RIDGE GENERATING STATION, L. P.

General Partners

DECKER ENERGY-RIDGE, INC. **WHEELABRATOR POLK INC.**

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October 29, 1993

Mr. John Reynolds, P.E.
Florida Department of Environmental Protection
Division of Air Resource Management
Twin Towers Office Building
2600 Blair Stone Road
Tallahassee, Florida 32399-2400

Re: Ridge Generating Station, Polk County
DER File No. AC 53-206244, PSD-FL-183

Dear Mr. Reynolds:

Pursuant to our telephone conversation on October 26, 1993 and Specific Condition 8 of the subject permit, a proposed protocol for the Comprehensive Emissions Testing Program is enclosed for your review and approval. The contractor is currently ahead of schedule and it is anticipated that the initial startup could occur early in March, 1994. We believe that the protocol includes all of the information required in the permit and that the approach for establishing the proposed emissions limits is reasonable. We would, however, be happy to meet with you to discuss the proposed protocol, if you feel that such a meeting would facilitate your review and approval.

Based on our telephone conversation, we have included the vent filter for the fuel transfer building in the proposed testing protocol and we will submit the additional details associated with this vent in the application for the operating permit. The addition of the fuel transfer building is beneficial because it will reduce the noise levels at the facility and the vent filter will reduce fugitive emissions.

Please call me at 1-800-682-0026 if you have questions or need any additional information. I will call you in a couple of weeks to determine if a meeting would be beneficial. Thank you for your assistance on this matter.

Very truly yours,

MPKilleen

Matthew P. Killeen
Manager, Environmental Permits

MPK220/ga

Att. - Two copies of Protocol

cc: Preston Lewis, P.E. (FLDEP) w/att.
D. Raymond
File Ridge 6.1

COMPREHENSIVE EMISSIONS TESTING PROGRAM PROTOCOL

for

RIDGE GENERATING STATION

3131 K-VILLE AVENUE

AUBURNDALE, POLK COUNTY, FL 33823

WHEELABRATOR ENVIRONMENTAL SYSTEMS, INC.

COMPREHENSIVE EMISSIONS TESTING PROGRAM PROTOCOL

for

RIDGE GENERATING STATION

3131 K-VILLE AVENUE

AUBURNDALE, POLK COUNTY, FL 33823

PSD-FL-183
FDEP AC 53-206244

Submitted by

WHEELABRATOR ENVIRONMENTAL SYSTEMS, INC.

LIBERTY LANE

HAMPTON, NH 03842

for

RIDGE GENERATING STATION LIMITED PARTNERSHIP

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1.0 General Emissions Test Program Description

In lieu of the usual compliance test requirement, a Comprehensive Emissions Testing Program will be performed at the Ridge Generating Station. The Emissions Test Program will be representative of the full range of operation of the facility. The Comprehensive Emissions Test Program will include an initial stack test and three additional quarterly stack tests. The initial test and one additional quarterly test program will consist of stack emissions testing for each limited and additional pollutant at 100 percent capacity while operating at both 80 percent wood/20 percent tire feed and 100% wood feed. One of the additional quarterly programs will consist of testing for each limited pollutant at 75 and 100 percent capacity, as well as testing for the additional pollutants at 100 percent capacity while operating on 80 percent wood and 20 percent tire feed. The remaining additional quarterly program will consist of testing for each limited and additional pollutant at 100 percent capacity while operating at 80 percent wood and 20 percent tire feed.

2.0 Facility Description

The Ridge Generating Station located off State Road 542 and Taylor Road near Auburndale, Polk County, Florida is an electric power generation facility with a permitted capacity of 50 megawatts or 630 million Btu per hour. The boiler is a conventional wood-fired boiler with waterwall construction which will burn a mixture of wood, tires and landfill gas.

Wood loading to the boiler will be at a rate of 75-100 percent of the heat input. Tire loading to the boiler will be limited to 20 percent of the heat input. Landfill gas, when available, will represent 5-10 percent of the heat input. Propane is utilized for start-up, shutdown and combustion stabilization fuel.

Wood fuel is obtained from independent contractors, and includes the following materials: construction and demolition material, forest residuals/land clearing material, industrial wood wastes and wood derived from residential yard waste. The wood is processed (chipped) both onsite and offsite, stockpiled then reclaimed and delivered to the boiler in a minus 2-inch processed form. Tires are received both whole and chipped and are free from dirt, metal rims and other foreign materials. Tires are processed to 3-inch nominal material. Two covered conveyors separately transport the processed fuels to feed bins located at the boiler front. Landfill gas will be obtained from Polk County's North Central Landfill.

A combination of combustion controls and selective noncatalytic reduction (SNCR) is utilized to control NO_x emissions from the boiler. The air pollution control system for this facility consists of a spray dryer absorber (SDA) and fabric filter (FF) to control acid gases, metals and particulate matter. The SDA system is equipped with redundant slakers and multiple atomizers for the addition of the lime slurry for acid gas control.

The FF is designed for collection of flyash at all boiler loads. A pulse jet type bag cleaning system will clean the bags and direct the flyash to the ash removal system.

An Altech Continuous Emissions Monitoring System (CEMS) is located at the FF outlet to continuously monitor sulfur dioxide (SO_2), nitrogen oxides (NO & NO_2), Carbon Monoxide (CO), and on a wet basis, Oxygen (O_2), Moisture, opacity and flue gas volumetric flowrate for compliance purposes. The Altech system also includes a multipoint mass flow meter to determine stack gas volumetric flowrate. SO_2, NO_x and CO concentrations will be measured in parts per million and converted to lbs/hr utilizing the values obtained for flue gas volumetric flow and molecular weight. O_2, CO_2, and moisture concentrations will be measured in percent by volume.

3.0 Sampling Location Descriptions

3.1 Fabric Filter Outlet (Stack)

Exhaust gases from the Ridge Generating Station (RGS) boiler flow through ductwork to the spray dry absorber and subsequently to the fabric filter. The emissions test program will be performed at the outlet to the fabric filter upstream of the induced draft fan. The stack sampling location is a rectangular duct which is 107.5 inches wide by 84 inches deep which corresponds to an equivalent diameter of 94.3 inches. The stack test ports are located 211.7 inches or 2.3 diameters from the nearest upstream disturbance and 69 inches or 0.7 diameters from the nearest downstream disturbance. This location has sufficient straight run to meet EPA Method 1 sampling location requirements. Five test ports are situated equidistantly across the duct. The CEMS are also located at the FF outlet duct (see Appendix A for drawings).

3.2 Fugitive

During the initial emissions test program, fugitive emissions will be determined from the material receiving, processing, storage and transfer operations. In accordance with EPA Method 22, locations of potential fugitive emissions will be confirmed in the field prior to the start of an observation period.

3.3 Ambient

Based on Tampa, Florida wind measurements made at a height of 22 feet above ground level, the most common near-surface wind direction in the vicinity of the RGS facility is a direction from east to west. Wind rose data for the years 1982 through 1986 were used for this determination. This same wind rose data was used in the PSD modeling evaluation. As a result of this information, Ammonia emissions will be continuously monitored at a location west of the stack near the fenceline of the RGS property (see Appendix A for location).

4.0 Detailed Emissions Test Program

A Comprehensive Emissions Test Program will be conducted at the Ridge Generating Station facility located off State Road 542 and Taylor Road near Auburndale, Polk County, Florida. The test program will commence after the facility has had a shakedown period and is considered to be in normal operation. The emissions test program will consist of the following three efforts.

4.1 Stack Emissions Tests

4.1.1 Objective

The objective of the stack emission tests is to collect data to evaluate compliance with the current emission limits as well as to establish proposed emission limits for the current limited pollutants and assess limits for any additional pollutants. In addition to the limited pollutants listed in Table 4-1, emission rates of the additional pollutants listed in Table 4-2 will also be determined. The initial test program will include certification of the CEMS and the quarterly test programs will include cylinder gas audits of the CEMS. Visible and fugitive emissions at the RGS facility will be determined at the locations and in accordance with the EPA Methods found in Table 4-3. The visible and fugitive emissions testing will only be performed during the initial test program.

4.1.2 Process Operating Conditions

The Comprehensive Emissions Test Program will include an initial stack test and three additional quarterly stack tests. The initial test and one additional quarterly test program will consist of stack emissions testing for each limited and additional pollutant at 100 percent capacity while operating at both 80 percent wood/20 percent tire feed and 100% wood feed. One of the additional quarterly programs will consist of testing for each limited pollutant at 75 and 100 percent capacity, as well as testing for the additional pollutants at 100 percent capacity while operating on 80 percent wood and 20 percent tire feed. The remaining additional quarterly program will consist of testing for each limited and additional pollutant at 100 percent capacity while operating at 80 percent wood and 20 percent tire feed. Table 4-4 details the boiler conditions during the stack emissions tests.

Process information will be collected by the Bailey distributed control system throughout the emissions test program. Process measurements will be provided in hourly averages during each test period.

TABLE 4-1
LIMITED POLLUTANTS

Pollutant	EPA Test Method	# Runs	Run Duration	Location	Initial BACT Limitation*
PM/PM10	201A (front ½ only)	3	120 Min	Stack	12.6 lb/hr
SO_2	6C	3	60 Min	Stack	109.4 lb/hr
NOx	7E	3	60 Min	Stack	94.5 lb/hr
CO	10	3	60 Min	Stack	315.0 lb/hr
VOC	25A	3	60 Min	Stack	22.1 lb/hr
HCl	26	3	60 Min	Stack	5.0 lb/hr
Hg	29	3	120 Min	Stack	0.022 lb/hr
Pb	29	3	120 Min	Stack	0.25 lb/hr
Be	29	3	120 Min	Stack	0.0063 lb/hr

* Based on 24 hour average

TABLE 4-2
ADDITIONAL POLLUTANTS

Pollutant	EPA Test Method	# Runs	Run Duration	Location
Ammonia (NH_3)	26 - 0050	3	60 Min	Stack
Arsenic (As)	29	3	60 Min	Stack
Cadmium (Cd)	29	3	120 Min	Stack
Total Chromium (Cr)	29	3	120 Min	Stack
Chromium VI (Cr^{+6})	13B	3	120 Min	Stack
Zinc Oxide	29	3	120 Min	Stack
Benzene	18	3	60 Min	Stack
Sulfuric Acid (H_2SO_4)	8	3	120 Min	Stack
PCB's Total mono-deca Congeners	23	3	180 Min	Stack
Dioxins/Furans	23	3	180 Min	Stack

TABLE 4-3

VISIBLE/FUGITIVE EMISSIONS

PROCESS/LOCATION	EPA TEST METHOD	TEST DURATION	FDEP LIMITATION
Boiler Stack	9	60 Mins.	10%
Ash Handling Vent Filter	9	60 Mins.	10%
Lime Silo Vent Filter	9	60 Mins.	10%
Fuel Transfer Bldg. Vent Filter	9	60 Mins.	10%*
Receiving	22	3 Days	N/A
Processing	22	3 Days	N/A
Transfer	22	3 Days	N/A
Storage	22	3 Days	N/A

* This limitation will be confirmed prior to the test

TABLE 4-4

STACK EMISSIONS TESTING BOILER CONDITIONS*

	75% LOAD	100% LOAD	100% LOAD
Generator Output (MW)	37.5	50	50
Total Heat Input (MMBtu/hr)	473	630	630
Steam Flow (Klb/hr)**	259	345	345
Fuel Feed (Heat Input)			
• Wood (%)	80	80	100
• Tires (%)	20	20	-
Fuel Feed (weight)			
• Wood (lb/hr)	69,358	92,477	115,596
• Tires (lb/hr)	6,750	9,000	-
Stack Emissions Testing			
• Initial Compliance***	-	Table 4-1	Table 4-1
	-	Table 4-2	Table 4-2
• Additional Quarterly Tests			
- 1 Quarter	-	Table 4-1	Table 4-1
	-	Table 4-2	Table 4-2
- 1 Quarter	Table 4-1	Table 4-1	-
	-	Table 4-2	-
- 1 Quarter	-	Table 4-1	-
	-	Table 4-2	-

* During the stack emissions testing, actual boiler conditions will be maintained within 10% of the values listed in this table.

** Actual determination of percent load will be based on steam flow.

*** Initial compliance will not included the 75% load condition due to the 30-day 100% capacity performance test.

The process data that will be collected will consist of the following:

1. Boiler Measurements
   a. Wood feed, lb/hr
   b. Tire feed, lb/hr
   c. Landfill gas, KPPH
   d. Propane, KPPH
   e. Generator Output, MW
   f. Steam production, klb/hr
   g. Furnace temperature, °F
   h. Furnace draft, inches H_2O
   i. Superheater outlet steam temperature, °F
   j. Superheater outlet steam pressure, psig
   k. Feed water flow, klb/hr
   l. Economizer water outlet temperature, °F
   m. Primary air heater gas outlet temperature, °F

2. Spray Dryer Absorber Measurements
   a. SDA inlet flue gas temperature, °F
   b. SDA outlet flue gas temperature, °F
   c. Lime slurry concentrations, %
   d. Dilution water flow, gpm
   e. SDA atomizer air flow, scfm
   f. SDA total slurry flow, gpm

3. Fabric Filter Measurements
   a. FF outlet flue gas temperature, °F
   b. FF pressure differential, inches H_2O

4. Hourly Plant CEM Data
   a. FF outlet - SO_2, NO_X, CO, opacity, stack gas volumetric flow
   b. Ambient - NH_3 (local recorder)

All test runs will be performed under normal, non-upset feed and operating conditions in order to obtain quality data. The wood and tire feed will represent the normal range of conditions for the facility. The following upset or atypical process conditions will be considered valid reasons for delaying or interrupting the testing:

1. Feed stoppage
2. Fan outage
3. Ash conveyor system shutdown
4. Turbine trip

5. Steam flow variation more than $\pm$10% of setpoint
6. SDA malfunction
7. FF malfunction
8. SNCR Malfunction

4.1.3 Sampling and Analytical Procedures

The stack emissions tests will be performed in accordance with EPA reference methods as outlined in 40 CFR 60 Appendix A and SW 846. The specific methods to be performed are outlined in Tables 4-1 and 4-2 for each pollutant. EPA draft method 29 "Determination of metals emissions from stationary sources" will be performed for all metals listed in Tables 4-1 and 4-2. EPA reference methods 1 through 4 will be performed in support of each isokinetic test. Copies of the individual test methods can be found in Appendix B.

Visible emissions from the RGS boiler stack, ash handling area vent filter, lime silo vent filter and fuel transfer building vent filter will be determined in accordance with EPA method 9. Fugitive emissions from the material receiving, processing, and storage operations will be determined in accordance with EPA method 22 over a three day period during normal operation.

4.2 Long Term CEMS Data Collection for BACT Determination

4.2.1 Objective

The objective of the long term CEMS data collection is to establish final SO_2, NO_x and CO emission limits and averaging times. In addition, the feasibility of establishing emission limits specific to startup and shutdown periods will be evaluated. The CEMS consists of an Altech Model MCS 100 analyzer to continuously measure SO_2, NO_X, CO, O_2, CO_2 and moisture. Opacity will be determined continuously by a TECO Model 400 monitor. Stack gas volumetric flow will be determined by a Kurz Model 4500 flow monitor.

4.2.2 Process Operating Conditions

During the long term CEMS data collection, three operational periods will be identified. These three periods will be normal operation, startup and shutdown. Normal operation will be considered operation between 70 and 100 percent capacity with all equipment outlined in section 4.1.2 operating correctly. During normal operation the fuel ratios will range from 80-100 percent wood to 0-20 percent tires. Startup periods will be defined as the period of time before which solid fuel feed has been started and steady

state conditions exist. Shutdown periods will be defined as the period of time after which solid fuel feed has been stopped and the boiler steam flow is less than 10% capacity. A shutdown may be the result of a malfunction or scheduled maintenance. During the long term CEMS data collection period, accurate records will be kept of normal operation, startup and shutdown periods.

4.2.3 Data Validation Procedures

A quality assurance/quality control (QA/QC) program will be followed in order to assure valid data is recorded during the long term CEMS data collection period. This program will include an initial CEMS certification (RATA), daily calibrations and subsequent cylinder gas audits (CGA) to include stack gas volumetric flow monitor calibrations. This QA/QC program will be performed in accordance with 40 CFR 60 Appendix B Performance Specifications 1, 2, 4 and 6 and 40 CFR 60 Appendix F Procedure 1.

4.3 Ambient Ammonia Monitoring

Ambient ammonia concentrations will be monitored at the Northwest corner fenceline of the RGS facility which has been determined to be the prevailing downwind location (see Appendix A). The ammonia monitor will be a TECO Model 17 chemiluminescence ammonia analyzer with converter, data logger and chart recorder. The equipment will be housed in a climate controlled shelter. The data will be collected from the initial startup through to the completion of the emissions test program. A meteorological station capable of measuring and recording wind speed and wind direction will be part of the ambient ammonia monitoring program. The Comprehensive Emissions Test Program report will include a discussion of this data and a recommendation related to the continuation of the ambient ammonia monitoring program.

5.0 Comprehensive Emissions Test Program Reporting

A Comprehensive Emissions Test Report will be submitted to the Florida Department of Environmental Protection - Southwest District Office within 15 months of initial startup of the facility. This report will include results of the stack emissions testing, long term CEMS data collection, ambient ammonia monitoring and the proposed emission limit determinations with revised BACT analyses.

Due to the amount of data which will be contained in the Comprehensive Emissions Test Report, a number of volumes will be needed. A sample would be to have Volume 1 contain a discussion of the overall test program, summary tables of the results of all efforts to include stack emissions tests, long term CEM data and ambient ammonia

results as well as a discussion of the proposed BACT limitations. Volumes 2-5 would contain the stack emission test reports for the initial and quarterly testing. Volumes 6 and 7 would contain the long term CEM data.

The stack emissions test report will include at a minimum a list of relevant personnel present during testing, a summary of results, description of the test procedures used, description of the source and it's operation during testing, test location description, example calculations, raw field data, laboratory analyses with chain of custody documentation, copies of the EPA test methods and equipment calibrations.

The summary tables will contain average test results in units of standard, the corresponding permit limitations, as well as the process data recorded during each test run. Individual test run averages will be in the following units where applicable: lbs/hr, gr/dscf @ 12% CO_2 and 7% O_2, ng/m^3 @ 12% CO_2 and 7% O_2 and ppm @ 12% CO_2 and 7% O_2.

A sample stack emissions test report will be submitted for review to the FDEP-Southwest District Office prior to the field testing, once a contractor has been chosen to perform the emissions test program.

6.0 Proposed Emission Limit Determinations and BACT Analyses

6.1 General Approach

In accordance with PSD Permit Conditions 5, 16 and 17, the results of the comprehensive emission testing program will be used to establish compliance with the initial permit limits and to evaluate the feasibility of proposing revised emission limits and/or averaging times for the operating permit. Specifically, the manual stack testing results from the initial compliance and subsequent quarterly stack testing will be used to evaluate revised limits for VOC, HCl, Hg, Pb and Be.

Long term SO_2, NOx and CO data from the plant CEMS will be analyzed to propose final CEM emission limits and averaging times. In addition, the feasibility of establishing emission limits specific to startup and shutdown periods will be evaluated. The long term CEM data analyses results, in conjunction with the air pollution control equipment annualized costs, will be incorporated in the revised BACT application proposing final SO_2, NOx and CO emission limits. Generally, both the manual stack test results and long term CEM data will be evaluated using several statistical analyses techniques. These techniques will include:

- routine summary statistics (mean, standard deviation),

- time series plots to examine trends in emissions over time and to identify data anomalies,

- normality testing and frequency distribution plots to evaluate distribution of data, and

- determining maximum estimated emissions based on appropriate statistical mean standard deviation and confidence level.

It should be noted that analyses of the long term CEM data will appropriately account for emission variations that are directly related to variations in fuel composition. For long term normal boiler operations the fuel ratios will range from 75-100% wood to 0-20% tires, and the final emission limits proposed as a result of the emission test program will account for these variations.

6.2 Determination of Manual Stack Test Emission Limits

Results from the initial compliance and subsequent quarterly manual stack testing will be analyzed to propose final limits for the following permit limited pollutants: total volatile organics (VOC), Hydrogen Chloride (HCl), Mercury (Hg), Lead (Pb) and Beryllium (Be). Manual stack test results from the non-limited pollutants will be analyzed using the same procedure in the event that limits for these pollutants might be included in the operating permit.

The following procedure will be followed to develop proposed emission limits from the manual stack test results:

- When results are below the method detection limit, the detection limit will be used in the statistical analyses.

- The sample ($\bar{x}$) mean and standard deviation (s) will be calculated from all data.

- The single tail 99% upper confidence limit will be determined using the Student t Test.

- The proposed emission limit will set at the 99% single tailed upper confidence limit.

The Student t Test 99% upper confidence limit has been established as the basis for the proposed or new emission limits due to the very low number of test results that will be used in the analyses, the heterogeneity of the fuel, sampling analytical method precision and bias limits. The 99% upper confidence limit will provide the assurance that the final emission limits will not be exceeded for the term of the operating permit if periodic manual stack testing is required.

The Student t Test confidence limit determination is the standard confidence limit determination calculation used for small sample populations.

The Student t 99% upper confidence limit equation is:

$CL_{99} = \bar{x} + t_{99} \times s$, where:

CL_{99} = Student t upper 99% confidence limit

$\bar{x}$ = Mean of test results

s = Standard deviation of test results

t_{99} = Standard Student t value for 99% confidence interval for n-1 degree of freedom (no of results - 1)

6.3 Long Term CEM Emission Limit Determinations

The long term data for SO_2, NOx and CO will be reduced to hourly averages in both lbs/hour and ppm @ 7% O_2. Hourly averages will be segregated into startup/shutdown and normal operating periods. These boiler operating conditions will be evaluated separately to determine appropriate revised emission limits. The CEM hourly data will be analyzed as follows:

1. Time series plots will be developed to visually examine trends in SO_2, NOx and CO emissions over time and to identify data gaps or anomalies.

2. Data anomalies identified in time series plots will be compared to actual wood/tire fuel ratios for the concurrent time periods. If frequent or extensive anomalies are found that directly correlate to specific wood/tire firing ratios, then the affected hourly averages will be separated and the data set evaluated independently in accordance with steps 3-7 below.

3. Hourly data will be tested for normality using the Shapiro-Wilke Normality Test statistic. Since environmental data tends to be high tailed where there are many data values grouped together and a few larger values, using the natural logarithm (ln) of the data will provide a more normal distribution. Therefore, raw hourly data and logarithms of the hourly data will be tested for normality. It is important to establish the normality of the data because probability statistics such as the confidence limit depend on the underlying sample data to be normally distributed.

4. To evaluate the effect of averaging times on data variability and maximum emission rates, both the raw and ln transformed hourly data will be reduced as follows:

   - SO_2 Data - 24 hour block and rolling averages
   - NOx Data - 24 hour block and rolling averages
   - CO Data - 24 and 8 hour block and rolling averages

   Raw hourly CEM data collected during startup and shutdown periods will be evaluated in 3 and 8 hour rolling and block averages.

5. Routine statistics will be performed in the raw and ln hourly data, and averaging times. Data means and standard deviations will be calculated. For ln data, the geometric mean and standard deviation will be calculated.

6. Distribution of the various normal and ln averaging times will be tested for normality using the Shapiro-Wilke Normality Test statistic. The raw or ln averaging time that is more normally distributed will be selected as the averaging time for the proposed emission limit.

7. The 99% upper confidence limit using the Student t distribution will be calculated using the final averaging time data sets selected for each emission using the following equation:

   $CI_{99} = \bar{x} + t_{99} \times s$, where:

   CI_{99} = 99% one tailed upper confidence limit

   $\bar{x}$ = Mean of the averaging time data set

   s = Standard deviation of the data set

   t_{99} = Student t value from Student t table

   The 99% upper confidence limit will be proposed as the final CEM emission limits.

   The statistical and averaging times evaluated for boiler startup/shutdown periods will be used to calculate the 99% upper confidence limit for these data. As necessary, specific startup/shutdown emission limits will be proposed for the operating permit.

6.4 Revised BACT Analyses

In accordance with Specific Condition 16 and the initial BACT determination, a revised BACT application will be submitted with the emissions test program report. The revised BACT application will include proposed final enforceable BACT limits for SO_2, NOx and CO and detailed cost analyses of the installed air pollution control systems. As determined in the initial BACT determination, the revised BACT application will be limited to SO_2, NOx and CO emissions where BACT/LAER clearinghouse data was used as the basis for the target emission limits for these emissions.

6.4.1 Final BACT Emission Limit

The final emission limits for SO_2, NOx and CO determined in CEM data analyses will not be used for the revised BACT determination cost analyses since there is a distinct difference between an enforceable "not to exceed" permit emission limit and the hourly average emission used to calculate annual emission reductions. These final proposed (upper 99% confidence limit) enforceable limits will represent the lowest level of emissions continuously achievable for the operating life of the facility which reflect the top control technologies selected in the initial BACT determination. Selection of the final emission limits at the 99% upper confidence limit will ensure that any reported excess emission will not be the result of natural fuel variations given that the boiler and air pollution control systems are being operated in a normal manner at the design control efficiencies. A conservative approach is warranted since this is the first facility of this type that will be combusting wood and tires simultaneously, and long term emission variations are unknown. The average 24 hour block average emissions rates for SO_2 and NOx will be used in conjunction with the design control efficiencies specified in the initial BACT application to calculate uncontrolled emissions for use as necessary in the BACT cost analyses.

6.4.2 BACT Cost Analyses

The BACT cost analyses will be specific for SO_2, and NOx emissions since operating costs for the respective best control technologies can be specifically defined. A cost analyses based on the final CO BACT emission limit will not be meaningful because operating costs for the good combustion practice best control technology cannot be accurately defined.

The capital and operating costs associated with the NOx and SO_2 best available control technologies will be based on the actual construction cost and from operating costs over the first year of facility operation.

Construction costs will include all costs associated with turnkey operation such as design, equipment purchase, and installation. Operating costs will include reagent usage, energy costs and routine repair and maintenance.

Cost effectiveness will be calculated using the annualized costs (annualized capital and operating) and total annual tons of SO_2 and NOx removed for the respective best control technology. Annual tons of pollutant removal will be calculated based on 100% annual boiler availability (8,760 hours/year). The average of the 24-block average and SO_2 and NOx CEM data from the emission test period will be used to calculate the annual uncontrolled pollutant emissions in accordance with the following equation:

$$E_a = \frac{8760 \times (\bar{x}_{24} \div (1 - RE/100))}{2000}, \text{ where:}$$

E_a = Total annual uncontrolled emission (tons/year)

$\bar{x}_{24}$ = Average of 24-hour block averages (lbs/hr)

RE = Air pollution control technology removal Efficiency (Thermal DeNOx = 40% and SDA/FF = 80%)

The total annual tons of pollutant removed will be calculated as follows:

$$T_R = \frac{E_a - (8760 \text{ hours} \times \bar{x}_{24})}{2000}, \text{ where:}$$

T_R = Total annual emissions removed (tons/year)

E_a = Total annual uncontrolled emissions (tons/year)

$\bar{x}_{24}$ = Average of the 24-hour block averages (lbs/hr)

The cost effectiveness is then calculated by the following equation:

$CE = C_a/T_R$

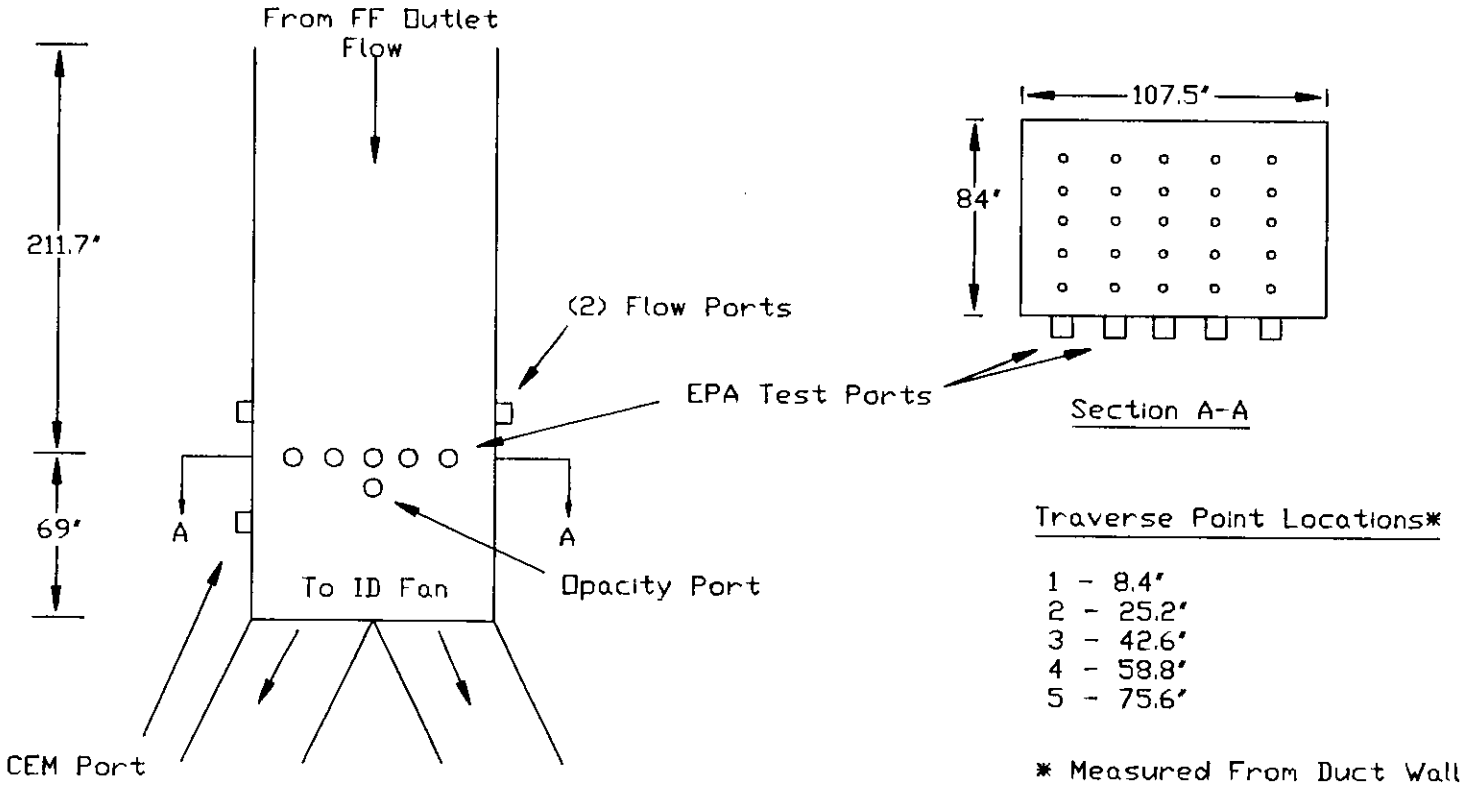
CE = Cost Effectiveness - $/ton removed

T_R = Total annual emissions removed

C_a = Total Annualized Costs

APPENDIX A

Sample Location Drawings



Traverse Point Locations*

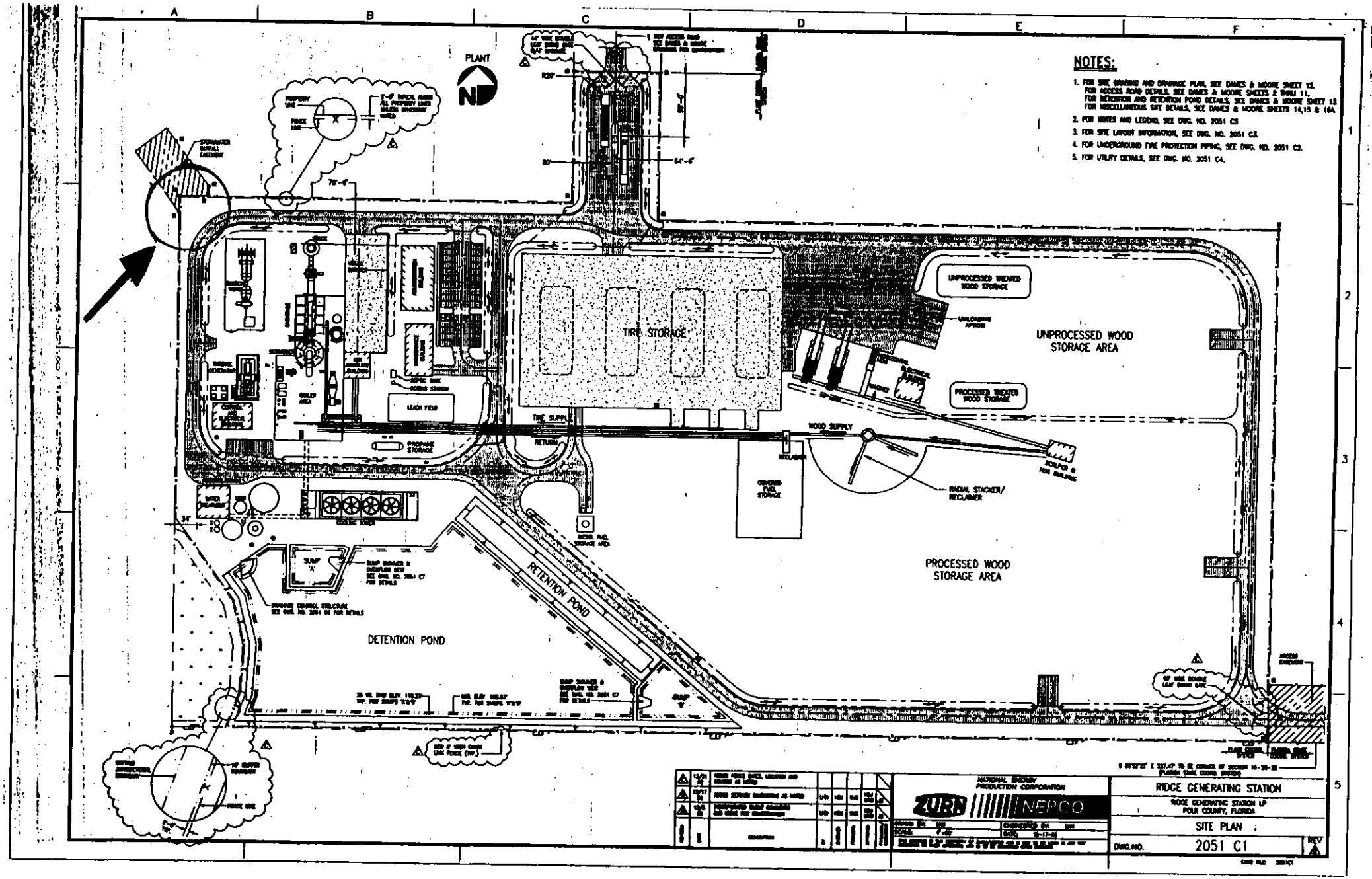
1 - 8.4'
2 - 25.2'
3 - 42.6'
4 - 58.8'
5 - 75.6'

* Measured From Duct Wall

Stack Location Schematic

Not Drawn to Scale

AMBIENT AMMONIA MONITOR LOCATION



APPENDIX B

EPA Sampling Methodologies

METHOD 1

Method 1—Sample and Velocity Traverses for Stationary Sources

1. Principle and Applicability

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

1.2 Applicability. This method is applicable to flowing gas streams in ducts, stacks, and flues. The method cannot be used when: (1) flow is cyclonic or swirling (see Section 2.4), (2) a stack is smaller than about 0.30 meter (12 in.) in diameter, or 0.071 m² (113 in.2) cross-sectional area, or (3) the measurement site is less than two stack or duct diameters downstream or less than a half diameter upstream from a flow disturbance.

The requirements of this method must be considered before construction of a new facility from which emissions will be measured; failure to do so may require subsequent alterations to the stack or deviation from the standard procedure. Cases involving variants are subject to approval by the Administrator, U.S. Environmental Protection Agency.

2. Procedure

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

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

Where L = length and W = width.

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

2.2 Determining the Number of Traverse Points.

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

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

Table 1-1. Cross-Section Layout for Rectangular Stacks

Number of traverse points	Matrix layout
8	3x3
12	4x3
16	4x4
20	5x4
25	5x5
30	6x5
36	6x6
42	7x6
49	7x7

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

2.3 Cross-sectional Layout and Location of Traverse Points.

2.3.1 Circular Stacks. Locate the traverse points on two perpendicular diameters according to Table 1-2 and the example shown in Figure 1-3. Any equation (for examples, see Citations 2 and 3 in the Bibliography) that gives the same values as those in Table 1-2 may be used in lieu of Table 1-2.

For particulate traverses, one of the diameters must be in a plane containing the greatest expected concentration variation, e.g., after bends, one diameter shall be in the plane of the bend. This requirement

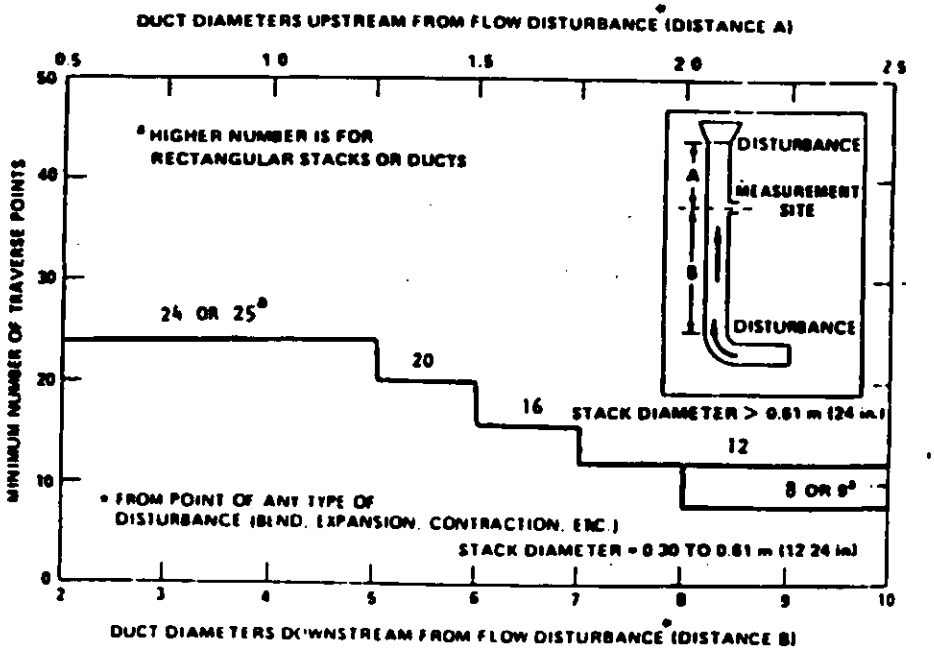


Figure 1-1. Minimum number of traverse points for particulate traverses.

becomes less critical as the distance from the disturbance increases; therefore, other diameter locations may be used, subject to approval of the Administrator.

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

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

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

2.3.1.2 Stacks With Diameters Equal to or Less Than 0.61 m (24 in.). Follow the procedure in Section 2.3.1.1, noting only that any "adjusted" points should be relocated away from the stack walls to: (1) a distance of 1.3 cm (0.50 in.); or (2) a distance equal to the nozzle inside diameter, whichever is larger.

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

If the tester desires to use more than the minimum number of traverse points, expand the "minimum number of traverse points" matrix (see Table 1-1) by adding the extra traverse points along one or the other or both legs of the matrix; the final matrix need not be balanced. For example, if a 4x3 "minimum number of points" matrix were expanded to 36 points, the final matrix could be 9x4 or 12x3, and would not necessarily have to be 6x6. After constructing the final matrix, divide the stack cross-section into as many equal rectangular, elemental areas as traverse points, and locate a traverse point at the centroid of each equal area.

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

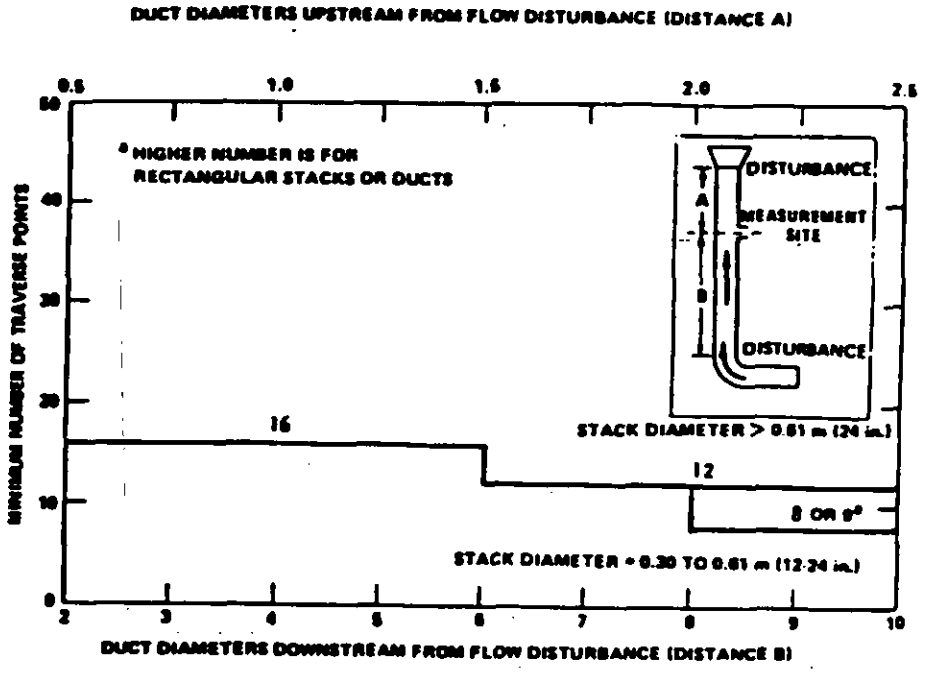


Figure 1-2. Minimum number of traverse points for velocity (nonparticulate) traverses.

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

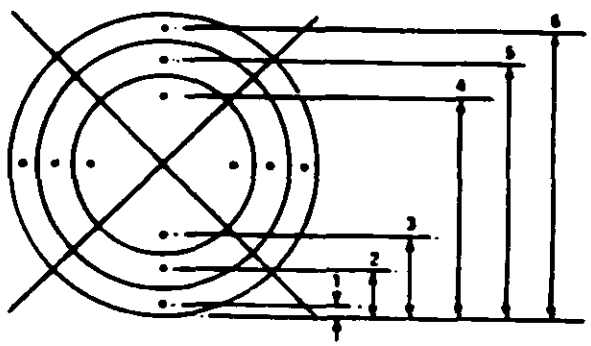


Figure 1-3. Example showing circular stack cross section divided into 12 equal areas, with location of traverse points indicated.

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

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

Traverse point number on a diameter	Number of traverse points on a diameter											
	2	4	6	8	10	12	14	16	18	20	22	24
1	14.6	6.7	4.4	3.2	2.6	2.1	1.8	1.6	1.4	1.3	1.1	1.1
2	85.4	25.0	14.6	10.5	8.2	6.7	5.7	4.9	4.4	3.9	3.5	3.2
3		75.0	29.6	19.4	14.6	11.8	9.9	8.5	7.5	6.7	6.0	5.5
4		93.3	70.4	32.3	22.6	17.7	14.6	12.5	10.9	9.7	8.7	7.9
5			85.4	67.7	34.2	25.0	20.1	16.9	14.6	12.9	11.6	10.5
6			95.6	80.6	65.8	35.6	26.9	22.0	18.8	16.5	14.6	13.2
7				89.5	77.4	64.4	36.8	28.3	23.6	20.4	18.0	16.1
8				96.8	85.4	75.0	63.4	37.5	29.6	25.0	21.8	19.4
9					91.8	82.3	73.1	62.5	38.2	30.6	26.2	23.0
10					97.4	88.2	79.9	71.7	61.8	38.8	31.5	27.2
11						93.3	85.4	78.0	70.4	61.2	38.3	32.3
12						97.9	90.1	83.1	76.4	69.4	60.7	39.8
13							94.3	87.5	81.2	75.0	68.5	60.2
14							98.2	91.5	85.4	79.6	73.8	67.7
15								95.1	88.1	83.5	78.2	72.8
16								98.4	92.5	87.1	82.0	77.0
17									95.6	90.3	85.4	80.6
18									98.6	93.3	88.4	83.9
19										96.1	91.3	86.8
20										98.7	94.0	89.5

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

[Percent of stack diameter from inside wall to traverse point]

Traverse point number on a diameter	Number of traverse points on a diameter											
	2	4	6	8	10	12	14	16	18	20	22	24
21											96.5	92.1
22											98.9	94.5
23												96.8
24												98.9

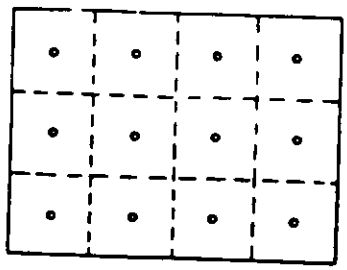


Figure 1-4. Example showing rectangular stack cross section divided into 12 equal areas, with a traverse point at centroid of each area.

2.4 Verification of Absence of Cyclonic Flow. In most stationary sources, the direction of stack gas flow is essentially parallel to the stack walls. However, cyclonic flow may exist (1) after such devices as cyclones and inertial demisters following venturi scrubbers, or (2) in stacks having tangential inlets or other duct configurations which tend to induce swirling; in these instances, the presence or absence of cyclonic flow at the sampling location must be determined. The following techniques are acceptable for this determination.

Level and zero the manometer. Connect a Type S pitot tube to the manometer. Position the Type S pitot tube at each traverse point, in succession, so that the planes of the face openings of the pitot tube are perpendicular to the stack cross-sectional plane; when the Type S pitot tube is in this position, it is at "0°reference." Note the differential pressure (delta p) reading at each traverse point. If a null (zero) pitot reading is obtained at 0°reference at a given traverse point, an acceptable flow condition exists at that point. If the pitot reading is not zero at 0°reference, rotate the pitot tube (up to ± 90°yaw angle), until a null reading is obtained. Carefully determine and record the value of the rotation angle (α) to the nearest degree. After the null technique has been applied at each traverse point, calculate the average of the absolute values of α; assign α values of 0°to those points for which no rotation was required, and include these in the overall average. If the average value of α is greater than 20°, the overall flow condition in the stack is unacceptable and alternative methodology, subject to the approval of the Administrator, must be used to perform accurate sample and velocity traverses.

The alternative procedure described in Section 2.5 may be used to determine the rotation angles in lieu of the procedure described above.

2.5 Alternative Measurement Site Selection Procedure. This alternative applies to sources where measurement locations are less than 2 equivalent stack or duct diameters downstream or less than ½ duct diameter upstream from a flow disturbance. The alternative should be limited to ducts larger than 24 in. in diameter where blockage and wall effects are minimal. A directional flow-sensing probe is used to measure pitch and yaw angles of the gas flow at 40 or more traverse points; the resultant angle is calculated and compared with acceptable criteria for mean and standard deviation.

Note: Both the pitch and yaw angles are measured from a line passing through the traverse point and parallel to the stack axis. The pitch angle is the angle of the gas flow component in the plane that INCLUDES the traverse line and is parallel to the stack axis. The yaw angle is the angle of the gas flow component in the plane PERPENDICULAR to the traverse line at the traverse point and is measured from the line passing through the traverse point and parallel to the stack axis.

2.5.1 Apparatus.

2.5.1.1 Directional Probe. Any directional probe, such as United Sensor Type DA Three-Dimensional Directional Probe, capable of measuring both the pitch and yaw angles of gas flows is acceptable. (Note: Mention of trade name or specific products does not constitute endorsement by the U.S. Environmental Protection Agency.) Assign an identification number to the directional probe, and permanently mark or engrave the number on the body of the probe. The pressure holes of directional probes are susceptible to plugging when used in particulate-laden gas streams. Therefore, a system for cleaning the pressure holes by "back-purging" with pressurized air is required.

2.5.1.2 Differential Pressure Gauges. Inclined manometers, U-tube manometers, or other differential pressure gauges (e.g., magnehelic gauges) that meet the specifications described in Method 2, section 2.2.

Note: If the differential pressure gauge produces both negative and positive readings, then both negative and positive pressure readings shall be calibrated at a minimum of three points as specified in Method 2, section 2.2.

2.5.2 Traverse Points. Use a minimum of 40 traverse points for circular ducts and 42 points for rectangular ducts for the gas flow angle determinations. Follow section 2.3 and Table 1-1 or 1-2 for the location and layout of the traverse points. If the measurement location is determined to be acceptable according to the criteria in this alternative procedure, use the same traverse point number and locations for sampling and velocity measurements.

2.5.3 Measurement Procedure.

2.5.3.1 Prepare the directional probe and differential pressure gauges as recommended by the manufacturer. Capillary tubing or surge tanks may be used to dampen pressure fluctuations. It is recommended, but not required, that a pretest leak check be conducted. To perform a leak check, pressurize or use suction on the impact opening until a reading of at least 7.6 cm (3 in.) H_2O registers on the differential pressure gauge, then plug the impact opening. The pressure of a leak-free system will remain stable for at least 15 seconds.

2.5.3.2 Level and zero the manometers. Since the manometer level and zero may drift because of vibrations and temperature changes, periodically check the level and zero during the traverse.

2.5.3.3 Position the probe at the appropriate locations in the gas stream, and rotate until zero deflection is indicated for the yaw angle pressure gauge. Determine and record the yaw angle. Record the pressure gauge readings for the pitch angle, and determine the pitch angle from the calibration curve. Repeat this procedure for each traverse point. Complete a "back-purge" of the pressure lines and the impact openings prior to measurements of each traverse point.

A post-test check as described in section 2.5.3.1 is required. If the criteria for a leak-free system are not met, repair the equipment, and repeat the flow angle measurements.

2.5.4 Calculate the resultant angle at each traverse point, the average resultant angle, and the standard deviation using the following equations. Complete the calculations retaining at least one extra significant figure beyond that of the acquired data. Round the values after the final calculations.

2.5.4.1 Calculate the resultant angle at each traverse point:

$$R_i = \text{arc cosine } [(\text{cosine } Y_i)(\text{cosine } P_i)] \quad \text{Eq. 1-2}$$

Where:

Ri = Resultant angle at traverse point i, degree.

Yi = Yaw angle at traverse point i, degree.

Pi = Pitch angle at traverse point i, degree.

2.5.4.2 Calculate the average resultant for the measurements:

$$\bar{R} = \frac{\Sigma Ri}{n} \quad \text{Eq. 1-3}$$

Where:

R *bar* = Average resultant angle, degree.

n = Total number of traverse points.

2.5.4.3 Calculate the standard deviations:

$$S_d = \sqrt{\frac{\sum_{i=1}^{n} (R_i - \bar{R})^2}{(n-1)}} \quad \text{Eq. 1-4}$$

Where:

Sd = Standard deviation, degree.

2.5.5 The measurement location is acceptable if R *bar* ≤ 20° and Sd ≤ 10°.

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

2.5.6.1 Cut two entry ports in the test section. The axes through the entry ports shall be perpendicular to each other and intersect in the centroid of the test section. The ports should be elongated slots parallel to the axis of the test section and of sufficient length to allow measurement of pitch angles while maintaining the pitot head position at the test-section centroid. To facilitate alignment of the directional probe during calibration, the test section should be constructed of plexiglass or some other transparent material. All calibration measurements should be made at the same point in the test section, preferably at the centroid of the test-section.

2.5.6.2 To ensure that the gas flow is parallel to the central axis of the test section, follow the procedure in Section 2.4 for cyclonic flow determination to measure the gas flow angles at the centroid of the test section from two test ports located 90° apart. The gas flow angle measured in each port must be ± 2° of 0°. Straightening vanes should be installed, if necessary, to meet this criterion.

2.5.6.3 Pitch Angle Calibration. Perform a calibration traverse according to the manufacturer's recommended protocol in 5° increments for angles from -60° to +60° at one velocity in each of the two ranges specified above. Average the pressure ratio values obtained for each angle in the two flow ranges, and plot a calibration curve with the average values of the pressure ratio (or other suitable measurement factor as recommended by the manufacturer) versus the pitch angle. Draw a smooth line through the data points. Plot also the data values for each traverse point. Determine the differences between the measured data values and the angle from the calibration curve at the same pressure ratio. The difference at each comparison must be within 2° for angles between 0° and 40° and within 3° for angles between 40° and 60°.

2.5.6.4 Yaw Angle Calibration. Mark the three-dimensional probe to allow the determination of the yaw position of the probe. This is usually a line extending the length of the probe and aligned with the impact opening. To determine the accuracy of measurements of the yaw angle, only the zero or null position need be calibrated as follows. Place the directional probe in the test section, and rotate the probe until the zero position is found. With a protractor or other angle measuring device, measure the angle indicated by the yaw angle indicator on the three-dimensional probe. This should be within 2° of 0°. Repeat this measurement for any other points along the length of the pitot where yaw angle measurements could be read in order to account for variations in the pitot markings used to indicate pitot head positions.

3. Bibliography

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Method 2—Determination of Stack Gas Velocity and Volumetric Flow Rate (Type S Pitot Tube)

1. Principle and Applicability

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

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

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

2. Apparatus

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

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

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

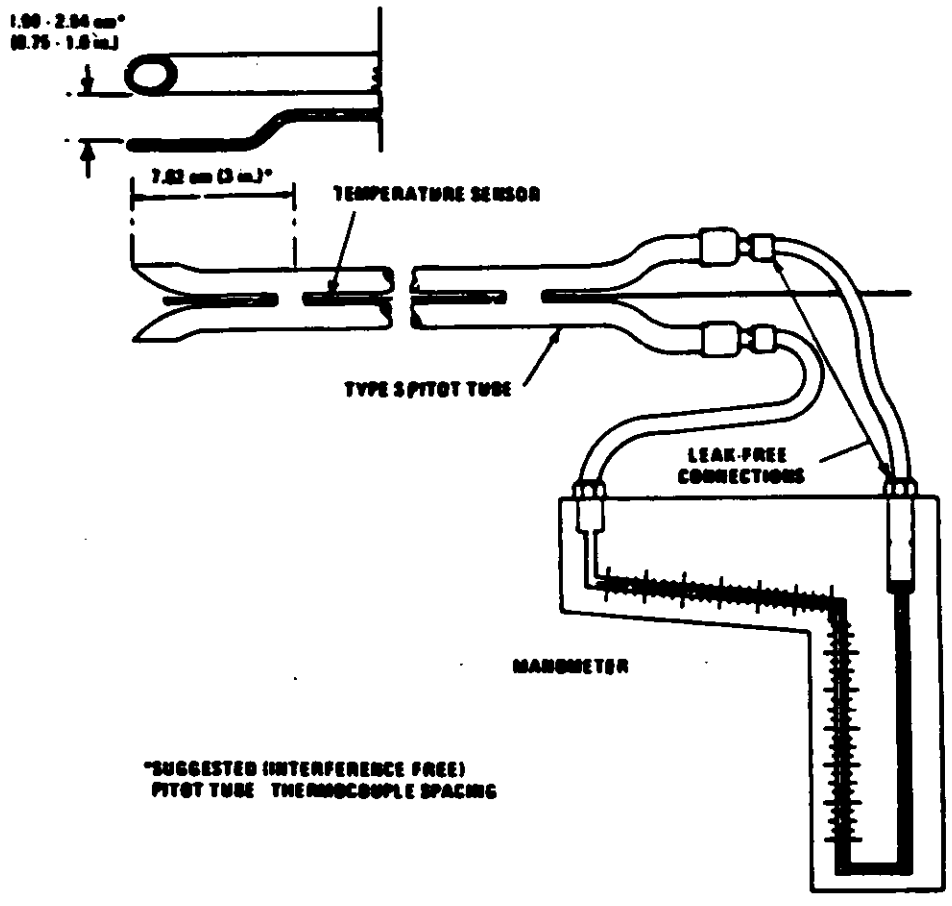


Figure 2-1. Type S pitot tube manometer assembly.

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

Figure 2-3. Types of face-opening misalignment that can result from field use or improper construction of Type S pitot tubes. These will not affect the baseline value of Cp(s) so long as $\alpha 1$ and $\alpha 2 \leq 10°$, $\beta 1$ and $\beta 2 \leq 5°$, $z \leq 0.32$ cm (1/8 in.) and $w \leq 0.08$ cm (1/32 in.) (citation 11 in Bibliography).

A standard pitot tube may be used instead of a Type S, provided that it meets the specifications of Sections 2.7 and 4.2; note, however, that the static and impact pressure holes of standard pitot tubes are susceptible to plugging in particulate-laden gas streams. Therefore, whenever a standard pitot tube is used to perform a traverse, adequate proof must be furnished that the openings of the pitot tube have not plugged up during the traverse period; this can be done by taking a velocity head (delta p) reading at the final traverse point, cleaning out the impact and static holes of the standard pitot tube by "back-purging" with pressurized air, and then taking another delta p reading. If the delta p readings made before and after the air purge are the same (± 5 percent), the traverse is acceptable. Otherwise, reject the run. Note that if delta p at the final traverse point is unsuitably low, another point may be selected. If "back-purging" at regular intervals is part of the procedure, then comparative delta p readings shall be taken, as above, for the last two back purges at which suitably high delta p readings are observed.

2.2 Differential Pressure Gauge. An inclined manometer or equivalent device is used. Most sampling trains are equipped with a 10—in. (water column) inclined-vertical manometer, having 0.01—in. H_2O divisions on the 0-to 1—in. inclined scale, and 0.1—in. H_2O divisions on the 1— to 10—in. vertical scale. This type of manometer (or other gauge of

equivalent sensitivity) is satisfactory for the measurement of delta p values as low as 1.3 mm (0.05 in.) H2O. However, a differential pressure gauge of greater sensitivity shall be used (subject to the approval of the Administrator), if any of the following is found to be true: (1) the arithmetic average of all delta p readings at the traverse points in the stack is less than 1.3 mm (0.05 in.) H2O; (2) for traverses of 12 or more points, more than 10 percent of the individual delta p readings are below 1.3 mm (0.05 in.) H2O; (3) for traverses of fewer than 12 points, more than one delta p reading is below 1.3 mm (0.05 in.) H2O. Citation 18 in Bibliography describes commercially available instrumentation for the measurement of low-range gas velocities.

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

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

Where:

delta pi = Individual velocity head reading at a traverse point, mm H2O (in. H2O).

n = Total number of traverse points.

K = 0.13 mm H2O when metric units are used and 0.005 in. H2O when English units are used.

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

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

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

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

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

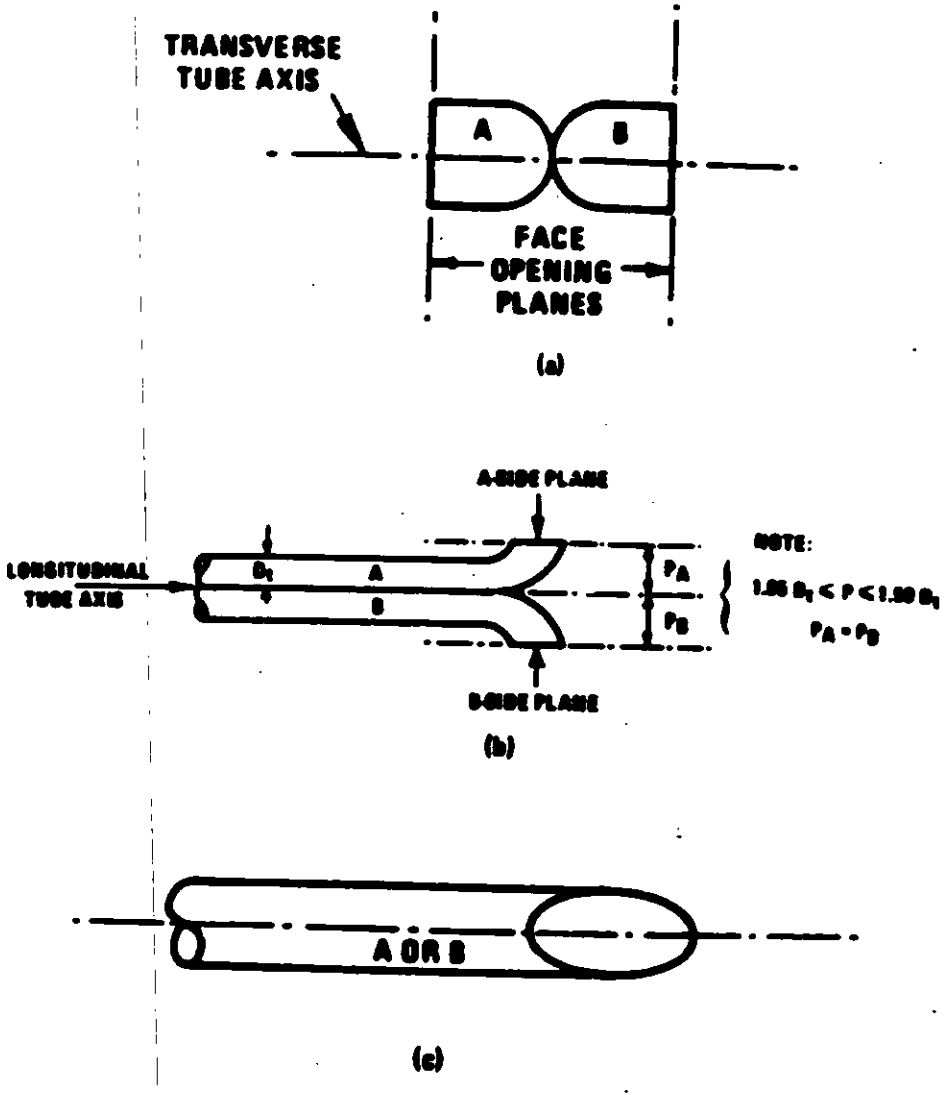


Figure 2-2. Properly constructed Type S pitot tube, shown in: (a) end view; face opening planes perpendicular to transverse axis; (b) top view; face opening planes parallel to longitudinal axis; (c) side view; both legs of equal length and centerlines coincident, when viewed from both sides. Baseline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

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

2.7 Calibration Pitot Tube. When calibration of the Type S pitot tube is necessary (see Section 4), a standard pitot tube is used as a reference. The standard pitot tube shall, preferably, have a known coefficient, obtained either (1) directly from the National Bureau of Standards, Route 270, Quince Orchard Road, Gaithersburg, Maryland, or (2) by calibration against another standard pitot tube with an NBS-traceable coefficient. Alternatively, a standard pitot tube designed according to the criteria given in 2.7.1 through 2.7.5 below and illustrated in Figure 2-4 (see also Citations 7, 8, and 17 in Bibliography) may be used. Pitot tubes designed according to these specifications will have baseline coefficients of about 0.99 ± 0.01.

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

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

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

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

2.7.5 Ninety degree bend, with curved or mitered junction.

2.8 Differential Pressure Gauge for Type S Pitot Tube Calibration. An inclined manometer or equivalent is used. If the single-velocity calibration technique is employed (see Section 4.1.2.3), the calibration differential pressure gauge shall be readable to the nearest 0.13 mm H2O (0.005 in. H2O). For multivelocity calibrations, the gauge shall be readable to the nearest 0.13 mm H2O (0.005 in. H2O) for delta p values between 1.3 and 25 mm H2O (0.05 and 1.0 in. H2O), and to the nearest 1.3 mm H2O (0.05 in. H2O) for delta p values above 25 mm H2O (1.0 in. H2O). A special, more sensitive gauge will be required to read delta p values below 1.3 mm H2O (0.05 in. H2O) (see Citation 18 in Bibliography).

3. Procedure

3.1 Set up the apparatus as shown in Figure 2-1. Capillary tubing or surge tanks installed between the manometer and pitot tube may be used to dampen delta p fluctuations. It is recommended, but not required, that a pretest leak-check be conducted, as follows: (1) blow through the pitot impact opening until at least 7.6 cm (3 in.) H2O velocity pressure registers on the manometer; then, close off the impact opening. The pressure shall remain stable for at least 15 seconds; (2) do the same for the static pressure side, except using suction to obtain the minimum of 7.6 cm (3 in.) H2O. Other leak-check procedures, subject to the approval of the Administrator, may be used.

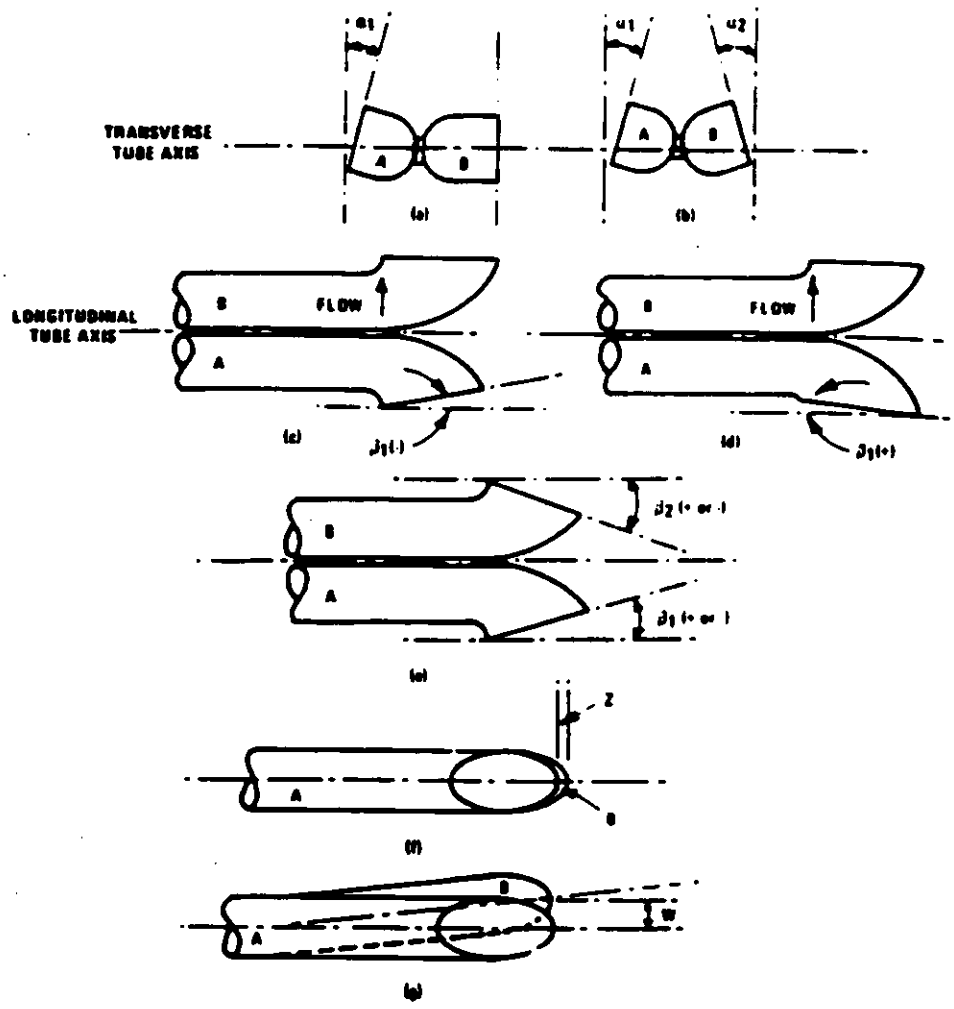


Figure 2-3. Types of face-opening misalignment that can result from field use or improper construction of Type S pitot tubes. These will not affect the baseline value of Cp(s) so long as $\alpha^1 \leq 10°$, β^1 and $\beta^2 \leq 5°$, $z \leq 0.32$ cm (1/8 in.) and $w \leq 0.08$ cm (1/32 in.) (citation 11 in Bibliography).

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

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

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

3.5 Determine the atmospheric pressure.

3.6 Determine the stack gas dry molecular weight. For combustion processes or processes that emit essentially CO2, O2, CO, and N2, use Method 3. For processes emitting ing essentially air, an analysis need not be conducted; use a dry molecular weight of 29.0. For other processes, other methods, subject to the approval of the Administrator, must be used.

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

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

blueprints.

4. Calibration

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

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

If Dt, PA, and PB are outside the specified limits, the pitot tube must be calibrated as outlined in 4.1.2 through 4.1.5 below.

4.1.1 Type S Pitot Tube Assemblies. During sample and velocity traverses, the isolated Type S pitot tube is not always used; in many instances, the pitot tube is used in combination with other source-sampling components (thermocouple, sampling probe, nozzle) as part of an "assembly." The presence of other sampling components can sometimes affect the baseline value of the Type S pitot tube coefficient (Citation 9 in Bibliography); therefore an assigned (or otherwise known) baseline coefficient value may or may not be valid for a given assembly. The baseline and assembly coefficient values will be identical only when the relative placement of the components in the assembly is such that aerodynamic interference effects are eliminated. Figures 2-6 through 2-8 illustrate interference-free component arrangements for Type S pitot tubes having external tubing diameters between 0.48 and 0.95 cm (3/16 and 3/8 in.). Type S pitot tube assemblies that fail to meet any or all of the specifications of Figures 2-6 through 2-8 shall be calibrated according to the procedure outlined in Sections 4.1.2 through 4.1.5 below, and prior to calibration, the values of the intercomponent spacings (pitot-nozzle, pitot-thermocouple, pitot-probe sheath) shall be measured and recorded.

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

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

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

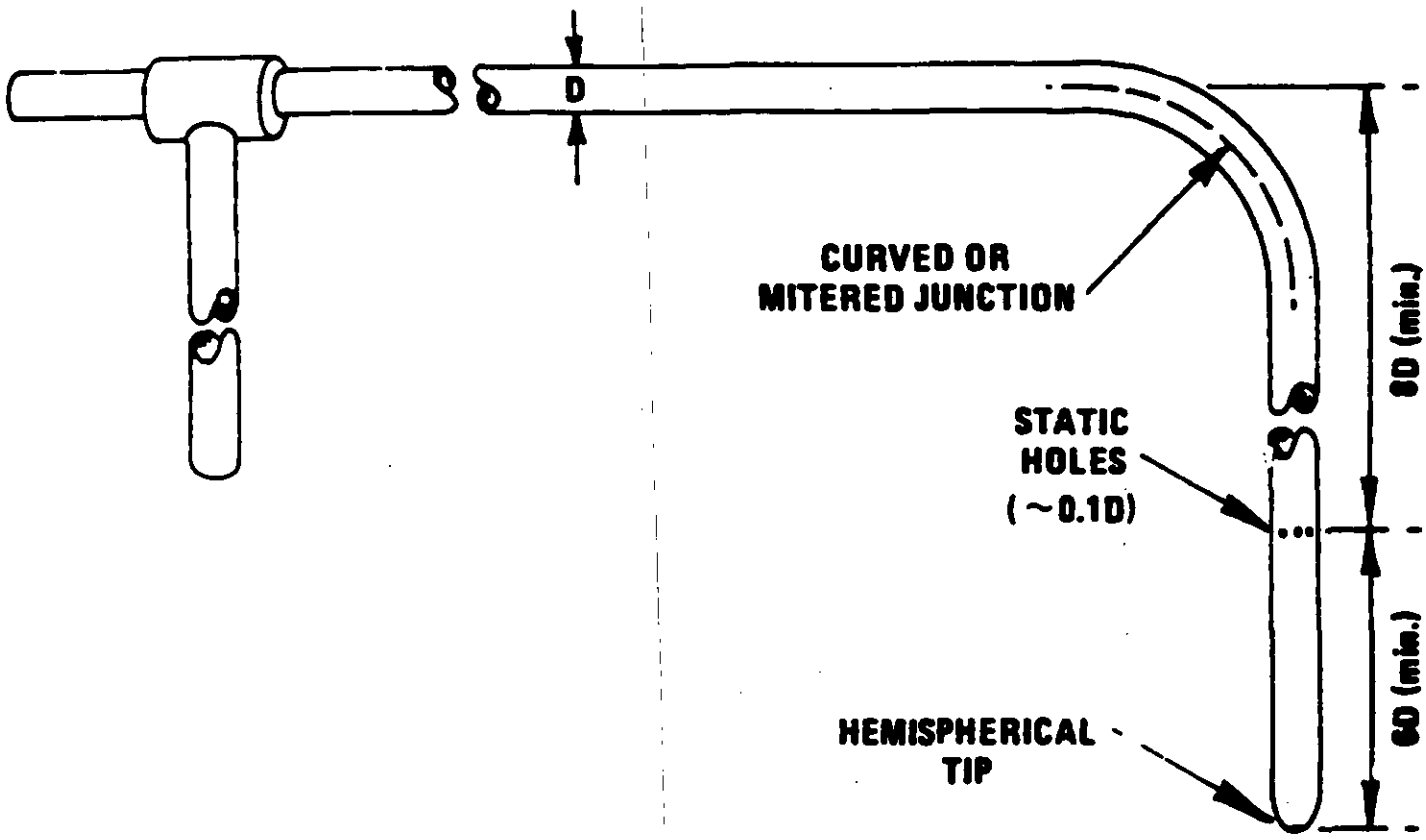


Figure 2-4. Standard pitot tube design specifications.

PLANT _____

DATE _____ RUN NO. _____

STACK DIAMETER OR DIMENSIONS, m(in.) _____

BAROMETRIC PRESSURE, mm Hg (in. Hg) _____

CROSS SECTIONAL AREA, $m^2(ft^2)$ _____

OPERATORS _____

PITOT TUBE I.D. NO. _____

AVG. COEFFICIENT, C_p = _____

LAST DATE CALIBRATED _____

SCHEMATIC OF STACK CROSS SECTION

Traverse Pt. No.	Vel. Hd., Δp mm (in.) H_2O	Stack Temperature t_s, °C (°F)	Stack Temperature T_s, °K (°R)	P_g mm Hg (in.Hg)	$\sqrt{\Delta p}$
		Average			

Figure 2-5. Velocity traverse data.

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

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

$$De = \frac{2LW}{(L+W)} \qquad \text{Eq. 2-1}$$

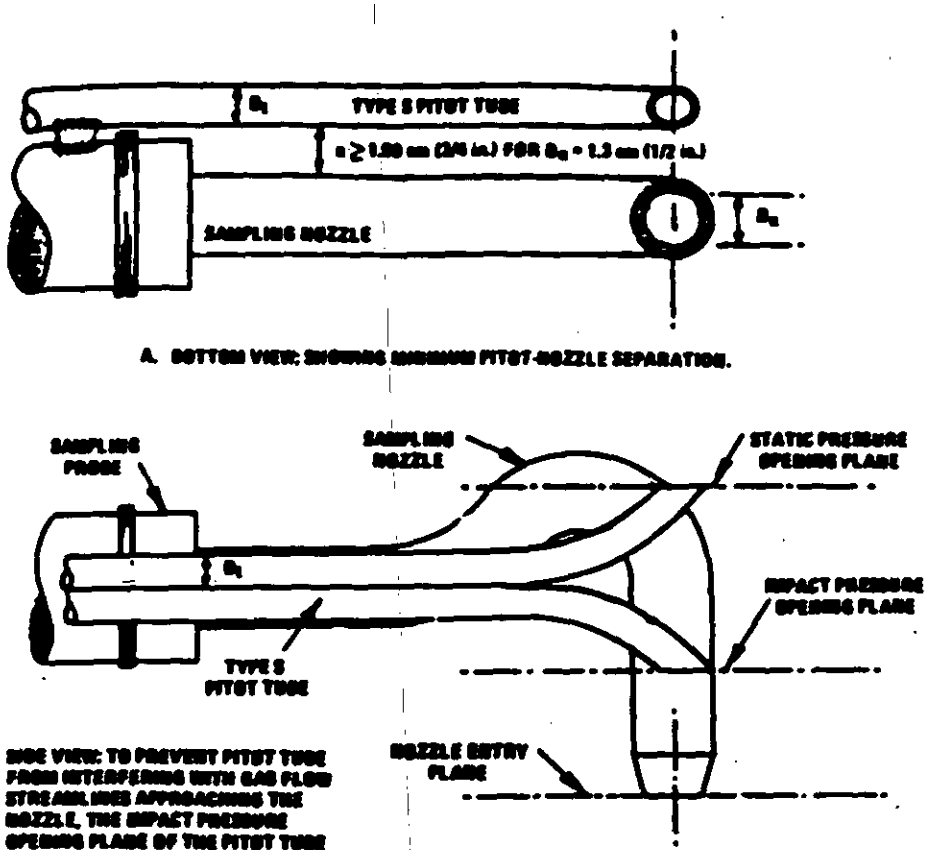
Where:
De = Equivalent diameter
L = Length
W = Width

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

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

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

4.1.2.4 Two entry ports, one each for the standard and Type S pitot tubes, shall be cut in the test section; the standard pitot entry port shall be located slightly downstream of the Type S port, so that the standard and Type S impact openings will lie in the same cross-sectional plane during



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

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

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

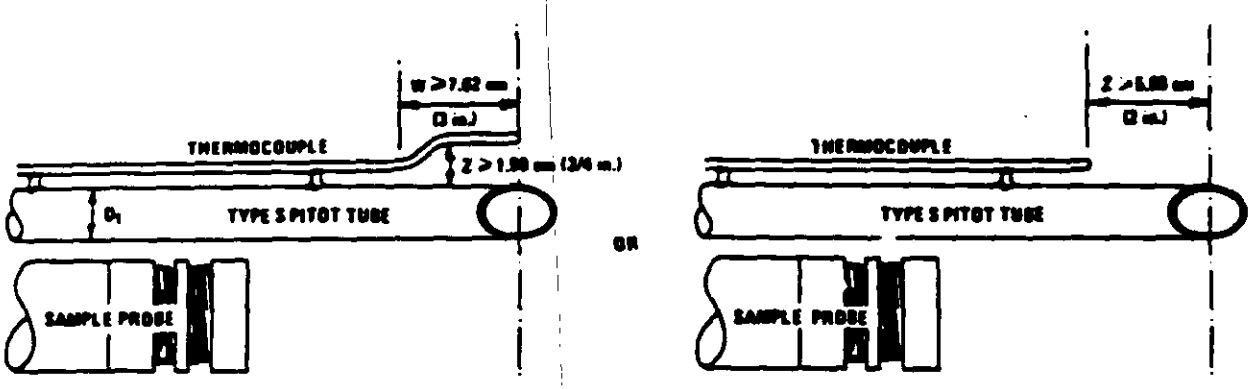


Figure 2-7. Proper thermocouple placement to prevent interference; D_t between 0.48 and 0.95 cm (3/16 and 3/8 in.).

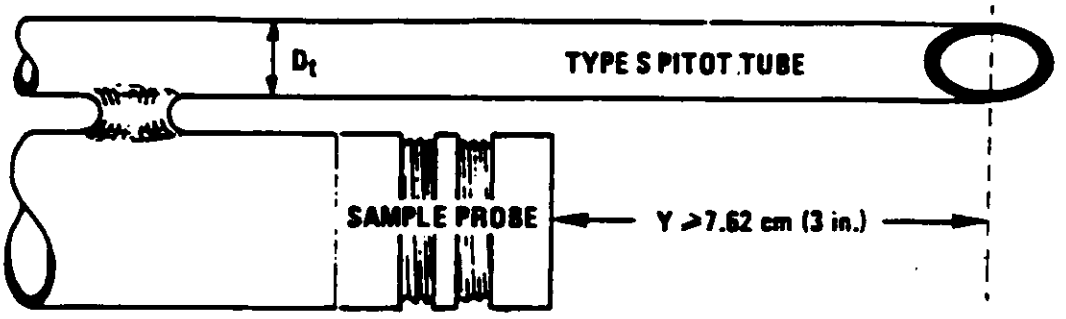


Figure 2-8. Minimum pitot-sample probe separation needed to prevent interference; D_t between 0.48 and 0.95 cm (3/16 and 3/8 in.).

PITOT TUBE IDENTIFICATION NUMBER: _____ DATE: _____

CALIBRATED BY: _____

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

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

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

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

Figure 2-9. Pitot tube calibration data.

calibration. To facilitate alignment of the pitot tubes during calibration, it is advisable that the test section be constructed of plexiglas or some other transparent material.

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

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

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

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

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

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

4.1.3.6 Read delta p8 and enter its value in the data table. Remove the Type S pitot tube from the duct and disconnect it from the manometer.

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

4.1.3.8 Repeat steps 4.1.3.3 through 4.1.3.7 above for the B side of the Type S pitot tube.

4.1.3.9 Perform calculations, as described in Section 4.1.4 below.

4.1.4 Calculations.

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

$$C_{p(s)} = C_{p(std)} \sqrt{\frac{\overline{\Delta p}_{std}}{\overline{\Delta p}_{s}}}$$

Equation 2-2

Where:

Cp(s) = Type S pitot tube coefficient

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

DELTA pstd = Velocity head measured by the standard pitot tube, cm H2O (in. H2O)

DELTA ps = Velocity head measured by the Type S pitot tube, cm H2O (in. H2O)

4.1.4.2 Calculate C *bar* p (side A), the mean A-side coefficient, and C *bar* p (side B), the mean B-side coefficient; calculate the difference between these two average values.

4.1.4.3 Calculate the deviation of each of the three A-side values of Cp(s) from C *bar* p (side A), and the deviation of each B-side value of Cp(s) from C *bar* p (side B). Use the following equation:

$$\text{Deviation} = Cp(s) - \overline{Cp}\ (\text{A or B})$$

Equation 2-3

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

$$\sigma\ (\text{side A or B}) = \frac{\sum_{1}^{3} |C_{p(s)} - \overline{C}_{p}(A \text{ or } B)|}{3}$$

Equation 2-4

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

4.1.5 Special considerations.

4.1.5.1 Selection of calibration point.

4.1.5.1.1 When an isolated Type S pitot tube is calibrated, select a calibration point at or near the center of the duct, and follow the procedures outlined in Sections 4.1.3 and 4.1.4 above. The Type S pitot coefficients so obtained, i.e., C *bar* p (side A) and C *bar* p (side B), will be valid, so long as either: (1) the isolated pitot tube is used; or (2) the pitot tube is used with other components (nozzle, thermocouple, sample probe) in an arrangement that is free from aerodynamic interference effects (see Figures 2-6 through 2-8).

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

4.1.5.1.3 For assemblies with sample probes, the calibration point should be located at or near the center of the duct; however, insertion of a probe sheath into a small duct may cause significant cross-sectional area blockage and yield incorrect coefficient values (Citation 9 in Bibliography). Therefore, to minimize the blockage effect, the calibration point may be a few inches off-center if necessary. The actual blockage effect will be negligible when the theoretical blockage, as determined by a projected-area model of the probe sheath, is 2 percent or less of the duct cross-sectional area for assemblies without external sheaths (Figure 2-10a), and 3 percent or less for assemblies with external sheaths (Figure 2-10b).

4.1.5.2 For those probe assemblies in which pitot tube-nozzle interference is a factor (i.e., those in which the pitot-nozzle separation distance fails to meet the specification illustrated in Figure 2-6a), the value of Cp(s) depends upon the amount of free-space between the tube and nozzle, and therefore is a function of nozzle size. In these instances, separate calibrations shall be performed with each of the commonly used nozzle sizes in place. Note that the single-velocity calibration technique is acceptable for this purpose, even though the larger nozzle sizes (> 0.635 cm or ¼ in.) are not ordinarily used for isokinetic sampling at velocities around 915 m/min (3,000 ft/min), which is the calibration velocity; note also that it is not necessary to draw an isokinetic sample during calibration (see Citation 19 in Section 6).

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

4.1.6 Field Use and Recalibration.

4.1.6.1 Field Use.

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

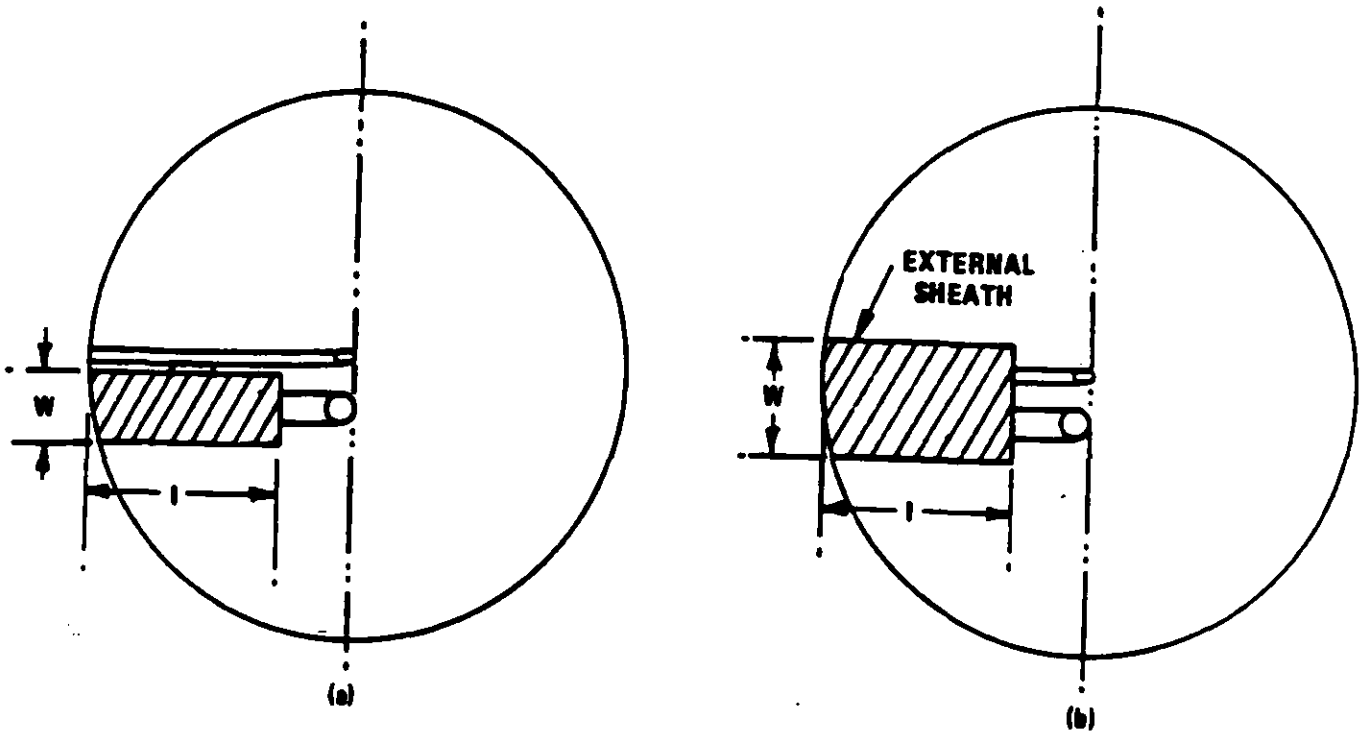
4.1.6.1.2 When a probe assembly is used to sample a small duct (12 to 36 in. in diameter), the probe sheath sometimes blocks a significant part of the duct cross-section, causing a reduction in the effective value of Cp(s). Consult Citation 9 in Bibliography for details. Conventional pitot-sampling probe assemblies are not recommended for use in ducts having inside diameters smaller than 12 inches (Citation 16 in Bibliography).

4.1.6.2 Recalibration.

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

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

4.2 Standard pitot tube (if applicable). If a standard pitot tube is used for the



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

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

velocity traverse, the tube shall be constructed according to the criteria of Section 2.7 and shall be assigned a baseline coefficient value of 0.99. If the standard pitot tube is used as part of an assembly, the tube shall be in an interference-free arrangement (subject to the approval of the Administrator).

4.3 Temperature Gauges. After each field use, calibrate dial thermometers, liquid-filled bulb thermometers, thermocouple-potentiometer systems, and other gauges at a temperature within 10 percent of the average absolute stack temperature. For temperatures up to 405°C (761°F), use an ASTM mercury—in—glass reference thermometer, or equivalent, as a reference; alternatively, either a reference thermocouple and potentiometer (calibrated by NBS) or thermometric fixed points, e.g., ice bath and boiling water (corrected for barometric pressure) may be used. For temperatures above 405°C (761°F), use an NBS-calibrated reference thermocouple-potentiometer system or an alternate reference, subject to the approval of the Administrator.

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

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

5. Calculations

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

5.1 Nomenclature.

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

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

Cp = Pitot tube coefficient, dimensionless.

Kp = Pitot tube constant,

$$34.97 - \left[\frac{m\ [(g/g\text{—mole})(mm\ Hg)]^{1/2}}{sec\ [\ (°K)(mmH2O)\ ]}\right]$$

for the metric system and

$$85.49 - \left[\frac{ft\ [(lb/lb\text{—mole})(in\ Hg)]^{1/2}}{sec\ [\ (°R)(in\ H2O)\ ]}\right]$$

for the English system.

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

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

$$= Md\ (1\text{-}Bws) + 18.0\ Bws \qquad \text{Eq. 2-5}$$

Pbar = Barometric pressure at measurement site, mm Hg (in. Hg).

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

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

$$= Pbar + Pg \qquad \text{Eq. 2-6}$$

Pstd = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).

Qsd = Dry volumetric stack gas flow rate corrected to standard conditions, dscm/hr (dscf/hr).

ts = Stack temperature, °C (°F).

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

= 273+ts for metric. Eq. 2-7

= 460+ts for English. Eq. 2-8

Tstd = Standard absolute temperature, 293 °K (528°R).

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

delta p = Velocity head of stack gas, mm H2O (in. H2O).

3,600 = Conversion factor, sec/hr.

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

5.2 Average Stack Gas Velocity.

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

Equation 2-9

5.3 Average Stack Gas Dry Volumetric Flow Rate.

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

Eq. 2-10

To convert Qsd from dscm/hr (dscf/hr) to dscm/min (dscf/min), divide Qsd by 60.

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Method 3—Gas Analysis for the Determination of Dry Molecular Weight

1. Applicability and Principle

1.1 Applicability.

1.1.1 This method is applicable for determining carbon dioxide (CO2) and oxygen (O2) concentrations and dry molecular weight of a sample from a gas stream of a fossil-fuel combustion process. The method may also be applicable to other processes where it has been determined that compounds other than CO2, O2, carbon monoxide (CO), and nitrogen (N2) are not present in concentrations sufficient to affect the results.

1.1.2 Other methods, as well as modifications to the procedure described herein, are also applicable for some or all of the above determinations. Examples of specific methods and modifications include: (1) A multi-point sampling method using an Orsat analyzer to analyze individual grab samples obtained at each point; (2) a method using CO2 or O2 and stoichiometric calculations to determine dry molecular weight; and (3) assigning a value of 30.0 for dry molecular weight, in lieu of actual measurements, for processes burning natural gas, coal, or oil. These methods and modifications may be used, but are subject to the approval of the Administrator, U.S. Environmental Protection Agency (EPA).

1.1.3 Note. Mention of trade names or specific products does not constitute endorsements by EPA.

1.2 Principle. A gas sample is extracted from a stack by one of the following methods: (1) Single-point, grab sampling; (2) single-point, integrated sampling; or (3) multi-point, integrated sampling. The gas sample is analyzed for pecent CO2, percent O2, and if necessary, for percent CO. For dry molecular weight determination, either an Orsat or a Fyrite analyzer may be used for the analysis.

2. Apparatus

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

2.1 Grab Sampling (Figure 3-1).

2.1.1 Probe. Stainless steel or borosilicate glass tubing equipped with an in-stack or out-stack filter to remove particulate matter (a plug of glass wool is satisfactory for this purpose). Any other materials, inert to O2, CO2, CO, and N2 and resistant to temperature at sampling conditions, may be used for the probe. Examples of such materials are aluminum, copper, quartz glass, and Teflon.

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

2.2 Integrated Sampling (Figure 3-2).

2.2.1 Probe. Same as in Section 2.1.1.

2.2.2 Condenser. An air-cooled or water-cooled condenser, or other condenser no greater than 250 ml that will not remove O2, CO2, CO, and N2, to remove excess moisture which would interfere with the operation of the pump and flowmeter.

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

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

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

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

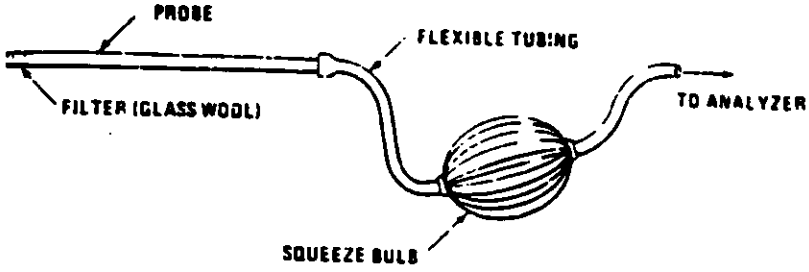

Figure 3-1. Grab sampling train.

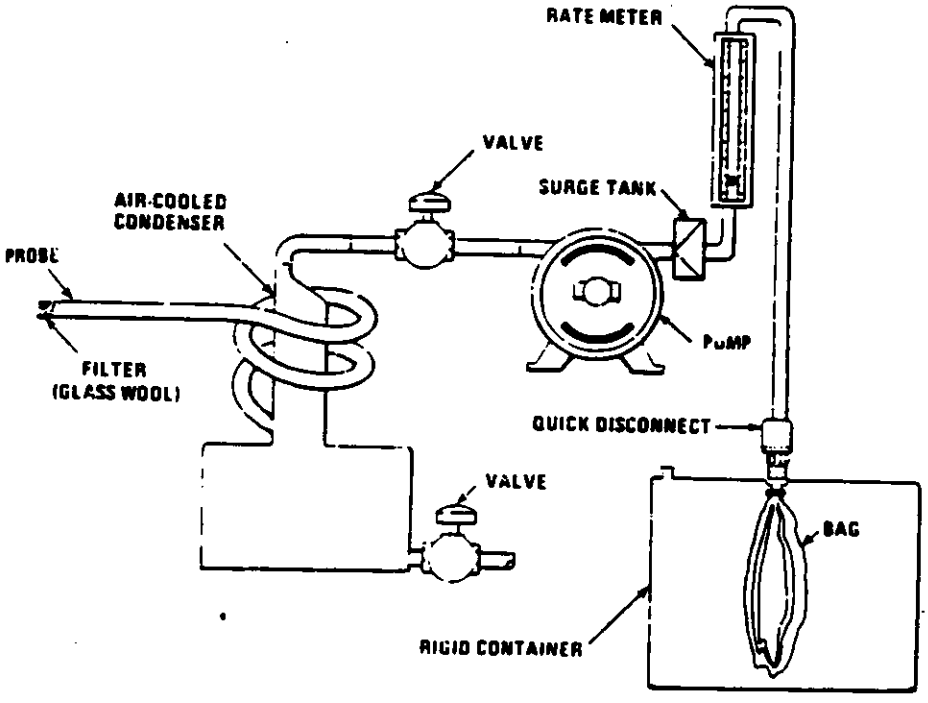

Figure 3-2. Integrated gas-sampling train.

it to a water manometer, and pressurize the bag to 5 to 10 cm H2O (2 to 4 in. H2O). Allow to stand for 10 minutes. Any displacement in the water manometer indicates a leak. An alternative leak-check method is to pressurize the bag to 5 to 10 cm (2 to 4 in.) H2O and allow to stand overnight. A deflated bag indicates a leak.

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

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

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

3. Single-Point, Grab Sampling and Analytical Procedure

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

3.2 Set up the equipment as shown in Figure 3-1, making sure all connections ahead of the analyzer are tight. If an Orsat analyzer is used, it is recommended that the analyzer be leak checked by following the procedure in Section 6; however, the leak check is optional.

3.3 Place the probe in the stack, with the tip of the probe positioned at the sampling point; purge the sampling line long enough to allow at least five exchanges. Draw a sample into the analyzer, and immediately analyze it for percent CO2 and percent O2. Determine the percentage of the gas that is N2 and CO by subtracting the sum of the percent CO2 and percent 02O from 100 percent. Calculate the dry molecular weight as indicated in Section 7.2.

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

4. Single-Point, Integrated Sampling and Analytical Procedure

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

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

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

4.4 Obtain one integrated flue gas sample during each pollutant emission rate determination. Within 8 hours after the sample is taken, analyze it for percent CO2 and percent O2 using either an Orsat analyzer or a Fyrite type combustion gas analyzer. If an Orsat analyzer is used, it is recommended that Orsat leak check described in Section 6, be performed before this determination; however, the check is optional. Determine the percentage of the gas that is N2 and CO by subtracting the sum of the percent CO2 and percent 0 from 100 percent. Calculate the dry molecular weight as indicated in Section 7.2.

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

5. Multi-Point, Integrated Sampling and Analytical Procedure

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

5.2 Follow the procedures outlined in Sections 4.2 through 4.5, except for the following: Traverse all sampling points, and sample at each point for an equal length of time. Record sampling data as shown in Figure 3-3.

Time	Traverse pt	Q, liter/min	% dev.*
Average			

a % dev. = (Q—Qavg)/Qavg X 100 (Must be | ± 10%)

Figure 3-3. Sampling rate data.

6. Leak-Check Procedure for Orsat Analyzer

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

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

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

6.3 Record the meniscus position.

6.4 Observe the menisus in the burette and the liquid level in the pipette for movement over the next 4 minutes.

6.5 For the Orsat analyzer to pass the leak check, two conditions must be met:

6.5.1 The liquid level in each pipette must not fall below the botton of the capillary tubing during this 4—minute interval.

6.5.2 The menisus in the burette must not change by more than 0.2 ml during this 4—minute interval.

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

7. Calculations

7.1 Nomenclature

Md = Dry molecular weight, g/g—mole (1b/1b—mole).

%CO2 = Percent CO2 by volume, dry basis.

%O2 = Percent O2 by volume, dry basis.

%CO = Percent CO by volume, dry basis.

%N2 = Percent N2 by volume, dry basis.

0.280 = Molecular weight of N2 or CO, divided by 100.

0.320 = Molecular wight of O2 divided by 100.

0.440 = Molecular weight of CO2 divided by 100.

7.2 Dry Molecular Weight. Use Equation 3-1 to calculate the dry molecular weight of the stack gas.

$$Md = 0.440(\%CO2) + 0.320(\%O2) + 0.280(\%N2 + \%CO) \quad \text{Eq. 3-1}$$

Note. The above equation does not consider argon in air (about 0.9 percent, molecular weight of 39.9). A negative error of about 0.4 percent is introduced. The tester may choose to include argon in the analysis using procedures subject to approval of the Administrator.

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Method 3A—Determination of Oxygen and Carbon Dioxide Concentrations in Emissions From Stationary Sources (Instrumental Analyzer Procedure)

1. Applicability and Principle

1.1 Applicability. This method is applicable to the determination of oxygen (O2) and carbon dioxide (CO2) concentrations in emissions from stationary sources only when specified within the regulations.

1.2 Principle. A sample is continuously extracted from the effluent stream; a portion of the sample stream is conveyed to an instrumental analyzer(s) for determination of O2 and CO2 concentration(s). Performance specifications and test procedures are provided to ensure reliable data.

2. Range and Sensitivity

Same as Method 6C, Sections 2.1 and 2.2, except that the span of the monitoring system shall be selected such that the average O2 or CO2 concentration is not less than 20 percent of the span.

3. Definitions

3.1 Measurement System. The total equipment required for the determination of the O2 or CO2 concentration. The measurement system consists of the same major subsystems as defined in Method 6C, Sections 3.1.1, 3.1.2, and 3.1.3.

3.2 Span, Calibration Gas, Analyzer Calibration Error, Sampling System Bias, Zero Drift, Calibration Drift, Response Time, and Calibration Curve. Same as Method 6C, Sections 3.2 through 3.8, and 3.10.

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

4. Measurement System Performance Specifications

Same as Method 6C, Sections 4.1 through 4.4.

5. Apparatus and Reagents

5.1 Measurement System. Any measurement system for O2 or CO2 that meets the specifications of this method. A schematic of an acceptable measurement system is shown in Figure 6C-1 of Method 6C. The essential components of the measurement system are described below:

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

5.1.2 Sample Line. Tubing, to transport the sample gas from the probe to the moisture removal system. A heated sample line is not required for systems that measure the O2 or CO2 concentration on a dry basis, or transport dry gases.

5.1.3 Sample Transport Line, Calibration Value Assembly, Moisture Removal System, Particulate Filter, Sample Pump, Sample Flow Rate Control, Sample Gas Manifold, and Data Recorder. Same as Method 6C, Sections 5.1.3 through 5.1.9, and 5.1.11, except that the requirements to use stainless steel, Teflon, and nonreactive glass filters do not apply.

5.1.4 Gas Analyzer. An analyzer to determine continuously the O2 or CO2 concentration in the sample gas stream. The analyzer shall meet the applicable performance specifications of Section 4. A means of controlling the analyzer flow rate and a device for determining proper sample flow rate (e.g., precision rotameter, pressure gauge downstream of all flow controls, etc.) shall be provided at the analyzer. The requirements for measuring and controlling the analyzer flow rate are not applicable if data are presented that demonstrate the analyzer is insensitive to flow variations over the range encountered during the test.

5.2 Calibration Gases. The calibration gases for CO2 analyzers shall be CO2 in N2 or CO2 in air. Alternatively, CO2/SO2, O2/SO2, or O2/CO2/SO2 gas mixtures in N2 may be used. Three calibration gases, as specified Section 5.3.1 through 5.3.3 of Method 6C, shall be used. For O2 monitors that cannot analyze zero gas, a calibration gas concentration equivalent to less than 10 percent of the span may be used in place of zero gas.

6. Measurement System Performance Test Procedures

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

6.1 Calibration Concentration Verification. Follow Section 6.1 of Method 6C, except if calibration gas analysis is required, use Method 3 and change the acceptance criteria for agreement among Method 3 results to 5 percent (or 0.2 percent by volume, whichever is greater).

6.2 Interference Response. Conduct an interference response test of the analyzer prior to its initial use in the field. Thereafter, recheck the measurement system if changes are made in the instrumentation that could alter the interference response (e.g., changes in the type of gas detector). Conduct the interference response in accordance with Section 5.4 of Method 20.

6.3 Measurement System Preparation, Analyzer Calibration Error, and Sampling System Bias Check. Follow Sections 6.2 through 6.4 of Method 6C.

7. Emission Test Procedure

7.1 Selection of Sampling Site and Sampling Points. Select a measurement site and sampling points using the same criteria that are applicable to tests performed using Method 3.

7.2 Sample Collection. Position the sampling probe at the first measurement point, and begin sampling at the same rate as used during the sampling system bias check. Maintain constant rate sampling (i.e., ± 10 percent) during the entire run. The sampling time per run shall be the same as for tests conducted using Method 3 plus twice the system response time. For each run, use only those measurements obtained after twice the response time of the measurement system has elapsed to determine the average effluent concentration.

7.3 Zero and Calibration Drift Test. Follow Section 7.4 of Method 6C.

8. Quality Control Procedures

The following quality control procedures are recommended when the results of this method are used for an emission rate correction factor, or excess air determination. The tester should select one of the following options for validating measurement results:

8.1 If both O2 and CO2 are measured using Method 3A, the procedures described in Section 4.4 of Method 3 should be followed to validate the O2 and CO2 measurement results.

8.2 If only O2 is measured using Method 3A, measurements of the sample stream CO2 concentration should be obtained at the sample by-pass vent discharge using an Orsat or Fyrite analyzer, or equivalent. Duplicate samples should be obtained concurrent with at least one run. Average the duplicate Orsat or Fyrite analysis results for each run. Use the average CO2 values for comparison with the O2 measurements in accordance with the procedures described in Section 4.4 of Method 3.

8.3 If only CO2 is measured using Method 3A, concurrent measurements of the sample stream CO2 concentration should be obtained using an Orsat or Fyrite analyzer as described in Section 8.2. For each run, differences greater than 0.5 percent between the Method 3A results and the average of the duplicate Fyrite analysis should be investigated.

9. Emission Calculation

For all CO2 analyzers, and for O2 analyzers that can be calibrated with zero gas, follow Section 8 of Method 6C, except express all concentrations as

percent, rather than ppm.

For O2 analyzers that use a low-level calibration gas in place of a zero gas, calculate the effluent gas concentration using Equation 3A-1.

$$C_{gas} = \frac{C_{ma} - C_{oa}}{C_m - C_o} (C - C_o) + C_{ma}$$

Where: Eq. 3A-1

Cgas = Effluent gas concentration, dry basis, percent.

Cma = Actual concentration of the upscale calibration gas, percent.

Coa = Actual concentration of the low-level calibration gas, percent.

Cm = Average of initial and final system calibration bias check responses for the upscale calibration gas, percent.

Co = Average of initial and final system calibration bias check responses for the low-level gas, percent.

C "bar" = Average gas concentration indicated by the gas analyzer, dry basis, percent.

10. Bibliography

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Method 4—Determination of Moisture Content in Stack Gases

1. Principle and Applicability

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

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

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

The reference method is often conducted simultaneously with a pollutant emission measurement run; when it is, calculation of percent isokinetic, pollutant emission rate, etc., for the run shall be based upon the results of the reference method or its equivalent; these calculations shall not be based upon the results of the approximation method, unless the approximation method is shown, to the satisfaction of the Administrator, U.S. Environmental Protection Agency, to be capable of yielding results within 1 percent H2O of the reference method.

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

2. Reference Method

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

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

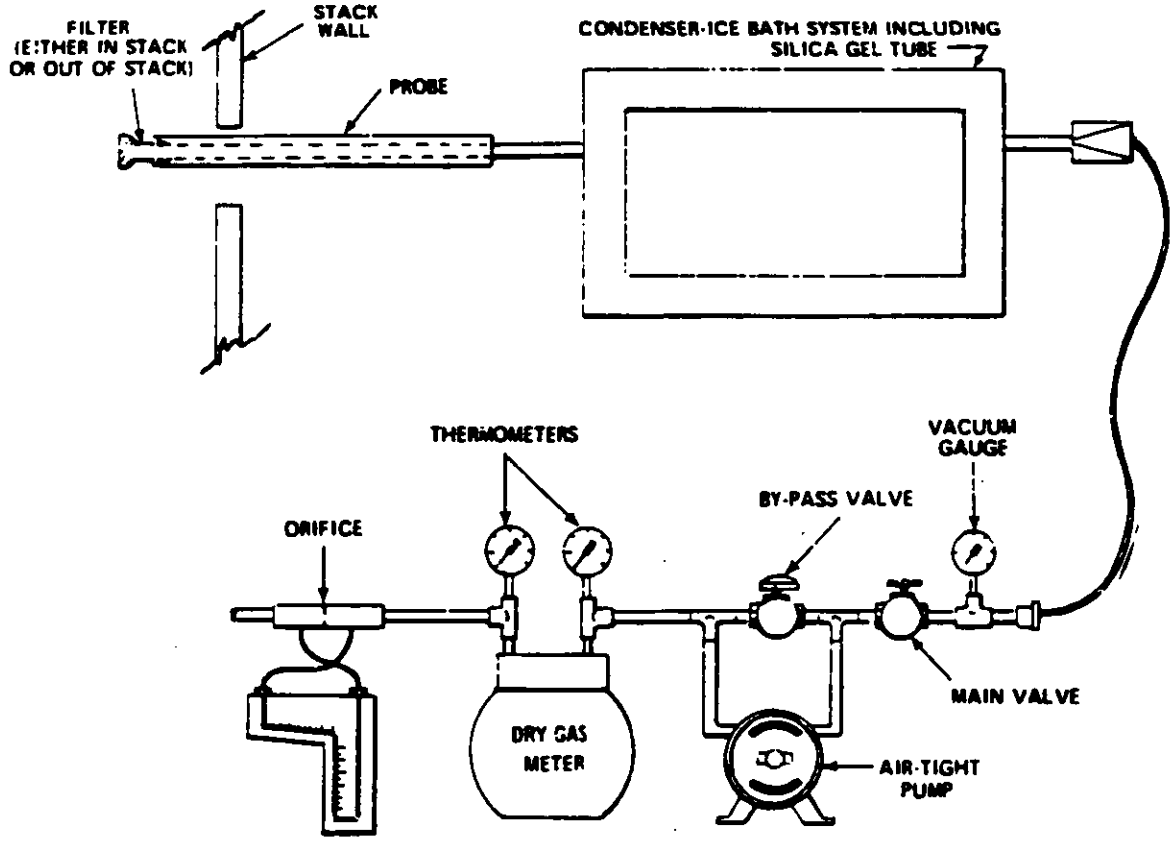

Figure 4-1. Moisture sampling train-reference method.

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

When stack conditions permit, other metals or plastic tubing may be used for the probe, subject to the approval of the Administrator.

2.1.2 Condenser. The condenser consists of four impingers connected in series with ground glass, leak-free fittings or any similarly leak-free non-contaminating fittings. The first, third, and fourth impingers shall be of the Greenburg-Smith design, modified by replacing the tip with a 1.3 centimeter (½ inch) ID glass tube extending to about 1.3 cm (½ in.) from the bottom of the flask. The second impinger shall be of the Greenburg-Smith design with the standard tip. Modifications (e.g., using flexible connections between the impingers, using materials other than glass, or using flexible vacuum lines to connect the filter holder to the condenser) may be used, subject to the approval of the Administrator.

The first two impingers shall contain known volumes of water, the third shall be empty, and the fourth shall contain a known weight of 6— to 16—mesh indicating type silica gel, or equivalent desiccant. If the silica gel has been previously used, dry at 175°C (350°F) for 2 hours. New silica gel may be used as received. A thermometer, capable of measuring temperature to within 1°C (2°F), shall be placed at the outlet of the fourth impinger, for monitoring purposes.

Alternatively, any system may be used (subject to the approval of the Administrator) that cools the sample gas stream and allows measurement of both the water that has been condensed and the moisture leaving the condenser, each to within 1 ml or 1 g. Acceptable means are to measure the condensed water, either gravimetrically or volumetrically, and to measure the moisture leaving the condenser by: (1) monitoring the temperature and pressure at the exit of the condenser and using Dalton's law of partial pressures, or (2) passing the sample gas stream through a tared silica gel (or equivalent desiccant) trap, with exit gases kept below 20°C (68°F), and determining the weight gain.

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

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

2.1.4 Metering System. This system includes a vacuum gauge, leak-free pump, thermometers capable of measuring temperature to within 3°C (5.4°F), dry gas meter capable of measuring volume to within 2 percent, and related equipment as shown in Figure 4-1. Other metering systems, capable of maintaining a constant sampling rate and determining sample gas volume, may be used, subject to the approval of the Administrator.

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

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

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

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

2.2.2 Select a total sampling time such that a minimum total gas volume of 0.60 scm (21 scf) will be collected, at a rate no greater than 0.021 m^3/min (0.75 cfm). When both moisture content and pollutant emission rate are to be determined, the moisture determination shall be simultaneous with, and for the same total length of time as, the pollutant emission rate run, unless otherwise specified in an applicable subpart of the standards.

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

2.2.4 During the sampling run, maintain a sampling rate within 10 percent of constant rate, or as specified by the Administrator. For each run, record the data required on the example data sheet shown in Figure 4-2. Be sure to record the dry gas meter reading at the beginning and end of each sampling time increment and whenever sampling is halted. Take other appropriate readings at each sample point, at least once during each time increment.

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

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

FIGURE 4-2—FIELD MOISTURE DETERMINATION REFERENCE METHOD

Plant.....
Location.....
Operator.....
Date.....
Run No.....
Ambient temperature.....
Barometric pressure.....
Probe length m (ft).....

SCHEMATIC OF STACK CROSS SECTION

Traverse point number	Sampling time (θ), min.	Stack temperature °C (°F)	Pressure differential across orifice meter ΔH mm (in.) H_2O	Meter reading gas sample volume m^3 (ft^3)	ΔV_m m^3 (ft^3)	Gas Sample temperature at dry gas meter: Inlet ($T_{m_{in}}$), °C (°F)	Gas Sample temperature at dry gas meter: Outlet ($T_{m_{out}}$), °C (°F)	Temperaturem of gas leaving condenser or last impinger °C (°F)
Total.....								
Average.....					Avg.	Avg.	Avg.	

information (see example data sheet, Figure 4-3) and calculate the moisture percentage, as described in 2.3 below.

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

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

Figure 4-3—Analytical Data—Reference Method

	Impinger volume, ml	Silica gel weight, g
Final.....		
Initial.....		
Difference.....		

2.3.1 Nomenclature.

B ws = Proportion of water vapor, by volume, in the gas stream.

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

P m = Absolute pressure (for this method, same as barometric pressure) at the dry gas meter, mm Hg (in. Hg).

P std = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).

R = Ideal gas constant, 0.06236 (mm Hg) (m^3)/(g—mole) (°K) for metric units and 21.85 (in. Hg) (ft^3)/(lb—mole) (°R) for English units.

T m = Absolute temperature at meter, °K (°R).

T std = Standard absolute temperature, 293°K (528°R).

V m = Dry gas volume measured by dry gas meter, dcm (dcf).

delta V m = Incremental dry gas volume measured by dry gas meter at each traverse point, dcm (dcf).

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

V wc(std) = Volume of water vapor condensed corrected to standard conditions, scm (scf).

V wsg(std) = Volume of water vapor collected in silica gel corrected to standard conditions, scm (scf).

V f = Final volume of condenser water, ml.

V i = Initial volume, if any, of condenser water, ml.

W f = Final weight of silica gel or silica gel plus impinger, g.

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

Y = Dry gas meter calibration factor.

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

2.3.2 Volume of Water Vapor Condensed.

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

$$= K_1 (V_f - V_i)$$

Eq. 4-1

Where:

K1 = 0.001333 m^3/ml for metric units
= 0.04707 ft^3/ml for English units

2.3.3 Volume of Water Vapor Collected in Silica Gel.

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

$$= K_2 (W_f - W_i)$$

Eq. 4-2

Where:

K 2 = 0.001335 m^3/g for metric units
= 0.04715 ft^3/g for English units

2.3.4 Sample Gas Volume.

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

$$= K_3 Y \frac{V_m P_m}{T_m}$$

Eq. 4-3

Where:

K 3 = 0.3858 °K/mm Hg for metric units

= 17.64 °R/in. Hg for English units

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

2.3.5 Moisture Content.

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

Eq. 4-4

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

2.3.6 Verification of Constant Sampling Rate. For each time increment, determine the delta V m. Calculate the average. If the value for any time increment differs from the average by more than 10 percent, reject the results and repeat the run.

3. Approximation Method

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

3.1 Apparatus.

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

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

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

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

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

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

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

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

3.1.9 Graduated Cylinder. 25 ml.

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

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

3.2 Procedure.

3.2.1 Place exactly 5 ml distilled water in each impinger.

Leak check the sampling train as follows: Temporarily insert a vacuum gauge at or near the probe inlet; then, plug the probe inlet and pull a vacuum of at least 250 mm Hg (10 in. Hg). Note the time rate of change of the dry gas meter dial; alternatively, a rotameter (0-40 cc/min) may be temporarily attached to the dry gas meter outlet to determine the leakage rate. A leak rate not in excess of 2 percent of the average sampling rate is acceptable.

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

FIGURE 4-5—FIELD MOISTURE DETERMINATION—APPROXIMATION METHOD

Location..... Comments:
Test.....
Date.....
Operator.....
Barometric pressure.....

Clock time	Gas volume through meter, (V_m), m³ (ft³)	Rate meter setting m³/min (ft³/min)	Meter temperature, °C (°F)

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

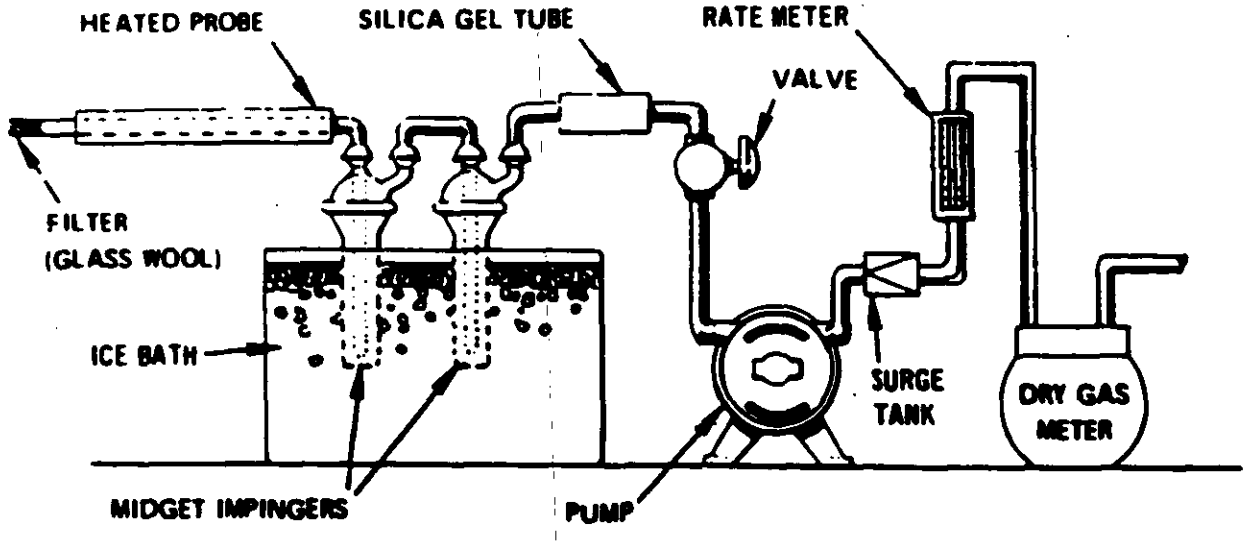

Figure 4-4. Moisture-sampling train - approximation method.

and dry gas meter readings as required by Figure 4-5.

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

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

3.3.1 Nomenclature.

Bwm = Approximate proportion, by volume, of water vapor in the gas stream leaving the second impinger, 0.025.

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

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

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

Pstd = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).

R = Ideal gas constant, 0.06236 (mm Hg) (m^3)/(g—mole) (°K) for metric units and 21.85 (in. Hg) (ft^3)/lb—mole) (°R) for English units.

Tm = Absolute temperature at meter, °K (°R).

Tstd = Standard absolute temperature, 293°K (528°R).

Vf = Final volume of impinger contents, ml.

Vi = Initial volume of impinger contents, ml.

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

Vm(std) = Dry gas volume measured by dry gas meter, corrected to standard conditions, dscm (dscf).

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

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

Y = Dry gas meter calibration factor.

3.3.2 Volume of Water Vapor Collected.

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

$$= K_1 (V_f - V_i)$$

Eq. 4-5

Where:

K1 = 0.001333 m^3/ml for metric units
= 0.04707 ft^3/ml for English units.

3.3.3 Gas Volume.

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

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

Equation 4-6

Where:

K2 = 0.3858 °K/mm Hg for metric units
= 17.64 °R/in. Hg for English units

3.3.4 Approximate Moisture Content.

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

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

Equation 4-7

4. Calibration

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

5. Bibliography

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

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

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

Method 6C—Determination of Sulfur Dioxide Emissions From Stationary Sources (Instrumental Analyzer Procedure)

1. Applicability and Principle

1.1 Applicability. This method is applicable to the determination of sulfur dioxide (SO2) concentrations in controlled and uncontrolled emissions from stationary sources only when specified within the regulations.

1.2 Principle. A gas sample is continuously extracted from a stack, and a portion of the sample is conveyed to an instrumental analyzer for determination of SO2 gas concentration using an ultraviolet (UV), nondispersive infrared (NDIR), or fluorescence analyzer. Performance specifications and test procedures are provided to ensure reliable data.

2. Range and Sensitivity

2.1 Analytical Range. The analytical range is determined by the instrumental design. For this method, a portion of the analytical range is selected by choosing the span of the monitoring system. The span of the monitoring system shall be selected such that the pollutant gas concentration equivalent to the emission standard is not less than 30 percent of the span. If at any time during a run the measured gas concentration exceeds the span, the run shall be considered invalid.

2.2 Sensitivity. The minimum detectable limit depends on the analytical range, span, and signal—to—noise ratio of the measurement system. For a well designed system, the minimum detectable limit should be less than 2 percent of the span.

3. Definitions

3.1 Measurement System. The total equipment required for the determination of gas concentration. The measurement system consists of the following major subsystems:

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

3.1.2 Gas Analyzer. That portion of the system that senses the gas to be measured and generates an output proportional to its concentration.

3.1.3 Data Recorder. A strip chart recorder, analog computer, or digital recorder for recording measurement data from the analyzer output.

3.2 Span. The upper limit of the gas concentration measurement range displayed on the data recorder.

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

3.4 Analyzer Calibration Error. The difference between the gas concentration exhibited by the gas analyzer and the known concentration of the calibration gas when the calibration gas is introduced directly to the analyzer.

3.5 Sampling System Bias. The difference between the gas concentrations exhibited by the measurement system when a known concentration gas is introduced at the outlet of the sampling probe and when the same gas is introduced directly to the analyzer.

3.6 Zero Drift. The difference in the measurement system output reading from the initial calibration response at the zero concentration level after a stated period of operation during which no unscheduled maintenance, repair, or adjustment took place.

3.7 Calibration Drift. The difference in the measurement system output reading from the initial calibration response at a mid-range calibration value after a stated period of operation during which no unscheduled maintenance, repair, or adjustment took place.

3.8 Response Time. The amount of time required for the measurement system to display 95 percent of a step change in gas concentration on the data recorder.

3.9 Interference Check. A method for detecting analytical interferences and excessive biases through direct comparison of gas concentrations provided by the measurement system and by a modified Method 6 procedure. For this check, the modified Method 6 samples are acquired at the sample by-pass discharge vent.

3.10 Calibration Curve. A graph or other systematic method of establishing the relationship between the analyzer response and the actual gas concentration introduced to the analyzer.

4. Measurement System Performance Specifications

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

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

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

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

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

5. Apparatus and Reagents

5.1 Measurement System. Any measurement system for SO2 that meets the specifications of this method. A schematic of an acceptable measurement system is shown in Figure 6C-1. The essential components of the measurement system are described below:

5.1.1 Sample Probe. Glass, stainless steel, or equivalent, of sufficient length to traverse the sample points. The sampling probe shall be heated to prevent condensation.

5.1.2 Sample Line. Heated (sufficient to prevent condensation) stainless steel or Teflon tubing, to transport the sample gas to the moisture removal system.

5.1.3 Sample Transport Lines. Stainless steel or Teflon tubing, to transport the sample from the moisture removal system to the sample pump, sample flow rate control, and sample gas manifold.

5.1.4 Calibration Valve Assembly. A three—way valve assembly, or equivalent, for blocking the sample gas flow and introducing calibration gases to the measurement system at the outlet of the sampling probe when in the calibration mode.

5.1.5 Moisture Removal System. A refrigerator-type condenser or similar device (e.g., permeation dryer), to remove condensate continuously from the sample gas while maintaining minimal contact between the condensate and the sample gas. The moisture removal system is not necessary for analyzers that can measure gas concentrations on a wet basis; for these analyzers, (1) heat the sample line and all interface components up to the inlet of the analyzer sufficiently to prevent condensation, and (2) determine the moisture content and correct the measured gas concentrations to a dry basis using appropriate methods, subject to the approval of the Administrator. The determination of sample moisture content is not necessary for pollutant analyzers that measure concentrations on a wet basis when (1) a wet basis CO2 analyzer operated according to Method 3A is used to obtain simultaneous measurements, and (2) the pollutant/CO2 measurements are used to determine emissions in units of the standard.

5.1.6 Particulate Filter. An in-stack or heated (sufficient to prevent water condensation) out—of—stack filter. The filter shall be borosilicate or quartz glass wool, or glass fiber mat. Additional filters at the inlet or outlet of the moisture removal system and inlet of the analyzer may be used to prevent accumulation of particulate material in the measurement system and extend the useful life of the

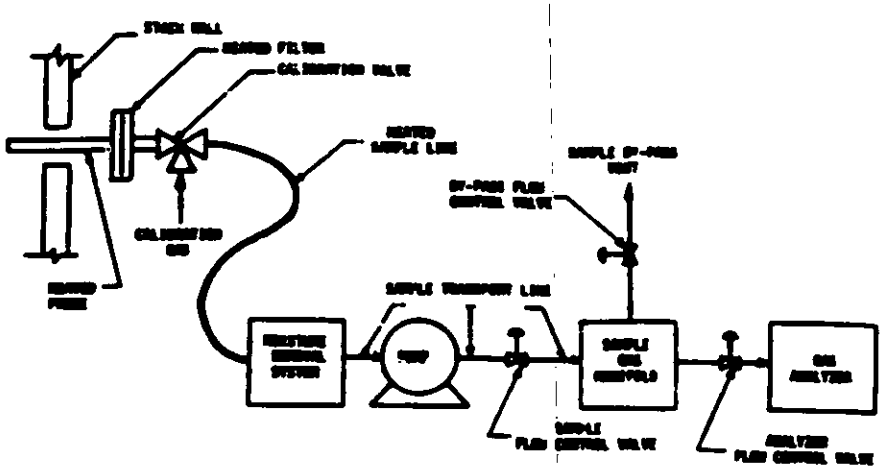

Figure 6C-1. [illegible]

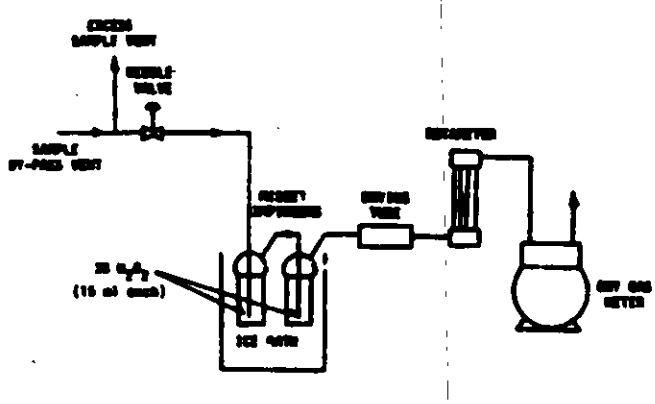

Figure 6C-2. [illegible]

components. All filters shall be fabricated of materials that are nonreactive to the gas being sampled.

5.1.7 Sample Pump. A leak-free pump, to pull the sample gas through the system at a flow rate sufficient to minimize the response time of the measurement system. The pump may be constructed of any material that is nonreactive to the gas being sampled.

5.1.8 Sample Flow Rate Control. A sample flow rate control valve and rotameter, or equivalent, to maintain a constant sampling rate within 10 percent.

(Note: The tester may elect to install a back-pressure regulator to maintain the sample gas manifold at a constant pressure in order to protect the analyzer(s) from overpressurization, and to minimize the need for flow rate adjustments.)

5.1.9 Sample Gas Manifold. A sample gas manifold, to divert a portion of the sample gas stream to the analyzer, and the remainder to the by-pass discharge vent. The sample gas manifold should also include provisions for introducing calibration gases directly to the analyzer. The manifold may be constructed of any material that is nonreactive to the gas being sampled.

5.1.10 Gas Analyzer. A UV or NDIR absorption or fluorescence analyzer, to determine continuously the SO2 concentration in the sample gas stream. The analyzer shall meet the applicable performance specifications of Section 4. A means of controlling the analyzer flow rate and a device for determining proper sample flow rate (e.g., precision rotameter, pressure gauge downstream of all flow controls, etc.) shall be provided at the analyzer.

(Note: Housing the analyzer(s) in a clean, thermally-stable, vibration-free environment will minimize drift in the analyzer calibration.)

5.1.11 Data Recorder. A strip chart recorder, analog computer, or digital recorder, for recording measurement data. The data recorder resolution (i.e., readability) shall be 0.5 percent of span. Alternatively, a digital or analog meter having a resolution of 0.5 percent of span may be used to obtain the analyzer responses and the readings may be recorded manually. If this alternative is used, the readings shall be obtained at equally spaced intervals over the duration of the sampling run. For sampling run durations of less than 1 hour, measurements at 1—minute intervals or a minimum of 30 measurements, whichever is less restrictive, shall be obtained. For sampling run durations greater than 1 hour, measurements at 2—minute intervals or a minimum of 96 measurements, whichever is less restrictive, shall be obtained.

5.2 Method 6 Apparatus and Reagents. The apparatus and reagents described in Method 6, and shown by the schematic of the sampling train in Figure 6C-2, to conduct the interference check.

5.3 SO2 Calibration Gases. The calibration gases for the gas analyzer shall be SO2 in N2 or SO2 in air. Alternatively, SO2/CO2, SO2/O2, or SO2/CO2/O2 gas mixtures in N2 may be used. For fluorescence-based analyzers, the O2 and CO2 concentrations of the calibration gases as introduced to the analyzer shall be within 1 percent (absolute) O2 and 1 percent (absolute) CO2 of the O2 and Co2 concentrations of the effluent samples as introduced to the analyzer. Alternatively, for fluorescence-based analyzers, use calibration blends of SO2 in air and the nomographs provided by the vendor to determine the quenching correction factor (the effluent O2 and CO2 concentrations must be known). Use three calibration gases as specified below:

5.3.1 High-Range Gas. Concentration equivalent to 80 to 100 percent of the span.

5.3.2 Mid-Range Gas. Concentration equivalent to 40 to 60 percent of the span.

5.3.3 Zero Gas. Concentration of less than 0.25 percent of the span. Purified ambient air may be used for the zero gas by passing air through a charcoal filter, or through one or more impingers containing a solution of 3 percent H2O2.

6. Measurement System Performance Test Procedures

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

6.1 Calibration Gas Concentration Verification. There are two alternatives for establishing the concentrations of calibration gases. Alternative Number 1 is preferred.

6.1.1 Alternative Number 1—Use of calibration gases that are analyzed following the Environmental Protection Agency Traceability Protocol Number 1 (see Citation 1 in the Bibliography). Obtain

a certification from the gas manufacturer that Protocol Number 1 was followed.

6.1.2 Alternative Number 2—Use of calibration gases not prepared according to Protocol Number 1. If this alternative is chosen, obtain gas mixtures with a manufacturer's tolerance not to exceed ± 2 percent of the tag value. Within 6 months before the emission test, analyze each of the calibration gases in triplicate using Method 6. Citation 2 in the Bibliography describes procedures and techniques that may be used for this analysis. Record the results on a data sheet (example is shown in Figure 6C-3). Each of the individual SO2 analytical results for each calibration gas shall be within 5 percent (or 5 ppm, whichever is greater) of the triplicate set average; otherwise, discard the entire set, and repeat the triplicate analyses. If the average of the triplicate analyses is within 5 percent of the calibration gas manufacturer's cylinder tag value, use the tag value; otherwise, conduct at least three additional analyses until the results of six consecutive runs agree with 5 percent (or 5 ppm, whichever is greater) of their average. Then use this average for the cylinder value.

6.2 Measurement System Preparation. Assemble the measurement system by following the manufacturer's written instructions for preparing and preconditioning the gas analyzer and, as applicable, the other system components. Introduce the calibration gases in any sequence, and make all necessary adjustments to calibrate the analyzer and the data recorder. Adjust system components to achieve correct sampling rates.

6.3 Analyzer Calibration Error. Conduct the analyzer calibration error check by introducing calibration gases to the measurement system at any point upstream of the gas analyzer as follows:

6.3.1 After the measurement system has been prepared for use, introduce the zero, mid-range, and high-range gases to the analyzer. During this check, make no adjustments to the system except those necessary to achieve the correct calibration gas flow rate at the analyzer. Record the analyzer responses to each calibration gas on a form similar to Figure 6C-4.

Note: A calibration curve established prior to the analyzer calibration error check may be used to convert the analyzer response to the equivalent gas concentration introduced to the analyzer. However, the same correction procedure shall be used for all effluent and calibration measurements obtained during the test.

FIGURE 6C-3—ANALYSIS OF CALIBRATION GASES

Date _____ Analytic method used _____

	Gas concentration (indicate units)		
	Zero [a]	Mid-range [b]	High-range [c]
Sample run:			
1			
2			
3			
Average			
Maximum percent deviation			

[a] Average must be less than 0.25 percent of span.
[b] Average must be 50 to 60 percent of span.
[c] Average must be 80 to 90 percent of span.

FIGURE 6C-4—ANALYZER CALIBRATION DATA

Source identification: _____ Analyzer calibration data for sampling runs: _____
Test personnel: _____ Span: _____
Date: _____

	Cylinder value (indicate units)	Analyzer calibration response (indicate units)	Absolute difference (indicate units)	Difference (percent of span)
Zero gas				
Mid-range gas				
High-range gas				

FIGURE 6C-5—SYSTEM CALIBRATION BIAS AND DRIFT DATA

Source identification: _____ Run number: _____
Test personnel: _____ Span: _____
Date: _____

	Analyzer calibration response	Initial values		Final values		Drift (percent of span)
		System calibration response	System cal. bias (percent of span)	System calibration response	System cal. bias (percent of span)	
Zero gas						
Upscale gas						

$$\text{System Calibration Bias} = \frac{\text{System Cal. Response-Analyzer Cal. Response}}{\text{Span}} \times 100$$

6.3.2 The analyzer calibration error check shall be considered invalid if the gas concentration displayed by the analyzer exceeds ± 2 percent of the span for any of the calibration gases. If an invalid calibration is exhibited, take corrective action, and repeat the analyzer calibration error check until acceptable performance is achieved.

6.4 Sampling System Bias Check. Perform the sampling system bias check by introducing calibration gases at the calibration valve installed at the outlet of the sampling probe. A zero gas and either the mid-range or high-range gas, whichever most closely approximates the effluent concentrations, shall be used for this check as follows:

6.4.1 Introduce the upscale calibration gas, and record the gas concentration

displayed by the analyzer on a form similar to Figure 6C-5. Then introduce zero gas, and record the gas concentration displayed by the analyzer. During the sampling system bias check, operate the system at the normal sampling rate, and make no adjustments to the measurement system other than those necessary to achieve proper calibration gas flow rates at the analyzer. Alternately introduce the zero and upscale gases until a stable response is achieved. The tester shall determine the measurement system response time by observing the times required to achieve a stable response for both the zero and upscale gases. Note the longer of the two times as the response time.

6.4.2 The sampling system bias check shall be considered invalid if the difference between the gas concentrations displayed by the measurement system for the analyzer calibration error check and for the sampling system bias check exceeds ± 5 percent of the span for either the zero or upscale calibration gas. If an invalid calibration is exhibited, take corrective action, and repeat the sampling system bias check until acceptable performance is achieved. If adjustment to the analyzer is required, first repeat the analyzer calibration error check, then repeat the sampling system bias check.

7. Emission Test Procedure

7.1 Selection of Sampling Site and Sampling Points. Select a measurement site and sampling points using the same criteria that are applicable to Method 6.

7.2 Interference Check Preparation. For each individual analyzer, conduct an interference check for at least three runs during the initial field test on a particular source category. Retain the results, and report them with each test performed on that source category.

If an interference check is being performed, assemble the modified Method 6 train (flow control valve, two midget impingers containing 3 percent H2O2, and dry gas meter) as shown in Figure 6C-2. Install the sampling train to obtain a sample at the measurement system sample by-pass discharge vent. Record the initial dry gas meter reading.

7.3 Sample Collection. Position the sampling probe at the first measurement point, and begin sampling at the same rate as used during the sampling system bias check. Maintain constant rate sampling (i.e., ± 10 percent) during the entire run. The sampling time per run shall be the same as for Method 6 plus twice the system response time. For each run, use only those measurements obtained after twice response time of the measurement system has elapsed, to determine the average effluent concentration. If an interference check is being performed, open the flow control valve on the modified Method 6 train concurrent with the initiation of the sampling period, and adjust the flow to 1 liter per minute (± 10 percent).

(Note: If a pump is not used in the modified Method 6 train, caution should be exercised in adjusting the flow rate since overpressurization of the impingers may cause leakage in the impinger train, resulting in positively biased results).

7.4 Zero and Calibration Drift Tests. Immediately preceding and following each run, or if adjustments are necessary for the measurement system during the run, repeat the sampling system bias check procedure described in Section 6.4 (Make no adjustments to the measurement system until after the drift checks are completed.) Record and analyzer's responses on a form similar to Figure 6C-5.

7.4.1 If either the zero or upscale calibration value exceeds the sampling system bias specification, then the run is considered invalid. Repeat both the analyzer calibration error check procedure (Section 6.3) and the sampling system bias check procedure (Section 6.4) before repeating the run.

7.4.2 If both the zero and upscale calibration values are within the sampling system bias specification, then use the average of the initial and final bias check values to calculate the gas concentration for the run. If the zero or upscale calibration drift value exceeds the drift limits, based on the difference between the sampling system bias check responses immediately before and after the run, repeat both the analyzer calibration error check procedure (Section 6.3) and the sampling system bias check procedure (Section 6.4) before conducting additional runs.

7.5 Interference Check (if performed). After completing the run, record the final dry gas meter reading, meter temperature, and barometric pressure. Recover and analyze the contents of the midget impingers, and determine the SO2 gas concentration using the procedures of Method 6. (It is not necessary to analyze EPA performance audit samples for Method 6.) Determine the average gas concentration exhibited by the analyzer for the run. If the gas concentrations provided by the analyzer and the modified Method 6 differ by more than 7 percent of the modified Method 6 result, the run is invalidated.

8. Emission Calculation

The average gas effluent concentration is determined from the average gas concentration displayed by the gas analyzer, and is adjusted for the zero and upscale sampling system bias checks, as determined in accordance with Section 7.4. The average gas concentration displayed by the analyzer may be determined by integration of the area under the curve for chart recorders, or by averaging all of the effluent measurements. Alternatively, the average may be calculated from measurements recorded at equally spaced intervals over the entire duration of the run. For sampling run durations of less than 1 hour, measurements at 1—minute intervals or a minimum of 30 measurements, whichever is less restrictive, shall be used. For sampling run durations greater than 1 hour, measurements at 2—minute intervals or a minimum of 96 measurements, whichever is less restrictive, shall be used. Calculate the effluent gas concentration using Equation 6C-1.

$$C_{gas} = (\bar{C} - C_o)\ \frac{C_{ma}}{C_m - C_o}$$

Eq. 6C-1

Where:

Cgas = Effluent gas concentration, dry basis, ppm.

$\bar{C}$ = Average gas concentration indicated by gas analyzer, dry basis, ppm.

Co = Average of initial and final system calibration bias check responses for the zero gas, ppm.

Cm = Average of initial and final system calibration bias check responses for the upscale calibration gas, ppm.

Cma = Actual concentration of the upscale calibration gas, ppm.

9. Bibliography

1. Traceability Protocol for Establishing True Concentrations of Gases Used for Calibrations and Audits of Continuous Source Emission Monitors: Protocol Number 1. U.S. Environmental Protection Agency, Quality Assurance Division. Research Triangle Park, NC. June 1978.

2. Westlin, Peter R. and J. W. Brown. Methods for Collecting and Analyzing Gas Cylinder Samples. Source Evaluation Society Newsletter. 3(3):5-15. September 1978.

Method 7E—Determination of Nitrogen Oxides Emissions From Stationary Sources (Instrumental Analyzer Procedure)

1. Applicability and Principle

1.1 Applicability. This method is applicable to the determination of nitrogen oxides (NOx) concentrations in emissions from stationary sources only when specified within the regulations.

1.2 Principle. A gas simple is continuously extracted from a stack, and a portion of the sample is conveyed to an instrumental chemiluminescent analyzer for determination of NOx concentration. Performance specifications and test procedures are provided to ensure reliable data.

2. Range and Sensitivity

Same as Method 6C, Sections 2.1 and 2.2.

3. Definitions

3.1 Measurement System. The total equipment required for the determination of NOx concentration. The measurement system consists of the following major subsystems:

3.1.1 Sample Interface, Gas Analyzer, and Data Recorder. Same as Method 6C, Sections 3.1.1, 3.1.2, and 3.1.3.

3.1.2 NO2 to NO Converter. A device that converts the nitrogen dioxide (NO2) in the sample gas to nitrogen oxide (NO).

3.2 Span, Calibration Gas, Analyzer Calibration Error, Sampling System Bias, Zero Drift, Calibration Drift, and Response Time. Same as Method 6C, Sections 3.2 through 3.8.

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

4. Measurement System Performance Specifications

Same as Method 6C, Sections 4.1 through 4.4.

5. Apparatus and Reagents

5.1 Measurement System. Any measurement system for NOx that meets the specifications of this method. A schematic of an acceptable measurement system is shown in Figure 6C-1 of Method 6C. The essential components of the measurement system are described below:

5.1.1 Sample Probe, Sample Line, Calibration Valve Assembly, Moisture Removal System, Particulate Filter, Sample Pump, Sample Flow Rate Control, Sample Gas Manifold, and Data Recorder. Same as Method 6C, Sections 5.1.1 through 5.1.9, and 5.1.11.

5.1.2 NO2 to NO Converter. That portion of the system that converts the nitrogen dioxide (NO2) in the sample gas to nitrogen oxide (NO). An NO2 to NO converter is not necessary if data are presented to demonstrate that the NO2 portion of the exhaust gas is less than 5 percent of the total NOx concentration.

5.1.3 NOx Analyzer. An analyzer based on the principles of chemiluminescence, to determine continuously the NOx concentration in the sample gas stream. The analyzer shall meet the applicable performance specifications of Section 4. A means of controlling the analyzer flow rate and a device for determining proper sample flow rate (e.g., precision rotameter, pressure gauge downstream of all flow controls, etc.) shall be provided at the analyzer.

5.2 NOx Calibration Gases. The calibration gases for the NOx analyzer shall be NO in N2. Three calibration gases, as specified in Sections 5.3.1 through 5.3.3. of Method 6C, shall be used. Ambient air may be used for the zero gas.

6. Measurement System Performance Test Procedures

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

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

6.2 Interference Response. Conduct an interference response test of the analyzer prior to its initial use in the field. Thereafter, recheck the measurement system if changes are made in the instrumentation that could alter the interference response (e.g., changes in the gas detector). Conduct the interference response in accordance with Section 5.4 of Method 20.

6.3 Measurement System Preparation, Analyzer Calibration Error, and Sample System Bias Check. Follow Sections 6.2 through 6.4 of Method 6C.

6.4 NO2 to NO Conversion Efficiency. Unless data are presented to demonstrate that the NO2 concentration within the sample stream is not greater than 5 percent of the NOx concentration, conduct an NO2 to NO conversion efficiency test in accordance with Section 5.6 of Method 20.

7. Emission Test Procedure

7.1 Selection of Sampling Site and Sampling Points. Select a measurement site and sampling points using the same criteria that are applicable to tests performed using Method 7.

7.2 Sample Collection. Position the sampling probe at the first measurement point, and begin sampling at the same rate as used during the system calibration drift test. Maintain constant rate sampling (i.e., ± 10 percent) during the entire run. The sampling time per run shall be the same as the total time required to perform a run using Method 7, plus twice the system response time. For each run, use only those measurements obtained after twice the response time of the measurement system has elapsed, to determine the average effluent concentration.

7.3 Zero and Calibration Drift Test. Follow Section 7.4 of Method 6C.

8. Emission Calculation

Follow Section 8 of Method 6C.

9. Bibliography

Same as bibliography of Method 6C.

Method 8—Determination of Sulfuric Acid Mist and Sulfur Dioxide Emissions From Stationary Sources

1. Principle and Applicability

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

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

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

Filterable particulate matter may be determined along with SO3 and SO2 (subject to the approval of the Administrator) by inserting a heated glass fiber filter between the probe and isopropanol impinger (see Section 2.1 of Method 6.) If this option is chosen, particulate analysis is gravimetric only; H2SO4 acid mist is not determined separately.

2. Apparatus

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

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

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

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

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

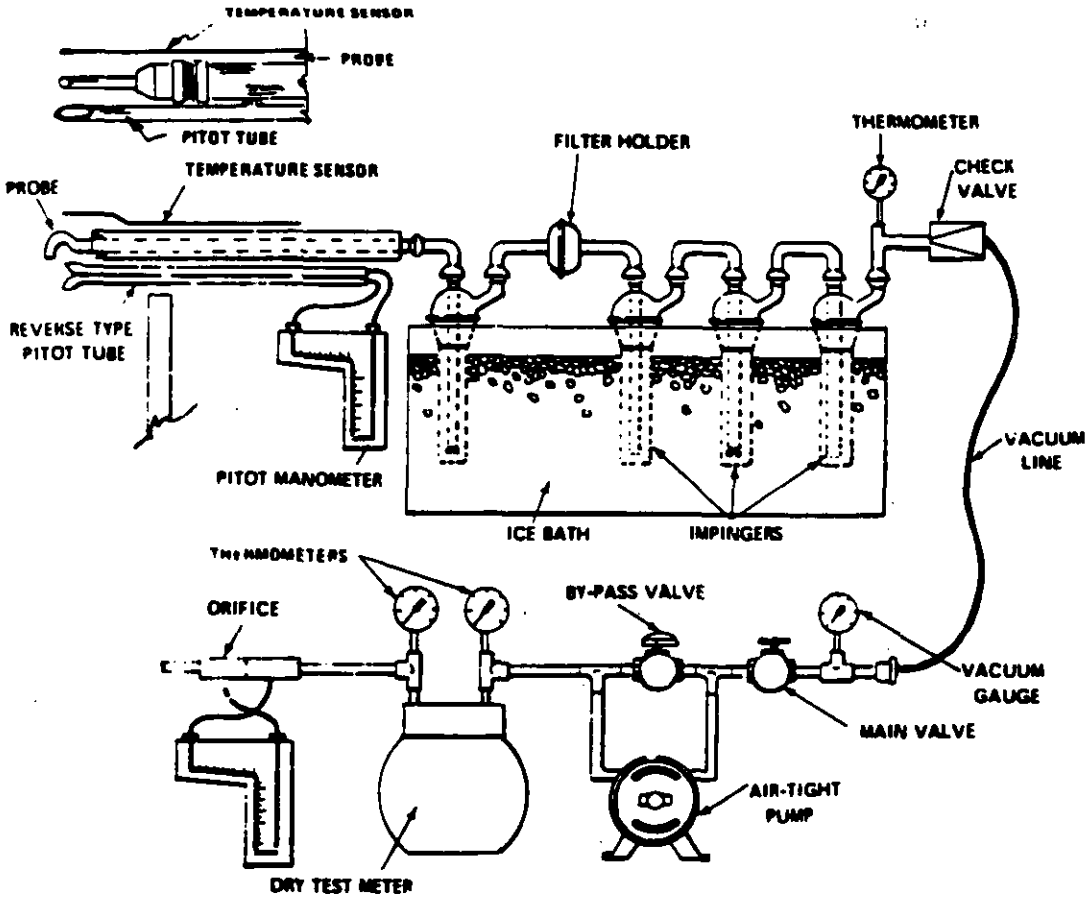

Figure 8-1. Sulfuric acid mist sampling train.

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

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

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

2.1.7 Metering System. Same as Method 5, Section 2.1.8.

2.1.8 Barometer. Same as Method 5, Section 2.1.9.

2.1.9 Gas Density Determination Equipment. Same as Method 5, Section 2.1.10.

2.1.10 Temperature Gauge. Thermometer, or equivalent, to measure the temperature of the gas leaving the impinger train to within 1°C (2°F).

2.2 Sample Recovery.

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

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

2.2.3 Storage Bottles. Leak-free polyethlene 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 Burette. 50 ml.

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

2.3.4 Graduated Cylinder. 100 ml.

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

2.3.6 Dropping Bottle. To add indicator solution. 125—ml size.

3. Reagents

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

3.1 Sampling.

3.1.1 Filters. Same as Method 5, Section 3.1.1.

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

3.1.3 Water. Deionized, distilled to conform to ASTM Specification D1193-77, Type 3 (incorporated by reference——see § 60.17). At the option of the analyst, the KMnO4 test for oxidizable organic matter may be omitted when high concentrations of organic matter are not expected to be present.

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

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

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

3.1.6 Crushed Ice.

3.2 Sample Recovery.

3.2.1 Water. Same as 3.1.3.

3.2.2 Isopropanol, 80 Percent. Same as 3.1.4.

3.3 Analysis.

3.3.1 Water. Same as 3.1.3.

3.3.2 Isopropanol, 100 Percent.

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

3.3.4 Barium Perchlorate (0.0100 Normal). Dissolve 1.95 g of barium perchlorate trihydrate (Ba(C104)2 + 3H2O) in 200 ml deionized, distilled water, and dilute to 1 liter with isopropanol; 1.22 g of barium chloride dihydrate (BaC12 + 2H2O) may be used instead of the barium perchlorate. Standardize with sulfuric acid as in Section 5.2. This solution must be protected against evaporation at all times.

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

3.3.6 Quality Assurance Audit Samples. Same as in Method 6, Section 3.3.6.

4. Procedure

4.1 Sampling.

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

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

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

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

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

4.1.5 Train Operation. Follow the basic procedures outlined in Method 5, Section 4.1.5, in conjunction with the following special instructions. Data shall be recorded on a sheet similar to the one in Figure 8-2. The sampling rate shall not exceed 0.030 m^3/min (1.0 cfm) during the run.

Periodically during the test, observe the connecting line between the probe and first impinger for signs of condensation. If it does occur, adjust the probe heater setting upward to the minimum temperature required to prevent condensation. If component changes become necessary during a run, a leak-check shall be done immediately before each change, according to the procedure outlined in Section 4.1.4.2 of Method 5 (with appropriate modifications, as mentioned in Section 4.1.4 of this method); record all leak rates. If the leakage rate(s) exceed the specified rate, the tester shall either void the run or shall plan to correct the sample volume as outlined in Section 6.3 of Method 5. Immediately after component changes, leak-checks are optional. If these leak-checks are done, the procedure outlined in Section 4.1.4.1 of Method 5 (with appropriate modifications) shall be used.

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

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

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

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

4.2 Sample Recovery.

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

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

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

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

4.3 Analysis.

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

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

FIGURE 8-2—FIELD DATA

Plant .....
Location .....
Operator .....
Date .....
Run No .....
Sample box No .....
Meter box No .....
Meter ΔH@ .....
C factor .....
Pitot tube coefficient, Cp .....

SCHEMATIC OF STACK CROSS SECTION

Static pressure, mm Hg (in. Hg) .....
Ambient temperature .....
Barometer pressure .....
Assumed moisture, % .....
Probe length, m (ft) .....
Nozzle identification No .....
Average calibrated nozzle diameter, cm (in.) .....
Probed heater setting .....
Leak rate, m³/min. (cfm) .....
Probe liner material .....
Filter No. .....

Traverse point number	Sampling time (θ), min.	Vacuum mm Hg (in. Hg)	Stack temperature (T_s) °C (°F)	Velocity head (ΔP) mm H_2O (in H_2O)	Pressure differential across orifice meter mm H_2O (in H_2O)	Gas sample volume m³ (ft³)	Gas sample temperature at dry gas meter: Inlet °C (°F)	Gas sample temperature at dry gas meter: Outlet °C (°F)	Temperature of gas leaving condenser or last impinger °C (°F)
Total									
Average							Avg	Avg	
							Avg		

agree within 1 percent or 0.2 ml, whichever is greater.

4.3.2 Container No. 2. Thoroughly mix the solution in the container holding the contents of the second and third impingers. Pipette a 10—ml aliquot of sample into a 250—ml Erlenmeyer flask. Add 40 ml of isopropanol, 2 to 4 drops of thorin indicator, and titrate to a pink endpoint using 0.0100 N barium perchlorate. Repeat the titration with a second aliquot of sample and average the titration values. Replicate titrations must agree within 1 percent or 0.2 ml, whichever is greater.

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

4.4 Quality Control Procedures. Same as in Method 5, Section 4.4.

4.5 Audit Sample Analysis. Same as in Method 6, Section 4.4.

5. Calibration

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

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

6. Calculations

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

6.1 Nomenclature.

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

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

CH2SO4 = Sulfuric acid (including SO3) concentration, g/dscm (lb/dscf).

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

I = Percent of isokinetic sampling.

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

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

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

Pstd = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).

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

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

Tstd = Standard absolute temperature, 293°K (528°R).

Va = Volume of sample aliquot titrated, 100 ml for H2SO4 and 10 ml for SO2.

Vlc = Total volume of liquid collected in impingers and silica gel, ml.

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

Vm(std) = Volume of gas sample measured by the dry gas meter corrected to standard conditions, dscm (dscf).

vs = Average stack gas velocity, calculated by Method 2, Equation 2-9, using data obtained from Method 8, m/sec (ft/sec).

Vsoln = Total volume of solution in which the sulfuric acid or sulfur dioxide sample is contained, 250 ml or 1,000 ml, respectively.

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

Vtb = Volume of barium perchlorate titrant used for the blank, ml.

Y = Dry gas meter calibration factor.

DELTA H = Average pressure drop across orifice meter, mm (in.) H2O.

Θ = Total sampling time, min.

13.6 = Specific gravity of mercury.

60 = sec/min.

100 = Conversion to percent.

6.2 Average Dry Gas Meter Temperature and Average Orifice Pressure Drop. See data sheet (Figure 8-2).

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

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

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

Equation 8-1

Where:

K1 = 0.3858 °K/mm Hg for metric units.

= 17.64 °R/in., Hg for English units.

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

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

6.5 Sulfuric Acid Mist (including SO3) Concentration.

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

Equation 8-2

Where:

K2 = 0.04904 g/milliequivalent for metric units.

= 1.081 x 10-4 lb/meq for English units.

6.6 Sulfur Dioxide Concentration.

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

Equation 8-3

Where:

K3 = 0.03203 g/meq for metric units.

= 7.061 x 10-5 lb/meq for English units.

6.7 Isokinetic Variation.

6.7.1 Calculation from Raw Data.

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

Eq. 8-4

Where:

K4 = 0.003464 mm Hg—m^3/ml-°K for metric units.

= 0.002676 in. Hg-ft^3/ml-°R for English units.

6.7.2 Calculation from Intermediate Values.

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

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

Equation 8-5

Where:

K5 = 4.320 for metric units.

= 0.09450 for English units

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

6.9 Stack Gas Velocity and Volumetric Flow Rate. Calculate the average stack gas velocity and volumetric flow rate, if needed, using data obtained in this method and equations in Sections 5.2 and 5.3 of Method 2.

6.10 Relative Error (RE) for QA Audit Samples. Same as in Method 6, Section 6.4.

7. Bibliography

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

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Method 9—Visual Determination of the Opacity of Emissions From Stationary Sources

Many stationary sources discharge visible emissions into the atmosphere; these emissions are usually in the shape of a plume. This method involves the determination of plume opacity by qualified observers. The method includes procedures for the training and certification of observers, and procedures to be used in the field for determination of plume opacity. The appearance of a plume as viewed by an observer depends upon a number of variables, some of which may be controllable and some of which may not be controllable in the field. Variables which can be controlled to an extent to which they no longer exert a significant influence upon plume appearance include: Angle of the observer with respect to the plume; angle of the observer with respect to the sun; point of observation of attached and detached steam plume; and angle of the observer with respect to a plume emitted from a rectangular stack with a large length to width ratio. The method includes specific criteria applicable to these variables.

Other variables which may not be controllable in the field are luminescence and color contrast between the plume and the background against which the plume is viewed. These variables exert an influence upon the appearance of a plume as viewed by an observer, and can affect the ability of the observer to accurately assign opacity values to the observed plume. Studies of the theory of plume opacity and field studies have demonstrated that a plume is most visible and presents the greatest apparent opacity when viewed against a contrasting background. It follows from this, and is confirmed by field trials, that the opacity of a plume, viewed under conditions where a contrasting background is present can be assigned with the greatest degree of accuracy. However, the potential for a positive error is also the greatest when a plume is viewed under such contrasting conditions. Under conditions presenting a less contrasting background, the apparent opacity of a plume is less and approaches zero as the color and luminescence contrast decrease toward zero. As a result, significant negative bias and negative errors can be made when a plume is viewed under less contrasting conditions. A negative bias decreases rather than increases the possibility that a plant operator will be cited for a violation of opacity standards due to observer error.

Studies have been undertaken to determine the magnitude of positive errors which can be made by qualified observers while reading plumes under contrasting conditions and using the procedures set forth in this method. The results of these studies (field trials) which involve a total of 769 sets of 25 readings each are as follows:

|_(1) For black plumes (133 sets at a smoke generator), 100 percent of the sets were read with a positive error|_\1\ of less than 7.5 percent opacity; 99 percent were read with a positive error of less than 5 percent opacity.

|_{Footnote}\1\ For a set, positive error = average opacity determined by observers' 25 observations——average opacity determined from transmissometer's 25 recordings.

|_(2) For white plumes (170 sets at a smoke generator, 168 sets at a coal-fired power plant, 298 sets at a sulfuric acid plant), 99 percent of the sets were read with a positive error of less than 7.5 percent opacity; 95 percent were read with a positive error of less than 5 percent opacity.

The positive observational error associated with an average of twenty-five readings is therefore established. The accuracy of the method must be taken into account when determining possible violations of applicable opacity standards.

1. Principle and Applicability

1.1 Principle. The opacity of emissions from stationary sources is determined visually by a qualified observer.

1.2 Applicability. This method is applicable for the determination of the opacity of emissions from stationary sources pursuant to § 60.11(b) and for qualifying observers for visually determining opacity of emissions.

2. Procedures

The observer qualified in accordance with section 3 of this method shall use the following procedures for visually determining the opacity of emissions:

2.1 Position. The qualified observer shall stand at a distance sufficient to provide a clear view of the emissions with the sun oriented in the 140°sector to his back. Consistent with maintaining the above requirement, the observer shall, as much as possible, make his observations from a position such that his line of vision is approximately perpendicular to the plume direction, and when observing opacity of emissions from rectangular outlets (e.g., roof monitors, open baghouses, noncircular stacks), approximately perpendicular to the longer axis of the outlet. The observer's line of sight should not include more than one plume at a time when multiple stacks are involved, and in any case the observer should make his observations with his line of sight perpendicular to the longer axis of such a set of multiple stacks (e.g., stub stacks on baghouses).

2.2 Field Records. The observer shall record the name of the plant, emission location, type facility, observer's name and affiliation, a sketch of the observer's position relative to the source, and the date on a field data sheet (Figure 9-1). The time, estimated distance to the emission location, approximate wind direction, estimated wind speed, description of the sky condition (presence and color of clouds), and plume background are recorded on a field data sheet at the time opacity readings are initiated and completed.

2.3 Observations. Opacity observations shall be made at the point of greatest opacity in that portion of the plume where condensed water vapor is not present. The observer shall not look continuously at the plume, but instead shall observe the plume momentarily at 15-second intervals.

2.3.1 Attached Steam Plumes. When condensed water vapor is present within the plume as it emerges from the emission outlet, opacity observations shall be made beyond the point in the plume at which condensed water vapor is no longer visible. The observer shall record the approximate distance from the emission outlet to the point in the plume at which the observations are made.

2.3.2 Detached Steam Plume. When water vapor in the plume condenses and becomes visible at a distinct distance from the emission outlet, the opacity of emissions should be evaluated at the emission outlet prior to the condensation of water vapor and the formation of the steam plume.

2.4 Recording Observations. Opacity observations shall be recorded to the nearest 5 percent at 15-second intervals on an observational record sheet. (See Figure 9-2 for an example.) A minimum of 24 observations shall be recorded. Each momentary observation recorded shall be deemed to represent the average opacity of emissions for a 15-second period.

2.5 Data Reduction. Opacity shall be determined as an average of 24 consecutive observations recorded at 15-second intervals. Divide the observations recorded on the record sheet into sets of 24 consecutive observations. A set is composed of any 24 consecutive observations. Sets need not be consecutive in time and in no case shall two sets overlap. For each set of 24 observations, calculate the average by summing the opacity of the 24 observations and dividing this sum by 24. If an applicable standard

specifies an averaging time requiring more than 24 observations, calculate the average for all observations made during the specified time period. Record the average opacity on a record sheet. (See Figure 9-1 for an example.)

3. Qualifications and Testing

3.1 Certification Requirements. To receive certification as a qualified observer, a candidate must be tested and demonstrate the ability to assign opacity readings in 5 percent increments to 25 different black plumes and 25 different white plumes, with an error not to exceed 15 percent opacity on any one reading and an average error not to exceed 7.5 percent opacity in each category. Candidates shall be tested according to the procedures described in section 3.2. Smoke generators used pursuant to section 3.2 shall be equipped with a smoke meter which meets the requirements of section 3.3.

The certification shall be valid for a period of 6 months, at which time the qualification procedure must be repeated by any observer in order to retain certification.

3.2 Certification Procedure. The certification test consists of showing the candidate a complete run of 50 plumes——25 black plumes and 25 white plumes——generated by a smoke generator. Plumes within each set of 25 black and 25 white runs shall be presented in random order. The candidate assigns an opacity value to each plume and records his observation on a suitable form. At the completion of each run of 50 readings, the score of the candidate is determined. If a candidate fails to qualify, the complete run of 50 readings must be repeated in any retest. The smoke test may be administered as part of a smoke school or training program, and may be preceded by training or familiarization runs of the smoke generator during which candidates are shown black and white plumes of known opacity.

3.3 Smoke Generator Specifications. Any smoke generator used for the purposes of section 3.2 shall be equipped with a smoke meter installed to measure opacity across the diameter of the smoke generator stack. The smoke meter output shall display instack opacity based upon a pathlength equal to the stack exit diameter, on a full 0 to 100 percent chart recorder scale. The smoke meter optical design and performance shall meet the specifications shown in Table 9-1. The smoke meter shall be calibrated as prescribed in section 3.3.1 prior to the conduct of each smoke reading test. At the completion of each test, the zero and span drift shall be checked and if the drift exceeds ± 1 percent opacity, the condition shall be corrected prior to conducting any subsequent test runs. The smoke meter shall be demonstrated, at the time of installation, to meet the specifications listed in Table 9-1. This demonstration shall be repeated following any subsequent repair or replacement of the photocell or associated electronic circuitry including the chart recorder or output meter, or every 6 months, whichever occurs first.

3.3.1 Calibration. The smoke meter is calibrated after allowing a minimum of 30 minutes warmup by alternately producing simulated opacity of 0 percent and 100 percent. When stable response at 0 percent or 100 percent is noted, the smoke meter is adjusted to produce an output of 0 percent or 100 percent, as appropriate. This calibration shall be repeated until

FIGURE 9-1
RECORD OF VISUAL DETERMINATION OF OPACITY

PAGE___of___

COMPANY_____
LOCATION_____
TEST NUMBER_____
DATE_____
TYPE FACILITY_____
CONTROL DEVICE_____

HOURS OF OBSERVATION_____
OBSERVER_____
OBSERVER CERTIFICATION DATE_____
OBSERVER AFFILIATION_____
POINT OF EMISSIONS_____
HEIGHT OF DISCHARGE POINT_____

	Initial			Final
CLOCK TIME				
OBSERVER LOCATION Distance to Discharge				
Direction from Discharge				
Height of Observation Point				
BACKGROUND DESCRIPTION				
WEATHER CONDITIONS Wind Direction				
Wind Speed				
Ambient Temperature				
SKY CONDITIONS (clear, overcast, % clouds, etc.)				
PLUME DESCRIPTION Color				
Distance Visible				
OTHER INFORMATION				

SUMMARY OF AVERAGE OPACITY

Set Number	Time	Opacity	
	Start--End	Sum	Average

Readings ranged from ____ to ____ % opacity

The source was/was not in compliance with ____ at the time evaluation was made.

stable 0 percent and 100 percent readings are produced without adjustment. Simulated 0 percent and 100 percent opacity values may be produced by alternately switching the power to the light source on and off while the smoke generator is not producing smoke.

3.3.2 Smoke Meter Evaluation. The smoke meter design and performance are to be evaluated as follows:

3.3.2.1 Light Source. Verify from manufacturer's data and from voltage measurements made at the lamp, as installed, that the lamp is operated within ± 5 percent of the nominal rated voltage.

3.3.2.2 Spectral Response of Photocell. Verify from manufacturer's data that the photocell has a photopic response; i.e., the spectral sensitivity of the cell shall closely approximate the standard spectral-luminosity curve for photopic vision which is referenced in (b) of Table 9-1.

TABLE 9-1—SMOKE METER DESIGN AND PERFORMANCE SPECIFICATIONS

Parameter	Specification
a. Light source	Incandescent lamp operated at nominal rated voltage.
b. Spectral response of photocell	Photopic (daylight spectral response of the human eye—Citation 3).
c. Angle of view	15° maximum total angle.
d. Angle of projection	15° maximum total angle.
e. Calibration error	±3% opacity, maximum
f. Zero and span drift	±1% opacity, 30 minutes
g. Response time	5 seconds.

3.3.2.3 Angle of View. Check construction geometry to ensure that the total angle of view of the smoke plume, as seen by the photocell, does not exceed 15°. The total angle of view may be calculated from: $\theta = 2 \tan^{-1} d/2L$, where θ = total angle of view; d = the sum of the photocell diameter + the diameter of the limiting aperture; and L = the distance from the photocell to the limiting aperture. The limiting aperture is the point in the path between the photocell and the smoke plume where the angle of view is most restricted. In smoke generator smoke meters this is normally an orifice plate.

3.3.2.4 Angle of Projection. Check construction geometry to ensure that the total angle of projection of the lamp on the smoke plume does not exceed 15°. The total angle of projection may be calculated from: $\theta = 2 \tan^{-1} d/2L$, where θ = total angle of projection; d = the sum of the length of the lamp filament + the diameter of the limiting aperture; and L = the distance from the lamp to the limiting aperture.

3.3.2.5 Calibration Error. Using neutral-density filters of known opacity, check the error between the actual response and the theoretical linear response of the smoke meter. This check is accomplished by first calibrating the smoke meter according to 3.3.1 and then inserting a series of three neutral-density filters of nominal opacity of 20, 50, and 75 percent in the smoke meter pathlength. Filters calibrated within ± 2 percent shall be used. Care should be taken when inserting the filters to prevent stray light from affecting the meter. Make a total of five nonconsecutive readings for each filter. The maximum error on any one reading shall be 3 percent opacity.

3.3.2.6 Zero and Span Drift. Determine the zero and span drift by calibrating and operating the smoke generator in a normal manner over a 1—hour period. The drift is measured by checking the zero and span at the end of this period.

3.3.2.7 Response Time. Determine the response time by producing the series of five simulated 0 percent and 100 percent opacity values and observing the time required to reach stable response. Opacity values of 0 percent and 100 percent may be simulated by alternately switching the power to the light source off and on while the smoke generator is not operating.

4. Bibliography.

1. Air Pollution Control District Rules

FIGURE 9-2—OBSERVATION RECORD

Page —— of ——

Company ..... Observer .....
Location ..... Type facility .....
Test Number ..... Point of emissions .....
Date .....

Hr.	Min.	Seconds				Steam plume (check if applicable)		Comments
		0	15	30	45	Attached	Detached	
	0							
	1							
	2							
	3							
	4							
	5							
	6							
	7							
	8							
	9							
	10							
	11							
	12							
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	25							
	26							
	27							
	28							
	29							

and Regulations, Los Angeles County Air Pollution Control District, Regulation IV, Prohibitions, Rule 50.

2. Weisburd, Melvin I., Field Operations and Enforcement Manual for Air, U.S. Environmental Protection Agency, Research Triangle Park, NC. APTD-1100, August 1972, pp. 4.1-4.36.

3. Condon, E.U., and Odishaw, H., Handbook of Physics, McGraw-Hill Co., New York, NY, 1958, Table 3.1, p. 6-52.

[s60, App. A, Alt. Meth.

Alternate Method 1—Determination of the Opacity of Emissions From Stationary Sources Remotely by Lidar

This alternate method provides the quantitative determination of the opacity of an emissions plume remotely by a mobile lidar system (laser radar; Light Detection and Ranging). The method includes procedures for the calibration of the lidar and procedures to be used in the field for the lidar determination of plume opacity. The lidar is used to measure plume opacity during either day or nighttime hours because it contains its own pulsed light source or transmitter. The operation of the lidar is not dependent upon ambient lighting conditions (light, dark, sunny or cloudy).

The lidar mechanism or technique is applicable to measuring plume opacity at numerous wavelengths of laser radiation. However, the performance evaluation and calibration test results given in support of this method apply only to a lidar that employs a ruby (red light) laser [Reference 5.1].

1. Principle and Applicability

1.1 Principle. The opacity of visible emissions from stationary sources (stacks, roof vents, etc.) is measured remotely by a mobile lidar (laser radar).

1.2 Applicability. This method is applicable for the remote measurement of the opacity of visible emissions from stationary sources during both nighttime and daylight conditions, pursuant to 40 CFR § 60.11(b). It is also applicable for the calibration and performance verification of the mobile lidar for the measurement of the opacity of emissions. A performance/design specification for a basic lidar system is also incorporated into this method.

1.3 Definitions.

Azimuth angle: The angle in the horizontal plane that designates where the laser beam is pointed. It is measured from an arbitrary fixed reference line in that plane.

Backscatter: The scattering of laser light in a direction opposite to that of the incident laser beam due to reflection from particulates along the beam's atmospheric path which may include a smoke plume.

Backscatter signal: The general term for the lidar return signal which results from laser light being backscattered by atmospheric and smoke plume particulates.

Convergence distance: The distance from the lidar to the point of overlap of the lidar receiver's field—of—view and the laser beam.

Elevation angle: The angle of inclination of the laser beam referenced to the horizontal plane.

Far region: The region of the atmosphere's path along the lidar line—of—sight beyond or behind the plume being measured.

Lidar: Acronym for Light Detection and Ranging.

Lidar range: The range or distance from the lidar to a point of interest along the lidar line—of—sight.

Near region: The region of the atmospheric path along the lidar line—of—sight between the lidar's convergence distance and the plume being measured.

Opacity: One minus the optical transmittance of a smoke plume, screen target, etc.

Pick interval: The time or range intervals in the lidar backscatter signal whose minimum average amplitude is used to calculate opacity. Two pick intervals are required, one in the near region and one in the far region.

Plume: The plume being measured by lidar.

Plume signal: The backscatter signal resulting from the laser light pulse passing through a plume.

1/R2 correction: The correction made for the systematic decrease in lidar backscatter signal amplitude with range.

Reference signal: The backscatter signal resulting from the laser light pulse passing through ambient air.

Sample interval: The time period between successive samples for a digital signal or between successive measurements for an analog signal.

Signal spike: An abrupt, momentary increase and decrease in signal amplitude.

Source: The source being tested by lidar.

Time reference: The time (to) when the laser pulse emerges from the laser, used as the reference in all lidar time or range measurements.

2. Procedures

The mobile lidar calibrated in accordance with Paragraph 3 of this method shall use the following procedures for remotely measuring the opacity of stationary source emissions:

2.1 Lidar Position. The lidar shall be positioned at a distance from the plume sufficient to provide an unobstructed view of the source emissions. The plume must be at a range of at least 50 meters or three consecutive pick intervals (whichever is greater) from the lidar's transmitter/receiver convergence distance along the line—of—sight. The maximum effective opacity measurement distance of the lidar is a function of local atmospheric conditions, laser beam diameter, and plume diameter. The test position of the lidar shall be selected so that the diameter of the laser beam at the measurement point within the plume shall be no larger than three-fourths the plume diameter. The beam diameter is calculated by Equation (AM1-1):

$$D(\text{lidar}) = A + R\phi \leq 0.75\ D(\text{Plume}) \quad \text{(AM1-1)}$$

Where:

D(Plume) = diameter of the plume (cm),

ϕ = laser beam divergence measured in radians

R = range from the lidar to the source (cm)

D(Lidar) = diameter of the laser beam at range R (cm),

A = diameter of the laser beam or pulse where it leaves the laser.

The lidar range, R, is obtained by aiming and firing the laser at the emissions source structure immediately below the outlet. The range value is then determined from the backscatter signal which consists of a signal spike (return from source structure) and the atmospheric backscatter signal [Reference 5.1]. This backscatter signal should be recorded.

When there is more than one source of emissions in the immediate vicinity of the plume, the lidar shall be positioned so that the laser beam passes through only a single plume, free from any interference of the other plumes for a minimum of 50 meters or three consecutive pick intervals (whichever is greater) in each region before and beyond the plume along the line—of—sight (determined from the backscatter signals). The lidar shall initially be positioned so that its line—of—sight is approximately perpendicular to the plume.

When measuring the opacity of emissions from rectangular outlets (e.g., roof monitors, open baghouses, noncircular stacks, etc.), the lidar shall be placed in a position so that its line—of—sight is approximately perpendicular to the longer (major) axis of the outlet.

2.2 Lidar Operational Restrictions. The lidar receiver shall not be aimed within an

Method 10—Determination of Carbon Monoxide Emissions From Stationary Sources

1. Principle and Applicability

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

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

2. Range and Sensitivity

2.1 Range. 0 to 1,000 ppm.

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

3. Interferences

Any substance having a strong absorption of infrared energy will interfere to some extent. For example, discrimination ratios for water (H2O) and carbon dioxide (CO2) are 3.5 percent H2O per 7 ppm CO and 10 percent CO2 per 10 ppm CO, respectively, for devices measuring in the 1,500 to 3,000 ppm range. For devices measuring in the 0 to 100 ppm range, interference ratios can be as high as 3.5 percent 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 ± 5 percent of span after calibration.

5. Apparatus

5.1 Continuous Sample (Figure 10-1).

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

|_{Footnote}\1\ Mention of trade names or specific products does not constitute endorsement by the Environmental Protection Agency.

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^3). Leak-test the bag in the laboratory before using by evacuating bag with a pump followed by a dry gas meter. When evacuation is complete, there should be no flow through the meter.

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

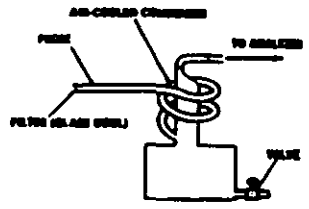
5.3 Analysis (Figure 10-3).

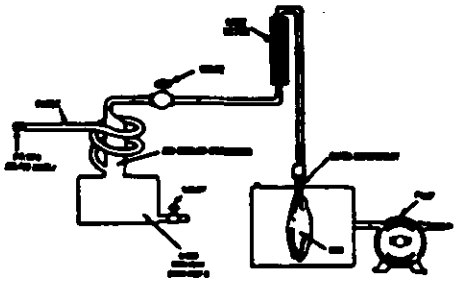
5.3.1 Carbon Monoxide Analyzer. Nondispersive infrared spectrometer, or equivalent. This instrument should be demonstrated, preferably by the manufacturer, to meet or exceed manufacturer's specifications and those described in this method.

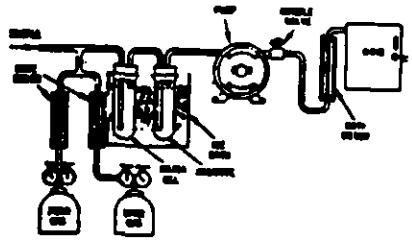
5.3.2 Drying Tube. To contain approximately 200 g of silica gel.

5.3.3 Calibration Gas. Refer to section 6.1.

5.3.4 Filter. As recommended by NDIR manufacturer.







5.3.5 CO2 Removal Tube. To contain approximately 500 g of ascarite.

5.3.6 Ice Water Bath. For ascarite and silica gel tubes.

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

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

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

6. Reagents

6.1 Calibration Gases. Known concentration of CO in nitrogen (N2) for instrument span, prepurified grade of N2 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.

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 section 7.2 and 8). CO2 content of the gas may be determined by using the Method 3 integrated sample procedure, or by weighing the ascarite CO2 removal tube and computing CO2 concentration from the gas volume sampled and the weight gain of the tube.

7.1.2 Integrated Sampling. Evacuate the flexible bag. Set up the equipment as shown in Figure 10-2 with the bag disconnected. Place the probe in the stack and purge the sampling line. Connect the

bag, making sure that all connections are leak free. Sample at a rate proportional to the stack velocity. CO2 content of the gas may be determined by using the Method 3 integrated sample procedures, or by weighing the ascarite CO2 removal tube and computing CO2 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 section 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 1 hour for warm-up. During this time check the sample conditioning apparatus, i.e., filter, condenser, drying tube, and CO2 removal tube, to ensure that each component is in good operating condition. Zero and calibrate the instrument according to the manufacturer's procedures using, respectively, nitrogen and the calibration gases.

TABLE 10-1—FIELD DATA

	Comments
Location	
Test	
Date	
Operator	

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

9. Calculation

Calculate the concentration of carbon monoxide in the stack using Equation 10-1.

$$C_{CO\ stack} = C_{CO\ wet}(1 - F_{w_2})$$

Eq. 10-1

Where:

CCO stack = Concentration of CO in stack, ppm by volume (dry basis).

CCO NDIR = Concentration of CO measured by NDIR analyzer, ppm by volume (dry basis).

FCO 2 = Volume fraction of CO2 in sample, i.e., percent CO2 from Orsat analysis divided by 100.

10. Alternative Procedures

10.1 Interference Trap. The sample conditioning system described in Method 10A, sections 2.1.2 and 4.2, may be used as an alternative to the silica gel and ascarite traps.

11. Bibliography

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

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.

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

4. Models 215A, 315A, and 415A Infrared Analyzers, Beckman Instruments, Inc., Beckman Instructions 1635-B, Fullerton, CA. October 1967.

5. Continuous CO Monitoring System, Model AS611, Intertech Corp., Princeton, NJ.

6. UNOR Infrared Gas Analyzers, Bendix Corp., Ronceverte, WV

ADDENDA

A. PERFORMANCE SPECIFICATIONS FOR NDIR CARBON MONOXIDE ANALYZERS

Range (minimum)	0–1000 ppm.
Output (minimum)	0–10mV.
Minimum detectable sensitivity.	20 ppm.
Rise time, 90 percent (maximum).	30 seconds.
Fall time, 90 percent (maximum).	30 seconds.
Zero drift (maximum)	10% in 8 hours.
Span drift (maximum)	10% in 8 hours.
Precision (minimum)	±2% of full scale.
Noise (maximum)	±1% of full scale.
Linearity (maximum deviation)	2% of full scale.
Interference rejection ratio	CO_2—1000 to 1, H_2O—50 to 1.

B. Definitions of Performance Specifications.

Range——The minimum and maximum measurement limits.

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

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

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

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

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

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

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

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

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

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

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

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

Method 13B—Determination of Total Fluoride Emissions From Stationary Sources——Specific Ion Electrode Method

1. Principle and Applicability

1.1 Applicability. This method applies to the determination of fluoride (F) emissions from stationary sources as specified in the regulations. It does not measure fluorocarbons, such as freons.

1.2 Principle. Gaseous and particulate F are withdrawn isokinetically from the source and collected in water and on a filter. The total F is then determined by the specific ion electrode method.

2. Range and Sensitivity

The range of this method is 0.02 to 2,000 μg F/ml; however, measurements of less than 0.1 μg F/ml require extra care. Sensitivity has not been determined.

3. Interferences

Grease on sample-exposed surfaces may cause low F results because of adsorption.

4. Precision and Accuracy

4.1 Precision. The following estimates are based on a collaborative test done at a primary aluminum smelter. In the test, six laboratories each sampled the stack simultaneously using two sampling trains for a total of 12 samples per sampling run. Fluoride concentrations encountered during the test ranged from 0.1 to 1.4 mg F/m^3. The within-laboratory and between-laboratory standard deviations, which include sampling and analysis errors, are 0.037 mg F/m^3 with 60 degrees of freedom and 0.056 mg F/m^3 with five degrees of freedom, respectively.

4.2 Accuracy. The collaborative test did not find any bias in the analytical method.

5. Apparatus

5.1 Sampling Train and Sample Recovery. Same as Method 13A, Sections 5.1 and 5.2, respectively.

5.2 Analysis. The following items are needed:

5.2.1 Distillation Apparatus, Bunsen Burner, Electric Muffle Furnace, Crucibles, Beakers, Volumetric Flasks, Erlenmeyer Flasks or Plastic Bottles, Constant Temperature Bath, and Balance. Same as Method 13A, Sections 5.3.1 to 5.3.9, respectively, except include also 100—ml polyethylene beakers.

5.2.2 Fluoride Ion Activity Sensing Electrode.

5.2.3 Reference Electrode. Single junction, sleeve type.

5.2.4 Electrometer. A pH meter with millivolt-scale capable of ± 0.1—mv resolution, or a specific ion meter made specifically for specific ion use.

5.2.5 Magnetic Stirrer and TFE 2 Fluorocarbon-Coated Stirring Bars. |_{Footnote} 2 Mention of any trade name or specific product does not constitute endorsement by the U.S. Environmental Protection Agency.

6. Reagents

6.1 Sampling and Sample Recovery. Same as Method 13A, Sections 6.1 and 6.2, respectively.

6.2 Analysis. Use ACS reagent grade chemicals (or equivalent), unless otherwise specified. The reagents needed for analysis are as follows:

6.2.1 Calcium Oxide (CaO). Certified grade containing 0.005 percent F or less.

6.2.2 Phenolphthalein Indicator. Dissolve 0.1 g of phenolphthalein in a mixture of 50 ml of 90 percent ethanol and 50 ml deionized distilled water.

6.2.3 Sodium Hydroxide (NaOH). Pellets.

6.2.4 Sulfuric Acid (H_2SO_4), Concentrated.

6.2.5 Filters. Whatman No. 541, or equivalent.

6.2.6 Water. From same container as 6.1.2 of Method 13A.

6.2.7 Sodium Hydroxide, 5 M. Dissolve 20 g of NaOH in 100 ml of deionized distilled water.

6.2.8 Sulfuric Acid, 25 percent (V/V). Mix 1 part of concentrated H_2SO_4 with 3 parts of deionized distilled water.

6.2.9 Total Ionic Strength Adjustment Buffer (TISAB). Place approximately 500 ml of deionized distilled water in a 1-liter beaker. Add 57 ml of glacial acetic acid, 58 g of sodium chloride, and 4 g of cyclohexylene dinitrilo tetraacetic acid. Stir to dissolve. Place the beaker in a water bath to cool it. Slowly add 5 M NaOH to the solution, measuring the pH continuously with a calibrated pH/reference electrode pair, until the pH is 5.3. Cool to room temperature. Pour into a 1-liter volumetric flask, and dilute to volume with deionized distilled water. Commercially prepared TISAB may be substituted for the above.

6.2.10 Fluoride Standard Solution, 0.1 M. Oven dry some sodium fluoride (NaF) for a minimum of 2 hours at 110°C, and store in a desiccator. Then add 4.2 g of NaF to a 1-liter volumetric flask, and add enough deionized distilled water to dissolve. Dilute to volume with deionized distilled water.

7. Procedure

7.1 Sampling, Sample Recovery, and Sample Preparation and Distillation. Same as Method 13A, Sections 7.1, 7.2, and 7.3, respectively, except the notes concerning chloride and sulfate interferences are not applicable.

7.2 Analysis.

7.2.1 Containers No. 1 and No. 2. Distill suitable aliquots from Containers No. 1 and No. 2. Dilute the distillate in the volumetric flasks to exactly 250 ml with deionized distilled water and mix thoroughly. Pipet a 25—ml aliquot from each of the distillate and separate beakers. Add an equal volume of TISAB, and mix. The sample should be at the same temperature as the calibration standards when measurements are made. If ambient laboratory temperature fluctuates more than ± 2°C from the temperature at which the calibration standards were measured, condition samples and standards in a constant-temperature bath before measurement. Stir the sample with a magnetic stirrer during measurement to minimize electrode response time. If the stirrer generates enough heat to change solution temperature, place a piece of temperature insulating material such as cork, between the stirrer and the beaker. Hold dilute samples (below 10-4 M fluoride ion content) in polyethylene beakers during measurement.

Insert the fluoride and reference electrodes into the solution. When a steady millivolt reading is obtained, record it. This may take several minutes. Determine concentration from the calibration curve. Between electrode measurements, rinse the electrode with deionized distilled water.

7.2.2 Container No. 3 (Silica Gel). Same as Method 13A, Section 7.4.2.

8. Calibration

Maintain a laboratory log of all calibrations.

8.1 Sampling Train. Same as Method 13A.

8.2 Fluoride Electrode. Prepare fluoride standardizing solutions by serial dilution of the 0.1 M fluoride standard solution. Pipet 10 ml of 0.1 M fluoride standard solution into a 100—ml volumetric flask, and make up to the mark with deionized distilled water for a 10-2 M standard solution. Use 10 ml of 10-2 M solution to make a 10-3 M solution in the same manner. Repeat the dilution procedure and make 10-4 and 10-5 solutions.

Pipet 50 ml of each standard into a

separate beaker. Add 50 ml of TISAB to each beaker. Place the electrode in the most dilute standard solution. When a steady millivolt reading is obtained, plot the value on the linear axis of semilog graph paper versus concentration on the log axis. Plot the nominal value for concentration of the standard on the log axis, e.g., when 50 ml of 10-2 M standard is diluted with 50 ml of TISAB, the concentration is still designated "10-2 M."

Between measurements soak the fluoride sensing electrode in deionized distilled water for 30 seconds, and then remove and blot dry. Analyze the standards going from dilute to concentrated standards. A straight-line calibration curve will be obtained, with nominal concentrations of 10-4, 10-3, 10-2, and 10-1 fluoride molarity on the log axis plotted versus electrode potential (in mv) on the linear scale. Some electrodes may be slightly nonlinear between 10-5 and 10-4 M. If this occurs, use additional standards between these two concentrations.

Calibrate the fluoride electrode daily, and check it hourly. Prepare fresh fluoride standardizing solutions daily (10-2 M or less). Store fluoride standardizing solutions in polyethylene or polypropylene containers.

Note: Certain specific ion meters have been designed specifically for fluoride electrode use and give a direct readout of fluoride ion concentration. These meters may be used in lieu of calibration curves for fluoride measurements over narrow concentration ranges. Calibrate the meter according to the manufacturer's instructions.)

9. Calculations

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

9.1 Nomenclature. Same as Method 13A, Section 9.1. In addition:

M = F concentration from calibration curve, molarity.

9.2 Average Dry Gas Meter Temperature and Average Orifice Pressure Drop, Dry Gas Volume, Volume of Water Vapor and Moisture Content, Fluoride Concentration in Stack Gas, and Isokinetic Variation and Acceptable Results. Same as Method 13A, Sections 9.2 to 9.4, 9.5.2, and 9.6, respectively.

9.3 Fluoride in Sample. Calculate the amount of F in the sample using the following:

$$F_t = K \frac{V_t}{A_t} V_a M \qquad \text{Eq. 13B-1}$$

Where:

K = 19 mg/millimole.

10. Bibliography

1. Same as Method 13A, Citations 1 and 2 of Bibliography.

2. MacLeod, Kathryn E. and Howard L. Crist. Comparison of the SPADNS—Zirconium Lake and Specific Ion Electrode Methods of Fluoride Determination in Stack Emission Samples. Analytical Chemistry. 45:1272-1273. 1973.

Method 18—Measurement of Gaseous Organic Compound Emissions by Gas Chromatography

Introduction

This method should not be attempted by persons unfamiliar with the performance characteristics of gas chromatography, nor by those persons who are unfamiliar with source sampling. Particular care should be exercised in the area of safety concerning choice of equipment and operation in potentially explosive atmospheres.

1. Applicability and Principle

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

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

1.2 Principle.

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

The retention times of each separated component are compared with those of known compounds under identical conditions. Therefore, the analyst confirms the identity and approximate concentrations of the organic emission components beforehand. With this information, the analyst then prepares or purchases commercially available standard mixtures to calibrate the GC under conditions identical to those of the samples. The analyst also determines the need for sample dilution to avoid detector saturation, gas stream filtration to eliminate particulate matter, and prevention of moisture condensation.

2. Range and Sensitivity

2.1 Range. The range of this method is from about 1 part per million (ppm) to the upper limit governed by GC detector saturation or column overloading. The upper limit can be extended by diluting the stack gases with an inert gas or by using smaller gas sampling loops.

2.2 Sensitivity. The sensitivity limit for a compound is defined as the minimum detectable concentration of that compound, or the concentration that produces a signal—to—noise ratio of three to one. The minimum detectable concentration is determined during the presurvey calibration for each compound.

3. Precision and Accuracy

Gas chromatographic techniques typically provide a precision of 5 to 10 percent relative standard deviation (RSD), but an experienced GC operator with a reliable instrument can readily achieve 5 percent RSD. For this method, the following combined GC/operator values are required.

|_(a) Precision. Duplicate analyses are within 5 percent of their mean value.

|_(b) Accuracy. Analysis results of prepared audit samples are within 10 percent of preparation values.

4. Interferences

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

The analytical system is demonstrated to be essentially free from contaminants by periodically analyzing blanks that consist of hydrocarbon-free air or nitrogen.

Sample cross-contamination that occurs when high-level and low-level samples or standards are analyzed alternately, is best dealt with by thorough purging of the GC sample loop between samples.

To assure consistent detector response, calibration gases are contained in dry air. To adjust gaseous organic concentrations when water vapor is present in the sample, water vapor concentrations are determined for those samples, and a correction factor is applied.

5. Presurvey and Presurvey Sampling.

Perform a presurvey for each source to be tested. Refer to Figure 18-1. Some of the information can be collected from literature surveys and source personnel. Collect gas samples that can be analyzed to confirm the identities and approximate concentrations of the organic emissions.

5.1 Apparatus. This apparatus list also applies to Sections 6 and 7.

5.1.1 Teflon Tubing. (Mention of trade names or specific products does not constitute endorsement by the U.S. Environmental Protection Agency.) Diameter and length determined by connection requirements of cylinder regulators and the GC. Additional tubing is necessary to connect the GC sample loop to the sample.

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

5.1.3 Pump. Capable of pumping 100 ml/min. For flushing sample loop.

5.1.4 Flowmeters. To measure flow rates.

5.1.5 Regulators. Used on gas cylinders for GC and for cylinder standards.

5.1.6 Recorder. Recorder with linear strip chart is minimum acceptable. Integrator (optional) is recommended.

5.1.7 Syringes. 0.5—ml, 1.0— and 10—microliter sizes, calibrated, maximum accuracy (gas tight), for preparing calibration standards. Other appropriate sizes can be used.

5.1.8 Tubing Fittings. To plumb GC and gas cylinders.

5.1.9 Septums. For syringe injections.

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

5.1.11 Soap Film Flow Meter. To determine flow rates.

5.1.12 Tedlar Bags. 10— and 50-liter capacity, for preparation of standards.

5.1.13 Dry Gas Meter with Temperature and Pressure Gauges. Accurate to ± 2 percent, for perparation of gas standards.

5.1.14 Midget Impinger/Hot Plate Assembly. For preparation of gas standards.

5.1.15 Sample Flasks. For presurvey samples, must have gas-tight seals.

5.1.16 Adsorption Tubes. If necessary, blank tubes filled with necessary adsorbent (charcoal, Tenax, XAD-2, etc.) for presurvey samples.

5.1.17 Personnel Sampling Pump. Calibrated, for collecting adsorbent tube presurvey samples.

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

5.1.19 Sample Probes. Pyrex or stainless steel, of sufficient length to reach centroid of stack, or a point no closer to the walls than 1 m.

5.1.20 Barometer. To measure barometric pressure.

5.2 Reagents.

5.2.1 Deionized Distilled Water.

5.2.2 Methylene Dichloride.

5.2.3 Calibration Gases. A series of standards prepared for every compound of interest.

5.2.4 Organic Compound Solutions. Pure

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

5.2.5 Extraction Solvents. For extraction of adsorbent tube samples in preparation for analysis.

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

5.2.7 Carrier Gas. Hydrocarbon free, as recommended by the manufacturer for operation of the detector and compatability with the column.

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

5.3 Sampling.

5.3.1 Collection of Samples with Glass Sampling Flasks. Presurvey samples can be collected in precleaned 250—ml double-ended glass sampling flasks. Teflon stopcocks, without grease, are preferred. Flasks should be cleaned as follows: Remove the stopcocks from both ends of the flasks, and wipe the parts to remove any grease. Clean the stopcocks, barrels, and receivers with methylene dichloride. Clean all glass ports with a soap solution, then rinse with tap and deionized distilled water. Place the flask in a cool glass annealing furnace and apply heat up to 500°C. Maintain at this temperature for 1 hour. After this time period, shut off and open the furnace to allow the flask to cool. Grease the stopcocks with stopcock grease and return them to the flask receivers. Purge the assembly with high-purity nitrogen for 2 to 5 minutes. Close off the stopcocks after purging to maintain a slight positive nitrogen pressure. Secure the stopcocks with tape.

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

5.3.1.1 Evacuated Flask Procedure. Use a high-vacuum pump to evacuate the flask to the capacity of the pump; then close off the stopcock leading to the pump. Attach a 6—mm outside diameter (OD) glass tee to the flask inlet with a short piece of Teflon tubing. Select a 6—mm OD borosilicate sampling probe, enlarged at one end to a 12—mm OD and of sufficient length to reach the centroid of the duct to be sampled. Insert a glass wool plug in the enlarged end of the probe to remove particulate matter. Attach the other end of the probe to the tee with a short piece of Teflon tubing. Connect a rubber suction bulb to the third leg of the tee. Place the filter end of the probe at the centroid of the duct, or at a point no closer to the walls than 1 m, and purge the probe with the rubber suction bulb. After the probe is completely purged and filled with duct gases, open the stopcock to the grab flask until the pressure in the flask reaches duct pressure. Close off the stopcock, and remove the probe from the duct. Remove the tee from the flask and tape the stopcocks to prevent leaks during shipment. Measure and record the duct temperature and pressure.

5.3.1.2 Purged Flask Procedure. Attach one end of the sampling flask to a rubber suction bulb. Attach the other end to a 6—mm OD glass probe as described in Section 5.3.1.1. Place the filter end of the probe at the centroid of the duct, or at a point no closer to the walls than 1 m, and apply suction with the bulb to completely purge the probe and flask. After the flask has been purged, close off the stopcock near the suction bulb, and then close the stopcock near the probe. Remove the probe from the duct, and disconnect both the probe and suction bulb. Tape the stopcocks to prevent leakage during shipment. Measure and record the duct temperature and pressure.

5.3.2 Flexible Bag Procedure. Tedlar or aluminized Mylar bags can also be used to obtain the presurvey sample. Use new bags, and leak check them before field use. In addition, check the bag before use for contamination by filling it with nitrogen or air, and analyzing the gas by GC at high sensitivity. Experience indicates that it is desirable to allow the inert gas to remain in the bag about 24 hours or longer to check for desorption of organics from the bag. Follow the leak check and sample collection procedures given in Section 7.1.

5.3.3 Determination of Moisture Content. For combustion or water-controlled processes, obtain the moisture content from plant personnel or by measurement during the presurvey. If the source is below 59°C, measure the wet bulb and dry bulb temperatures, and calculate the moisture content using a psychrometric chart. At higher temperatures, use Method 4 to determine the moisture content.

5.4 Determination of Static Pressure. Obtain the static pressure from the plant personnel or measurement. If a type S pitot tube and an inclined manometer are used, take care to align the pitot tube 90°from the direction of the flow. Disconnect one of the tubes to the manometer, and read the static pressure; note whether the reading is positive or negative.

5.5 Collection of Presurvey Samples with Adsorption Tube. Follow Section 7.4 for presurvey sampling.

6. Analysis Development

6.1 Selection of GC Parameters.

6.1.1 Column Choice. Based on the initial contact with plant personnel concerning the plant process and the anticipated emissions, choose a column that provides good resolution and rapid analysis time. The choice of an appropriate column can be aided by a literature search, contact with manufacturers of GC columns, and discussion with personnel at the emission source.

Most column manufacturers keep excellent records of their products. Their technical service departments may be able to recommend appropriate columns and detector type for separating the anticipated compounds, and they may be able to provide information on interferences, optimum operating conditions, and column limitations.

Plants with analytical laboratories may also be able to provide information on appropriate analytical procedures.

6.1.2 Preliminary GC Adjustment. Using the standards and column obtained in Section 6.1.1, perform initial tests to determine appropriate GC conditions that provide good resolution and minimum analysis time for the compounds of interest.

6.1.3 Preparation of Presurvey Samples. If the samples were collected on an adsorbent, extract the sample as recommended by the manufacturer for removal of the compounds with a solvent suitable to the type of GC analysis. Prepare other samples in an appropriate manner.

6.1.4 Presurvey Sample Analysis. Before analysis, heat the presurvey sample to the duct temperature to vaporize any condensed material. Analyze the samples by the GC procedure, and compare the retention times against those of the calibration samples that contain the components expected to be in the stream. If any compounds cannot be identified with certainty by this procedure, identify them by other means such as GC/mass spectroscopy (GC/MS) or GC/infrared techniques. A GC/MS system is recommended.

Use the GC conditions determined by the procedures of Section 6.1.2 for the first injection. Vary the GC parameters during subsequent injections to determine the optimum settings. Once the optimum settings have been determined, perform repeat injections of the sample to determine the retention time of each compound. To inject a sample, draw sample through the loop at a constant rate (100 ml/min for 30 seconds). Be careful not to pressurize the gas in the loop. Turn off the pump and allow the gas in the sample loop to come to ambient pressure. Activate the sample valve, and record injection time, loop temperature, column temperature, carrier flow rate, chart speed,

and attenuator setting. Calculate the retention time of each peak using the distance from injection to the peak maximum divided by the chart speed. Retention times should be repeatable within 0.5 seconds.

If the concentrations are too high for appropriate detector response, a smaller sample loop or dilutions may be used for gas samples, and, for liquid samples, dilution with solvent is appropriate. Use the standard curves (Section 6.3) to obtain an estimate of the concentrations.

Identify all peaks by comparing the known retention times of compounds expected to be in the retention times of peaks in the sample. Identify any remaining unidentified peaks which have areas larger than 5 percent of the total using a GC/MS, or estimation of possible compounds by their retention times compared to known compounds, with confirmation by further GC analysis.

6.2 Calibration Standards. Prepare or obtain enough calibration standards so that there are three different concentrations of each organic compound expected to be measured in the source sample. For each organic compound, select those concentrations that bracket the concentrations expected in the source samples. A calibration standard may contain more than one organic compound. If available, commercial cylinder gases may be used if their concentrations have been certified by direct analysis.

If samples are collected in adsorbent tubes (charcoal, XAD-2, Tenax, etc.), prepare or obtain standards in the same solvent used for the sample extraction procedure. Refer to Section 7.4.3.

Verify the stability of all standards for the time periods they are used. If gas standards are prepared in the laboratory, use one or more of the following procedures.

6.2.1 Preparation of Standards from High Concentration Cylinder Standards. Obtain enough high concentration cylinder standards to represent all the organic compounds expected in the source samples.

Use these high concentration standards to prepare lower concentration standards by dilution, as shown by Figures 18-5 and 18-6.

To prepare the diluted calibration samples, calibrated rotameters are normally used to meter both the high concentration calibration gas and the diluent gas. Other types of flowmeters and commercially available dilution systems can also be used.

Calibrate each flowmeter before use by placing it between the diluent gas supply and suitably sized bubble meter, spirometer, or wet test meter. Record all data shown on Figure 18-4. While it is desirable to calibrate the cylinder gas flowmeter with cylinder gas, the available quantity and cost may preclude it. The error introduced by using the diluent gas for calibration is insignificant for gas mixtures of up to 1,000 to 2,000 ppm of each organic component.

Once the flowmeters are calibrated, connect the flowmeters to the calibration and diluent gas supplies using 6—mm Teflon tubing. Connect the outlet side of the flowmeters through a connector to a leak-free Tedlar bag as shown in Figure 18-5. (See Section 7.1 for bag leak-check procedures.) Adjust the gas flow to provide the desired dilution, and fill the bag with sufficient gas for GC calibration. Be careful not to overfill and cause the bag to apply additional pressure on the dilution system. Record the flow rates of both flowmeters, and the laboratory temperature and atmospheric pressure. Calculate the concentration Cs in ppm of each organic in the diluted gas as follows:

$$C_s = \frac{10^6 \ (\bar{X} \ q_c)}{q_c + q_d}$$

Eq. 18-1

Where:

10\6\ = Conversion to ppm.

X = Mole or volume fraction of the organic in the calibration gas to be diluted.

qc = Flow rate of the calibration gas to be diluted.

qd = Diluent gas flow rate.

Single-stage dilutions should be used to prepare calibration mixtures up to about 1:20 dilution factor.

For greater dilutions, a double dilution system is recommended, as shown in Figure 18-6. Fill the Tedlar bag with the dilute gas from the second stage. Record the laboratory temperature, barometric pressure, and static pressure readings. Correct the flow reading for temperature and pressure. Calculate the concentration Cs in ppm of the organic in the final gas mixture as follows:

$$C_s = 10^6 \ \bar{X} \left(\frac{q_{c1}}{q_{c1} + q_{d1}} \right) \left(\frac{q_{c2}}{q_{c2} + q_{d2}} \right)$$

Eq. 18-2

Where:

10\6\ = Conversion to ppm.

X = Mole or volume fraction of the organic in the calibration gas to be diluted.

qc1 = Flow rate of the calibration gas to be diluted in stage 1.

qc2 = Flow rate of the calibration gas to be diluted in stage 2.

qd1 = Flow rate of diluent gas in stage 1.

qd2 = Flow rate of diluent gas in stage 2.

Further details of the calibration methods for flowmeters and the dilution system can be found in Citation 21 in the Bibliography.

6.2.2 Preparation of Standards from Volatile Materials. Record all data shown on Figure 18-3.

6.2.2.1 Gas Injection Technique. This procedure is applicable to organic compounds that exist entirely as a gas at ambient conditions. Evacuate a 10-liter Tedlar bag that has passed a leak-check (see Section 7.1), and meter in 5.0 liters of air or nitrogen through a dry gas meter that has been calibrated in a manner consistent with the procedure described in Section 5.1.1 of Method 5. While the bag is filling use a 0.5—ml syringe to inject a known quantity of "pure" gas of the organic compound through the wall of the bag, or through a septum-capped tee at the bag inlet. Withdraw the syringe needle, and immediately cover the resulting hole with a piece of masking tape. In a like manner, prepare dilutions having other concentrations. Prepare a minimum of three concentrations. Place each bag on a smooth surface, and alternately depress opposite sides of the bag 50 times to mix the gases Record the average meter temperature and pressure, the gas volume and the barometric pressure. Record the syringe temperature and pressure before injection.

Calculate each organic standard concentration Cs in ppm as follows:

$$C_s = \frac{G_v \times 10^6 \ \frac{293}{T_s} \ \frac{P_s}{760}}{V_m \ Y \ \frac{293}{T_m} \ \frac{P_m}{760} \ 1000} = \frac{G_v \times 10^3 \ P_s \ T_m}{V_m \ Y \ T_s \ P_m}$$

Eq. 18-3

Where:

Gv = Gas volume or organic compound njected, ml.

10^6 = Conversion to ppm.

Ps = Absolute pressure of syringe before injection, mm Hg.

Ts = Absolute temperature of syringe before injection, °K.

Vm = Gas volume indicated by dry gas meter, liters.

Y = Dry gas meter calibration factor, dimensionless.

Pm = Absolute pressure of dry gas meter, mm Hg.

Tm = Absolute temperature of dry gas meter, °K.

1000 = Conversion factor, ml/liter.

6.2.2.2 Liquid Injection Technique. Use the equipment shown in Figure 18-8. Calibrate the dry gas meter as described in Section 6.2.2.1 with a wet test meter or a spirometer. Use a water manometer for the pressure gauge and glass, Teflon, brass, or stainless steel for all connections. Connect a valve to the inlet of the 50-liter Tedlar bag.

To prepare the standards, assemble the equipment as shown in Figure 18-8, and leak-check the system. Completely evacuate the bag. Fill the bag with hydrocarbon-free air, and evacuate the bag again. Close the inlet valve.

Turn on the hot plate, and allow the water to reach boiling. Connect the bag to the impinger outlet. Record the initial meter reading, open the bag inlet valve, and open the cylinder. Adjust the rate so that the bag will be completely filled in approximately 15 minutes. Record meter pressure and temperature, and local barometric pressure.

Allow the liquid organic to equilibrate to room temperature. Fill the 1.0— or 10—microliter syringe to the desired liquid volume with the organic. Place the syringe needle into the impinger inlet using the septum provided, and inject the liquid into the flowing air stream. Use a needle of sufficient length to permit injection of the liquid below the air inlet branch of the tee. Remove the syringe.

When the bag is filled, stop the pump, and close the bag inlet valve. Record the final meter reading, temperature, and pressure.

Disconnect the bag from the impinger outlet, and either set it aside for at least 1 hour, or massage the bag to insure complete mixing.

Measure the solvent liquid density at room temperature by accurately weighing a known volume of the material on an analytical balance to the nearest 1.0 milligram. A ground-glass stoppered 25—mil volumetric flask or a glass-stoppered specific gravity bottle is suitable for weighing. Calculate the result in terms of g/ml. As an alternative, literature values of the density of the liquid at 20 °C may be used.

Calculate each organic standard concentration Cs in ppm as follows:

$$C_s = \frac{\frac{L_v \rho}{M}(24.055 \times 10^6)}{V_m Y \frac{293}{T_m}\frac{P_m}{760}(1000)}$$

$$= 6.24 \times 10^4 \frac{L_v \rho T_m}{M V_m Y P_m}$$

Eq. 18-4

Where:

Lv = Liquid volume of organic injected, ul.

ul = Liquid organic density as determined, g/ml.

M = Molecular weight of organic, g/g—mole.

24.055 = Ideal gas molar volume at 293 °K and 760 mm Hg, liters/g—mole.

10^6 = Conversion to ppm.

1000 = Conversion factor, ul/ml.

6.3 Preparation of Calibration Curves. Establish proper GC conditions, then flush the sampling loop for 30 seconds at a rate of 100 ml/min. Allow the sample loop pressure to equilibrate to atmospheric pressure, and activate the injection valve. Record the standard concentration, attenuator factor, injection time, chart speed, retention time, peak area, sample loop temperature, column temperature, and carrier gas flow rate. Repeat the standard injection until two consecutive injections give area counts within 5 percent of their average. The average value multiplied by the attenuator factor is then the calibration area value for the concentration.

Repeat this procedure for each standard. Prepare a graphical plot of concentration (Cs) versus the calibration area values. Perform a regression analysis, and draw the least squares line.

6.4 Relative Response Factors. The calibration curve generated from the standards for a single organic can usually be related to each of the individual GC response curves that are developed in the laboratory for all the compounds in the source. In the field, standards for that single organic can then be used to "calibrate" the GC for all the organics present. This procedure should first be confirmed in the laboratory by preparing and analyzing calibration standards containing multiple organic compounds.

6.5 Quality Assurance for Laboratory Procedures. Immediately after the preparation of the calibration curves and prior to the presurvey sample analysis, the analysis audit described in 40 CFR Part 61, Appendix C, Procedure 2: "Procedure for Field Auditing GC Analysis," should be performed. The information required to document the analysis of the audit samples has been included on the example data sheets shown in Figures 18-3 and 18-7. The audit analyses should agree with the audit concentrations within 10 percent. When available, the tester may obtain audit cylinders by contacting: U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Quality Assurance Division (MD-77), Research Triangle Park, North Carolina 27711. Audit cylinders obtained from a commercial gas manufacturer may be used provided that (a) the gas manufacturer certifies the audit cylinder in a manner similar to the procedure described in 40 CFR Part 61, Appendix B, Method 106, Section 5.2.3.1, and (b) the gas manufacturer obtains an independent analysis of the audit cylinders to verify this analysis. Independent analysis is defined as an analysis performed by an individual other than the individual who performs the gas manufacturer's analysis, while using calibration standards and analysis equipment different from those used for the gas manufacturer's analysis. Verification is complete and acceptable when the independent analysis concentration is within 5 percent of the gas manufacturer's concentration.

7. Final Sampling and Analysis Procedure

Considering safety (flame hazards) and the source conditions, select an appropriate sampling and analysis procedure (Section 7.1, 7.2, 7.3, or 7.4). In situations where a hydrogen flame is a hazard and no intrinsically safe GC is suitable, use the flexible bag collection technique or an adsorption technique. If the source temperature is below 100°C, and the organic concentrations are suitable for the detector to be used, use the direct interface method. If the source gases require dilution, use a dilution interface and either the bag sample or adsorption tubes. The choice between these two techniques will depend on the physical layout of the site, the source temperature, and the storage stability of the compounds if collected in the bag. Sample polar compounds by direct interfacing or dilution interfacing to prevent sample loss by adsorption on the bag.

7.1 Integrated Bag Sampling and Analysis.

7.1.1 Evacuated Container Sampling Procedure. In this procedure, the bags are filled by evacuating the rigid air-tight

containers that hold the bags. Use a field sample data sheet as shown in Figure 18-10. Collect triplicate sample from each sample location.

7.1.1.1 Apparatus.

7.1.1.1.1 Probe. Stainless steel, Pyrex glass, or Teflon tubing probe, according to the duct temperature, with 6.4—mm OD Teflon tubing of sufficient length to connect to the sample bag. Use stainless steel or Teflon unions to connect probe and sample line.

7.1.1.1.2 Quick Connects. Male (2) and female (2) of stainless steel construction.

7.1.1.1.3 Needle Valve. To control gas flow.

7.1.1.1.4 Pump. Leakless Teflon-coated diaphragm-type pump or equivalent. To deliver at least 1 liter/min.

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

7.1.1.1.6 Flowmeter. 0 to 500—ml flow range; with manufacturer's calibration curve.

7.1.1.2 Sampling Procedure. To obtain a sample, assemble the sample train as shown in Figure 18-9. Leak check both the bag and the container. Connect the vacuum line from the needle valve to the Teflon sample line from the probe. Place the end of the probe at the centroid of the stack, or at a point no closer to the walls than 1 m, and start the pump with the needle valve adjusted to yield a flow of 0.5 liter/minute. After allowing sufficient time to purge the line several times, connect the vacuum line to the bag, and evacuate until the rotameter indicates no flow. Then position the sample and vacuum lines for sampling, and begin the actual sampling, keeping the rate proportional to the stack velocity. As a precaution, direct the gas exiting the rotameter away from sampling personnel. At the end of the sample period, shut off the pump, disconnect the sample line from the bag, and disconnect the vacuum line from the bag container. Record the source temperature, barometric pressure, ambient temperature, sampling flow rate, and initial and final sampling time on the data sheet shown in Figure 18-10. Protect the Tedlar bag and its container from sunlight. When possible, perform the analysis within 2 hours of sample collection.

7.1.2 Direct Pump Sampling Procedure. Follow 7.1.1, except place the pump and needle valve between the probe and the bag. Use a pump and needle valve constructed of stainless steel or some other material not affected by the stack gas. Leak check the system, and then purge with stack gas before the connecting to the previously evacuated bag.

7.1.3 Explosion Risk Area Bag Sampling Procedure. Follow 7.1.1 except replace the pump with another evacuated can (see Figure 18-9a). Use this method whenever there is a possibility of an explosion due to pumps, heated probes, or other flame producing equipment.

7.1.4 Other Modified Bag Sampling Procedures. In the event that condensation is observed in the bag while collecting the sample and a direct interface system cannot be used, heat the bag during collection, and maintain it at a suitably elevated temperature during all subsequent operations. (Note: Take care to leak check the system prior to the dilutions so as not to create a potentially explosive atmosphere.) As an alternative, collect the sample gas, and simultaneously dilute it in the Tedlar bag.

In the first procedure, heat the box containing the sample bag to the source temperature, provided the components of the bag and the surrounding box can withstand this temperature. Then transport the bag as rapidly as possible to the analytical area while maintaining the heating, or cover the box with an insulating blanket. In the analytical area, keep the box heated to source temperature until analysis. Be sure that the method of heating the box and the control for the heating circuit are compatible with the safety restrictions required in each area.

To use the second procedure, prefill the Tedlar bag with a known quantity of inert gas. Meter the inert gas into the bag according to the procedure for the preparation of gas concentration standards of volatile liquid materials (Section 6.2.2.2), but eliminate the midget impinger section. Take the partly filled bag to the source, and meter the source gas into the bag through heated sampling lines and a heated flowmeter, or Teflon positive displacement pump. Verify the dilution factors periodically through dilution and analysis of gases of known concentration.

7.1.5 Analysis of Bag Samples.

7.1.5.1 Apparatus. Same as Section 5. A minimum of three gas standards are required.

7.1.5.2 Procedure. Establish proper GC operating conditions as described in Section 6.3, and record all data listed in Figure 18-7. Prepare the GC so that gas can be drawn through the sample valve. Flush the sample loop with gas from one of the three calibration mixtures, and activate the valve. Obtain at least two chromatograms for the mixture. The results are acceptable when the peak areas from two consecutive injections agree to within 5 percent of their average. If they do not, run additional analyses or correct the analytical techniques until this requirement is met. Then analyze the other two calibration mixtures in the same manner. Prepare a calibration curve as described in the same manner. Prepare a calibration curve as described in Section 6.3.

Analyze the source gas samples by connecting each bag to the sampling valve with a piece of Teflon tubing identified for that bag. Follow the specifications on replicate analyses specified for the calibration gases. Record the data listed in Figure 18-11. If certain items do not apply, use the notation "N.A." After all samples have been analyzed, repeat the analyses of the calibration gas mixtures, and generate a second calibration curve. Use an average of the two curves to determine the sample gas concentrations. If the two calibration curves differ by more than 5 percent from their mean value, then report the final results by comparison to both calibration curves.

7.1.6 Determination of Bag Water Vapor Content. Measure and record the ambient temperature and barometric pressure near the bag. From a water saturation vapor pressure table, determine and record the water vapor content as a decimal figure. (Assume the relative humidity to be 100 percent unless a lesser value is known.) If the bag has been maintained at an elevated temperature as described in Section 7.1.4, determine the stack gas water content by Method 4.

7.1.7 Quality Assurance. Immediately prior to the analysis of the stack gas samples, perform audit analyses as described in Section 6.5. The audit analyses must agree with the audit concentrations within 10 percent. If the results are acceptable, proceed with the analyses of the source samples. If they do not agree within 10 percent, then determine the reason for the discrepancy, and take corrective action before proceeding.

7.1.8 Emission Calculations. From the average calibration curve described in Section 7.1.5., select the value of Cs that corresponds to the peak area. Calculate the concentration Cc in ppm, dry basis, of each organic in the sample as follows:

$$C_c = \frac{C_s P_r T_i F_r}{P_i T_r (1-B_{ws})} \qquad \text{Eq. 18-5}$$

Where:

Cs = Concentration of the organic from the calibration curve, ppm.

Pr = Reference pressure, the barometric pressure or absolute sample loop pressure recorded during calibration, mm Hg.

Ti = Sample loop temperature at the time of sample analysis, °K.

Fr = Relative response factor (if applicable, see Section 6.4).

Pi = Barometric or absolute sample loop pressure at time of sample analysis, mm Hg.

Tr = Reference temperature, the termperature of the sample loop recorded during calibration, °K.

Bws = Water vapor content of the bag sample or stack gas, proportion by volume.

7.2 Direct Interface Sampling and Analysis Procedure. The direct interface procedure can be used provided that the moisture content of the gas does not interfere with the analysis procedure, the physical requirements of the equipment can be met at the site, and the source gas concentration is low enough that detector saturation is not a problem. Adhere to all safety requirements with this method.

7.2.1 Apparatus.

7.2.1.1 Probe. Constructed of stainless steel, Pyrex glass, or Teflon tubing as required by duct temperature, 6.4—mm OD, enlarged at duct end to contain glass wool plug. If necessary, heat the probe with heating tape or a special heating unit capable of maintaining duct temperature.

7.2.1.2 Sample Lines. 6.4—mm OD Teflon lines, heat-traced to prevent condensation of material.

7.2.1.3 Quick Connects. To connect sample line to gas sampling valve on GC instrument and to pump unit used to withdraw source gas. Use a quick connect or equivalent on the cylinder or bag containing calibration gas to allow connection of the calibration gas to the gas sampling valve.

7.2.1.4 Thermocouple Readout Device. Potentiometer or digital thermometer, to measure source temperature and probe temperature.

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

7.2.1.6 Needle Valve. To control gas sampling rate from the source.

7.2.1.7 Pump. Leakless Teflon-coated diaphragm-type pump or equivalent, capable of at least 1 liter/minute sampling rate.

7.2.1.8 Flowmeter. Of suitable range to measure sampling rate.

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

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

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

7.2.1.12 Recorder/Integrator. To record results.

7.2.2 Procedure. To obtain a sample, assemble the sampling system as shown in Figure 18-12. Make sure all connections are tight. Turn on the probe and sample line heaters. As the temperature of the probe and heated line approaches the source temperature as indicated on the thermocouple readout device, control the heating to maintain a temperature of 0 to 3°C above the source temperature. While the probe and heated line are being heated, disconnect the sample line from the gas sampling valve, and attach the line from the calibration gas mixture. Flush the sample loop with calibration gas and analyze a portion of that gas. Record the results. After the calibration gas sample has been flushed into the GC instrument, turn the gas sampling valve to flush position, then reconnect the probe sample line to the valve. Place the inlet of the probe at the centroid of the duct, or at a point no closer to the walls than 1 m, and draw source gas into the probe, heated line, and sample loop. After thorough flushing, analyze the sample using the same conditions as for the calibration gas mixture. Repeat the analysis on an additional sample. Measure the peak areas for the two samples, and if they do not agree to within 5 percent of their mean value, analyze additional samples until two consecutive analyses meet this criteria. Record the data. After consistent results are obtained, remove the probe from the source and analyze a second calibration gas mixture. Record this calibration data and the other required data on the data sheet shown in Figure 18-11, deleting the dilution gas information.

(Note: Take care to draw all samples, calibration mixtures, and audits through the sample loop at the same pressure.)

7.2.3 Determination of Stack Gas Moisture Content. Use Method 4 to measure the stack gas moisture content.

7.2.4 Quality Assurance. Same as Section 7.1.7. Introduce the audit gases in the sample line immediately following the probe.

7.2.5 Emission Calculations. Same as Section 7.1.8.

7.3 Dilution Interface Sampling and Analysis Procedure. Source samples that contain a high concentration of organic materials may require dilution prior to analysis to prevent saturating the GC detector. The apparatus required for this direct interface procedure is basically the same as that described in the Section 7.2, except a dilution system is added between the heated sample line and the gas sampling valve. The apparatus is arranged so that either a 10:1 or 100:1 dilution of the source gas can be directed to the chromatograph. A pump of larger capacity is also required, and this pump must be heated and placed in the system between the sample line and the dilution apparatus.

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

7.3.1.1 Sample Pump. Leakless Teflon-coated diaphragm-type that can withstand being heated to 120°C and deliver 1.5 liters/minute.

7.3.1.2 Dilution Pumps. Two Model A-150 Komhyr Teflon positive displacement type delivering 150 cc/minute, or equivalent. As an option, calibrated flowmeters can be used in conjunction with Teflon-coated diaphragm pumps.

7.3.1.3 Valves. Two Teflon three—way valves, suitable for connecting to 6.4—mm OD Teflon tubing.

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

7.3.1.5 Diluent Gas with Cylinders and Regulators. Gas can be nitrogen or clean dry air, depending on the nature of the source gases.

7.3.1.6 Heated Box. Suitable for being heated to 120°C, to contain the three pumps, three—way valves, and associated connections. The box should be equipped with quick connect fittings to facilitate connection of: (1) The heated sample line from the probe, (2) the gas sampling valve, (3) the calibration gas mixtures, and (4) diluent gas lines. A schematic diagram of the components and connections is shown in Figure 18-13.

(Note: Care must be taken to leak check the system prior to the dilutions so as not to create a potentially explosive atmosphere.)

The heated box shown in Figure 18-13 is designed to receive a heated line from the probe. An optional design is to build a probe unit that attaches directly to the heated box. In this way, the heated box contains the controls for the probe heaters, or, if the box is placed against the duct being sampled, it may be possible to eliminate the probe heaters. In either case, a heated Teflon line is used to connect the heated box to the gas sampling valve on

7.3.2 Procedure. Assemble the apparatus by connecting the heated box, shown in Figure 18-13, between the heated sample line from the probe and the gas sampling valve on the chromatograph. Vent the source gas from the gas sampling valve directly to the charcoal filter, eliminating the pump and rotameter. Heat the sample probe, sample line, and heated box. Insert the probe and source thermocouple to the centroid of the duct, or to a point no closer to the walls than 1 m. Measure the source temperature, and adjust all heating units to a temperature 0 to 3°C above this temperature. If this temperature is above the safe operating temperature of the Teflon components, adjust the heating to maintain a temperature high enough to prevent condensation of water and organic compounds. Verify the operation of the dilution system by analyzing a high concentration gas of known composition through either the 10:1 or 100:1 dilution stages, as appropriate. (If necessary, vary the flow of the diluent gas to obtain other dilution ratios.) Determine the concentration of the diluted calibration gas using the dilution factor and the calibration curves prepared in the laboratory. Record the pertinent data on the data sheet shown in Figure 18-11. If the data on the diluted calibration gas are not within 10 percent of the expected values, determine whether the chromatograph or the dilution system is in error, and correct it. Verify the GC operation using a low concentration standard by diverting the gas into the sample loop, bypassing the dilution system. If these analyses are not within acceptable limits, correct the dilution system to provide the desired dilution factors. Make this correction by diluting a high-concentration standard gas mixture to adjust the dilution ratio as required.

Once the dilution system and GC operations are satisfactory, proceed with the analysis of source gas, maintaining the same dilution settings as used for the standards. Repeat the analyses until two consecutive values do not vary by more than 5 percent from their mean value are obtained.

Repeat the analysis of the calibration gas mixtures to verify equipment operation. Analyze the two field audit samples using either the dilution system, or directly connect to the gas sampling valve as required. Record all data and report the results to the audit supervisor.

7.3.3 Determination of Stack Gas Moisture Content. Same as Section 7.2.3.

7.3.4 Quality Assurance. Same as Section 7.2.4.

7.3.5 Emission Calculations. Same as Section 7.2.5, with the dilution factor applied.

7.4 Adsorption Tube Procedure (Alternative Procedure). It is suggested that the tester refer to the National Institute of Occupational Safety and Health (NIOSH) method for the particular organics to be sampled. The principal interferent will be water vapor. If water vapor is present at concentrations above 3 percent, silica gel should be used in front of the charcoal. Where more than one compound is present in the emissions, then develop relative adsorptive capacity information.

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

7.4.1.1 Probe (Optional). Borosilicate glass or stainless steel, approximately 6—mm ID, with a heating system if water condensation is a problem, and a filter (either in-stack or out-stack heated to stack temperature) to remove particulate matter. In most instances, a plug of glass wool is a satisfactory filter.

7.4.1.2 Flexible Tubing. To connect probe to adsorption tubes. Use a material that exhibits minimal sample adsorption.

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

7.4.1.4 Bubble-Tube Flowmeter. Volume accuracy within ± 1 percent, to calibrate pump.

7.4.1.5 Stopwatch. To time sampling and pump rate calibration.

7.4.1.6 Adsorption Tubes. Similar to ones specified by NIOSH, except the amounts of adsorbent per primary/backup sections are 800/200 mg for charcoal tubes and 1040/260 mg for silica gel tubes. As an alternative, the tubes may contain a porous polymer adsorbent such as Tenax GC or XAD-2.

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

7.4.1.8 Rotameter. 0 to 100 cc/min, to detect changes in flow rate during sampling.

7.4.2 Sampling and Analysis. It is suggested that the tester follow the sampling and analysis portion of the respective NIOSH method section entitled "Procedure." Calibrate the pump and limiting orifice flow rate through adsorption tubes with the bubble tube flowmeter before sampling. The sample system can be operated as a "recirculating loop" for this operation. Record the ambient temperature and barometric pressure. Then, during sampling, use the rotameter to verify that the pump and orifice sampling rate remains constant.

Use a sample probe, if required, to obtain the sample at the centroid of the duct, or at a point no closer to the walls than 1 m. Minimize the length of flexible tubing between the probe and adsorption tubes. Several adsorption tubes can be connected in series, if the extra adsorptive capacity is needed. Provide the gas sample to the sample system at a pressure sufficient for the limiting orifice to function as a sonic orifice. Record the total time and sample flow rate (or the number of pump strokes), the barometric pressure, and ambient temperature. Obtain a total sample volume commensurate with the expected concentration(s) of the volatile organic(s) present, and recommended sample loading factors (weight sample per weight adsorption media). Laboratory tests prior to actual sampling may be necessary to predetermine this volume. When more than one organic is present in the emissions, then develop relative adsorptive capacity information. If water vapor is present in the sample at concentrations above 2 to 3 percent, the adsorptive capacity may be severely reduced. Operate the gas chromatograph according to the manufacture's instructions. After establishing optimum conditions, verify and document these conditions during all operations. Analyze the audit samples (see Section 7.4.4.3), then the emission samples. Repeat the analysis of each sample until the relative deviation of two consecutive injections does not exceed 5 percent.

7.4.3 Standards and Calibration. The standards can be prepared according to the respective NIOSH method. Use a minimum of three different standards; select the concentrations to bracket the expected average sample concentration. Perform the calibration before and after each day's sample analyses. Prepare the calibration curve by using the least squares method.

7.4.4 Quality Assurance.

7.4.4.1 Determination of Desorption Efficiency. During the testing program, determine the desorption efficiency in the expected sample concentration range for each batch of adsorption media to be used. Use an internal standard. A minimum desorption efficiency of 50 percent shall be obtained. Repeat the desorption determination until the relative deviation of two consecutive determinations does not exceed 5 percent. Use the average desorption efficiency of these two consecutive determinations for the correction specified in Section 7.4.4.5. If the desorption efficiency of the compound(s) of interest is questionable under actual sampling conditions, use of the Method of Standard Additions may be helpful to determine this value.

7.4.4.2 Determination of Sample Collection Efficiency. For the source samples, analyze the primary and backup portions of the adsorption tubes separately. If the backup portion exceeds 10 percent of the total amount (primary and backup), repeat the sampling with a larger sampling portion.

7.4.4.3 Analysis Audit. Immediately before the sample analyses, analyze the two audits in accordance with Section 7.4.2. The analysis audit shall agree with the audit concentration within 10 percent.

7.4.4.4 Pump Leak Checks and Volume Flow Rate Checks. Perform both of these checks immediately after sampling with all sampling train components in place. Perform all leak checks according to the manufacturer's instructions, and record the results. Use the bubble-tube flowmeter to measure the pump volume flow rate with the orifice used in the test sampling, and the result. If it has changed by more than 5 but less than 20 percent, calculate an average flow rate for the test. If the flow rate has changed by more than 20 percent, recalibrate the pump and repeat the sampling.

7.4.4.5 Calculations. All calculations can be performed according to the respective NIOSH method. Correct all sample volumes to standard conditions. If a sample dilution system has been used, multiply the results by the appropriate dilution ratio. Correct all results by dividing by the desorption efficiency (decimal value). Report results as ppm by volume, dry basis.

7.5 Reporting of Results. At the completion of the field analysis portion of the study, ensure that the data sheets shown in Figure 18-11 have been completed. Summarize this data on the data sheets shown in Figure 18-15.

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I. Name of company _____ Date _____
Address _____
_____
Contacts _____ Phone _____
_____
Process to be sampled _____
_____
_____
Duct or vent to be sampled _____
_____

II. Process description _____
_____
_____
_____
_____
Raw material _____
_____
_____
Products _____
_____
_____
Operating cycle
Check: Batch _____ Continuous _____ Cyclic _____
Timing of batch or cycle _____
Best time to test _____

Figure 18-1. Preliminary survey data sheet.

III. Sampling site
A. Description
Site description _____
Duct shape and size _____
Material _____
Wall thickness _____ inches
Upstream distance _____ inches _____ diameter
Downstream distance _____ inches _____ diameter
Size of port _____
Size of access area _____
Hazards _____ Ambient temp. _____ °F

B. Properties of gas stream
Temperature ____°C ____°F, Data source _____
Velocity _____, Data source _____
Static pressure ___ inches H_2O, Data source _____
Moisture content _____%, Data source _____
Particulate content _____, Data source _____
Gaseous components

N_2	_____%	Hydrocarbons	_____ ppm
O_2	_____%	_____	_____
CO	_____%	_____	_____
CO_2	_____%	_____	_____
SO_2	_____%	_____	_____

Hydrocarbon components

_____	_____ ppm
_____	_____ ppm
_____	_____ ppm
_____	_____ ppm
_____	_____ ppm
_____	_____ ppm

Figure 18-1 (continued). Preliminary survey data sheet.

C. Sampling considerations
Location to set up GC _____
_____
Special hazards to be considered _____
_____
Power available at duct _____
Power available for GC _____
Plant safety requirements _____
_____
Vehicle traffic rules _____
_____
Plant entry requirements _____
_____
Security agreements _____
_____
Potential problems _____
_____

D. Site diagrams. (Attach additional sheets if required).

Figure 18-1 (continued). Preliminary survey data sheet.

Components to be analyzed	Expected concentration
_____	_____
_____	_____
_____	_____
_____	_____
_____	_____
_____	_____

Suggested chromatographic column _____
_____
Column flow rate ____ ml/min Head pressure____ mm Hg
Column temperature:
Isothermal _____°C
Programmed from ____°C to ____°C at ____°C/min
Injection port/sample loop temperature _____°C
Detector temperature _____°C
Detector flow rates: Hydrogen _____ ml/min.
head pressure____ mm Hg
Air/Oxygen _____ ml/min,
head pressure____ mm Hg
Chart speed _____ inches/minute
Compound data:

Compound	Retention time	Attenuation
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____

Figure 18-2. Chromatographic conditions data sheet.

Preparation of Standards in Tedlar Bags and Calibration Curve

Standards Preparation Data:	Standards Mixture #1	Standards Mixture #2	Standards Mixture #3
Organic: _____			
Bag number or identification			
Dry gas meter calibration factor			
Final meter reading (liters)			
Initial meter reading (liters)			
Metered volume (liters)			
Average meter temperature (°K)			
Average meter pressure, gauge (mm Hg)			
Average atmospheric pressure (mm Hg)			
Average meter pressure, absolute (mm Hg)			
Syringe temperature (°K) (Section 6.2.2.1)			
Syringe pressure, absolute (mm Hg) (Section 6.2.2.1)			
Volume of gas in syringe (ml) (Section 6.2.2.1)			
Density of liquid organic (g/ml) (Section 6.2.2.2)			
Volume of liquid in syringe (µl) (Section 6.2.2.2)			
GC Operating Conditions:			
Sample loop volume (ml)			
Sample loop temperature (°C)			
Carrier gas flow rate (ml/min)			
Column temperature			
Initial (°C)			
Rate change (°C/min)			
Final (°C)			
Organic Peak Identification and Calculated Concentrations:			
Injection time (24-hr clock)			
Distance to peak (cm)			
Chart speed (cm/min)			
Organic retention time (min)			
Attenuation factor			
Peak height (mm)			
Peak area (mm^2)			
Peak area x attenuation factor (mm^2)			
Calculated concentration (ppm) (Equation 18-3 or 18-4)			

Plot peak area x attenuation factor against calculated concentration to obtain calibration curve.

Figure 18-3. Standards prepared in Tedlar bags and calibration curve.

Flowmeter Calibration

Flowmeter number or identification _____

Flowmeter type _____

Calibration device (a): Bubble meter ___ Spirometer ___ Wet test meter ___

Readings at laboratory conditions:

Laboratory temperature (T_{lab}) _____ °K

Laboratory barometric pressure (P_{lab}) _____ mm Hg

Flow data:

Flowmeter reading (as marked)	Temp. (°K)	Pressure (absolute)	Calibration device time (min)	Gas volume[a]	Flow rate[b]

a = Volume of gas measured by calibration device, corrected to standard conditions (liters).

b = Calibration device gas volume/time.

Plot flowmeter reading against flow rate (standard conditions), and draw a smooth curve. If the flowmeter being calibrated is a rotameter or other flow device that is viscosity dependent, it may be necessary to generate a "family" of calibration curves that cover the operating pressure and temperature ranges of the flowmeter.

While the following technique should be verified before application, it may be possible to calculate flow rate readings for rotameters at standard conditions Q_{std} as follows:

$$Q_{std} = Q_{lab}\left(\frac{760 \times T_{lab}}{P_{lab} \times 293}\right)^{1/2}$$

Flow rate (laboratory conditions)	Flow rate (standard conditions)

Figure 18-4. Flowmeter calibration.

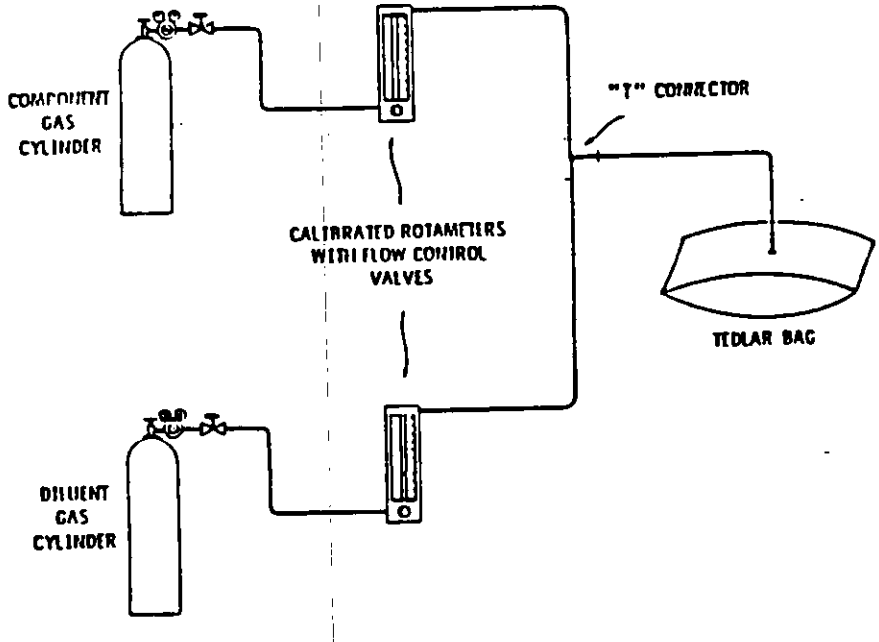

Figure 18-5. Single-stage calibration gas dilution system.

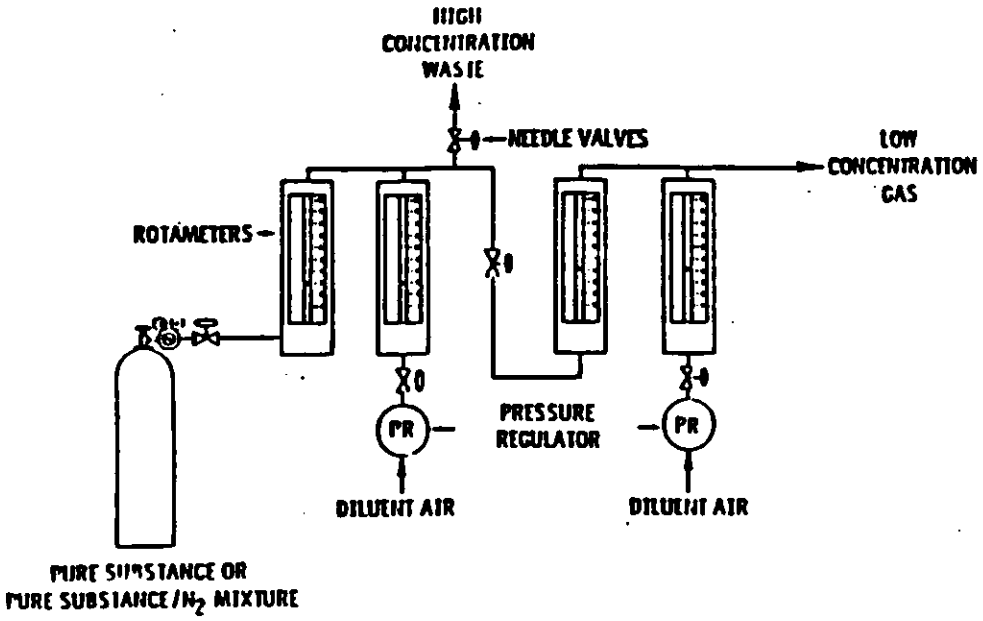

Figure 18-6. Two-stage dilution apparatus.

Preparation of Standards by Dilution of Cylinder Standard

Cylinder standard: Organic _____ Certified concentration _____ ppm

Standards Preparation Data: Date _____

Stage 1	Mixture 1	Mixture 2	Mixture 3
Standard gas flowmeter reading			
Diluent gas flowmeter reading			
Laboratory temperature (°K)			
Barometric pressure (mm Hg)			
Flowmeter gage pressure (mm Hg)			
Flow rate cylinder gas at standard conditions (ml/min)			
Flow rate diluent gas at standard conditions (ml/min)			
Calculated concentration (ppm)			
Stage 2 (if used)			
Standard gas flowmeter reading			
Diluent gas flowmeter reading			
Flow rate stage 1 gas at standard conditions (ml/min)			
Flow rate diluent gas at standard conditions (ml/min)			
Calculated concentration (ppm)			
Operating Conditions:			
Sample loop volume (ml)			
Sample loop temperature (°C)			
Carrier gas flow rate (ml/min)			
Column temperature:			
Initial (°C)			
Program rate (°C/min)			
Final (°C)			
Organic Peak Identification and Calculated Concentrations:			
Injection time (24-hr clock)			
Distance to peak (cm)			
Chart speed (cm/min)			
Retention time (min)			
Attenuation factor			
Peak area (mm^2)			
Peak area x attenuation factor			

Plot peak area x attenuation factor against calculated concentration to obtain calibration curve.

Figure 18-7. Standards prepared by dilution of cylinder standard.

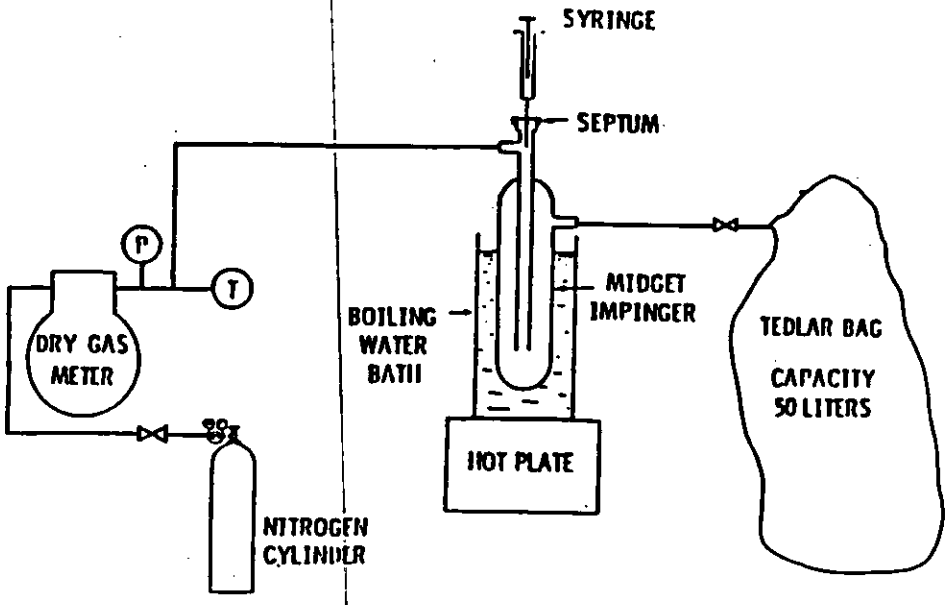

Figure 18-8. Apparatus for preparation of liquid materials.

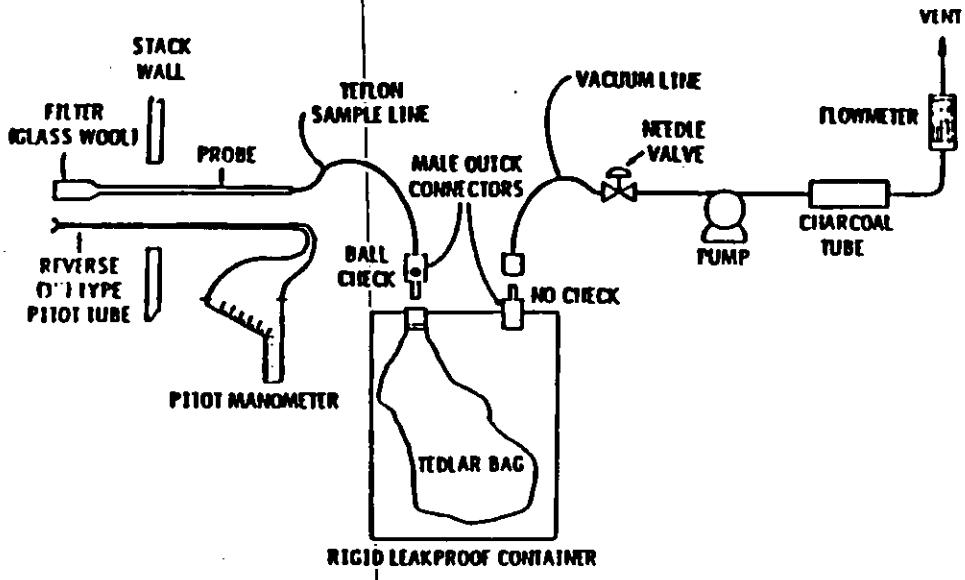

Figure 18-9. Integrated bag sampling train.

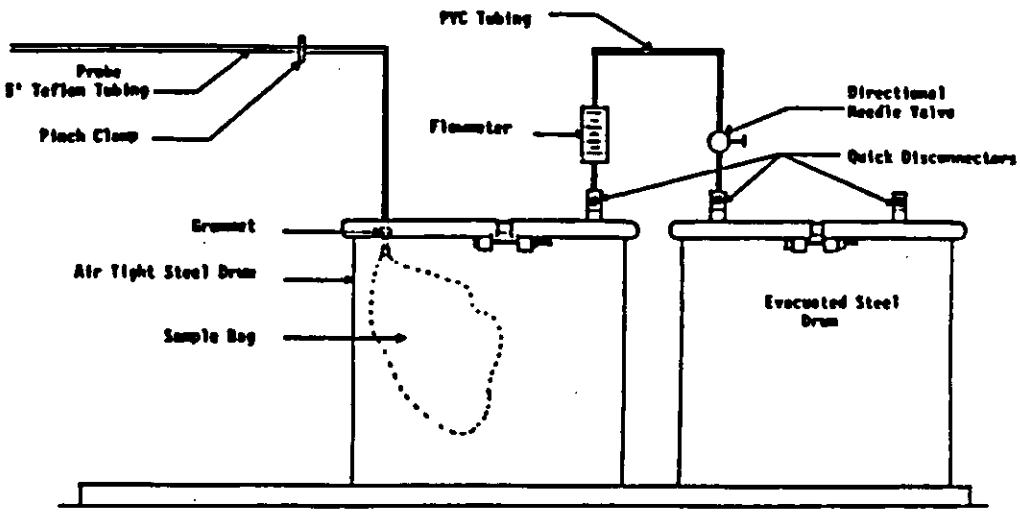

Figure 18-9a. Explosion risk gas sampling method.

Plant_____ Date_____

Site_____

	Sample 1	Sample 2	Sample 3
Source temperature (°C)			
Barometric pressure (mm Hg)			
Ambient temperature (°C)			
Sample flow rate (appr.)			
Bag number			
Start time			
Finish time			

Figure 18-10. Field sample data sheet - Tedlar bag collection method.

Plant_____ Date_____

Location_____

1. General information

Source temperature (°C)	
Probe temperature (°C)	
Ambient temperature (°C)	
Atmospheric pressure (mm)	
Source pressure (°Hg)	
Absolute source pressure (mm)	
Sampling rate (liter/min)	
Sample loop volume (ml)	
Sample loop temperature (°C)	
Columnar temperature:	
Initial (°C)/time (min)	
Program rate (°C/min)	
Final (°C)/ time (min)	
Carrier gas flow rate (ml/min)	
Detector temperature (°C)	
Injection time (24-hour basis)	
Chart speed (mm/min)	
Dilution gas flow rate (ml/min)	
Dilution Gas used (symbol)	
Dilution ratio	

Figure 18-11. Field analysis data sheets.

2. Field Analysis Data - Calibration Gas

Run No._____ Time_____

Components	Area	Attenuation	A x A Factor	Conc. (ppm)

Run No._____ Time_____

Components	Area	Attenuation	A x A Factor	Conc. (ppm)

Run No._____ Time_____

Components	Area	Attenuation	A x A Factor	Conc. (ppm)

Figure 18-11 (continued). Field analysis data sheets.

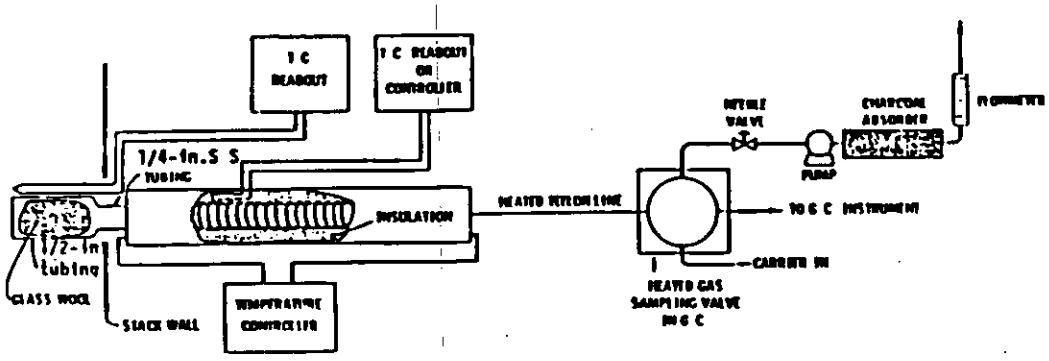

Figure 18-12. Direct interface sampling system.

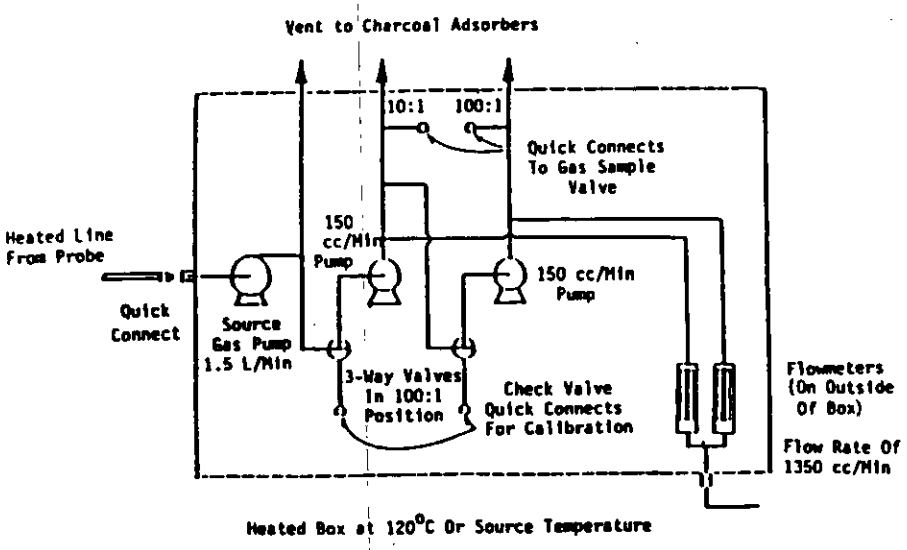

Figure 18-13. Schematic diagram of the heated box required for dilution of sample gas.

GASEOUS ORGANIC SAMPLING AND ANALYSIS CHECK LIST

(Respond with initials or number as appropriate)

		Date
1. Presurvey data:		
A. Grab sample collected	☐	_____
B. Grab sample analyzed for composition	☐	_____
Method GC	☐	☐
GC/MS	☐	☐
Other	☐	☐
C. GC-FID analysis performed	☐	_____
2. Laboratory calibration data:		
A. Calibration curves prepared	☐	_____
Number of components	☐	☐
Number of concentrations/component (3 required)	☐	☐
B. Audit samples (optional):		
Analysis completed	☐	_____
Verified for concentration	☐	_____
OK obtained for field work	☐	_____
3. Sampling procedures:		
A. Method:		
Bag sample	☐	☐
Direct interface	☐	☐
Dilution interface	☐	☐
B. Number of samples collected	☐	_____
4. Field analysis:		
A. Total hydrocarbon analysis performed	☐	_____
B. Calibration curve prepared	☐	_____
Number of components	☐	☐
Number of concentrations per component (3 required)	☐	☐

Figure 18-14. Sampling and analysis check.

GASEOUS ORGANIC SAMPLING AND ANALYSIS DATA

Plant— _____

Date— _____

Location— _____

	Source sample 1	Source sample 2	Source sample 3
1. General information:			
Source temperature (°C)			
Probe temperature (°C)			
Ambient temperature (°C)			
Atmospheric pressure (mm Hg)			
Source pressure (mm Hg)			
Sampling rate (ml/min)			
Sample loop volume (ml)			
Sample loop temperature (°C)			
Sample collection time (24-hr basis)			
Column temperature:			
Initial (°C)			
Program rate (°C/min)			
Final (°C)			
Carrier gas flow rate (ml/min)			

	Source sample 1	Source sample 2	Source sample 3
Detector temperature (°C)			
Chart speed (cm/min)			
Dilution gas flow rate (ml/min)			
Diluent gas used (symbol)			
Dilution ratio			

Performed by (signature): _____

Date: _____

Figure 18-14. Sampling and analysis sheet.

Method 22—Visual Determination of Fugitive Emissions From Material Sources and Smoke Emissions from Flares

1. Introduction

This method involves the visual determination of fugitive emissions, i.e., emissions not emitted directly from a process stack or duct. Fugitive emissions include emissions that (1) escape capture by process equipment exhaust hoods; (2) are emitted during material transfer; (3) are emitted from buildings housing material processing or handling equipment; and (4) are emitted directly from process equipment. This method is used also to determine visible smoke emissions from flares used for combustion of waste process materials.

This method determines the amount of time that any visible emissions occur during the observation period, i.e., the accumulated emission time. This method does not require that the opacity of emissions be determined. Since this procedure requires only the determination of whether a visible emission occurs and does not require the determination of opacity levels, observer certification according to the procedures of Method 9 are not required. However, it is necessary that the observer is educated on the general procedures for determining the presence of visible emissions. As a minimum, the observer must be trained and knowledgeable regarding the effects on the visibility of emissions caused by background contrast, ambient lighting, observer position relative to lighting, wind, and the presence of uncombined water (condensing water vapor). This training is to be obtained from written materials found in Citations 1 and 2 of Bibliography or from the lecture portion of the Method 9 certification course.

2. Applicability and Principle

2.1 Applicability. This method applies to the determination of the frequency of fugitive emissions from stationary sources (located indoors or outdoors) when specified as the test method for determining compliance with new source performance standards.

This method also is applicable for the determination of the frequency of visible smoke emissions from flares.

2.2 Principle. Fugitive emissions produced during material processing, handling, and transfer operations or smoke emissions from flares are visually determined by an observer without the aid of instruments.

3. Definitions

3.1 Emission Frequency. Percentage of time that emissions are visible during the observation period.

3.2 Emission Time. Accumulated amount of time that emissions are visible during the observation period.

3.3 Fugitive Emissions. Pollutant generated by an affected facility which is not collected by a capture system and is released to the atmosphere.

3.4 Smoke Emissions. Pollutant generated by combustion in a flare and occurring immediately downstream of the flame. Smoke occurring within the flame, but not downstream of the flame, is not considered a smoke emission.

3.5 Observation Period. Accumulated time period during which observations are conducted, not to be less than the period specified in the applicable regulation.

4. Equipment

4.1 Stopwatches. Accumulative type with unit divisions of at least 0.5 seconds; two required.

4.2 Light Meter. Light meter capable of measuring illuminance in the 50— to 200-lux range; required for indoor observations only.

5. Procedure

5.1 Position. Survey the affected facility or building or structure housing the process to be observed and determine the locations of potential emissions. If the affected facility is located inside a building, determine an observation location that is consistent with the requirements of the applicable regulation (i.e., outside observation of emissions escaping the building/structure or inside observation of emissions directly emitted from the affected facility process unit). Then select a position that enables a clear view of the potential emission point(s) of the affected facility or of the building or structure housing the affected facility, as appropriate for the applicable subpart. A position at least 15 feet, but not more than 0.25 miles, from the emission source is recommended. For outdoor locations, select a position where the sun is not directly in the observer's eyes.

5.2 Field Records.

5.2.1 Outdoor Location. Record the following information on the field data sheet (Figure 22-1): company name, industry, process unit, observer's name, observer's affiliation, and date. Record also the estimated wind speed, wind direction, and sky condition. Sketch the process unit being observed and note the observer location relative to the source and the sun. Indicate the potential and actual emission points on the sketch.

5.2.2 Indoor Location. Record the following information on the field data sheet (Figure 22-2): company name, industry, process unit, observer's name, observer's affiliation, and date. Record as appropriate the type, location, and intensity of lighting on the data sheet. Sketch the process unit being observed and note observer location relative to the source. Indicate the potential and actual fugitive emission points on the sketch.

5.3 Indoor Lighting Requirements. For indoor locations, use a light meter to measure the level of illumination at a location as close to the emission source(s) as is feasible. An illumination of greater than 100 lux (10 foot candles) is considered necessary for proper application of this method.

5.4 Observations. Record the clock time when observations begin. Use one stopwatch to monitor the duration of the observation period; start this stopwatch when the observation period begins. If the observation period is divided into two or more segments by process shutdowns or observer rest breaks, stop the stopwatch when a break begins and restart it without resetting when the break ends. Stop the stopwatch at the end of the observation period. The accumulated time indicated by this stopwatch is the duration of the observation period. When the observation period is completed, record the clock time.

During the observation period, continously watch the emission source. Upon observing an emission (condensed water vapor is not considered an emission), start the second accumulative stopwatch; stop the watch when the emission stops. Continue this procedure for the entire observation period. The accumulated elapsed time on this stopwatch is the total time emissions were visible during the observation period, i.e., the emission time.

5.4.1 Observation Period. Choose an observation period of sufficient length to meet the requirements for determining compliance with the emission regulation in the applicable subpart. When the length of the observation period is specifically stated in the applicable subpart, it may not be necessary to observe the source for this entire period if the emission time required to indicate noncompliance (based on the specified observation period) is observed in a shorter time period. In other words, if the regulation prohibits emissions for more than 6 minutes in any hour, then observations may (optional) be stopped after an emission time of 6 minutes is exceeded. Similarly, when the regulation is expressed as an emission frequency and

the regulation prohibits emissions for greater than 10 percent of the time in any hour, then observations may (optional) be terminated after 6 minutes of emissions are observed since 6 minutes is 10 percent of an hour. In any case, the observation period shall not be less than 6 minutes in duration. In some cases, the process operation may be intermittent or cyclic. In such cases, it may be convenient for the observation period to coincide with the length of the process cycle.

5.4.2 Observer Rest Breaks. Do not observe emissions continuously for a period of more than 15 to 20 minutes without taking a rest break. For sources requiring observation periods of greater than 20 minutes, the observer shall take a break of not less than 5 minutes and not more than 10 minutes after every 15 to 20 minutes of observation. If continuous observations are desired for extended time periods, two observers can alternate between making observations and taking breaks.

5.4.3 Visual Interference. Occasionally, fugitive emissions from sources other than the affected facility (e.g., road dust) may prevent a clear view of the affected facility. This may particularly be a problem during periods of high wind. If the view of the potential emission points is obscured to such a degree that the observer questions the validity of continuing observations, then the observations are terminated, and the observer clearly notes this fact on the data form.

5.5 Recording Observations. Record the accumulated time of the observation period on the data sheet as the observation period duration. Record the accumulated time emissions were observed on the data sheet as the emission time. Record the clock time the observation period began and ended, as well as the clock time any observer breaks began and ended.

6. Calculations

If the applicable subpart requires that the emission rate be expressed as an emission frequency (in percent), determine this value as follows: Divide the accumulated emission time (in seconds) by the duration of the observation period (in seconds) or by any minimum observation period required in the applicable subpart, if the acutal observation period is less than the required period and multiply this quotient by 100.

7. Bibliography

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2. Wohlschlegel, P. and D. E. Wagoner. Guideline for Development of a Quality Assurance Program: Volume IX—Visual Determination of Opacity Emissions From Stationary Sources. EPA Publication No. EPA-650/4-74-005-i. November 1975.

FUGITIVE OR SMOKE EMISSION INSPECTION
OUTDOOR LOCATION

Company _____	Observer _____
Location _____	Affiliation _____
Company representative _____	Date _____
Sky Conditions _____	Wind direction _____
Precipitation _____	Wind speed _____
Industry _____	Process unit: _____

Sketch process unit; indicate observer position relative to source and sun; indicate potential emission points and/or actual emission points.

OBSERVATIONS	Clock time	Observation period duration, min:sec	Accumulated emission time, min:sec
Begin Observation			
End observation			

Figure 22-1

Fugitive Emission Inspection Indoor Location Table

FUGITIVE EMISSION INSPECTION
INDOOR LOCATION _____

Company _____ Observer _____

Location _____ Affiliation _____

Company Representative _____ Date _____

Industry _____ Process unit _____

Light type (fluorescent, incandescent, natural _____

Light location (overhead, behind observer, etc.) _____

Illuminance (lux or footcandles) _____

Sketch process unit; indicate observer position relative to source; indicate potential emission points and/or actual emission points.

OBSERVATIONS	Clock time	Observation period duration, min:sec	Accumulated emission, time, min:sec
Beginning observation			
End observation			

Figure 22-2

Method 23—Determination of Polychlorinated Dibenzo-p-Dioxins and Polychlorinated Dibenzofurans From Stationary Sources

1. Applicability and Principle

1.1 Applicability. This method is applicable to the determination of polychlorinated dibenzo-p-dioxins (PCDD's) and polychlorinated dibenzofurans (PCDF's) from stationary sources.

1.2 Principle. A sample is withdrawn from the gas stream isokinetically and collected in the sample probe, on a glass fiber filter, and on a packed column of adsorbent material. The sample cannot be separated into a particle vapor fraction. The PCDD's and PCDF's are extracted from the sample, separated by high resolution gas chromatography, and measured by high resolution mass spectrometry.

2. Apparatus

2.1 Sampling. A schematic of the sampling train used in this method is shown in Figure 23-1. Sealing greases may not be used in assembling the train. The train is identical to that described in section 2.1 of Method 5 of this appendix with the following additions:

2.1.1 Nozzle. The nozzle shall be made of nickel, nickel-plated stainless steel, quartz, or borosilicate glass.

2.1.2 Sample Transfer Lines. The sample transfer lines, if needed, shall be heat traced, heavy walled TFE (½ in. OD with 1/8 in. wall) with connecting fittings that are capable of forming leak-free, vacuum-tight connections without using sealing greases. The line shall be as short as possible and must be maintained at 120 °C.

2.1.1 Filter Support. Teflon or Teflon-coated wire.

2.1.2 Condenser. Glass, coil type with compatible fittings. A schematic diagram is shown in Figure 23-2.

2.1.3 Water Bath. Thermostatically controlled to maintain the gas temperature exiting the condenser at >20 °C (68 °F).

2.1.4 Adsorbent Module. Glass container to hold the solid adsorbent. A schematic diagram is shown in Figure 23-2. Other physical configurations of the resin trap/condenser assembly are acceptable. The connecting fittings shall form leak-free, vacuum tight seals. No sealant greases shall be used in the sampling train. A coarse glass frit is included to retain the adsorbent.

2.2 Sample Recovery.

2.2.1 Fitting Caps. Ground glass, Teflon tape, or aluminum foil (Section 2.2.6) to cap off the sample exposed sections of the train.

2.2.2 Wash Bottles. Teflon, 500—ml.

2.2.3 Probe-Liner Probe-Nozzle, and Filter-Holder Brushes. Inert bristle brushes with precleaned stainless steel or Teflon handles. The probe brush shall have extensions of stainless steel or Teflon, at least as long as the probe. The brushes shall be properly sized and shaped to brush

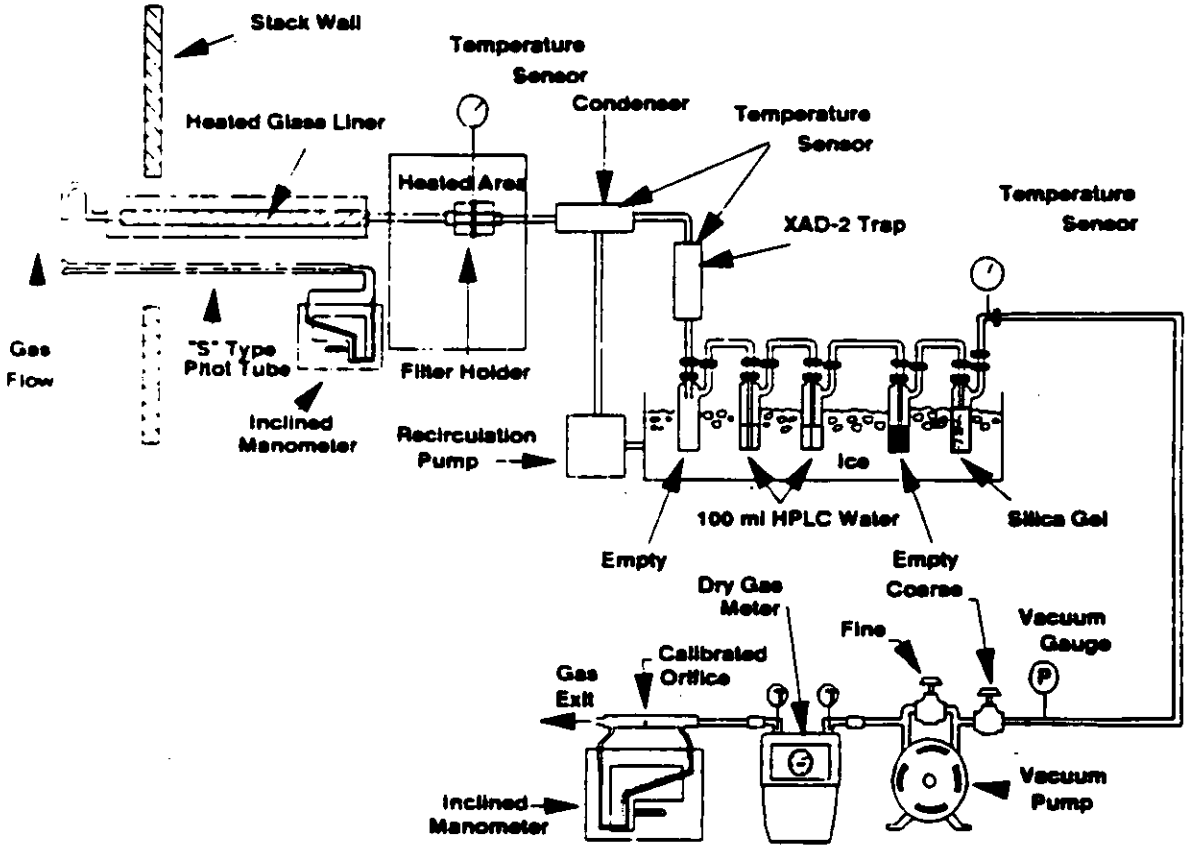

Figure 23.1 Sampling train

out the nozzle, probe liner, and transfer line, if used.

2.2.4 Filter Storage Container. Sealed filter holder, wide—mouth amber glass jar with Teflon-lined cap, or glass petri dish.

2.2.5 Balance. Triple beam.

2.2.6 Aluminum Foil. Heavy duty, hexane-rinsed.

2.2.7 Metal Storage Container. Air tight container to store silica gel.

2.2.8 Graduated Cylinder. Glass, 250—ml with 2—ml graduation.

2.2.9 Glass Sample Storage Container. Amber glass bottle for sample glassware washes, 500— or 1000—ml, with leak free Teflon-lined caps.

2.3 Analysis.

2.3.1 Sample Container. 125— and 250—ml flint glass bottles with Teflon-lined caps.

2.3.2 Test Tube. Glass.

2.3.3 Soxhlet Extraction Apparatus. Capable of holding 43 x 123 mm extraction thimbles.

2.3.4 Extraction Thimble. Glass, precleaned cellulosic, or glass fiber.

2.3.5 Pasteur Pipettes. For preparing liquid chromatographic columns.

2.3.6 Reacti-vials. Amber glass, 2—ml, silanized prior to use.

2.3.7 Rotary Evaporator. Buchi/Brinkman RF-121 or equivalent.

2.3.8 Nitrogen Evaporative Concentrator. N-Evap Analytical Evaporator Model III or equivalent.

2.3.9 Separatory Funnels. Glass, 2-liter.

2.3.10 Gas Chromatograph. Consisting of the following components:

2.3.10.1 Oven. Capable of maintaining the separation column at the proper operating temperature ± °C and performing programmed increases in temperature at rates of at least 40 °C/min.

2.3.10.2 Temperature Gauge. To monitor column oven, detector, and exhaust temperatures ± 1 °C.

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

2.3.10.4 Capillary Columns. A fused silica column, 60 x 0.25 mm inside diameter (ID), coated with DB-5 and a fused silica column, 30 m x 0.25 mm ID coated with DB-225. Other column systems may be used provided that the user is able to demonstrate using calibration and performance checks that the column system is able to meet the specifications of section 6.1.2.2.

2.3.11 Mass Spectrometer. Capable of routine operation at a resolution of 1:10000 with a stability of ± 5 ppm.

2.3.12 Data System. Compatible with the mass spectrometer and capable of monitoring at least five groups of 25 ions.

2.3.13 Analytical Balance. To measure within 0.1 mg.

3. Reagents

3.1 Sampling.

3.1.1 Filters. Glass fiber filters, without organic binder, exhibiting at least 99.95 percent efficiency (<0.05 percent penetration) on 0.3—micron dioctyl phthalate smoke particles. The filter efficiency test shall be conducted in accordance with ASTM Standard Method D 2986-71 (Reapproved 1978) (incorporated by reference——see § 60.17).

3.1.1.1 Precleaning. All filters shall be cleaned before their initial use. Place a glass extraction thimble and 1 g of silica gel and a plug of glass wool into a Soxhlet apparatus, charge the apparatus with toluene, and reflux for a minimum of 3 hours. Remove the toluene and discard it, but retain the silica gel. Place no more than 50 filters in the thimble onto the silica gel bed and top with the cleaned glass wool. Charge the Soxhlet with toluene and reflux for 16 hours. After extraction, allow the Soxhlet to cool, remove the filters, and dry them under a clean N2 stream. Store the filters in a glass petri dish sealed with Teflon tape.

3.1.2 Adsorbent Resin. Amberlite XAD-2 resin. Thoroughly cleaned before initial use.

3.1.2.1 Cleaning Procedure. This procedure may be carried out in a giant Soxhlet extractor. An all-glass filter thimble containing an extra-course frit is used for extraction of XAD-2. The frit is recessed 10-15 mm above a crenelated ring at the bottom of the thimble to facilitate drainage. The resin must be carefully retained in the extractor cup with a glass wool plug and a stainless steel ring because it floats on methylene chloride. This process involves sequential extraction in the following order.

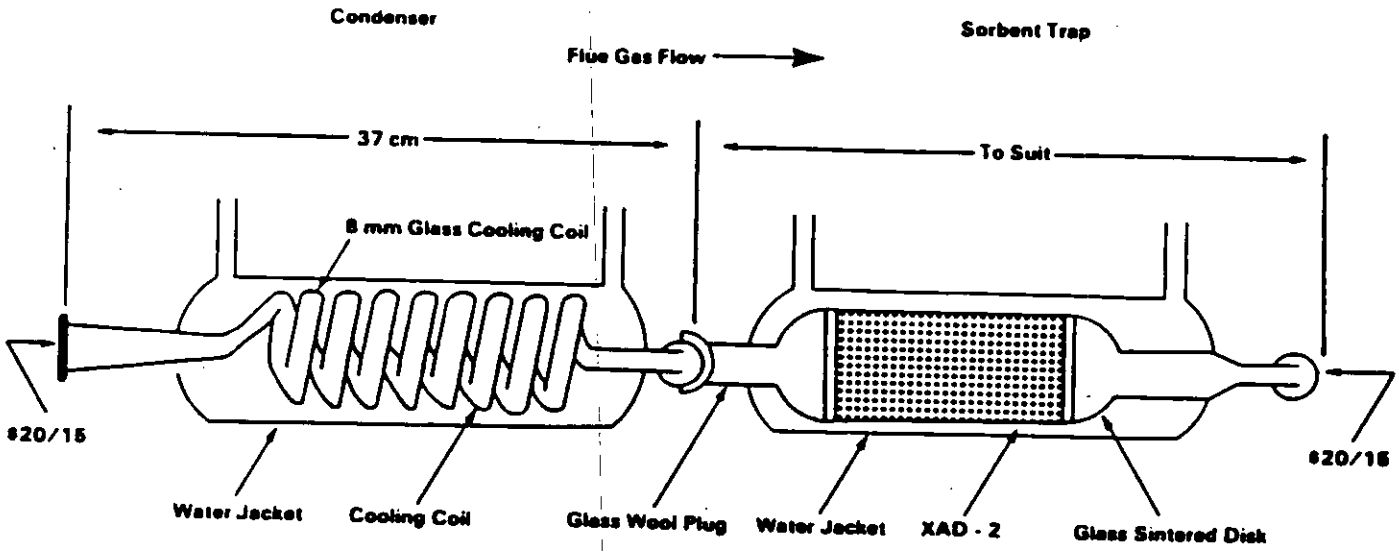

Figure 23.2. Condenser and adsorbent trap

Solvent	Procedure
Water	Initial rinse: Place resin in a beaker, rinse once with water, and discard. Fill with water a second time, let stand overnight, and discard.
Water	Extract with water for 8 hours.
Methanol	Extract for 22 hours.
Methylene Chloride	Extract for 22 hours.
Toluene	Extract for 22 hours.

3.1.2.2 Drying.

3.1.2.2.1 Drying Column. Pyrex pipe, 10.2 cm ID by 0.6 m long, with suitable retainers.

3.1.2.2.2 Procedure. The adsorbent must be dried with clean inert gas. Liquid nitrogen from a standard commercial liquid nitrogen cylinder has proven to be a reliable source of large volumes of gas free from organic contaminants. Connect the liquid nitrogen cylinder to the column by a length of cleaned copper tubing, 0.95 cm ID, coiled to pass through a heat source. A convenient heat source is a water-bath heated from a steam line. The final nitrogen temperature should only be warm to the touch and not over 40 °C. Continue flowing nitrogen through the adsorbent until all the residual solvent is removed. The flow rate should be sufficient to gently agitate the particles but not so excessive as the cause the particles to fracture.

3.1.2.3 Quality Control Check. The adsorbent must be checked for residual toluene.

3.1.2.3.1 Extraction. Weigh 1.0 g sample of dried resin into a small vial, add 3 ml of toluene, cap the vial, and shake it well.

3.1.2.3.2 Analysis. Inject a 2 ul sample of the extract into a gas chromatograph operated under the following conditions: Column: 6 ft x 1/8 in stainless steel containing 10 percent OV-101 on 100/120 Supelcoport. Carrier Gas: Helium at a rate of 30 ml/min. Detector: Flame ionization detector operated at a sensitivity of 4 x 10-11 A/mV. Injection Port Temperature: 250 °C. Detector Temperature: 305 °C. Oven Temperature: 30 °C for 4 min; programmed to rise at 40 °C/min until it reaches 250 °C; return to 30 °C after 17 minutes.

Compare the results of the analysis to the results from the reference solution. Prepare the reference solution by injection 2.5 ul of methylene chloride into 100 ml of toluene. This corresponds to 100 μg of methylene chloride per g of adsorbent. The maximum acceptable concentration is 1000 μg/g of adsorbent. If the adsorbent exceeds this level, drying must be continued until the excess methylene chloride is removed.

3.1.2.4 Storage. The adsorbent must be used within 4 weeks of cleaning. After cleaning, it may be stored in a wide mouth amber glass container with a Teflon-lined cap or placed in one of the glass adsorbent modules tightly sealed with glass stoppers. If precleaned adsorbent is purchased in sealed containers, it must be used within 4 weeks after the seal is broken.

3.1.3 Glass Wool. Cleaned by sequential immersion in three aliquots of methylene chloride, dried in a 110 °C oven, and stored in a methylene chloride—washed glass jar with a Teflon-lined screw cap.

3.1.4 Water. Deionized distilled and stored in a methylene chloride-rinsed glass container with a Teflon-lined screw cap.

3.1.5 Silica Gel. Indicating type, 6 to 16 mesh. If previously used, dry at 175 °C (350 °F) for two hours. New silica gel may be used as received. Alternately other types of desiccants (equivalent or better) may be used, subject to the approval of the Administrator.

3.1.6 Chromic Acid Cleaning Solution. Dissolve 20 g of sodium dichromate in 15 ml of water, and then carefully add 400 ml of concentrated sulfuric acid.

3.2 Sample Recovery.

3.2.2 Acetone. Pesticide quality.

3.2.2 Methylene Chloride. Pesticide quality.

3.2.3 Toluene. Pesticide quality.

3.3 Analysis.

3.3.1 Potassium Hydroxide. ACS grade, 2-percent (weight/volume) in water.

3.3.2 Sodium Sulfate. Granulated, reagent grade. Purify prior to use by rinsing with methylene chloride and oven drying. Store the cleaned material in a glass container with a Teflon-lined screw cap.

3.3.3 Sulfuric Acid. Reagent grade.

3.3.4 Sodium Hydroxide. 1.0 N. Weigh 40 g of sodium hydroxide into a 1-liter volumetric flask. Dilute to 1 liter with water.

3.3.5 Hexane. Pesticide grade.

3.3.6 Methylene Chloride. Pesticide grade.

3.3.7 Benzene. Pesticide Grade.

3.3.8 Ethyl Acetate.

3.3.9 Methanol. Pesticide Grade.

3.3.10 Toluene. Pesticide Grade.

3.3.11 Nonane. Pesticide Grade.

3.3.12 Cyclohexane. Pesticide Grade.

3.3.13 Basic Alumina. Activity grade 1, 100-200 mesh. Prior to use, activate the alumina by heating for 16 hours at 130 °C before use. Store in a desiccator. Pre-activated alumina may be purchased from a supplier and may be used as received.

3.3.14 Silica Gel. Bio-Sil A, 100-200 mesh. Prior to use, activate the silica gel by heating for at least 30 minutes at 180 °C. After cooling, rinse the silica gel sequentially with methanol and methylene chloride. Heat the rinsed silica gel at 50 °C for 10 minutes, then increase the temperature gradually to 180 °C over 25 minutes and maintain it at this temperature for 90 minutes. Cool at room temperature and store in a glass container with a Teflon-lined screw cap.

3.3.15 Silica Gel Impregnated with Sulfuric Acid. Combine 100 g of silica gel with 44 g of concentrated sulfuric acid in a screw capped glass bottle and agitate thoroughly. Disperse the solids with a stirring rod until a uniform mixture is obtained. Store the mixture in a glass container with a Teflon-lined screw cap.

3.3.16 Silica Gel Impregnated with Sodium Hydroxide. Combine 39 g of 1 N sodium hydroxide with 100 g of silica gel in a screw capped glass bottle and agitate thoroughly. Disperse solids with a stirring rod until a uniform mixture is obtained. Store the mixture in glass container with a Teflon-lined screw cap.

3.3.17 Carbon/Celite. Combine 10.7 g of AX-21 carbon with 124 g of Celite 545 in a 250—ml glass bottle with a Teflon-lined screw cap. Agitate the mixture thoroughly until a uniform mixture is obtained. Store in the glass container.

3.3.18 Nitrogen. Ultra high purity.

3.3.19 Hydrogen. Ultra high purity.

3.3.20 Internal Standard Solution. Prepare a stock standard solution containing the isotopically labelled PCDD's and PCDF's at the concentrations shown in Table 1 under the heading "Internal Standards" in 10 ml of nonane.

3.3.21 Surrogate Standard Solution. Prepare a stock standard solution containing the isotopically labelled PCDD's and PCDF's at the concentrations shown in Table 1 under the heading "Surrogate Standards" in 10 ml of nonane.

3.3.22 Recovery Standard Solution. Prepare a stock standard solution containing the isotopically labelled PCDD's and PCDF's at the concentrations shown in Table 1 under the heading "Recovery Standards" in 10 ml of nonane.

4. Procedure

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

4.1.1 Pretest Preparation.

4.1.1.1 Cleaning Glassware. All glass components of the train upstream of ... including the adsorbent module, shall be cleaned as described in section 3A of the "Manual of Analytical Methods for the Analysis of Pesticides in Human and Environmental Samples." Special care

shall be devoted to the removal of residual silicone grease sealants on ground glass connections of used glassware. Any residue shall be removed by soaking the glassware for several hours in a chromic acid cleaning solution prior to cleaning as described above.

4.1.1.2 Adsorbent Trap. The traps must be loaded in a clean area to avoid contamination. They may not be loaded in the field. Fill a trap with 20 to 40 g of XAD-2. Follow the XAD-2 with glass wool and tightly cap both ends of the trap. Add 100 ul of the surrogate standard solution (section 3.3.21) to each trap.

4.1.1.3 Sample Train. It is suggested that all components be maintained according to the procedure described in APTD-0576.

4.1.1.4 Silica Gel. Weigh several 200 to 300 g portions of silica gel in an air tight container to the nearest 0.5 g. Record the total weight of the silica gel plus container, on each container. As an alternative, the silica gel may be weighed directly in its impinger or sampling holder just prior to sampling.

4.1.1.5 Filter. Check each filter against light for irregularities and flaws or pinhole leaks. Pack the filters flat in a clean glass container.

4.1.2 Preliminary Determinations. Same as section 4.1.2 of Method 5.

4.1.3 Preparation of Collection Train.

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

Note: Do not use sealant grease in assembling the train.

4.1.3.2 Place approximately 100 ml of water in the second and third impingers, leave the first and fourth impingers empty, and transfer approximately 200 to 300 g of preweighed silica gel from its container to the fifth impinger.

4.1.3.3 Place the silica gel container in a clean place for later use in the sample recovery. Alternatively, the weight of the silica gel plus impinger may be determined to the nearest 0.5 g and recorded.

4.1.3.4 Assemble the train as shown in Figure 23-1.

4.1.3.5 Turn on the adsorbent module and condenser coil recirculating pump and begin monitoring the adsorbent module gas entry temperature. Ensure proper sorbent temperature gas entry temperature before proceeding and before sampling is initiated. It is extremely important that the XAD-2 adsorbent resin temperature never exceed 50 °C because thermal decomposition will occur. During testing, the XAD-2 temperature must not exceed 20 °C for efficient capture of the PCDD's and PCDF's.

4.1.4 Leak-Check Procedure. Same as Method 5, section 4.1.4.

4.1.5 Sample Train Operation. Same as Method 5, section 4.1.5.

4.2 Sample Recovery. Proper cleanup procedure begins as soon as the probe is removed from the stack at the end of the sampling period. Seal the nozzle end of the sampling probe with Teflon tape or aluminum foil.

When the probe can be safely handled, wipe off all external particulate matter near the tip of the probe. Remove the probe from the train and close off both ends with aluminum foil. Seal off the inlet to the train with Teflon tape, a ground glass cap, or aluminum foil.

Transfer the probe and impinger assembly to the cleanup area. This area shall be clean and enclosed so that the chances of losing or contaminating the sample are minimized. Smoking, which could contaminate the sample, shall not be allowed in the cleanup area.

Inspect the train prior to and during disassembly and note any abnormal conditions, e.g., broken filters, colored impinger liquid, etc. Treat the samples as follows:

4.2.1 Container No. 1. Either seal the filter holder or carefully remove the filter from the filter holder and place it in its identified container. Use a pair of cleaned tweezers to handle the filter. If it is necessary to fold the filter, do so such that the particulate cake is inside the fold. Carefully transfer to the container any particulate matter and filter fibers which adhere to the filter holder gasket, by using a dry inert bristle brush and a sharp-edged blade. Seal the container.

4.2.2 Adsorbent Module. Remove the module from the train, tightly cap both ends, label it, cover with aluminum foil, and store it on ice for transport to the laboratory.

4.2.3 Container No. 2. Quantitatively recover material deposited in the nozzle, probe transfer lines, the front half of the filter holder, and the cyclone, if used, first, by brushing while rinsing three times each with acetone and then, by rinsing the probe three times with methylene chloride. Collect all the rinses in Container No. 2.

Rinse the back half of the filter holder three times with acetone. Rinse the connecting line between the filter and the condenser three times with acetone. Soak the connecting line with three separate portions of methylene chloride for 5 minutes each. If using a separate condenser and adsorbent trap, rinse the condenser in the same manner as the connecting line. Collect all the rinses in Container No. 2 and mark the level of the liquid on the container.

4.2.4 Container No. 3. Repeat the methylene chloride-rinsing described in Section 4.2.3 using toluene as the rinse solvent. Collect the rinses in Container No. 3 and mark the level of the liquid on the container.

4.2.5 Impinger Water. Measure the liquid in the first three impingers to within ± 1 ml by using a graduated cylinder or by weighing it to within ± 0.5 g by using a balance. Record the volume or weight of liquid present. This information is required to calculate the moisture content of the effluent gas.

Discard the liquid after measuring and recording the volume or weight.

4.2.7 Silica Gel. Note the color of the indicating silica gel to determine if it has been completely spent and make a mention of its condition. Transfer the silica gel from the fifth impinger to its original container and seal.

5. Analysis

All glassware shall be cleaned as described in section 3A of the "Manual of Analytical Methods for the Analysis of Pesticides in Human and Environmental Samples." All samples must be extracted within 30 days of collection and analyzed within 45 days of extraction.

5.1 Sample Extraction.

5.1.1 Extraction System. Place an extraction thimble (section 2.3.4), 1 g of silica gel, and a plug of glass wool into the Soxhlet apparatus, charge the apparatus with toluene, and reflux for a minimum of 3 hours. Remove the toluene and discard it, but retain the silica gel. Remove the extraction thimble from the extraction system and place it in a glass beaker to catch the solvent rinses.

5.1.2 Container No. 1 (Filter). Transfer the contents directly to the glass thimble of the extraction system and extract them simultaneously with the XAD-2 resin.

5.1.3 Adsorbent Cartridge. Suspend the adsorbent module directly over the extraction thimble in the beaker (See section 5.1.1). The glass frit of the module should be in the up position. Using a Teflon squeeze bottle containing toluene, flush the XAD-2 into the thimble onto the bed of cleaned silica gel. Thoroughly rinse the glass module catching the rinsings in the beaker containing the thimble. If the resin is wet, effective extraction can be accomplished by loosely packing the resin in the thimble. Add the XAD-2 glass wool plug into the thimble.

5.1.4 Container No. 2 (Acetone and

Methylene Chloride). Concentrate the sample to a volume of about 1-5 ml using the rotary evaporator apparatus, at a temperature of less than 37 °C. Rinse the sample container three times with small portions of methylene chloride and add these to the concentrated solution and concentrate further to near dryness. This residue contains particulate matter removed in the rinse of the train probe and nozzle. Add the concentrate to the filter and the XAD-2 resin in the Soxhlet apparatus described in section 5.1.1.

5.1.5 Extraction. Add 100 ul of the internal standard solution (Section 3.3.20) to the extraction thimble containing the contents of the adsorbent cartridge, the contents of Container No. 1, and the concentrate from section 5.1.4. Cover the contents of the extraction thimble with the cleaned glass wool plug to prevent the XAD-2 resin from floating into the solvent reservoir of the extractor. Place the thimble in the extractor, and add the toluene contained in the beaker to the solvent reservoir. Pour additional toluene to fill the reservoir approximately 2/3 full. Add Teflon boiling chips and assemble the apparatus. Adjust the heat source to cause the extractor to cycle three times per hour. Extract the sample for 16 hours. After extraction, allow the Soxhlet to cool. Transfer the toluene extract and three 10—ml rinses to the rotary evaporator. Concentrate the extract to approximately 10 ml. At this point the analyst may choose to split the sample in half. If so, split the sample, store one half for future use, and analyze the other according to the procedures in sections 5.2 and 5.3. In either case, use a nitrogen evaporative concentrator to reduce the volume of the sample being analyzed to near dryness. Dissolve the residue in 5 ml of hexane.

5.1.6 Container No. 3 (Toluene Rinse). Add 100 ul of the Internal Standard solution (section 3.3.2) to the contents of the container. Concentrate the sample to a volume of about 1-5 ml using the rotary evaporator apparatus at a temperature of less than 37 °C. Rinse the sample container apparatus at a temperature of less than 37 °C. Rinse the sample container three times with small portions of toluene and add these to the concentrated solution and concentrate further to near dryness. Analyze the extract separately according to the procedures in sections 5.2 and 5.3, but concentrate the solution in a rotary evaporator apparatus rather than a nitrogen evaporative concentrator.

5.2 Sample Cleanup and Fractionation.

5.2.1 Silica Gel Column. Pack one end of a glass column, 20 mm x 230 mm, with glass wool. Add in sequence, 1 g silica gel, 2 g of sodium hydroxide impregnated silica gel, 1 g silica gel, 4 g of acid—modified silica gel, and 1 g of silica gel. Wash the column with 30 ml of hexane and discard it. Add the sample extract, dissolved in 5 ml of hexane to the column with two additional 5—ml rinses. Elute the column with an additional 90 ml of hexane and retain the entire eluate. Concentrate this solution to a volume of about 1 ml using the nitrogen evaporative concentrator (section 2.3.7).

5.2.2 Basic Alumina Column. Shorten a 25—ml disposable Pasteur pipette to about 16 ml. Pack the lower section with glass wool and 12 g of basic alumina. Transfer the concentrated extract from the silica gel column to the top of the basic alumina column and elute the column sequentially with 120 ml of 0.5 percent methylene chloride in hexane followed by 120 ml of 35 percent methylene chloride in hexane. Discard the first 120 ml of eluate. Collect the second 120 ml of eluate and concentrate it to about 0.5 ml using the nitrogen evaporative concentrator.

5.2.3 AX-21 Carbon/Celite 545 Column. Remove the bottom 0.5 in. from the tip of a 9—ml disposable Pasteur pipette. Insert a glass fiber filter disk in the top of the pipette 2.5 cm from the constriction. Add sufficient carbon/celite mixture to form a 2 cm column. Top with a glass wool plug. In some cases AX-21 carbon fines may wash through the glass wool plug and enter the sample. This may be prevented by adding a celite plug to the exit end of the column. Rinse the column in sequence with 2 ml of 50 percent benzene in ethyl acetate, 1 ml of 50 percent methylene chloride in cyclohexane, and 2 ml of hexane. Discard these rinses. Transfer the concentrate in 1 ml of hexane from the basic alumina column to the carbon/celite column along with 1 ml of hexane rinse. Elute the column sequentially with 2 ml of 50 percent methylene chloride in hexane and 2 ml of 50 percent benzene in ethyl acetate and discard these eluates. Invert the column and elute in the reverse direction with 13 ml of toluene. Collect this eluate. Concentrate the eluate in a rotary evaporator at 50 °C to about 1 ml. Transfer the concentrate to a Reacti-vial using a toluene rinse and concentrate to a volume of 200 ul using a stream of N2. Store extracts at room temperature, shielded from light, until the analysis is performed.

5.3 Analysis. Analyze the sample with a gas chromatograph coupled to a mass spectrometer (GC/MS) using the instrumental parameters in sections 5.3.1 and 5.3.2. Immediately prior to analysis, add a 20 ul aliquot of the Recovery Standard solution from Table 1 to each sample. A 2 ul aliquot of the extract is injected into the GC. Sample extracts are first analyzed using the DB-5 capillary column to determine the concentration of each isomer of PCDD's and PCDF's (tetra-through octa-). If tetra-chlorinated dibenzofurans are detected in this analysis, then analyze another aliquot of the sample in a separate run, using the DB-225 column to measure the 2,3,7,8 tetra-chloro dibenzofuran isomer. Other column systems may be used, provided that the user is able to demonstrate using calibration and performance checks that the column system is able to meet the specifications of section 6.1.2.2.

5.3.1 Gas Chromatograph Operating Conditions.

5.3.1.1 Injector. Configured for capillary column, splitless, 250°C.

5.3.1.2 Carrier Gas. Helium, 1-2 ml/min.

5.3.1.3 Oven. Initially at 150°C. Raise by at least 40°C/min to 190°C and then at 3°C/min up to 300°C.

5.3.2 High Resolution Mass Spectrometer.

5.3.2.1 Resolution. 10000 m/e.

5.3.2.2 Ionization Mode. Electron impact.

5.3.2.3 Source Temperature 250°C.

5.3.2.4 Monitoring Mode. Selected ion monitoring. A list of the various ions to be monitored is summarized in Table 3.

5.3.2.5 Identification Criteria. The following identification criteria shall be used for the characterization of polychlorinated dibenzodioxins and dibenzofurans.

1. The integrated ion-abundance ratio (M/M+2 or M+2/M+4) shall be within 15 percent of the theoretical value. The acceptable ion-abundance ratio ranges for the identification of chlorine-containing compounds are given in Table 4.

2. The retention time for the analytes must be within 3 seconds of the corresponding \1\3\ C-labeled internal standard, surrogate or alternate standard.

3. The monitored ions, shown in Table 3 for a given analyte, shall reach their maximum within 2 seconds of each other.

4. The identification of specific isomers that do not have corresponding \1\3\ C-labeled standards is done by comparison of the relative retention time (RRT) of the analyte to the nearest internal standard retention time with reference (i.e., within 0.005 RRT units) to the comparable RRT's found in the continuing calibration.

5. The signal to noise ratio for all monitored ions must be greater than 2.5.

6. The confirmation of 2, 3, 7, 8-TCDD and 2, 3, 7, 8-TCDF shall satisfy all of the above identification criteria.

7. For the identification of PCDF's, no

signal may be found in the corresponding PCDPE channels.

5.3.2.6 Quantification. The peak areas for the two ions monitored for each analyte are summed to yield the total response for each analyte. Each internal standard is used to quantify the indigenous PCDD's or PCDF's in its homologous series. For example, the \1\\3\ C 12-2,3,7,8-tetra chlorinated dibenzodioxin is used to calculate the concentrations of all other tetra chlorinated isomers. Recoveries of the tetra— and penta— internal standards are calculated using the \1\\3\ C 12-1,2,3,4-TCDD. Recoveries of the hexa— through octa— internal standards are calculated using \1\\3\ C 12-1,2,3,7,8,9-HxCDD. Recoveries of the surrogate standards are calculated using the corresponding homolog from the internal standard.

6. Calibration

Same as Method 5 with the following additions.

6.1 GC/MS System.

6.1.1 Initial Calibration. Calibrate the GC/MS system using the set of five standards shown in Table 2. The relative standard deviation for the mean response factor from each of the unlabeled analytes (Table 2) and of the internal, surrogate, and alternate standards shall be less than or equal to the values in Table 5. The signal to noise ratio for the GC signal present in every selected ion current profile shall be greater than or equal to 2.5. The ion abundance ratios shall be within the control limits in Table 4.

6.1.2 Daily Performance Check.

6.1.2.1 Calibration Check. Inject on ul of solution Number 3 from Table 2. Calculate the relative response factor (RRF) for each compound and compare each RRF to the corresponding mean RRF obtained during the initial calibration. The analyzer performance is acceptable if the measured RRF's for the labeled and unlabeled compounds for the daily run are within the limits of the mean values shown in Table 5. In addition, the ion-abundance ratios shall be within the allowable control limits shown in Table 4.

6.1.2.2 Column Separation Check. Inject a solution of a mixture of PCDD's and PCDF's that documents resolution between 2,3,7,8-TCDD and other TCDD isomers. Resolution is defined as a valley between peaks that is less than 25 percent of the lower of the two peaks. Identify and record the retention time windows for each homologous series.

Perform a similar resolution check on the confirmation column to document the resolution between 2,3,7,8 TCDF and other TCDF isomers.

6.2 Lock Channels. Set mass spectrometer lock channels as specified in Table 3. Monitor the quality control check channels specified in Table 3 to verify instrument stability during the analysis.

7. Quality Control

7.1 Sampling Train Collection Efficiency Check. Add 100 ul of the surrogate standards in Table 1 to the absorbent cartridge of each train before collecting the field samples.

7.2 Internal Standard Percent Recoveries. A group of nine carbon labeled PCDD's and PCDF's representing, the tetra-through octachlorinated homologues, is added to every sample prior to extraction. The role of the internal standards is to quantify the native PCDD's and PCDF's present in the sample as well as to determine the overall method efficiency. Recoveries of the internal standards must be between 40 to 130 percent for the tetra-through hexachlorinated compounds while the range is 25 to 130 percent for the higher hepta— and octachlorinated homologues.

7.3 Surrogate Recoveries. The five surrogate compounds in Table 2 are added to the resin in the adsorbent sampling cartridge before the sample is collected. The surrogate recoveries are measured relative to the internal standards and are a measure of collection efficiency. They are not used to measure native PCDD's and PCDF's. All recoveries shall be between 70 and 130 percent. Poor recoveries for all the surrogates may be an indication of breakthrough in the sampling train. If the recovery of all standards is below 70 percent, the sampling runs must be repeated. As an alternative, the sampling runs do not have to be repeated if the final results are divided by the fraction of surrogate recovery. Poor recoveries of isolated surrogate compounds should not be grounds for rejecting an entire set of the samples.

7.4 Toluene QA Rinse. Report the results of the toluene QA rinse separately from the total sample catch. Do not add it to the total sample.

8. Quality Assurance

8.1 Applicability. When the method is used to analyze samples to demonstrate compliance with a source emission regulation, an audit sample must be analyzed, subject to availability.

8.2 Audit Procedure. Analyze an audit sample with each set of compliance samples. The audit sample contains tetra through octa isomers of PCDD and PCDF. Concurrently, analyze the audit sample and a set of compliance samples in the same manner to evaluate the technique of the analyst and the standards preparation. The same analyst, analytical reagents, and analytical system shall be used both for the compliance samples and the EPA audit sample.

8.3 Audit Sample Availability. Audit samples will be supplied only to enforcement agencies for compliance tests. The availability of audit samples may be obtained by writing: Source Test Audit Coordinator (MD-77B), Quality Assurance Division, Atmospheric Research and Exposure Assessment Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711, or by calling the Source Test Audit Coordinator (STAC) at (919) 541-7834. The request for the audit sample must be made at least 30 days prior to the scheduled compliance sample analysis.

8.4 Audit Results. Calculate the audit sample concentration according to the calculation procedure described in the audit instructions included with the audit sample. Fill in the audit sample concentration and the analyst's name on the audit response form included with the audit instructions. Send one copy to the EPA Regional Office or the appropriate enforcement agency and a second copy to the STAC. The EPA Regional office or the appropriate enforcement agency will report the results of the audit to the laboratory being audited. Include this response with the results of the compliance samples in relevant reports to the EPA Regional Office or the appropriate enforcement agency.

9. Calculations

Same as Method 5, section 6 with the following additions.

9.1 Nomenclature.

Aai = Integrated ion current of the noise at the retention time of the analyte. A*ci = Integrated ion current of the two ions characteristic of the internal standard i in the calibration standard. Acij = Integrated ion current of the two ions characteristic of compound i in the jth calibration standard. A*cij = Integrated ion current of the two ions characteristic of the internal standard i in the jth calibration standard. Acsi = Integrated ion current of the two ions characteristic of surrogate compound i in the calibration standard. Ai = Integrated ion current of the two ions characteristic of compound i in the sample. A*i = Integrated ion current of the two ions characteristic of internal standard i in the sample. Ars = Integrated ion current of the two ions characteristic of the recovery standard. Asi = Integrated ion current of the two ions characteristic of surrogate compound i in the sample. Ci = Concentration of PCDD or PCDF i in the sample, pg/M \3\. CT = Total

concentration of PCDD's or PCDF's in the sample, pg/M \3\. mci = Mass of compound i in the calibration standard injected into the analyzer, pg. mrs = Mass of recovery standard in the calibration standard injected into the analyzer, pg. msi = Mass of surrogate compound i in the calibration standard, pg. RRFi = Relative response factor. RRFrs = Recovery standard response factor. RRFs = Surrogate compound response factor.

9.2 Average Relative Response Factor.

$$RRF_i = \frac{1}{n}\sum_{j=1}^{n}\frac{A_{is}\, m^*_{cs}}{A^*_{cs}\, m_{is}} \quad \text{Eq. 23-1}$$

9.3 Concentration of the PCDD's and PCDF's.

$$C_i = \frac{m_i^* A_i}{A_i^* RRF_i V_{soln}} \quad \text{Eq. 23-2}$$

9.4 Recovery Standard Response Factor.

$$RRF_{rs} = \frac{A_{ri}^* m_{rs}}{A_{rs} m_{ri}^*} \quad \text{Eq. 23-3}$$

9.5 Recovery of Internal Standards (R*).

$$R^* = \frac{A_i^* m_{rs}}{A_{rs} RF_{is} m_i^*} \times 100\% \quad \text{Eq. 23-4}$$

9.6 Surrogate Compound Response Factor

$$RRF_s = \frac{A_s^* m_i}{A_{is} m_s^*} \quad \text{Eq. 23-5}$$

9.7 Recovery of Surrogate Compounds (Rs).

$$R_s = \frac{A_s m_i^*}{A_i^* RRF_s m_s} \times 100\% \quad \text{Eq. 23-6}$$

9.8 Minimum Detectable Limit (MDL).

$$MDL = \frac{2.5\, A_{is} m_i^*}{A_{is}^* RRF_i} \quad \text{Eq. 23-7}$$

9.9 Total Concentration of PCDD's and PCDF's in the Sample.

$$C_T = \sum_{i=1}^{n} C_i \quad \text{Eq. 23-8}$$

Any PCDD's or PCDF's that are reported as nondetected (below the MDL) shall be counted as zero for the purpose of calculating the total concentration of PCDD's and PCDF's in the sample.

10. Bibliography

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2. American Society of Mechanical Engineers. Analytical Procedures to Assay Stack Effluent Samples and Residual Combustion Products for Polychlorinated Dibenzo-p-Dioxins (PCDD) and Polychlorinated Dibenzofurans (PCDF). Prepared for the U.S. Department of Energy and U.S. Environmental Protection Agency. Washington, DC. December 1984. 23 p.

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TABLE 1—COMPOSITION OF THE SAMPLE FORTIFICATION AND RECOVERY STANDARDS SOLUTIONS

Analyte	Concentration (pg/μl)
Internal Standards	
$^{13}C_{12}$-2,3,7,8-TCDD	100
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	100
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100
$^{13}C_{12}$-OCDD	100
$^{13}C_{12}$-2,3,7,8-TCDF	100
$^{13}C_{12}$-1,2,3,7,8-PeCDF	100
$^{13}C_{12}$-1,2,3,6,7,- HxCDF	100
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100
Surrogate Standards	
$^{37}Cl_4$-2,3,7,8-TCDD	100
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	100
$^{13}C_{12}$-2,3,4,7,8-PeCDF	100
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	100
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	100
Recovery Standards	
$^{13}C_{12}$-1,2,3,4-TCDD	500
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	500

TABLE 2—COMPOSITION OF THE INITIAL CALIBRATION SOLUTIONS

Compound	Concentrations (pg/μL)				
	Solution No				
	1	2	3	4	5
Alternate Standard					
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	2.5	5	25	250	500
Recovery Standards					
$^{13}C_{12}$-1,2,3,4-TCDD	100	100	100	100	100
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	100	100	100	100	100

TABLE 3—ELEMENTAL COMPOSITIONS AND EXACT MASSES OF THE IONS MONITORED BY HIGH RESOLUTION MASS SPECTROMETRY FOR PCDD'S AND PCDF'S

Descriptor No	Accurate mass	Ion type	Elemental composition	Analyte
2	292.9825	LOCK	C_9F_{11}	PFK
	303.9016	M	$C_{12}H_4{}^{35}Cl_4O$	TCDF
	305.8987	M+2	$C_{12}H_4{}^{35}Cl_3{}^{37}ClO$	TCDF
	315.9419	M	$^{13}C_{12}H_4{}^{35}Cl_4O$	TCDF (S)
	317.9389	M+2	$^{13}C_{12}H_4{}^{35}Cl_3{}^{37}ClO$	TCDF (S)
	319.8965	M	$C_{12}H_4{}^{35}Cl_4O_2$	TCDD
	321.8936	M+2	$C_{12}H_4{}^{35}Cl_3{}^{37}ClO_2$	TCDD
	327.8847	M	$C_{12}H_4{}^{37}Cl_4O_2$	TCDD (S)
	330.9792	QC	C_9F_{11}	PFK
	331.9368	M	$^{13}C_{12}H_4{}^{35}Cl_4O_2$	TCDD (S)
	333.9339	M+2	$^{13}C_{12}H_4{}^{35}Cl_3{}^{37}ClO_2$	TCDD (S)
	339.8597	M+2	$C_{12}H_5{}^{35}Cl_3{}^{37}ClO$	PECDF
	341.8567	M+4	$C_{12}H_5{}^{35}Cl_2{}^{37}Cl_2O$	PeCDF
	351.9000	M+2	$^{13}C_{12}H_5{}^{35}Cl_3{}^{37}ClO$	PeCDF (S)
	353.8970	M+4	$^{13}C_{12}H_5{}^{35}Cl^{37}Cl_2O$	PeCDF (S)
	355.8546	M+2	$C_{12}H_5{}^{35}Cl_3{}^{37}ClO_2$	PeCDD
	357.8516	M+4	$C_{12}H_5{}^{35}Cl_2{}^{37}Cl_2O_2$	PeCDD
	367.8949	M+2	$^{13}C_{12}H_5{}^{35}Cl_3{}^{37}ClO_2$	PeCDD (S)
	369.8919	M+4	$^{13}C_{12}H_5{}^{35}Cl_2{}^{37}Cl_2O_2$	PeCDD (S)
	375.8364	M+2	$C_{12}H_3{}^{35}Cl_5{}^{37}ClO$	HxCDPE
	409.7974	M+2	$C_{12}H_3{}^{35}Cl_6{}^{37}ClO$	HpCPDE
3	373.8208	M+2	$C_{12}H_3{}^{35}Cl_5{}^{37}ClO$	HxCDF
	375.8178	M+4	$C_{12}H_3{}^{35}Cl_4{}^{37}Cl_2O$	HxCDF
	383.8639	M	$^{13}C_{12}H_3{}^{35}Cl_6O$	HxCDF (S)
	385.8610	M+2	$^{13}C_{12}H_3{}^{35}Cl_5{}^{37}ClO$	HxCDF (S)
	389.8157	M+2	$C_{12}H_3{}^{35}Cl_5{}^{37}ClO_2$	HxCDD
	391.8127	M+4	$C_{12}H_3{}^{35}Cl_4{}^{37}Cl_2O_2$	HxCDD
	392.9760	LOCK	C_8F_{13}	PFK
	401.8559	M+2	$^{13}C_{12}H_3{}^{35}Cl_5{}^{37}ClO_2$	HxCDD (S)
	403.8529	M+4	$^{13}C_{12}H_3{}^{35}Cl_4{}^{37}Cl_2O$	HxCDD (S)
	445.7555	M+4	$C_{12}H_3{}^{35}Cl_6{}^{37}Cl_2O$	OCDPE
	430.9729	QC	C_8F_{13}	PFK
4	407.7818	M+2	$C_{12}H^{35}Cl_6{}^{37}ClO$	HpCDF
	409.7789	M+4	$C_{12}H^{35}Cl_5{}^{37}Cl_2O$	HpCDF
	417.8253	M	$^{13}C_{12}H^{35}Cl_7O$	HpCDF (S)
	419.8220	M+2	$^{13}C_{12}H^{35}Cl_6{}^{37}ClO$	HpCDF (S)
	423.7766	M+2	$C_{12}H^{35}Cl_6{}^{37}ClO_2$	HpCDD
	425.7737	M+4	$C_{12}H^{35}Cl_5{}^{37}Cl_2O_2$	HpCDD
	435.8169	M+2	$^{13}C_{12}H^{35}Cl_6{}^{37}ClO_2$	HpCDD (S)
	437.8140	M+4	$^{13}C_{12}H^{35}Cl_5{}^{37}Cl_2O_2$	HpCDD (S)
	479.7185	M+4	$C_{12}H^{35}Cl_7{}^{37}Cl_2O$	NCPDE
	430.9729	LOCK	C_8F_{13}	PFK
	441.7428	M+2	$C_{13}{}^{35}Cl_7{}^{37}ClO$	OCDF
	443.7399	M+4	$C_{13}{}^{35}Cl_6{}^{37}Cl_2O$	OCDF
	457.7377	M+2	$C_{13}{}^{35}Cl_7{}^{37}ClO_2$	OCDD
	459.7348	M+4	$C_{13}{}^{35}Cl_6{}^{37}Cl_2O_2$	OCDD
	469.7779	M+2	$^{13}C_{12}{}^{35}Cl_7{}^{37}ClO_2$	OCDD (S)
	471.7750	M+4	$^{13}C_{12}{}^{35}Cl_6{}^{37}Cl_2O_2$	OCDD (S)
	513.6775	M+4	$C_{13}{}^{35}Cl_8{}^{37}Cl_2O_2$	DCDPE
	442.9728	QC	$C_{10}F_{11}$	PFK

(a) The following nuclidic masses were used
H = 1.007825
C = 12.000000
^{13}C = 13.003355
F = 18.9984
O = 15.994915
^{35}Cl = 34.968853
^{37}Cl = 36.965903
S = Labeled Standard
QC = Ion selected for monitoring instrument stability during the GC/MS analysis

TABLE 4—ACCEPTABLE RANGES FOR ION-ABUNDANCE RATIOS OF PCDD'S AND PCDF'S

No. of chlorine atoms	Ion type	Theoretical ratio	Control limits	
			Lower	Upper
4	M/M+2	0.77	0.65	0.89
5	M+2/M+4	1.55	1.32	1.78
6	M+2/M+4	1.24	1.05	1.43
6[a]	M/M+2	0.51	0.43	0.59
7[b]	M/M+2	0.44	0.37	0.51
7	M+2/M+4	1.04	0.88	1.20
8	M+2/M+4	0.89	0.76	1.02

[a] Used only for ^{13}C-HxCDF
[b] Used only for ^{13}C-HpCDF

TABLE 5—MINIMUM REQUIREMENTS FOR INITIAL AND DAILY CALIBRATION RESPONSE FACTORS

Compound	Relative response factors	
	Initial calibration RSD	Daily calibration % difference
Unlabeled Analytes		
2,3,7,8-TCDD	25	25
2,3,7,8-TCDF	25	25
1,2,3,7,8-PeCDD	25	25
1,2,3,7,8-PeCDF	25	25
2,3,4,7,8-PeCDF	25	25
1,2,4,5,7,8-HxCDD	25	25
1,2,3,6,7,8-HxCDD	25	25
1,2,3,7,8,9-HxCDD	25	25
1,2,3,4,7,8-HxCDF	25	25
1,2,3,6,7,8-HxCDF	25	25
1,2,3,7,8,9-HxCDF	25	25
2,3,4,6,7,8-HxCDF	25	25
1,2,3,4,6,7,8-HpCDD	25	25
1,2,3,4,6,7,8-HpCDF	25	25
OCDD	25	25
OCDF	30	30
Internal Standards		
$^{13}C_{12}$-2,3,7,8-TCDD	25	25
$^{13}C_{12}$-1,2,3,7,8-PeCDD	30	30
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	25	25
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	30	30
$^{13}C_{12}$-OCDD	30	30
$^{13}C_{12}$-2,3,7,8-TCDF	30	30
$^{13}C_{12}$-1,2,3,7,8-PeCDF	30	30
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	30	30
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	30	30
Surrogate Standards		
$^{37}Cl_4$-2,3,7,8-TCDD	25	25
$^{13}C_{12}$-2,3,4,7,8-PeCDF	25	25
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	25	25
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	25	25
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	25	25
Alternate Standard		
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	25	25

Method 25A—Determination of Total Gaseous Organic Concentration Using a Flame Ionization Analyzer

|s60xA_Meth_25A

1. Applicability and Principle

1.1 Applicability. This method applies to the measurement of total gaseous organic concentration of vapors consisting primarily of alkanes, alkenes, and/or arenes (aromatic hydrocarbons). The concentration is expressed in terms of propane (or other appropriate organic calibration gas) or in terms of carbon.

1.2 Principle. A gas sample is extracted from the source through a heated sample line, if necessary, and glass fiber filter to a flame ionization analyzer (FIA). Results are reported as volume concentration equivalents of the calibration gas or as carbon equivalents.

2. Definitions

2.1 Measurement System. The total equipment required for the determination of the gas concentration. The system consists of the following major subsystems:

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

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

2.2 Span Value. The upper limit of a gas concentration measurement range that is specified for affected source categories in the applicable part of the regulations. The span value is established in the applicable regulation and is usually 1.5 to 2.5 times the applicable emission limit. If no span value is provided, use a span value equivalent to 1.5 to 2.5 times the expected concentration. For convenience, the span value should correspond to 100 percent of the recorder scale.

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

2.4 Zero Drift. The difference in the measurement system response to a zero level calibration gas before and after a stated period of operation during which no unscheduled maintenance, repair, or adjustment took place.

2.5 Calibration Drift. The difference in the measurement system response to a mid-level calibration gas before and after a stated period of operation during which no unscheduled maintenance, repair or adjustment took place.

2.6 Response Time. The time interval from a step change in pollutant concentration at the inlet to the emission measurement system to the time at which 95 percent of the corresponding final value is reached as displayed on the recorder.

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

3. Apparatus

A schematic of an acceptable measurement system is shown in Figure 25A-1. The essential components of the measurement system are described below:

3.1 Organic Concentration Analyzer. A flame ionization analyzer (FIA) capable of meeting or exceeding the specifications in this method.

3.2 Sample Probe. Stainless steel, or equivalent, three-hole rake type. Sample holes shall be 4 mm in diameter or smaller and located at 16.7, 50, and 83.3 percent of the equivalent stack diameter. Alternatively, a single opening probe may be used so that a gas sample is collected from the centrally located 10 percent area of the stack cross-section.

3.3 Sample Line. Stainless steel or Teflon* tubing to transport the sample gas to the analyzer. The sample line should be heated, if necessary, to prevent condensation in the line.

|_{Footnote} * Mention of trade names or specific products does not constitute endorsement by the Environmental Protection Agency.

3.4 Calibration Valve Assembly. A three—way valve assembly to direct the zero and calibration gases to the analyzers is recommended. Other methods, such as quick-connect lines, to route calibration gas to the analyzers are applicable.

3.5 Particulate Filter. An in-stack or an out—of—stack glass fiber filter is recommended if exhaust gas particulate loading is significant. An out—of—stack filter should be heated to prevent any condensation.

3.6 Recorder. A strip-chart recorder, analog computer, or digital recorder for recording measurement data. The minimum data recording requirement is one measurement value per minute. Note. This method is often applied in highly explosive areas. Caution and care should be exercised in choice of equipment and installation.

4. Calibration and Other Gases

Gases used for calibrations, fuel, and combustion air (if required) are contained in compressed gas cylinders. Preparation of calibration gases shall be done according to the procedure in Protocol No. 1, listed in Citation 2 of Bibliography. Additionally, the manufacturer of the cylinder should provide a recommended shelf life for each calibration gas cylinder over which the concentration does not change more than ± 2 percent from the certified value. For calibration gas values not generally available (i.e., organics between 1 and 10 percent by volume), alternative methods for preparing calibration gas mixtures, such as dilution systems, may be used with prior approval of the Administrator.

Calibration gases usually consist of propane in air or nitrogen and are determined in terms of the span value. Organic compounds other than propane can be used following the above guidelines and making the appropriate corrections for

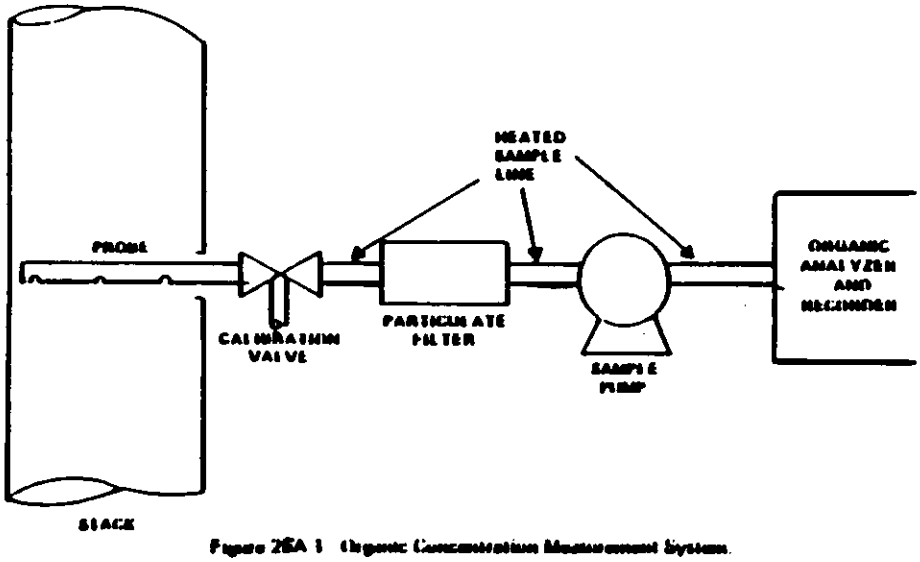


Figure 25A-1 Organic Concentration Measurement System.

response factor.

4.1 Fuel. A 40 percent H2/60 percent He or 40 percent H2/60 percent N2 gas mixture is recommended to avoid an oxygen synergism effect that reportedly occurs when oxygen concentration varies significantly from a mean value.

4.2 Zero Gas. High purity air with less than 0.1 parts per million by volume (ppmv) of organic material (propane or carbon equivalent) or less than 0.1 percent of the span value, whichever is greater.

4.3 Low-level Calibration Gas. An organic calibration gas with a concentration equivalent to 25 to 35 percent of the applicable span value.

4.4 Mid-level Calibration Gas. An organic calibration gas with a concentration equivalent to 45 to 55 percent of the applicable span value.

4.5 High-level Calibration Gas. An organic calibration gas with a concentration equivalent to 80 to 90 percent of the applicable span value.

5. Measurement System Performance Specifications

5.1 Zero Drift. Less than ± 3 percent of the span value.

5.2 Calibration Drift. Less than ± 3 percent of span value.

5.3 Calibration Error. Less than ± 5 percent of the calibration gas value.

6. Pretest Preparations

6.1 Selection of Sampling Site. The location of the sampling site is generally specified by the applicable regulation or purpose of the test; i.e., exhaust stack, inlet line, etc. The sample port shall be located at least 1.5 meters or 2 equivalent diameters upstream of the gas discharge to the atmosphere.

6.2 Location of Sample Probe. Install the sample probe so that the probe is centrally located in the stack, pipe, or duct and is sealed tightly at the stack port connection.

6.3 Measurement System Preparation. Prior to the emission test, assemble the measurement system following the manufacturer's written instructions in preparing the sample interface and the organic analyzer. Make the system operable.

FIA equipment can be calibrated for almost any range of total organics concentrations. For high concentrations of organics (> 1.0 percent by volume as propane) modifications to most commonly available analyzers are necessary. One accepted method of equipment modification is to decrease the size of the sample to the analyzer through the use of a smaller diameter sample capillary. Direct and continuous measurement of organic concentration is a necessary consideration when determining any modification design.

6.4 Calibration Error Test. Immediately prior to the test series, (within 2 hours of the start of the test) introduce zero gas and high-level calibration gas at the calibration valve assembly. Adjust the analyzer output to the appropriate levels, if necessary. Calculate the predicted response for the low-level and mid-level gases based on a linear response line between the zero and high-level responses. Then introduce low-level and mid-level calibration gases successively to the measurement system. Record the analyzer responses for low-level and mid-level calibration gases and determine the differences between the measurement system responses and the predicted responses. These differences must be less than 5 percent of the respective calibration gas value. If not, the measurement system is not acceptable and must be replaced or repaired prior to testing. No adjustments to the measurement system shall be conducted after the calibration and before the drift check (Section 7.3). If adjustments are necessary before the completion of the test series, perform the drift checks prior to the required adjustments and repeat the calibration following the adjustments. If multiple electronic ranges are to be used, each additional range must be checked with a mid-level calibration gas to verify the multiplication factor.

6.5 Response Time Test. Introduce zero gas into the measurement system at the calibration valve assembly. When the system output has stabilized, switch quickly to the high-level calibration gas. Record the time from the concentration change to the measurement system response equivalent to 95 percent of the step change. Repeat the test three times and average the results.

7. Emission Measurement Test Procedure

7.1 Organic Measurement. Begin sampling at the start of the test period, recording time and any required process information as appropriate. In particular, note on the recording chart periods of process interruption or cyclic operation.

7.2 Drift Determination. Immediately following the completion of the test period and hourly during the test period, reintroduce the zero and mid-level calibration gases, one at a time, to the measurement system at the calibration valve assembly. (Make no adjustments to the measurement system until after both the zero and calibration drift checks are made.) Record the analyzer response. If the drift values exceed the specified limits, invalidate the test results preceding the check and repeat the test following corrections to the measurement system. Alternatively, recalibrate the test measurement system as in Section 6.4 and report the results using both sets of calibration data (i.e., data determined prior to the test period and data determined following the test period).

8. Organic Concentration Calculations

Determine the average organic concentration in terms of ppmv as propane or other calibration gas. The average shall be determined by the integration of the output recording over the period specified in the applicable regulation.

If results are required in terms of ppmv as carbon, adjust measured concentrations using Equation 25A-1.

$$Cc = K\ Cmeas \qquad \text{Eq. 25A-1}$$

Where:

Cc = Organic concentration as carbon, ppmv.

Cmeas = Organic concentration as measured, ppmv.

K = Carbon equivalent correction factor. K = 2 for ethane. K = 3 for propane. K = 4 for butane. K = Appropriate response factor for other organic calibration gases.

9. Bibliography

1. Measurement of Volatile Organic Compounds——Guideline Series. U.S. Environmental Protection Agency. Research Triangle Park, NC. Publication No. EPA-450/2-78-041. June 1978. p. 46-54.

2. Traceability Protocol for Establishing True Concentrations of Gases Used for Calibration and Audits of Continuous Source Emission Monitors (Protocol No. 1). U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory. Research Triangle Park, NC. June 1978.

3. Gasoline Vapor Emission Laboratory Evaluation——Part 2. U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards. Research Triangle Park, NC. EMB Report No. 75-GAS-6. August 1975.

Method 26—Determination of Hydrogen Chloride Emissions From Stationary Sources

1. Applicability, Principle, Interferences, Precision, Bias, and Stability

1.1 Applicability. This method is applicable for determining hydrogen chloride (HCl) emissions from stationary sources.

1.2 Principle. An integrated sample is extracted from the stack and passed through dilute sulfuric acid. In the dilute acid, the HCl gas is dissolved and forms chloride (Cl-) ions. The Cl— is analyzed by ion chromatography (IC).
{**new-92-2 revised; Source: 57 FR 24551, June 10, 1992}

1.3 Interferences. Volatile materials which produce chloride ions upon dissolution during sampling are obvious interferences. Another likely interferent is diatomic chlorine (Cl2) gas which reacts to form HCl and hypochlorous acid (HOCl) upon dissolving in water. However, Cl2 gas exhibits a low solubility in water and the use of acidic, rather than neutral or basic collection solutions, greatly reduces the chance of dissolving any chlorine present.
{**new text ending}

1.4 Precision and Bias. The within-laboratory relative standard deviations are 6.2 and 3.2 percent at HCl concentrations of 3.9 and 15.3 ppm, respectively. The method does not exhibit a bias to Cl2 when sampling at concentrations less than 50 ppm.

1.5 Stability. The collected samples can be stored for up to 4 weeks before analysis.

1.6 Detection Limit. The analytical detection limit of the method is 0.1 μg/ml.

2. Apparatus

2.1 Sampling. The sampling train is shown in Figure 26-1, and component parts are discussed below.
{**new-92-2 revised; Source: 57 FR 24551, June 10, 1992}

2.1.1 Probe. Borsilicate glass, approximately 3/8—in. (9—mm) I.D. with a heating system to prevent moisture condensation. A Teflon-glass filter in a mat configuration shall be installed behind the probe to remove particulate matter from the gas stream (see section 2.1.5). A glass wool plug should not be used to remove particulate matter since a negative bias in the data could result.

2.1.2 Three-Way Stopcock. A borosilicate glass three—way stopcock with a heating system to prevent moisturecondensation. The heated stopcock should connect to the outlet of the heated filter and the inlet of the first impinger. The heating system shall be capable of preventing condensation up to the inlet of the first impinger. Silicone grease may be used, if necessary, to prevent leakage.
{**new text ending}

2.1.3 Impingers. Four 30—ml midget impingers with leak-free glass connectors. Silicone grease may be used, if necessary, to prevent leakage. For sampling at high

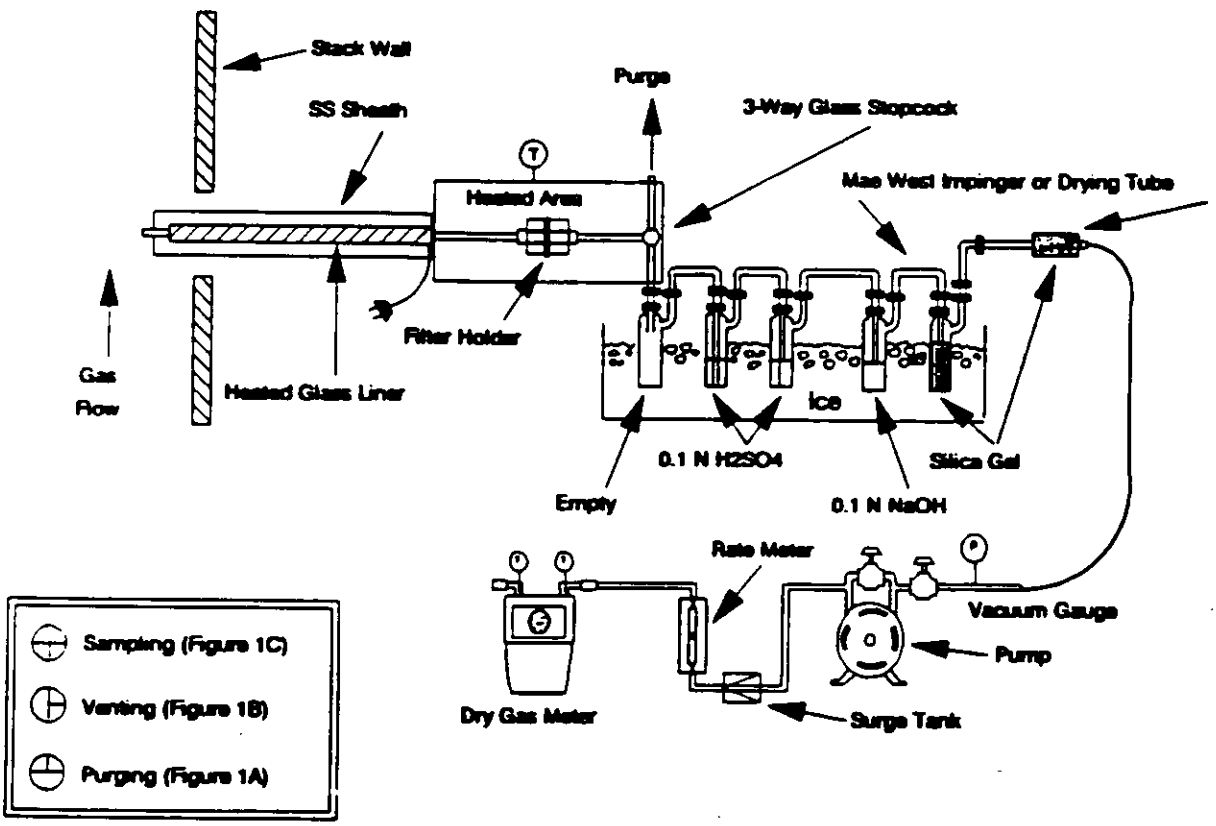


Figure 26-1. Sampling train.

moisture sources or for sampling times greater than 1 hour, a midget impinger with a shortened stem (such that the gas sample does not bubble through the collected condensate) should be used in front of the first impinger.

2.1.4 Drying Tube or Impinger. Tube or impinger, of Mae West design, filled with 6— to 16—mesh indicating type silica gel, or equivalent, to dry the gas sample and to protect the dry gas meter and pump. If the silica gel has been used previously, dry at 175 °C (350 °F) for 2 hours. New silica gel may be used as received. Alternatively, other types of desiccants (equivalent or better) may be used.
{**new-92-2 revised; Source: 57 FR 24551, June 10, 1992}

2.1.5 Filter. A 25—mm (or other size) Teflon-glass mat, Pallflex TX40HI75 (Pallflex Inc., 125 Kennedy Drive, Putnam, CT 06260). This filter is in a mat configuration to prevent fine particulate matter from entering the sampling train. Its composition is 75 percent Teflon/25 percent borosilicate glass. Other filters may be used, but they must be in a mat (as opposed to a laminate) configuration and contain at least 75 percent Teflon.
{**new text ending}
{**new-92-2 added; Source: 57 FR 24551, June 10, 1992}

2.1.6 Filter Holder and Support. The filter holder should be made of Teflon or quartz. The filter support shall be made of Teflon. All-Teflon filter holders and supports are available from Savillex Corp., 5325 Hwy 101, Minnetonka, MN 55345.
{**new text ending}
{**new-92-2 redesignated; Source: 57 FR 24551, June 10, 1992}

2.1.7 Sample Line. Leak-free, with compatible fittings to connect the last impinger to the needle valve.

2.1.8 Rate Meter. Rotameter, or equivalent, capable of measuring flow rate to within 2 percent of the selected flow rate of 2 liters/min.

2.1.9 Purge Pump, Purge Line, Drying Tube, Needle Valve, and Rate Meter. Pump capable of purging the sampling probe at 2 liters/min, with drying tube, filled with silica gel or equivalent, to protect pump, and a rate meter capable of measuring 0 to 5 liters/min.

2.1.10 Stopcock Grease, Valve, Pump, Volume Meter, Barometer, and Vacuum Gauge. Same as in Method 6, Sections 2.1.4, 2.1.7, 2.1.8, 2.1.10, 2.1.11, and 2.1.12.
{**new text ending}
{**new-92-2 added; Source: 57 FR 24551, June 10, 1992}

2.1.11 Temperature Measuring Devices. Temperature measuring device to monitor the temperature of the probe and a thermometer or other temperature measuring device to monitor the temperature of the sampling system from the outlet of the probe to the inlet of the first impinger.

2.1.12 Ice Water Bath. To minimize loss of absorbing solution.
{**new text ending}

2.2 Sample Recovery.

2.2.1 Wash Bottles. Polyethylene or glass, 500—ml or larger, two.
{**new-92-2 revised; Source: 57 FR 24551, June 10, 1992}

2.2.2 Storage Bottles. 100—ml glass, with Teflon-lined lids, to store impinger samples (two per sampling run).
{**new text ending}

2.3 Sample Preparation and Analysis. The materials required for volumetric dilution and chromatographic analysis of samples are described below.

2.3.1 Volumetric Flasks. Class A, 100—ml size.

2.3.2 Volumetric Pipets. Class A, assortment. To dilute samples into the calibration range of the instrument.
{**new-92-2 revised; Source: 57 FR 24551, June 10, 1992}

2.3.3 Ion Chromatograph. Suppressed or nonsuppressed, with a conductivity detector and electronic integrator operating in the peak area mode. Other detectors, strip chart recorders, and peak height measurements may be used.
{**new text ending}

3. Reagents

Unless otherwise indicated, all reagents must conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society (ACS reagent grade). When such specifications are not available, the best available grade shall be used.

3.1. Sampling.

3.1.1 Water. Deionized, distilled water that conforms to ASTM Specification D 1193-77, Type 3.

3.1.2 Absorbing solution, 0.1 N Sulfuric Acid (H_2SO_4). To prepare 100 ml of the absorbing solution for the front impinger pair, slowly add 0.28 ml of concentrated H_2SO_4 to about 90 ml of water while stirring, and adjust the final volume to 100 ml using additional water. Shake well to mix the solution.

3.1.3. Chlorine Scrubber Solution, 0.1 N Sodium Hydroxide (NaOH). To prepare 100 ml of the scrubber solution for the back pair of impingers, dissolve 0.40 g of solid NaOH in about 90 ml of water, and adjust the final solution volume to 100 ml using additional water. Shake well to mix the solution.

3.2 Sample Preparation and Analysis.

3.2.1 Water. Same as in Section 3.1.1.

3.2.2 Blank Solution. A separate blank solution of the absorbing reagent should be prepared for analysis with the field samples. Dilute 30 ml of absorbing solution to 100 ml with water in a separate volumetric flask.
{**new-92-2 revised; Source: 57 FR 24551, June 10, 1992}

3.2.3 Sodium Chloride (NaCl) Stock Standard Solution. Solutions containing a nominal certified concentration of 1000 mg/l are commercially available as convenient stock solutions from which working standards can be made by appropriate volumetric dilution. Alternately, concentrated stock solutions may be produced from reagent grade NaCl. The NaCl should be dried at 110 °C for 2 or more hours and cooled to room temperature in a desiccator immediately before weighing. Accurately weigh 1.6 to 1.7 g of the dried NaCl to within 0.1 mg, dissolve in water, and dilute to 1 liter. The exact Cl concentration can be calculated using Eq. 26-1.
{**new text ending}

3.2.4 Chromatographic Eluent. Effective eluents for nonsuppressed IC using a resin— or silica-based weak ion exchange column are a 4 mM potassium hydrogen phthalate solution, adjusted to pH 4.0 using a saturated sodium borate solution, and a 4 mM 4-hydroxy benzoate solution, adjusted to pH 8.6 using 1 N NaOH. An effective eluent for suppressed ion chromatography is a solution containing 3 mM sodium bicarbonate and 2.4 mM sodium carbonate. Other dilute solutions buffered to a similar pH and containing no interfering ions may be used. When using suppressed ion chromatography, if the "water dip" resulting from sample injection interferes with the chloride peak, use a 2 mM NaOH/2.4 mM sodium bicarbonate eluent.

$$\mu g\ Cl^-/ml = R \text{ of } NaCl \times 10^3 \times 35.45/58.44 \qquad \text{Eq. 26-1}$$

Refrigerate the stock standard solution and store no longer than 1 month.

4. Procedure

4.1 Sampling.

4.1.1 Preparation of Collection Train. Prepare the sampling train as follows: Pour 15 ml of the aborbing solution into each of the first two impingers, and add 15 ml of scrubber solution to the third and fourth impingers. Connect the impingers in series with the knockout impinger first, followed by the two impingers containing absorbing solution and the two containing the scrubber solution. Place a fresh charge of silica gel, or equivalent, in the drying tube or Mae West impinger.
{**new-92-2 revised; Source: 57 FR 24551, June 10, 1992}

4.1.2 Adjust the probe temperature and the temperature of the filter and the stopcock, i.e., the heated area in Figure 26-1 to a temperature sufficient to prevent water condensation. This temperature should be at least 20° C above the source temperature, but not greater than 120° C. The temperature should be monitored throughout a sampling run to ensure that the desired temperature is maintained.

4.1.3 Leak-Check Procedure. A leak-check prior to the sampling run is optional; however, a leak-check after the sampling run is mandatory. The leak-check procedure is as follows: Temporarily attach a suitable (e.g., 0–40 cc/min) rotameter to the outlet of the dry gas meter and place a vacuum gauge at or near the probe inlet. Plug the probe inlet, pull a vacuum of at least 250 mm Hg (10 in. Hg), and note the flow rate as indicated by the rotameter. A leakage rate not in excess of 2 percent of the average sampling rate is acceptable. (NOTE: Carefully release the probe inlet plug before turning off the pump.) It is suggested (not mandatory) that the pump be leak-checked separately, either prior to or after the sampling run. If done prior to the sampling run, the pump leak-check shall precede the leak-check of the sampling train described immediately above; if done after the sampling run, the pump leak-check shall follow the train leak-check. To leak-check the pump, proceed as follows: Disconnect the drying tube from the probe-impinger assembly. Place a vacuum gauge at the inlet to either the drying tube or pump, pull a vacuum of 250 mm (10 in.) Hg, plug or pinch off the outlet of the flowmeter, and then turn off the pump. The vacuum should remain stable for at least 30 sec. Other leak-check procedures may be used, subject to the approval of the Administrator, U.S. Environmental Protection Agency.
{**new text ending}

4.1.4 Purge Procedure. Immediately before sampling, connect the purge line to the stopcock, and turn the stopcock to permit the purge pump to purge the probe (see Figure 1A of Figure 26-1). Turn on the purge pump, and adjust the purge rate to 2 liters/min. Purge for at least 5 minutes before sampling.
{**new-92-2 revised; Source: 57 FR 24551, June 10, 1992}

4.1.5 Sample Collection. Turn on the sampling pump, pull a slight vacuum of approximately 25 mm Hg (1 in. Hg) on the impinger train, and turn the stopcock to permit stack gas to be pulled through the impinger train (see Figure 1C of Figure 26-1). Adjust the sampling rate to 2 liters/min, as indicated by the rate meter, and maintain this rate to within 10 percent during the entire sampling run. Take readings of the dry gas meter volume and temperature, rate meter, and vacuum gauge at least once every 5 minutes during the run. A sampling time of 1 hour is recommended. Shorter sampling times may introduce a significant negative bias in the HCl concentration. At the conclusion of the sampling run, remove the train from the stack, cool, and perform a leak-check as described in section 4.1.2.
{**new text ending}

4.2 Sample Recovery. Disconnect the impingers after sampling. Quantitatively transfer the contents of the first three impingers (the knockout impinger and the two absorbing solution impingers) to a leak-free storage bottle. Add the water rinses of each of these impingers and connecting glassware to the storage bottle. The contents of the scrubber impingers and connecting glassware rinses may be discarded. The sample bottle should be sealed, shaken to mix, and labeled. The fluid level should be marked so that if any sample is lost during transport, a correction proportional to the lost volume can be applied.

4.3 Sample Preparation for Analysis. Check the liquid level in each sample, and determine if any sample was lost during shipment. If a noticeable amount of leakage has occurred, the volume lost can be determined from the difference between the initial and final solution levels, and this value can be used to correct the analytical results. Quantitatively transfer the sample solution to a 100—ml volumetric flask, and dilute the solution to 100 ml with water.

4.4 Sample Analysis.
{**new-92-2 revised; Source: 57 FR 24551, June 10, 1992}

{ 4.4.1 The IC conditions will depend upon analytical column type and whether suppressed or nonsuppressed IC is used. An example chromatogram from a nonsuppressed system using a 150—mm Hamilton PRP-X100 anion column, a 2 ml/min flow rate of 4 mM 4-hydroxy benzoete solution adjusted to a pH of 8.6 using 1 N NaOH, a 50-μl sample loop, and a conductivity detector set on 1.0 μS full scale is shown in Figure 26-2.
**new text ending}

4.4.2 Before sample analysis, establish a stable baseline. Next, inject a sample of water, and determine if any Cl^- appears in the chromatogram. If Cl^- is present, repeat the load/injection procedure until no Cl^- is present. At this point, the instrument is ready for use.

4.4.3 First, inject the calibration standards covering an appropriate concentration range, starting with the lowest concentration standard. Next, inject in duplicate, a QC sample followed by a water blank and the field samples. Finally, repeat the injection of calibration standards to allow compensation for any drift in the instrument during analysis of the field samples. Measure the Cl^- peak areas or heights of the samples. Use the average response from the duplicate injections to determine the field sample concentrations using a linear calibration curve generated from the standards.

4.5 Audit Analysis. An audit sample must be analyzed, subject to availability.

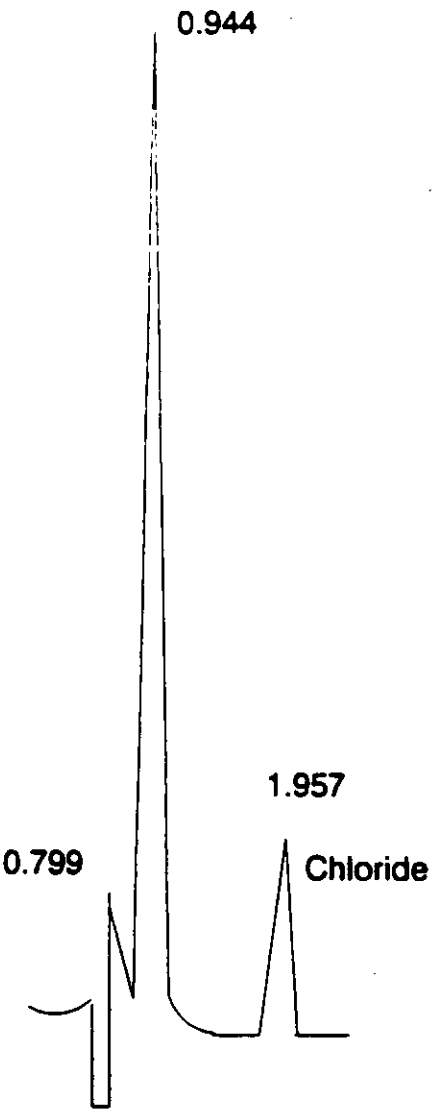


Figure 26-2. Example Chromatogram

5. Calibration

5.1 Dry Gas Metering System, Thermometers, Rate Meter, and Barometer. Same as in Method 6, sections 5.1, 5.2, 5.3, and 5.4.

5.2 Calibration Curve for Ion Chromatograph. To prepare calibration standards, dilute given volumes (1.0 ml or greater) of the stock standard solution, with 0.1 N H2SO4 (section 3.1.2) to convenient volumes. Prepare at least four standards that are within the linear range of the instrument and which cover the expected concentration range of the field samples. Analyze the standards as instructed in section 4.4.3, beginning with the lowest concentration standard. Determine the peak measurements, and plot individual values versus Cl' concentration in μg/ml. Draw a smooth curve through the points. Use linear regression to calculate a formula describing the resulting linear curve.

6. Quality Assurance

6.1 Applicability. When the method is used to analyze samples to demonstrate compliance with a source emission regulation, a set of two audit samples must be analyzed.

6.2 Audit Procedure. The audit sample are chloride solutions. Concurrently analyze the two audit samples and a set of compliance samples in the same manner to evaluate the technique of the analyst and the standards preparation. The same analyst, analytical reagents, and analytical system shall be used both for compliance samples and the EPA audit samples. If this condition is met, auditing the subsequent compliance analyses for the same enforcement agency within 30 days is not required. An audit sample set may not be used to validate different sets of compliance samples under the jurisdiction of different enforcement agencies, unless prior arrangements are made with both enforcement agencies.

6.3 Audit Sample Availability. The audit samples may be obtained by writing or calling the EPA Regional Office or the appropriate enforcement agency. The request for the audit samples must be made at least 30 days prior to the scheduled compliance sample analyses.

{**new-92-2 revised; Source: 57 FR 24551, June 10, 1992}

6.4 Audit Results.

6.4.1 Calculate the concentrations in mg/dscm using the specified sample volume in the audit instructions.

Note: Indication of acceptable results may be obtained immediately by reporting the audit results in mg/dscm and compliance results in total μg HCl/sample to the responsible enforcement agency. Include the results of both audit samples, their identification numbers, and the analyst's name with the results of the compliance determination samples in appropriate reports to the EPA Regional Office or the appropriate enforcement agency. Include this information with subsequent analyses for the same enforcement agency during the 30—day period.

6.4.2 The concentrations of the audit samples obtained by the analyst shall agree within 10 percent of the actual concentrations. If the 10 percent specification is not met, reanalyze the compliance samples and audit samples, and include initial and reanalysis values in the test report.

6.4.3 Failure to meet the 10 percent specification may require retests until the audit problems are resolved. However, if the audit results do no affect the compliance or noncompliance status of the affected facility, the Administrator may waive the reanalysis requirement, further audits, or retests and accept the results of the compliance test. While steps are being taken to resolve audit analysis problems, the Administrator may also choose to use the data to determine the compliance or noncompliance status of the affected facility.

{**new text ending}

7. Calculations

Retain at least one extra decimal figure beyond those contained in the available data in intermediate calculations, and round off only the final answer appropriately.

7.1 Sample Volume, Dry Basis, Corrected to Standard Conditions. Calculate the sample volume using Eq. 5-1 of Method 6.

7.2 Total μg HCl Per Sample.

$$m = \frac{(S-B)\times 100\times 36.46}{(35.45)}$$

$$= (102.8)(S-B) \qquad \text{Eq. 26-2}$$

Where:

m = Mass of HCl in sample, μg.

S = Concentration of sample, μg Cl—/ml.

B = Concentration of blank, μg Cl—/ml.

100 = Volume of filtered and diluted sample, ml.

36.46 = Molecular weight of HCl, μg/μg—mole.

35.45 = Atomic weight of Cl, μg/μg—mole.

7.3 Concentration of HCl in the Flue Gas.

$$C = Km/Vm(std) \qquad \text{Eq. 26-3}$$

Where:

C = Concentration of HCl, dry basis, mg/dscm.

K = 10^-3 mg/ μg.

m = Mass of HCl in sample, μg.

Vm(std) = Dry gas volume measured by the dry gas meter, corrected to standard conditions, dscm.

8. Bibliography

{**new-92-2 revised; Source: 57 FR 24551, June 10, 1992}

1. Steinsberger, S.C. and J.H Margeson, "Laboratory and Field Evaluation of a Methodology for Determination of Hydrogen Chloride Emissions form Municipal and Hazardous Waste Incinerators," U.S. Environmental Protection Agency, Office of Research and Development, Report No. 600/3-89/064, April 1989. Available from the National Technical Information Service, Springfield, VA 22161 as PB89220586/AS.

{**new text ending}

2. State of California, Air Resources Board. Method 421. "Determination of Hydrochloric Acid Emissions from Stationary Sources." March 18, 1987.

{**new-92-2 revised; Source: 57 FR 24551, June 10, 1992}

3. Cheney, J.L. and C.R. Fortune. Improvements in the Methodology for Measuring Hydrochloric Acid in Combustion Source Emissions. J. Environ. Sci. Health. A19(3): 337-350. 1984.

{**new text ending}

It is proposed that 40 CFR Parts 60 and 61 be amended as follows:

1. The authority citations for Parts 60 and 61 continue to read as follows:

42 U.S.C. 7401, 7411, 7412, 7414, 7416, and 7601.

2. In Part 60, by adding Method 29 to Appendix A as follows:

Appendix A - Test Methods

* * * * *

Method 29 - Determination of Metals Emissions from Stationary Sources

1. Applicability and Principle

1.1 Applicability. This method is applicable to the determination of total chromium (Cr), cadmium (Cd), arsenic (As), nickel (Ni), manganese (Mn), beryllium (Be), copper (Cu), zinc (Zn), lead (Pb), selenium (Se), phosphorus (P), thallium (Tl), silver (Ag), antimony (Sb), barium (Ba), and mercury (Hg) emissions from stationary sources This method may also be used for determining particulate emissions when the prescribed procedures and precautions are followed. Changes in the procedures to further facilitate particulate determination may affect the front-half mercury determination.

1.2 Principle. A stack sample is withdrawn isokinetically from the source, with particulate emissions collected in the probe and on a heated filter and gaseous emissions collected in solutions of acidic hydrogen peroxide and acidic potassium permanganate. The recovered samples are digested, and

appropriate fractions are analyzed for mercury by cold vapor atomic absorption spectroscopy (CVAAS) and for Cr, Cd, Ni, Mn, Be, Cu, Zn, Pb, Se, P, Tl, Ag, Sb, Ba, and As by inductively coupled argon plasma emission spectroscopy (ICAP) or atomic absorption spectroscopy (AAS). Graphite furnace atomic absorption spectroscopy (GFAAS) is used for analysis of Sb, As, Dc, Pb, Se, and Tl if these elements require greater analytical sensitivity than can be obtained by ICAP. Additionally, if desired, the tester may use AAS for analysis of all metals if the resulting in-stack method detection limits meet the goal of the testing program.

2. Range, Sensitivity, Precision, and Interferences

2.1 Range. For the analysis described and for similar analyses, the ICAP response is linear over several orders of magnitude. Samples containing metal concentrations in the nanograms per ml (ng/ml) to micrograms per ml (μg/ml) range in the final analytical solution can be analyzed using this method. Samples containing greater than approximately 50 μg/ml Cr, Pb, or As should be diluted to that level or lower for final analysis. Samples containing greater than approximately 20 μg/ml of Cd should be diluted to that level before analysis.

2.2 Analytical Sensitivity. ICAP analytical detection limits for the sample solutions (based on SW-846, Method 6010) are approximately as follows: Sb (32 ng/ml), As (53 ng/ml), Ba (2 ng/ml), Be (0.3 ng/ml), Cd (4 ng/ml), Cr (7 ng/ml), Cu (6 ng/ml), Pb (42 ng/ml), Mn (2 ng/ml), Ni (15 ng/ml),

P (75 ng/ml), Se (75 ng/ml), Ag (7 ng/ml), Tl (40 ng/ml), and Zn (2 ng/ml). The actual method detection limits are sample dependent and may vary as the sample matrix may affect the limits. The analytical detection limits for analysis by direct aspiration AAS (based on SW-846, Method 7000 series) are approximately as follows: Sb (200 ng/ml), As (2 ng/ml), Ba (100 ng/ml), Be (5 ng/ml), Cd (5 ng/ml), Cr (50 ng/ml), Cu (20 ng/ml), Pb (100 ng/ml), Mn (10 ng/ml), Ni (40 ng/ml), Se (2 ng/ml), Ag (10 ng/ml), Tl (100 ng/ml), and Zn (5 ng/ml). The detection limit for mercury by CVAAS is approximately 0.2 ng/ml. The use of GFAAS can give added sensitivity compared to direct aspiration AAS for the following metals: Sb (3 ng/ml), As (1 ng/ml), Be (0.2 ng/ml), Cd (0.1 ng/ml), Cr (1 ng/ml), Pb (1 ng/ml), Se (2 ng/ml), and Tl (1 ng/ml).

2.3 In-stack Detection Limit.

2.3.1 Using (1) the procedures described in this method, (2) the analytical detection limits described in the previous paragraph, (3) a volume of 300 ml (Fraction 1) for the front-half and 150 ml (Fraction 2A) for the back-half samples, and (4) a stack gas sample volume of 1.25 m^3, the corresponding in-stack method detection limits are presented in Table 29-1 and calculated using Eq. 29-1.

$$A \times B/C = D \qquad \text{Eq. 29-1}$$

where:

A = Analytical detection limit, $\mu g/ml$.

B = Volume of sample prior to aliquotting for analysis, ml.

C = Stack sample volume, dsm^3.

D = In-stack detection limit, $\mu g/m^3$.

Values in Table 29-1 are calculated for the front- and back-half and/or the total train.

2.3.2 To ensure optimum sensitivity in the measurements, the concentrations of target metals in the solutions are suggested to be at least ten times the analytical detection limits. Under certain conditions, and with greater care in the analytical procedure, this concentration can be as low as approximately three times the analytical detection limit. In all cases, on at least one sample (run) in the source test and for each metal analyzed, repetitive analyses, method of standard additions (MSA), serial dilution, or matrix spike addition, etc., shall be used to establish the quality of the data.

2.3.3 Actual in-stack method detection limits will be determined based on actual source sampling parameters and analytical results as described above. If required, the method in-stack detection limits can be made more sensitive than those shown in Table 29-1 for a specific test by using one or more of the following options:

2.3.4 A 1-hour sampling run may collect a stack gas sampling volume of about 1.25 m^3. If the sampling time is

increased and 5 m^3 are collected, the in-stack method detection limits would be one fourth the values shown in Table 29-1 (with this change, the method is four times more sensitive than a 1-hour run. Larger sample volumes (longer runs) would make it even more sensitive.

2.3.5 The in-stack detection limits assume that all of the sample is digested (except the aliquot for mercury) and the final liquid volumes for analysis are 300 ml (Fraction 1) for the front-half and 150 ml (Fraction 2A) for the back-half sample. If the front-half volume is reduced from 300 to 30 ml, the front-half in-stack detection limits would be one tenth the values shown above (ten times more sensitive). If the back-half volume is reduced from 150 to 25 ml, the in-stack detection limits would be one sixth the above values. Matrix effect checks are necessary on sample analyses and typically are of greater significance for samples that have been concentrated to less than the normal original sample volume. Reduction to a volume of less than 25 ml may not allow redissolving of the residue and may increase interference by other compounds.

2.3.6 When both of the above modifications are used simultaneously on one sample, the resultant improvements are multiplicative. For example, where stack gas volume is increased by a factor of five and the total liquid sample digested volume of both the front- and back-halves is reduced by a factor of six, the in-stack method detection limit is reduced by a factor of thirty (the method is thirty times more sensitive). Conversely,

reducing stack sample volume and increasing sample liquid volume will increase in-stack detection limits (the method would then be less sensitive). The front-half and back-half samples (Fractions 1A and 2A) can be combined proportionally (see Section 1.2) prior to analysis. The resultant liquid volume (excluding the mercury fractions, which must be analyzed separately) is recorded. Combining the sample in this manner does not allow the point of capture in the train to be determined. The in-stack method detection limit then becomes a single value for all metals except mercury (due to exclusion of the mercury fraction). This discussion assumes no blank correction. Blank corrections are discussed later in this method.

2.4 Precision. The precision (relative standard deviation) for each metal detected in a method development test at a sewage sludge incinerator are as follows: Sb (12.7 percent), As (13.5 percent), Ba (20.6 percent), Cd (11.5 percent), Cr (11.2 percent), Cu (11.5 percent), Pb (11.6 percent), P (14.6 percent), Se (15.3 percent), Tl (12.3 percent), and Zn (11.8 percent). The precision for Ni was 7.7 percent for another test conducted at a source simulator. Beryllium, Mn, and Ag were not detected in the tests; however, based on the analytical sensitivity of the ICAP for these metals, it is assumed that their precisions should be similar to those for the other metals when detected at similar levels.

2.5 Interferences. Iron can be a spectral interference during the analysis of As, Cr, and Cd by ICAP. Al can be a

spectral interference during the analysis of As and Pb by ICAP. Generally, these interferences can be reduced by diluting the sample, but this increases the method detection limit (in-stack detection limit). Refer to Method 6010 of Citation 1 of the Bibliography or the other analytical methods used for details on potential interferences to this method. The analyst must eliminate or reduce interferences to acceptable levels. For all GFAAS analyses, matrix modifiers should be used to limit interferences, and standards should be matrix matched.

3. Apparatus

3.1 Sampling Train. A schematic of the sampling train is shown in Figure 29-1. It is similar to the Method 5 train and consists of the following components.

3.1.1 Probe Nozzle (Probe Tip) and Borosilicate or Quartz Glass Probe Liner. Same as Method 5, Sections 2.1.1 and 2.1.2, except that glass nozzles are required unless alternate tips are constructed of materials that are free from contamination and will not interfere with the sample. If a probe tip other than glass is used, no correction to the sample test results may be made to compensate for its effect on the sample. Probe fittings of plastic such as Teflon, polypropylene, etc. are recommended over metal fittings to prevent contamination; further, if desired, a single glass piece consisting of a combined probe tip and probe liner may be used, but such a single glass piece is <u>not</u> a requirement of this methodology)

3.1.2 Pitot Tube and Differential Pressure Gauge. Same as Method 2, Sections 2.1 and 2.2, respectively.

3.1.3 Filter Holder. Glass, same as Method 5, Section 2.1.5, except a Teflon filter support or other non-metallic, non-contaminating support must be used in place of the glass frit.

3.1.4 Filter Heating System. Same as Method 5, Section 2.1.6.

3.1.5 Condenser. The following system shall be used for condensing and collecting gaseous metals and determining the moisture content of the stack gas. The condensing system should consist of four to seven impingers connected in series with leak-free ground glass fittings or other leak-free, non-contaminating fittings. The first impinger is optional and is recommended as a moisture trap. The second impinger (or the first HNO_3/H_2O_2 impinger) shall be as described for the first impinger in Method 5. The third impinger (or second HNO_3/H_2O_2 impinger) shall be the Greenburg Smith impinger with the standard tip described as the second impinger in Method 5, Section 2.1.7. All other impingers are the same as the first HNO_3/H_2O_2 impinger previously described. A thermometer capable of measuring to within 1°C (2°F) shall be placed at the outlet of the last impinger. If mercury analysis is not to be performed, the potassium permanganate impingers and the empty impinger preceding them are removed.

3.1.6 Metering System, Barometer, and Gas Density Determination Equipment. Same as Method 5, Sections 2.1.8 through 2.1.10, respectively.

3.1.7 Teflon Tape. For capping openings and sealing connections, if necessary, on the sampling train.

3.2 Sample Recovery. Same as Method 5, Sections 2.2.1 through 2.2.8 (Probe-Liner and Probe-Nozzle Brushes or Swabs, Wash Bottles, Sample Storage Containers, Petri Dishes, Glass Graduated Cylinder, Plastic Storage Containers, Funnel and Rubber Policeman, and Glass Funnel), respectively, with the following exceptions and additions:

3.2.1 Non-metallic Probe-Liner and Probe-Nozzle Brushes or Swabs. For quantitative recovery of materials collected in the front-half of the sampling train. A description of acceptable all-Teflon component brushes or swabs are to be included in EPA's Emission Measurement Technical Information Center (EMTIC) files.

3.2.2 Sample Storage Containers. Glass bottles with Teflon-lined caps which are non-reactive to the oxidizing solutions, with capacities of 1000- and 500-ml shall be used for $KMnO_4$-containing samples and blanks. Polyethylene bottles may be used for other sample types.

3.2.3 Graduated Cylinder. Glass or equivalent.

3.2.4 Funnel. Glass or equivalent.

3.2.5 Labels. For identifying samples.

3.2.6 Polypropylene Tweezers and/or Plastic Gloves. For recovery of the filter from the sampling train filter holder.

3.3 Sample Preparation and Analysis. For the analysis, the following equipment is needed:

3.3.1 Volumetric Flasks, 100-ml, 250-ml, and 1000-ml. For preparation of standards and sample dilutions.

3.3.2 Graduated Cylinders. For preparation of reagents.

3.3.3 Parr^{R} Bombs or Microwave Pressure Relief Vessels with Capping Station (CEM Corporation model or equivalent).

3.3.4 Beakers and Watch Glasses. 250-ml beakers for sample digestion with watch glasses to cover the tops.

3.3.5 Ring Stands and Clamps. For securing equipment such as filtration apparatus.

3.3.6 Filter Funnels. For holding filter paper.

3.3.7 Disposable Pasteur Pipets and Bulbs.

3.3.8 Volumetric Pipets.

3.3.9 Analytical Balance. Accurate to within 0.1 mg.

3.3.10 Microwave or Conventional Oven. For heating samples at fixed power levels or temperatures.

3.3.11 Hot Plates.

3.3.12 Atomic Absorption Spectrometer (AAS). Equipped with a background corrector.

3.3.12.1 Graphite Furnace Attachment. With Sb, As, Cd, Pb, Se, and Tl hollow cathode lamps (HCLs) or electrodeless discharge lamps (EDLs). Same as Bibliography Citation 1 Methods 7041 (Sb), 7060 (As), 7131 (Cd), 7421 (Pb), 7740 (Se), and 7841 (Tl).

3.3.12.2 Cold Vapor Mercury Attachment. With a mercury HCL or EDL. The equipment needed for the cold vapor mercury

attachment includes an air recirculation pump, a quartz cell, an aerator apparatus, and a heat lamp or desiccator tube. The heat lamp should be capable of raising the ambient temperature at the quartz cell by 10°C such that no condensation forms on the wall of the quartz cell. Same as Method 7470 in Citation 2 of the Bibliography.

3.3.13 Inductively Coupled Argon Plasma Spectrometer. With either a direct or sequential reader and an alumina torch. Same as EPA Method 6010 in Citation 1 of the Bibliography.

4. Reagents

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

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

4.2.1 Filters. The filters shall contain less than 1.3 $\mu g/in.^2$ of each of the metals to be measured. Analytical results provided by filter manufacturers are acceptable. However, if no such results are available, filter blanks must be analyzed for each target metal prior to emission testing. Quartz or glass fiber filters without organic binders shall be used. The filters should exhibit at least 99.95 percent efficiency (<0.05 percent penetration) on 0.3-μ dioctyl phthalate smoke particles. The filter efficiency test shall be conducted in

accordance with ASTM Standard Method D2986-71 (incorporated by reference). For particulate determination in sources containing sulfur dioxide (SO_2) or sulfur trioxide (SO_3), the filter material must be of a type that is unreactive to SO_2 or SO_3, as described in Method 5. Quartz fiber filters meeting these requirements are recommended.

4.2.2 Water. To conform to ASTM Specification D1193-77, Type II (incorporated by reference). If necessary, analyze the water for all target metals prior to field use. All target metals should be less than 1 ng/ml.

4.2.3 Nitric Acid. Concentrated. Baker Instra-analyzed or equivalent.

4.2.4 Hydrochloric Acid. Concentrated. Baker Instra-analyzed or equivalent.

4.2.5 Hydrogen Peroxide, 30 Percent (V/V).

4.2.6 Potassium Permanganate.

4.2.7 Sulfuric Acid. Concentrated.

4.2.8 Silica Gel and Crushed Ice. Same as Method 5, Sections 3.1.2 and 3.1.4, respectively.

4.3 Pretest Preparation of Sampling Reagents.

4.3.1 Nitric Acid (HNO_3)/Hydrogen Peroxide (H_2O_2) Absorbing Solution, 5 Percent HNO_3/10 Percent H_2O_2. Add carefully with stirring 50 ml of concentrated HNO_3 to a 1000-ml volumetric flask containing approximately 500 ml of water, and then add carefully with stirring 333 ml of 30 percent H_2O_2. Dilute to volume with

water. Mix well. The reagent shall contain less than 2 ng/ml of each target metal.

4.3.2 Acidic Potassium Permanganate ($KMnO_4$) Absorbing Solution, 4 Percent $KMnO_4$ (W/V), 10 Percent H_2SO_4 (V/V). Prepare fresh daily. Mix carefully, with stirring, 100 ml of concentrated H_2SO_4 into approximately 800 ml of water, and add water with stirring to make a volume of 1 liter: this solution is 10 percent H_2SO_4 (V/V). Dissolve, with stirring, 40 g of $KMnO_4$ into 10 percent H_2SO_4 (V/V) and add 10 percent H_2SO_4 (V/V) with stirring to make a volume of 1 liter: this is the acidic potassium permanganate absorbing solution. Prepare and store in glass bottles to prevent degradation. The reagent shall contain less than 2 ng/ml of Hg.

Precaution: To prevent autocatalytic decomposition of the permanganate solution, filter the solution through Whatman 541 filter paper. Also, due to the potential reaction of the potassium permanganate with the acid, there may be pressure buildup in the sample storage bottle; these bottles shall not be fully filled and shall be vented to relieve excess pressure and prevent explosion potentials. Venting is required, but should not allow contamination of the sample; a No. 70-72 hole drilled in the container cap and Teflon liner has been used.

4.3.3 Nitric Acid, 0.1 N. Add with stirring 6.3 ml of concentrated HNO_3 (70 percent) to a flask containing approximately 900 ml of water. Dilute to 1000 ml with water.

Mix well. The reagent shall contain less than 2 ng/ml of each target metal.

4.3.4 Hydrochloric Acid (HCl), 8 N. Make the desired volume of 8N HCl in the following proportions. Carefully add with stirring 690 ml of concentrated HCl to a flask containing 250 ml of water. Dilute to 1000 ml with water. Mix well. The reagent shall contain less than 2 ng/ml of Hg.

4.4 Glassware Cleaning Reagents.

4.4.1 Nitric Acid, Concentrated. Fisher ACS grade or equivalent.

4.4.2 Water. To conform to ASTM Specifications D1193-77, Type II.

4.4.3 Nitric Acid, 10 Percent (V/V). Add with stirring 500 ml of concentrated HNO_3 to a flask containing approximately 4000 ml of water. Dilute to 5000 ml with water. Mix well. Reagent shall contain less than 2 ng/ml of each target metal.

4.5 Sample Digestion and Analysis Reagents.

4.5.1 Hydrochloric Acid, Concentrated.

4.5.2 Hydrofluoric Acid, Concentrated.

4.5.3 Nitric Acid, Concentrated. Baker Instra-analyzed or equivalent.

4.5.4 Nitric Acid, 50 Percent (V/V). Add with stirring 125 ml of concentrated HNO_3 to 100 ml of water. Dilute to 250 ml with water. Mix well. Reagent shall contain less than 2 ng/ml of each target metal.

4.5.5 Nitric Acid, 5 Percent (V/V). Add with stirring 50 ml of concentrated HNO_3 to 800 ml of water. Dilute to 1000 ml with water. Mix well. Reagent shall contain less than 2 ng/ml of each target metal.

4.5.6 Water. To conform to ASTM Specifications D1193-77, Type II.

4.5.7 Hydroxylamine Hydrochloride and Sodium Chloride Solution. See Citation 2 of the Bibliography for preparation.

4.5.8 Stannous Chloride. See Citation 2 of the Bibliography for preparation.

4.5.9 Potassium Permanganate, 5 Percent (W/V). See Citation 2 of the Bibliography for preparation.

4.5.10 Sulfuric Acid, Concentrated.

4.5.11 Nitric Acid, 50 Percent (V/V).

4.5.12 Potassium Persulfate, 5 Percent (W/V). See Citation 2 of the Bibliography for preparation.

4.5.13 Nickel Nitrate, $Ni(NO_3)_2 \cdot 6H_2O$.

4.5.14 Lanthanum Oxide, La_2O_3.

4.5.15 Hg Standard (AAS Grade), 1000 µg/ml.

4.5.16 Pb Standard (AAS Grade), 1000 µg/ml.

4.5.17 As Standard (AAS Grade), 1000 µg/ml.

4.5.18 Cd Standard (AAS Grade), 1000 µg/ml.

4.5.19 Cr Standard (AAS Grade), 1000 µg/ml.

4.5.20 Sb Standard (AAS Grade), 1000 µg/ml.

4.5.21 Ba Standard (AAS Grade), 1000 µg/ml.

4.5.22 Be Standard (AAS Grade), 1000 µg/ml.

4.5.23 Cu Standard (AAS Grade), 1000 μg/ml.

4.5.24 Mn Standard (AAS Grade), 1000 μg/ml.

4.5.25 Ni Standard (AAS Grade), 1000 μg/ml.

4.5.26 P Standard (AAS Grade), 1000 μg/ml.

4.5.27 Se Standard (AAS Grade), 1000 μg/ml.

4.5.28 Ag Standard (AAS Grade), 1000 μg/ml.

4.5.29 Tl Standard (AAS Grade), 1000 μg/ml.

4.5.30 Zn Standard (AAS Grade), 1000 μg/ml.

4.5.31 Al Standard (AAS Grade), 1000 μg/ml.

4.5.32 Fe Standard (AAS Grade), 1000 μg/ml.

4.5.33 The metals standards may also be made from solid chemicals as described in Citation 3 of the Bibliography. Citations 1, 2, or 4 of the Bibliography should be referred to for additional information on mercury standards.

4.5.34 Mercury Standards and Quality Control Samples. Prepare fresh weekly a 10 μg/ml intermediate mercury standard by adding 5 ml of 1000 μg/ml mercury stock solution to a 500-ml volumetric flask; dilute with stirring to 500 ml by first carefully adding 20 ml of 15 percent HNO_3 and then adding water to the 500-ml volume. Mix well. Prepare a 200 ng/ml working mercury standard solution fresh daily: add 5 ml of the 10 μg/ml intermediate standard to a 250-ml volumetric flask, and dilute to 250 ml with 5 ml of 4 percent $KMnO_4$, 5 ml of 15 percent HNO_3, and then water. Mix well. At least six separate aliquots of the working mercury standard solution should be used to prepare the standard curve. These aliquots should contain 0.0, 1.0, 2.0,

3.0, 4.0, and 5.0 ml of the working standard solution containing 0, 200, 400, 600, 800, and 1000 ng mercury, respectively. Quality control samples should be prepared by making a separate 10 µg/ml standard and diluting until in the range of the calibration.

4.5.35 ICAP Standards and Quality Control Samples. Calibration standards for ICAP analysis can be combined into four different mixed standard solutions as shown below.

MIXED STANDARD SOLUTIONS FOR ICAP ANALYSIS

Solution	Elements
I	As, Be, Cd, Mn, Pb, Se, Zn
II	Ba, Cu, Fe
III	Al, Cr, Ni
IV	Ag, P, Sb, Tl

Prepare these standards by combining and diluting the appropriate volumes of the 1000 µg/ml solutions with 5 percent HNO_3. A minimum of one standard and a blank can be used to form each calibration curve. However, a separate quality control sample spiked with known amounts of the target metals in quantities in the mid-range of the calibration curve should be prepared. Suggested standard levels are 25 µg/ml for AL, Cr and Pb, 15 µg/ml for Fe, and 10 µg/ml for the remaining elements. Prepare any standards containing less than 1 µg/ml of metal on a daily basis. Standards containing greater than 1 µg/ml of metal should be stable for a minimum of 1 to 2 weeks.

4.5.36 Graphite Furnace AAS Standards. Sb, As, Cd, Pb, Se, and Tl. Prepare a 10 µg/ml standard by adding 1 ml of 1000 µg/ml standard to a 100-ml volumetric flask. Dilute with stirring to

100 ml with 10 percent HNO_3. For graphite furnace AAS, the standards must be matrix matched. Prepare a 100 ng/ml standard by adding 1 ml of the 10 µg/ml standard to a 100-ml volumetric flask, and dilute to 100 ml with the appropriate matrix solution. Other standards should be prepared by diluting the 100 ng/ml standards. At least five standards should be used to make up the standard curve. Suggested levels are 0, 10, 50, 75, and 100 ng/ml. Quality control samples should be prepared by making a separate 10 µg/ml standard and diluting until it is in the range of the samples. Any standards containing less than 1 µg/ml of metal should be prepared on a daily basis. Standards containing greater than 1 µg/ml of metal should be stable for a minimum of 1 to 2 weeks.

4.5.37 Matrix Modifiers.

4.5.37.1 Nickel Nitrate, 1 Percent (V/V). Dissolve 4.956 g of $Ni(NO_3)_2 \cdot 6H_2O$ in approximately 50 ml of water in a 100-ml volumetric flask. Dilute to 100 ml with water.

4.5.37.2 Nickel Nitrate, 0.1 Percent (V/V). Dilute 10 ml of the 1 percent nickel nitrate solution from Section 4.5.37.1 above to 100 ml with water. Inject an equal amount of sample and this modifier into the graphite furnace during AAS analysis for As.

4.5.37.3 Lanthanum. Carefully dissolve 0.5864 g of La_2O_3 in 10 ml of concentrated HNO_3, and dilute the solution by adding it with stirring to approximately 50 ml of water. Dilute to 100 ml with water, and mix well. Inject an equal amount of

sample and this modifier into the graphite furnace during AAS analysis for Pb.

4.5.38 Whatman 541 Filter Paper (or equivalent). For filtration of digested samples.

5. Procedure

5.1 Sampling. The complexity of this method is such that, to obtain reliable results, testers and analysts should be trained and experienced with the test procedures, including source sampling, reagent preparation and handling, sample handling, safety equipment, analytical calculations, reporting, and specific descriptions throughout this method.

5.1.1 Pretest Preparation. Follow the same general procedure given in Method 5, Section 4.1.1, except that, unless particulate emissions are to be determined, the filter need not be desiccated or weighed. All sampling train glassware should first be rinsed with hot tap water and then washed in hot soapy water. Next, glassware should be rinsed three times with tap water, followed by three additional rinses with water. All glassware should then be soaked in a 10 percent (V/V) nitric acid solution for a minimum of 4 hours, rinsed three times with water, rinsed a final time with acetone, and allowed to air dry. All glassware openings where contamination can occur should be covered until the sampling train is assembled for sampling.

5.1.2 Preliminary Determinations. Same as Method 5, Section 4.1.2.

5.1.3 Preparation of Sampling Train.

5.1.3.1 Follow the same general procedures given in Method 5, Section 4.1.3, except place 100 ml of the HNO_3/H_2O_2 solution (Section 4.2.1) in each of the two impingers as shown in Figure 29-1 (normally the second and third impingers). Place 100 ml of the acidic $KMnO_4$ absorbing solution (Section 4.2.2) in each of the two impingers as shown in Figure 29-1, and transfer approximately 200 to 300 g of preweighed silica gel from its container to the last impinger. Alternatively, the silica gel may be weighed directly in the impinger just prior to train assembly.

5.1.3.2 Several options are available to the tester based on the sampling requirements and conditions. The use of an empty first impinger can be eliminated if the moisture to be collected in the impingers will be less than approximately 100 ml. If necessary, use as applicable to this methodology the procedure described in Section 7.1.1 of Method 101A, 40 CFR Part 61, Appendix B, to maintain the desired color in the last permanganate impinger.

5.1.3.3 Retain for reagent blanks volumes of the HNO_3/H_2O_2 solution per Section 5.2.16 of this method and of the acidic $KMnO_4$ solution per Section 5.2.17. These reagent blanks should be labeled and analyzed as described in Section 7. Set up the sampling train as shown in Figure 29-1. If mercury analysis is not desired, delete the empty impinger and the two permanganate impingers following the HNO_3/H_2O_2 impingers. If necessary to

ensure leak-free sampling train connections, Teflon tape or other non-contaminating material should be used instead of silicone grease to prevent contamination. Precaution: Extreme care should be taken to prevent contamination within the train. Prevent the mercury collection reagent (acidic $KMnO_4$) from contacting any glassware of the train which is washed and analyzed for Mn. Prevent H_2O_2 from mixing with the acidic $KMnO_4$.

5.1.3.4 Mercury emissions can be measured, alternatively, in a separate train using EPA Method 101A with the modifications for processing the permanganate containers as described in the precaution in Section 4.3.2 and the note in Section 5.2.11 of this method). This alternative method is applicable for measurement of mercury emissions, and it may be of special interest to sources which must measure both mercury and manganese emissions.

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

5.1.5 Sampling Train Operation. Follow the procedures given in Method 5, Section 4.1.5. For each run, record the data required on a data sheet such as the one shown in Figure 5-2 of Method 5.

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

5.2 Sample Recovery.

5.2.1 Begin cleanup procedures as soon as the probe is removed from the stack at the end of a sampling period. The probe should be allowed to cool prior to sample recovery. When it can be safely handled, wipe off all external particulate matter near the tip of the probe nozzle and place a rinsed, non-contaminating cap over the probe nozzle to prevent losing or gaining particulate matter. Do not cap the probe tip tightly while the sampling train is cooling; a vacuum may form in the filter holder with the undesired result of drawing liquid from the impingers onto the filter.

5.2.2 Before moving the sampling train to the cleanup site, remove the probe from the sampling train and cap the open outlet. Be careful not to lose any condensate that might be present. Cap the filter inlet where the probe was fastened. Remove the umbilical cord from the last impinger and cap the impinger. Cap off the filter holder outlet and impinger inlet. Use non-contaminating caps, whether ground-glass stoppers, plastic caps, serum caps, or Teflon tape to close these openings.

5.2.3 Alternatively, the train can be disassembled before the probe and filter holder/oven are completely cooled if this procedure is followed: Initially disconnect the filter holder outlet/impinger inlet and loosely cap the open ends. Then disconnect the probe from the filter holder or cyclone inlet and loosely cap the open ends. Cap the probe tip and remove the umbilical cord as previously described.

5.2.4 Transfer the probe and filter-impinger assembly to a cleanup area that is clean and protected from the wind and other potential causes of contamination or loss of sample. Inspect the train before and during disassembly and note any abnormal conditions. The sample is recovered and treated as follows (see schematic in Figures 29-2a and 29-2b). Assure that all items necessary for recovery of the sample do not contaminate it.

5.2.5 Container No. 1 (Filter). Carefully remove the filter from the filter holder and place it in its identified petri dish container. Acid-washed polypropylene or Teflon coated tweezers or clean, disposable surgical gloves rinsed with water and dried should be used to handle the filters. If it is necessary to fold the filter, make certain the particulate cake is inside the fold. Carefully transfer the filter and any particulate matter or filter fibers that adhere to the filter holder gasket to the petri dish by using a dry (acid-cleaned) nylon bristle brush. Do not use any metal-containing materials when recovering this train. Seal the labeled petri dish.

5.2.6 Container No. 2 (Acetone Rinse). **NOTE**: Perform this section only if determination of particulate emissions are desired in addition to metals emissions. Ensuring that dust on the outside of the probe or other exterior surfaces does not get into the sample, quantitatively recover particulate matter and any condensate from the probe nozzle, probe fitting, probe liner, and front half of the filter holder by washing these components with 100 ml of acetone and placing the wash in a glass container.

NOTE: The use of exactly 100 ml is necessary for the subsequent blank correction procedures. Distilled water may be used instead of acetone when approved by the Administrator and shall be used when specified by the Administrator; in these cases, save a water blank and follow the Administrator's directions on analysis. Perform the acetone rinse as follows: Carefully remove the probe nozzle and clean the inside surface by rinsing with acetone from a wash bottle and brushing with a non-metallic brush. Brush until the acetone rinse shows no visible particles, after which make a final rinse of the inside surface with acetone.

5.2.7 Brush and rinse the sample exposed inside parts of the fitting with acetone in a similar way until no visible particles remain. Rinse the probe liner with acetone by tilting and rotating the probe while squirting acetone into its upper end so that all inside surfaces will be wetted with acetone. Allow the acetone to drain from the lower end into the sample container. A funnel may be used to aid in transferring liquid washings to the container. Follow the acetone rinse with a non-metallic probe brush. Hold the probe in an inclined position, squirt acetone into the upper end as the probe brush is being pushed with a twisting action through the probe. Hold a sample container underneath the lower end of the probe, and catch any acetone and particulate matter which is brushed through the probe three times or more until no visible particulate matter is carried out with the acetone or until none remains in the probe liner on visual inspection. Rinse the brush with acetone, and

quantitatively collect these washings in the sample container. After the brushing, make a final acetone rinse of the probe as described above.

5.2.8 It is recommended that two people clean the probe to minimize sample losses. Between sampling runs, keep brushes clean and protected from contamination. Clean the inside of the front-half of the filter holder by rubbing the surfaces with a non-metallic nylon bristle brush and rinsing with acetone. Rinse each surface three times or more if needed to remove visible particulate. Make a final rinse of the brush and filter holder. After all acetone washings and particulate matter have been collected in the sample container, tighten the lid so that acetone will not leak out when shipped to the laboratory. Mark the height of the fluid level to determine whether or not leakage occurred during transport. Label the container clearly to identify its contents.

5.2.9 Container No. 3 (Probe Rinse). Keep the probe assembly clean and free from contamination during the probe rinse. Rinse the probe nozzle and fitting, probe liner, and front-half of the filter holder thoroughly with 100 ml of 0.1 N HNO_3, and place the wash into a sample storage container. **NOTE**: The use of exactly 100 ml is necessary for the subsequent blank correction procedures. Perform the rinses as applicable and generally as described in Method 12, Section 5.2.2. Record the volume of the combined rinse. Mark the height of the fluid level on the outside of the storage container and use this mark

to determine if leakage occurs during transport. Seal the container, and clearly label the contents. Finally, rinse the nozzle, probe liner, and front-half of the filter holder with water followed by acetone, and discard these rinses.

5.2.10 Container No. 4 (Impingers 1 through 3, HNO_3/H_2O_2 Impingers and Moisture Knockout Impinger, when used, Contents and Rinses). Due to the potentially large quantity of liquid involved, the tester may place the impinger solutions from impingers 1 through 3 in more than one container. Measure the liquid in the first three impingers to within 0.5 ml using a graduated cylinder. Record the volume. This information is required to calculate the moisture content of the sampled flue gas. Clean each of the first three impingers, the filter support, the back half of the filter housing, and connecting glassware by thoroughly rinsing with 100 ml of 0.1 N HNO_3 using the procedure as applicable in Method 12, Section 5.2.4. **NOTE**: The use of exactly 100 ml of 0.1 N HNO_3 rinse is necessary for the subsequent blank correction procedures. Combine the rinses and impinger solutions, measure and record the volume. Mark the height of the fluid level, seal the container, and clearly label the contents.

5.2.11 Container Nos. 5A (0.1 N HNO_3), 5B ($KMnO_4/H_2SO_4$ absorbing solution), and 5C (8 N HCl rinse and dilution). Pour all the liquid, if any, from the impinger which was empty at the start of the run and which immediately precedes the two permanganate impingers (normally impinger No. 4) into a graduated

cylinder and measure the volume to within 0.5 ml. This information is required to calculate the moisture content of the sampled flue gas. Place the liquid in Sample Container No. 5A. Rinse the impinger (No. 4) with 100 ml of 0.1 N HNO_3 and place this into Container No. 5A.

5.2.12 Pour all the liquid from the two permanganate impingers into a graduated cylinder and measure the volume to within 0.5 ml. This information is required to calculate the moisture content of the sampled flue gas. Place this $KMnO_4$ solution into Container No. 5B. Using 100 ml total of fresh acidified $KMnO_4$ solution, rinse the two permanganate impingers and connecting glass a minimum of three times. Pour the rinses into Container No. 5B, carefully assuring transfer of all loose precipitated materials from the two impingers. Using 100 ml total of water, rinse the permanganate impingers and connecting glass a minimum of three times, and pour the rinses into Container 5B, carefully assuring transfer of all loose precipitated material, if any. Mark the height of the fluid level, and clearly label the contents. Note the precaution in Section 4.3.2. **NOTE**: Due to the potential reaction of $KMnO_4$ with acid, there may be pressure buildup in the sample storage bottles. These bottles shall not be filled completely and shall be vented to relieve excess pressure. A No. 70-72 hole drilled in the container cap and Teflon liner has been used successfully.

5.2.13 If no visible deposits remain after the above described water rinse, no further rinse is necessary. However,

if deposits do remain on the glassware, wash the impinger surfaces with 25 ml of 8 N HCl, and place the wash in a separate sample container labeled Container No. 5C containing 200 ml of water as follows. Place 200 ml of water in a sample container labeled Container No. 5C. Wash the impinger walls and stem with the HCl by turning the impinger on its side and rotating it so that the HCl contacts all inside surfaces. Use a total of only 25 ml of 8 N HCl for rinsing <u>both permanganate impingers combined</u>. Rinse the first impinger, then pour the actual rinse used for the first impinger into the second impinger for its rinse. Finally, pour the 25 ml of 8 N HCl rinse carefully into Container No. 5C. Mark the height of the fluid level on the outside of the bottle to determine if leakage occurs during transport.

5.2.14 Container No. 6 (Silica Gel). Note the color of the indicating silica gel to determine whether it has been completely spent and make a notation of its condition. Transfer the silica gel from its impinger to its original container and seal. The tester may use a funnel to pour the silica gel and a rubber policeman to remove the silica gel from the impinger. The small amount of particles that may adhere to the impinger wall need not be removed. Do not use water or other liquids to transfer the silica gel since weight gained in the silica gel impinger is used for moisture calculations. Alternatively, if a balance is available in the field, record the weight of the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g.

5.2.15 Container No. 7 (Acetone Blank). If particulate emissions are to be determined, at least once during each field test, place a 100-ml portion of the acetone used in the sample recovery process into a labeled container for use in the front-half field reagent blank. Seal the container.

5.2.16 Container No. 8A (0.1 N HNO_3 Blank). At least once during each field test, place 300 ml of the 0.1 N HNO_3 solution used in the sample recovery process into a labeled container for use in the front-half and back-half field reagent blanks. Seal the container.

5.2.17 Container No. 8B (water blank). At least once during each field test, place 100 ml of the water used in the sample recovery process into a labeled Container No. 8B. Seal the container.

5.2.18 Container No. 9 (5 Percent HNO_3/10 Percent H_2O_2 Blank). At least once during each field test, place 200 ml of the 5 Percent HNO_3/10 Percent H_2O_2 solution used as the nitric acid impinger reagent into a labeled container for use in the back-half field reagent blank. Seal the container.

5.2.19 Container No. 10 (Acidified $KMnO_4$ Blank). At least once during each field test, place 100 ml of the acidified $KMnO_4$ solution used as the impinger solution and in the sample recovery process into a labeled container for use in the back-half field reagent blank for mercury analysis. Prepare the container as described in Section 5.2.11. See the note in Section 5.2.12.

5.2.20 Container No. 11 (8 N HCl Blank). At least once during each field test, perform both of the following. Place 200 ml of water into a sample container. Pour 25 ml of 8 N HCl carefully with stirring into the container. Mix well and seal the container.

5.2.21 Container No. 12 (Filter Blank). Once during each field test, place three unused blank filters from the same lot as the sampling filters in a labeled petri dish. Seal the petri dish. These will be used in the front-half field reagent blank.

5.3 Sample Preparation. Note the level of the liquid in each of the containers and determine if any sample was lost during shipment. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results. A diagram illustrating sample preparation and analysis procedures for each of the sample train components is shown in Figure 29-3.

5.3.1 Container No. 1 (Filter). If particulate emissions are being determined, desiccate the filter and filter catch without added heat and weigh to a constant weight as described in Section 4.3 of Method 5. For analysis of metals, divide the filter with its filter catch into portions containing approximately 0.5 g each and place into the analyst's choice of either individual microwave pressure relief vessels or Parr^{R} Bombs. Add 6 ml of concentrated HNO_3 and 4 ml of concentrated HF to each vessel. For microwave heating, microwave the sample vessels for approximately 12-15 minutes in intervals of 1 to 2

minutes at 600 Watts. For conventional heating, heat the Parr^{R} Bombs at 140°C (285°F) for 6 hours. Then cool the samples to room temperature, and combine with the acid digested probe rinse as required in Section 5.3.3, below. **NOTES**:

5.3.1.1 Suggested microwave heating times are approximate and are dependent upon the number of samples being digested. Twelve to 15 minute heating times have been found to be acceptable for simultaneous digestion of up to 12 individual samples. Sufficient heating is evidenced by sorbent reflux within the vessel.

5.3.1.2 If the sampling train uses an optional cyclone, the cyclone catch should be prepared and digested using the same procedures described for the filters and combined with the digested filter samples.

5.3.2 Container No. 2 (Acetone Rinse). Note the level of liquid in the container and confirm on the analysis sheet whether or not leakage occurred during transport. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results. Measure the liquid in this container either volumetrically within 1 ml or gravimetrically within 0.5 g. Transfer the contents to an acid-cleaned, tared 250-ml beaker and evaporate to dryness at ambient temperature and pressure. If particulate emissions are being determined, desiccate for 24 hours without added heat, weigh to a constant weight according to the procedures described in Section 4.3 of Method 5, and

report the results to the nearest 0.1 mg. Redissolve the residue with 10 ml of concentrated HNO_3. Quantitatively combine the resultant sample, including all liquid and any particulate matter, with Container No. 3 before beginning Section 5.3.3.

5.3.3 Container No. 3 (Probe Rinse). The pH of this sample shall be 2 or lower. If the pH is higher, the sample should be acidified by careful addition with stirring of concentrated HNO_3 to pH 2. The sample should be rinsed into a beaker with water, and the beaker should be covered with a ribbed watch glass. The sample volume should be reduced to approximately 20 ml by heating on a hot plate at a temperature just below boiling. Digest the sample in microwave vessels or Parr^R Bombs by quantitatively transferring the sample to the vessel or bomb, carefully adding the 6 ml of concentrated HNO_3, 4 ml of concentrated HF, and then continuing to follow the procedures described in Section 5.3.1. Then combine the resultant sample directly with the acid digested portions of the filter prepared previously in Section 5.3.1. The resultant combined sample is referred to as Fraction 1 precursor. Filter the combined solution of the acid digested filter and probe rinse samples using Whatman 541 filter paper. Dilute to 300 ml (or the appropriate volume for the expected metals concentration) with water. This dilution is Fraction 1. Measure and record the volume of the Fraction 1 solution to within 0.1 ml. Quantitatively remove a 50-ml aliquot and label as Fraction 1B. Label the remaining 250-ml portion as

Fraction 1A. Fraction 1A is used for ICAP or AAS analysis. Fraction 1B is used for the determination of front-half mercury.

5.3.4 Container No. 4 (Impingers 1-3). Measure and record the total volume of this sample (Fraction 2) to within 0.5 ml. Remove a 75- to 100-ml aliquot for mercury analysis and label as Fraction 2B. Label the remaining portion of Container No. 4 as aliquot Fraction 2A. Aliquot Fraction 2A defines the volume of 2A prior to digestion. All of aliquot Fraction 2A is digested to produce concentrated Fraction 2A. Concentrated Fraction 2A defines the volume of 2A after digestion and is normally 150 ml. Only concentrated Fraction 2A is analyzed for metals (except that it is not analyzed for mercury). The Fraction 2B aliquot should be prepared and analyzed for mercury as described in Section 5.4.3. Aliquot Fraction 2A shall have a pH of 2 or lower. If necessary, use concentrated HNO_3 by careful addition and stirring to lower aliquot Fraction 2A to pH 2. The sample should be rinsed into a beaker with water and the beaker covered with a ribbed watchglass. The sample volume should be reduced to approximately 20 ml by heating on a hot plate at a temperature just below boiling. Then follow either of the digestion procedures described in Sections 5.3.4.1 and 5.3.4.2, below.

5.3.4.1 Conventional Digestion Procedure. Add 30 ml of 50 percent HNO_3, and heat for 30 minutes on a hot plate to just below boiling. Add 10 ml of 3 percent H_2O_2 and heat for 10 more minutes. Add 50 ml of hot water, and heat the sample for an additional 20 minutes. Cool, filter the sample, and dilute to

150 ml (or the appropriate volume for the expected metals concentrations) with water. This dilution is concentrated Fraction 2A. Measure and record the volume of the Fraction 2A solution to within 0.1 ml.

5.3.4.2 Microwave Digestion Procedure. Add 10 ml of 50 percent HNO_3 and heat for 6 minutes in intervals of 1 to 2 minutes at 600 Watts. Allow the sample to cool. Add 10 ml of 3 percent H_2O_2 and heat for 2 more minutes. Add 50 ml of hot water, and heat for an additional 5 minutes. Cool, filter the sample, and dilute to 150 ml (or the appropriate volume for the expected metals concentrations) with water. This dilution is concentrated Fraction 2A. Measure and record the volume of the Fraction 2A solution to within 0.1 ml. **NOTE**: All microwave heating times given are approximate and are dependent upon the number of samples being digested at a time. Heating times as given above have been found acceptable for simultaneous digestion of up to 12 individual samples. Sufficient heating is evidenced by solvent reflux within the vessel.

5.3.5 Container Nos. 5A, 5B, and 5C (Impingers 4, 5, and 6). Keep these samples separate from each other and measure and record the volumes of 5A and 5B separately to within 0.5 ml. Dilute sample 5C to 500 ml with water. These samples 5A, 5B, and 5C are referred to respectively as Fractions 3A, 3B, and 3C. Follow the analysis procedures described in Section 5.4.3. Because the permanganate rinse and water rinse have the capability to recover a high percentage of the mercury from the

permanganate impingers, the amount of mercury in the HCl rinse (Fraction 3C) may be very small, possibly even insignificantly small. However, as instructed in this method, add the total of any mercury measured in and calculated for the HCl rinse (Fraction 3C) to that for Fractions 1B, 2B, 3A, and 3B for calculation of the total sample mercury concentration.

5.3.6 Container No. 6 (Silica Gel). Weigh the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g using a balance. (This step may be conducted in the field.)

5.4 Sample Analysis. For each sampling train, seven individual samples are generated for analysis. A schematic identifying each sample and the prescribed sample preparation and analysis scheme is shown in Figure 29-3. The first two samples, labeled Fractions 1A and 1B, consist of the digested samples from the front-half of the train. Fraction 1A is for ICAP or AAS analysis as described in Sections 5.4.1 and/or 5.4.2. Fraction 1B is for determination of front-half mercury as described in Section 5.4.3. The back-half of the train was used to prepare the third through seventh samples. The third and fourth samples, labeled Fractions 2A and 2B, contain the digested samples from the moisture knockout, if used, and HNO_3/H_2O_2 Impingers 1 through 3. Fraction 2A is for ICAP or AAS analysis. Fraction 2B will be analyzed for mercury. The fifth through seventh samples, labeled Fractions 3A, 3B, and 3C, consist of the impinger contents and rinses from the empty and permanganate impingers 4, 5, and 6. These samples are analyzed for mercury as

described in Section 5.4.3. The total back-half mercury catch is determined from the sum of Fraction 2B and Fractions 3A, 3B, and 3C.

5.4.1 ICAP Analysis. Fraction 1A and Fraction 2A are analyzed by ICAP using Method 6010 or Method 200.7 (40 CFR 136, Appendix C). Calibrate the ICAP, and set up an analysis program as described in Method 6010 or Method 200.7. The quality control procedures described in Section 7.3.1 shall be followed. Recommended wavelengths for use in the analysis are listed below.

Element	Wavelength (nm)
Aluminum	308.215
Antimony	206.833
Arsenic	193.696
Barium	455.403
Beryllium	313.042
Cadmium	226.502
Chromium	267.716
Copper	324.754
Iron	259.940
Lead	220.353
Manganese	257.610
Nickel	231.604
Phosphorous	214.914
Selenium	196.026
Silver	328.068
Thallium	190.864
Zinc	213.856

The wavelengths listed are recommended because of their sensitivity and overall acceptance. Other wavelengths may be substituted if they can provide the needed sensitivity and are treated with the same corrective techniques for spectral interference. Initially, analyze all samples for the desired target metals (except mercury) plus iron and aluminum. If iron and aluminum are present, the sample may have to be diluted so that each of these elements is at a concentration of less than

50 ppm to reduce their spectral interferences on arsenic, cadmium, chromium, and lead. **NOTE**: When analyzing samples in a HF matrix, an alumina torch should be used; since all front-half samples will contain HF, use an alumina torch.

5.4.2 AAS by Direct Aspiration and/or Graphite Furnace. If analysis of metals in Fraction 1A and Fraction 2A using graphite furnace or direct aspiration AAS is desired, Table 29-2 should be used to determine which techniques and methods should be applied for each target metal. Table 29-2 should also be consulted to determine possible interferences and techniques to be followed for their minimization. Calibrate the instrument according to Section 6.3 and follow the quality control procedures specified in Section 7.3.2.

5.4.3 Cold Vapor AAS Mercury Analysis. Fractions 1B, 2B, 3A, 3B, and 3C should be analyzed separately for mercury using CVAAS following the method outlined in EPA SW-846 Method 7470 or in Standard Methods for Water and Wastewater Analysis, 15th Edition, Method 303F. Set up the calibration curve (zero to 1000 ng) as described in SW-846 Method 7470 or similar to Method 303F using 300-ml BOD bottles instead of Erlenmeyers. Dilute separately, as described below, an aliquot sized from 1 ml to 10 ml of each original sample to 100 ml with water. Record the amount of the aliquot used for dilution to 100 ml. If no prior knowledge exists of the expected amount of mercury in the sample, a 5-ml aliquot is suggested for the first dilution to 100 ml and analysis. In determining the emission value for mercury, the

size of the sample aliquot used for dilution and analysis is dependent upon its mercury content. The total amount of mercury in the aliquot shall be less than 1 μg and within the range (zero to 1000 ng) of the calibration curve. Place each sample aliquot into a separate 300-ml BOD bottle, and add enough water to make a total volume of 100 ml. Then analyze the sample for mercury by adding to it sequentially the sample preparation solutions and performing the sample preparation and analysis as described in the procedures of SW-846 Method 7470 or Method 303F. If the reading maximums are off-scale (because mercury in the aliquot exceeded the calibration range), including the dilution of 1-ml aliquots of the original sample, then perform the following: dilute the original sample (or a portion of it) with 0.15 percent HNO_3 (1.5 ml concentrated HNO_3 per liter aqueous solution) so that when a 1- to 10-ml aliquot of the original sample is further diluted to 100 ml and analyzed by the procedures described above, it will yield an analysis within the range of the calibration curve.

6. Calibration

Maintain a laboratory log of all calibrations.

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

6.2 Inductively Coupled Argon Plasma Spectrometer Calibration. Prepare standards as outlined in Section 4.5. Profile and calibrate the instrument according to the manufacturer's recommended procedures using the above standards. The calibration should be checked once per hour. If the instrument does not reproduce the standard concentrations within 10 percent, the complete calibration procedures should be performed.

6.3 Atomic Absorption Spectrometer - Direct Aspiration, Graphite Furnace and Cold Vapor Mercury Analyses. Prepare the standards as outlined in Section 4.5 and use to calibrate the spectrometer. Calibration procedures are also outlined in the EPA methods referred to in Table 29-2 and in SW-846 Method 7470 or Standard Methods for Water and Wastewater Method 303F (for mercury). Each standard curve should be run in duplicate and the mean values used to calculate the calibration line. The instrument should be recalibrated approximately once every 10 to 12 samples.

7. Quality Control

7.1 Sampling. Field Reagent Blanks. When analyzed, the blanks in Container Nos. 7 through 12 produced previously in Sections 5.2.14 through 5.2.19, respectively, shall be processed, digested, and analyzed as follows. Digest and process one of the filters from Container No. 12 per Section 5.3.1, 100 ml from Container No. 7 per Section 5.3.2, and 100 ml from Container No. 8A per Section 5.3.3. This produces Fraction Blanks 1A and

1B from Fraction Blank 1. [If desired, the other two filters may be digested separately according to Section 5.3.1, diluted separately to 300 ml each, and analyzed separately to produce a blank value for each of the two additional filters. If these analyses are performed, they will produce two additional values for each of Fraction Blanks 1A and 1B. The three Fraction Blank 1A values will be calculated as three values of M_{fhb} in Equation 3 of Section 8.4.3, then the three values shall be totalled and divided by 3 to become the value M_{fhb} to be used in computing M_t by Equation 3. Similarly, the three Fraction Blank 1B values will be calculated separately as three values, totalled, averaged, and used as the value for Hg_{fhb} in Equation 8 of Section 8.5.3. The analyses of the two extra filters are optional and are <u>not</u> a requirement of this method, but if the analyses are performed, the results must be considered as described above.] Combine 100 ml of Container No. 8A with 200 ml from Container No. 9, and digest and process the resultant volume per Section 5.3.4. This produces concentrated Fraction Blanks 2A and 2B from Fraction Blank 2. A 100-ml portion of Container No. 8A is Fraction Blank 3A. Combine 100 ml from Container No. 10 with 33 ml from Container No. 8B. This produces Fraction Blank 3B (use 400 ml as the volume of Fraction Blank 3B when calculating the blank value. Use the actual volumes when calculating all the other blank values). Dilute 225 ml from Container No. 11 to 500 ml with water. This produces Fraction Blank 3C. Analyze Fraction Blank 1A and Fraction Blank 2A per

Section 5.4.1 and/or 5.4.2. Analyze Fraction Blank 1B, Fraction Blank 2B, and Fraction Blanks 3A, 3B, and 3C per Section 5.4.3. The analysis of Fraction Blank 1A produces the front-half reagent blank correction values for the metals except for mercury; the analysis of Fraction Blank 1B produces the front-half reagent blank correction value for mercury. The analysis of concentrated Fraction Blank 2A produces the back-half reagent blank correction values for the metals except for mercury, while separate analyses of Fraction Blanks 2B, 3A, 3B, and 3C produce the back-half reagent blank correction value for mercury.

7.2 An attempt may be made to determine if the laboratory reagents used in Section 5.3 caused contamination. They should be analyzed by the procedures in Section 5.4. The Administrator will determine whether or not the laboratory blank reagent values can be used in the calculation of the test results.

7.3 Quality Control Samples. The following quality control samples should be analyzed.

7.3.1 ICAP Analysis. Follow the quality control shown in Section 8 of Method 6010. For the purposes of a three run test series, these requirements have been modified to include the following: two instrument check standard runs, two calibration blank runs, one interference check sample at the beginning of the analysis (must be within 25 percent or analyze by standard additions), one quality control sample to check the accuracy of the calibration standards (must be within 25 percent of

calibration), and one duplicate analysis (must be within 10 percent of average or repeat all analyses).

7.3.2 Direct Aspiration and/or Graphite Furnace AAS Analysis for Sb, As, Ba, Be, Cd, Cu, Cr, Pb, Ni, Mn, Hg, P, Se, Ag, Tl, and Zn. All samples should be analyzed in duplicate. Perform a matrix spike on at least one front-half sample and one back-half sample or one combined sample. If recoveries of less than 75 percent or greater than 125 percent are obtained for the matrix spike, analyze each sample by the method of additions. A quality control sample should be analyzed to check the accuracy of the calibration standards. The results must be within 10 percent or the calibration repeated.

7.3.3 Cold Vapor AAS Analysis for Mercury. All samples should be analyzed in duplicate. A quality control sample should be analyzed to check the accuracy of the calibration standards (within 15 percent or repeat calibration). Perform a matrix spike on one sample from the HNO_3 impinger portion (must be within 25 percent or samples must be analyzed by the method of standard additions). Additional information on quality control can be obtained from EPA SW-846 Method 7470 or in Standard Methods for Water and Wastewater Method 303F.

8. Calculations

8.1 Dry Gas Volume. Using the data from this test, calculate $V_{m(std)}$, the dry gas sample volume at standard conditions as outlined in Section 6.3 of Method 5.

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

8.3 Stack Gas Velocity. Using the data from this test and Equation 2-9 of Method 2, calculate the average stack gas velocity.

8.4 Metals (Except Mercury) in Source Sample.

8.4.1 Fraction 1A, Front-Half, Metals (except Hg). Calculate separately the amount of each metal collected in Fraction 1 of the sampling train using the following equation:

$$M_{fh} = C_{a1} F_d V_{soln,1} \qquad \text{Eq. 29-1}$$

where:

M_{fh} = Total mass of each metal (except Hg) collected in the front half of the sampling train (Fraction 1), μg.

C_{a1} = Concentration of metal in sample Fraction 1A as read from the standard curve, $\mu g/ml$.

F_d = Dilution factor (F_d = the inverse of the fractional portion of the concentrated sample in the solution actually used in the instrument to produce the reading C_{a1}. For example, when 2 ml of Fraction 1A are diluted to 10 ml, $F_d = 5$).

$V_{soln,1}$ = Total volume of digested sample solution (Fraction 1), ml.

NOTE: If Fractions 1A and 2A are combined, proportional aliquots must be used. Appropriate changes must be made in Equations 29-1 to 29-3 to reflect this approach.

8.4.2 Fraction 2A, Back-Half, Metals (except Hg). Calculate separately the amount of each metal collected in Fraction 2 of the sampling train using the following equation.

$$M_{bh} = C_{a2} F_a V_a \qquad \text{Eq. 29-2}$$

where:

M_{bh} = Total mass of each metal (except Hg) collected in the back-half of the sampling train (Fraction 2), μg.

C_{a2} = Concentration of metal in sample concentrated Fraction 2A as read from the standard curve, (μg/ml).

F_a = Aliquot factor, volume of Fraction 2 divided by volume of aliquot Fraction 2A (see Section 5.3.4).

V_a = Total volume of digested sample solution (concentrated Fraction 2A), ml (see Section 5.3.4.1 or 5.3.4.2, as applicable).

8.4.3 Total Train, Metals (except Hg). Calculate the total amount of each of the quantified metals collected in the sampling train as follows:

$$M_t = (M_{fh} - M_{fhb}) + (M_{bh} - M_{bhb}) \qquad \text{Eq. 29-3}$$

where:

M_t = Total mass of each metal (separately stated for each metal) collected in the sampling train, μg.

M_{fhb} = Blank correction value for mass of metal detected in front-half field reagent blank, μg.

M_{bhb} = Blank correction value for mass of metal detected in back-half field reagent blank, μg.

NOTE: If the measured blank value for the front half (m_{fhb}) is in the range 0.0 to A μg [where A μg equals the value determined by multiplying 1.4 μg/in.^{2} times the actual area in in.^{2} of the filter used in the emission sample], m_{fhb} may be used to correct the emission sample value (m_{fh}); if m_{fhb} exceeds A μg, the greater of the two following values may be used:

I. A μg, or

II. the lesser of (a) m_{fhb}, or (b) 5 percent of m_{fh}.

If the measured blank value for the back-half (m_{bhb}) is in the range 0.0 to 1 μg, m_{bhb} may be used to correct the emission sample value (m_{bh}); if m_{bhb} exceeds 1 μg, the greater of the two following values may be used: 1 μg or 5 percent of m_{bh}.

8.5 Mercury in Source Sample.

8.5.1 Fraction 1B, Front-Half, Mercury. Calculate the amount of mercury collected in the front-half, Fraction 1, of the sampling train using the following equation:

$$Hg_{fh} = \frac{Q_{fh}}{V_{f1B}} (V_{soln,1}) \qquad \text{Eq. 29-4}$$

where:

Hg_{fh} = Total mass of mercury collected in the front-half of the sampling train (Fraction 1), μg.

Q_{fh} = Quantity of mercury in analyzed sample, μg.

$V_{soln,1}$ = Total volume of digested sample solution (Fraction 1), ml.

V_{f1B} = Volume of Fraction 1B analyzed, ml. See the following Note.

Note: V_{f1B} is the actual amount of Fraction 1B analyzed. For example, if 1 ml of Fraction 1B were diluted to 100 ml to bring it into the proper analytical range, and 1 ml of the 100-ml dilution were analyzed, V_{f1B} would be 0.01.

8.5.2 Fractions 2B, 3A, 3B, and 3C, Back Half, Mercury. Calculate the amount of mercury collected in Fractions 2 using Equation 5 and in Fractions 3A, 3B, and 3C using Equation 6. Calculate the total amount of mercury collected in the back-half of the sampling train using Eq. 29-7.

$$Hg_{bh2} = \frac{Q_{bh2}}{V_{f2B}} (V_{soln,2}) \qquad \text{Eq. 29-5}$$

where:

Hg_{bh2} = Total mass of mercury collected in Fraction 2, μg.

Q_{bh2} = Quantity of mercury in analyzed sample, μg.

$V_{soln,2}$ = Total volume of Fraction 2, ml.

V_{f2B} = Volume of Fraction 2B analyzed, ml (see the following note).

Note: V_{f2B} is the actual amount of Fraction 2B analyzed. For example, if 1 ml of Fraction 2B were diluted to 10 ml to bring it into the proper analytical range, and 5 ml of the 10-ml dilution was analyzed, V_{f2B} would be 0.5. Use Equation 6 to calculate separately the back-half mercury for Fractions 3A, then 3B, then 3C.

$$Hg_{bh3(A,B,C)} = \frac{Q_{bh3(A,B,C)}}{V_{f3(A,B,C)}} (V_{soln,3(A,B,C,)} \qquad \text{Eq. 29-6}$$

where:

$Hg_{bh3(A,B,C)}$ = Total mass of mercury collected separately in Fraction 3A, 3B, or 3C, µg.

$Q_{bh3(A,B,C)}$ = Quantity of mercury in separately analyzed samples, µg.

$V_{f3(A,B,C)}$ = Volume of Fraction 3A, 3B, or 3C analyzed, ml (see note in Sections 8.5.1 and 8.5.2, and calculate similarly).

$V_{soln,3(A,B,C)}$ = Total volume of Fraction 3A, 3B, or 3C, ml.

$$Hg_{bh} = Hg_{bh2} + Hg_{bh3A} + Hg_{bh3B} + Hg_{bh3C} \qquad \text{Eq. 29-7}$$

where:

Hg_{bh} = Total mass of mercury collected in the back-half of the sampling train, µg.

8.5.3 Total Train Mercury Catch. Calculate the total amount of mercury collected in the sampling train using Eq 29-8.

$$Hg_t = (Hg_{fh} - Hg_{fhb}) + (Hg_{bh} - Hg_{bhb}) \qquad \text{Eq. 29-8}$$

where:

Hg_t = Total mass of mercury collected in the sampling train, ug.

Hg_{fhb} = Blank correction value for mass of mercury detected in front-half field reagent blank, μg.

Hg_{bhb} = Blank correction value for mass of mercury detected in back-half field reagent blanks, μg.

Note: If the total of the measured blank values ($Hg_{fhb} + Hg_{bhb}$) is in the range of 0 to 6 μg, then the total may be used to correct the sample value ($Hg_{fh} + Hg_{bh}$); if it exceeds 6 μg, the greater of the following two values may be used: 6 μg or 5 percent of the sample value ($Hg_{fh} + Hg_{bh}$).

8.6 Metal Concentration in Stack Gas. Calculate each metal separately for the Cd, total Cr, As, Ni, Mn, Be, Cu, Pb, P, Tl, Ag, Ba, Zn, Se, Sb, and Hg concentrations in the stack gas (dry basis, adjusted to standard conditions) as follows:

$$C_s = \frac{K_4 M_t}{V_{m(std)}} \qquad \text{Eq. 29-9}$$

where:

C_s = Concentration of each metal in the stack gas, mg/dscm.

$K_4 = 10^{-3}$ mg/μg.

M_t = Total mass of each metal collected in the sampling train, μg; (substitute Hg_t for M_t for the mercury calculation).

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

8.7 Isokinetic Variation and Acceptable Results. Same as Method 5, Sections 6.11 and 6.12, respectively.

9. Bibliography

1. Method 303F in Standard Methods for the Examination of Water Wastewater, 15th Edition, 1980. Available from the American Public Health Association, 1015 18th Street N.W., Washington, D.C. 20036.

2. EPA Methods 6010, 7000, 7041, 7060, 7131, 7421, 7470, 7740, and 7841, Test Methods for Evaluating Solid Waste: Physical/Chemical Methods. SW-846, Third Edition. September 1988. Office of Solid Waste and Emergency Response, U. S. Environmental Protection Agency, Washington, D.C. 20460.

3. EPA Method 200.7, Code of Federal Regulations, Title 40, Part 136, Appendix C. July 1, 1987.

4. EPA Methods 1 through 5, Code of Federal Regulations, Title 40, Part 60, Appendix A, July 1, 1991.

* * * * *

METHOD 201A - DETERMINATION OF PM_{10} EMISSIONS

(Constant Sampling Rate Procedure)

1. Applicability and Principle

1.1 Applicability. This method applies to the measurement of particulate matter (PM) emissions with an aerodynamic diameter equal to or less than nominally 10 μm (PM_{10}) from stationary sources. This method does not measure condensible emissions; it measures only PM_{10} as it occurs in the stack and at 120°C (248°F).

1.2 Principle. A gas sample is extracted at a constant flow rate through an in-stack sizing device, which separates PM greater than PM_{10}, and two glass fiber filters are used to collect the PM_{10}. Variations from isokinetic sampling conditions are maintained within well-defined limits. The particulate mass is determined gravimetrically after removal of uncombined water.

2. Apparatus

2.1 Sampling Train. A schematic of the Method 201A sampling train is shown in Figure 1. With the exception of the PM_{10} sizing device and in-stack filter, this train is the same as a standard Method 5 train.

NOTE: Method 5 as cited in this method is part of 40 CFR Part 60, Appendix A.

2.1.1 Nozzle. Stainless steel (316 or equivalent) with a sharp tapered leading edge. Eleven nozzles that meet the design specifications in Figure 2 are recommended. A large number of nozzles with small nozzle increments increase the likelihood that a single nozzle can be used for the

entire traverse. If the nozzles do not meet the design specifications in Figure 2, then the nozzles must meet the criteria in Section 5.2.

2.1.2 Sizing Device. Stainless steel (316 or equivalent), capable of determining the PM_{10} fraction. The sizing device shall be either a cyclone that meets the specifications in Section 5.2 or a cascade impactor that meets the specifications in Section 5.3.

2.1.3 Probe Liner. Same as in Method 5, Section 2.1.2.

2.1.4 Pitot Tube. Same as in Method 5, Section 2.1.3. The pitot lines shall be made of heat resistant tubing and attached to the probe with stainless steel fittings.

2.1.5 Differential Pressure Gauge, Filter Holders, Filter Heating System, Condenser, Metering System, Barometer, and Gas Density Determination Equipment. Same as in Method 5, Sections 2.1.4 through 2.1.10, respectively.

2.2 Sample Recovery.

2.2.1 Nozzle, Sizing Device, Probe, and Filter Holder Brushes. Nylon bristle brushes with stainless steel wire shafts and handles, properly sized and shaped for cleaning the nozzle, sizing device, probe or probe liner, and filter holders.

2.2.2 Wash Bottles, Glass Sample Storage Containers, Petri Dishes, Graduated Cylinder and Balance, Plastic Storage Containers, Funnel and Rubber Policeman, and Funnel. Same as in Method 5, Sections 2.2.2 through 2.2.8, respectively.

2.3 Analysis. Same as in Method 5, Section 2.3.

3. Reagents

The reagents for sampling, sample recovery, and analysis are the same as that specified in Method 5, Sections 3.1, 3.2, and 3.3, respectively.

4. Procedure

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

4.1.1 Pretest Preparation. Same as in Method 5, Section 4.1.1.

4.1.2 Preliminary Determinations. Same as in Method 5, Section 4.1.2, except use the directions on nozzle size selection and sampling time in this section. Use of any nozzles greater than 0.16 in. in diameter require a minimum sampling port diameter of 6 inches. Also, the required maximum number of traverse points at any location shall be 12.

4.1.2.1 The sizing device must be in-stack or maintained at stack temperature during sampling. The blockage effect of the EGR sampling assembly will be minimal if the cross-sectional area of the sampling assembly is 3 percent or less of the cross-sectional area of the duct. If the cross-sectional area of the assembly is greater than 3 percent of the cross-sectional area of the duct, then use the procedures in Method 1A to determine the sampling site, flow measurements, and the number of traverse points.

4.1.2.2 The setup calculations can be performed by using the following procedures.

4.1.2.2.1 In order to maintain a cut size of 10 μm in the sizing device, the flow rate through the sizing device must be maintained at a constant, discrete value during the run. If the sizing device is a cyclone that meets the design specifications in Figure 3, use the equations in Figure 4 to calculate three orifice pressure heads (ΔH): one at the

average stack temperature, and the other two at temperatures ±28°C (±50°F) of the average stack temperature. Use the ΔH calculated at the average stack temperature as the pressure head for the sample flow rate as long as the stack temperature during the run is within 28°C (50°F) of the average stack temperature. If the stack temperature varies by more than 28°C (50°F), then use the appropriate ΔH.

4.1.2.2.2 If the sizing device is a cyclone that does not meet the design specifications in Figure 3, use the equations in Figure 4, except use the equation for cyclone flow rate derived in Section 5.2.6.

4.1.2.2.3 To select a nozzle, use the equations in Figure 5 to calculate Δp_{min} and Δp_{max} for each nozzle at all three temperatures. If the sizing device is a cyclone that does not meet the design specifications in Figure 3, the example worksheets can be used except use the procedures in Section 5.2.6 to determine Q_s, the correct cyclone flow rate for a 10 μm cut size.

4.1.2.2.4 Correct the Method 2 pitot readings to Method 201A pitot readings by multiplying the Method 2 pitot readings by the square of a ratio of the Method 201A pitot coefficient to the Method 2 pitot coefficient. Select the nozzle for which Δp_{min} and Δp_{max} bracket all of the corrected Method 2 pitot readings. If more than one nozzle meets this requirement, select the nozzle giving the greatest symmetry. Note that if the expected pitot reading for one or more points is near a limit for a chosen nozzle, it may be outside the limits at the time of the run.

4.1.2.2.5 Vary the dwell time, or sampling time, at each traverse point proportionately with the point velocity. Use the equations in Figure 6 to calculate the dwell time at the first point and at each

subsequent point. It is recommended that the number of minutes sampled at each point be rounded to the nearest 15 seconds.

4.1.3 Preparation of Collection Train. Same as in Method 5, Section 4.1.3, except omit directions about a glass cyclone.

4.1.4 Leak-Check Procedure.

4.1.4.1 Pretest Leak-Check. Same as in Method 5, Section 4.1.4.1.

4.1.4.2 Leak-Checks During Sample Run. Same as in Method 5, Section 4.1.4.1.

4.1.4.3 Post-Test Leak-Check. Same as in Method 5, Section 4.1.4.3.

4.1.5 Method 201A Train Operation. Same as in Method 5, Section 4.1.5, except use the procedures in this section for isokinetic sampling and flow rate adjustment. Maintain the flow rate calculated in Section 4.1.2 throughout the run provided the stack temperature is within 28°C (50°F) of the temperature used to calculate ΔH. If stack temperatures vary by more than 28°C (50°F), use the appropriate ΔH value calculated in Section 4.1.2. Calculate the dwell time at each traverse point as in Figure 6.

4.1.6 Calculation of Percent Isokinetic Rate and Aerodynamic Cut Size (D_{50}). Calculate percent isokinetic rate and D_{50} (see Calculations, Section 6) to determine whether the test was valid or another test run should be made. If there was difficulty in maintaining isokinetic sampling rates within the prescribed range, or if the D_{50} is not in its proper range because of source conditions, the Administrator may be consulted for possible variance.

4.2 Sample Recovery. If a cascade impactor is used, use the manufacturer's recommended procedures for sample recovery. If a cyclone is used, use the same sample recovery as that in Method 5, Section 4.2, except an increased number of sample recovery containers is required.

4.2.1 Container No. 1 (In-Stack Filter). The recovery shall be the same as that for Container No. 1 in Method 5, Section 4.2.

4.2.2 Container No. 2 (Out-of-Stack Filter). The recovery shall be the same as that for Container No. 1 in Method 5, Section 4.2.

4.2.3 Container No. 3 (Cyclone or Large PM Catch). This step is optional. The anisokinetic error for the cyclone PM is theoretically larger than the error for the PM_{10} catch. Therefore, adding all the fractions to get a total PM catch is not as accurate as Method 5 or Method F2. Disassemble the cyclone and remove the nozzle to recover the large PM catch. Quantitatively recover the PM from the interior surfaces of the nozzle and cyclone, excluding the "turn around" cup and the interior surfaces of the exit tube. The recovery shall be the same as that for Container No. 2 in Method 5, Section 4.2.

4.2.4 Container No. 4 (PM_{10}). Quantitatively recover the PM from all of the surfaces from the cyclone exit to the front half of the in-stack filter holder, including the "turn around" cup inside the cyclone and the interior surfaces of the exit tube. The recovery shall be the same as that for Container No. 2 in Method 5, Section 4.2.

4.2.5 Container No. 5 (PM_{10}). Quantitatively recover PM between the back half of the in-stack filter holder and the front half of the out-of-stack filter. The recovery shall be the same as that for Container No. 2 in Method 5, Section 4.2.

4.2.6 Container No. 6 (Silica Gel). The recovery shall be the same as that for Container No. 3 in Method 5, Section 4.2.

4.2.7 Impinger Water. Same as Method 5, Section 4.2, under "Impinger Water."

4.3 Analysis. Same as in Method 5, Section 4.3, except handle Method 201A Containers No. 1 and No. 2 like Container No. 1, Method 201A Containers No. 3, No. 4, and No. 5 like Container No. 2, and Method 201A Container No. 6 like Container No. 3. Use Figure 7 to record the weights of PM collected. Use Figure 5-3 in Method 5, Section 4.3, to record the volume of water collected.

4.4 Quality Control Procedures. Same as in Method 5, Section 4.4.

5. Calibration

Maintain an accurate laboratory log of all calibrations.

5.1 Probe Nozzle, Pitot Tube, Metering System, Probe Heater Calibration, Temperature Gauges, Leak-check of Metering System, and Barometer. Same as in Method 5, Sections 5.1 through 5.7, respectively.

5.2 Probe Cyclone and Nozzle Combinations. The probe cyclone and nozzle combinations need not be calibrated if both meet design specifications in Figures 2 and 3. If the nozzles do not meet design specifications, then the cyclone and nozzle combinations shall be tested for conformity with performance specifications (PS's) in Table 1. If the cyclone does not meet design specifications, then the cyclone and nozzle combination shall conform to PS's and the cyclone shall be calibrated to determine the relationship between flow rate, gas viscosity, and gas density. Use the procedures in Section 5.2.4 to conduct PS tests and the procedures in Section 5.2.6 to calibrate the cyclone.

5.2.1 Conduct the PS tests in a wind tunnel described in Section 5.2.2 and particle generation system described in Section 5.2.3. Use five particle sizes and three wind velocities as listed in Table 2. A minimum of three replicate measurements of collection efficiency shall be performed for each of the 15 conditions listed, for a minimum of 45 measurements.

5.2.2 Wind Tunnel. The calibration and PS tests shall be performed in a wind tunnel (or equivalent test apparatus) capable of establishing and maintaining the required gas stream velocities within 10 percent.

5.2.3 Particle Generation System. The particle generation system shall be capable of producing solid monodispersed dye particles with the mass median aerodynamic diameters specified in Table 2. The particle size distribution verification should be performed on an integrated sample obtained during the sampling period of each test. An acceptable alternative is to verify the size distribution of samples obtained before and after each test, with both samples required to meet the diameter and monodispersity requirements for an acceptable test run.

5.2.4 Establish the size of the solid dye particles delivered to the test section of the wind tunnel by using the operating parameters of the particle generation system, and verify them during the tests by microscopic examination of samples of the particles collected on a membrane filter. The particle size, as established by the operating parameters of the generation system, shall be within the tolerance specified in Table 2.

The precision of the particle size verification technique shall be at least ±0.5 μm, and particle size determined by the verification technique shall not differ by more than 10 percent from that established by the operating parameters of the particle generation system.

5.2.5 The monodispersity of the particles shall be certified for each test either by microscopic inspection of collected particles on filters or by other suitable monitoring techniques such as an optical particle counter followed by a multichannel pulse height analyzer. If the proportion of multiplets and satellites in an aerosol exceeds 10 percent by mass, the particle generation system is unacceptable for purposes of this test. Multiplets are particles that are agglomerated, and satellites are particles that are smaller than the specified size range.

5.2.6 Schematic drawings of the wind tunnel and blower system and other information showing complete procedural details of the test atmosphere generation, verification, and delivery techniques shall be furnished with calibration data to the reviewing agency.

5.2.7 Flow Measurements. Measure the cyclone air flow rates with a dry gas meter and a stopwatch, or a calibrated orifice system capable of measuring flow rates to within 2 percent.

5.2.8 Performance Specification Procedure. Establish test particle generator operation and verify particle size microscopically. If monodispersity is to be verified by measurements at the beginning and the end of the run rather than by an integrated sample, these measurements may be made at this time.

5.2.9 The cut size, or D_{50}, of a cyclone is defined here as the particle size having a 50 percent probability of penetration. Determine

the cyclone flow rate at which the D_{50} is 10 μm. A suggested procedure is to vary the cyclone flow rate while keeping a constant particle size of 10 μm. Measure the PM collected in the cyclone (m_c), the exit tube (m_t), and the filter (m_f). Calculate cyclone efficiency (E_c) for each flow rate as follows:

$$E_c = \frac{m_c}{(m_c + m_t + m_f)} \times 100$$

5.2.10 Do three replicates and calculate the average cyclone efficiency [$E_{c(avg)}$] as follows:

$$E_{c(avg)} = (E_1 + E_2 + E_3)/3$$

where E_1, E_2, and E_3 are replicate measurements of E_c.

5.2.11 Calculate the standard deviation (σ) for the replicate measurements of E_c as follows.

$$\sigma = \left[\frac{(E_1^2 + E_2^2 + E_3^2) - \frac{(E_1 + E_2 + E_3)^2}{3}}{2} \right]^{0.5}$$

If σ exceeds 0.10, or if $E_{c(avg)}$ is not 50 $\pm$ 0.5 percent, repeat the replicate runs.

5.2.12 Measure the overall efficiency of the cyclone and nozzle, E_o, at the particle sizes and nominal gas velocities in Table 2 using the following procedure.

5.2.13 Set the air velocity and particle size from one of the conditions in Table 2. Establish isokinetic sampling conditions and the correct flow rate in the cyclone (obtained by procedures in this section)

such that the D_{50} is 10 μm. Sample long enough to obtain ±5 percent precision on total collected mass as determined by the precision and the sensitivity of measuring technique. Determine separately the nozzle catch (m_n), cyclone catch (m_c), cyclone exit tube (m_t), and collection filter catch (m_f) for each particle size and nominal gas velocity in Table 2. Calculate overall efficiency (E_o) as follows:

$$E_o = \frac{(m_n + m_c)}{(m_n + m_c + m_t + m_f)} \times 100$$

5.2.14 Do three replicates for each combination of gas velocity and particle size in Table 2. Use the equation below to calculate the average overall efficiency [$E_{o(avg)}$] for each combination following the procedures described in this section for determining efficiency.

$$E_{o(avg)} = (E_1 + E_2 + E_3)/3$$

where E_1, E_2, and E_3 are replicate measurements of E_o.

5.2.15 Use the appropriate formula in this section to calculate σ for the replicate measurements. If σ exceeds 0.10 or if the particle sizes and nominal gas velocities are not within the limits specified in Table 2, repeat the replicate runs.

5.2.16 Criteria for Acceptance. For each of the three gas stream velocities, plot the $E_{o(avg)}$ as function of particle size on Figure 8. Draw smooth curves through all particle sizes. $E_{o(avg)}$ shall be within the banded region for all sizes, and the $E_{c(avg)}$ shall be 50 ± 0.5 percent at 10 μm.

5.3 Cyclone Calibration Procedure. The purpose of this section is to develop the relationship between flow rate, gas viscosity, gas density, and D_{50}.

5.3.1 Determine flow rates and D_{50}'s for three different particle sizes between 5 μm and 15 μm, one of which shall be 10 μm. All sizes must be determined within 0.5 μm. For each size, use a different temperature within 60°C (108°F) of the temperature at which the cyclone is to be used and conduct triplicate runs. A suggested procedure is to keep the particle size constant and vary the flow rate.

5.3.2 On log-log graph paper, plot the Reynolds number (Re) on the abscissa, and the square root of the Stokes 50 number $[(Stk_{50})^{0.5}]$ on the ordinate for each temperature. Use the following equations to compute both values:

$$Re = \frac{4\ \rho\ Q_{cyc}}{d_{cyc}\ \pi\ \mu_{cyc}}$$

$$(Stk_{50})^{0.5} = \left[\frac{4\ Q_{cyc}\ (D_{50})^2}{9\ \pi\ \mu_{cyc}\ (d_{cyc})^3}\right]^{0.5}$$

where:

Q_{cyc} = Cyclone flow rate, cm^3/sec.

ρ = Gas density, g/cm^3.

d_{cyc} = Diameter of cyclone inlet, cm.

μ_{cyc} = Viscosity of gas through the cyclone, micropoise.

D_{50} = Aerodynamic diameter of a particle having a 50 percent probability of penetration, cm.

5.3.3 Use a linear regression analysis to determine the slope (m) and the y-intercept (b). Use the following formula to determine Q, the cyclone flow rate required for a size cut of 10 μm.

$$Q = \frac{\pi \mu_{cyc}}{4} \left[(3000)(K_1)^b \right]^{-(0.5-m)} \left[\frac{T_s}{M_c P_s} \right]^{m/(m-0.5)} d^{(m-1.50)/(m-0.5)}$$

where:

m = Slope of the calibration line.

b = y-interept of the calibration line.

Q = Cyclone flow rate for a size cut of 10 μm, cm^3/sec.

d = Diameter of nozzle, cm.

T_s = Stack gas temperature, °R.

P_s = Absolute stack pressure, in. Hg.

M_c = Molecular weight of the stack gas, lb/lb-mole.

$K_1 = 4.077 \times 10^{-3}$.

5.3.4 Refer to the Method 201A operators manual, entitled Measurement of Size Selective Particulate Emissions from Stationary Sources by Constant Sampling Rate, for directions in the use of this equation for Q in the setup calculations.

5.4 Cascade Impactor Calibration Procedure. The purpose of calibrating a cascade impactor is to determine the empirical constant (Stk_{50}), which is specific to the impactor and which permits the accurate determination of the cut sizes of the impactor stages at field conditions. It is not necessary to calibrate each individual impactor. Once an impactor has been calibrated, the calibration data can be applied to other impactors of identical design.

5.4.1 Wind Tunnel. Same as in Section 5.2.2.

5.4.2 Particle Generation System. Same as in Section 5.2.3.

5.4.4 Hardware Configuration for Calibrations. An impaction stage constrains an aerosol to form circular or rectangular jets, which are directed toward a suitable substrate where the larger aerosol particles are collected. For calibration purposes, three stages of the cascade impactor shall be discussed and designated calibration stages 1, 2, and 3. The first calibration stage consists of the collection substrate of an impaction stage and all upstream surfaces up to and including the nozzle. This may include other preceding impactor stages. The second and third calibration stages consist of each respective collection substrate and all upstream surfaces up to but excluding the collection substrate of the preceding calibration stage. This may include intervening impactor stages which are not designated as calibration stages. The cut size, or D_{50}, of the adjacent calibration stages shall differ by a factor of not less than 1.5 and not more than 2.0. For example, if the first calibration stage has a D_{50} of 12 μm, then the D_{50} of the downstream stage shall be between 6 and 8 μm.

5.4.5 It is expected, but not necessary, that the complete hardware assembly will be used in each of the sampling runs of the calibration and performance determinations. Only the first calibration stage must be tested under isokinetic sampling conditions. The second and third calibration stages must be calibrated with the collection substrate of the preceding calibration stage in place, so that gas flow patterns existing in field operation will be simulated.

5.4.6 Each of the PM_{10} stages should be calibrated with the type of collection substrate, viscid material (such as grease) or glass fiber, used in PM_{10} measurements. Note that most materials used as substrates at elevated temperatures are not viscid at normal laboratory conditions. The substrate material used for calibrations should minimize particle bounce yet be viscous enough to withstand erosion or deformation by the impactor jets and not interfere with the procedure for measuring the collected PM.

5.4.7 Calibration Procedure. Establish test particle generator operation and verify particle size microscopically. If monodispersity is to be verified by measurements at the beginning and the end of the run rather than by an integrated sample, these measurements shall be made at this time. Measure in triplicate the PM collected by the calibration stage (m) and the PM on all surfaces downstream of the respective calibration stage (m') for all of the flow rates and particle size combinations shown in Table 2. Techniques of mass measurement may include the use of a dye and spectrophotometer. Particles on the upstream side of a jet plate shall be included with the substrate downstream, except agglomerates of particles, which shall be included with the preceding or upstream substrate. Use the following formula to calculate the collection efficiency (E) for each stage.

$$E = \frac{m}{m + m'} \times 100$$

5.4.8 Use the appropriate formula in Section 5.2.4 to calculate the standard deviation (σ) for the replicate measurements. If σ exceeds 0.10, repeat the replicate runs.

5.4.9 Use the following formula to calculate the average collection efficiency (E_{avg}) for each set of replicate measurements.

$$E_{avg} = (E_1 + E_2 + E_3)/3$$

where E_1, E_2, and E_3 are replicate measurements of E.

5.4.10 Use the following formula to calculate Stk for each E_{avg}.

$$Stk = \frac{D^2 Q}{9 \mu A d_j}$$

where:

D = Aerodynamic diameter of the test particle, cm $(g/cm^3)0.5$.

Q = Gas flow rate through the calibration stage at inlet conditions, cm^3/sec.

μ = Gas viscosity, micropoise.

A = Total cross-sectional area of the jets of the calibration stage, cm^2.

d_j = Diameter of one jet of the calibration stage, cm.

5.4.11 Determine Stk_{50} for each calibration stage by plotting E_{avg} versus Stk on log-log paper. Stk_{50} is the Stk number at 50 percent efficiency. Note that particle bounce can cause efficiency to decrease at high values of Stk. Thus, 50 percent efficiency can occur at multiple values of Stk. The calibration data should clearly indicate the value of Stk_{50} for minimum particle bounce. Impactor efficiency versus Stk with minimal particle bounce is characterized by a monotonically increasing function with constant or increasing slope with increasing Stk.

5.4.12 The Stk_{50} of the first calibration stage can potentially decrease with decreasing nozzle size. Therefore, calibrations should be performed with enough nozzle sizes to provide a measured value within 25 percent of any nozzle size used in PM_{10} measurements.

5.4.13 Criteria For Acceptance. Plot E_{avg} for the first calibration stage versus the square root of the ratio of Stk to Stk_{50} on Figure 9. Draw a smooth curve through all of the points. The curve shall be within the banded region.

6. Calculations

6.1 Nomenclature.

B_{ws} = Moisture fraction of stack, by volume, dimensionless.

C_1 = Viscosity constant, 51.12 micropoise for °K (51.05 micropoise for °R).

C_2 = Viscosity constant, 0.372 micropoise/°K (0.207 micropoise/°R).

C_3 = Viscosity constant, 1.05×10^{-4} micropoise/$°K^2$ (3.24×10^{-5} micropoise/$°R^2$).

C_4 = Viscosity constant, 53.147 micropoise/fraction O_2.

C_5 = Viscosity constant, 74.143 micropoise/fraction H_2O.

D_{50} = Diameter of particles having a 50 percent probability of penetration, μm.

f_{O_2} = Stack gas fraction O_2, by volume, dry basis.

K_1 = 0.3858 °K/mm Hg (17.64 °R/in. Hg).

M_c = Wet molecular weight of mixed gas through the PM_{10} cyclone, g/g-mole (lb/lb-mole).

M_d = Dry molecular weight of stack gas, g/g-mole (lb/lb-mole).

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

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

Q_s = Total cyclone flow rate at wet cyclone conditions, m^3/min (ft^3/min).

$Q_{s(std)}$ = Total cyclone flow rate at standard conditions, dscm/min (dscf/min).

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

T_s = Average absolute stack gas temperature, °K (°R).

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

θ = Total sampling time, min.

μ_{cyc} = Viscosity of mixed cyclone gas, micropoise.

μ_{std} = Viscosity of standard air, 180.1 micropoise.

6.2 Analysis of Cascade Impactor Data. Use the manufacturer's recommended procedures to analyze data from cascade impactors.

6.3 Analysis of Cyclone Data. Use the following procedures to analyze data from a single stage cyclone.

6.3.1 PM_{10} Weight. Determine the PM catch in the PM_{10} range from the sum of the weights obtained from Containers Nos. 1, 2, 4, and 5 less the acetone blank.

6.3.2 Total PM Weight (optional). Determine the PM catch for greater than PM_{10} from the weight obtained from Container No. 3 less the acetone blank, and add it to the PM_{10} weight.

6.3.3 Aerodynamic Cut Size. Calculate the stack gas viscosity as follows:

$$\mu_{cyc} = C_1 + C_2\ T_s + C_3\ T_s^2 + C_4\ f_{O_2} - C_5\ B_{ws}$$

6.3.3.1 The PM_{10} flow rate, at actual cyclone conditions, is calculated as follows:

$$Q_s = \frac{T_s\ V_{m(std)}}{K_1\ P_s\ (1-B_{ws})\ \theta}$$

6.3.3.2 Calculate the molecular weight on a wet basis of the stack gas as follows:

$$M_c = M_d(1 - B_{ws}) + 18.0(B_{ws})$$

6.3.3.3 Calculate the actual D_{50} of the cyclone for the given conditions as follows:

$$D_{50} = \beta_1 \left[\frac{T_s}{M_c\ \ P_s}\right]^{0.2091} \left[\frac{\mu_{cyc}}{Q_s}\right]^{0.7091}$$

where $\beta_1 = 0.027754$ for metric units (0.15625 for English units).

6.3.4 Acceptable Results. The results are acceptable if two conditions are met. The first is that 9.0 μm $\leq D_{50} \leq$ 11.0 μm. The second is that no sampling points are outside Δp_{min} and Δp_{max}, or that 80 percent $\leq I \leq$ 120 percent and no more than one sampling point is outside Δp_{min} and Δp_{max}. If D_{50} is less than 9.0 μm, reject the results and repeat the test, unless the total particulate catch is less than the PM_{10}

standard. In this case, or if D_{50} is greater than 11 μm, the Administrator may accept the results.

7. Bibliography

1. Same as Bibliography in Method 5.

2. McCain, J.D., J.W. Ragland, and A.D. Williamson. Recommended Methodology for the Determination of Particle Size Distributions in Ducted Sources, Final Report. Prepared for the California Air Resources Board by Southern Research Institute. May 1986.

3. Farthing, W.E., S.S. Dawes, A.D. Williamson, J.D. McCain, R.S. Martin, and J.W. Ragland. Development of Sampling Methods for Stationary Source PM-10 Particulate Emissions. Southern Research Institute for the Environmental Protection Agency. 1986 (Unpublished).

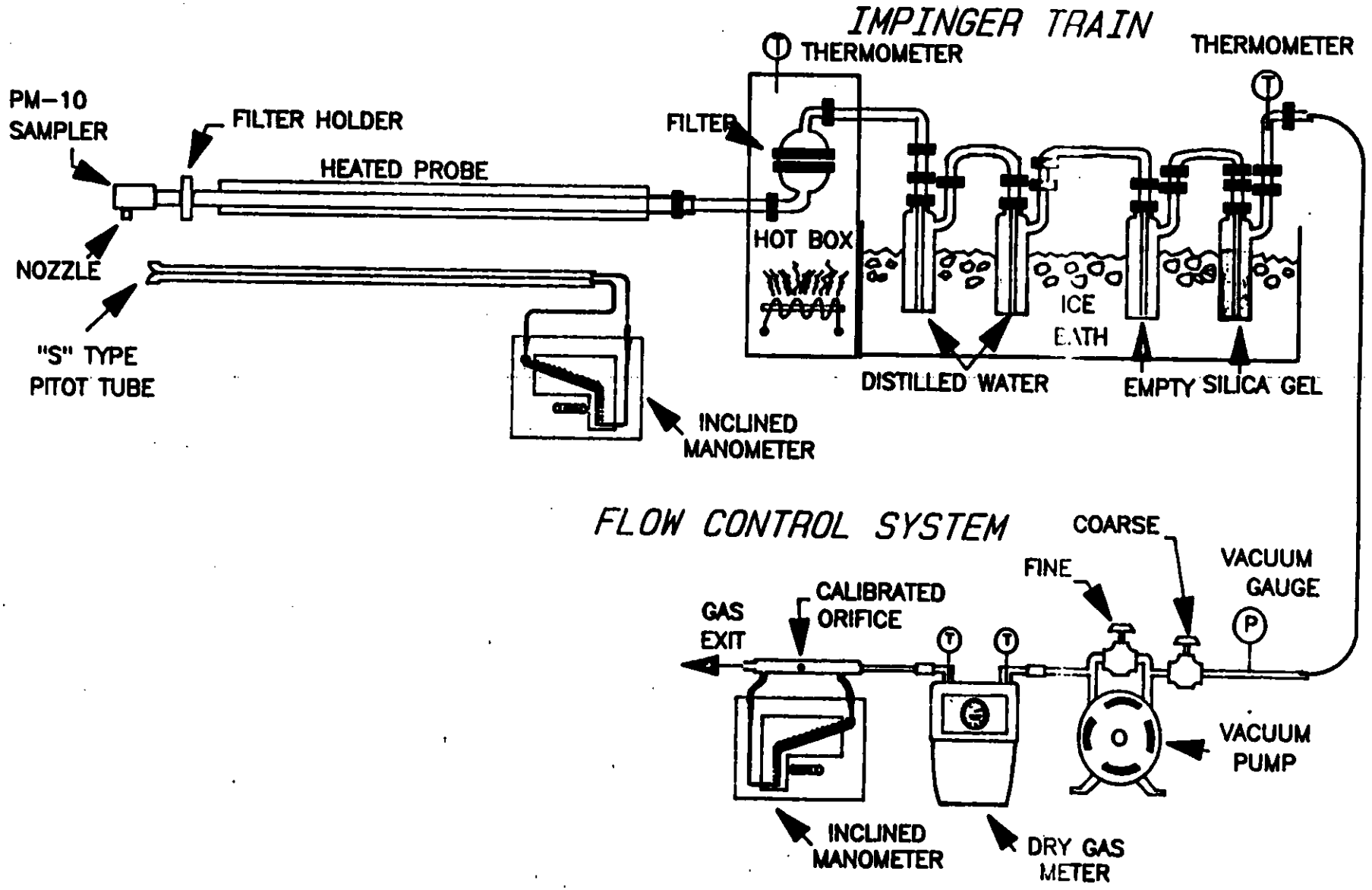
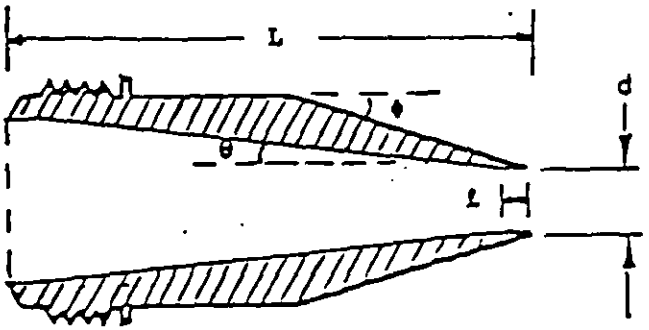


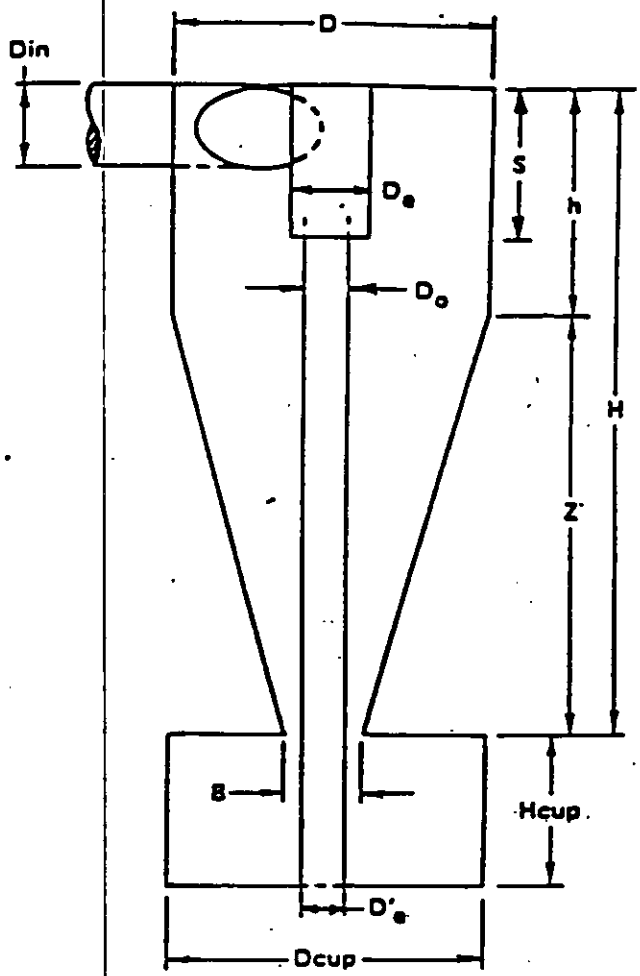
Figure 1. CSR Sampling Train



Nozzle Diameter (inches)	Cone Angle, θ (degrees)	Outside taper, ϕ (degrees)	Straight inlet length, ℓ (inches)	Total Length L (inches)
0.136	4	15	<0.05	2.653±0.05
0.150	4	15	<0.05	2.553±0.05
0.164	5	15	<0.05	1.970±0.05
0.180	6	15	<0.05	1.572±0.05
0.197	6	15	<0.05	1.491±0.05
0.215	6	15	<0.05	1.45 ±0.05
0.233	6	15	<0.05	1.45 ±0.05
0.264	5	15	<0.05	1.45 ±0.05
0.300	4	15	<0.05	1.48 ±0.05
0.342	4	15	<0.05	1.45 ±0.05
0.390	3	15	<0.05	1.45 ±0.05

Figure 2. Nozzle design specifications.

Cyclone Interior Dimensions



	Dimensions, ± 0.013 cm (± 0.005 in.)											
	Din	D	De	B	H	h	Z	S	Hcup	Dcup	D'_e	D_o
cm	1.27	4.47	1.50	1.88	6.95	2.24	4.71	1.57	2.25	4.45	1.02	1.24
inches	0.50	1.76	0.59	0.74	2.74	0.88	1.85	0.62	0.89	1.75	0.40	0.49

Figure 3. Cyclone design specifications.

Barometric pressure, P_{bar}, in. Hg = _____
Stack gauge pressure, P_g, in. H_2O = _____
Average stack temperature, t_s, °F = _____
Meter temperature, t_m, °F = _____
Orifice $\Delta H_@$, in. H_2O = _____

Gas analysis:

% CO_2 = _____
% O_2 = _____
% N_2 + % CO = _____
Fraction moisture content, B_{ws} = _____

Molecular weight of stack gas, dry basis:
$M_d = 0.44\ (\%CO_2) + 0.32\ (\%O_2) + 0.28\ (\%N_2 + \%CO)$ = _____ lb/lb mole

Molecular weight of stack gas, wet basis:
$M_w = M_d\ (1-B_{ws}) + 18\ (B_{ws})$ = _____ lb/lb mole

Absolute stack pressure:

$$P_s = P_{bar} + \frac{P_g}{13.6} = \text{_____ in. Hg}$$

Viscosity of stack gas:
$\mu_s = 152.418 + 0.2552\ t_s + 3.2355 \times 10^{-5}\ t_s^2 + 0.53147\ (\%\ O_2)$
$- 74.143\ B_{ws}$ = _____ micropoise

Cyclone flow rate:

$$Q_s = 0.002837\ \mu_s \left[\frac{(t_s + 460)}{M_w\ P_s}\right]^{0.2949} = \text{_____ ft}^3\text{/min}$$

Figure 4. Example worksheet 1 (Page 1 of 2), cyclone flow rate and ΔH.

Orifice pressure head (ΔH) needed for cyclone flow rate:

$$\Delta H = \left[\frac{Q_s\ (1-B_{ws})\ P_s}{t_s + 460}\right]^2 \frac{t_m\ M_d\ 1.083\ \Delta H@}{P_{bar}} = _____ \text{ in. } H_2O$$

Calculate ΔH for three temperatures:

t_s, °F				
ΔH, in. H_2O				

Figure 4. Example worksheet 1 (Page 2 of 2), cyclone flow rate and ΔH.

Stack viscosity, μ_s, micropoise = _____

Absolute stack pressure, P_s, in. Hg = _____

Average stack temperature, t_s, °F = _____

Meter temperature, t_m, °F = _____

Method 201A pitot coefficient, C_p = _____

Cyclone flow rate, ft^3/min, Q_s = _____

Method 2 pitot coefficient, C_p = _____

Molecular weight of stack gas, wet basis, M_w = _____

Nozzle diameter, D_n, in. = _____

Nozzle velocity

$$v_n = \frac{3.056\ Q_s}{D_n^{\ 2}} = _____ \text{ft/sec}$$

Maximum and minimum velocities:

$$v_{min} = v_n \left[0.2457 + \left[0.3072 - \frac{0.2603\ Q_s^{\ 0.5}\ \mu_s}{v_n^{\ 1.5}} \right]^{0.5} \right] = _____ \text{ft/sec}$$

$$v_{max} = v \left[0.4457 + \left[0.5690 + \frac{0.2603\ Q_s^{\ 0.5}\ \mu_s}{v_n^{\ 1.5}} \right]^{0.5} \right] = _____ \text{ft/sec}$$

Figure 5. Example worksheet 2 (page 1 of 2), nozzle selection.

Maximum and minimum velocity head values:

$$\Delta p_{min} = 1.3686 \times 10^{-4} \frac{P_s M_w (v_{min})^2}{(t_s + 460) C_p^2} = _____ \text{in. } H_2O$$

$$\Delta p_{max} = 1.3686 \times 10^{-4} \frac{P_s M_w (v_{max})^2}{(t_s + 460) C_p^2} = _____ \text{in. } H_2O$$

Nozzle number				
D_n, in.				
v_n, ft/sec				
v_{min}, ft/sec				
v_{max}, ft/sec				
Δp_{min}, in. H_2O				
Δp_{max}, in. H_2O				

Velocity traverse data:

$$\Delta p(\text{Method 201A}) = \Delta p(\text{Method 2}) \left[\frac{C_p}{C_p'}\right]^2 = _____ \text{ in. } H_2O$$

Figure 5. Example worksheet 2 (page 2 of 2), nozzle selection.

Total run time, minutes = _____

No. traverse points = _____

$$t_1 = \left[\frac{\overline{\Delta p'_1}}{\overline{\Delta p'_{avg}}}\right]^{0.5} \frac{\text{(Total run time)}}{\text{(No. points)}}$$

where:

t_1 = dwell time at first traverse point, minutes.

$\Delta p'_1$ = the velocity head at the first traverse point (from a previous traverse), in. H_2O.

$\Delta p'_{avg}$ = the square of the average square root of the Δp's (from a previous velocity traverse), in. H_2O.

At subsequent traverse points, measure the velocity Δp and calculate the dwell time by using the following equation:

$$t_n = \frac{t_1}{(\Delta p_1)^{0.5}} \quad (\Delta p_n)^{0.5}, \; n = 2,3,\ldots \text{ total number of sampling points}$$

where:

t_n = dwell time at traverse point n, minutes.

Δp_n = measured velocity head at point n, in. H_2O.

Δp_1 = dwell time at first traverse point, minutes.

Figure 6. Example worksheet 3 (page 1 of 2), dwell time.

	Port_____		Port_____		Port_____		Port_____	
Point No.	Δp	t	Δp	t	Δp	t	Δp	t
1	____	____	____	____	____	____	____	____
2	____	____	____	____	____	____	____	____
3	____	____	____	____	____	____	____	____
4	____	____	____	____	____	____	____	____
5	____	____	____	____	____	____	____	____
6	____	____	____	____	____	____	____	____

Figure 6. Example worksheet 3 (page 2 of 2), dwell time.

Plant _____
Date _____
Run no. _____
Filter no. (in-stack) _____
Filter no. (out-of-stack) _____
Amount of liquid lost during transport _____
Acetone blank volume, ml _____
Acetone wash volume, ml (4) _____ (5) _____
Acetone blank conc., mg/mg (Equation 5-4, Method 5) _____
Acetone wash blank, mg (Equation 5-5, Method 5) _____

Container number	Weight of PM_{10} mg		
	Final weight	Tare weight	Weight gain
1			
2			
4			
5			
		Total.....	
		Less acetone blank.....	
		Weight of PM_{10}.....	

Figure 7. Method 201A analysis sheet

TABLE 1. PERFORMANCE SPECIFICATIONS FOR SOURCE PM_{10} CYCLONES AND NOZZLE COMBINATIONS

Parameter	Units	Specification
1. Collection efficiency	Percent	Such that collection efficiency falls within envelope specified by Section 5.2.5 and Figure 8.
2. Cyclone cut size (D_{50})	μm	10 ± 1 μm aerodynamic diameter.

TABLE 2. PARTICLE SIZES AND NOMINAL GAS VELOCITIES FOR EFFICIENCY

Particle size (μm)[a]	Target gas velocities (m/sec)		
	7 ± 1.0	15 ± 1.5	25 ± 2.5
5 ± 0.5			
7 ± 0.5			
10 ± 0.5			
14 ± 1.0			
20 ± 1.0			

(a) Mass median aerodynamic diameter.

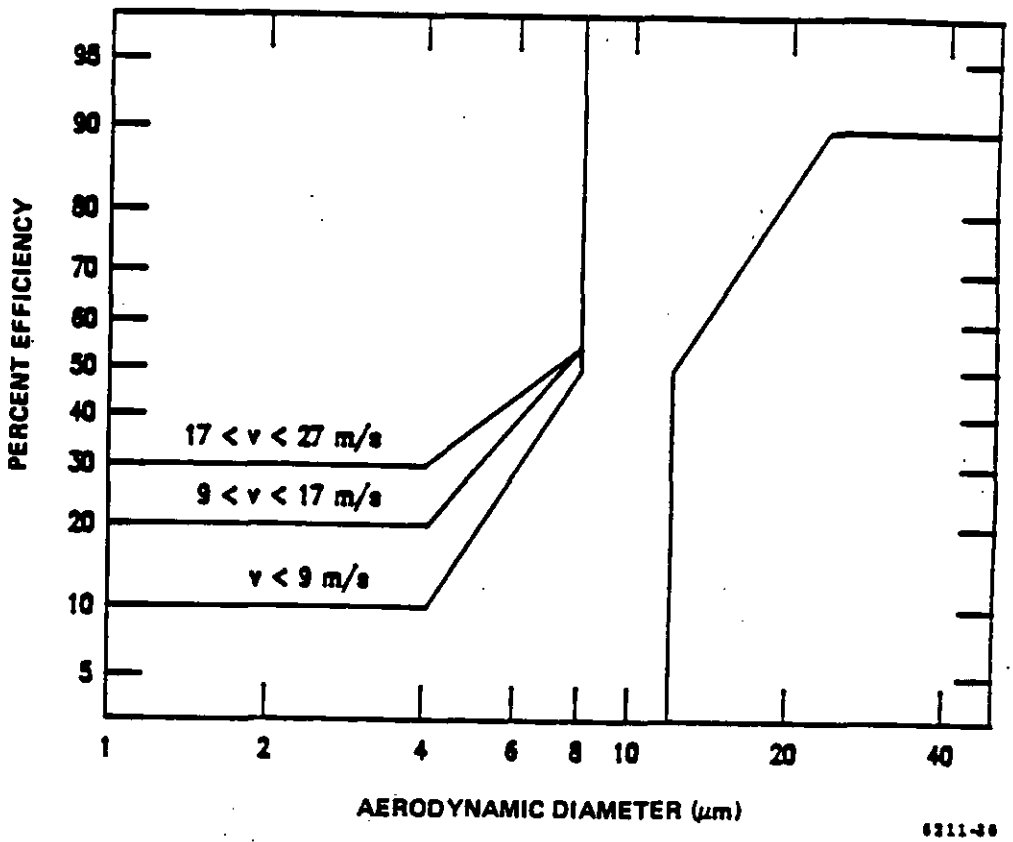


Figure 8. Efficiency envelope for the PM_{10} cyclone.

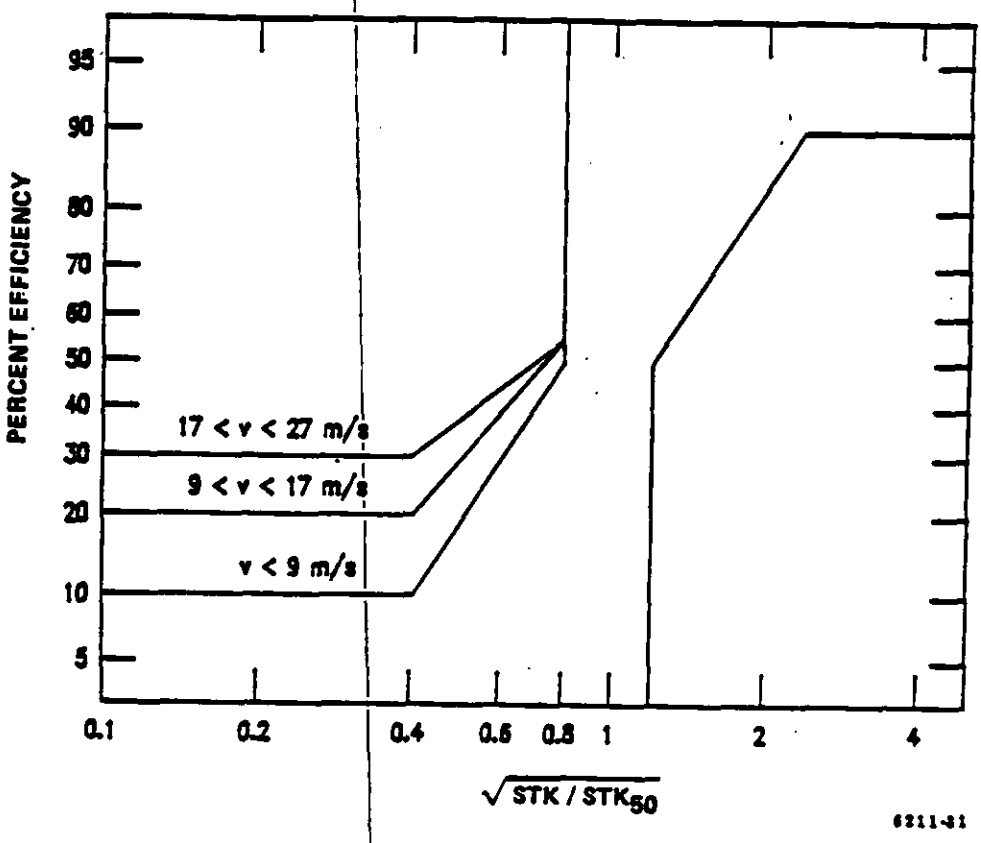


Figure 9. Efficiency envelope for first calibration stage.