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12

EMISSIONS TEST REPORT:
CITY OF PHILADELPHIA NORTHWEST AND
EAST CENTRAL MUNICIPAL INCINERATORS

By

Roy Neulicht
Midwest Research Institute
Kansas City, Missouri 64110

VOLUME I - TECHNICAL REPORT

EPA Contract No. 68-02-3891
MRI Project No. 3281-L(1)

October 31, 1985

For

Mr. Victor Guide
Region III
U.S. Environmental Protection Agency
841 Chestnut Street
Philadelphia, Pennsylvania 19146

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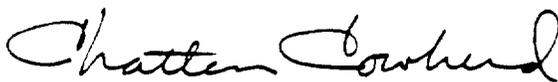
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PREFACE

This final report presents the results for emission tests conducted by Midwest Research Institute at the City of Philadelphia Northwest and East Central Municipal incinerators. The objective of the project was to quantify the polychlorinated dibenzo-p-dioxin and polychlorinated dibenzofuran emissions from these two facilities. The work was conducted under EPA Contract No. 68-02-3891. Primary responsibility for the project resided within the Environmental Systems Department with analytical support provided by the Chemical and Biological Sciences Department. Mr. Roy Neulicht was project leader. Mr. Tom Walker was responsible for supervising all emissions testing; Drs. John Stanley and Tom Capps acted as task leaders for the analytical aspects of the project. Ms. Carol Green, Mr. Scott Meeks, and Mr. Jack Balsinger monitored quality assurance for the project.

Approved for:

MIDWEST RESEARCH INSTITUTE



Chatten Cowherd, Director
Environmental Systems Department

October 31, 1985

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LIST OF ABBREVIATIONS AND SYMBOLS

ABBREVIATIONS

CEMS	-- Continuous Emission Monitoring System
dscf	-- dry standard cubic feet (68°F, 29.92 in.Hg)
EC	-- east central incinerator
ESP	-- electrostatic precipitator
°F	-- degrees Farenheit
ft	-- feet
g	-- gram
gr	-- grain
hr	-- hour
kg	-- kilogram
lb	-- pound
M3	-- Reference Method 3 (40CFR 60 Appendix A)
MM5	-- Method Method 5
mg	-- milligram
ng	-- nanogram
Nm ³	-- Normal cubic meter (20°C, 760 mmHg)
NW	-- northwest incinerator
ppm	-- parts per million (volume/volume)
QA	-- Quality Assurance
sec	-- second

SYMBOLS

CO	-- carbon monoxide
CO ₂	-- carbon dioxide
HCl	-- hydrogen chloride
HxCDD	-- hexachlorodibenzo-p-dioxin
HxCDF	-- hexachlorodibenzofuran
HpCDD	-- heptachlorodibenzo-p-dioxin
HpCDF	-- heptachlorodibenzofuran
NO _x	-- nitrogen oxide
O ₂	-- oxygen
OCDD	-- octachlorodibenzo-p-dioxin
OCDF	-- octachlorodibenzofuran
PCDD	-- polychlorinated dibenzo-p-dioxins
PCDF	-- polychlorinated dibenzofurans
P ₅ CDD	-- pentachlorodibenzo-p-dioxin
P ₅ CDF	-- pentachlorodibenzofuran
SO ₂	-- sulfur dioxide
TCDD	-- tetrachlorodibenzo-p-dioxin
TCDF	-- tetrachlorodibenzofuran
THC	-- total hydrocarbon
%	-- percent

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Assistance with Quality Assurance review by Mr. John Austin and Ms. Diana Pickens of EPA's Central Regional Laboratory is also acknowledged and appreciated.

SECTION 1.0

INTRODUCTION

The primary objective of this project was to quantify emissions of polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) at four City of Philadelphia municipal incinerator units operating under normal conditions. The project involved sampling and analysis for PCDDs and PCDFs at the City of Philadelphia's Northwest (NW) Unit 1, NW Unit 2, East Central (EC) Unit 1, and EC Unit 2.

Work at all four incinerator units included sampling and analyses of ESP fly ash and incinerator bottom ash for PCDDs and PCDFs; continuous monitoring of stack gas emissions for carbon monoxide (CO), carbon dioxide (CO₂), oxygen (O₂), total hydrocarbons (THC), nitrogen oxides (NO_x), and sulfur dioxide (SO₂); and recording of incinerator operating parameters. In addition, the project included emissions sampling by Modified Method 5 (MM5) to determine the PCDDs, PCDFs, total particulate matter, and hydrogen chloride (HCl) stack emissions from NW Unit 1 and NW Unit 2. Two identical Modified Method 5 (MM5) sampling trains were used during the test program; these trains are referred to as the "A" train and the "B" train. One sample train was analyzed for PCDDs and PCDFs; the other train was analyzed for particulate matter and HCl.

Although stack gas emissions of PCDD, PCDF, and particulate were not sampled from the EC units because of limited project resources, the NW and EC units are very similar in design. The intent of the study was to gather the monitoring data (CO, CO₂, O₂, and THC), opacity observations, and process operating data from all four units to verify that both the EC and NW units were operating similarly. If the units operate in a similar manner

and the monitored emissions are similar, one could hypothesize that the PCDD and PCDF emissions are similar (same order of magnitude). This report presents the results of the emissions tests, but does not compare data from the different units, nor draw any conclusions regarding the measured emissions levels.

The emission tests were conducted by MRI during the period of February 27 through March 7, 1985. Table 1 is a log of the test runs conducted during the study.

A summary of results is presented in Section 2. Section 3 presents a brief description of the facilities tested and a summary of the process operating parameters during the test period. Section 4 presents the complete results of the emissions tests and provides a discussion of the results; quality assurance results also are summarized in this section. Descriptions of the sampling and analysis protocols are provided in Section 5.

The appendices for this project are presented in eight separate volumes. The contents of the appendices are listed in the Table of Contents.

TABLE 1. TEST LOG

Run No.	Date	Facility ^a	Start time	End time	Type of test
1A	2/27/85	NW2	1545	1721	Dioxin
1B	2/27/85	NW2	1547	2006	Particulate/HCl
1A/B	2/27/85	NW2	1545	2006	CEMS ^b /fly ash/bottom ash
2A	2/28/85	NW2	1200	1712	Dioxin
2B	2/28/85	NW2	1212	1710	Particulate/HCl
2A/B	2/28/85	NW2	1200	1712	CEMS/fly ash/bottom ash
3A	3/01/85	NW2	0935	1425	Particulate ^c /HCl
3B	3/01/85	NW2	0941	1427	Dioxin
3A/B	3/01/85	NW2	0935	1427	CEMS/fly ash/bottom ash
4A	3/02/85	NW1	1130	1710	Dioxin
4B	3/02/85	NW1	1132	1712	Particulate/HCl
4A/B	3/02/85	NW1	1130	1712	CEMS/fly ash/bottom ash
5A	3/03/85	NW1	0940	1410	Dioxin
5B	3/03/85	NW1	0942	1412	Particulate/HCl
5A/B	3/03/85	NW1	0940	1412	CEMS/fly ash/bottom ash
5C	3/03/85	NW2	1610	1902	Particulate/HCl
6A	3/05/85	NW1	1340	1850	Dioxin
6B	3/05/85	NW1	1342	1852	Particulate/HCl
6A/B	3/05/85	NW1	1340	1852	CEMS/fly ash/bottom ash
7	3/07/85	EC1	1150	1516	CEMS/fly ash/bottom ash
8	3/07/85	EC2	1646	2012	CEMS/fly ash/bottom ash

^a
 NW1 = Northwest Unit No. 1
 NW2 = Northwest Unit No. 2
 EC1 = East Central Unit No. 1
 EC2 = East Central Unit No. 2

^b Continuous emission monitoring for O₂, CO₂, CO, THC, SO₂, NO_x.

^c Probe liner broken at end of test; post test leak check failed.

SECTION 2.0

SUMMARY OF RESULTS

Table 2 summarizes the test results for all four incinerator units. Total tetra-octa chlorinated dibenzodioxin (PCDDs), total tetra-octa chlorinated dibenzofuran (PCDFs), 2,3,7,8-tetraCDD, and 2,3,7,8-tetraCDF results are reported for the stack emissions, electrostatic precipitator (ESP) fly ash, and bottom ash. Particulate matter, HCl, opacity, and continuous emission monitoring (O_2 , CO_2 , CO, THC, SO_2 , and NO_x) results also are presented.

For the two NW incinerator units, the measured total tetra-octaCDD concentrations range from 1,000 to 4,700 nanograms/normal cubic meter (ng/Nm^3), resulting in measured emission rates of 41,000 to 170,000 ng/sec ; total tetra-octaCDF concentrations range from 1,000 to 5,000 ng/Nm^3 , resulting in measured emission rates of 41,000 to 180,000 ng/sec .

Measured particulate matter concentrations corrected to 12% CO_2 range from 0.21 to 3.5 g/Nm^3 (0.09 to 1.5 $gr/dscf$). All measurements except Test 1B at NW Unit 2 were in the 0.21 to 0.43 g/Nm^3 (0.09 to 0.19 $gr/dscf$) range. Calculated particulate matter emission rates range from 13 to 175 kg/hr (29 to 385 lb/hr); without Test 1B, the range is 13 to 24 kg/hr (29 to 52 lb/hr). Measured HCl emission rates range from 7 to 32 kg/hr .

For the four incinerator units, the measured average oxygen concentration ranged from 13.4 to 16.6%, and the measured average carbon dioxide concentration ranged from 3.3 to 5.6%. Average carbon monoxide concentrations ranged from 16 to 240 ppm, while the average total hydrocarbon concentration ranged from less than 1 (< 1) ppm to 7 ppm.

TABLE 2. (continued)

Run No.:	Northwest Unit No. 1		Northwest Unit No. 2		East Central Unit No. 1	East Central Unit No. 2				
	4AB	5AB	6AB	7AB			2AB	3AB	5C	
Avg. CO ₂	%	5.5	4.8	5.6	5.2	4.4	4.5	NH	4.2	3.3
Avg. CO	ppm	238	240	204	150	193	202	NH	57	16
Avg. THC	ppm	3	2	7	6	5	< 1	NH	< 1	1
Avg. SO ₂ ^d	ppm	203	156	173	122	167	152	NH	40	26
Avg. NO _x	ppm	84	78	96	93	79	81	NH	62	48
FLY Ash										
2,3,7,8-TCDD	ng/g	6.6	6.2 ^e	3.9	5.0 ^e	3.7	f	NH	3.0 ^e	0.57 ^e
2,3,7,8-TCDF	ng/g	13	11 ^e	6.8	8.7 ^e	6.3	f	NH	6.1 ^e	1.4 ^e
Total tetra-octa CDD	ng/g	1,900	2,100 ^e	1,800	1,500 ^e	1,000	f	NH	1,900 ^e	720 ^e
Total tetra-octa CDF	ng/g	1,300	1,600 ^e	1,600	1,200 ^e	900	f	NH	940 ^e	270 ^e
Bottom Ash										
2,3,7,8-TCDD	ng/g	1.5	0.59 ^e	0.92	0.34 ^e	0.79	0.83	NH	0.38 ^e	0.02 ^e
2,3,7,8-TCDF	ng/g	2.7	0.90 ^e	1.5	0.56 ^e	0.86	1.4	NH	0.29 ^e	0.04 ^e
Total tetra-octa CDD	ng/g	260	111 ^e	170	48 ^e	98	120	NH	76 ^e	7.0 ^e
Total tetra-octa CDF	ng/g	160	64 ^e	110	32 ^e	43	79	NH	34 ^e	< 3

^a NH = not measured.

^b Low surrogate recovery for this sample; reported value should be considered an estimate.

^c Broken probe at end of test; leak check failed; particulate test repeated as Run 5C.

^d SO₂ results are probably biased high; interference due to stack gas moisture is suspected.

^e Average of replicate analyses.

^f To be reanalyzed and reported at a later date.

The total tetra-octaCDD measured in the ESP fly ash samples ranges from 720 to 2,100 ng/g; the measured total tetra-octaCDF ranges from 270 to 1,600 ng/g. The total tetra-octaCDD measured in the bottom ash samples ranges from 7.0 to 260 ng/g; the measured total tetra-octaCDF ranges from < 3 to 160 ng/g.

SECTION 3.0

INCINERATOR DESCRIPTION AND OPERATION

The City of Philadelphia's municipal incinerators are briefly described in Section 3.1. The operating conditions of the incinerator during the test period are presented in Section 3.2.

3.1 DESCRIPTION OF CITY OF PHILADELPHIA NORTHWEST AND EAST CENTRAL INCINERATORS

The City of Philadelphia northwest incinerator plant operates two refuse furnaces which can each process up to 375 tons of trash per day. The operation of the units is designed to achieve a 90% volume reduction in refuse. Each furnace consists of a single (primary) excess air combustion chamber with air cooled walls. Exhausts from each furnace pass through cooling sprays, two evaporation towers, a two-stage (field) ESP, and the stack. Figure 1 is a schematic of the northwest incinerator furnace.

An elevated crane with a clam-shell bucket lifts the refuse from the storage bin into a charging hopper and water-cooled gravity chute. Refuse drops from the chute onto the inclined traveling grate, which continuously feeds the refuse onto a horizontal traveling grate. Each grate is driven by independent variable speed motors. The total effective grate area provided by the two grates is 480 ft² per furnace. Combustion air (taken from outside the building) is provided to each furnace by a 50 hp forced draft fan. The underfire/overfire air ratio is adjusted by dampers in the forced draft ductwork. The refractory lined furnaces are designed to operated at a maximum temperature of 2100°F.

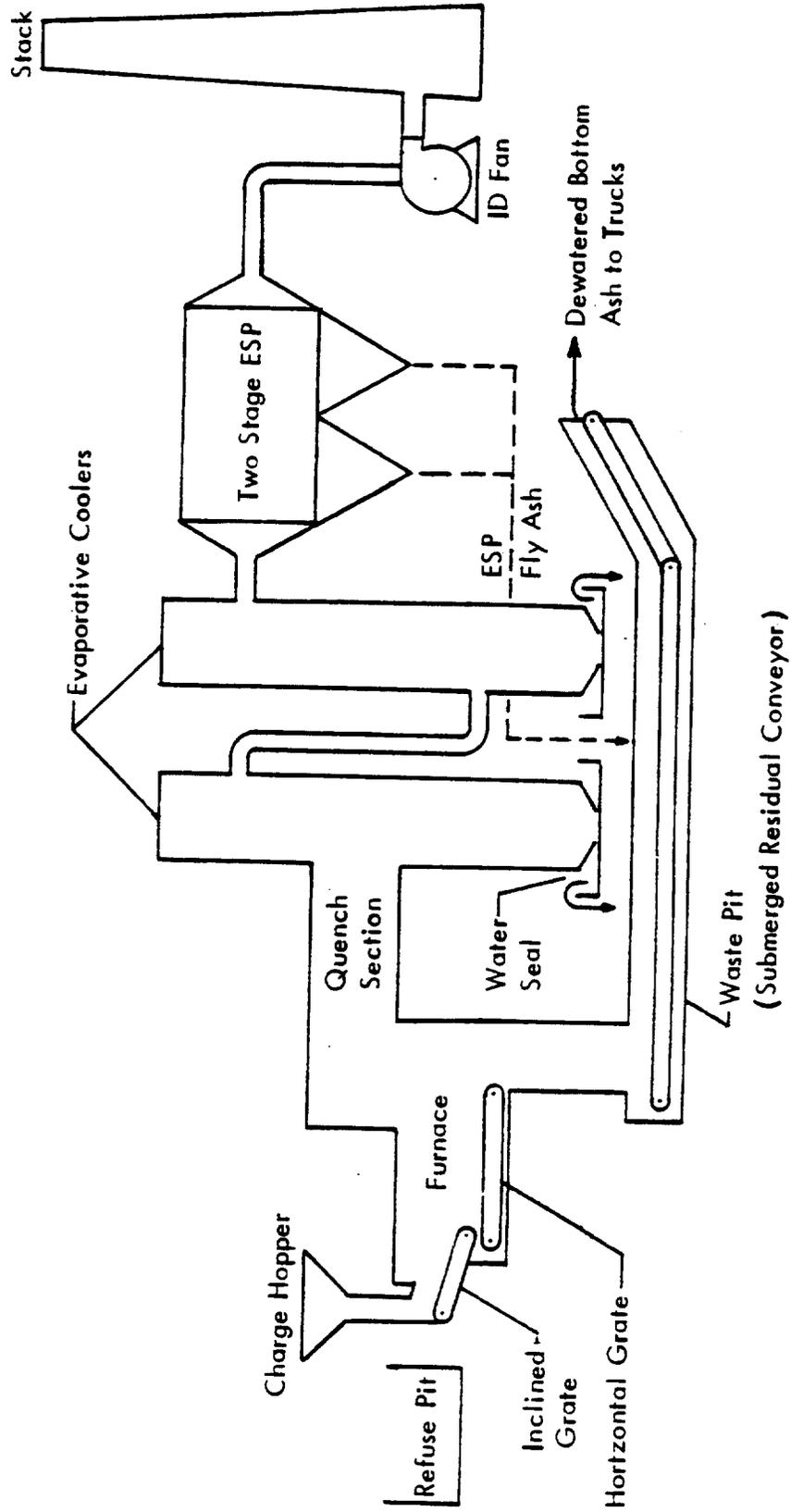


Figure 1. Simplified schematic of Northwest incinerator (Unit 1 or 2)

Incinerator residues drop off the edge of the horizontal grate and fall through a series of residue-quenching sprays and onto a submerged residue conveyor. The ESP fly ash also is discharged onto the submerged residue conveyor. Residue is discharged into trucks.

Furnace flue gases exit the furnaces through spray chambers where atomized water cools the gases to the designed ESP operating temperature. The cooling water evaporates in the two evaporation towers so that flue gases entering the ESP are between 550° and 600°F. The cyclonic flow in the towers is also designed to remove the largest particles from the flue gases prior to their entry into the ESP.

Flue gases leave the towers and travel through the precipitator breeching where turning vanes and baffle plates ensure even gas distribution throughout the device. Treated flue gases are drawn from each precipitator by an induced draft variable speed fan and exit the plant through a single stack.

The EC incinerator units are similar in design to the NW incinerator units, with only minor differences.

3.2 INCINERATOR OPERATION

The incinerator and electrostatic precipitator operating conditions during the tests are summarized in Tables 3, 4, and 5 for NW Unit 1, NW Unit 2, and EC Units 1 and 2, respectively.

The purpose of the test primarily was to determine PCDD, PCDF, and particulate emissions from the incinerator during normal operation. Two main criteria were agreed upon by the EPA and the City of Philadelphia as indicating normal operation:

TABLE 3. SUMMARY OF PROCESS OPERATING DATA, NW UNIT NO. 1

Run Date	4A/B	5A/B	6A/B
	3/02/85	3/03/85	3/05/85
Time period	1130-1716	0938-1415	1336-1855
Indicated inclined stoker speed, avg. ft/hr (range)	66 (61-70)	60 (60)	70 (70)
Measured ^a inclined stoker speed, avg. ft/hr (range)	75 ^b c	74 (74)	86 (86)
Indicated horizontal stoker speed, avg. ft/hr (range)	89 (80-95)	70 (70)	80 (78-90)
Measured horizontal stoker speed, avg. ft/hr (range)	123 (120-128)	115 (113-115)	140 (132-160)
Furnace temperature, avg. °F ^d (range)	1910 (1700-2100)	1770 (1600-2000)	1760 (1550-2000)
Furnace draft, avg. in. H ₂ O (range)	0.50 (0.50-0.55)	0.50 (0.45-0.50)	0.40 (0.35-0.45)
Field A, primary voltage, avg. volts (range)	250 (230-270)	240 (230-250)	230 (210-240)
Field A, primary current, avg. amps (range)	105 (90-115)	105 (90-125)	110 (105-120)
Field A, secondary current, avg. MA (range)	460 (330-480)	410 (340-490)	420 (380-480)
Field B, primary voltage, avg. volts (range)	235 (185-260)	250 (250-260)	270 (270)
Field B, primary current, avg. amps (range)	120 (120)	120 (120)	100 (95-105)
Field B, secondary current, avg. MA (range)	375 (300-415)	285 (240-410)	235 (230-240)

a Visually timed.

b At indicated speed of 61.

c Only one reading.

d Average temperature calculated from 1/2-hr readings recorded during each test; ranges are minimum/maximum values on the chart record for each test period.

TABLE 4. SUMMARY OF PROCESS OPERATING DATA, NW UNIT NO. 2

Run Date Time period	1A/B 2/27/85 1530-2010	2A/B 2/28/85 1200-1717	3A/B 3/01/85 0935-1427	5C 3/03/85 1610-1902
Indicated inclined stoker speed, avg. ft/hr (range)	70 (70)	70 (70)	71 (71)	61 (61)
Measured ^a inclined stoker speed, avg. ft/hr (range)	b	b	b	73 (72-73)
Indicated horizontal stoker speed, avg. ft/hr (range)	65 (65)	90 (75-100)	93 (70-100)	86 (75-105)
Measured horizontal stoker speed, avg. ft/hr (range)	b	b	150 (133-160)	144 (131-167)
Furnace temperature, avg. °F ^c (range)	1,730 (1600-2000)	1,740 (1550-1900)	1,700 (1550-1850)	1,750 (1650-1950)
Furnace draft, avg. in. H ₂ O (range)	0.40 (0.35-0.50)	0.40 (0.35-0.42)	0.30 (0.30-0.35)	0.30 (0.25-0.35)
Field A, primary voltage, avg. volts (range)	225 (210-230)	215 (210-240)	215 (210-220)	215 (200-220)
Field A, primary current, avg. amps (range)	80 (60-90)	70 (60-90)	80 (65-100)	85 (75-95)
Field A, secondary current, avg. MA (range)	245 (200-280)	280 (240-300)	290 (260-310)	285 (260-300)
Field B, primary voltage, avg. volts (range)	185 (155-220)	180 (165-200)	170 (160-190)	175 (165-180)
Field B, primary current, avg. amps (range)	100 (95-100)	95 (80-110)	100 (95-100)	100 (100)
Field B, secondary current, avg. MA (range)	550 (550)	550 (550)	650 (600-700)	550 (550)

a Visually limited.

b Not measured.

c Average temperature calculated from 1/2-hr readings recorded during each test; ranges are minimum/maximum values on the chart record for each test period.

TABLE 5. SUMMARY OF PROCESS OPERATING DATA: EC UNIT NOS. 1 AND 2

Run Date Time period	7 3/07/85 1150-1513	8 3/07/85 1646-2012
Unit	1	2
Indicated inclined grate speed, avg. ft/hr (range)	80 (80)	79 (62-83)
Measured inclined grate speed, avg. ft/hr (range)	101 (91-103)	84 (72-98)
Indicated horizontal grate speed, avg. ft/hr (range)	a	a
Measured horizontal grate speed, avg. ft/hr (range)	147 (145-150)	160 (160)
Furnace temperature, avg. °F (range)	1840 (1740-1940)	1890 (1760-2000)
Furnace draft, avg. in. H ₂ O (range)	0.15 ^b (0.1-0.2)	0.20 (0.10-0.20)
Field A, primary voltage, avg. volts (range)	240 (190-280)	230 (220-230)
Field A, primary current, avg. amps (range)	115 (70-175)	145 (145)
Field A, secondary current, avg. MA (range)	390 (300-600)	590 (550-600)
Field B, primary voltage, avg. volts (range)	360 (360-380)	430 (410-450)
Field B, primary current, avg. amps (range)	170 (150-190)	195 (180-200)
Field B, secondary current, avg. MA (range)	720 (670-790)	840 (790-880)

^a No working indicator.

^b Gauge at furnace, not at control panel.

1. Furnace temperature between 1400° and 1800°F; and
2. An indicated inclined grate speed of 70 ft/hr.

The Inclined grate speed is used as the indicator of feedrate to the incinerator. Another indicator of feedrate is the number of charges (crane loads) per hour to the charge hopper. Previous tests at these facilities indicate 20 charges per hour is normal. Both these parameters were monitored during the emission testing in order to verify that the facilities were operating normally. Actual measurements of the weight of refuse being charged to the incinerator were not taken.

With the exception of run 4 on NW Unit 1, the furnace temperature during the tests averaged between 1600° to 1800°F. Occasional excursions above 1800°F to as high as 2100°F were noted. The furnace high temperature warning is at 2100°F.

The indicated inclined stoker speeds ranged from 60 (one test) to 70 ft/hr at the NW Units 1 and 2. During the tests, the indicated inclined stoker speeds for both East Central units was 80 ft/hr. During the testing a discrepancy between the indicated grate speeds and the observed (measured) grate speeds was noted. Therefore, the grate speeds were occasionally measured by timing the number of grate sections passing a fixed point. Table 6 summarizes the comparison of the measured and indicated grate speeds for each unit; speeds for both the inclined and the horizontal grates are presented.

Table 7 summarizes the observed charging rate (crane loads/hr) of refuse to the feed hopper. Hourly readings of observed charging rates ranged from 12 to 24 charges per hour, and averaged 18.5 charges per hour.

TABLE 6. SUMMARY OF INDICATED VERSUS MEASURED GRATE SPEEDS (ft/hr)

	NW Unit 1		NW Unit 2		EC Unit 1		EC Unit 2	
	Indicated	Measured ^a						
Inclined grate:	60	74	61	73	80	101	62	72
	70	86	70	84			71	84
Correction factor ^b		1.2		1.2		1.3		1.2
Horizontal grate:	70	114	80	132				
	80	130	105	167				
Correction factor ^b		1.6		1.6				

^a Average of all measurements taken at listed indicated speed.

^b Actual (measured) speed = indicated speed x correction factor.

TABLE 7. REFUSE CHARGE RATE TO FEED HOPPER

Run	Facility	Date	Begin time	End time	Observed charges (charges/hr)
1AB	NW No. 2	2/27/85	1545	1645	17
			1645	1730	12/45 min
			1820	1920	20
			1920	2000	11/40 min
2AB	NW No. 2	2/28/85	1200	1300	20
			1300	1400	18
			1400	1500	17
			1500	1600	21
			1600	1700	18
			1700	1715	3
3AB	NW No. 2	3/01/85	0930	1030	18
			1030	1130	20
			1130	1230	18
			1230	1330	18
			1330	1430	17
4AB	NW No. 1	3/02/85	1115	1215	24
			1215	1315	24
			1315	1415	15
			1415	1515	19
			1515	1615	18
			1615	1715	18
5AB	NW No. 1	3/03/85	0940	1040	12
			1040	1140	21
			1140	1240	16
			1240	1340	18
			1340	1410	9/30 min
5C	NW No. 2	3/03/85	1610	1710	18
			1710	1810	21
			1810	1901	15/50 min
6	NW No. 1	3/05/85	1348	1448	22
			1448	1548	21
			1655	1755	23
			1755	1855	17
7	EC No. 1	3/07/85	1206	1306	19
			1306	1406	19
			1406	1506	19
8	EC No. 2	3/07/85	1707	1807	17
			1807	1907	13
			1907	2007	12

SECTION 4.0

RESULTS AND DISCUSSION OF RESULTS

4.1 POLYCHLORINATED DIBENZO-p-DIOXINS (PCDDs) AND POLYCHLORINATED DIBENZOFURANS (PCDFs)

4.1.1 Stack Gas Emissions

Tables 8 and 9 present the PCDD and PCDF results of the stack emissions measurements from NW Units 1 and 2, respectively. Low surrogate recoveries were obtained during analysis of Run 6A. Although the results are reported, the results should be considered an estimate. The particulate sample taken simultaneously, Run 6B, currently is being analyzed for PCDDs and PCDFs. The results of this analysis will be reported as an addendum to this report. Results for the field blank sampling train also are reported in Table 9; no blank problems were identified.

Tables 10 and 11 present the 2,3,7,8-substituted tetra-octa isomers of dibenzodioxin and dibenzofuran measured in the stack gas emissions from NW Units 1 and 2, respectively. These results were obtained by identifying the chromatogram peaks for the specific isomers of interest by their relative retention times. Results for the specific isomer were then calculated using the response factor for the homolog group, in general; the response factors for each homolog group were calculated from the calibration standard. A more detailed explanation of the analyses and calculations conducted is presented in Section 5.

TABLE 8. SUMMARY OF TOTAL TETRA-OCTA DIBENZO-P-DIOXIN AND DIBENZOFURAN EMISSIONS, MW UNIT NO. 1

Run No.	4A	5A	6A ^a	6B
Date	3/02/85	3/03/85	3/05/85	3/05/85
Start time	1130	0940	1340	1342
End time	1710	1410	1850	1852
Sample time, min	240	240	240	240
Sample volume, Nm ³ (dscf)	2,607 (92,065)	2,486 (87,803)	2,543 (89,798)	2,466 (87,074)
Stack volumetric flow rate, Nm ³ /min (dscfm)	2,131 (75,262)	2,221 (78,450)	2,106 (74,389)	2,103 (74,262)
Stack gas velocity, m/min (ft/sec)	1,551 (84.8)	1,509 (82.5)	1,527 (83.5)	1,529 (82.6)
Stack gas temp., °C (°F)	268 (514)	267 (513)	265 (508)	268 (515)
Stack gas moisture, % vol.	26.9	22.9	26.7	26.4
Oxygen concentration, %	14.4	15.1	14.2	14.2
Carbon dioxide concentration, %	5.7	5.1	5.7	5.7
Percent isokinetic	106	97	104	103
	ng	ng/Nm ³	ng	ng/Nm ³
2,3,7,8-TCDF	14	5.4	11	4.4
TCDF	510	190	370	160
P ₅ CDF	1,600	610	1,100	400
HxCDF	810	310	860	910
HpCDF	320	120	370	3,000
OCDF	160	61	130	2,500
Total Tetra-Octa CDF	3,400	1,300	2,800	12,000
	ng	ng/Nm ³	ng	ng/Nm ³
2,3,7,8-TCDF	70	27	36	8.3
TCDF	1,400	540	900	160
P ₅ CDF	1,700	650	1,000	360
HxCDF	800	310	800	402
HpCDF	260	100	290	320
OCDF	26	10	25	120
Total Tetra-Octa CDF	4,200	1,600	3,000	1,200
	ng/sec	ng/sec	ng/sec	ng/sec
2,3,7,8-TCDF	190	160	21	290
TCDF	6,900	5,500	400	5,500
P ₅ CDF	22,000	16,000	910	13,000
HxCDF	11,000	13,000	7,300	100,000
HpCDF	4,400	5,500	2,500	34,000
OCDF	2,200	1,900	950	13,000
Total Tetra-Octa CDF	46,000	42,000	12,000	170,000
	ng	ng	ng	ng
2,3,7,8-TCDF	70	14	88	35
TCDF	1,400	13,000	1,400	19,000
P ₅ CDF	1,700	15,000	1,400	19,000
HxCDF	800	12,000	7,900	110,000
HpCDF	260	4,300	1,900	26,000
OCDF	26	370	110	1,500
Total Tetra-Octa CDF	4,200	45,000	13,000	180,000

^a Low surrogate recovery on this sample.

^b Results not yet available; results to be reported as an addendum to this report.

TABLE 9. SUMMARY OF TOTAL TETRA-OCTA DIBENZO-p-DIOXIN AND DIBENZOFURAN EMISSIONS, NW UNIT NO. 2

Run No.	IA			2A			3B			Blank			
	Date	Start time	End time	2/27/85	2/28/85	3/01/85	3/04/85	ng	ng/Nm ³	ng/sec	ng	ng/Nm ³	ng/sec
2,3,7,8-TCDD		1549	1712	7.1	19	11	0.073 ^b	230	600	260	NA	NA	NA
TCDD		540	940	18	600	260	0.073 ^b	540	1,700	900	NA	NA	NA
P ₅ CDF		940	340	460	780	880	0.044	940	360	880	NA	NA	NA
HxCDF		340	130	170	360	430	0.038	340	360	430	NA	NA	NA
HpCDF		130	63	63	2,500	190	0.005	130	160	190	NA	NA	NA
OCDF		2,200	1,000	1,000	42,000	2,700	0.010	2,200	3,600	2,700	NA	NA	NA
Total Tetra-Octa CDD		2,200	1,000	1,000	42,000	2,700	< 0.17	2,200	3,600	2,700	NA	NA	NA
2,3,7,8-TCDF		18	360	8.7	51	34	0.012 ^b	18	18	34	NA	NA	NA
TCDF		360	520	170	1,200	700	0.012 ^b	360	1,200	700	NA	NA	NA
P ₅ CDF		520	930	250	1,600	1,000	0.022	520	1,600	1,000	NA	NA	NA
HxCDF		930	310	450	580	710	0.005	930	580	710	NA	NA	NA
HpCDF		310	150	150	6,000	220	0.005	310	210	220	NA	NA	NA
OCDF		2,200	1,000	1,000	42,000	2,700	0.0023	2,200	3,600	2,700	NA	NA	NA
Total Tetra-Octa CDF		2,200	1,000	1,000	42,000	2,700	< 0.047	2,200	3,600	2,700	NA	NA	NA

a NA = not applicable.

b Carry over from previous standard injection.

TABLE 10. SUMMARY OF EMISSIONS OF 2,3,7,8-SUBSTITUTED DIBENZO-p-DIOXIN AND DIBENZOFURAN ISOMERS, NW UNIT NO. 1

Run No.	4A			5A			6A ^a			6B				
	Date	ng	ng/Nm ³	ng/sec	ng/Nm ³	ng/sec	Date	ng	ng/Nm ³	ng/sec	Date	ng	ng/Nm ³	ng/sec
2,3,7,8-TCDF	14	5.4	190	11	4.4	164	21	8.3	290	2,106 (74,389)	2,103 (74,262)	2,103 (74,262)	2,103 (74,262)	2,103 (74,262)
1,2,3,7,8-PCDD	130	50	1,800	85	34	1,270	61	24	842	1,527 (83.5)	1,529 (82.6)	1,529 (82.6)	1,529 (82.6)	1,529 (82.6)
1,2,3,4,7,8-PCDF	100	38	1,400	98 ^c	39	1,500	810	320	11,000	265 (508)	268 (515)	268 (515)	268 (515)	268 (515)
1,2,3,4,6,7,8-PCDF	160	61	2,200	190 ^c	76	2,800	1,200	470	17,000	26.7	26.6	26.6	26.6	26.6
1,2,3,4,7,8-PCDF	160	61	2,200	190 ^c	76	2,800	1,200	470	17,000	14.2	14.2	14.2	14.2	14.2
1,2,3,4,6,7,8-PCDF	190	73	2,600	220 ^c	88	3,300	950	370	13,000	5.7	5.7	5.7	5.7	5.7
1,2,3,4,7,8,9-PCDF	18	6.9	245	17 ^c	6.8	250	97	38	1,300	104	103	103	103	103
OCDF	26	10	350	25	10	370	110	43	1,500	2,466 (87.074)	2,466 (87.074)	2,466 (87.074)	2,466 (87.074)	2,466 (87.074)
Stack volumetric flow rate, Nm ³ /min (discfm)	2,131 (75,262)	2,221 (78,450)	2,221 (78,450)	2,221 (78,450)	2,221 (78,450)	2,221 (78,450)	2,221 (78,450)	2,221 (78,450)	2,221 (78,450)	2,221 (78,450)	2,221 (78,450)	2,221 (78,450)	2,221 (78,450)	2,221 (78,450)
Stack gas velocity, m/min (ft/sec)	1,551 (84.8)	1,551 (84.8)	1,551 (84.8)	1,551 (84.8)	1,551 (84.8)	1,551 (84.8)	1,551 (84.8)	1,551 (84.8)	1,551 (84.8)	1,551 (84.8)	1,551 (84.8)	1,551 (84.8)	1,551 (84.8)	1,551 (84.8)
Stack gas temp., °C (°F)	268 (514)	268 (514)	268 (514)	268 (514)	268 (514)	268 (514)	268 (514)	268 (514)	268 (514)	268 (514)	268 (514)	268 (514)	268 (514)	268 (514)
Stack gas moisture, % vol.	26.9	26.9	26.9	26.9	26.9	26.9	26.9	26.9	26.9	26.9	26.9	26.9	26.9	26.9
Oxygen concentration, %	14.4	14.4	14.4	14.4	14.4	14.4	14.4	14.4	14.4	14.4	14.4	14.4	14.4	14.4
Carbon dioxide concentration, %	5.7	5.7	5.7	5.7	5.7	5.7	5.7	5.7	5.7	5.7	5.7	5.7	5.7	5.7
Percent isokinetic	106	106	106	106	106	106	106	106	106	106	106	106	106	106

^a Low surrogate recovery on this sample; results should be considered an estimate.

^b Results not yet available.

^c Only first replicate reported.

With the exception of the low surrogate recoveries for Run 6A, no serious anomalies in sampling or analysis were noted for the measurement of PCDDs and PCDFs in the stack gas emissions.

4.1.2 ESP Fly Ash Samples

Tables 12 and 13 report the PCDD and PCDF concentrations measured in the ESP fly ash samples from the NW and EC facilities, respectively. Where applicable, results are reported for replicate analyses and/or multiple GC/MS injections. Results for replicate sample analyses (i.e., extraction and analysis of multiple aliquots of the sample) are reported as Replicate 1, Replicate 2, etc. Multiple analyses of the same aliquot (i.e., same sample extract) are reported as Replicate 1A, 1B, etc. Note that, in some cases (e.g., Table 12, Run 1A/B, Replicate 2B), replicate analyses are reported for only some homologs. This situation occurs because multiple GC/MS injections are required to quantitate the five PCDD and PCDF homologs; in some cases, all the injections required to quantitate all homologs were not replicated.

The only anomaly related to the sampling and analysis of fly ash samples noted during the study, was that samples from runs 1 and 5 contained considerable amounts of charred paper flakes. This resulted in composites of a fairly nonhomogeneous nature.

4.1.3 Bottom Ash Samples

Tables 14 and 15 report the PCDD and PCDF concentrations measured in the bottom ash samples taken from the NW and EC facilities, respectively. Note that the bottom ash samples were often nonhomogeneous; relatively large pieces of inert materials (e.g., pebbles) and unburned refuse (e.g., metal) often were contained in the ash samples. Large objects such as pebbles and pieces of metal were removed from the sample aliquot prior to extraction by sieving. The calculated concentration (ng/g) is based on the final weight of the sample fraction after sieving. The final sieved fraction which was extracted ranged from 26 to 73% of the original aliquot weight. More detail of the procedure used to prepare the bottom ash samples for analysis is presented in Section 5.

TABLE 12. SUMMARY OF TOTAL TETRA-OCTA DIBENZO-p-DIOXIN AND DIBENZO FURAN CONCENTRATION IN FLY ASH, NW UNIT NOS. 1 AND 2 (ng/g)

Run No. Date Start time ^a End time ^b	NW Unit 1			NW Unit 2		
	4 A/B 3/02/85 1142 1700	5 A/B 3/03/85 0950 1420	6 A/B 3/05/85 1352 1833	1 A/B 2/27/85 1553 2000	2 A/B 2/28/85 1215 1725	3 A/B 3/01/85 0945 1435
2,3,7,8-TCDD	6.6	5.9	6.4	6.0	4.9	3.7
TCDD	340	330	410	270	230	160
PCDD	640	730	800	660	450	380
HxCDD	660	1,000	510	350	NA ^e	390
HpCDD	170	240	120	110	NA	95
OCDD	42	49	28	31	NA	20
Total Tetra-Octa CDD	1,900	2,300	1,900	1,400	1,000	1,000
2,3,7,8-TCDF	13	11	11	11	8.0	6.3
TCDF	330	300	350	280	200	170
PCDF	370	430	520	410	220	260
HxCDF	500	920	570	350	NA	390
HpCDF	112	210	110	100	NA	72
OCDF	6.2	11	6.8	6.2	NA	1.8
Total Tetra-Octa CDF	1,300	1,900	1,200	1,100	1,200	900

^a Time when first grab sample was taken.

^b Time when last grab sample was taken.

^c To be reanalyzed and results reported at a later date.

^d Replicates 1 and 2 indicate replicate extraction/analysis of sample; letter suffix (i.e., A, B) indicates duplicate analysis of same sample extract.

^e NA = not analyzed.

TABLE 13. SUMMARY OF TOTAL TETRA-OCTA DIBENZO-p-DIOXIN AND DIBENZOFURAN CONCENTRATION IN FLY ASH, EC UNIT NOS. 1 AND 2 (ng/g)

Run No.	EC Unit 1		EC Unit 2		Bottle blank	Method blank	Method blank
	7	8	7	8			
Date	3/07/85		3/17/85		-	-	-
Start time ^a	1159		1700		-	-	-
End time ^b	1502		2005		-	-	-
	Rep. 1	Rep. 2	Rep. 1	Rep. 2	Rep. 3A	Rep. 3B ^c	
2,3,7,8-TCDD	3.5	2.5	0.60	0.62	0.48	0.56	ND ^d (0.025)
TCDD	210	170	46	44	35	44	ND (0.020)
PCDD	730	610	230	210	140	160	ND (0.020)
HxCDD	530	680	150	170	140	NA ^e	ND (0.037)
HpCDD	270	270	133	140	150	NA	ND (0.020)
OCDD	170	140	190	190	180	NA	ND (0.037)
Total Tetra-Octa CDD	1,900	1,900	750	750	650	-	ND (0.025)
	6.4	5.7	1.4	1.5	1.2	1.4	< 0.1
2,3,7,8-TCDF	180	150	34	39	28	31	0.03 (0.020)
TCDF	270	250	64	81	46	54	ND (0.020)
PCDF	330	350	71	73	62	NA	ND (0.020)
HxCDF	160	150	76	98	62	NA	ND (0.025)
HpCDF	24	19	23	23	20	NA	ND (0.037)
OCDF	960	920	270	310	220	-	ND (0.037)
Total Tetra-Octa CDF	1,900	1,900	750	750	650	-	ND (0.025)
	6.4	5.7	1.4	1.5	1.2	1.4	< 0.1

^a Time when first grab sample was taken.

^b Time when last grab sample was taken.

^c Replicates 1 and 2 indicate replicate extraction/analysis of sample; letter suffix (i.e., A, B) indicates duplicate analysis of same sample extract.

^d ND = Not detected; detection limit stated in parenthesis.

^e NA = not analyzed.

TABLE 14. SUMMARY OF TOTAL TETRA-OCTA DIBENZO-p-DIOXIN AND DIBENZO FURAN CONCENTRATION IN
 BOTTOM ASH, NW UNIT NOS. 1 AND 2 (ng/g)

Run No.	NW Unit 1				NW Unit 2			
	4 A/B	5 A/B	6 A/B	1 A/B	2 A/B	3 A/B	2 A/B	3 A/B
Date	3/02/85	3/03/85	3/05/85	2/27/85	2/28/85	3/01/85	2/28/85	3/01/85
Start time ^a	1145	0955	1357	1600	1210	0950	1210	0950
End time ^b	1705	1425	1831	2003	1720	1440	1720	1440
	Rep. 1A	Rep. 1B	Rep. 1	Rep. 2	Rep. 1A	Rep. 1B	Rep. 2	Rep. 2
2,3,7,8-TCDD	1.5	NA ^c	0.77	0.41	0.47	NA	0.21	0.79
TCDD	47	NA	33	16	12	NA	7.0	23
PCDD	92	NA	71	25	32	NA	14	42
HxCDD	69	50	35	12	13	11	6.5	18
HpCDD	31	20	11	4.8	4.2	3.9	2.6	9.1
OCDD	21	17	5.9	2.9	2.9	2.9	1.8	5.7
Total Tetra-Octa CDD	260	-	160	61	64	-	32	98
2,3,7,8-TCDF	2.7	NA	1.1	0.69	0.74	NA	0.38	0.86
TCDF	47	NA	25	13	13	NA	8.2	18
PCDF	49	NA	29	16	14	NA	7.2	18
HxCDF	48	37	24	8.1	12	9.1	4.5	0.84
HpCDF	15	11	7.8	2.6	2.2	2.8	1.4	5.3
OCDF	1.9	1.9	0.95	0.40	0.22	0.27	0.20	0.75
Total Tetra-Octa CDF	160	-	87	40	41	-	22	43

^a Time when first grab sample was taken.

^b Time when last grab sample was taken.

^c NA = not analyzed.

TABLE 15. SUMMARY OF TOTAL TETRA-OCTA DIBENZO-p-DIOXIN AND DIBENZOFURAN CONCENTRATION IN BOTH ASH, EC UNIT NOS. 1 AND 2 (ng/g)

Run No.	EC Unit 1		EC Unit 2		Bottle blank	Method blank	Method blank
	3/07/85	7	3/07/85	8			
Date	1156		1710		-	-	-
End time	1508		2009		-	-	-
	Rep. 1	Rep. 2	Rep. 1	Rep. 2	Rep. 3		
2,3,7,8-TCDD	0.18	0.17	ND	0.016	0.031	ND	ND
			(0.045)			(0.014)	(0.010)
TCDD	6.7	7.1	0.14	0.20	0.16	ND	ND
						(0.030)	(0.010)
PCDD	16	23	0.67	1.2	0.70	ND	ND
						(0.018)	(0.010)
HxCDD	18	25	0.76	1.0	1.9	ND	ND
						(0.069)	(0.026)
HpCDD	10	15	1.3	1.3	1.9	0.090	ND
							(0.010)
OCDD	13	17	3.2	3.2	3.4	0.14	ND
							(0.014)
Total Tetra-Octa CDD	64	87	6.1	6.9	8.1	< 0.36	(0.010)
							(< 0.08)
							(< 0.09)
2,3,7,8-TCDF	0.25	0.32	0.041	0.029	0.041	ND	ND
						(0.014)	(0.010)
TCDF	5.0	7.6	0.55	0.70	0.38	ND	ND
						(0.014)	(0.010)
PCDF	7.1	11	0.24	0.82	0.76	ND	ND
						(0.030)	(0.010)
HxCDF	10	9.1	0.39	0.52	0.77	ND	ND
						(0.022)	(0.045)
HpCDF	6.0	7.6	0.35	0.57	0.70	0.11	ND
							(0.023)
OCDF	1.7	2.0	ND	ND	ND	0.18	ND
			(0.24)	(0.29)	(0.39)		(0.015)
Total Tetra-Octa CDF	30	37	< 1.8	< 2.9	< 3.0	< 0.37	ND
							(< 0.10)
							(< 0.08)

a Time when first grab sample was taken.

b Time when last grab sample was taken.

4.2 PARTICULATE MATTER AND HYDROGEN CHLORIDE EMISSIONS

Table 16 presents the results of the particulate matter and HCl stack emissions measurements from NW Units 1 and 2. Run 3A failed the final leak check because of a broken probe liner. The results of this test run are reported, although the run technically is invalid. An additional particulate test run (5C) on NW Unit 2 was conducted to obtain three valid tests.

The particulate matter results from Run 1B on Unit No. 2 are significantly higher (an order of magnitude) than for the other five test runs. The measurements and calculations for this test were rechecked and found to be valid. Visual examination of the filter during reweighing revealed a wax-like substance on the filter.

The results of blank analyses for particulate matter and HCl are reported with the Quality Assurance Results, Section 4.5.1, Table 20; no problems with sample blanks were identified.

4.3 CONTINUOUS EMISSION MONITORING

Table 17 presents a summary of all continuous emission monitoring results. The results are reported as the average concentration for the test period; the range of concentrations measured during the test run also is reported.

An NDIR analyzer was used to monitor the SO₂ emissions. When using an NDIR, moisture can interfere with the measurement of pollutants at low levels. Consequently, the SO₂ measurements are suspect and are likely biased high. Moisture interference is not a major concern with the CO₂ measurements because of the high level of CO₂ in the stack gas (i.e., percent instead of ppm). To assure no interference from water or carbon dioxide during the CO measurements, an ascarite scrubber was used prior to the CO monitor.

TABLE 16. SUMMARY OF PARTICULATE AND HCl EMISSIONS

Run No.	NW Unit No. 1				NW Unit No. 2			
	4B	5B	6B	1B	2B	3A ^a	5C	
Date	3/02/85	3/03/85	3/05/85	2/27/85	2/28/85	3/01/85	3/03/85	
Start time	1132	0942	1342	1547	1212	0935	1610	
End time	1712	1412	1852	2006	1710	1425	1902	
Sample time, min	240	240	240	192	240	240	144	
Sample volume, Nm ³ (dscf)	2,562 (90.481)	2,475 (87.415)	2,466 (87.074)	2,042 (72.106)	2,739 (96.714)	2,746 (96.964)	1,566 (55.309)	
Stack volumetric flow rate, Nm ³ /min (dscfm)	2,190 (77.351)	2,267 (80.074)	2,103 (74.262)	2,414 (85.256)	2,512 (88.724)	2,359 (83.292)	2,207 (77.925)	
Stack gas velocity, m/min (ft/sec)	1,563 (85.5)	1,537 (84.1)	1,529 (82.6)	1,675 (91.6)	1,654 (90.5)	1,558 (85.2)	1,509 (82.5)	
Stack gas temp., °F (°C)	265 (508)	269 (517)	268 (515)	270 (518)	267 (512)	270 (518)	262 (503)	
Stack gas moisture, % vol	25.8	22.5	26.4	23.9	20.6	20.9	25.1	
Oxygen concentration, %	14.4	15.1	14.2	15.9	15.4	15.5	14.8	
Carbon dioxide conc., %	5.7	5.1	5.7	4.2	4.7	4.7	5.3	
Percent isokinetic	103	96	103	94	96	101	103	
Particulate weight, g ^b	0.3720	0.2665	0.2420	2.4682	0.3505	0.4606	0.1571	
Particulate conc., g/Nm ³ (gr/dscf)	0.1452 (0.0633)	0.1077 (0.0469)	0.0981 (0.0428)	1.2089 (0.5271)	0.1279 (0.0558)	0.1677 (0.0731)	0.1003 (0.0438)	
Corrected particulate conc. at 12% CO ₂ , g/Nm ³ (gr/dscf)	0.31 (0.13)	0.25 (0.11)	0.21 (0.09)	3.5 (1.5)	0.33 (0.14)	0.43 (0.19)	0.23 (0.10)	
Particulate emission rate kg/hr (lb/hr)	19 (42)	15 (32)	12 (27)	175 (385)	19 (42)	24 (52)	13 (29)	
HCl amount detected, mg B ₂ C ₁₀	626	359	607	98.5	198	482	f	
HCl concentration, mg/Nm ³	244	145	246	48	72	175	f	
HCl emission rate, kg/hr	32	20	31	7.0	11	25	f	

^a Probe liner broken; final leak check failed.

^b Blank corrected.

^c As HCl.

^d HCl detected in blank train = 0.4 mg.

^e Correction calculated using CO₂ obtained by IHH (integrated bag/hrsat); not (EMS data).

^f Particulate matter test only.

TABLE 17. SUMMARY OF CONTINUOUS EMISSION MONITORING RESULTS

Facility Run no. Date	NW Unit No. 1		NW Unit No. 2		EC 1 7 3/07/85	EC 2 8 3/07/85	
	4A/B 3/02/85	5A/B 3/03/85	6A/B 3/15/85	1A/B 2/27/85			2A/B 2/28/85
Time periods Monitored ^a	1130-1201 1206-1337 1420-1430 1520-1712	0940-1142 1210-1412	1340-1353 1403-1552 1650-1852	1545-1723 1824-2006	1200-1215 1230-1255 1302-1434 1510-1712	0935-1141 1225-1427	1646-2012
Average O ₂ , % (range)	13.4 (11.4-15.0)	14.7 (12.7-16.6)	13.6 (12.2-15.8)	14.4 (12.8-15.9)	15.1 (13.7-16.7)	14.9 (13.2-16.3)	15.3 (14.4-17)
Average CO ₂ , % (range)	5.5 (3.6-7.6)	4.8 (3.0-6.8)	5.6 (3.4-6.9)	5.2 (3.8-6.7)	4.4 (3.0-5.7)	4.5 (3.0-6.0)	4.2 (3.0-5.5)
Average CO, ppm (range)	238 (95-1,230)	240 (95-496)	204 (119-468)	150 (69-388)	193 (123-342)	202 (127-334)	57 (17-222)
Average THC, ppm (range)	3 (2-15)	2 (0-24)	7 (2-46)	6 (0-12)	5 (4.6-6.8)	< 1 (0-6)	< 1 (0-6)
Average SO ₂ , ppm ^b (range)	203 (160-280)	156 (126-234)	173 (134-239)	122 (91-187)	167 (146-212)	152 (88-197)	40 (16-231)
Average NO _x , ppm (range)	84 (56-104)	78 (52-106)	96 (78-111)	93 (66-111)	79 (60-96)	81 (62-114)	62 (40-83)

^a Monitor data logger was stopped when sample trains were stopped; therefore, monitored time period coincides with actual MM5 sampling; strip charts were operated continuously.

^b SO₂ results are probably biased high; interference due to stack gas moisture is suspected.

The data were recorded on a data logger; measurements recorded every 3 sec were used to calculate 1-min averages. A continuous strip chart record also was obtained. The data logger printouts (1-min averages) and the strip charts are included as Appendix G of this report. Calibration results for the monitors also are reported in Appendix G.

4.4 OPACITY

Tables 18 and 19 present results of visual readings of the opacity of emissions recorded during each test run. The data are tabulated as 6-min averages (Table 18) and total minutes observed at each opacity level (Table 19). The visual emission readings were taken and recorded by EPA observers.

4.5 QUALITY ASSURANCE

The Quality Assurance (QA) program for this project was extensive. The QA program included analyzing blank samples, spiked samples, control samples, and blind audit samples. All samples were spiked with internal standards and surrogates. Duplicate analyses were conducted to assess precision. Depending upon the type of sample, accuracy was assessed by several different means including: (a) analysis of audit samples; (b) analysis of spiked blanks; and (c) surrogate recovery. In addition, several of the samples were analyzed by a second laboratory.

This section is divided into two subsections; Section 4.5.1 summarizes the QA results of MRI's laboratory; and Section 4.5.2 summarizes the results of the second laboratory, Triangle Laboratories, Inc.. All results obtained by MRI in regards to Quality Assurance are reported along with the analytical results for the samples in Appendix C--Laboratory Report: Dioxins. Appendix L provides the complete report of results from Triangle Laboratories, Inc.

TABLE 18. SUMMARY OF OPACITY OBSERVATIONS: 6-MIN AVERAGE OPACITY

Facility Run No. Date	NW Unit No. 1			NW Unit No. 2			EC 1	EC 2		
	4A/B 3/02/85	5A/B 3/03/85	6A/B 3/05/85	1A/B 2/27/85	2A/B 2/28/85	3A/B 3/01/85			2A/B 2/28/85	3A/B 3/03/85
Observation begin Time	1222	1030	1407	1545	1324	1609	1038	1631	1225	1700
Observation end time	1321	1129	1506	1644	1423	1708	1137	1730	1324	1744
6-Min ^b observation period	Average percent opacity									
0-6	4.8	26.0	2.9	30.6	13.5	12.1	10.6	5.6	0.8	7.7
6-12	7.3	30.4	2.1	17.3	22.1	15.8	12.3	2.9	3.3	2.3
12-18	6.9	27.3	7.1	11.3	18.6	15.4	9.2	11.3	0.8	2.7
18-24	4.2	28.3	6.5	9.2	18.6	12.9	16.5	6.7	0.8	4.8
24-30	4.8	30.6	3.8	13.8	15.8	10.8	15.6	5.8	2.9	6.9
30-36	6.0	22.5	0.4	26.0	17.5	12.7	17.1	7.7	2.9	1.0
36-42	4.4	22.3	2.9	29.2	24.2	8.5	18.3	5.8	1.7	0.2
42-48	10.2	21.7	2.3	36.0	14.6	10.6	20.4	4.4	1.9	-
48-54	7.9	18.1	2.9	37.7	20.2	7.9	16.0	5.2	2.9	-
54-60	5.2	19.0	1.9	35.2	9.4	6.0	19.6	6.3	6.9	-
Overall average	6.2	24.6	3.3	25.0	17.4	11.3	15.6	6.2	2.5	3.4

^a MN5 run number.

^b Observation periods are block periods; running 6-min averages were not calculated to determine the highest 6-min average.

^c Observations discontinued.

TABLE 19. SUMMARY OF OPACITY OBSERVATIONS: TOTAL MINUTES AT SPECIFIED OPACITY LEVEL

Facility Run No. Date	NW Unit No. 1			NW Unit No. 2			EC 1	EC 2
	4A/B 3/02/85	5A/B 3/03/85	6A/B 3/05/85	1A/B 2/27/85	2A/B 2/28/85	3A/B 3/01/85		
Observation begin time	1222	1030	1407	1545	1324	1609	1225	1700
Observation end time	1321	1129	1506	1644	1423	1708	1324	1744
Opacity level (%)	Observed minutes							
0	6.75	0	32.25	0	0	0	0	12.75
5	36.75	0	19	3	4.25	14.25	7	28
10	13.5	0.75	6.25	11.25	15	26.50	15.5	14.75
15	1.75	8.5	2.25	6.75	13.25	12.25	14.5	3.25
20	1.25	19.25	0.25	4.75	12	4.25	16.5	0.50
25		9.75		4.25	8.25	2.25	0	0.25
30		13.25		9.75	5.25	0.25	6.27	0.25
35		5.5		12.75	1.75	0.25	0	0
40		2.25		5.75	0		0.25	
45		0.75		1.75	0.25			0.25
50								
55								
60								
65								
70								
75								
80								
85								
90								
95								
100								

a MM5 run number.

4.5.1 MRI Quality Assurance Results

4.5.1.1 Particulate/HCl--

Table 20 reports the results of the blank analyses for the particulate and HCl sampling. No problems were identified.

4.5.1.2 PCDD/PCDF Analyses--

Audit results

Prior to initiating analysis of any samples, accuracy was checked by analyzing blind audit samples provided by MRI's Quality Assurance Unit. Two different samples were submitted to the laboratory; one sample was analyzed on two separate occasions. Results of the blind audit analyses are presented in Table 21. All accuracy results were within the range of 88 to 134%; the quality assurance objective of 60 to 115% accuracy, as assessed by the audit samples, was exceeded for some analyses.

ESP fly ash

Precision of the analysis for PCDDs and PCDFs in fly ash was assessed by conducting duplicate and triplicate analyses; accuracy was assessed by calculating percent recovery of the spiked surrogate. Table 22 summarizes the results of replicate analyses for the four ESP fly ash samples which were analyzed in duplicate. For each sample analyzed in duplicate the range percent difference was calculated for each homolog. Range percent is calculated as follows:

TABLE 20. PARTICULATE/HCl BLANK RESULTS

Sample No.	Type of blank	Measured value
157	Particulate, Filter No. 10	0.0003 g ^a
164	Particulate, acetone/hexane	0.0010 g/260 ml, 0.004 mg/ml
166	HCl, water	0 µg/mL Cl ⁻
167	HCl, water	0 µg/mL Cl ⁻
168	HCl, KOH	6 µg/mL Cl ⁻
169	HCl, KOH	6 µg/mL Cl ⁻

^a Difference between final weight and tare weight.

TABLE 21. RESULTS OF AUDIT SAMPLES

Sample	Analyzed	Analyte	Conc. (ng/ μ L)		Accuracy (%)
			Actual	Found	
QA-1	04/09/85	Tetra CDD	17	17.9	106
QA-1	04/09/85	Tetra CDF	17	17.7	104
QA-2	04/25/85	Tetra CDD	122	141	116
QA-2	04/25/85	Tetra CDF	122	145	119
QA-1	04/09/85	Penta CDD	17	22.8	134
QA-1	04/09/85	Penta CDF	17	17.2	101
QA-2	04/25/85	Penta CDD	122	159	130
QA-2	04/25/85	Penta CDF	122	155	127
QA-1	05/02/85	Hexa CDD	87	83	95
QA-1	05/02/85	Hexa CDF	87	87	100
QA-1	05/02/85	Hepta CDD	87	91	105
QA-1	05/02/85	Hepta CDF	87	91	105
QA-1	05/02/85	Octa CDD	173	176	102
QA-1	05/02/85	Octa CDF	173	153	88

TABLE 22. RESULTS OF REPLICATE ANALYSES FOR ESP
FLY ASH SAMPLES

Analyte	Range percent difference for replicate analyses	
	Mean ^a (%)	Range of values (%)
2,3,7,8-TCDD	22	(8-33)
Tetra CDD	22	(14-35)
Penta CDD	30	(9-51)
Hexa CDD	46	(19-77)
Hepta CDD	38	(0-71)
Octa CDD	34	(5-56)
2,3,7,8-TCDF	16	(0-37)
Tetra CDF	26	(9-41)
Penta CDF	33	(8-56)
Hexa CDF	32	(6-59)
Hepta CDF	39	(6-63)
Octa CDF	30	(14-47)

^a Mean of range percent calculated for replicate analyses of four samples [runs 1,5,7,8].

$$R\% = \frac{C_1 - C_2}{\bar{C}} \times 100$$

where: C_1 = highest value determined
 C_2 = lowest value determined
 \bar{C} = mean value of set

and

$$\bar{C} = \sum_{i=1}^n \frac{C_i}{n}$$

where: C_i = ith determination
 n = number of determinations

The four precision values for each homolog obtained from the four samples were averaged to calculate the mean value reported in Table 22. The range of values for the calculated precision (range percent difference) of the four samples also are reported for each homolog in Table 22. For example, for 2,3,7,8-TCDD the range percent difference for the duplicate analyses of samples from runs 1, 5, 7, and 8 were 40, 8, 33, and 25%, respectively. Therefore, the mean precision value is $[(40\% + 8\% + 33\% + 25\%) \div 4 = 27\%]$; the values ranged from (8 to 40%). The results generally were within the QA precision objective of $\leq 30\%$ for 2,3,7,8-TCDD/TCDF, tetra CDD/CDF, and octa CDD/CDF, and $\leq 60\%$ for the penta, hexa, and hepta CDD/CDF homologs.

Accuracy of the fly ash analyses was assessed by calculating the percent recovery for the surrogate $^{37}\text{Cl}_4$ TCDD. Table 23 reports the recovery results for the ESP fly ash. The calculated recoveries are very good and within the QA objective of 60 to 115%. The surrogate recovery of $^{37}\text{Cl}_4$ -1,2,3,4,6,7,8-HPCDD could not be measured because of interference due to the large (relative to the spiked amount) quantity of 1,2,3,4,6,7,8-HPCDD in the samples. This is also true for the bottom ash and MM5 stack emission samples.

TABLE 23. RESULTS OF SURROGATE RECOVERY
FOR FLY ASH SAMPLES

Run	% Accuracy ^a
1A/B (replicate 1)	105
1A/B (replicate 2)	73
1A/B (replicate 3)	102
2A/B	90
3A/B	NA ^b
4A/B	79
5A/B (replicate 1)	82
5A/B (replicate 2)	101
6A/B	96
7 (replicate 1)	95
7 (replicate 2)	69
8 (replicate 1)	89
8 (replicate 2)	97
8 (replicate 3)	82
8 (replicate 4)	99

^a Percent recovery of ³⁷Cl₄ TCDD.

^b Not available; sample being reanalyzed.

Two fly ash method blanks and a field sample bottle blank were analyzed; all results were below detection limits.

Bottom ash

The same procedures that were used to assess precision and accuracy for the ESP fly ash samples were used for the bottom ash samples. Table 24 reports the precision results for replicate analyses and Table 25 reports the accuracy results as surrogate percent recovery.

The precision for the bottom ash samples is not as good as the precision measured for the fly ash samples. The nonhomogeneity of the bottom ash samples is expected to be the cause of the greater imprecision. The percent accuracy (surrogate recovery) is very good and within the desired range of 60 to 115%, with the exception of sample 4A/B (replicate 1) which was 53%.

Two bottom ash method blanks and a field sample bottle blank were analyzed; all results were below detection limits.

Stack emissions

Precision for the analysis of MM5 stack emissions samples was assessed by analyzing spiked blanks. Two filters and two XAD resin traps were spiked and analyzed. Table 26 reports the results of the analyses. The range percent differences were all less than 30%, except for one analyte which was 34%.

Accuracy for the MM5 samples was assessed by calculating percent recoveries for the surrogate $^{37}\text{Cl}_4\text{-TCDD}$ for each emissions sample and the spiked blanks. Table 27 reports the surrogate recovery results. With the exception of run 6A, the surrogate recoveries were within the QA objectives (60 to 115%). Because the surrogate recovery on run 6A is so low (21%), the results from this sample should be considered as estimates.

TABLE 24. RESULTS OF REPLICATE ANALYSES
FOR BOTTOM ASH SAMPLES

Analyte	Range percent difference for replicate analyses	
	Mean ^a (%)	Range of values (%)
2,3,7,8-TCDD	54	(16-76)
Tetra CDD	41	(6-69)
Penta CDD	68	(36-96)
Hexa CDD	71	(32-98)
Hepta CDD	51	(40-78)
Octa CDD	37	(6-68)
2,3,7,8-TCDF	42	(25-64)
Tetra CDF	51	(41-63)
Penta CDF	65	(43-95)
Hexa CDF	64	(9-99)
Hepta CDF	61	(24-100)
Octa CDF	29	(0-81)

^a Mean of range percent calculated for replicate analyses of four samples [runs 1, 5, 7, 8].

TABLE 25. RESULTS OF SURROGATE RECOVERY
FOR BOTTOM ASH SAMPLES

Run	% Accuracy ^a
1A/B (replicate 1)	85
1A/B (replicate 2)	99
2A/B	89
3A/B	85
4A/B (replicate 1)	53
5A/B (replicate 1)	96
5A/B (replicate 2)	94
6A/B	89
7A/B (replicate 1)	87
7A/B (replicate 2)	92
8A/B (replicate 1)	78
8A/B (replicate 2)	95
8A/B (replicate 3)	69

^a Percent recovery of ³⁷Cl₄ TCDD.

TABLE 26. RESULTS OF REPLICATE ANALYSES FOR
MODIFIED METHOD 5 SAMPLES

Analyte	Range percent difference for replicate analyses	
	Spiked filter blank ^a (%)	Spiked XAD resin blank ^a (%)
2,3,7,8-TCDD	21	1
Tetra CDD	21	1
Penta CDD	13	10
Hexa CDD	29	5
Hepta CDD	34	18
Octa CDD	25	3
2,3,7,8-TCDF	7	2
Tetra CDF	7	2
Penta CDF	ND ^b	ND ^b
Hexa CDF	c	c
Hepta CDF	c	c
Octa CDF	28	13

^a Two samples.

^b Not detected.

^c HxCDF and HpCDF not spiked.

TABLE 27. RESULTS OF SURROGATE RECOVERY
FOR MODIFIED METHOD 5
SAMPLES

Run	% Accuracy ^a
1A	58
2A	96
3B	100
4A	122
5A	96
6A	21
XAD spike (1)	80
XAD spike (2)	100
Filter spike (1)	101
Filter spike (2)	102
Blank train	103

^a Percent recovery of ³⁷Cl₄ TCDD.

A MM5 blank train was set up in the field and the recovered sample analyzed along with the emissions sample. The results of this blank train were reported in Table 9. With the exception of two analytes where very low levels were found (contamination from previous GC/MS injection suspected) all analytes were below the detection limit.

Control samples

In order to obtain data comparable to data obtained by other laboratories, two control samples were analyzed. The samples were National Bureau of Standards (NBS) urban dust and a fly ash composite ("Eastern Fly Ash"). The eastern fly ash (EFA) was provided by MRI and had been previously analyzed by MRI and other laboratories. Results of the analyses are provided in Table 28. Previously reported results for the NBS dust are 0.12 ng/g for 2,3,7,8-TCDD (plus four isomers) and 0.28 ng/g for TCDD. The previously reported result for the EFA is 2.0 ng/g for 2,3,7,8-TCDD. The results obtained during this project compare reasonably well with the results reported for the NBS dust and compare very well with the previously reported results for the EFA.

4.5.2 Second Laboratory Results (Triangle Laboratories, Inc.)

Samples from test run 5 were split and submitted to a second laboratory for analysis. The eight samples which were split and sent were:

1. ESP fly ash, replicate 1
2. ESP fly ash, replicate 2
3. Bottom ash, replicate 1
4. Bottom ash, replicate 2
5. NBS urban dust
6. Eastern coast fly ash (EFA)
7. MM5 extract
8. MRI calibration standard

TABLE 28. RESULTS FOR NBS DUST AND EASTERN FLY ASH

	Concentration ng/g			
	NBS replicate 1	NBS replicate 2	EFA replicate 1	EFA replicate 2
2,3,7,8-TCDD	0.06 ^a	b	2.3 ^c	1.9 ^c
TCDD	0.12 ^a	b	75	71
PCDD	2.2	b	230	220
HxCDD	3.8	5.3	b	112
HpCDD	19	16	b	68
OCDD	67	61	b	96
2,3,7,8-TCDF	0.21	b	4.0	4.2
TCDF	1.4	b	110	120
PCDF	3.1	b	160	170
HxCDF	d	0.94	b	108
HpCDF	4.7	4.9	b	76
OCDF	2.6	5.3	b	19

^a Data reported by L. Lamparski and T. J. Nestruck (Anal. Chem. 1980, 52, 2045-54); TCDD (0.28 ng/g) and 2,3,7,8-TCDD plus four isomers (0.12 ng/g).

^b Not analyzed.

^c Data reported by Kuehl et al. (4th International Dioxin Symposium, Ottawa, October 1984); 2,3,7,8-TCDD (2.0 ng/g).

^d Not detected.

The fly ash, bottom ash, NBS urban dust, and EFA were sent to the second laboratory for extraction and analysis; aliquots of the extracted MM5 sample and the calibration sample were sent for analysis. Table 29 summarizes the results of the analyses by the second laboratory. MRI's results for the same samples also are presented in Table 29 for comparison. Percent accuracy of the second lab compared to MRI's standard was calculated; the accuracy for the different homologs ranged from 27% (HxCDF) to 298% (HpCDD).

TABLE 29. SECOND LABORATORY (TRIANGLE LABORATORIES, INC.) RESULTS

Lab ^a	Sample	2,3,7,8-TCDF		TCDD	P ₅ CDD	HxCDD	HpCDD	Octa CDD	2,3,7,8-TCDF		P ₅ CDF	HxCDF	HpCDF	Octa CDF
		Surrogate recovery	%						TCDF	TCDF				
TL	Fly ash, Run 5 (rep. 1)	93	15.8	357	274	343	(ng/g) 62	178	43.2	353	232	127	237	34
TL	Fly ash, Run 5 (rep. 2)	100	17.4	64	56	75	303	145	39.2	148	78	22	30	12.3
TL	Fly ash, Run 5 (dup. analysis)	107	18.3	63	72	95	345	152	b	154	78	22.5	25	8.1
HRI	Fly ash, Run 5 (rep. 1)	82	5.9	330	730	1,000	240	49	11	300	430	920	210	11
HRI	Fly ash, run 5 (rep. 2)	101	6.4	410	800	510	120	26	11	350	520	570	110	6.8
TL	Bottom ash, Run 5 (rep. 1) ^d	158	0.88	1.2	1.1	2.1	4.9	4.8	1.2	7.4	3.4	0.6	0.4	0.3
TL	Bottom ash, Run 5 (rep. 2)	109	0.72	2.9	2.5	3.9	10.6	5.8	1.3	5.9	3.4	0.9	0.7	0.3
HRI	Bottom ash, Run 5 (rep. 1)	96	0.77	33	71	35	11	5.9	1.1	25	29	24	7.8	0.95
HRI	Bottom ash, Run 5 (rep. 2)	94	0.41	16	25	12	4.8	2.9	0.69	13	16	8.1	2.6	0.4
TL	EFA ^{c,d}	97	4.6	6.6	4.9	17.8	93	351	8.9	28.3	17.5	5.5	2.9	6.7
HRI	EFA (rep. 1)	102	2.3	75	230	e	e	e	4	110	160	e	e	e
HRI	EFA (rep. 2)	92	1.9	71	220	112	68	96	4.2	120	170	108	76	19
	Literature value		2											
TL	MBS dust ^{d,h}	47	0.2	0.2	0.2	1.8	5.8	21	ND ^f	0.6	1	1.1	2.8	2.4
HRI	MBS dust (rep. 1)	106	0.059	0.12	2.2	3.8	19	67	0.21	1.4	3.1	ND	4.7	2.6
	Literature value		0.12	0.28										
TL	HHS ^g	97.6	9.4	426	318	386	265	78	b	1,110	838	367	158	22
HRI	HHS (rep. 1)	96	11	370	1,100	1,200	450	170	36	900	1,100	1,300	390	32
HRI	HHS (rep. 2)	-	e	e	e	860	390	130	e	e	e	800	290	25
TL	HRI standard	-	78.5	83.2	61.4	397	1,490	1,649	42.3	51.6	62	137	1,153	1,497
HRI	HRI standard	-	100	-	100	500	500	1,000	100	100	100	500	500	1,000
	Percent accuracy versus HRI standard		78.5	-	61.4	79.4	298	165	42.3	62	27.4	231	150	

^a TL = Triangle Labs; HRI = Midwest Research Institute.
^b Not available; peak outside acceptance window.
^c Eastern fly ash.
^d High signal to noise ratio; results should be considered estimated.
^e Not analyzed.
^f Not detected.
^g HHS = Modified Method 5 stack emissions sample.
^h Percent recovery outside EPA acceptance range (60-140% recovery).

SECTION 5.0

SAMPLING AND ANALYSIS PROCEDURES

This section briefly describes the sampling, sample recovery/preparation, and analytical procedures used during the test program. Table 30 presents an overview of the sampling/analysis protocol.

Section 5.1 identifies the sampling locations. Section 5.2 presents the sampling procedures and the sample recovery/handling procedures. Section 5.3 briefly describes the analytical procedures.

5.1 SAMPLING LOCATIONS

5.1.1 Stack Emissions

Figure 2 identifies the MM5 sampling locations for the NW Units 1 or 2 (units are nearly identical). The sample was collected at 24 traverse points chosen according to EPA Reference Method 1 (40CFR60). The CEM sampling location for the NW units also is shown in Figure 2; the CEM sample was taken from a single point in the stack of each unit.

The continuous emission monitor sampling location for the EC Units 1 or 2 is depicted in Figure 3; the sample was taken from a single point in the breeching of each unit.

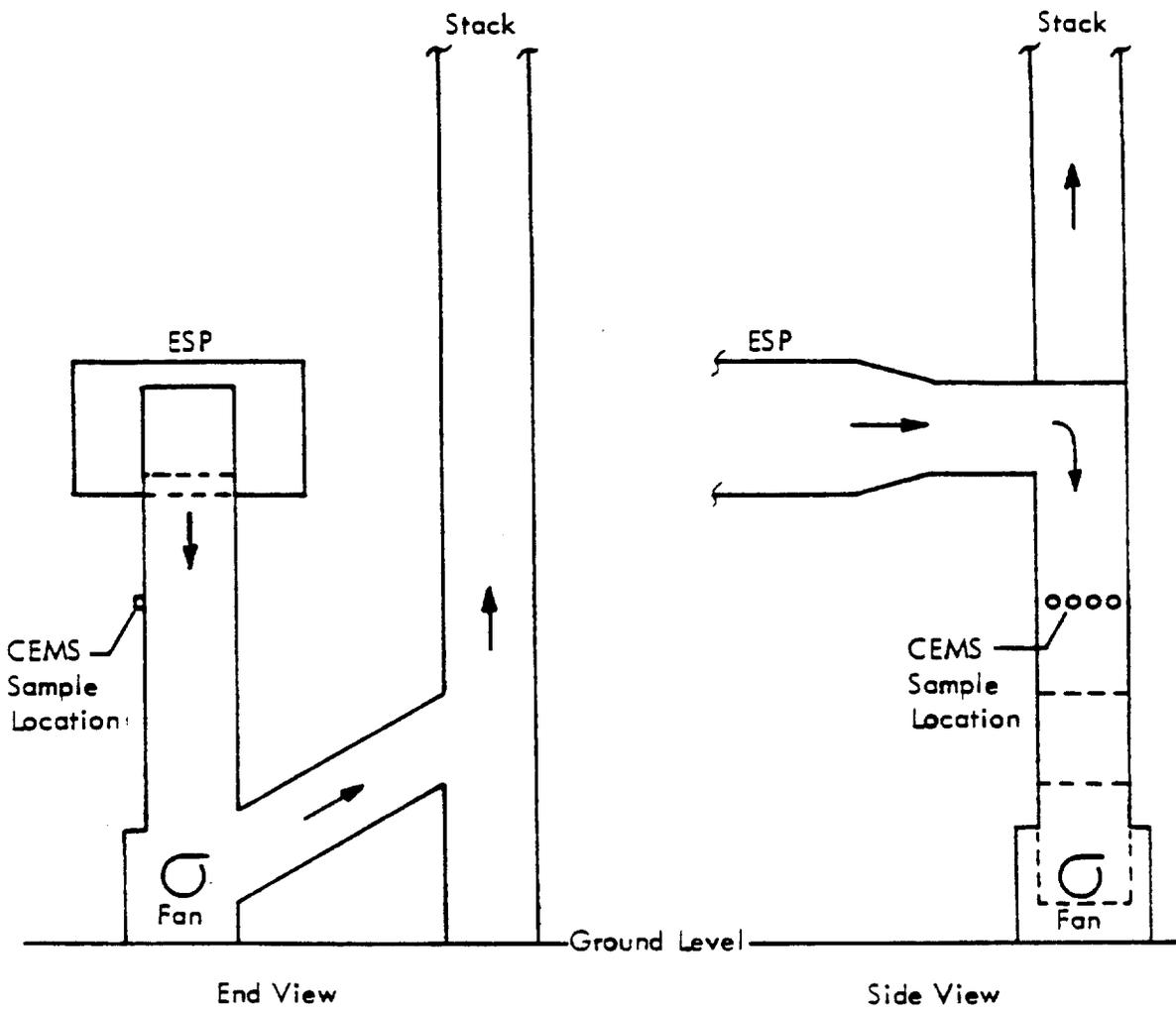
TABLE 30. SAMPLING AND ANALYSIS AT FOUR CITY OF PHILADELPHIA INCINERATORS

Sample	Sampling method/frequency	Analysis parameters	Number of runs at each unit ^{a,b}		
			NW 1	NW 2	EC 1 EC 2
A. Operating parameters	Record plant instrument readings every 1/2 hr.	Feedrate; incinerator temperature; incinerator pressure; ESP parameters.	3	3	1 1
B. Bottom ash	Grab samples taken every 1/2 hr and composited into one sample.	PCDD/PCDF ^c	3	3	1 1
C. ESP ash	Grab samples taken every 1/2 hr and composited into one sample.	PCDD/PCDF ^c	3	3	1 1
D. Stack gas	Continuous monitoring over the test period.	CO ₂ , CO, O ₂ , SO ₂ , HC, NO _x	3	3	1 1
	Visual (EPA Method 9) 1-hr during the test period.	Opacity	3	3	1 1
	MM5-Train A (4 hr) MM5-Train B (4 hr) MM5-Train C (blank)	Particulate, HCl PCDD/PCDF ^c PCDD/PCDF ^c	3 3 1	3 3 0	0 0 0

^a NW 1 = Northwest incinerator Unit 1, NW 2 = Northwest incinerator Unit 2.
EC 1 = East Central incinerator Unit 1, EC 2 = East Central incinerator Unit 2.

^b First test at Northwest Unit 2 was 192 min, all other tests at NW incinerator were 240 min; tests at EC incinerator were 180 min.

^c 2,3,7,8-TCDD, 2,3,7,8-TCDF, Tetra CDD, Penta CDD, Hexa CDD, Hepta CDD, Octa CDD, Tetra CDF, Penta CDF, Hexa CDF, Hepta CDF, Octa CDF.



Not To Scale

Figure 3. Continuous emission monitoring sampling location East Central incinerator.

5.1.2 Fly Ash

For both units the ESP fly ash is discharged to the atmosphere just above the wasting pit. The fly ash samples were taken from the discharge of the ESP hoppers before the ash entered the wasting pit.

Figure 4 shows the ESP ash sampling locations for the NW facility. Sampling locations for Units 1 and 2 are essentially the same. The fly ash samples were taken from locations C and D (Figure 4); grab samples were taken alternately from locations C and D.

Figure 5 shows the ESP fly ash sampling location for the East Central incinerator Units 1 and 2. The units are essentially the same. At the EC facility there is a single ESP screw feed (for each unit) to the waste pit; therefore, all ESP fly ash samples were taken from point C (Figure 5).

5.1.3 Bottom Ash

The bottom ash samples were taken from the inclined grate at the discharge end of the waste pit; the location is depicted as location E, Figure 4, for the NW facility units; the bottom ash sampling location for the EC units is depicted as location D, Figure 5. Note that at this sampling location the bottom ash is composed of both the ESP fly ash and the furnace bottom ash.

5.2 SAMPLING AND SAMPLE HANDLING PROCEDURES

Table 30 summarized the sampling procedures used during the test program. The following paragraphs briefly describe the sampling and sample handling procedures used in the field.

5.2.1 Fly Ash Sampling

Individual grab samples of the fly ash were collected at 1/2-hr intervals during the test period.

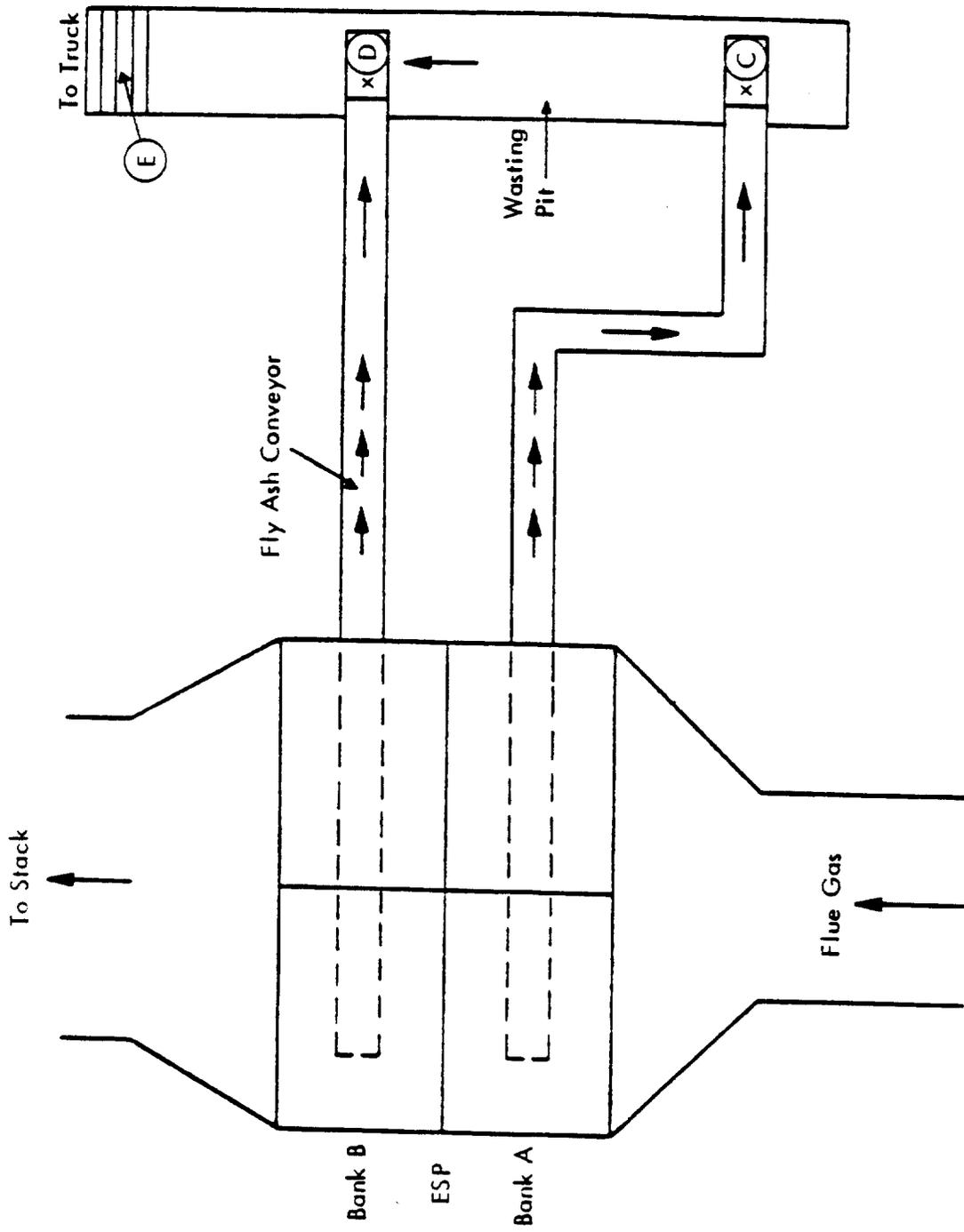


Figure 4. Ash sampling locations NW facility (Units 1 and 2 identical).

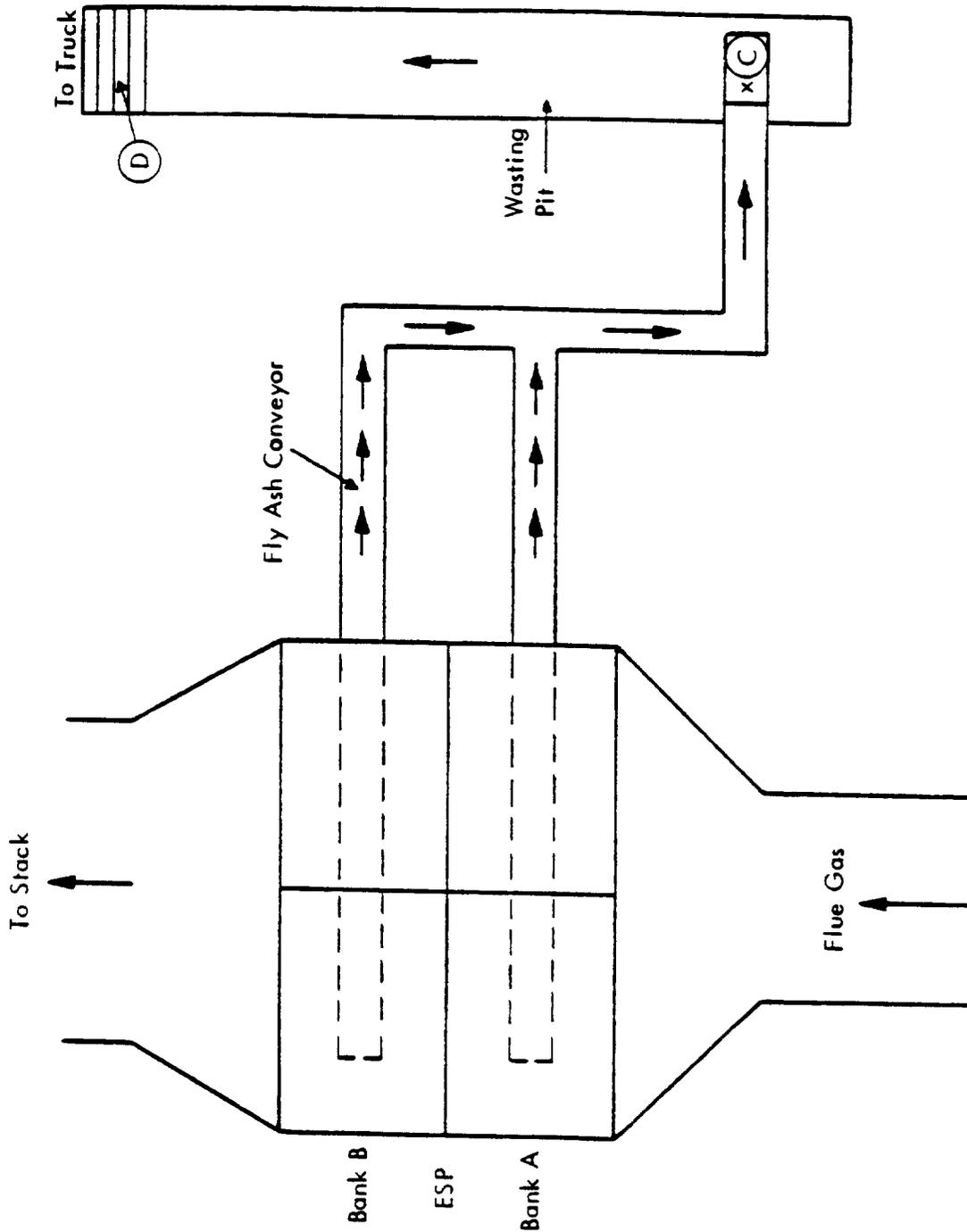
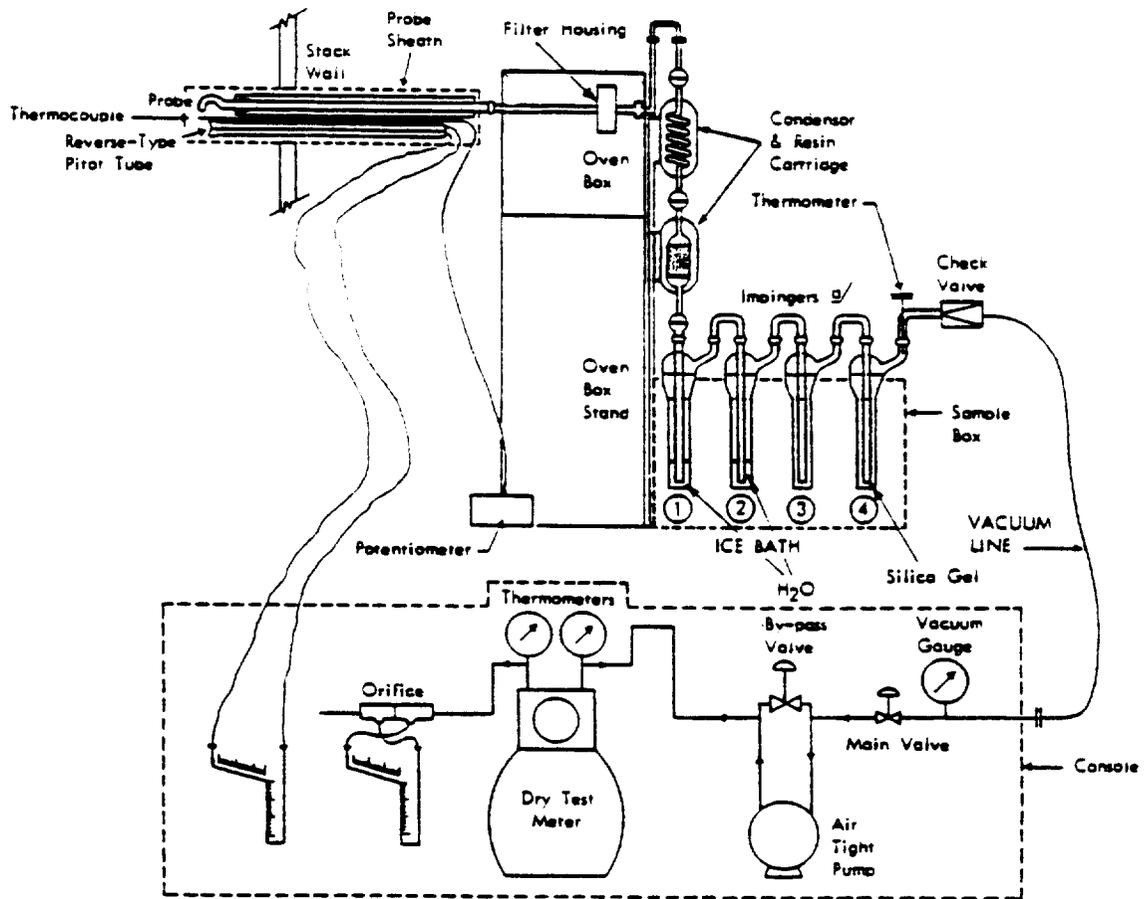


Figure 5. Ash sampling locations East Central facility (Units 1 and 2 identical).



g/ All Impingers are of the Modified Greenburg-Smith Type

- Impinger 1 and 2 Contain 100 ml Water
- Impinger 3 Contains 100 ml 0.1 N KOH
- Impinger 4 Contains 200-300 Grams Silica Gel

All Joints Up to and Not Including the Second Impinger Have Viton "O" Rings, All Other Joints Use Apiezon "L"

Figure 6. Modified Method 5 (MM5) train.

Impinger 1: 100 mL water
Impinger 2: 100 mL water
Impinger 3: 100 mL 0.1 N KOH
Impinger 4: 200 g silica gel

One of the requirements of the method is that no grease be used for sealing joints in the train. Viton® O-rings were used to seal all joints prior to and including the first impinger; Apeiezon "L" grease was used for sealing the remaining impinger joints.

With the exception of Run 1, the sampling time for each test was 4-hr (240 min); test 1 was 192 min long. The sampling time was increased after test 1 to increase the sample volume collected to over 3 m³.

Sample recovery--Both sampling trains were recovered using identical procedures. The containers recovered included:

Container 1: Probe, nozzle, and filter front half rinse (hexane/acetone)
Container 2: Filter
Container 3: XAD resin cartridge
Container 4: Hexane/acetone rinse of filter back half, condensor, and glassware connecting the filter and condensor ("organic rinse")
Container 5: First impinger condensate and organic rinse of impinger
Container 6: Second impinger condensate and impinger rinse
Container 7: Third (KOH) impinger contents and impinger rinse
Container 8: 25-mL aliquot of first impinger condensate (for HCl analyses)

The contents of all four impingers were gravimetrically measured during sample recovery to calculate stack gas percent moisture.

All samples were recovered in the field laboratory; the samples were stored in chilled containers in the field, during transport to the laboratory, and at the laboratory.

Oxygen measurement

An integrated bag sample was collected according to the procedures of EPA Reference Method 3. The bag sample was collected from a single point in the stack throughout the duration of the MMS test. The sample was analyzed for oxygen and carbon dioxide by Orsat immediately after the test. The measured carbon dioxide concentration was used to correct the measured particulate concentration to a 12% CO₂ concentration basis.

5.2.3.2 Continuous Emission Monitoring--

Stack effluent gases were continuously monitored during each 4-hr test period. The gas sample was drawn from a single point in the stack through a single heated Teflon line to a common sampling manifold mounted in a field van. The gas sample was split from the manifold so that all monitors continuously obtained a sample of the gas. Figure 7 is a simplified schematic of the continuous emission monitoring system. Gases monitored and the instruments used are shown in Table 31. Prior to initiating any testing, the calibration of each monitor was checked and documented by a three-point calibration. All calibration gases were certified calibration gases (certified $\pm 2\%$ accuracy by the manufacturer); to verify monitor calibration, one of the three gases used for calibration of each monitor was an EPA protocol gas. Before every run, each monitor was zeroed and spanned with zero and high level calibration gases. At the completion of every run, the calibration of each instrument was rechecked, and documented using the same zero/span gases. Sample line integrity was verified prior to each run by plugging the sample line inlet and monitoring the gas volumetric flow rate at the manifold to assure a no-flow condition.

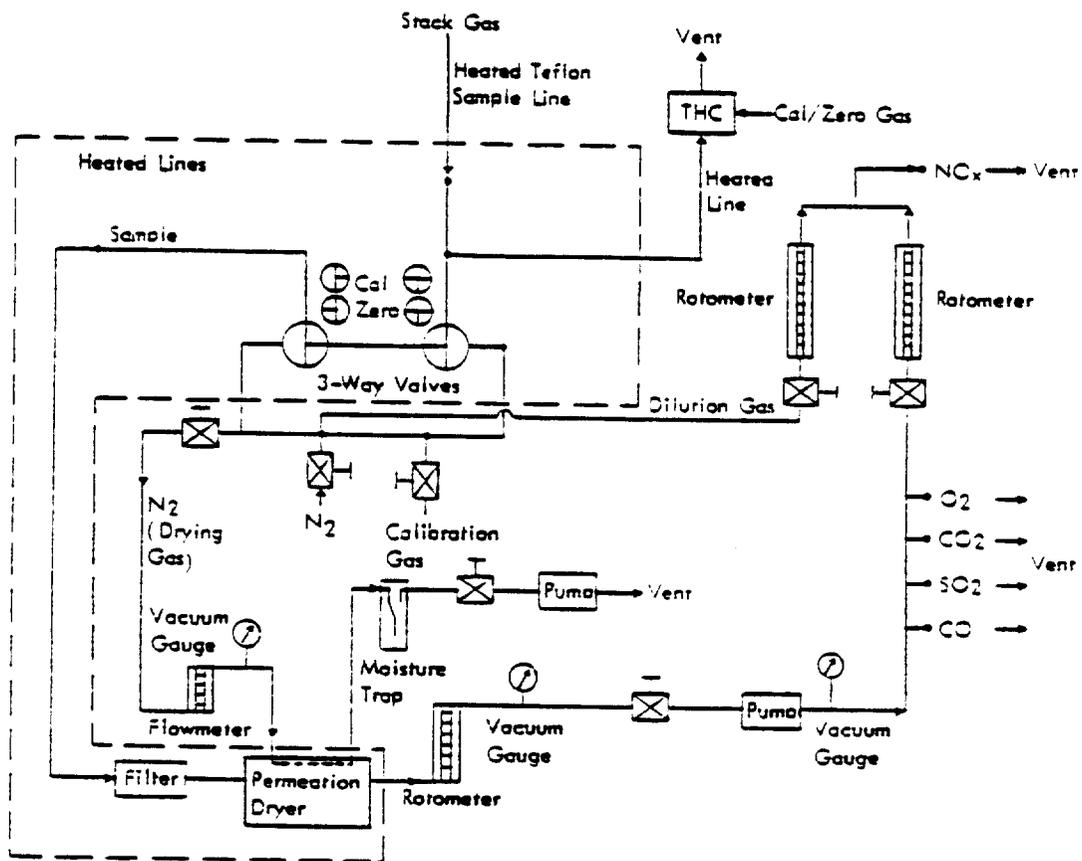


Figure 7. Simplified schematic of continuous monitoring system.

TABLE 31. SUMMARY OF CONTINUOUS MONITORING PARAMETERS

Parameter	Monitor	Instrument range
CO ₂	Horiba PIR-2000	0-15%
CO	Horiba PIR-2000	0-1,700 ppm
O ₂	Beckman 741	0-25%
SO ₂	Beckman 865	500 ppm
THC	Beckman 402	10 ppm propane
NO _x	Bendix 8101-R	5 ppm with 1:50 dilution

5.2.3 Opacity--

A certified (Method 9) opacity reader recorded stack opacity readings every 15 sec per EPA Method 9. The visible emission observers were EPA inspectors from Region III.

5.3 ANALYTICAL PROCEDURES

5.3.1 PCDD/PCDF Analyses

A brief summary of the procedures used for compositing, extracting, and analyzing the samples for PCDDs and PCDFs are presented in the following paragraphs.

5.3.1.1 Sample Compositing--

Fly ash

For each test run, 10 g of each of the 10 grab samples were composited to form a single composite fly ash sample. Therefore, the final composite fly ash sample was 100 g, except for run 1 which was 80 g (run 1 was a shorter test); a 10 g aliquot of the composite was taken for extraction.

Bottom ash

The bottom ash samples presented some problems for compositing since the samples were very wet and contained materials of varying size fractions (glass, wire, bottle tops, etc.). In order to achieve more uniform composites, the bottom ashes were air dried and separated into three size fractions. A 0.250-in. mesh screen was used to separate the largest pieces of debris (fraction 1) from the composited materials. A second cut of the bottom ashes using a 0.0937-in. sieve resulted in the removal of additional fragments of glass, rock, paper, etc. (fraction 2). The resulting sieved materials (fraction 3) were mixed well and were analyzed as the final composites. Table 32 provides the masses of the three size fractions for the composited bottom ash samples.

TABLE 32. SAMPLE COMPOSITES - BOTTOM ASH

Run No.	Composite fraction	Mass	Laboratory ^b sample No.	Extract sample No.
1	Fraction 1	c	120-BA-8281	121-BA-8281-14 122-BA-8281-15 (duplicate)
	Fraction 2	196 g		
	Fraction 3	<u>373 g</u>		
	Total	569+g		
2	Fraction 1	c	220-BA-8281	220-BA-8281-16
	Fraction 2	195 g		
	Fraction 3	<u>330 g</u>		
	Total	525+g		
3	Fraction 1	c	320-BA-8281	320-BA-8281-17
	Fraction 2	111 g		
	Fraction 3	<u>198 g</u>		
	Total	309+g		
4	Fraction 1	111 g	420-BA-8281	420-BA-8281-18
	Fraction 2	147 g		
	Fraction 3	<u>238 g</u>		
	Total	496 g		
5	Fraction 1	341 g	520-BA-8281	521-BA-8281-19 522-BA-8281-20 (duplicate)
	Fraction 2	249 g		
	Fraction 3	<u>410 g</u>		
	Total	1,000 g		
6	Fraction 1	28 g	620-BA-8281	620-BA-8281-21
	Fraction 2	48 g		
	Fraction 3	<u>206 g</u>		
	Total	282 g		
7	Fraction 1	128 g	720-BA-8281	721-BA-8281-21 722-BA-8281-22 (duplicate)
	Fraction 2	131 g		
	Fraction 3	<u>176 g</u>		
	Total	435 g		
8	Fraction 1	105 g	820-BA-8281	821-BA-8281-23 822-BA-8281-34 823-BA-8281-35 (triplicate)
	Fraction 2	127 g		
	Fraction 3	<u>167 g</u>		
	Total	399 g		

^a Contents of all field samples were combined, mixed, and allowed to air dry. Each composited sample was sieved through a 0.250-in. mesh screen. The residual materials from this step are classified as fraction 1. The sieved material was taken through a second sieve (0.0937 in.). The retained material is considered fraction 2 and the sieved material is fraction 3.

^b Fraction 3 was given the laboratory sample number. Fractions 1 and 2 were returned to the sample bottles.

^c This material was erroneously discarded prior to weighing.

MM5 samples

The MM5 sample fractions for each test run were:

- a. filter
- b. XAD resin
- c. first impinger contents/rinse ("condensate")
- d. back-half organic rinse
- e. front half probe rinse

For each run, the back-half organic rinse and the front-half probe rinse were combined prior to extraction. All other fractions were extracted separately, and the extracts combined for analysis (see Section 5.3.1.2 for extraction procedures).

5.3.1.2 Sample Extraction--

MM5 trains

Each MM5 sample consisted of the components presented in Table 33. For each run, one component of the MM5 train was spiked with 20 μ L of a solution containing the internal standards and surrogates as specified in Table 33. The composition of the spiking solution is presented in Table 34. The final impinger contents (water/hexane) were allowed to come to room temperature, spiked as necessary, and transferred to 1-L separatory funnels. The contents were shaken vigorously, allowed to separate, and the hexane fractions were removed. The aqueous condensates were each extracted with three aliquots of 60 mL of methylene chloride (Burdick and Jackson, distilled in glass). The methylene chloride extracts were combined with the hexane fraction and the combined extracts were back extracted with Milli-Q water. The organic layers were separated, dried over sodium sulfate, and stored in a walk-in cooler until combined with the remaining train component extracts.

The organic rinses and MM5 probe rinses were spiked (20 μ L of internal standards and surrogates solution), where necessary, and were concentrated

TABLE 33. MODIFIED METHOD 5 SAMPLE FRACTIONS AND SPIKING SCHEME

Sample fraction	Fraction spiked						Blank
	Run						
	1	2	3	4	5	6	
Filter	X					X	
XAD resin		X			X		
First impinger condensate and rinse			X				
Organic/probe rinse				X			X

TABLE 34. SPIKING SOLUTION

Compound	Mass of compound in 20 μ L
$^{13}\text{C}_{12}$ -2,3,7,8-TCDD	2.5 ng
$^{37}\text{Cl}_4$ -2,3,7,8-TCDD	12 ng
$^{13}\text{C}_{12}$ -2,3,7,8-TCDF	2.5 ng
$^{37}\text{Cl}_4$ -1,2,3,4,6,7,8-HpCDD	10 ng
$^{13}\text{C}_{12}$ -OCDD	10 ng

using flowing prepurified nitrogen to approximately 5 mL. The extracts and associated particulate were quantitatively transferred to 6-dram vials with additional hexane rinses and were concentrated to 1 mL.

The MM5 filters and particulate were placed in Soxhlet apparatus. The filter samples for runs 1 and 6 were spiked with 20 μ L of the surrogate and internal standards. The combined organic rinses and MM5 probe rinses were added to the respective filter extractions. The extractors were charged with 350 mL of benzene and the systems were allowed to cycle for 16 hr. The extracts from this procedure were combined with the first impinger extracts and were concentrated to 2 mL using Kuderna-Danish evaporators and flowing prepurified nitrogen.

The contents of the MM5 XAD-2 resin cartridges were transferred to large Soxhlet extractors. Samples from runs 2 and 5 were each spiked with 20 μ L of the internal standard and surrogate spiking solution. The Soxhlet apparatus were charged with 500 mL of benzene (Burdick and Jackson, distilled in glass) and were allowed to extract for at least 16 hr. The resulting extracts were combined with the extracts from the other MM5 train components and reduced in volume to 1 mL using Kuderna-Danish evaporators and flowing prepurified nitrogen.

One complete MM5 field blank was prepared along with the actual samples. In addition, a laboratory method blank was prepared to parallel all actual sample preparations.

Fly ash/bottom ash samples

Ten-gram aliquots of the composite fly ash samples were each mixed with anhydrous sodium sulfate, spiked with 200 μ L of the internal standard/surrogate spiking solution, and transferred to Soxhlet extractors. Each extractor was charged with 350 mL of benzene and the samples were extracted overnight (16 hr). The extracts were removed and concentrated as described above.

Replicate sample analyses were completed for runs 1, 5, 7, and 8. Two fly ash method blanks and one field blank were extracted along with the actual samples. However, only 20 μ L of the internal standard/surrogate spiking solution was added to the blanks.

Bottom ash samples were prepared following the same procedures as discussed for the fly ash except 20-g aliquots of the bottom ash composites were spiked with 20 μ L of the internal standard/surrogate spiking solution.

5.3.1.3 Extract Cleanup--

All sample extracts were cleaned using a two-part column chromatography procedure. The first column (1 x 30 cm) was packed with 1.0 g of silica gel and 4.0 g of 40% (w/w) sulfuric acid modified silica gel. The second column (1 x 30 m) was packed with 6.0 g of acidic alumina topped with 1 cm of anhydrous sodium sulfate. The sample extracts were added at approximately 1-mL final volume in benzene to the silica/sulfuric acid modified silica column, followed by 90 mL of hexane. This eluent was collected and eluted through the acidic alumina column, followed by 45 mL of additional hexane and 20 mL of 20% methylene chloride in hexane. The 20% methylene chloride fraction was collected for PCDD/PCDF analysis. The extracts were concentrated using flowing prepurified nitrogen and transferred to 1-mL reactivials. The final extracts were concentrated just to dryness and refrigerated until HRGC/MS analysis.

5.3.1.4 High Resolution Gas Chromatography/Mass Spectrometry (HRGC/MS)

Analysis--

The sample extracts were analyzed by high resolution gas chromatography/mass spectrometry with selected ion monitoring (HRGC/MS-SIM) using the parameters specified in Table 35. The level of the PCDDs and PCDFs were calculated by comparison of the response of the samples to calibration standards which contained the compounds listed in Table 36.

TABLE 35. INSTRUMENT AND OPERATING PARAMETERS FOR HRGC/MS-SIM ANALYSES OF PCDDs/PCDFs

Instrument:	Finnigan MAT 311A			
Column:	60-m fused silica, wall-coated with SP-2330 (TCDD/F-P ₅ CDD/F) or with DB-5 (HxCDD/F-OCDD/F)			
Column temperature:	110°C hold 2 min, 10°C/min to 340°C, hold 10 min (HxCDD/F-OCDD/F)			
Carrier gas:	Helium			
Injector:	Grob type split/splitless (1-μL injection)			
Mass resolution:	~ 1,000 (M/ΔM, 10% valley)			
Ions measured:				
<u>Homolog</u>	<u>Dioxins (m/e)</u>	<u>Furans (m/e)</u>	<u>PFK (reference)</u>	<u>Diphenyl ether Interference</u>
Tetrachloro-	319.9/321.9	303.9/305.9	330.9	373.8
Pentachloro-	355.9/357.9	337.9/339.9		407.8
Hexachloro-	389.8/391.8	373.8/375.8	380.9	443.7
Heptachloro-	423.8/425.8	407.8/409.8		477.7
Octachloro-	457/459.7	441.7/443.7		511.7
<u>Internal standards</u>				
Tetrachloro- (³⁷ Cl ₄)	327.9	-	330.9	
Tetrachloro- (¹³ C ₁₂)	331.9/333.9	315.9/317.9		
Heptachloro- (³⁷ Cl ₄)	329/331		380.9	
Octachloro (¹³ C ₁₂)	469.7/471.71	-		

TABLE 36. ANALYTICAL STANDARDS AND SOURCES

Analyte	Compounds in calibration standard	Source	Internal quantitation standard
Tetra-CDD	2,3,7,8-TCDD	EPA QA Materials Branch	2,3,7,8-TCDD- $^{13}\text{C}_{12}$ ^a
$^{37}\text{Cl}_4$ - Tetra-CDD	$^{37}\text{Cl}_4$ -2,3,7,8-TCDD	KOR Isotopes	2,3,7,8-TCDD- $^{13}\text{C}_{12}$
Tetra-CDF	2,3,7,8-TCDF	Cambridge Isotope Laboratories	2,3,7,8-TCDF- $^{13}\text{C}_{12}$
Penta-CDD	1,2,3,7,8-P ₅ CDD	Cambridge Isotope Laboratories	2,3,7,8-TCDD- $^{13}\text{C}_{12}$
Penta-CDF	1,2,3,8,9-P ₅ CDF	Cambridge Isotope Laboratories	2,3,7,8-TCDF- $^{13}\text{C}_{12}$
Hexa-CDD	1,2,3,4,7,8-HxCDD	Cambridge Isotope Laboratories	OCDD- $^{13}\text{C}_{12}$
Hexa-CDF	1,2,3,4,7,8-HxCDF	Cambridge Isotope Laboratories	OCDD- $^{13}\text{C}_{12}$
Hepta-CDD	1,2,3,4,6,7,8-HpCDD	Cambridge Isotope Laboratories	OCDD- $^{13}\text{C}_{12}$
$^{37}\text{Cl}_4$ - Hepta-CDD	$^{37}\text{Cl}_4$ -1,2,3,4,6,7,8-HpCDD	KOR Isotopes	OCDD- $^{13}\text{C}_{12}$
Hepta-CDF	1,2,3,4,6,7,8-HpCDF	Cambridge Isotope Laboratories	OCDD- $^{13}\text{C}_{12}$
Octa-CDD	OCDD	Ultra Scientific	OCDD- $^{13}\text{C}_{12}$
Octa-CDF	OCDF	Ultra Scientific	OCDD- $^{13}\text{C}_{12}$

^a The $^{13}\text{C}_{12}$ -2,3,7,8-TCDD, $^{13}\text{C}_{12}$ -2,3,7,8-TCDF, and the $^{13}\text{C}_{12}$ -OCDD were from Cambridge Isotope Laboratories.

Concentrations of each dioxin or furan homolog were calculated by first calculating a relative response factor, then calculating a final concentration in nanograms per sample using the following equations, which are an example for TCDD.

$$\text{Relative Response Factor (RRF)} = \frac{A_{(\text{std})}}{A_{(\text{IS})}} \times \frac{C_{(\text{IS})}}{C_{(\text{std})}}$$

where: $A_{(\text{std})}$ = area of ions m/z 320 and 322 for the unlabeled 2,3,7,8-TCDD in the standard
 $A_{(\text{IS})}$ = area of ions m/z 332 and 334 for the $^{13}\text{C}_{12}$ -2,3,7,8-TCDD in the standard
 $C_{(\text{IS})}$ = concentration of $^{13}\text{C}_{12}$ -2,3,7,8-TCDD in the standard
 $C_{(\text{std})}$ = concentration of unlabeled 2,3,7,8-TCDD in the standard (ng)

$$C_{(\text{sample})} = \frac{A_{(\text{sample})}}{A_{(\text{IS})}} \times \frac{C_{(\text{IS})}}{\text{RRF}}$$

where: $C_{(\text{sample})}$ = total concentration of all TCDD isomers in the sample (ng)
 $A_{(\text{sample})}$ = total area of ions m/z 320 and 322 for all TCDD isomers in the sample
 $A_{(\text{IS})}$ = area of ions m/z 332 and 334 for the $^{13}\text{C}_{12}$ -2,3,7,8-TCDD in the sample
 $C_{(\text{IS})}$ = concentration of $^{13}\text{C}_{12}$ -2,3,7,8-TCDD in the sample (ng)

The concentration of total TCDF was calculated with the above equations using the response of ions m/z 304 and 306 to measure the concentration of unlabeled TCDF and the response of ions m/z 316 and 318 for the $^{13}\text{C}_{12}$ -2,3,7,8-TCDF. Similar procedures were used for each of the PCDD/PCDF homologs. Table 36 indicates the internal standard used to calculate the RRF values for each of the PCDD/PCDF homologs.

The calibration standard included 2,3,7,8-TCDD and 2,3,7,8-TCDF; therefore, concentrations of these isomers in the stack gas emissions were determined by quantifying directly against the internal standard.

Stack gas concentrations of specific 2,3,7,8-substituted isomers for the penta-hepta dioxin and furan homologs also were of interest. There are thirteen 2,3,7,8-substituted dioxin/furan isomers; these are listed in Table 37. Nine of the 13 isomers were identified by matching their retention times to the retention time of the isomer included in the calibration standard. Information on relative retention times was provided by the two sources:

1. Rappe, C., "Analysis of Polychlorinated Dioxins and Furans," Environ. Sci. Tech., 18, 78A-90A (1984).
2. Hale, D. H., F. D. Hileman, T. Mazer, T. L. Shell, R. W. Noble, and J. J. Brooks, "Mathematical Modeling of Temperature Programmed Capillary Gas Chromatographic Retention Indexes of Polychlorinated Dibenzofurans," Anal. Chem., 57 640-648 (1985).

Once the isomer peaks were identified, concentrations were calculated using peak areas and the relative response factor previously calculated for each homolog.

5.3.2 Particulate Matter Concentrations

The probe rinse and particulate filter from the separate sample train designated as the particulate sample (train B, except run 3) were analyzed gravimetrically according to EPA Reference Method 5 procedures. The probe rinse was transferred to a tared 250 mL beaker, evaporated to dryness at room temperature, desiccated for 24 hr and weighed to a constant weight. The filter was desiccated for 24 hr and weighed to a constant weight.

TABLE 37. 2,3,7,8-SUBSTITUTED DIOXIN/FURAN ISOMERS

Isomer	Results reported ^a
1,2,3,7,8 P ₅ CDD	Yes
1,2,3,7,8 P ₅ CDF	Yes (with 1,2,3,4,8 PCDF)
2,3,4,7,8 P ₅ CDF	Yes
1,2,3,4,7,8 HxCDD	Yes
1,2,3,6,7,8 HxCDD	No
1,2,3,7,8,9 HxCDD	No
1,2,3,4,7,8 HxCDF	Yes
1,2,3,6,7,8 HxCDF	Yes
2,3,4,6,7,8 HxCDF	No
1,2,3,7,8,9 HxCDF	No
1,2,3,4,6,7,8 HpCDD	Yes
1,2,3,4,6,7,8 HPCDF	Yes
1,2,3,4,7,8,9 HpCDF	Yes

^a Stack gas concentration results are reported in Tables 10 and 11.

5.3.3 HCl Analysis

The first, second, and third impinger contents/rinse of the designated particulate sampling train were analyzed for Cl^- . A Technicon autoanalyzer was used to conduct the analyses by the colorimetric, ferricyanide method (Method 325.2, "Methods for Chemical Analysis of Water and Wastes," EPA-600/4-79-020, March 1979).