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Asphalt Roofing Industry
Manual Emission Testing
Modified Bitumen

U.S. Intec
Port Arthur, Texas



Asphalt Roofing Industry

Final Report

Contract No. 68-D7-0001
Work Assignment 2-002

U. S. Intec Modified Bitumen Facility
Port Arthur, Texas

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1.0 INTRODUCTION

The asphalt roofing industry is among the categories of major sources for which national emission standards for hazardous air pollutants (NESHAPS) are to be issued by November 2000 pursuant to Section 112 of the Clean Air Act. The asphalt roofing industry category includes facilities that have the following specific processes: asphalt blowing stills; modified bitumen production; a saturator/coater process; and fiberglass mat production.

Source tests are required to quantify and characterize the particulate matter (PM) and hazardous air pollutant (HAP) emissions, and the performance of a thermal oxidizer used to control emissions associated with a modified bitumen facility.

1.1 Objective

The objective of the testing at the U. S. Intec modified bitumen facility in Port Arthur, Texas, was to perform all activities necessary to characterize the thermal oxidizer for the following emission components:

- Determination of particulate matter (PM) using EPA Method 5A; and
- Determination of dioxins and furans (D/F) using EPA Method 23.

The roof top vents for the atactic polypropylene (APP) coater and the styrene butadiene styrene (SBS) coater were tested for the following component:

- Determination of particulate matter (PM) using EPA Method 5A.

In addition, the determination of total hydrocarbons using Method 25A and preliminary screenings for organic HAPs using a Fourier Transform Infrared (FTIR) monitoring instrument were conducted by Midwest Research Institute (MRI) under a separate work assignment. Testing

by ERG and MRI occurred simultaneously. The FTIR element is not included within this final report.

Testing was performed at the inlet and outlet simultaneously at the thermal oxidizer and at the outlet only of the two roof top vents (APP and SBS). ERG coordinated all field test activities with MRI personnel.

1.2 Brief Site Description

The asphalt roofing industry produces roofing and siding materials for weather-proofing various structures. The process involves the saturation of a substrate with modified bitumen (asphalt) which is then coated with materials such as sand before being cut to size and packaged. Typical emission controls include a thermal oxidizer.

The U. S. Intec plant, located in Port Arthur, Texas, produces rolled roofing products by saturating a polyester substrate or a fiberglass substrate with bitumen that has been modified with either APP or SBS. The entire manufacturing process is housed under a single roof with the production beginning on each Monday morning, operating 24 hours per day and ending production on each Friday night, leaving Saturday and Sunday for maintenance. Production is greatest during the spring and summer months to accommodate increases in construction and decreases in the fall and winter months. A thermal oxidizer is used to control emissions from various plant processes, such as the holding, mixing, and storage tanks.

The facility produces rolled roofing products by saturating a polyester substrate or a fiberglass substrate with bitumen (modified with either APP or SBS) on two separate production lines. Both substrates enter their respective production lines through a web unwind stand and then go through a dry hooper. Asphalt is loaded from tanker trucks into two 100 ton, 400°F mixing tanks for the polyester substrate and two 10.5 ton, 390°F mixing tanks for the fiberglass substrate line. Tanker trucks also unload polymer liquid into two steam jacketed storage tanks.

Modified bitumen is produced by combining the asphalt with polypropylene and fillers in the six mixing tanks for the polyester substrate line and the SBS in the first mixing tank and fillers in the second mixing tank for the fiberglass substrate line. The modified bitumen from the mixing tanks is transferred to two holding tanks for the polypropylene substrate line and one holding tank for the fiberglass substrate line before going to the respective coaters. Once the saturated polyester substrate leaves the vat, it is coated with granules and talc. The saturated fiberglass substrate is coated with granules and sand. After both products are cooled, the substrates go through separate finish loopers and roll winders.

Emissions from the mixing tanks and holding tanks for both production lines and the blended polymer operation go to the thermal oxidizer. The thermal oxidizer has an operating temperature of 1440°F and a residence time of 0.5 seconds. The emissions from the coaters are uncontrolled. Emissions from the coater areas are collected by overhead hoods and are each vented through the roof with separate vents. The flow rate at the outlet of the thermal oxidizer is approximately 12,000 actual cubic feet per minute (acfm) at a temperature of 479°F.

1.3 Emissions Measurement Program

This section provides an overview of the emissions measurement program conducted at the U. S. Intec facility in Port Arthur, Texas. Included in this section are summaries of the test matrix, sampling locations, sampling methods, and laboratory analysis. Additional detail on these topics is provided in the sections that follow.

1.3.1 Test Matrix

The sampling and analytical matrix is presented in Table 1-1. Manual emissions tests were employed; detailed descriptions of these sampling and analytical procedures are provided in Section 5.0.

Table 1-1. U. S. Intec Facility (Port Arthur, Texas) Sampling and Analytical Matrix

Sampling Location	Number of Runs	Sample Type	EPA Reference Method	Sampling Period (Duration)	Analytical Method	Laboratory Performing Analysis
Thermal Oxidizer Inlet/Outlet	3	Gas Velocity Volume Moisture	1-4	4 hrs	Volumetric/ Gravimetric	ERG
Thermal Oxidizer Inlet/Outlet	3	Total PM	5A	4 hrs	Gravimetric	ERG
Thermal Oxidizer Inlet/Outlet	3	Dioxins/ Furans	23	4 hrs	HRGC/HRMS ¹	Triangle Laboratories
APP and SBS Roof Vent Outlets	3	Gas Velocity Volume Moisture	1-4	1 hr	Volumetric/ Gravimetric	ERG
APP and SBS Roof Vent Outlets	3	Total PM	5A	1 hr	Gravimetric	ERG

¹HRGC/HRMS = High Resolution Gas Chromatography/High Resolution Mass Spectrometry.

1.3.2 Test Schedule

The daily test schedule is presented in Table 1-2. The test required two days of set-up, four test days, and one tear-down day. Each test day was approximately 12-16 hours in length with a typical working period between 6:00 a.m. and 8:00 p.m. A typical set-up, tear-down day was 8-10 hours in length, with working hours between 7:00 a.m. and 7:00 p.m. The test schedule was based on the test duration shown in Table 1-1.

Table 1-2. U. S. Intec Facility (Port Arthur, Texas) Test Schedule

Test Day	Date	Activity
1	9/18/97	Travel
2	9/19/97	Travel
3	9/20/97	Setup
4	9/21/97	Setup
5	9/22/97	Test Day #1: Thermal Oxidizer
6	9/23/97	Test Day #2: Thermal Oxidizer
7	9/24/97	Test Day #3: Coater Vents
8	9/25/97	Test Day #4: Coater Vents
9	9/26/97	Travel

1.3.3 Sampling Locations

The sampling locations used during the emissions testing program at the U. S. Intec facility are described below. Flue gas samples were collected at the inlet and outlet of the thermal oxidizer using two ports at each location and at the outlet of the APP coater vent and the SBS coater vent.

The test ports and their locations met the requirements of EPA Method 1. The thermal oxidizer inlet location is a circular duct with an inside diameter (i.d.) of 36". At the time of the pre-test survey there were no ports in place at the inlet location, but two 4" i.d. ports had been installed at 90 degrees to each other, one horizontally and one vertically on top of the duct, by the time of the test. The thermal oxidizer outlet location is a vertical circular stack with an i.d. of 36". Two new 4" i.d. ports 90 degrees to each other were also installed at this location. The two roof top vents were similar in size and shape and had an inside diameter of 24". Two 4" i.d. sampling points, 90 degrees to each other were installed on each vent approximately two feet above the roof line. A new sampling port for FTIR sampling was installed at the thermal oxidizer inlet and outlet as well as both roof top vents.

1.3.4 Sampling and Analytical Methods

Total particulate matter emissions were determined using EPA Method 5A, with particulate mass emissions collected on a glass fiber filter together with any material that condensed at or above the filter temperature of 42°C. Particulate concentrations are based on the weight gain of the filter and any condensible PM recovered from the 1,1,1-trichloroethane (TCE) rinses of the probe, nozzle, and front half of the glass filter holder.

Flue gas samples for D/F were collected using EPA Method 23. Flue gas was extracted isokinetically and any D/F present was collected on the filter, the XAD-2® resin trap, and in the probe and condenser. The analysis was performed using HRGC coupled with HRMS.

1.4 Quality Assurance/Quality Control (QA/QC)

All flue gas testing procedures followed comprehensive QA/QC procedures as outlined in the Site Specific Test Plan (SSTP) and the Quality Assurance Project Plan (QAPP). A full description of the resulting QA parameters is presented in Section 6.

All post-test and port change leak checks met the criteria prescribed in the manual methods procedure. The allowable isokinetic QC range of $\pm 10\%$ was met for all PM and D/F sampling runs. All post-test dry gas meter calibration checks were within 5% of the full calibration factor. Field blanks (FB) for the D/F and PM tests showed virtually no contamination.

All analyses were completed under a strict QA/QC regimen. For the D/F results, percent recoveries of all isotopically-labeled compounds were within the lower and upper limits of recovery as specified in the method.

The manual flue gas flow rates test data reflected very little variation over the test runs. The percent relative standard deviation (% RSD) observed during each set of tests runs ranged from 1 to 6. These values indicate that the process was very stable during the test period.

1.5 Test Report

This final report, presenting all data collected and the results of the analyses, has been prepared in six sections, as described below:

- Section 1 provides an introduction to the testing effort and includes a brief description of the test site, an overview of the emissions measurement program, and a brief overview of the QC results;
- Section 2 gives a summary of the test results for the PM and D/F tests;
- Section 3 provides a description of the process and plant operation during the field test. These data are to be supplied by EPA and are not included in this report;
- Section 4 gives a discussion of the sampling locations;
- Section 5 presents detailed descriptions of the sampling and analysis procedures; and
- Section 6 provides details of the quality assurance/quality control procedures used on this program and the QC results.

The appendices containing copies of the actual field data sheets and the results of the laboratory analyses are also contained as part of this report.

2.0 SUMMARY OF RESULTS

This section provides the results of the emissions test program conducted at the U. S. Intec asphalt roofing facility (Port Arthur, Texas) from September 22 to September 25, 1997. Included in this section are results of manual tests conducted for PM and D/F.

2.1 Emissions Test Log

Eighteen tests were conducted over a four-day period (6 D/F and 12 PM). Table 2-1 presents the emissions test log which shows the test date, location, run number, test type, run times and port change times for each test method.

Table 2-2 shows the volume of stack gas sampled for each run in dry standard cubic meters (dscm) and Table 2-3 shows the stack gas volumetric flow rate during each run in dry standard cubic meters per minute (dscmm). The percent relative standard deviation (%RSD) calculated for the three runs for each test method (shown in Table 2-3) was less than 6%, indicating that the process flow was relatively constant over the four test days. All related field sheets are given in Appendix A.

2.2 PM Emission Results

Particulate matter emissions were determined from EPA Method 5A sampling trains, with testing performed at the inlet and outlet of the thermal oxidizer, and at the roof vent outlets of the APP and SBS production lines. PM collected on the train filter and in the 1,1,1-trichloroethane probe rinse of the Method 5A sampling train was analyzed gravimetrically. PM stack concentrations, in grams per dry standard cubic meter (g/dscm), the average and %RSD for the three test runs at the inlet and outlet of the thermal oxidizer and for the three test runs at each of the roof top vents are shown in Table 2-4. The % RSD for both the inlet and outlet of the thermal oxidizer was less than 32, showing good reproducibility for the sampling and analysis method as well as relatively constant process conditions over the four-day test period. The

Table 2-1. Emissions Log, U. S. Intec

Date	Location	Run Number	Test Type	Run Time
9/22/97	Thermal Oxidizer Inlet, Port B	1	PM	1450-1650
	Thermal Oxidizer Inlet, Port A	1	PM	1725-1925
	Thermal Oxidizer Inlet, Port A	1	D/F	1450-1650
	Thermal Oxidizer Inlet, Port B	1	D/F	1725-1925
	Thermal Oxidizer Outlet, Port B	1	PM	1450-1650
	Thermal Oxidizer Outlet, Port A	1	PM	1725-1925
	Thermal Oxidizer Outlet, Port A	1	D/F	1450-1650
	Thermal Oxidizer Outlet, Port B	1	D/F	1725-1925
9/23/97	Thermal Oxidizer Inlet, Port B	2	PM	1015-1240
	Thermal Oxidizer Inlet, Port A	2	PM	1245-1440
	Thermal Oxidizer Inlet, Port B	3	PM	1710-1910
	Thermal Oxidizer Inlet, Port A	3	PM	1940-2140
	Thermal Oxidizer Inlet, Port A	2	D/F	1015-1215
	Thermal Oxidizer Inlet, Port B	2	D/F	1240-1440
	Thermal Oxidizer Inlet, Port A	3	D/F	1710-1910
	Thermal Oxidizer Inlet, Port B	3	D/F	1940-2140
	Thermal Oxidizer Outlet, Port B	2	PM	1015-1215
	Thermal Oxidizer Outlet, Port A	2	PM	1240-1440
	Thermal Oxidizer Outlet, Port B	3	PM	1710-1910
	Thermal Oxidizer Outlet, Port A	3	PM	1940-2140
	Thermal Oxidizer Outlet, Port A	2	D/F	1015-1215
	Thermal Oxidizer Outlet, Port B	2	D/F	1240-1440
	Thermal Oxidizer Outlet, Port A	3	D/F	1710-1910
	Thermal Oxidizer Outlet, Port B	3	D/F	1940-2140
9/24/97	APP Stack, Port Y	1	PM	1325-1401
	APP Stack, Port X	1	PM	1406-1431
	APP Stack, Port X	2	PM	1510-1545
	APP Stack, Port Y	2	PM	1550-1615
	APP Stack, Port Y	3	PM	1632-1703
	APP Stack, Port X	3	PM	1705-1735
	SBS Stack, Port X	1	PM	1435-1505
	SBS Stack, Port Y	1	PM	1513-1538
9/25/97	SBS Stack, Port Y	2	PM	0922-0952
	SBS Stack, Port X	2	PM	0956-1026
	SBS Stack, Port X	3	PM	1040-1110
	SBS Stack, Port Y	3	PM	1114-1144

Table 2-2. Sample Volume Collected, dscm¹

Location	Parameter	Run 1	Run 2	Run 3	Average	% RSD
Thermal Oxidizer Inlet	PM	4.34	4.06	4.04	4.15	4.04
Thermal Oxidizer Inlet	D/F	4.45	4.21	4.31	4.32	2.79
Thermal Oxidizer Outlet	PM	4.18	4.00	3.93	4.04	3.19
Thermal Oxidizer Outlet	D/F	3.90	3.96	3.87	3.91	1.17
APP Stack, Outlet	PM	1.24	1.26	1.27	1.26	1.21
SBS Stack, Outlet	PM	1.26	1.41	1.33	1.33	5.64

¹Standard conditions are defined as 1 atm and 68°F.

Table 2-3. Flue Gas Volumetric Flow Rates, dscmm¹

Location	Parameter	Run 1	Run 2	Run 3	Average	% RSD
Thermal Oxidizer Inlet	PM	227	209	206	214	5.36
Thermal Oxidizer Inlet	D/F	218	212	213	214	1.72
Thermal Oxidizer Outlet	PM	215	207	206	209	2.32
Thermal Oxidizer Outlet	D/F	212	209	210	210	0.91
APP Stack, Outlet	PM	308	314	317	313	1.45
SBS Stack, Outlet	PM	306	329	323	319	3.67

¹Standard conditions are defined as 1 atm and 68°F.

Table 2-4. Particulate Matter Concentration, EPA Method 5A

Location	gr/dscm				% RSD
	Run 1	Run 2	Run 3	Average	
Thermal Oxidizer, Inlet	0.23	0.15	0.12	0.17	31.3
Thermal Oxidizer, Outlet	0.0093	0.0077	0.011	0.0093	16.7
APP Stack, Outlet	0.13	0.14	0.099	0.12	17.3
SBS Stack, Outlet	0.13	0.056	0.068	0.085	46.7

%RSD for the three runs at SBS vent was 46.7. The variability in these results is most likely due to gravimetric measurements made on very low amounts of PM. Increased variability would not be unusual in this case. Since no measurable PM was detected in the blanks, the blank correction was not necessary.

Table 2-5 shows the average PM emission rate in pounds per hour (lb/hr), for each of the three outlet test locations. These values were calculated from the average outlet concentration from Table 2-4 and the average stack flow rate from Table 2-3. Using this value in conjunction with the equivalent value for the inlet (see Table 2-5), a PM removal efficiency for the thermal oxidizer was calculated to be 94.6%. Table 2-6 shows the average PM emissions, in pounds per ton of product, for each of the three test location outlets. These values were calculated from the results presented in Table 2-5 and the summary of the process data presented in Appendix D, Tables D-2 through D-4. The average total tons produced during the test period were divided by the length of the test run. This value was divided into the emission rate from Table 2-5. The data presented in Appendix D are a summary of the process information extracted from the information supplied by the facility. Although much of the process data was present, several clarifications and supplemental data were requested from and supplied by the facility after several iterations. The PM analytical raw data are given in Appendix B.

Table 2-5. Particulate Matter Emission Rate, lb/hr, and Thermal Oxidizer Removal Efficiency, %

Location	lb/hr		Removal Efficiency ² %
	Average Inlet Rate ¹	Average Outlet Rate ¹	
Thermal Oxidizer	0.308	0.0166	94.6
APP Vent	NT ³	0.331	NA ⁴
SBS Vent	NT	0.228	NA

¹ Average of three test runs.

² Percent Removal Efficiency = (Inlet - Outlet) / Inlet x 100

³ NT = Not Tested

⁴ NA = Not Applicable

Table 2-6. Particulate Matter Emission Rate, lbs/Ton of Product

Location	lbs/ton of Product
Thermal Oxidizer Outlet	1.9×10^{-3}
APP Vent Outlet	4.5×10^{-2}
SBS Vent Outlet	2.9×10^{-1}

2.3 D/F Emission Results

2.3.1 Overview

Six 4-hour D/F emission test runs were completed at U.S. Intec during the week of September 21, 1997. Three test runs were completed at the inlet and at the outlet of the thermal oxidizer which is associated with various plant processes, such as holding, mixing, and storage tanks. The sample collection protocol followed EPA Method 23, while the analysis protocol followed EPA Method 23/8290. The sample preparation and analytical procedure is discussed in Section 5 of this report.

2.3.2 D/F Emission Results

Table 2-7 presents the concentration, in nanograms per dry standard cubic meter (ng/dscm) for the selected D/F congeners by run number, the average concentration over the three runs and the %RSD. All results were determined by HRGC/HRMS using a DB-5 capillary gas chromatographic column.

Any compound that was not detected is reported as a "less than" value with this value being the instrumental detection limit. A "less than" value rather than "0" is used in all appropriate calculations. The % RSD values reported in Table 2-7 for each test run by compound range widely, but are not indicative of poor sampling/analytical reproducibility because almost all values are reported as "less than" values. Increased variability is not unusual in these cases.

Table 2-8 shows the D/F stack emission rates, in $\mu\text{g/hr}$, from the thermal oxidizer inlet and outlet. These values were calculated from the average concentrations from Table 2-7 and the average stack flow rate from Table 2-3.

Table 2-7. Thermal Oxidizer Dioxin/Furan Stack Gas Concentrations

Congener	ng/dscm				% RSD
	Run 1	Run 2	Run 3	Average	
Inlet					
2,3,7,8-TCDD	<0.001	<0.001	<0.001	<0.001	0.0
1,2,3,7,8-PeCDD	<0.002	<0.002	<0.002	<0.002	0.0
1,2,3,4,7,8-HxCDD	<0.002	<0.002	<0.002	<0.002	0.0
1,2,3,6,7,8-HxCDD	<0.002	<0.002	<0.002	<0.002	0.0
1,2,3,7,8,9-HxCDD	<0.002	<0.002	<0.002	<0.002	0.0
1,2,3,4,6,7,8-HpCDD	<0.002	<0.002	<0.002	<0.002	0.0
OCDD	0.005 ¹	<0.005	<0.005	<0.005	0.0
2,3,7,8-TCDF	<0.001	<0.001	<0.001	<0.001	0.0
1,2,3,7,8-PeCDF	<0.002	<0.001	<0.001	<0.001	63.2
2,3,4,7,8-PeCDF	<0.002	<0.001	<0.001	<0.001	63.2
1,2,3,4,7,8-HxCDF	<0.002	<0.001	<0.001	<0.001	63.2
1,2,3,6,7,8-HxCDF	<0.001	<0.001	<0.001	<0.001	0.0
2,3,4,6,7,8-HxCDF	<0.002	<0.001	<0.001	<0.001	63.2
1,2,3,7,8,9-HxCDF	<0.002	<0.001	<0.002	<0.002	66.7
1,2,3,4,6,7,8-HpCDF	<0.002	<0.002	<0.002	<0.002	0.0
1,2,3,4,7,8,9-HpCDF	<0.002	<0.002	<0.002	<0.002	0.0
OCDF	<0.004	<0.002	<0.002	<0.003	38.5
Outlet					
2,3,7,8-TCDD	0.002 ¹	<0.002	<0.003	<0.002	28.9
1,2,3,7,8-PeCDD	<0.002	<0.003	<0.005	<0.003	50.9
1,2,3,4,7,8-HxCDD	<0.002	<0.003	<0.005	<0.003	50.9
1,2,3,6,7,8-HxCDD	<0.002	<0.003	<0.005	<0.003	50.9
1,2,3,7,8,9-HxCDD	<0.002	<0.003	<0.005	<0.003	50.9
1,2,3,4,6,7,8-HpCDD	<0.002	0.005 ¹	<0.005	<0.004	37.6
OCDD	<0.02	<0.005	<0.008	<0.011	72.1

Table 2-7. Continued

Congener	ng/dscm				% RSD
	Run 1	Run 2	Run 3	Average	
2,3,7,8-TCDF	<0.001	<0.002	<0.002	<0.002	83.3
1,2,3,7,8-PeCDF	<0.001	<0.002	<0.002	<0.002	50.0
2,3,4,7,8-PeCDF	<0.001	<0.002	<0.002	<0.002	50.0
1,2,3,4,7,8-HxCDF	<0.001	<0.002	<0.002	<0.002	50.0
1,2,3,6,7,8-HxCDF	<0.001	<0.002	<0.002	<0.002	50.0
2,3,4,6,7,8-HxCDF	0.002 ¹	<0.002	<0.003	<0.002	37.6
1,2,3,7,8,9-HxCDF	<0.001	<0.003	<0.003	<0.002	57.7
1,2,3,4,6,7,8-HpCDF	<0.002	<0.003	<0.005	<0.003	50.9
1,2,3,4,7,8,9-HpCDF	<0.002	<0.005	<0.005	<0.003	96.2
OCDF	<0.002	<0.005	<0.005	<0.003	96.2

¹ Amount detected is less than 5 times the detection limit and should be considered only an estimate.

Table 2-8. Dioxin/Furan Stack Emission Rate, µg/hr, Thermal Oxidizer Inlet and Outlet

Congener	Average Concentration ng/dscm	Average Emission Rate µg/hr	Average Concentration ng/dscm	Average Emission Rate µg/hr
	Inlet		Outlet	
2,3,7,8-TCDD	<0.001	<0.013	<0.002	<0.025
1,2,3,7,8-PeCDD	<0.002	<0.026	<0.003	<0.038
1,2,3,4,7,8-HxCDD	<0.002	<0.026	<0.003	<0.038
1,2,3,6,7,8-HxCDD	<0.002	<0.026	<0.003	<0.038
1,2,3,7,8,9-HxCDD	<0.002	<0.026	<0.003	<0.038
1,2,3,4,6,7,8-HpCDD	<0.002	<0.026	<0.004	<0.050
OCDD	<0.005	<0.064	<0.011	<0.139
2,3,7,8-TCDF	<0.001	<0.013	<0.002	<0.025
1,2,3,7,8-PeCDF	<0.001	<0.013	<0.002	<0.025
2,3,4,7,8-PeCDF	<0.001	<0.013	<0.002	<0.025
1,2,3,4,7,8-HxCDF	<0.001	<0.013	<0.002	<0.025
1,2,3,6,7,8-HxCDF	<0.001	<0.013	<0.002	<0.025
2,3,4,6,7,8-HxCDF	<0.001	<0.013	<0.002	<0.025
1,2,3,7,8,9-HxCDF	<0.002	<0.026	<0.002	<0.025
1,2,3,4,6,7,8-HpCDF	<0.002	<0.026	<0.003	<0.038
1,2,3,4,7,8,9-HpCDF	<0.002	<0.026	<0.003	<0.038
OCDF	<0.003	<0.039	<0.003	<0.038

Table 2-9 shows the average D/F emissions, in micrograms per megagram ($\mu\text{g}/\text{Mg}$) of product, for the thermal oxidizer outlet. These values were calculated from the results presented in Table 2-8 and the summary of the process data presented in Appendix D, Tables D-1 and D-2. The average total tons produced during the test period were divided by the length of the test run. This value was divided into the emission rate for each congener from Table 2-8. The data presented in Appendix D are a summary of the process information extracted from the information supplied by the facility. Although much of the process data was present, several clarifications and supplemental data were requested from and supplied by the facility after several iterations.

Table 2-10 shows the congener concentrations in ng/dscm converted to 2,3,7,8-tetrachlorodibenzo-*p*-dioxin toxicity equivalents as well as a summation of the values presented as total chlorinated dioxins and total chlorinated furans. All D/F analytical raw data can be found in Appendix C.

Table 2-9. Dioxin/Furan Stack Emission Rate, Thermal Oxidizer Outlet, µg/Mg Product

Congener	Average Emission Rate µg/Mg Product
2,3,7,8-TCDD	<0.0032
1,2,3,7,8-PeCDD	<0.0048
1,2,3,4,7,8-HxCDD	<0.0048
1,2,3,6,7,8-HxCDD	<0.0048
1,2,3,7,8,9-HxCDD	<0.0048
1,2,3,4,6,7,8-HpCDD	<0.0064
OCDD	<0.018
2,3,7,8-TCDF	<0.0032
1,2,3,7,8-PeCDF	<0.0032
2,3,4,7,8-PeCDF	<0.0032
1,2,3,4,7,8-HxCDF	<0.0032
1,2,3,6,7,8-HxCDF	<0.0032
2,3,4,6,7,8-HxCDF	<0.0032
1,2,3,7,8,9-HxCDF	<0.0032
1,2,3,4,6,7,8-HpCDF	<0.0048
1,2,3,4,7,8,9-HpCDF	<0.0048
OCDF	<0.0048

Table 2-10. Dioxin/Furan 2,3,7,8-TCDD Toxicity Equivalent Stack Gas Concentrations, Thermal Oxidizer Inlet and Outlet

Congener	2,3,7,8-TCDD TEF ¹	ng/dscm			
		Run 1	Run 2	Run 3	Average
Inlet					
2,3,7,8-TCDD	1.0	<0.001	<0.001	<0.001	<0.001
1,2,3,7,8-PeCDD	0.5	<0.001	<0.001	<0.001	<0.001
1,2,3,4,7,8-HxCDD	0.1	<0.0002	<0.0002	<0.0002	<0.0002
1,2,3,6,7,8-HxCDD	0.1	<0.0002	<0.0002	<0.0002	<0.0002
1,2,3,7,8,9-HxCDD	0.1	<0.0002	<0.0002	<0.0002	<0.0002
1,2,3,4,6,7,8-HpCDD	0.01	<0.00002	<0.00002	<0.00002	<0.00002
OCDD	0.001	0.000005 ²	<0.000005	<0.000005	<0.000005
Total PCDD					<0.0026
2,3,7,8-TCDF	0.1	<0.0001	<0.0001	<0.0001	<0.0001
1,2,3,7,8-PeCDF	0.05	<0.0001	<0.00005	<0.00005	<0.00005
2,3,4,7,8-PeCDF	0.5	<0.001	<0.0005	<0.0005	<0.0007
1,2,3,4,7,8-HxCDF	0.1	<0.0002	<0.0001	<0.0001	<0.0001
1,2,3,6,7,8-HxCDF	0.1	<0.0001	<0.0001	<0.0001	<0.0001
2,3,4,6,7,8-HxCDF	0.1	<0.0002	<0.0001	<0.0001	<0.0001
1,2,3,7,8,9-HxCDF	0.1	<0.0002	<0.0002	<0.0002	<0.0002
1,2,3,4,6,7,8-HpCDF	0.01	<0.00002	<0.00002	<0.00002	<0.00002
1,2,3,4,7,8,9-HpCDF	0.01	<0.00002	<0.00002	<0.00002	<0.00002
OCDF	0.001	<0.000004	<0.000002	<0.000002	<0.000003
Total PCDF					<0.0014
Outlet					
2,3,7,8-TCDD	1.0	0.002 ²	<0.002	<0.003	<0.002
1,2,3,7,8-PeCDD	0.5	<0.001	<0.0015	<0.0025	<0.0015

Table 2-10. Continued

Congener	2,3,7,8-TCDD TEF ¹	ng/dscm			
		Run 1	Run 2	Run 3	Average
1,2,3,4,7,8-HxCDD	0.1	<0.0002	<0.0003	<0.0005	<0.0003
1,2,3,6,7,8-HxCDD	0.1	<0.0002	<0.0003	<0.0005	<0.0003
1,2,3,7,8,9-HxCDD	0.1	<0.0002	<0.0003	<0.0005	<0.0003
1,2,3,4,6,7,8-HpCDD	0.01	<0.00002	0.00005 ²	<0.00005	<0.00004
OCDD	0.001	<0.000002	<0.000005	<0.000008	<0.000005
Total PCDD					<0.0044
2,3,7,8-TCDF	0.1	<0.0001	<0.0002	<0.0002	<0.0002
1,2,3,7,8-PeCDF	0.05	<0.00005	<0.0001	<0.00015	<0.0001
2,3,4,7,8-PeCDF	0.5	<0.0005	<0.001	<0.0005	<0.001
1,2,3,4,7,8-HxCDF	0.1	<0.0001	<0.0002	<0.0003	<0.0002
1,2,3,6,7,8-HxCDF	0.1	<0.0001	<0.0002	<0.0003	<0.0002
2,3,4,6,7,8-HxCDF	0.1	0.0002 ²	<0.0002	<0.0003	<0.0002
1,2,3,7,8,9-HxCDF	0.1	<0.0001	<0.0003	<0.0003	<0.0002
1,2,3,4,6,7,8-HpCDF	0.01	<0.00002	<0.00003	<0.00005	<0.00003
1,2,3,4,7,8,9-HpCDF	0.01	<0.00002	<0.00005	<0.00005	<0.00004
OCDF	0.001	<0.000002	<0.000005	<0.000005	<0.000003
Total PCDF					<0.0022

¹TEF, Toxicity Equivalence Factor

²The amount detected is less than 5 times the detection limit and should be considered an estimated value.

3.0 PROCESS DESCRIPTION AND PROCESS DATA

The facility produces rolled roofing products by saturating a polyester substrate and a fiberglass substrate with modified bitumen on two separate production lines. Both substrates enter their respective production lines through a web unwind stand and then go through a dry looper. Asphalt is loaded from tanker trucks into two 100-ton, 350°F asphalt storage tanks. Asphalt from the storage tanks is distributed to six 10.5-ton, 400°F mixing tanks for the polyester substrate line and two 10.5-ton, 390°F mixing tanks for the fiberglass substrate line. Tanker trucks also load polymer liquid into two steam jacket storage tanks.

Modified bitumen is produced by combining the asphalt with polypropylene and fillers in the six mixing tanks for the polyester substrate line and SBS in the first mixing tank and fillers in the second mixing tank for the fiberglass substrate line. The modified bitumen from the mixing tanks is transferred to two holding tanks for the polyester substrate line and one holding tank for the fiberglass substrate line before going to their respective coaters. The coaters are impregnation vats which saturate both substrates with the modified bitumen. Once the saturated polyester substrate leaves the vat it is coated with granules and talc. The saturated fiberglass substrate is coated with granules and sand. After both products are cooled, the substrates go through separate finish loopers and roll winders.

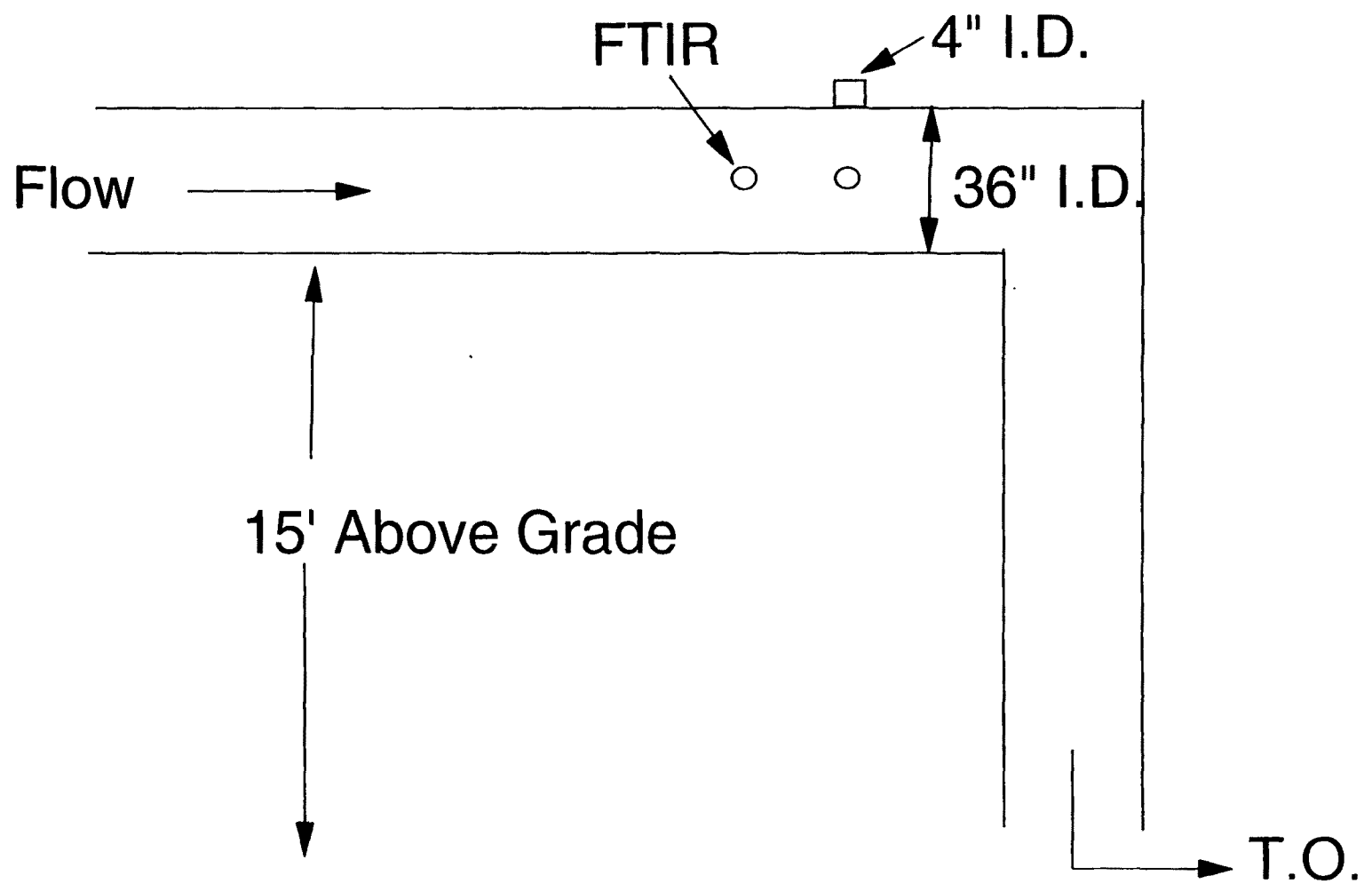
Emissions from the mixing tanks and holding tanks for both production lines and the blended polymer operation go to the thermal oxidizer. The thermal oxidizer has an operating temperature of 1400°F and a residence time of 0.5 seconds. The talc applicator for the polyester substrate production line is controlled by a baghouse. The baghouse (fabric filter) has an air-to-cloth ratio of 5:1 actual cubic feet per minute (acfm), an inlet volumetric flow rate of 5000 dry standard cubic feet per minute (dscfm), and an inlet gas temperature of 100°F. Emissions from the coaters are uncontrolled and vent to the atmosphere through roof top vents.

4.0 SAMPLING LOCATIONS

The sampling locations used during the emission testing program at the U. S. Intec, Port Arthur, Texas, plant are described in this section. Flue gas samples were collected at the inlet and outlet of the thermal oxidizer scrubber using two ports at each location and at the outlet of the APP coater vent and the SBS coater vent. The configurations of the sampling locations are shown in Figures 4-1, 4-2, and 4-3. The configurations for the two roof top vents are similar.

The test ports and their locations met the requirements of EPA Method 1. The thermal oxidizer inlet is a circular duct with an i.d. of 36". At the time of the pre-test survey there were no ports in place at the inlet location, but ERG requested that two 4" i.d. ports be installed at 90 degrees to each other, one horizontally and one vertically on top of the duct; these ports were in place for the field testing effort. The thermal oxidizer outlet is a vertical circular stack with an i.d. of 36" with two 4" ports installed at 90 degrees to each other. The two roof top vents have an inside diameter of 24" and each has two 3" outside diameter (o.d.) ports installed at 90 degrees to each other. The 3" ports were enlarged to 4" prior to the testing effort in order to accommodate the sampling probes. The position and number of traverse points for the outlet and inlet locations are shown in Figures 4-4, 4-5, and 4-6, respectively.

4-2



4-3

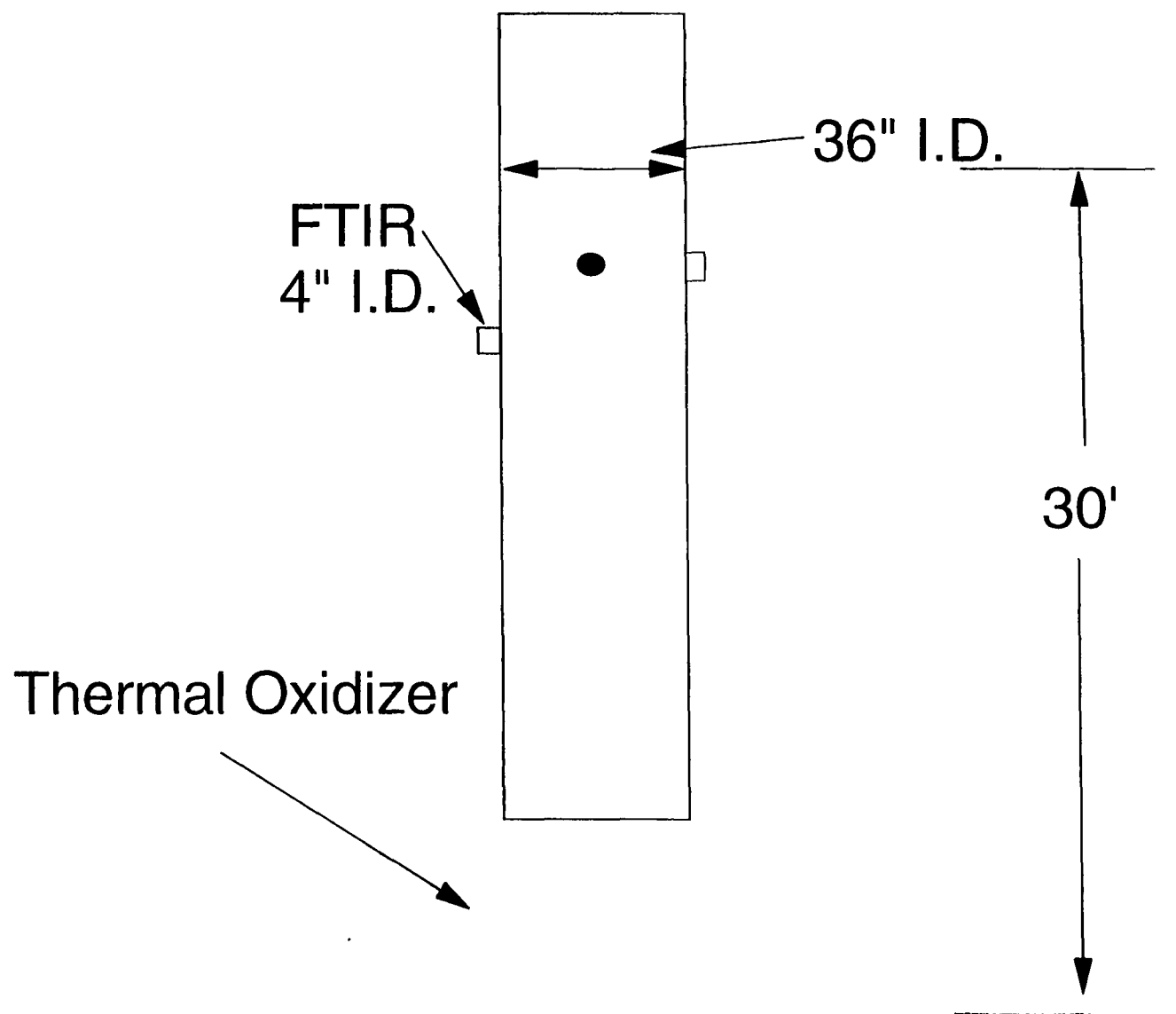
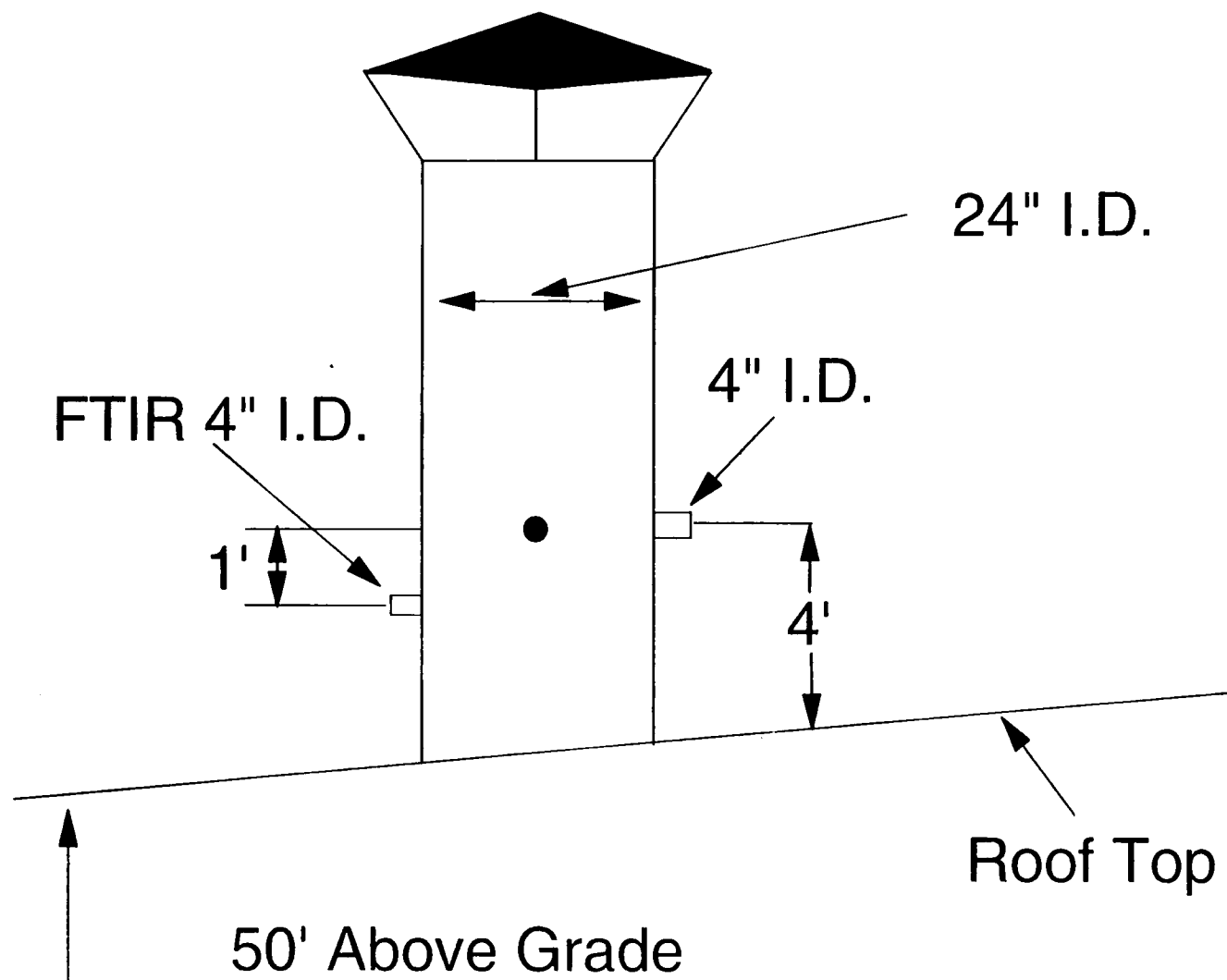


Figure 4-2. Thermal Oxidizer Outlet Sampling Location



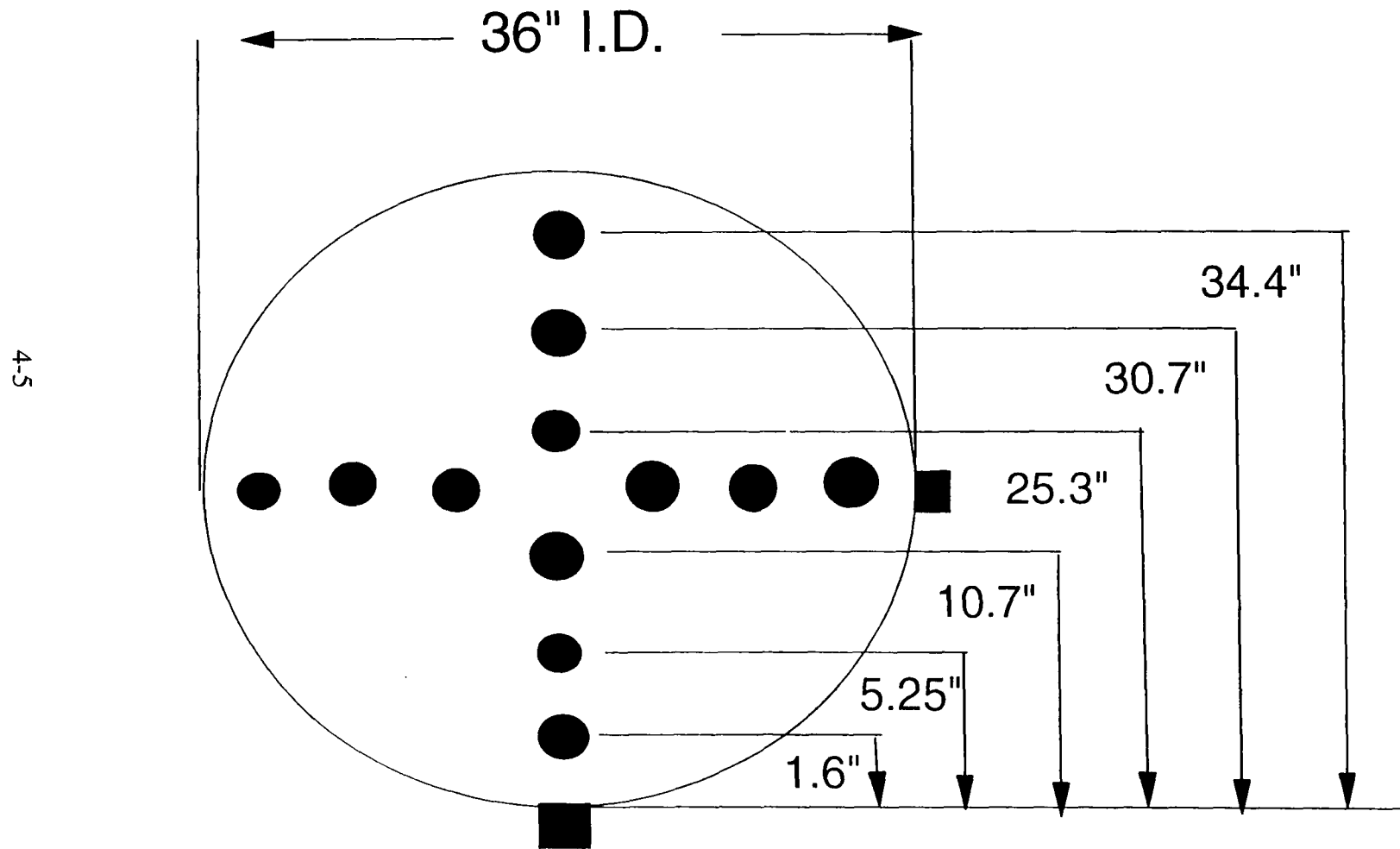
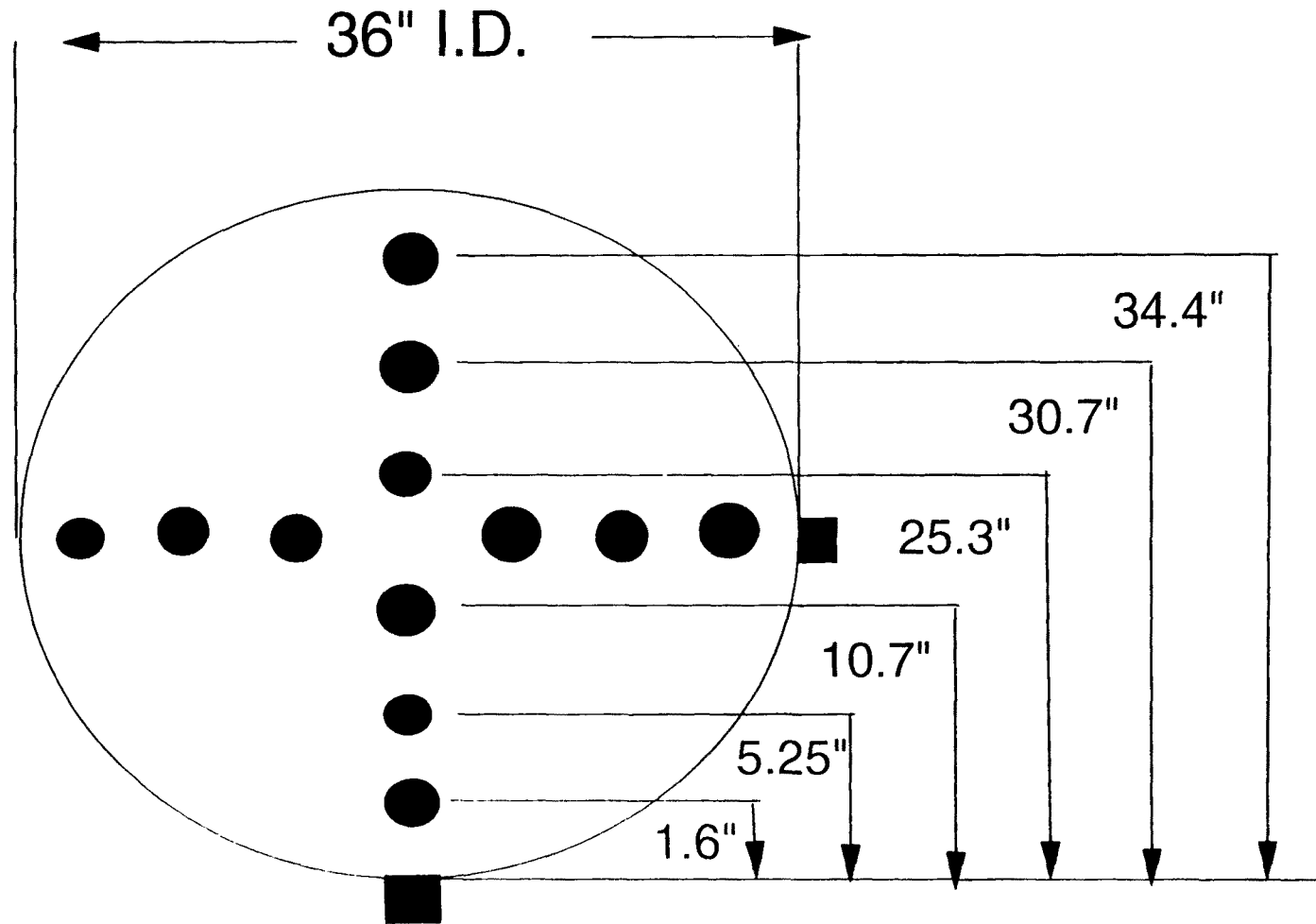


Figure 4-4. Thermal Oxidizer Inlet Traverse Point Layout

4-6



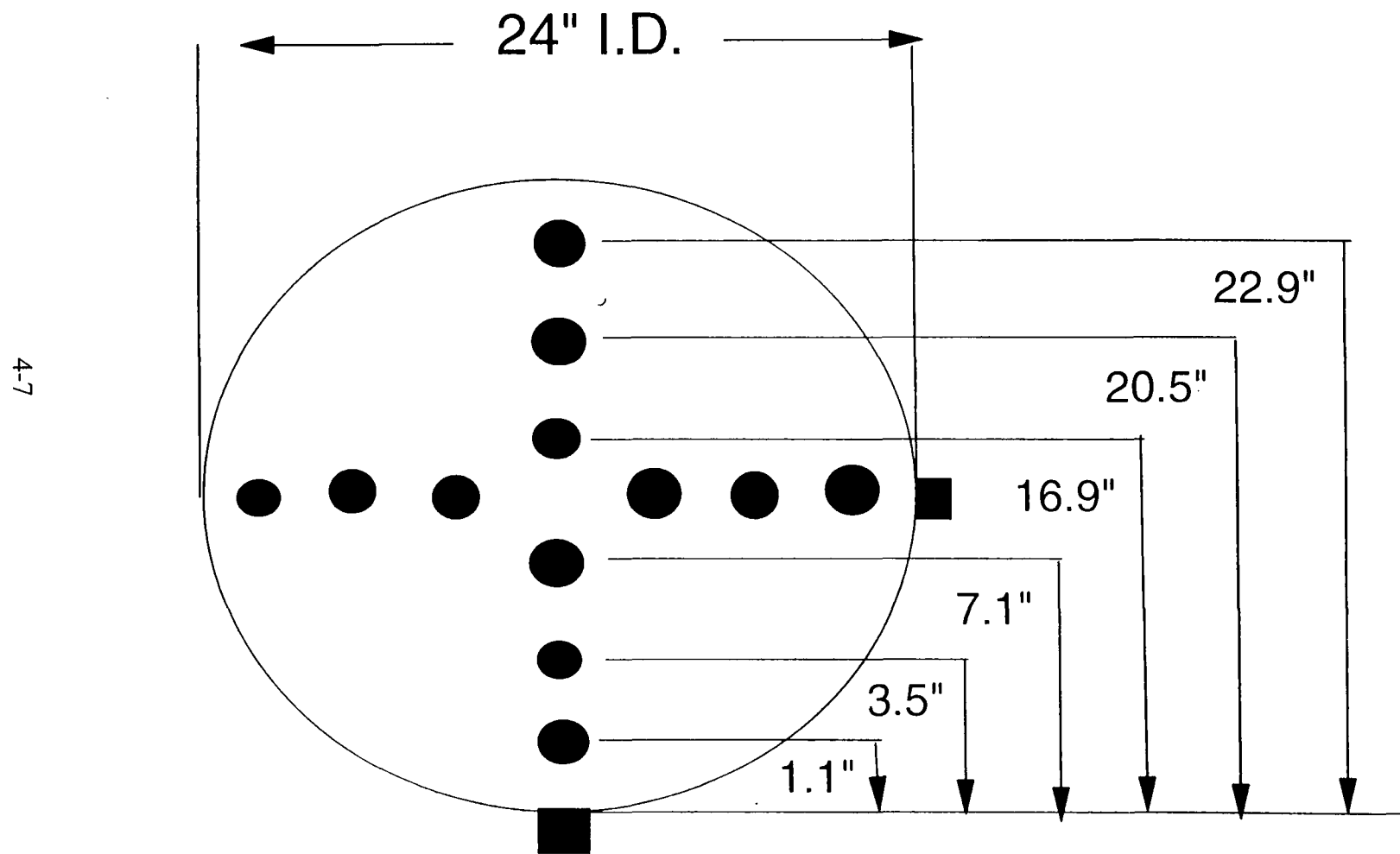


Figure 4-6. APP and SBS Outlet Traverse Point Layout

5.0 SAMPLING AND ANALYTICAL PROCEDURES BY ANALYTE

The sampling and analytical procedures used for the asphalt roofing test program are the most recent revisions of the published EPA methods. In this section, descriptions of each sampling and analytical method by analyte are provided.

5.1 Particulate Matter (PM) Emissions Testing Using EPA Method 5A

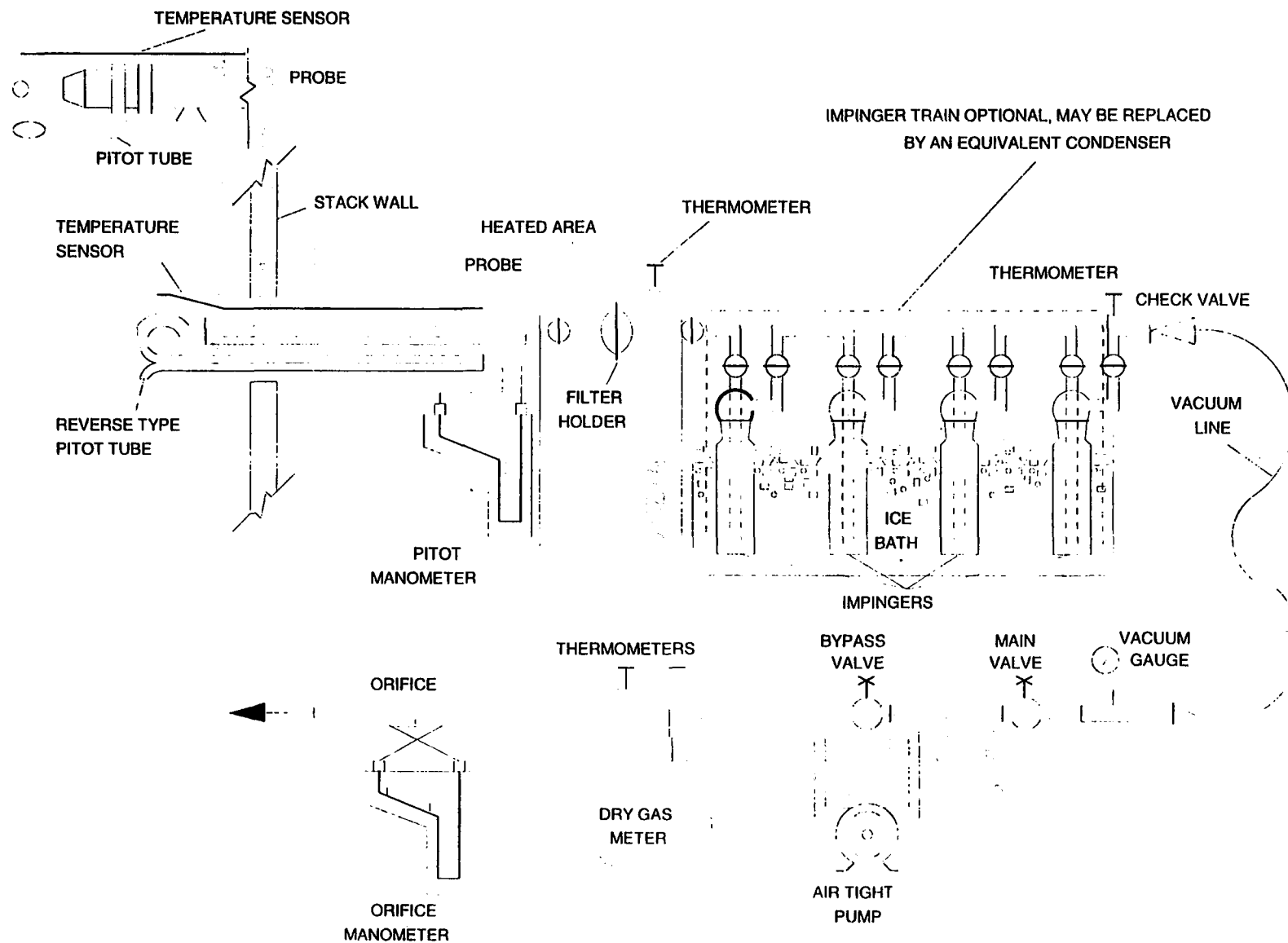
Sampling for Particulate Matter (PM) was performed according to the EPA Method 5A protocol. This method is applicable to the determination of particulate mass emissions collected on a glass fiber filter and any material that condenses at or above the filter temperature of 42°C from various types of process controls and combustion sources associated with the asphalt industry.

Particulate concentrations are based on the weight gain of the filter and any condensible PM recovered from the 1,1,1-trichloroethane (TCE) rinses of the probe, nozzle, and front half of the glass filter holder.

5.1.1 Method 5A Sampling Equipment

The Method 5A methodology uses the sampling train shown in Figure 5-1.

The 4-impinger train consists of a borosilicate glass nozzle/probe liner followed by a heated filter assembly with a Teflon® filter support, a series of impingers and a meter box and vacuum pump as specified in EPA Method 5. The sample is not exposed to any metal surfaces in this train.



The design and contents of the sequential impingers are:

- Impinger 1 (modified Greenburg-Smith) and Impinger 2 (Greenburg-Smith), known volumes of deionized water (nominal 100 mL);
- Impinger 3 (modified Greenburg-Smith), empty; and
- Impinger 4 (modified Greenburg-Smith), silica gel.

5.1.2 Method 5A Sampling Equipment Preparation

5.1.2.1 Glassware Preparation

Glassware is washed in soapy water, rinsed with hot tap water, rinsed with Type II water, rinsed with acetone to remove the water, rinsed three times with TCE and then air-dried. This procedure is used on all the glass components of the sampling train including the glass nozzles plus any sample bottles, Erlenmeyer flasks, petri dishes and graduated cylinders. Non-glass components (such as the Teflon[®]-coated filter screens and seals, tweezers, Teflon[®] squeeze bottles, Teflon[®] probe brushes) are cleaned following the same procedure. The cleaning procedure is summarized in Table 5-1.

Table 5-1. Glassware Cleaning Procedure for Method 5A Sampling Train Components

NOTE: USE DISPOSABLE GLOVES AND ADEQUATE VENTILATION

1. Soak all glassware in hot soapy water (laboratory detergent).
2. Rinse with tap water to remove soap.
3. Rinse three times with HPLC-grade water.
4. Rinse three times with acetone.
5. Rinse three times with TCE.
6. Air dry.
7. Cap glassware with clean glass plugs or Parafilm[®].
8. Mark cleaned glassware with color-coded identification sticker.

5.1.2.2 Reagent Preparation

The filters in the sampling train were Whatman 94 AH glass fiber filters, without organic binders, that met the criteria specified in EPA Method 5 Section 3.1.1. These filters were used as received. The TCE was purchased as HPLC-grade to ensure a low residue after evaporation.

The reagent water is HPLC-grade or equivalent. The lot number, manufacturer and grade of each reagent that was used was recorded.

The analyst wears both safety glasses (with side shields) and protective gloves when the reagents are mixed or handled. Each reagent had its own designated transfer Teflon® squeeze bottle and was marked for identification and used only for the reagent for which it was designated.

5.1.2.3 Equipment Preparation

The remaining equipment preparation included calibration and leak checking of all of the train equipment, including meter boxes, thermocouples, nozzles, pitot tubes, and umbilicals. Referenced calibration procedures were followed when available, and the results were properly documented and retained. A discussion of the techniques used to calibrate the sampling equipment is presented below.

Type S Pitot Tube Calibration. The EPA has specified guidelines concerning the construction and geometry of an acceptable Type S pitot tube. If the specified design and construction guidelines are met, a pitot tube coefficient of 0.84 is used. Information pertaining to the design and construction of the Type S pitot tube may be found in detail in Section 3.1.1 of EPA Document 600/4-77-027b. Only Type S pitot tubes meeting the required EPA specifications were used. Pitot tubes were inspected and documented as meeting EPA specifications prior to field sampling.

Sampling Nozzle Calibration. Glass nozzles are used for isokinetic sampling.

Calculation of the isokinetic sampling rate requires that the cross-sectional area of the sampling nozzle be accurately known. All nozzles were thoroughly cleaned, visually inspected and calibrated according to the procedure outlined in Section 3.4.2 of EPA Document 600/4-77-027b.

Temperature Measuring Device calibration. Accurate temperature measurements are required during stationary source sampling. Bimetallic stem thermometers and thermocouple temperature sensors are calibrated using the procedure described in Section 3.4.2 of EPA Document 600/4-77-027b. Each temperature sensor was calibrated at a minimum of two points over the anticipated range of use against an NBS-traceable mercury-in-glass thermometer. All sensors were calibrated prior to field sampling.

Dry Gas Meter Device Calibration. Dry gas meters (DGMs) are used in the Method 5A sampling trains to monitor the sampling rate and to measure the sample volume. All DGMs were calibrated to document the volume correction factor just prior to shipping of the equipment to the field. Post-test calibration checks are performed as soon as possible after the equipment has been returned to the ERG laboratory. Pre- and post-test calibration should agree to within 5%.

Prior to calibration, a positive pressure leak check of the system was performed using the procedure outlined in Section 3.3.2 of EPA Document 600/4-77-023b. The system was placed under approximately 10 inches of water pressure and a gauge oil manometer was used to determine if a pressure increase could be detected over a one-minute period. If leaks are detected at this point, they are repaired before actual calibration are performed and a successful leak check is obtained for each system.

After the sampling console was assembled and leak checked, the pump ran for 15 minutes to allow the pump and DGM to warm up. The valve was then adjusted to obtain the desired flow rate. For the pre-test calibration, data were collected at orifice manometer settings

(ΔH) of 0.5, 1.0, 1.5, 2.0, 3.0 and 4.0 in H_2O . Gas volumes of 5 ft³ were used for the two lower orifice settings, and volumes of 10 ft³ were used for the higher settings. The individual gas meter correction factors (Y_i) were calculated for each orifice setting and averaged. The method requires that each of the individual correction factors fall within $\pm 2\%$ of the average correction factor or the meter must be cleaned, adjusted, and recalibrated. In addition, ERG requires that the average correction factor be within $1.00 \pm 1\%$. For the post-test calibration, the meter was calibrated three times at the average orifice setting and vacuum which were used during the actual field test.

5.1.3 Method 5A Sampling Operations

5.1.3.1 Preliminary Measurements

Prior to sampling, preliminary measurements are required to ensure isokinetic sampling. These preliminary measurements include determining the traverse point locations, performing a preliminary velocity traverse and a cyclonic flow check. These measurements are used to calculate a "K factor." The K factor is used to determine an isokinetic sampling rate from stack gas flow readings taken during sampling. Preliminary measurement datasheets from the field test are shown in Appendix A.

Measurements are then made of the duct inside diameter, port nozzle length, and the distances to the nearest upstream and downstream flow disturbances. These measurements are then used to determine sampling point locations by following EPA Reference Method 1 guidelines. The distances are then marked on the sampling probe using an indelible marker.

5.1.3.2 Assembling the Train

Assembly of the EPA Method 5A sampling train components was begun in the recovery trailer and final train assembly was performed at the specific stack testing location. First, the empty, clean impingers were assembled and laid out in the proper order in the recovery trailer.

Each ground glass joint was carefully inspected for hairline cracks. After the impingers were loaded, each impinger was weighed, and the initial weight and contents of each impinger were recorded on a recovery data sheet (see Appendix A).

The impingers were connected together using clean glass U-tube connectors and arranged in the impinger bucket. The height of all the impingers is approximately the same to aid in obtaining a leak-free seal. The open ends of the train were sealed with Parafilm® or clean ground glass caps.

The pre-weighed filter was then loaded into the filter holder in the recovery trailer. The filter holder was then capped off and placed into the impinger bucket. To avoid contamination of the sample, sealing greases were not used. The train components were then transferred to the sampling location and assembled as shown in Figure 5-1.

5.1.3.3 Sampling Procedures

After the train is assembled, the heaters for the probe liner and filter box were turned on. When the system reached the appropriate temperatures, the sampling train was ready for pre-test leak checking. The gas stream exiting the heated filter was maintained at a temperature of $42\pm 10^{\circ}\text{C}$ ($108\pm 18^{\circ}\text{F}$). To monitor this temperature during sampling, a thermocouple was inserted directly into the gas stream at the end of the heated filter. The filter temperature was initially set at $42\pm 10^{\circ}\text{C}$ ($108\pm 18^{\circ}\text{F}$) and the probe temperature at 100°C (212°F). The temperature of these two heated zones was regulated as necessary to maintain the proper temperature of the gas exiting the filter. Due to the physical constraints of vertical sampling at the thermal oxidizer inlet, a flexible Teflon® line was used to connect the exit of the filter to the first impinger. The heated probe and filter box were a single unit mounted on a vertical monorail. The chilled impinger box was placed on the floor of the scaffolding.

The sampling trains were leak checked at the start and finish of sampling. EPA Method 5 protocol requires post-test leak checks and recommends pre-test leak checks. ERG protocol

also incorporates leak checks before and after every port change. An acceptable pre-test leak rate is less than 0.02 acfm (ft³/min) at approximately 15 inches of mercury (in. Hg). If, during testing, a piece of glassware needed to be emptied or replaced, a leak check was performed before the glassware piece was removed and after the train was re-assembled.

To perform a leak check of an assembled train, the nozzle end was capped off and a vacuum of 15 in. Hg was pulled in the system. When the system was evacuated, the volume of gas flowing through the system was timed for 60 seconds. After the leak rate was determined, the cap was slowly removed from the nozzle end until the vacuum dropped off, and then the pump was turned off. If the leak rate requirement was not met, the train was systematically checked by first capping the train at the filter, at the first impinger, etc., until the leak was located and corrected.

After a successful pre-test leak check had been conducted, all train components were at their specified temperatures and initial data were recorded (DGM reading), the test was initiated. Sampling train data were recorded every five minutes on standard data forms.

A checklist for sampling is included in Table 5-2.

The leak rates and sampling start and stop times are recorded in the sampling task log. Any other events that occur during sampling are also recorded on the sampling task log, such as pitot cleaning, thermocouple malfunctions, heater malfunctions, or any other unusual occurrences.

At the conclusion of the test run, the sample pump (or flow) was turned off, the probe was removed from the duct, a final DGM reading was taken, and a post-test leak check was completed. The procedure was identical to the pre-test procedure. However, the vacuum was at least one inch Hg higher than the highest vacuum attained during sampling. An acceptable leak

Table 5-2. Sampling Checklist, EPA Method 5A

Prior to Test:

1. Check the set of impingers to ensure that the number of impingers is correct and that the impingers are in the right order. Verify that the markings on the probe are correct; re-mark, if necessary.
2. Check that the set of glassware is complete and that all the pieces are correct and in the proper order and orientation.
3. Check that a sufficient number of the correct datasheets are available, and check barometric pressure.
4. Check that sampling equipment is ready for Method 3 analysis.
5. Leak check pitot tubes.
6. Examine meter box - level it and confirm that the pump is operational.
7. Assemble train to the filter and leak check at 20 in. Hg. Attach probe to train and perform final leak check; record leak rate and pressure on sampling log.
8. Check out thermocouples to verify that they are all reading correctly.
9. Turn on heaters and ensure that their temperatures are increasing.
10. Check that cooling water is on and flowing (if required). Add ice to impinger bucket(s).
11. Check isokinetic K Factor to be sure it has been calculated correctly. Refer to previous results to confirm assumptions. Two people should perform this calculation independently to double check the accuracy.
12. Have a spare probe liner, probe sheath, meter box, and filter prepared at the testing location.

During the Test:

1. Notify Test Crew Leader of any sampling problems ASAP. Fill in sampling log.
2. Perform simultaneous/concurrent testing with other locations (if applicable). Maintain filter temperature at $42 \pm 10^{\circ}\text{C}$ ($108 \pm 18^{\circ}\text{F}$), and keep temperature as steady as possible. Maintain impinger temperatures below 68°F . Maintain probe temperature above 212°F or at the temperature required to maintain the correct filter temperature.
3. Perform leak checks between ports and record on sampling log.
4. Record sampling rate, times, and location for the fixed gas (CO_2 , O_2) sample (if applicable).
5. Blow back pitot tubes every 15 minutes.

Table 5-2. Continued

6. Change filter if pressure drop exceeds 20 in. Hg.
7. Check impinger containing silica gel every 0.5 hour. If indicator changes color, request a pre-filled impinger from the recovery trailer and replace.
8. Check manometer fluid levels and zero every hour.

After Test is Completed:

1. Record final meter reading.
2. Check data sheet for completeness.
3. Perform final leak check of sampling train at maximum vacuum achieved during test.
4. Leak check each leg of pitot tubes.
5. Disassemble train. Cap sections. Take sections to recovery trailer.
6. Probe/cyclone recovery (use 500 mL bottles)

For TCE rinses (all trains)

- Attach flask to end of probe (use separate recovery containers for each sampling location)
- Add 50 mL TCE.
Put a brush down the probe, and brush back and forth
- Rinse back and forth in probe with TCE
- Empty TCE rinse into sample jar
- Repeat brushing and TCE rinse three times, so that the final combined TCE rinse volume is ≤ 150 mL.

7. Reattach nozzle and cap for next day. Store in dry safe place.
8. Make sure that data sheets are filled out completely and give to test crew leader.

rate is less than 4% of the average sampling rate or 0.02 acfm (whichever is lower). All final leak rates on site met the acceptance criterion.

5.1.4 Method 5A Sample Recovery

Recovery procedures were initiated as soon as the probe was removed from the stack and the post-test leak check was completed.

To facilitate transfer from the sampling location to the recovery trailer, the sampling train was disassembled into three sections:

- Nozzle/probe liner;
- Filter holder; and
- Impingers in their bucket.

Each of these sections was capped with Teflon[®] tape before removal to the recovery trailer. All train components were rinsed and the samples were collected in separate, pre-labeled, pre-cleaned sample containers to avoid cross-contamination of inlet and outlet samples. Trains of each type were recovered in separate areas of the recovery trailer to avoid cross-contamination or mistakes in recovery sequences.

Once in the recovery trailer, the sampling trains were recovered as separate front and back half fractions. A diagram illustrating front half and back half sampling train recovery procedures is shown in Figure 5-2.

No equipment with exposed metal surfaces was used in the recovery procedures. The weight gain in each of the impingers was recorded to determine the moisture content in the flue gas. Following weighing of the impingers, the front half of the train was recovered, including the front one half of the filter holder, filter and all sample-exposed surfaces forward of the filter. The probe liner was rinsed with TCE by tilting and rotating the probe while squirting TCE into its

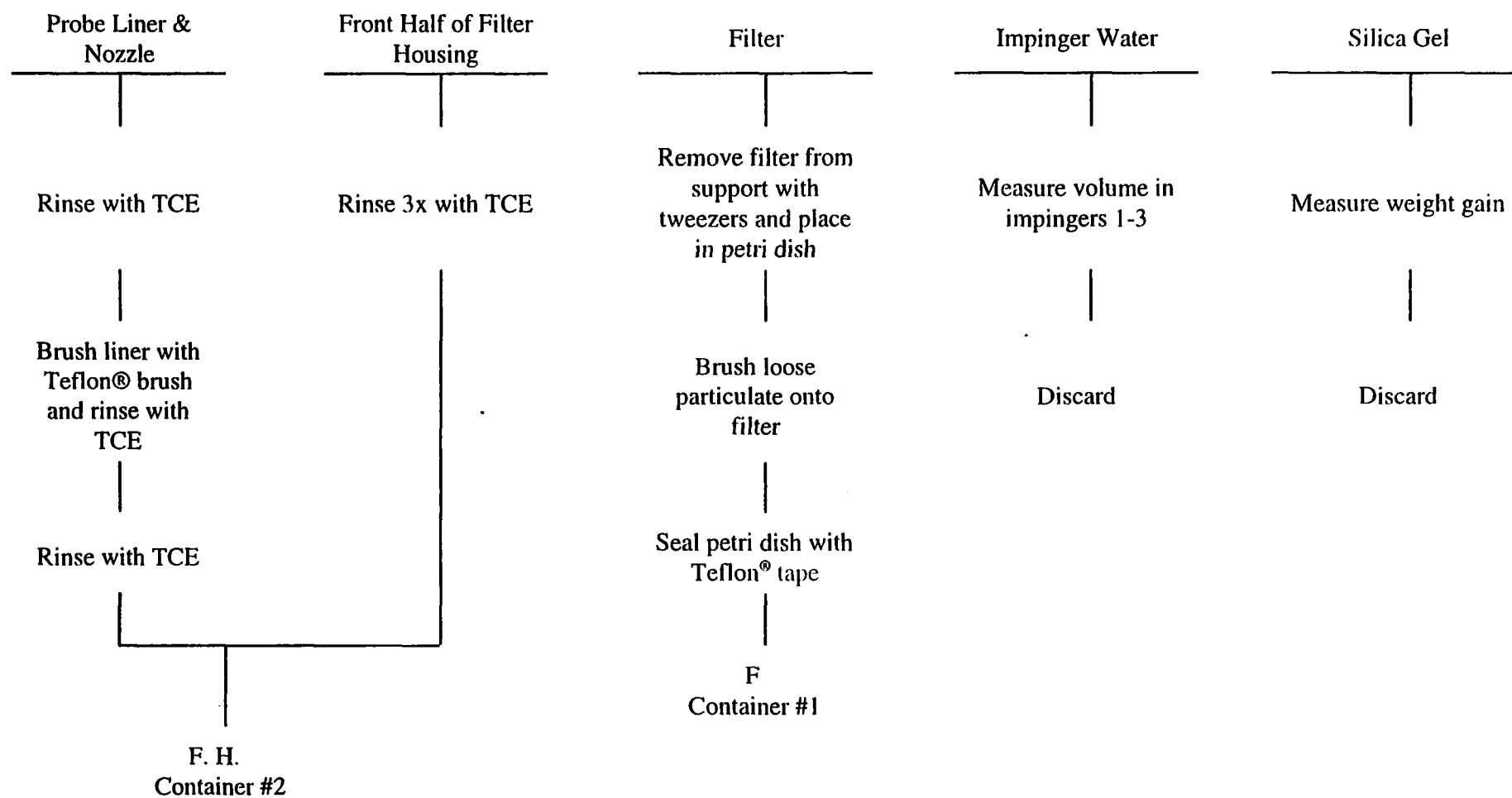


Figure 5-2. Method 5A Sample Recovery Scheme

upper end so that all inside surfaces were wetted. The TCE was quantitatively collected into the appropriate bottle. This rinse was followed by two additional brush/rinse sequences, using a non-metallic brush; the probe was held in an inclined position and TCE was squirted into the upper end as the brush was pushed through with a twisting action. All of the TCE and particulate material were caught in the sample container. The brush/rinse procedure was repeated until no visible particulate matter remained and finished with a final TCE rinse of the probe and brush. The front half of the glass filter holder was also rinsed with TCE until all visible particulate matter was removed. These rinses were added to the probe rinses. After all front half TCE washes were collected, the cap of the container was tightened, the liquid level was marked, and the bottle was weighed to determine the TCE rinse volume. This sample was labeled as Container #2. EPA Method 5A specifies that a nominal volume of 100 mL of TCE must be used for rinsing these sampling train components. For blank correction purposes, the exact weight or volume of TCE used was measured. A TCE reagent blank of approximately the same volume as the TCE rinses was analyzed with the samples.

The filter was carefully removed from the filter support and placed in a clean, well-marked glass petri dish (labeled Container #1) and sealed with Teflon® tape.

After the volume of liquid in the first three impingers was measured and the weight gain of the desiccant in the fourth impinger was determined, the contents of the impingers were discarded. The measured volume of water was used to adjust the moisture content of the sampled gas stream calculations.

5.1.5 Quality Control for Gravimetric Procedures

All quality control procedures specified in the test method were followed. All field reagent blanks were processed and analyzed as specified in the test method. Prior to each gravimetric determination, the balance calibration was verified using a series of certified weights covering the range of weights encountered for the samples.

5.2 Chlorinated Dibenzo-*p*-Dioxin and Chlorinated Dibenzofuran Emissions Testing Using EPA Method 23

The sampling and analytical method for determining flue gas emissions of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/PCDF) is EPA Method 23.

5.2.1 Method 23 Sampling Equipment

EPA Method 23 requires the sampling train shown in Figure 5-3.

The EPA Method 23 sampling train is similar to a Method 5 sampling train, with the following exceptions:

- All components (glass probe/nozzle, probe liner, all other glassware, filters) are pre-cleaned using solvent rinses and extraction procedures; and
- A condensing coil and XAD-2[®] resin sorbent module are located between the filter and the impinger train.

All sampling equipment specifications are detailed in EPA Method 23.

5.2.2 Method 23 Equipment Preparation

In addition to the standard EPA Method 5 requirements, Method 23 includes several unique preparation steps which ensure that the sampling train components are not contaminated with organic compounds that may interfere with analysis. The glassware, glass fiber filters, and sorbent resin were cleaned and the filters and resin were checked for 42 residuals before they were packed for shipment to the test site.

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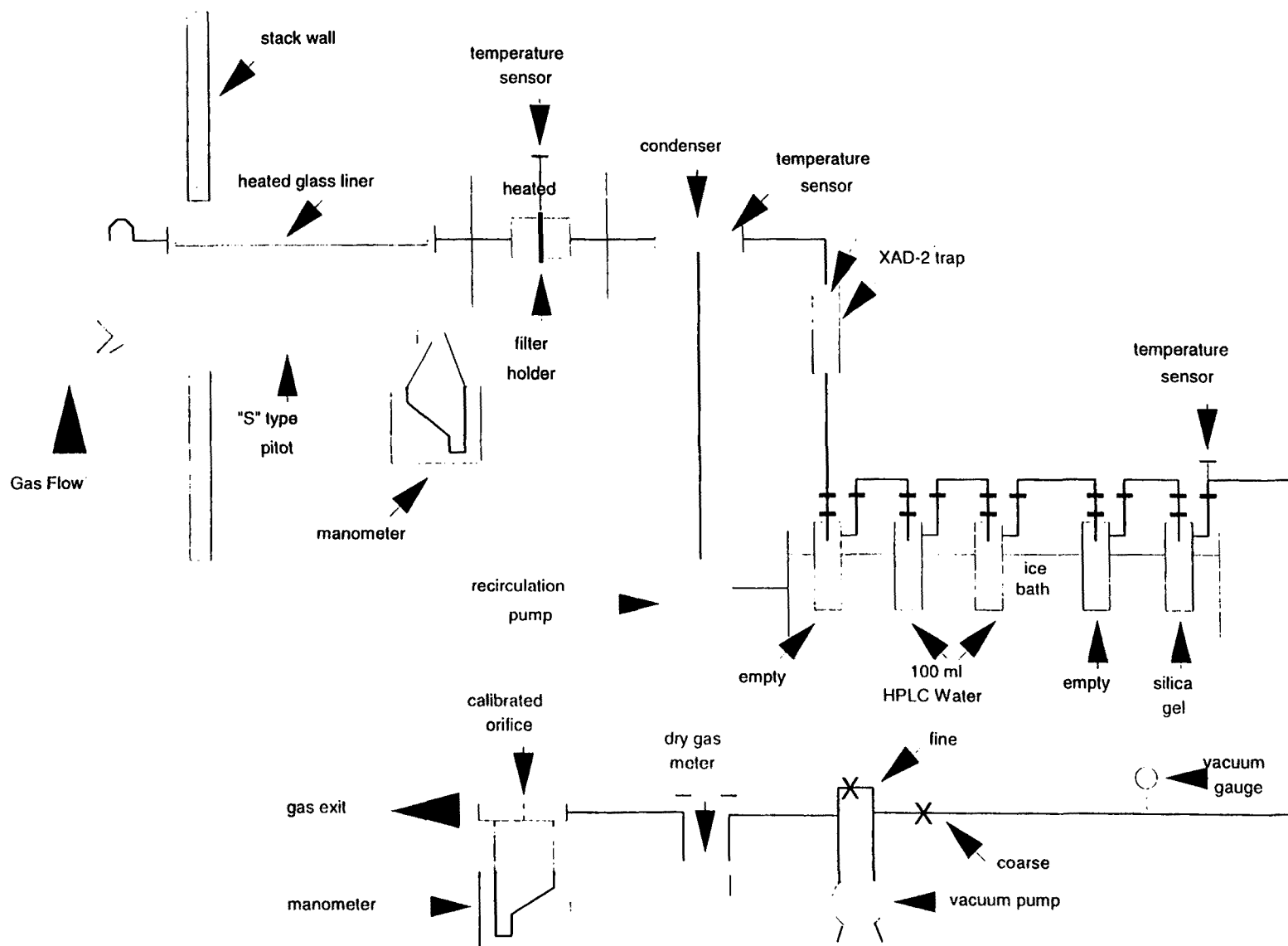


Figure 5-3. Method 23 Sampling Train Configuration

5.2.2.1 Glassware Preparation

Glassware was cleaned as shown in Table 5-3. Glassware was washed in soapy water, rinsed with distilled water, baked, and then rinsed with acetone followed by methylene chloride. Clean glassware was allowed to dry under a hood loosely covered with aluminum foil to prevent laboratory contamination. Once the glassware was dry, the ends exposed to air were sealed with methylene chloride-rinsed aluminum foil. All the glass components of the sampling train, including the glass nozzles plus any flasks, petri dishes, graduated cylinders, and pipets that are used during sampling and recovery were cleaned according to this procedure. Non-glass components (such as the Teflon[®]-coated filter screens and seals, tweezers, Teflon[®] squeeze bottles, Teflon[®] probe/nozzle brushes) were cleaned following the same procedure except that no baking was performed.

5.2.2.2 XAD-2[®] Sorbent Resin and Filter Preparation

XAD-2[®] sorbent resin and glass fiber filters were pre-cleaned by separate procedures according to EPA Method 23. Only pesticide-grade solvents and HPLC-grade water were used to prepare for D/F sampling, and to recover these sampling trains. The lot number, manufacturer, and grade of each reagent were recorded in the laboratory notebook.

To prepare the filters, a batch of 50 filters was placed in a Soxhlet extractor pre-cleaned by extraction with toluene. The Soxhlet extractor was charged with fresh toluene and refluxed for 16 hours. After the extraction, the toluene was analyzed as described in Sections 5.2 and 5.3 of EPA Method 23 for the presence of polychlorinated dibenzodioxins and dibenzofurans. If these analytes were found, the filters were re-extracted until the analyte was not detected. The cleaned filters were then dried under a clean nitrogen stream. Each filter was individually checked for holes, tears, creases or discoloration and, if any were found, was discarded. Acceptable filters were stored in a pre-cleaned petri dish, labeled by date of analysis, and sealed with Teflon[®] tape.

Table 5-3. EPA Method 23 Glassware Cleaning Procedure for Train Components, Sample Containers, and Laboratory Glassware

1. Soak all glassware in hot soapy water (laboratory detergent).
2. Rinse with tap water to remove soap.
3. Rinse three times with distilled/deionized water.
4. Bake at 450°F for 2 hours.^a
5. Rinse three times with pesticide-grade acetone.
6. Rinse three times with pesticide-grade methylene chloride.
7. Cap rinsed glassware with clean glass plugs or methylene chloride-rinsed aluminum foil.
8. Mark cleaned glassware with color-coded identification sticker.
9. Rinse glassware immediately before using with acetone and methylene chloride (laboratory proof).

^aStep (4) has been added to the cleanup procedure to replace the dichromate soak specified in the reference method. ERG has demonstrated in the past that Step (4) sufficiently removes organic artifacts. Step (4) is not used for probe liners and non-glass components of the sampling train that cannot withstand a temperature of 450°F (i.e., Teflon®-coated filter screens and seals, tweezers, Teflon® squeeze bottles, Teflon® probe/nozzle brushes).

To prepare the sorbent resin, the XAD-2® polymer resin was cleaned in the following order:

- Rinse with HPLC-grade water; discard water;
- Soak in HPLC-grade water overnight; discard water;
- Extract in a Soxhlet extractor with HPLC-grade water for 8 hours; discard water;
- Extract in a Soxhlet extractor with methanol for 22 hours; discard methanol;

- Extract in a Soxhlet extractor with methylene chloride for 22 hours; discard methylene chloride;
- Extract in a Soxhlet extractor with methylene chloride for 22 hours, retain an aliquot of the solvent for analysis for PCDDs/PCDFs by HRGC/HRMS; and
- Dry resin under a clean nitrogen stream.

Once the resin was completely dry, it was checked for the presence of methylene chloride, PCDDs, and PCDFs as described in Section 3.1.2.3.1 of EPA Method 23. If any analytes were found, the resin was re-extracted. If methylene chloride was found, the resin was dried until the excess solvent was removed. The sorbent was used within four weeks of cleaning.

The cleaned XAD-2[®] resin was spiked before shipment to the field test site with five PCDD/PCDF internal standards. Due to the special handling considerations required for the internal standards, the spiking was performed by Triangle Laboratories. For convenience and to minimize the potential for contamination, Triangle Laboratories also performed the resin and filter cleanup procedures and loaded the resin into the glass sampling modules.

5.2.2.3 Method 23 Sampling Train Preparation

The remaining preparation of the Method 23 sampling train included calibration and leak checking of all sampling train equipment, including meter boxes, thermocouples, nozzles, pitot tubes, and umbilicals. Referenced calibration procedures were followed when available. The results were properly documented and retained.

5.2.3 Method 23 Sampling Operations

5.2.3.1 Preliminary Measurements

Prior to sampling, preliminary measurements were taken to ensure isokinetic sampling. These preliminary measurements included determining the traverse point locations, performing a

preliminary velocity traverse, cyclonic flow check and moisture determination. These measurements were used to calculate a K factor. The K factor was used to determine an isokinetic sampling rate from stack gas flow readings taken during sampling. Measurements were then made of the duct inside diameter, port nozzle length, and the distances to the nearest upstream and downstream flow disturbances. These measurements were then used to determine sampling point locations by following EPA Reference Method 1 guidelines. The distances were then marked on the sampling probe using an indelible marker.

5.2.3.2 Assembling the EPA Method 23 Sampling Train

The components of the EPA Method 23 sampling train components were gathered in the recovery trailer and final assembly of the sampling train was performed at the stack location. First, the empty clean impingers were assembled and laid out in the proper order in the recovery trailer. Each ground glass joint was carefully inspected for hairline cracks. The first impinger was a knockout impinger which has a short tip. The purpose of this impinger was to collect condensate which formed in the coil and XAD-2[®] resin sampling module. The next two impingers were modified-tip impingers, which each contained 100 mL of HPLC-grade water. The fourth impinger was empty, and the fifth impinger contained 200-300 grams of blue indicating silica gel. After the impingers were loaded, each impinger was weighed, and the initial weights and contents of each impinger were recorded on a recovery data sheet. The heights of all the impingers were approximately the same to aid in obtaining a leak-free seal. The open ends of the train were sealed with methylene chloride-rinsed aluminum foil, or clean ground glass caps.

The filter was loaded into the filter holder in the recovery trailer. The filter holder was then capped off and placed with the sorbent resin sampling module and condenser coil (capped) into the impinger bucket. A supply of pre-cleaned foil and socket joints was also placed in the bucket inside a clean plastic bag for the convenience of the samplers. Sealing greases were not used to avoid contamination of the sample. The train components were transferred to the sampling location and assembled as shown in Figure 5-3.

5.2.3.3 Sampling Procedures

After the train was assembled, the heaters were turned on for the probe liner and heated filter box, and the sorbent module/condenser coil recirculating pump was turned on. When the system reached the appropriate temperatures, the sampling train was ready for a pre-test leak check. The temperature of the sorbent resin sampling module must not exceed 50°C (120°F) at any time and during testing the temperature must not exceed 20°C (68°F). The filter temperature was maintained at 120±14°F (248±25°F). The probe temperature was maintained above 100°C (212°F).

The sampling trains were leak checked at the start and finish of sampling. (EPA Method 5/23 protocol requires only post-test leak checks and recommends pre-test leak checks.) ERG protocol also incorporates leak checks before and after every port change. An acceptable pre-test leak rate is less than 0.02 acfm (ft³/min) at approximately 15 in. Hg. If, during the testing, a piece of glassware needed to be replaced or emptied, a leak check was performed before the glassware piece was removed, and after the train was re-assembled.

To perform a leak check of the assembled sampling train, the nozzle end was capped off and a vacuum of 15 in. Hg was pulled in the system. When the system was evacuated, the volume of gas flowing through the system was timed for 60 seconds. After the leak rate was determined, the cap was slowly removed from the nozzle end until the vacuum dropped off, and then the pump was turned off. If the leak rate requirement was not met, the sampling train was systematically checked by first capping the train at the filter, at the first impinger, etc., until the leak was located and corrected.

After a successful pre-test leak check has been conducted, all train components were at their specified temperatures, and initial data and DGM readings were recorded, the test was initiated. Sampling train data were recorded every five minutes on standard data forms. A checklist for PCDD/PCDF sampling is shown in Table 5-4. In performing PCDD/PCDF

Table 5-4. EPA Method 23 Sampling Checklist

Prior to Testing:

1. Check impinger set to verify the correct number, order, and orientation of impingers. Verify probe markings, and re-mark if necessary.
2. Check glassware to ensure that the number of pieces of each type is correct. Have a spare probe liner, probe sheath, meter box, and filter prepared at the test location.
3. Check that a sufficient number of the correct data sheets are available; check barometric pressure.
4. Prepare sampling equipment for CO₂/O₂, unless CEMs are being used for CO₂/O₂ determination.
5. Examine meter box: level, zero the manometers, and confirm that the pump is operational.
6. Verify that the filter is loaded correctly and as tightly as possible. Place filter in line with the train and leak check at 15 in. Hg.
7. Add probe to sampling train.
8. Check thermocouples; make sure that they are reading correctly.
9. Conduct pitot leak check and recheck manometer zero.
10. Perform final leak check: record leak rate and vacuum on sampling log.
11. Turn on heaters and verify that heat is increasing.
12. Check that cooling water is on and flowing. Add ice to impinger bucket(s).
13. Check isokinetic K factor to be sure that it has been calculated correctly. Refer to previous results to confirm assumptions. Two people should perform this calculation independently to double check it.

During Test:

1. Notify Test Crew Chief of any sampling problems ASAP. Train operator should fill in sampling log and document any abnormalities.
2. Perform simultaneous/concurrent testing with other locations (if applicable). Maintain filter temperature between 248°F±25°F. Keep temperature as steady as possible. Maintain the sorbent sampling module and impinger temperatures below 68°F. Maintain probe temperature above 212°F.
3. Perform leak checks between ports and record on data sheet. Perform a leak check if the test is stopped to change silica gel, to decant condensate, or to change filters.

Table 5-4. Continued

4. Record sampling times, rate, and location for the fixed gas bag sampling (CO, CO₂, O₂), if applicable.
5. Blow back pitot tubes periodically if moisture entrapment is expected.
6. Change filter if vacuum suddenly increases or exceeds 20 in. Hg.
7. Check impinger solutions every 0.5 hour. If the knockout impinger is approaching full, stop the test and empty the knockout impinger into a pre-weighed bottle and replace the empty knockout impinger in the train. Perform a leak check, and continue testing.
8. Check the silica gel impinger every 0.5 hour. If the color of the indicator begins to fade, request a pre-filled, pre-weighed impinger from the recovery trailer.
9. Check the ice in the impinger bucket frequently. If stack gas temperatures are high or the moisture content of the emission stream is high, the ice at the bottom of the impinger bucket will melt rapidly. Add more ice, as needed. Maintain the temperature of the gas at the condenser coil and silica gel impinger below 20°C (68°F).

After Test is Completed:

1. Record final DGM reading.
2. Perform final leak check of the sampling train at the maximum vacuum achieved during the test.
3. Perform final pitot leak check, check the functions (level, zero, etc.), and inspect for tip damage.
4. Check that the data sheet has been filled out completely. Verify that the impinger bucket identification is recorded on the data sheets. Note any abnormal conditions.
5. Disassemble sampling train, cap sections, and take each section and all data sheets down to the recovery trailer.
6. Use 500 mL bottles to recover the probe.
 - a) Bring probes into the recovery trailer (or other enclosed area).
 - b) Wipe the exterior of the probe to remove any loose material that could contaminate the sample.
 - c) Carefully remove the nozzle/probe liner and cap it off with aluminum foil that has been rinsed with methylene chloride.
 - d) For acetone rinses (all trains)
 - Attach a pre-cleaned cyclone flask to the probe to catch rinses.

Table 5-4. Continued

	Wet all sides of the probe interior with acetone
-	While holding the probe in an inclined position, put pre-cleaned probe brush down into probe and brush it in and out
-	Rinse the brush, while in the probe, with acetone
-	Repeat the brush/rinse sequence at least three times until all of the particulate material has been removed
	Recover acetone into a pre-weighed, pre-labeled sample container
e)	Repeat the brush/rinse sequence at least three times using methylene chloride. Recover the methylene chloride into the same acetone recovery bottle.
f)	Repeat the brush/rinse sequence at least three times using toluene. Recover the toluene into a separate pre-weighed pre-labeled sample container.
7.	Cap both ends of the nozzle/probe liner for the next day, and store in a dry safe place.
8.	Make sure that data sheets are completely filled out and legible, and give completed data sheets to the Test Crew Chief.

sampling, the temperature of the gas entering the resin sampling module must be below 20°C (68°F). The gas was cooled by a water jacket condenser through which ice water was circulated.

The leak rates and sampling start and stop times were recorded on the field sampling data sheets. Also, any other events that occurred during sampling were recorded on the task log (e.g., sorbent module heat excursions, pitot cleaning, thermocouple malfunctions, heater malfunctions, or any other unusual occurrences).

At the conclusion of the sampling run, the sample pump (or flow) was turned off, the probe was removed from the duct, a final DGM reading was taken, and a post-test leak check was completed. The leak test procedure is identical to the pre-test procedure. However, the vacuum for the post-test leak check should be at least one inch Hg higher than the highest vacuum attained during sampling. An acceptable leak rate is less than 4% of the average sampling rate or 0.02 acfm (whichever is lower).

5.2.4 PCDD/PCDF Sample Recovery

To facilitate transfer from the sampling location to the recovery trailer, the sampling train was disassembled into the following sections:

- Probe liner;
- Filter holder;
- Filter to condenser glassware;
- Condenser and sorbent module; and
- Impingers in their bucket.

Each of these sections was capped with ground glass caps or aluminum foil that had been rinsed with methylene chloride before removal to the recovery trailer. Once in the recovery trailer, field recovery followed the scheme shown in Figure 5-4.

The samples were recovered and stored in cleaned amber glass bottles to prevent degradation by light.

The probe and nozzle were first rinsed with approximately 100 mL of acetone and brushed to remove any particulate matter. This first rinse was followed with a rinse of methylene chloride. Both of these rinses were collected in the same bottle. The same two solvents were used to rinse the cyclone, front/back half of the filter holder, filter support, connecting glassware, and condenser. These rinses were added to the probe rinse bottle. All of the components listed above were again rinsed with toluene and the toluene rinses were collected in a separate container.

The contents of Impingers 1-4 (water) were discarded.

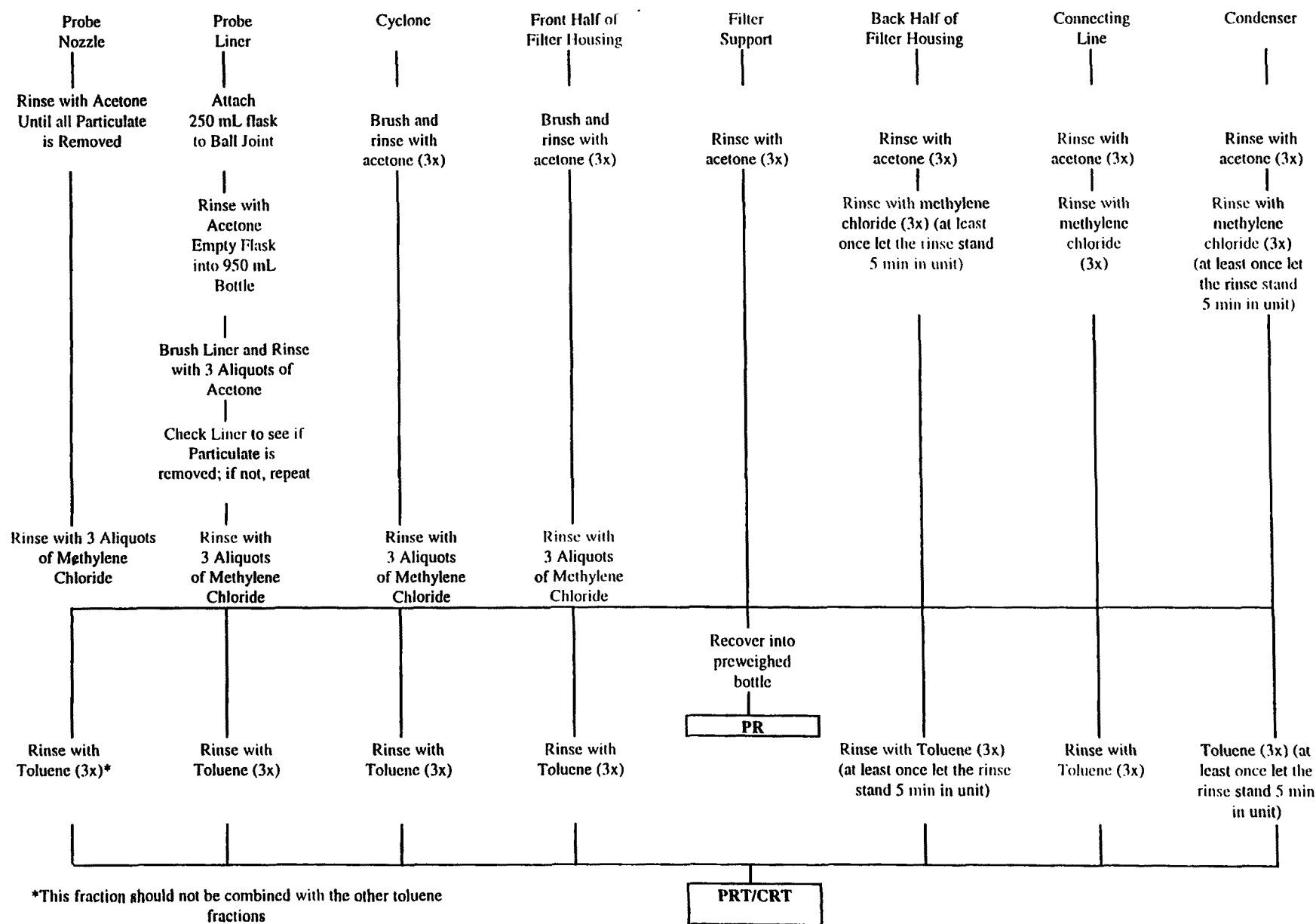


Figure 5-4. Method 23 Field Recovery Scheme

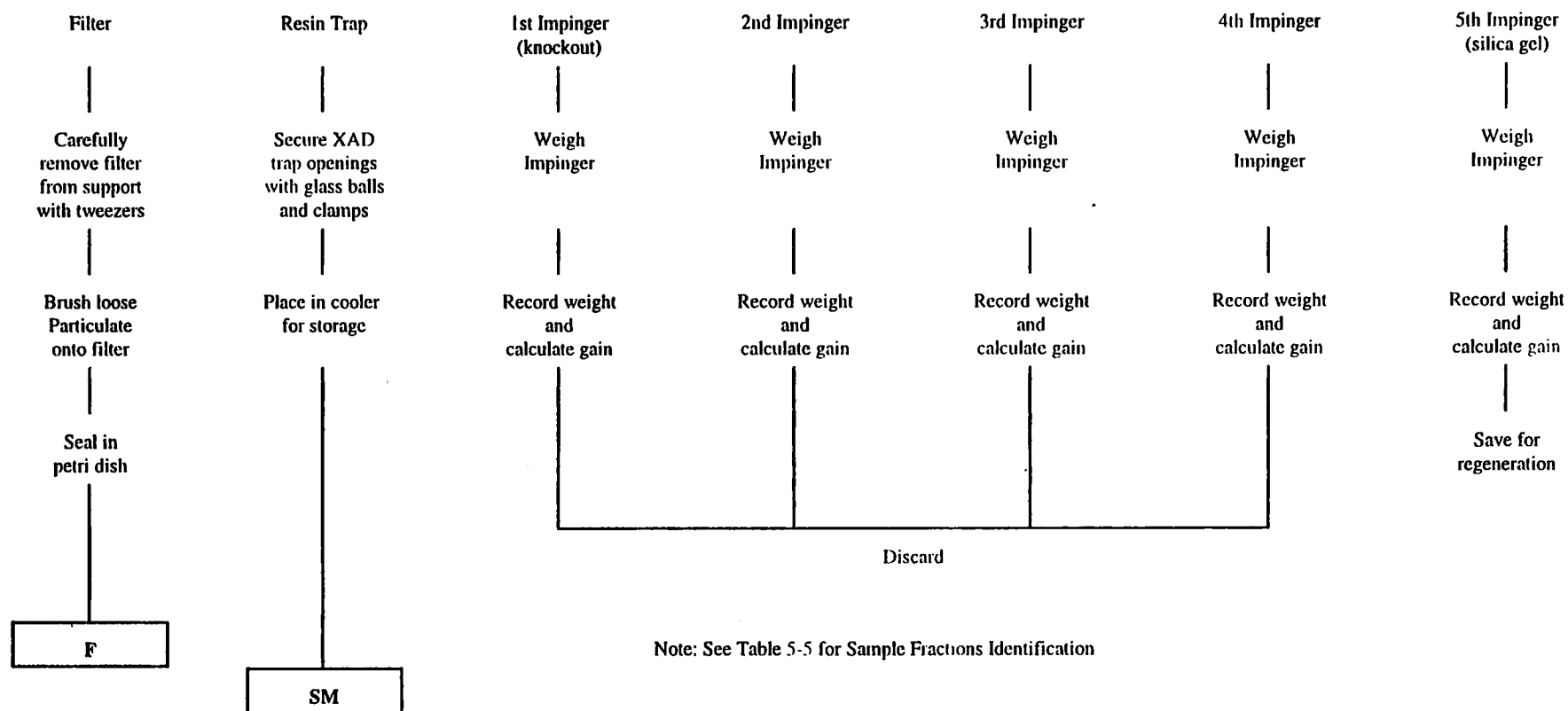


Figure 5-4. Method 23 Field Recovery Schedule (continued)

All solvents used for sampling train recovery were pesticide-grade. The use of the highest grade of reagents for sampling train recovery was essential to prevent the introduction of chemical impurities which interfere with the quantitative analytical determinations.

The sampling train components recovered in the field are listed in Table 5-5. The XAD-2[®] sorbent module was stored in coolers on ice at all times. The samples were delivered to the analytical laboratory upon return to ERG, accompanied by written information designating the analyses to be performed.

Table 5-5. Method 23 Sample Fractions Shipped to the Analytical Laboratory

Container	Code	Fraction
1	F	Filter(s)
2	Pr ^a	Acetone and methylene chloride rinses of nozzle/probe, cyclone, front half/back half filter holder, filter support, connecting glassware, condenser
3	PRT CRT	Toluene rinse of nozzle/probe, cyclone, front half/back half filter holder, filter support, connecting line and condenser
4	SM	XAD-2 [®] sorbent module

^aRinses include acetone and methylene chloride recovered into the same sample bottle.

5.2.5 PCDD/PCDF Analytical Procedures

The analytical procedure used to obtain analyte concentrations from a single flue gas sample incorporates HRGC and HRMS, with mass spectrometric resolution from 8000-10000. The PCDD/PCDF congeners that were designated as target analytes are listed in Table 5-6. The analyses were performed by Triangle Laboratories, Inc., using EPA Method 23/8290.

The Method 23 samples were prepared and analyzed according to the scheme shown in Figure 5-5. The XAD-2[®] and filter (along with the concentrated acetone/methylene chloride

Table 5-6. PCDD/PCDF Congeners To Be Analyzed

DIOXINS:

2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD)
1,2,3,7,8-pentachlorodibenzo-*p*-dioxin (1,2,3,7,8-PeCDD)
1,2,3,4,7,8-hexachlorodibenzo-*p*-dioxin (1,2,3,4,7,8-HxCDD)
1,2,3,6,7,8-hexachlorodibenzo-*p*-dioxin (1,2,3,6,7,8-HxCDD)
1,2,3,7,8,9-hexachlorodibenzo-*p*-dioxin (1,2,3,7,8,9-HxCDD)
1,2,3,4,6,7,8-heptachlorodibenzo-*p*-dioxin (1,2,3,4,6,7,8-HpCDD)
Total octachlorinated dibenzo-*p*-dioxin (OCDD)

FURANS:

2,3,7,8-tetrachlorodibenzofuran (2,3,7,8-TCDF)
1,2,3,7,8-pentachlorodibenzofuran (1,2,3,7,8-PeCDF)
2,3,4,7,8-pentachlorodibenzofuran (2,3,4,7,8-PeCDF)
1,2,3,4,7,8-hexachlorodibenzofuran (1,2,3,4,7,8-HxCDF)
1,2,3,6,7,8-hexachlorodibenzofuran (1,2,3,6,7,8-HxCDF)
2,3,4,6,7,8-hexachlorodibenzofuran (2,3,4,6,7,8-HxCDF)
1,2,3,7,8,9-hexachlorodibenzofuran (1,2,3,7,8,9-HxCDF)
1,2,3,4,6,7,8-heptachlorodibenzofuran (1,2,3,4,6,7,8-HpCDF)
1,2,3,4,7,8,9-heptachlorodibenzofuran (1,2,3,4,7,8,9-HpCDF)
Total octachlorinated dibenzofuran (OCDF)

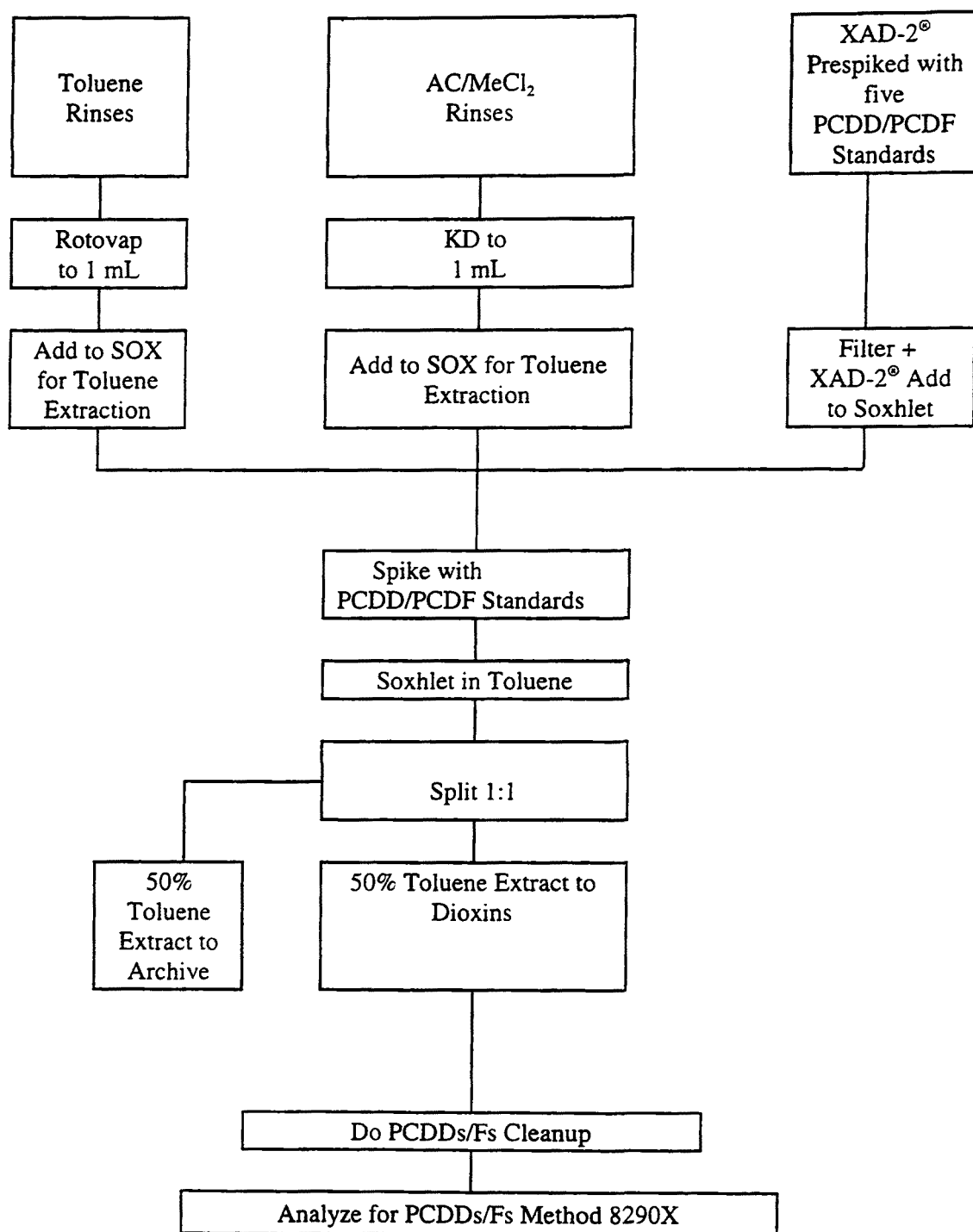


Figure 5-5. Extraction and Analysis Schematic for Method 23 Samples

rinses) were extracted with toluene, the extract processed through a column cleanup procedure, concentrated, and analyzed. For the D/F analysis, isotopically-labeled surrogate compounds and internal standards and surrogates that were used are described in detail in EPA Method 23/8290.

Data from the mass spectrometer were recorded and stored on a computer file as well as printed on paper. Results such as amount detected, detection limit, retention time, and internal standard and surrogate standard recoveries were calculated by computer. The chromatograms were retained by the analytical laboratory with copies included in the analytical report delivered to ERG.

5.2.5.1 Preparation of Samples for Extraction

Upon receipt of the sample shipment at Triangle Laboratories, the samples were checked against the Chain of Custody forms and then assigned an analytical laboratory sample number. Each sample component was re-weighed to determine if leakage had occurred during travel. Color, appearance, and other particulars of the samples were noted. Samples were extracted within 21 days of collection and processed through cleanup procedures before concentration and analysis.

5.2.5.2 Calibration of the GC/MS System

A five-point calibration curve for the GC/MS was prepared to demonstrate the linearity of the instrument response over the concentration range of interest. Relative response factors were calculated for each congener shown in Table 5-6; the response factors from the multipoint curve were verified on a daily basis using a continuing calibration standard consisting of a mid-level calibration standard. Instrument performance was acceptable only if the measured response factors for the labeled and unlabeled compounds and the ion abundance ratios were within the allowable limits specified in EPA Method 23.

5.2.6 PCDD/PCDF Analytical Quality Control

All quality control procedures specified in Method 23 were followed. Blanks were used to determine analytical contamination, calibration standards were used for instrument calibration and linearity checks, internal standards were used to determine isomer recoveries and adjust response factors for matrix effects, surrogate standards were used to measure the collection efficiency of the sampling methodology, and an alternate standard was used as a column efficiency check.

5.2.6.1 PCDD/PCDF Quality Control Blanks

Four different types of sample blanks were collected for D/F analysis. The types of blanks that were required are shown in Table 5-7.

Table 5-7. Method 23 Blanks Collected in the Field

Blank	Collection	Analysis
Field Blanks	One blank collected and analyzed for each sample location	Analyze with field samples
Glassware Proof Blank	Each train to be used (2) will be loaded and quantitatively recovered prior to sampling	Archive for potential analysis
Method Blank	At least one for each analytical batch (laboratory generated)	Analyze with each analytical batch of field samples
Reagent Blanks	One 500 mL sample for each reagent and lot	Archive for potential analysis

Reagent blanks consisting of 1000 mL of each reagent used at the test site were saved for potential analysis. Each reagent blank was of the same lot as was used during the sampling program. Each lot number and reagent grade was recorded on the field blank label and in the laboratory notebook (acetone, methylene chloride, toluene HPLC-grade water, filter, XAD-2®).

A glassware blank (proof blank) was recovered from each set of sampling train glassware that was used to collect the samples in the field. The pre-cleaned glassware, which consists of a probe liner, filter holder, condenser coil, and impinger set, was loaded as if for sampling and then used to check the effectiveness of the glassware cleaning procedure only if sample analysis indicated a potential contamination problem.

A field blank was collected from a set of D/F glassware that had been used to collect at least one sample and had been recovered. The sampling train was re-loaded, leak checked, and left at a sampling location during a test run. The train was then recovered. The purpose of the field blank was to measure the level of contamination that occurs from handling, loading, recovering, and transporting the sampling train. The field blanks were analyzed with the flue gas samples. If the field blank results are unsatisfactory in terms of contamination, reagent blanks may be analyzed to determine the specific source of the contamination.

In addition to the three types of blanks that are required for the sampling program, the analytical laboratory analyzed a method blank with each set of flue gas samples. This method blank consisted of preparing and analyzing an aliquot of toluene by the exact procedure used for the field sample analysis. The purpose of the method blank was to verify that there was no laboratory contamination of the field samples.

5.2.6.2 Quality Control Standards and Duplicates

Recoveries of the internal standards must be between 40 and 130% for the tetra- through hexachlorinated congeners and in the range of 25 to 130% for the hepta- and octachlorinated homologs. If these requirements are not met, the data will be acceptable if the signal-to-noise ratio is greater than or equal to 10. If these requirements are met, the results for the compounds sampled can be adjusted according to the internal standard recoveries.

Surrogate standard recoveries must be between 70 and 130%. If the recoveries of all surrogate standards are less than 70%, the surrogate standard recovery results can be used to adjust the results for the sampled species.

5.2.7 Analytes and Detection Limits for Method 23

The compounds of interest are the tetra- through octachlorinated dibenzodioxins and tetra- through octachlorinated dibenzofurans. The detection limit for the individual compounds is dependent upon the detection limit of the analytical method, the volume of the final extract, and the total volume of gaseous sample collected in the sampling train. Following the Method 23 protocol, the fractions to be analyzed from each sampling train include:

- Fraction 1—Filter;
- Fraction 2—XAD-2[®] sorbent module;
- Fraction 3—Acetone and methylene chloride rinses of all train components prior to sorbent module; and
- Fraction 4—Toluene rinses of all train components prior to the sorbent module.

Following the sample preparation protocol of EPA Method 23, a single combined sample is prepared for analysis for D/F by HRGC/HRMS. The individual components of this sample are no longer available for analysis. The final volume of this combined sample was 200 μ L; the injection into the HRGC/HRMS was 2 μ L. Using an instrument detection limit of 50 pg for tetra-, 250 pg for penta- through hepta-, and 500 pg for octachlorinated compounds, the total minimum detectable amounts were calculated and are shown in Table 5-8. Using a four-hour sampling time as selected by the EPA Work Assignment Manager at an assumed sampling rate of 0.75 cfm, the Method Detection Limits shown in Table 5-9 were achieved. The sampling flow rate at the outlet location was dictated by the flow rate of the stack gas since isokinetic sampling was performed.

Table 5-8. Analytical Detection Limits (HRGC/HRMS) for Dioxins/Furans

Analyte	Total Detectable Amount, ng
Tetra CDDs	5
Penta CDDs	25
Hexa CDDs	25
Hepta CDDs	25
Octa CDD	50
Tetra CDFs	5
Penta CDFs	25
Hexa CDFs	25
Hepta CDFs	25
Octa CDF	50

NOTE: D/F analysis by High Resolution Mass Spectrometry assumes a 2 μL injection of a 200 μL sample extract.

Table 5-9. PCDD/PCDF Method Detection Limits HRGC/HRMS

Sampling Time, Hours	4
Sampling Rate, cfm	0.75
Sample Volume, m^3	5.1
	MDL, ng/m^3
Tetra CDDs	0.98
Penta CDDs	4.9
Hexa CDDs	4.9
Hepta CDDs	4.9
Octa CDD	9.8
Tetra CDFs	0.98
Penta CDFs	4.9
Hexa CDFs	4.9
Hepta CDFs	4.9
Octa CDF	9.8

5.3 EPA Methods 1-4

5.3.1 *Traverse Point Location by EPA Method 1*

The number and location of sampling traverse points necessary for isokinetic and flow sampling were dictated by the EPA Method 1 protocol. These parameters were based upon the duct distance separating the sampling ports from the closest downstream and upstream flow disturbances. The minimum number of traverse points for a circular duct with an i.d. of 12 feet is 12.

5.3.2 *Volumetric Flow Rate Determination by EPA Method 2*

Volumetric flow rate was measured according to EPA Method 2. A Type K thermocouple was used to measure flue gas temperature and a Type S pitot tube was used to measure flue gas velocity.

5.3.2.1 Sampling Equipment Preparation

The pitot tubes were calibrated before use following the directions presented in EPA Method 2. The pitot tubes were leak checked before and after each sampling run.

5.3.2.2 Sampling Operations

The parameters that were measured include the pressure drop across the pitot tubes, stack temperature, stack static and ambient pressure. These parameters were measured at each traverse point, as applicable. A computer program was used to calculate the average velocity during the sampling period.

5.3.3 *O₂ and CO₂ Concentrations by EPA Method 3*

The O₂ and CO₂ concentrations were determined by Fyrite following EPA Method 3. Flue gas was extracted from the duct for analysis. The Method 3 analysis for O₂ and CO₂ were performed approximately every 30 minutes as a grab sample at the outlet and at the inlet.

5.3.4 *Average Moisture Determination by EPA Method 4*

The average flue gas moisture content was determined according to EPA Method 4. Before sampling, the initial weight of the impingers was recorded. When sampling was completed, the final weights of the impingers were recorded, and the weight gain was calculated. The weight gain and the volume of gas sampled were used to calculate the average moisture content (%) of the flue gas. The calculations were performed by computer. Method 4 was incorporated in the technique used for the Method 5A manual sampling method that was used during the test.

6.0 QUALITY ASSURANCE/QUALITY CONTROL

Specific Quality Assurance/Quality Control (QA/QC) procedures were strictly followed during this test program to ensure the production of useful and valid data throughout the course of the project. A detailed presentation of QC procedures for all sampling and analysis activities can be found in the Site Specific Test Plan and Quality Assurance Project Plan for this program. This section reports the results of all QC analyses so that the degree of data quality can be ascertained.

In summary, a high degree of data quality was maintained throughout the project. All sampling train leak checks met the QC criteria as specified in the methods. Isokinetic sampling rates were maintained within 10% of 100% isokinetic for all test runs. Good spike recoveries and close agreement between duplicate analyses were shown for the sample analyses.

6.1 Sampling QC Results

The following sections discuss the QC results of the specific sampling methods employed during this program.

6.2 D/F Sampling QC

Table 6-1 lists the pre- and post-test and port change leak check results. The acceptance criteria are that all post-test leak checks must be less than 0.02 cfm or 4% of the average sampling rate, whichever is less. All D/F leak checks met this criterion.

Table 6-2 presents the isokinetic sampling rates for the D/F sampling runs. The acceptance criterion is that the average sampling rate must be within 10% of 100% isokinetic. All D/F sampling runs met this criterion.

Table 6-1. Summary of Leak Checks Performed, Per Port, Method 23 Testing, Thermal Oxidizer, Inlet and Outlet

Date	Run #/Port	Initial Leak Check	Leak Check	Final Leak Check
Inlet				
9/22/97	1/A	0.004 @ 15" Hg	Passed ^a	0.011 @ 12" Hg
	1/B		Passed ^a	
9/23/97	2/A	0.01 @ 10" Hg	Passed ^a	Passed ^a
	2/B		Passed ^a	
	3/A	0.008 @ 15" Hg	Passed ^a	0.002 @ 15" Hg
	3/B		Passed ^a	
Outlet				
9/22/97	1/A	0.012 @ 15" Hg	0.007 @ 9" Hg	0.011 @ 5" Hg
	1/B		0.011 @ 5" Hg	
9/23/97	2/A	0.017 @ 10" Hg	0.007 @ 10" Hg	0.008 @ 10" Hg
	2/B		0.008 @ 10" Hg	
	3/A	0.014 @ 10" Hg	0.009 @ 9" Hg	0.009 @ 9" Hg
	3/B		0.009 @ 9" Hg	

^aActual value of leak check not recorded on field data sheet.

Table 6-2. Summary of Isokinetic Percentages

Date	Run #	Percent Isokinetic
Method 23, Thermal Oxidizer Inlet		
9/22/97	1	105
9/23/97	2	102
9/23/97	3	108
Method 23, Thermal Oxidizer Outlet		
9/22/97	1	98
9/23/97	2	101
9/23/97	3	98
Method 5A, Thermal Oxidizer Inlet		
9/22/97	1	98
9/23/97	2	103
9/23/97	3	104
Method 5A, Thermal Oxidizer Outlet		
9/22/97	1	104
9/23/97	2	103
9/23/97	3	102
Method 5A, APP Stack		
9/24/97	1	100
9/24/97	2	99
9/24/97	3	99
Method 5A, SBS Stack		
9/24/97	1	102
9/25/97	2	106
9/25/97	3	102

All dry gas meters are fully calibrated every six months against an EPA-approved intermediate standard. The full calibration factor is used to correct the actual metered sample volume to the true sample volume. To verify the full calibration, a post-test calibration is performed. The full and post-test calibration coefficients must be within 5% to meet ERG's internal QA/QC acceptance criterion. As shown in Table 6-3, the meter boxes used for the D/F and PM testing met this criterion.

Table 6-3. Dry Gas Meter Post-Test Calibration Results

Sampling Train	Meter Box Number	Full Calibration Factor	Post-Test Calibration Factor	Post Test Deviation^a %
D/F, TO Inlet	A-39	0.996	0.974	-2.2
D/F, TO Outlet	A-38	0.984	0.981	-0.30
PM, TO Inlet	A-40	0.984	0.980	-0.41
PM, TO Outlet	A-37	0.999	0.988	-1.1
PM, APP Stack	A-40	0.984	0.980	-0.41
PM, SBS Stack	A-39	0.996	0.974	-2.2

^aPost-Test Deviation (%) = (Post Test Factor - Full Factor) / Full Factor x 100.

Field blanks are collected to verify the absence of any sample contamination. A D/F train was assembled as if for sampling, leak checked at the sampling location, left at the sampling location for the duration of a test run, and then recovered. Table 6-4 presents the analytical results for the field blank and reagent blank as well as the laboratory method blank. No analytes were observed above method detection limits in any of the blank samples.

Table 6-4. Dioxin/Furan Field Blank Analysis Results

Congener	Reagent Blank ng Detected	Field Blank 1 ng Detected	Field Blank 2 ng Detected	Cleanup Blank ng Detected
2,3,7,8-TCDD	<0.006	<0.009	<0.005	<0.002
1,2,3,7,8-PeCDD	<0.009	<0.01	<0.007	<0.003
1,2,3,4,7,8-HxCDD	<0.009	<0.01	<0.009	<0.004
1,2,3,6,7,8-HxCDD	<0.007	<0.01	<0.007	<0.003
1,2,3,7,8,9-HxCDD	<0.008	<0.01	<0.007	<0.003
1,2,3,4,6,7,8-HpCDD	<0.01	<0.01	<0.01	<0.004
OCDD	<0.02	<0.01	<0.01	<0.007
2,3,7,8-TCDF	<0.004	<0.006	<0.003	<0.001
1,2,3,7,8-PeCDF	<0.006	<0.009	<0.005	<0.002
2,3,4,7,8-PeCDF	<0.006	<0.009	<0.005	<0.002
1,2,3,4,7,8-HxCDF	<0.006	0.008	<0.005	<0.002
1,2,3,6,7,8-HxCDF	<0.004	<0.006	<0.004	<0.002
2,3,4,6,7,8-HxCDF	<0.005	<0.008	<0.005	<0.006
1,2,3,7,8,9-HxCDF	<0.006	<0.008	<0.006	<0.003
1,2,3,4,6,7,8-HpCDF	<0.008	<0.01	<0.007	<0.003
1,2,3,4,7,8,9-HpCDF	<0.01	<0.01	<0.009	<0.004
OCDF	<0.01	<0.01	<0.01	<0.005

6.2.1 PM Sampling QC

Table 6-5 lists the pre- and post-test and port change leak check results for the thermal oxidizer inlet and outlet, the APP Stack, and the SBS Stack. The acceptance criterion of less than 0.02 cfm or 4% of the sampling rate, whichever is less, was met by all of the sampling trains.

Table 6-5. Summary of Leak Checks Performed, Per Port, Method 5A

Date	Run #/Port	Initial Leak Check	Leak Check	Final Leak Check
Thermal Oxidizer Inlet				
9/22/97	1/B	0.016 @ 15" Hg	Passed ^a	Passed ^a
	1/A		Passed ^a	
9/23/97	2/B	0.01 @ 10" Hg	Passed ^a	Passed ^a
	2/A		Passed ^a	
	3/B	0.001 @ 10" Hg	Passed ^a	0.002 @ 10" Hg
	3/A		Passed ^a	
Thermal Oxidizer Outlet				
9/22/97	1/B	0.007 @ 15" Hg	0.010 @ 5" Hg	0.020 @ 5" Hg
	1/A		0.020 @ 5" Hg	
9/23/97	2/B	0.010 @ 10" Hg	0.010 @ 10" Hg	0.006 @ 10" Hg
	2/A		0.006 @ 10" Hg	
	3/B	0.006 @ 9" Hg	0.007 @ 7" Hg	0.007 @ 7" Hg
	3/A		0.007 @ 7" Hg	
APP Stack				
9/24/97	1/Y	0.008 @ 15" Hg	Passed ^a	0.005 @ 15" Hg
	1/X		Passed ^a	
	2/X	0.012 @ 15" Hg	Passed ^a	0.014 @ 15" Hg
	2/Y		0.014 @ 15" Hg	
	3/Y	0.011 @ 15" Hg	Passed ^a	0.005 @ 15" Hg
	3/X		Passed ^a	
SBS Stack				
9/24/97	1/X	0.010 @ 15" Hg	Passed ^a	
	1/Y		Passed ^a	0.016 @ 15" Hg
9/25/97	2/Y	0.006 @ 15" Hg	Passed ^a	0.006 @ 15" Hg
	2/X		Passed ^a	
	3/X	0.008 @ 15" Hg	Passed ^a	0.007 @ 15" Hg
	3/Y		Passed ^a	

^aNumerical value not recorded.

Table 6-2 presents the isokinetic sampling rates for the PM sampling runs. The sampling rate acceptance criterion of being within 10% of 100% isokinetic was met for all sampling runs at the thermal oxidizer inlet and outlet, at the APP Stack, and at the SBS Stack.

As shown in Table 6-3, the calibration coefficients of the meter boxes used for the PM testing were within 5% of their full calibration coefficient, thus meeting the acceptance criterion.

6.3 Analytical QC Results

The following section reports QC parameters for the D/F and PM analytical results.

6.3.1 D/F Analytical Quality Control

One sample was generated for D/F analyses for each flue gas sample collected; the sample was subjected to a full screen analysis conducted using a DB-5[®] capillary gas chromatographic column which allows the separation of each class of chlorinated dioxins and furans (i.e., tetra-, penta-, etc.) and fully resolves 2,3,7,8-TCDD from the other TCDD isomers. Since no D/F were observed at a level five times the method detection limit, confirmation analysis to resolve the 2,3,7,8-TCDF from the other TCDF isomers (performed, if required, on a DB-225[®] capillary gas chromatographic column) was not required.

A component of the D/F QC program consists of the addition of isotopically labeled standards to each sample during various stages of analysis to determine recovery efficiencies and to aid in the quantitation of sampled D/F species. Four different types of standards are added:

- Surrogate standards are usually spiked onto the XAD-2[®] sorbent prior to shipment to the test site. Recovery of these compounds allows for the evaluation of overall sample collection efficiency and analytical matrix effects;
- Internal standards are spiked after sampling but prior to extraction.
- Alternate standards are also spiked after sampling but prior to extraction.

- Recovery percentages of internal standards are used in quantifying the D/F sampled from the stack gas. Recovery of alternate standards is used for determination of extraction/fractionation efficiencies.
- Recovery standards are added after fractionation, just prior to analysis by HRGC/HRMS.

The recovery of each of the spiked isotopically-labeled compounds was within the acceptance criteria of Method 23 (see Appendix C for analytical data).

6.3.2 PM Quality Control

All filters and TCE probe rinse residues were weighed to a constant weight following the procedures given in EPA Method 5A. The TCE probe rinse residues were blank-corrected using a known volume of TCE reagent. The five-place analytical balance calibration was verified prior to use by weighing a series of Class S weights which covered the range of weights encountered with the samples.

TECHNICAL REPORT DATA

(Please read Instructions on reverse before completing)

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