

NATIONAL DIOXIN STUDY TIER 4 — COMBUSTION SOURCES

Final Test Report — Site 10 Secondary Copper Recovery Cupola Furnace MET — A

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FOREWORD

This report is the result of a cooperative effort between the Office of Research and Development's Hazardous Waste Engineering Research Laboratory (HWERL) and the Office of Air Quality Planning and Standard's Monitoring and Data Analysis Division (MDAD). The overall management of Tier 4 of the National Dioxin Study was the responsibility of MDAD. In addition, MDAD provided technical guidance for the source test covered by this report. HWERL was directly responsible for the management and technical direction of the source test.

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1.0 INTRODUCTION

This report summarizes the results of a dioxin/furan^a emissions test of a secondary copper recovery cupola furnace equipped with an afterburner for hydrocarbon emissions control and two baghouses for particulate emissions control. The cupola furnace is used for recovery of copper from telephone scrap and other copper-bearing materials. The test was the tenth in a series of dioxin/furan emissions tests conducted under Tier 4 of the National Dioxin Study. The primary objective of Tier 4 is to determine if various combustion sources are sources of dioxin and/or furan emissions. If any of the combustion sources are found to emit dioxin or furan, the secondary objective of Tier 4 is to quantify these emissions.

Secondary copper recovery cupola furnaces are one of 8 combustion source categories that have been tested in the Tier 4 program. The tested cupola furnace, hereafter referred to as cupola furnace MET-A, was selected for this test after an initial information screening and a one-day pretest survey visit. Cupola furnace MET-A is a large secondary copper recovery cupola furnace relative to others in the United States. The furnace feed includes plastic-bearing materials of various types, some of which may contain chlorinated organic compounds.

This test report is organized as follows. A summary of test results and conclusions is provided in Section 2.0, followed by a detailed process description in Section 3.0. The source sampling and analysis plan is outlined in Section 4.0, and the field sampling and analytical data are presented in Section 5.0. Sections 6.0 through 9.0 present various testing details. These include descriptions of the sampling locations and procedures (Section 6.0), descriptions of the analytical procedures (Section 7.0), and a summary of the quality assurance/quality control results (Section 8.0). The appendices contain data generated during the field sampling and analytical activities.

^a The term "dioxin/furan" as used in this report refers to the polychlorinated dibenzo-p-dioxin and dibenzofuran isomers with four or more chlorine atoms.

2.0 TEST PROGRAM SUMMARY

2.1 SOURCE SAMPLING AND ANALYSIS OVERVIEW

The host plant is a secondary copper smelter that recovers copper and precious metals from a variety of metal-bearing scrap. The smelter cupola furnace was tested for dioxin/furan emissions in the Tier 4 program, and is referred to as cupola furnace MET-A in this report. Cupola furnace MET-A processes iron and copper-bearing scrap that includes various plastic materials. Hydrocarbon and particulate emissions in the exhaust gas from the blast furnace are controlled by an afterburner and a fabric filter system that consists of two baghouses in parallel. A simplified process flow diagram of the cupola furnace and fabric filter system is shown in Figure 2-1.

The gaseous, liquid and solid sampling performed are summarized in Table 2-1. Sampling for dioxin and furan emissions was performed at the common exhaust stack for the two baghouses. The dioxin/furan sampling was based on the October 1984 draft of the Modified Method 5 (MM5) procedure developed by the American Society of Mechanical Engineers (ASME) for measuring emissions of chlorinated organic compounds. Three modifications were made to the ASME protocol for these tests: (1) the sample train clean-up solvents used were acetone and methylene chloride instead of water, acetone, and hexane, (2) the condenser preceding the XAD sorbent traps was oriented horizontally instead of vertically, and (3) a back-up sorbent module was placed in between the water knockout impinger and the two water-filled impingers. Reasons for these modifications are discussed in Section 6.1.2. MM5 sample train components and rinses were analyzed for dioxins and furans by EMSL-RTP and ECL-Bay St. Louis, two of three EPA laboratories collectively referred to as Troika in the National Dioxin Study. The dioxin/furan analysis quantified the 2,3,7,8-tetrachlorodibenzo-p-dioxin isomer (2378 TCDD), the tetra- through octa- polychlorinated dioxin homologues (PCDD), the 2,3,7,8-tetrachlorodibenzo furan isomer (2378 TCDF), and the tetra- through octa- polychlorinated dibenzo furan homologues (PCDF).

Dioxin precursor analyses were performed by the Radian/RTP laboratory on samples of various cupola furnace feed materials. Specific precursors

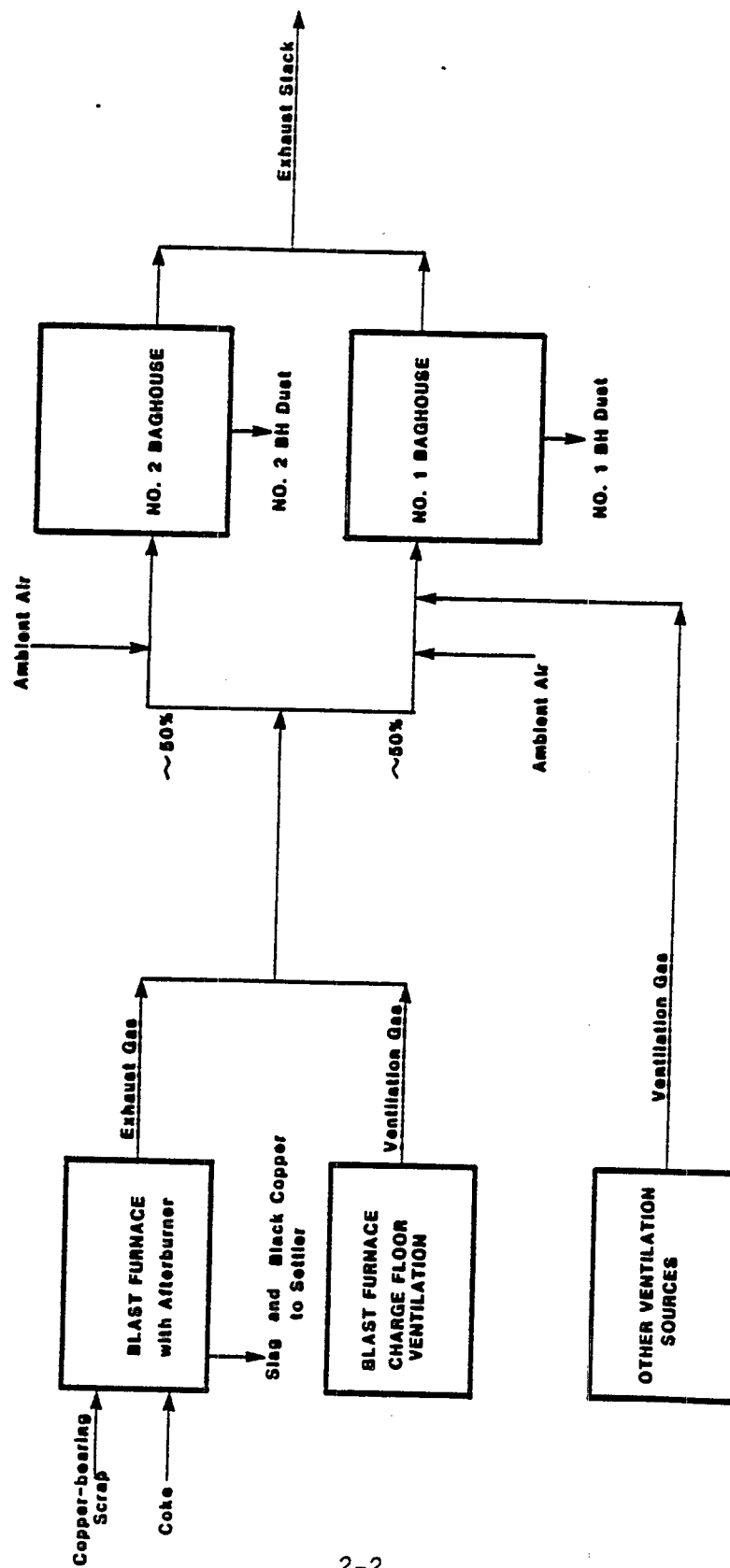


Figure 2-1. Simplified process flow diagram of Site MET-A.

TABLE 2-1. SOURCE SAMPLING AND ANALYSIS OVERVIEW FOR SITE MET-A

Item	Item Description
1. Number of test runs	- Three identical test runs (Runs 2,3,4) ^a
2. Gaseous sampling	<ul style="list-style-type: none"> - MM5 dioxin sampling at the common exhaust stack for the two baghouses (Runs 2,3,4). Dioxin/furan analysis. - HCl train sampling at the common exhaust stack for the two baghouses (Runs 2,3,4). Total chloride analysis. - Ambient air sampling near the baghouse dilution air intake point (two identical composites for Runs 2,3,4). Dioxin/furan and precursor analysis. - EPA Reference Methods 2 and 4 at exhaust stack (Runs 2,3,4). Gas velocity and moisture. - Integrated bag sampling (EPA Reference Method 3) at exhaust stack. (Runs 2,3,4). CO₂, O₂, and N₂ analysis for molecular weight determination. - Continuous monitoring of CO, CO₂, O₂, NO_x, SO₂, and THC (total hydrocarbons) at breeching to exhaust stack. (Runs 2,3,4).
3. Solid sampling	<ul style="list-style-type: none"> - Plastic-bearing cupola furnace feed sampling. Dioxin/furan precursor analysis. - Coke feed sampling. Dioxin/furan precursor analysis. - No. 1 baghouse dust sampling (Runs 2,3,4). Dioxin/furan analysis. - No. 2 baghouse dust sampling (Runs 2,3,4). Dioxin/furan analysis. - Soil sampling (one composite sample from ten locations). Potential dioxin/furan analysis.

^aOne test run (Run 01) was aborted due to sampling errors.

analyzed for were chlorophenols, chlorobenzenes, and polychlorinated biphenyls. In addition, total organic halide (TOX) analysis was performed on a composite feed sample. Samples of dust from each baghouse were collected for dioxin/furan analysis by Troika. A single set of soil samples was collected by Radian and potentially will be analyzed by Troika for dioxin/furan content.

Continuous emission monitors were operated during the test periods to measure CO_2 , O_2 , CO , NO_x , SO_2 , and total hydrocarbon (THC) concentrations in the baghouse exhaust gases. Total chloride emissions sampling was also performed at the exhaust stack during each test. Ambient air monitoring was performed at the baghouse dilution air intake point using an ambient XAD train. The ambient air samples were analyzed for dioxin/furan content by Troika and for dioxin/furan precursor content by Radian.

2.2 SUMMARY OF RESULTS

Figure 2-2 summarizes the data obtained at Site MET-A during the Tier 4 test program. Values shown in the figure correspond to the average* results for the three test runs. According to plant personnel, the cupola furnace, afterburner, and baghouse were operated under conditions representative of normal operation during the sampling periods. Detectable quantities of all targeted dioxin and furan species were found in the stack gas emissions. As shown in Table 2-2, average as-measured stack gas concentrations of 2378 TCDD, total PCDD, and total PCDF were 10.6 ng/dscm, 558 ng/dscm, and 2820 ng/dscm, respectively. This corresponded to hourly mass emission rates of 0.0054 g/hr 2378 TCDD, 0.28 g/hr total PCDD, and 1.4 g/hr total PCDF. Total dioxin emissions were fairly evenly distributed among the tetra- through octa-chlorinated dioxin homologues, while the tetra-chlorinated furan homologue was significantly more prevalent than the penta- through octa-chlorinated furan homologues.

* Surrogate recoveries could not be determined for Runs 02 and 04 dioxin/furan samples because of the large quantities of native CDD and CDF species present; therefore, no measure of extraction method efficiency was available. All three runs gave similar results, tending to lend credibility to the validity of the estimated values for the Runs 02 and 04 samples. See Section 8.3.1.2 for more details.

Flue Gas Parameter Data (A)

Flow Rate: 8400 dscmm
Temperature: 103°C
Moisture: 6.3% vol

Cupola Furnace Operating Data (F)

Feed Rate 48TPH
Charge Rate 10/hr
Roof Temperature 1610°F

Baghouse Operating Data (C)

Inlet Temp 230-300°F
P 0.5 - 8.5 in H₂O
Air:Cloth Ratio 2:1

Feed Precursor Data (G)(H)

Telephone Scrap	not detected
chlorobenzenes	detected
PCB's	not detected
Chlorophenols	detected
TOX	not detected
Coke	not detected
chlorobenzenes	not detected
PCB's	not detected
chlorophenols	not detected
TOX	not analyzed

Continuous Monitoring Data (A)

O ₂	20.2% vol
CO ₂	1.8% vol
CO	1220 ppmv
THC	15 ppmv
SO ₂	203 ppmv
NO _x	38 ppmv

Ambient Air Data (E)

Species	Concentration (ng/dscm)
2378 TCDD	ND
Total PCDD	0.15
Total PCDF	1.1

ND = not detected

Copper-Bearing Scrap Composition (coke-free basis) (G)

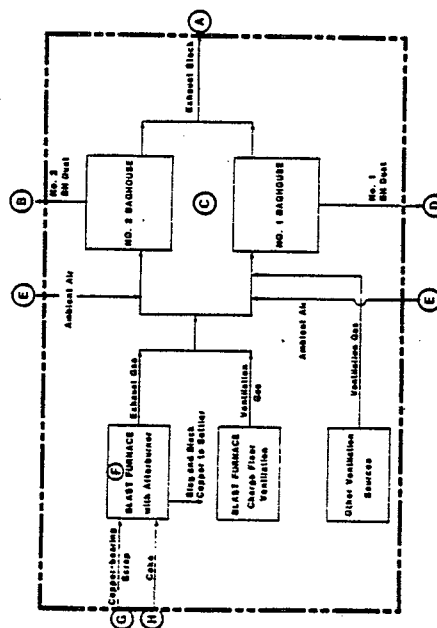
Telephone Scrap	22.1 wt%
Metallurgical Scrap	8.0 wt%
Cu Residues	26.5 wt%
Plant Reverts	9.1 wt%
Slags	34.3 wt%

No. 1 Baghouse Dust Analysis (D)

Species	Concentration (ppb)
2378 TCDD	0.17
Total PCDD	127
Total PCDF	711

No. 2 Baghouse Dust Analysis (B)

Species	Concentration (ppb)
2378 TCDD	0.12
Total PCDD	86
Total PCDF	433



Dioxin/Furan Emissions Data (A)

Species	Concentration (ng/dscm)	Emission Rate (ug/hr)	Emissions Factor (ug/kg)
2378 TCDD	10.6	5,400	0.13
Total PCDD	558	283,000	6.4
Total PCDF	2,820	1,420,000	32.5

Chloride Emission Data (A)

Emissions Type	Concentration mg/dscm	Emission Rate (kg/hr)	Emission Factor (mg/kg)
Front Half	1.4	0.7	16.1
Back Half	1.1	0.5	11.5
Train Total	2.4	1.2	27.5

note: Emission factors shown are based on copper-bearing feed input (coke-free basis). Concentrations shown are at as-measured oxygen concentrations.

Figure 2-2. Data Summary for Site MET-A

TABLE 2-2. SUMMARY OF MEAN DIOXIN/FURAN EMISSIONS DATA FOR SITE MET-A
(STACK LOCATION)

PARAMETER	2378 TCDD	TOTAL PCDD	TOTAL PCDF
<u>Emissions Concentration (ng/dscm)</u>			
As-measured	10.6	558	2,820
Corrected to 3%O ₂	232	11,900	60,700
<u>Emissions Rate (ug/hr)</u>	5360	283,000	1,420,000

Baghouse dust samples were found to contain detectable quantities of all targeted dioxin and furan species. The mean 2378 TCDD content of the baghouse dusts was 0.15 ppb; total PCDD, 107 ppb; and total PCDF, 572 ppb. The dioxin and furan homologue distributions of the baghouse dust were shifted towards the more highly chlorinated dioxin and furan species relative to the homologue distributions of the stack emissions.

Detectable quantities of all targeted dioxin and furan species except 2378 TCDD and penta-CDD were found in the ambient air samples taken near the baghouse dilution air intake point. The measured concentrations of total PCDD and total PCDF were 0.15 ng/dscm and 1.1 ng/dscm, respectively.

The copper-bearing scrap feed to the cupola furnace (i.e., coke-free feed) was reported by plant personnel to contain about 22 weight percent telephone scrap, which was the only source of plastic-bearing materials in the feed. Small quantities of polychlorinated biphenyls were detected in two components of the telephone scrap, but chlorobenzenes and chlorophenols were not detected. Total organic halide (TOX) analysis of a composite sample of telephone scrap indicated potential for the presence of significant quantities of TOX in the furnace feed. There were no unusual process upsets in cupola furnace, afterburner, or baghouse operation during the test periods. Furnace feed rates during the test periods averaged 43.5 Mg/hr (48 TPH) on a coke-free basis. The blast furnace roof temperature averaged 877°C (1610°F), and the inlet gas temperatures to the two baghouses ranged from 110°C to 150°C (230°F - 300°F).

Average flue gas concentrations measured in the exhaust stack breeching by the Radian continuous emissions monitoring system were: O₂, 20.2 vol %; CO₂, 1.8 vol %; CO, 1220 ppmv; THC, 15 ppmv as propane; SO₂, 203 ppmv; and NO_x, 38 ppmv. Total chloride emissions concentrations measured using the HCl train at the exhaust gas stack were 2.4 mg/dscm (as measured), and the total HCl emission rate was 1.2 kg/hr. The front-half of the HCl train (i.e., probe rinse and filter) accounted for about 60 percent of the total chloride emissions and the back-half (i.e., impingers and back-half rinse) accounted for the remaining 40 percent.

The composite soil sample obtained at Site MET-A has not yet been analyzed for dioxin/furan content.

3.0 PROCESS DESCRIPTION

This section describes the host site and the cupola furnace/baghouse system that was tested.

3.1 HOST SITE DESCRIPTION

The host site is a secondary copper smelter that recovers copper and precious metals from copper and iron-bearing scrap. A process flow diagram of the copper recovery system is shown in Figure 3-1. Copper and iron-bearing scrap is fed to the cupola furnace, which produces a mixture of slag and black copper. The settler separates the black copper from the slag. The black copper is further processed in converter and anode furnaces before going on to copper and precious metal refining processes. The slag from the settler goes to an electric arc furnace to recover copper remaining in the slag.

Two baghouses control particulate emissions from a gas stream consisting of the cupola furnace process offgases, cupola furnace charge floor ventilation, electric arc furnace ladle ventilation, settler tap hole ventilation, settler ladle ventilation, and silo bin ventilation. The cupola furnace and baghouse emissions control system are described in more detail in Section 3.2.

3.2 CUPOLA FURNACE DESCRIPTION

Cupola furnace MET-A is a batch-fed cupola furnace. Four to five tons of metal-bearing scrap are fed to the furnace per charge, with materials being charged eight to twelve times an hour. The furnace operates 24 hours a day for a maximum of 340 days each year. Coke is used to fuel the furnace, and represents approximately 14 percent by weight of the total feed.

The feed to the furnace is a heterogeneous mixture of several raw materials. These include telephone scrap, other metallic scrap, copper-bearing residues, plant reverts, metallurgical slags, coke, and limestone. The electronic telephone scrap contains various plastic-bearing components that may contain chlorinated organic plastics such as polyvinylchloride (PVC).

The feed to the furnace is prepared in large batches (1250 to 3750 tons, or 2 to 6 days worth of charges). Copper-bearing scrap is bedded in the raw materials storage area by layering the different types of materials. A front end loader is used to mix the bed. Mixed portions of the bed are transferred to a charge car that is transported to the cupola furnace charge floor. Approximately 4 to 5 tons of the copper-bearing scrap material and a half ton of coke are fed from the charge car to the cupola furnace 8 to 12 times each hour.

The cupola furnace is a 13 foot vertical shaft with a base of 20 feet 8 inches by 8 feet, and an uncovered top of 20 feet 8 inches by 5 feet. Oxygen enriched air for coke combustion is blown through tuyeres at the bottom of the furnace. Four Linde type AB-1-1/2 natural gas-fired afterburners at the top of the furnace aid in completing combustion. Combustion gas temperatures after the afterburner average approximately 815°C (1500°F).

Exhaust gases from the cupola furnace are cooled with water in a spray chamber and mixed with ventilation gases from the furnace charge floor. Approximately 50% of the composite cupola furnace offgas/charge floor ventilation gas stream is diluted with ambient air and vented through baghouse No. 2. The remaining 50% of the composite cupola furnace offgas/charge floor ventilation gas stream is diluted with ambient air and mixed with ventilation gases from the settler, arc furnace and silo bins. The combined gas stream is vented through baghouse No. 1.

The following cupola furnace operating parameters are monitored by the host plant: cupola roof temperatures, downcomer temperature, spray chamber temperature, cupola tuyere pressure, cupola blast air volume, cupola draft, cupola water jacket temperatures, flue gas opacity, baghouse inlet temperatures, and baghouse pressure drops. The data are recorded continuously on strip charts in the control room.

3.3 EMISSIONS CONTROL DEVICES

As discussed above, particulate emissions from cupola furnace MET-A are controlled by two Wheelabrator Corporation Model 8-320-240 baghouses in

parallel. Figure 3-2 shows the sources, flowrates and temperatures of the gas streams treated by the baghouse system. The flowrate through baghouse No. 1 is approximately 178,000 scfm. Approximately 20% of the volume through baghouse No. 1 is cupola furnace exhaust, 14% is cupola furnace charge floor ventilation gas, 48% is ambient dilution air, and 18% is ventilation gas from the arc furnace ladles, settler tap holes, settler ladles, and silo bin. The flowrate through baghouse No. 2 is approximately 118,000 scfm. Approximately 27% of the volume through baghouse No. 2 is cupola furnace exhaust, 20% is cupola furnace charge floor ventilation gas, and 53% is ambient dilution air.

The No. 1 baghouse has eight modules and the No. 2 baghouse has six modules. The baghouses use fiberglass bags and are operated at an air/cloth ratio of approximately 2 to 1. The bags are shaker cleaned. Dust from both baghouses is screw conveyed to a bucket elevator and stored in a silo. Ventilation gas from the silo is exhausted to baghouse No. 2. The baghouse dust is mixed with water and converted into pellets.

The inlet and outlet temperatures of each baghouse are monitored and recorded on strip charts in the control room. Pressure drop data across each baghouse is also maintained. The exhausts from baghouse No. 1 and baghouse No. 2 discharge to a common 250 ft. stack. Continuous monitors maintained by the plant record O_2 , THC, CO, and benzene concentrations in the breeching to the exhaust stack.

4.0 TEST DESCRIPTION

This section describes the field sampling, process monitoring, and analytical activities that were performed for Site MET-A. The purpose of the section is to provide sufficient descriptive information about the test so that the data presented in Section 5.0 can be easily understood. Details on specific sampling locations and procedures will be presented in Section 6.0.

This section is divided into three parts. Section 4.1 summarizes field sampling activities, Section 4.2 summarizes process monitoring activities, and Section 4.3 summarizes analytical activities performed during the test program.

4.1 FIELD SAMPLING

Table 4-1 shows the source sampling and analysis matrix for test Site MET-A. Three valid dioxin/furan emissions tests (Runs 02-04) were performed at the baghouse outlet exhaust stack, which is shown as location A on Figure 4-1. An additional test (Run 01) was aborted due to an error in the MM5 dioxin/furan filter housing assembly. The dioxin/furan sampling was based on the Modified Method 5 (MM5) protocol developed by the American Society of Mechanical Engineers (ASME) for measuring emissions of chlorinated organic compounds. A back-up XAD-2 resin trap was added to the MM5 sample train specified in the ASME protocol to ensure high capture efficiency of dioxins and furans. A minimum of 240 minutes of on-line sampling was performed for each test run.

Concentrations of HCl in the flue gas were determined for each test run at the baghouse outlet exhaust stack using another modification of EPA Method 5 (MM5/HCl). Continuous emissions monitoring (CEM) of O₂, CO, CO₂, NO_x, SO₂, and total hydrocarbons was performed during each test run at the breeching leading to the outlet exhaust stack. Ambient air samples were taken near the baghouse dilution air intake dampers using two ambient XAD trains. These samples were taken to quantify the levels of dioxin/furan and dioxin/furan precursors present in the cupola furnace combustion air and the baghouse dilution air.

TABLE 4-1. SOURCE SAMPLING AND ANALYSIS MATRIX FOR SITE WET-A

Sample Location	Sample Type or Parameter	Sampling Method	Analytical Method	Number of Samples/ Sample Frequency
1. Baghouse Outlet Exhaust Stack (Point A, Figure 4-1)	Dioxin/furan emissions	Modified EPA Method 5 with back-up XAD trap	Gas Chromatography/ Mass Spectrometer	Three test runs (Runs 02,03,04); one proof blank; one field recovery blank
	Volumetric gas flow rate	EPA Method 2	Not applicable	Once per MMS test run
	Molecular Weight	EPA Method 3	Gas Chromatograph/ thermal conductivity detector	Two integrated bag samples per MMS test run
	Moisture	EPA Method 4	Gravimetric Balance	Once per MMS test run
	HCl emissions	Modified EPA Method 5 (MMS/HCl)	Ion Chromatography	Once per MMS test run
2. Breaching to Exhaust Stack	CO, CO ₂ concentration	In-stack filter probe and heat- traced Teflon sample line	Non-dispersive infrared analyzer	Continuously during MMS test runs
	O ₂ concentration	Same as CO/CO ₂	Paramagnetic analyzer	Continuously during MMS test runs
	NO _x concentration	Same as CO/CO ₂	Chemiluminescent analyzer	Continuously during MMS test runs
	SO ₂ concentration	Same as CO/CO ₂	Pulsed fluorescence analyzer	Continuously during MMS test runs
	THC concentration	Same as CO/CO ₂	Flame ionization detector	Continuously during MMS test runs

TABLE 4-1. SOURCE SAMPLING AND ANALYSIS MATRIX FOR SITE HET-A (Continued)

Sample Location	Sample Type or Parameter	Sampling Method	Analytical Method	Number of Samples/ Sample Frequency
3. Ambient Dilution Air Intake Dampers	Ambient concentrations of dioxin/furan and precursors	Ambient XAD Train	Gas Chromatograph/ Mass Spectrometer	Two identical samples integrated over the 445 test periods
4. No. 1 and No. 2 Baghouse Screw Conveyors	Dioxin/furan content of baghouse dusts	Grab samples	Gas Chromatograph/ Mass Spectrometer	Samples taken twice per 445 test run
5. Raw Material Storage Yard	Precursor content of coke, telephone parts, wire, circuit boards, electronic switching gear samples	Grab samples	Gas Chromatograph/ Mass Spectrometer	Samples of each material taken once during the test program
6. Plant Property	Dioxin/furan content of a composite soil sample	Core samples	Gas Chromatograph/ Mass Spectrometer	Ten individual soil cores composited into one sample

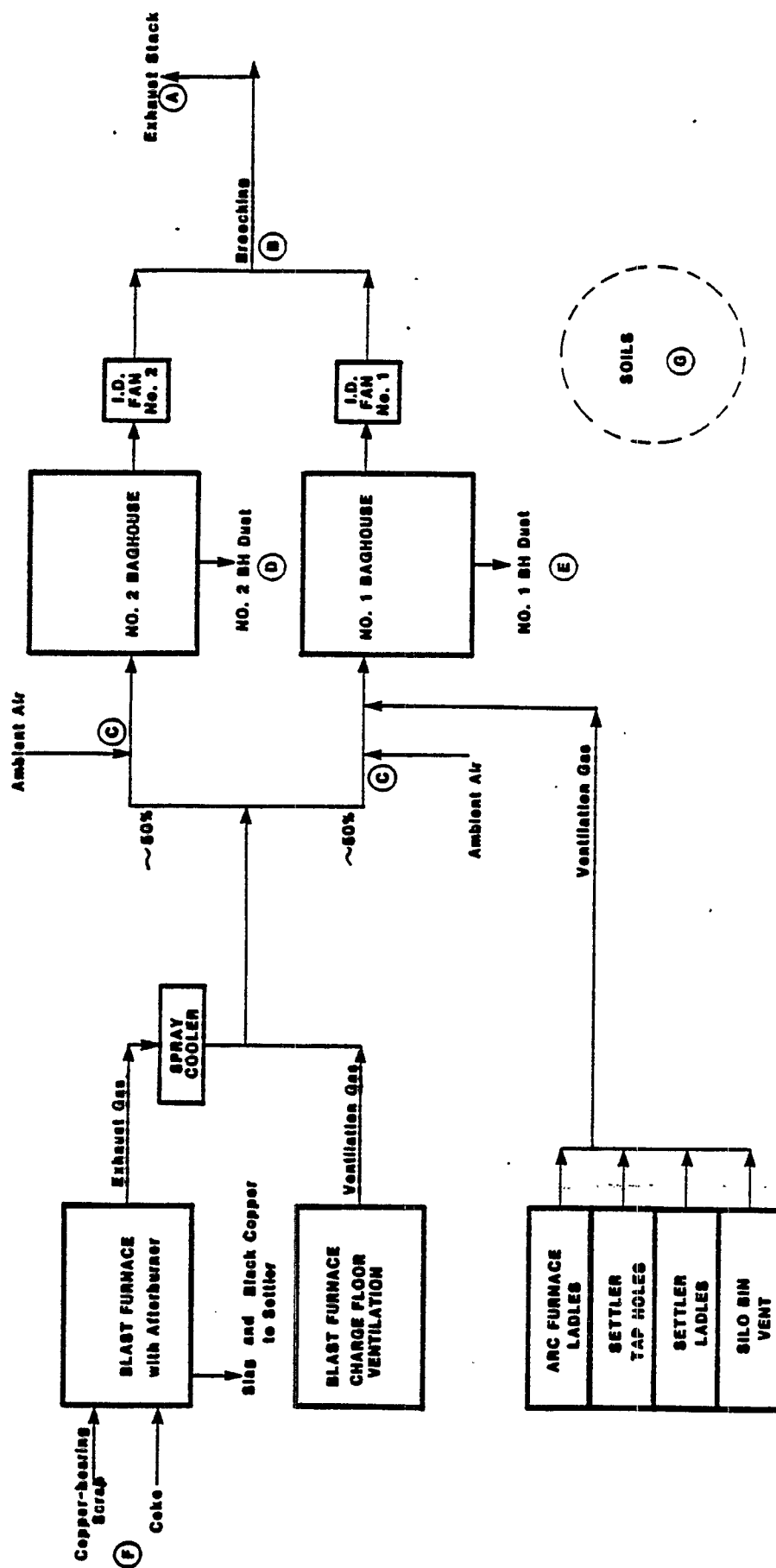


Figure 4-1. Sample point diagram for Site MET-A.

Two types of process samples were taken at Site MET-A: cupola furnace feed material samples, and cupola furnace baghouse dust samples. The feed samples were taken once during the test program and were analyzed for dioxin/furan precursor content. The baghouse dust samples were taken twice during each test run and were analyzed for dioxin/furan content. Separate samples were taken for the No. 1 and No. 2 baghouses.

Soil samples were collected from ten locations at the plant site. The ten samples were combined into a single composite that will potentially be analyzed for dioxin/furan content.

4.2 PROCESS DATA COLLECTION

Process data were collected to characterize the operation of the cupola furnace and the baghouse system during the MM5 test periods. A complete record of blast furnace charges was maintained, and data on the weight of individual charges were developed. Operating data normally monitored by the host plant were also obtained. These included various process temperatures (i.e., cupola roof temperatures, spray chamber temperature, baghouse temperatures, etc.), pressure drop data for the No. 1 and No. 2 baghouses, and continuous baghouse exhaust gas monitoring data (O_2 , CO, THC, and benzene)

4.3 LABORATORY ANALYSES

Laboratory analyses performed on samples from Site MET-A included dioxin/furan analyses, dioxin/furan precursor analyses, and total chloride analyses. These analyses are discussed in Sections 4.3.1, 4.3.2, and 4.3.3, respectively. Details on the analytical procedures are contained in Section 7.0.

4.3.1 Dioxin/Furan Analysis

All dioxin/furan analyses for Site MET-A were performed by EMSL-RTP and ECL-Bay St. Louis, Mississippi, laboratories, two of the three laboratories known as Troika. Field samples requiring dioxin/furan analysis were

prioritized based on their relative importance to the Tier 4 program objectives. The priority levels, in order of decreasing importance, were designated Priority 1 through Priority 3.

Priority 1 samples were sent to Troika with instructions to perform immediate extraction and analysis. These included the MM5 train components for the baghouse outlet exhaust stack sampling location (including the back-up XAD trap), an MM5 field recovery train blank, an MM5 proof train blank, field solvent blanks, the baghouse dust samples, and the ambient XAD train samples.

Priority 2 samples were sent to Radian/RTP for archiving. These samples may be analyzed for dioxin/furan in the future, pending the results of the Priority 1 analyses. Priority 2 samples at Site MET-A included the blast furnace feed samples.

Priority 3 samples included only the composite soil sample. The soil sample was shipped to Troika for potential dioxin/furan analysis.

4.3.2 Dioxin/Furan Precursor Analysis

Dioxin/furan precursor analyses of blast furnace feed samples were performed by Radian/RTP. The specific dioxin/furan precursors analyzed for were chlorophenols, chlorobenzenes, PCB's and total organic halide (TOX).

4.3.3 Total Chloride Analysis

Total chloride analysis was performed on front-half and back-half HCl samples by Radian's Austin, Texas laboratory.

5.0 TEST RESULTS

The results of the Tier 4 dioxin/furan emission tests of cupola furnace MET-A are presented in this section. The individual test runs are designated as Runs 01-04. Run 01 was aborted due to an error in the MM5 dioxin/furan filter housing assembly. Runs 02, 03 and 04 were performed under stable process conditions with no unusual sampling abnormalities.

Process data obtained during Runs 02-04 are presented in Section 5.1, and continuous emission monitoring results for O_2 , CO, CO_2 , NO_x , SO_2 , and THC are presented in section 5.2. Dioxin/furan and HCl emissions data are contained in Sections 5.3 and 5.4, respectively. Results of dioxin/furan analyses of the baghouse dust samples are contained in Section 5.5. Precursor and dioxin/furan analyses of the cupola furnace feed samples and the ambient XAD train samples are summarized in Section 5.6 and 5.7. Soil sampling data are presented in Section 5.8.

5.1 PROCESS DATA

Process data were obtained to document the operation of blast furnace MET-A and the baghouse during the test runs. Feed composition and feed rate data are presented in Section 5.1.1. Cupola furnace operating data are summarized in Section 5.1.2, and baghouse operating data are summarized in Section 5.1.3. In general the data indicate that process operations were stable within test runs and similar between test runs.

5.1.1 Feed Composition and Feed Rate Data

A large bed of copper-bearing materials that was prepared prior to the start of the Tier 4 tests served as the source of cupola furnace charge materials during the test runs. Five categories of materials were contained in the bed: telephone scrap, copper-bearing metallic scrap, copper-bearing residues, plant reverts, and metallurgical slag reverts. Telephone scrap was

the only category that contained plastic-bearing components. The telephone scrap included circuit boards, electronic switching gear, telephone parts, and other miscellaneous plastic materials.

The approximate composition of the charge bed reported by the host plant is presented in Table 5-1. These data were developed by multiplying the number of buckets of each feed component placed on the charge bed by the approximate weight per bucket of each component. The bucket weight data shown in Table 5-1 for the various charge bed components were developed in a previous study at this facility.

Telephone scrap accounted for about 22 weight percent of the materials in the charge bed (coke-free basis). According to plant personnel, metallurgical constraints limit the amount of telephone scrap that can be charged to the cupola furnace. The 22 percent charged represents the maximum possible amount for the particular type of telephone scrap currently used by the host plant. A different type of telephone scrap no longer processed by this facility was fed during previous tests for which higher percentages of telephone scrap were reported.

The hourly feed rate (coke-free basis) to cupola furnace MET-A during the test runs was estimated by multiplying the number of furnace charges per hour by the approximate weight per charge (coke-free basis). The number of charges per hour was counted manually during the test runs. It was not possible to weigh each individual cupola furnace charge because of the remote location of the plant scale used. A scale located on the cupola furnace charge floor was not used due to the logistics of transporting the charge cars containing the copper scrap to the charge floor scale. An average weight per charge was determined by weighing pairs of randomly selected furnace charges that were dumped into a tared skiff. The skiff was then transported to the remote plant scale and weighed. The contents of the skiff were returned to the furnace feed bed.

Charge weight data developed using this method are presented in Table 5-2. The average weight per charge was determined to be approximately 4.3 Mg (4.7 tons). This number was used to compute furnace feed rates for each test run. At an average of 10.2 charges per hour, this corresponded to an average

TABLE 5-1. CHARGE BED COMPOSITION DATA FOR THE TIER 4 TESTS AT SITE MET-A^a

Material	Raw Charge Bed Preparation Data		Calculated Charge Bed Composition Data	
	Number of Buckets	Bucket Weight (tons)	Total Weight (tons)	Weight % of Bed
Telephone Scrap	110	3.0	330	22.1
Copper-Bearing Metallic Scrap	24	5.0	120	8.0
Copper-Bearing Residues	72	5.5	396	26.5
Plant Reverts	18	7.5	135	9.1
Slag Reverts Type A Type B	24	8.2	197	13.2
	42	7.5	315	21.1
Total (All copper-bearing materials)	-	-	1493	100%

^aThe composition data shown in this table is on a coke-free basis. Coke accounts for about 15 weight percent of the total cupola furnace feed.

TABLE 5-2. CHARGE WEIGHT DATA FOR THE TIER 4 TESTS AT SITE MET-A

Sample Date/Time	Sample Weight Data ^a		Weight Per Charge (tons)
	Scale Reading (lb)	Tare Weight (lb)	Sample Weight (lb)
5/22/85 Samples			
0953	31550	6030	25520
1102	26290	6030	20260
1308	24840	6030	18810
1436	25180	6030	19150
1630	21590	6030	15560
1749	25630	6030	19600
1845	21680	6030	15650
5/23/85 Samples			
1401	23690	6030	17660
1510	24310	6030	18280
1640	22330	6030	16300
Total (10 Samples)	247090	60300	186790
			4.7

^aEach sample weight shown corresponds to two cupola furnace charges (coke-free basis).

furnace feed rate of approximately 43.5 Mg/hr (48 TPH). As shown in Table 5-3, feed rates for individual test runs ranged from 39.7 Mg/hr (43.8 TPH) for Run 02 to 49.0 Mg/hr (54.0 TPH) for Run 03. Random and operator-specific variability in the weight of charge buckets fed to the furnace accounts for much of the deviation between test runs.

5.1.2 Cupola Furnace Operating Data

Table 5-4 summarizes the mean values and standard deviations of several important cupola furnace process parameters measured during the test runs. The mean values and ranges of additional cupola furnace parameters are presented in Table 5-5. These data were reduced from strip charts obtained from the host plant.

Process temperatures were very consistent during the test runs. The cupola roof temperature, which is measured downstream of the afterburners that fire across the top of cupola furnace shaft, averaged 877°C (1610°F) for the three test runs. The maximum deviation of the mean cupola roof temperature for any test run from the average for all test runs was 5°C (9°F). Figure 5-1 shows that within-run cupola roof temperature variations were on the order of $\pm 55^{\circ}\text{C}$ ($\pm 100^{\circ}\text{F}$). Downcomer and spray chamber temperatures showed similar consistency. These temperatures averaged 300°C (572°F) and 294°C (562°F), respectively.

Flue gas concentration data monitored by the host plant at the breeching leading to the baghouse exhaust stack are also summarized in Table 5-4. The high oxygen content of the flue gas stream (avg. 19.3 vol %) reflects the large amount of ambient dilution air that is introduced prior to the baghouse system. Measured carbon monoxide concentrations at the breeching averaged 1900 ppmv and total hydrocarbon concentrations averaged 16 ppmv (as methane). Run 04 showed the highest mean CO and THC concentrations. Figure 5-2 gives a graphical representation of the THC concentration data obtained from the host plant strip charts. The data show similar within-run variability for the three test runs, with peak THC values ranging from 50 to 70 ppmv. Benzene emissions were not detected during any of the test runs.

TABLE 5-3. CUPOLA FURNACE FEED RATE DATA FOR SITE MET-A

	Run 02 (5/22/85)	Run 03 (5/22/85)	Run 04 (5/23/85)	Total Runs 02-04
Sample Period	0750-1240	1440-1910	1215-1646	-
Elapsed Time (hr)	4.8	4.5	4.5	13.8
No. Charges (North)	20	24	24	68
No. Charges (South)	25	28	20	73
No. Charges (Total)	45	52	44	141
No. Charges/hr	9.4	11.6	9.8	10.2
Furnace Charge Rate (TPH) ^a	43.8	54.0	45.7	47.7

^aCharge rate based on the total number of charges per hour and an average charge weight of 4.67 tons (coke-free basis).

TABLE 5-4 MEAN VALUES AND STANDARD DEVIATIONS OF THE MAJOR CUPOLA FURNACE PROCESS PARAMETERS AT SITE MET-A^{a, b}

Parameter	Run 02	Run 03	Run 04	Average
Cupola Furnace Feed Rate (TPH)	43.8	54.0	45.7	47.7
<u>Process Temperatures (°F)</u>				
Cupola Roof	1619 (29)	1605 (37)	1605 (62)	1610 (43)
Downcomer	590 (33)	576 (33)	551 (22)	572 (29)
Spray Chamber	571 (43)	566 (37)	549 (23)	562 (34)
<u>Flue Gas Monitoring^c</u>				
O ₂ (% vol)	19.3 (0.2)	19.5 (0.2)	19.2 (0.3)	19.3 (0.2)
CO (ppmv)	1900 (1000)	1600 (1200)	2200 (1000)	1900 (1070)
THC (ppmv) ^d	14.4 (14.4)	12.8 (15.8)	21.0 (13.8)	16.1 (14.7)
Benzene (ppmv) ^d	ND ^e	ND ^e	ND ^e	ND ^e

^aData obtained from plant-maintained strip charts. Mean value shown on top with standard deviation below in parenthesis.

^bTo convert to alternate units:

$$\text{Mg/hr} = \text{TPH} \times 0.907$$

$$^{\circ}\text{C} = (^{\circ}\text{F} - 32)/1.8$$

^cFlue gas concentration data obtained from plant-maintained continuous monitoring instruments. Sample probe was located at the breeching leading to the outlet stack, downstream of the ambient air dilution.

^dTotal hydrocarbon and benzene concentrations are reported as methane and correspond to the as-measured oxygen concentration.

^eND=not detected

TABLE 5-5 MEAN VALUES AND RANGES OF ADDITIONAL CUPOLA FURNACE
PROCESS PARAMETERS AT SITE MET-A^{a,b}

	Run 02	Run 03	Run 04
Cupola Tuyere Pressure (Oz/in ²)	30 (26 - 37)	27 (23 - 34)	29 (24 - 35)
Cupola Blast Air Volume (CFM)	20 (19 - 22)	20 (19 - 23)	20 (19 - 22)
Cupola Draft (in H ₂ O)	-.10 (-.07 - -.15)	-.12 (-.08 - -.16)	-.11 (-.09 - -.13)
Inlet Cupola Water Jacket Temp. (°F)	80 (78 - 82)	80 (78 - 82)	NA ^c
Outlet Cupola Water Jacket Temp. (°F)	105 (103 - 108)	105 (103 - 108)	NA ^c
Lear Siegler Opacity Monitor ^d (% transmittance)	7 (0 - 30)	7 (0 - 30)	7 (0 - 30)

^aData obtained from plant-maintained strip charts

^bTo convert to alternate units:

$$\text{kPa} = \text{Oz/in}^2 \times 0.430$$

$$\text{cmH}_2\text{O} = \text{cfm} \times 0.0283$$

$$\text{kPa} = \text{in H}_2\text{O} \times 0.249$$

$$\text{O}_2 = (\text{°F} - 32)/1.8$$

^cCupola water jacket temperature data were not retained by plant personnel for Run 04.

^dOpacity monitor was located at breeching leading to stack (i.e., downstream of the baghouses).

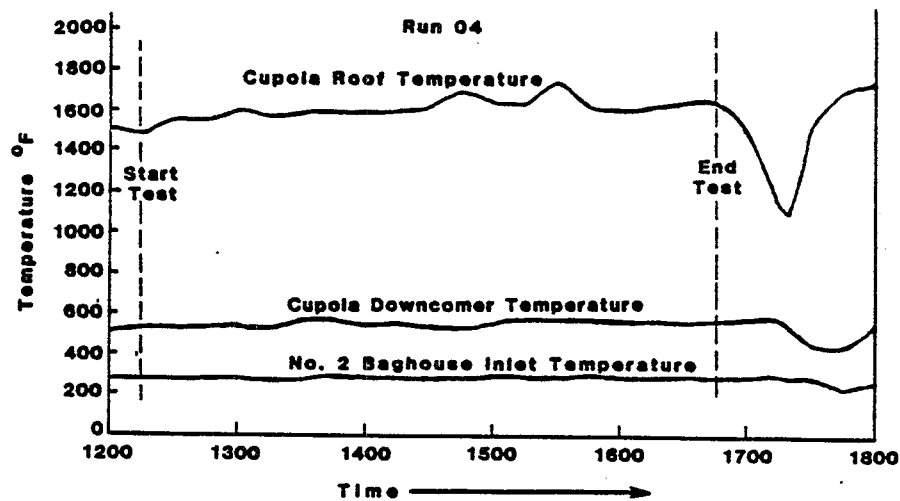
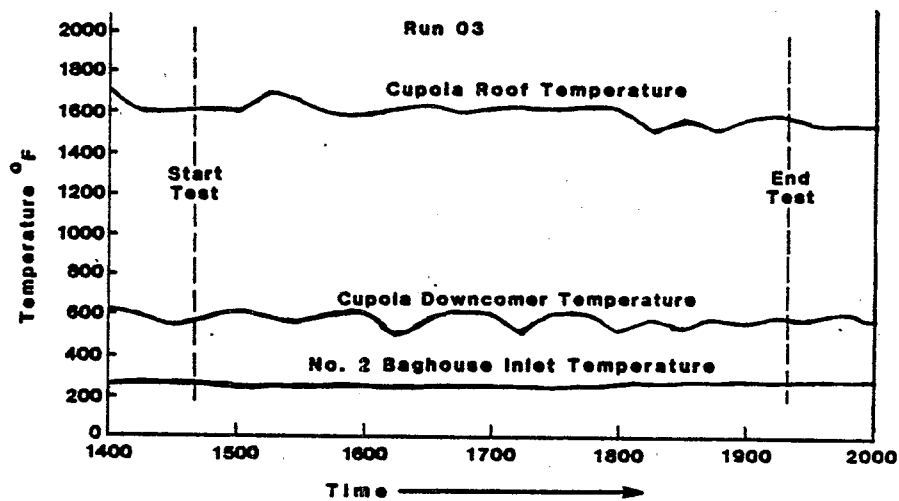
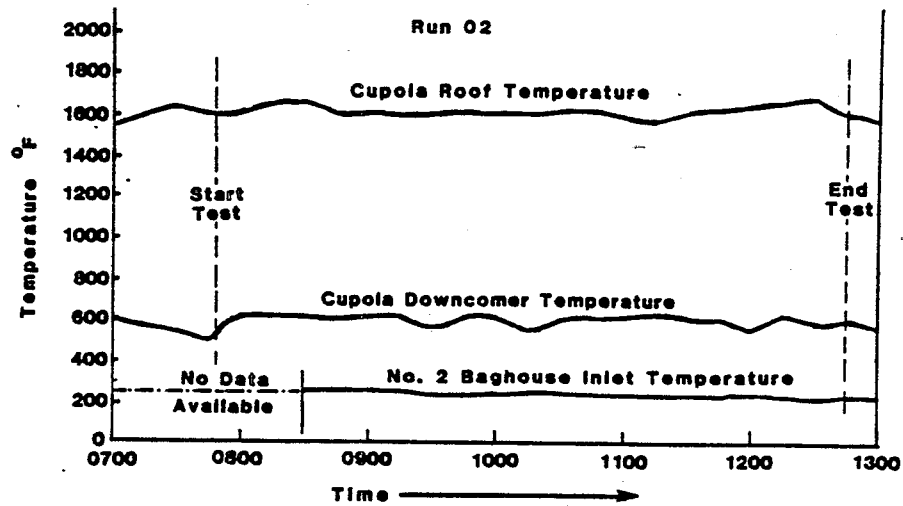


Figure 5-1. Process Temperature Histories During the Test Runs

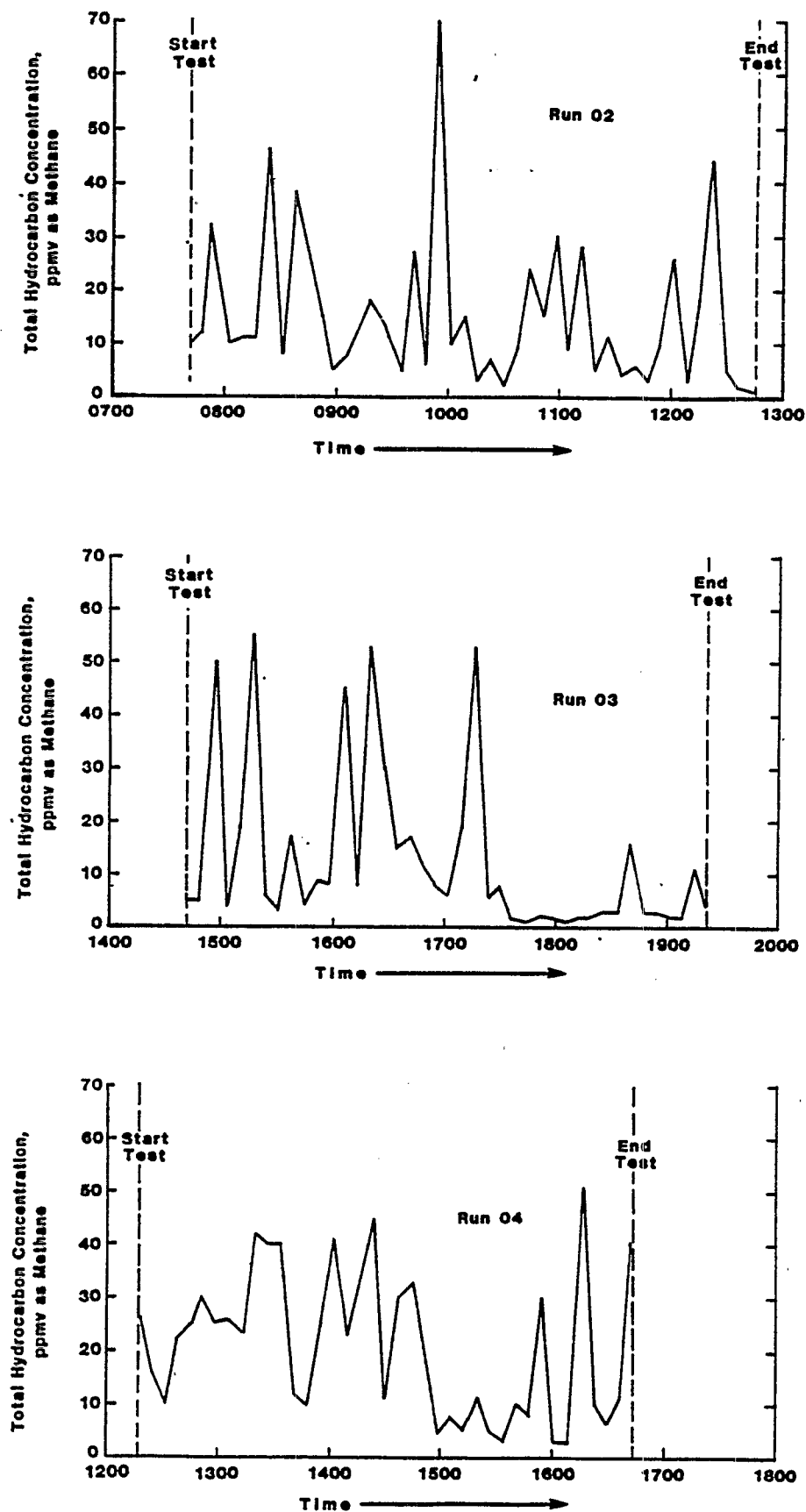


Figure 5-2. Total Hydrocarbon Concentration Histories During the Test Runs (Plant Data)

5.1.3 Baghouse Operating Data

Table 5-6 summarizes the mean values and ranges of several baghouse operating parameters measured during the test runs. The inlet gas temperature to the No. 1 and No. 2 baghouses averaged 142°C (288°F) and 130°C (266°F), respectively. Within-run baghouse inlet temperature variabilities were on the order of $\pm 11^{\circ}\text{C}$ (20°F) for the No. 1 baghouse and $\pm 22^{\circ}\text{C}$ (40°F) for the No. 2 baghouse. An explanation for these apparent differences between baghouses is not readily apparent.

5.2 FLUE GAS PARAMETER DATA

Table 5-7 summarizes flue gas temperature, moisture, volumetric flow rate, and oxygen concentration data obtained at Site MET-A. These parameters were consistent between test runs. The average flue gas temperature and moisture content measured at the exhaust stack location were 103°C (217°F) and 6.3% vol, respectively. The average exhaust gas flow rate under actual stack temperature and moisture conditions was 11,500 acmm (406,000 acfm), and the average dry, standard flow rate was 8,400 dscmm (297,000 dscfm). Standard EPA conditions are 20°C (68°F) and 1 atm.

Flue gas oxygen concentration data were obtained from the plant continuous emissions monitoring (CEM) system, the Radian CEM system, and integrated bag samples (EPA Method 3). The average O_2 concentrations of the flue gas as measured by these three techniques were 19.3 vol%, 20.2 vol%, and 20.5 vol%, respectively. The Radian CEM data will be used in subsequent sections of this report when normalizing as-measured flue gas concentrations of other species (e.g., dioxin, furan, CO, THC, etc.)-to a reference oxygen level.

5.3 CONTINUOUS EMISSIONS MONITORING DATA

As-measured mean values and standard deviations of the combustion gases continuously monitored by Radian at the stack breeching location (O_2 , CO, CO_2 ,

TABLE 5-6 MEAN VALUES AND RANGES OF BAGHOUSE OPERATING
PARAMETERS AT SITE MET-A^{a, b}

Parameter	Run 02	Run 03	Run 04	Average
<u>Temperature Data (^oF)</u>				
#1 Baghouse Inlet	288 (280-300)	289 (285-290)	288 (285-295)	288 (280-300)
#2 Baghouse Inlet	247 (230-265)	270 (250-295)	280 (260-295)	266 (230-295)
<u>Pressure Drop Data (inches H₂O)</u>				
#1 Baghouse	5.0 (0.5 - 8.5)	6.0 (4.0 - 8.0)	6.5 (3.5 - 8.5)	5.8 (0.5 - 8.5)
#2 Baghouse	8.0 (6.5 -10.0)	8.5 (7.0 -10.0)	8.5 (6.0 -10.5)	8.3 (6.5 - 10.5)
Gas Flow Rate (dscfm) ^c	296,000	307,000	286,000	296,000

^aBaghouse temperature and pressure drop data obtained from plant-maintained strip charts. Gas flow rate data obtained by Radian using EPA Method 2.

^bTo convert values to alternate units:

$$^{\circ}\text{C} = (^{\circ}\text{F} - 32)/1.8$$

$$\text{kPa} = \text{in. H}_2\text{O} \times 0.249$$

$$\text{dscmm} = \text{dscfm} \times 0.0283$$

^cTotal gas flow rate measured by Radian at stack.

TABLE 5-7 FLUE GAS PARAMETERS AT SITE MET-A^a
(STACK LOCATION)

Flue Gas Parameters	Run 02	Run 03	Run 04	Average
Temperature (°C)	101	106	101	103
Moisture (vol. %)	6.4	6.3	6.3	6.3
<u>Volumetric Flow Rate</u>				
Actual (acmm)	11,500	12,000	11,100	11,500
Dry Standard (dscmm)	8,400	8,700	8,100	8,400
<u>Oxygen Content (vol. %)</u>				
Plant CEM	19.3	19.5	19.2	19.3
Radian CEM	20.2	20.1	20.2	20.2
EPA Method 3	20.4	20.4	20.7	20.5

a. Metric units are reported for all flue gas measurement data.
 To convert to alternate units: °F = 1.8 x °C + 32
 cfm = cmm x 35.3

THC, NO_x , and SO_2) are shown for each MM5 test run in Table 5-8. The as-measured overall mean values for the three test runs are as follows: oxygen, 20.2 percent by volume (dry); carbon monoxide, 1220 ppmv (dry); carbon dioxide, 1.8 percent by volume (dry); sulfur oxides, 203 ppmv (dry); nitrogen oxides, 38 ppmv (dry); and total hydrocarbons, 15 ppmv (wet, as propane).

Table 5-9 shows the mean values and standard deviations of these concentrations corrected to 3% O_2 , for comparison to other combustion sources tested in the Tier 4 program. The factor for correcting gas phase concentration data to a reference oxygen level is very sensitive to small changes in the measured oxygen level when the measured oxygen level is near 20 percent. For example, a change in the measured oxygen level from 19% O_2 to 20% O_2 results in a change in the concentration correction factor of more than a factor of 2. Thus, the numbers in Table 5-8 should be regarded as estimates only.

The mean oxygen, carbon dioxide, sulfur oxides and nitrogen oxide concentrations showed reasonably small between-run variability. The maximum deviation between the mean concentration for any run and the overall average for all runs was less than 20 percent for these species. The mean carbon monoxide and THC concentrations had a greater degree of between-run variability, with Run 04 showing the highest as-measured mean values (1500 ppmv and 18.5 ppmv, respectively) and Run 03 showing the lowest as-measured mean values (844 ppmv and 11.7 ppmv, respectively). The between-run trends measured by Radian for CO and THC were consistent with those measured by the host plant.

Five-minute average values of the continuously monitored combustion gas concentrations are tabulated in Appendix A-2 and are shown graphically as functions of time in Figures 5-3 through 5-8. In general, concentrations of oxygen and CO_2 were reasonably stable while concentrations of CO, THC, NO_x , and SO_2 all showed considerable within-run variability. This is most likely due to the semi-batch feed nature of the cupola furnace (i.e., roughly one charge every six minutes). The small cyclic variations shown for the O_2 concentration in Figure 5-3 have not been explained.

TABLE 5-8. MEAN VALUES AND STANDARD DEVIATIONS OF CONTINUOUSLY MONITORED COMBUSTION GASES AT SITE MET-A (BREECHING LOCATION, AS-MEASURED VALUES)^{a,b}

Species ^{c,d}	Run 02	Run 03	Run 04	Average
O ₂ (% vol)	20.2 (0.6)	20.1 (0.3)	20.2 (0.6)	20.2 (0.5)
CO (ppmv)	1320 (1090)	844 (890)	1500 (871)	1220 (951)
CO ₂ (% vol)	1.8 (0.2)	1.6 (0.2)	1.9 (0.2)	1.8 (0.2)
SO ₂ (ppmv)	193 (46)	176 (55)	240 (48)	203 (49)
NO _x (ppmv)	38.9 (12.3)	40.9 (9.4)	34.8 (6.1)	38.2 (9.3)
THC (ppmv)	14.7 (11.5)	11.7 (11.2)	18.5 (11.9)	15.0 (11.5)

^aMean value shown on top, with standard deviation below in parenthesis.

^bGas sampling for the continuous monitors was performed at the stack breeching location.

^cAll concentrations expressed on a dry volume basis except for total hydrocarbon concentrations, which are expressed on a wet volume basis.

^dTotal hydrocarbon data are expressed in units of ppmv (wet) as propane.

TABLE 5-9. MEAN VALUES AND STANDARD DEVIATIONS OF CONTINUOUSLY
MONITORED COMBUSTION GASES AT SITE MET-A^{a,b}
(BREECHING LOCATION, CORRECTED TO 3% O₂)^{a,b}

Species ^{c,d}	Run 02	Run 03	Run 04	Average
O ₂ (% vol)	20.2 (0.6)	20.1 (0.3)	20.2 (0.6)	20.2 (0.5)
CO (ppmv @ 3% O ₂)	36,600 (29,300)	18,700 (19,700)	37,200 (21,600)	30,800 23,500
CO ₂ (% vol @ 3% O ₂)	48.7 (5.4)	36.4 (4.6)	46.2 (4.9)	43.8 (5.0)
SO ₂ (ppmv @ 3% O ₂)	7,560 (1,800)	5,660 (1,760)	8,650 (1,720)	7,290 (1,760)
NO _x (ppmv @ 3% O ₂)	1,050 (331)	907 (208)	863 (151)	940 (230)
THC (ppmv @ 3% O ₂)	395 (309)	260 (249)	458 (295)	371 (284)

^aMean values shown on top, with standard deviation below in parenthesis.

^bGas sampling for the continuous monitors was performed at the stack breeching location.

^cAll concentrations expressed on a dry volume basis except for total hydrocarbon concentrations, which are expressed on a wet volume basis.

^dTotal hydrocarbon data are expressed in units of ppmv (wet) as propane.

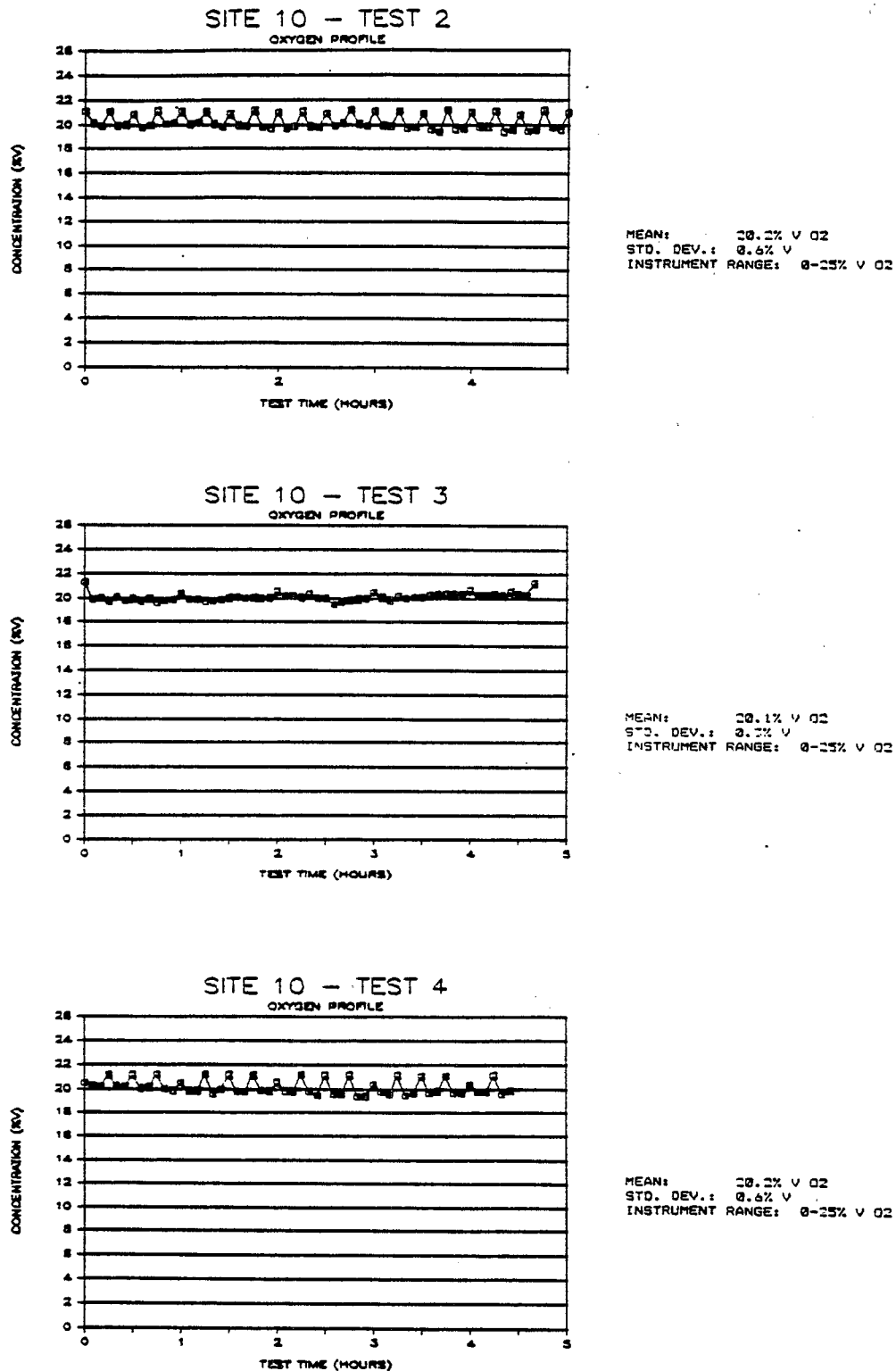


Figure 5-3. Oxygen Concentration Data at the Stack Breeching Location

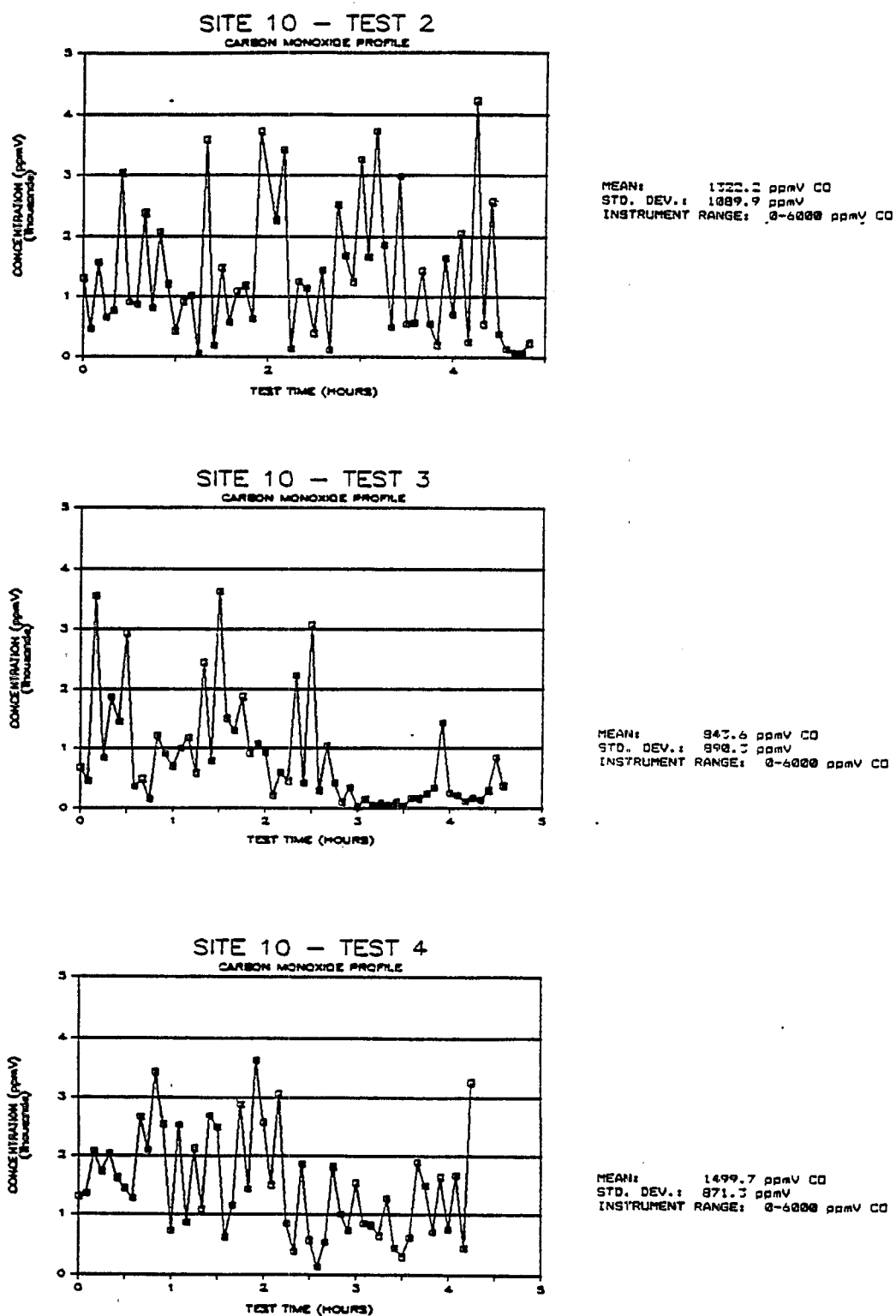


Figure 5-4. Carbon Monoxide Concentration Data
at the Stack Breaching (as-measured values)

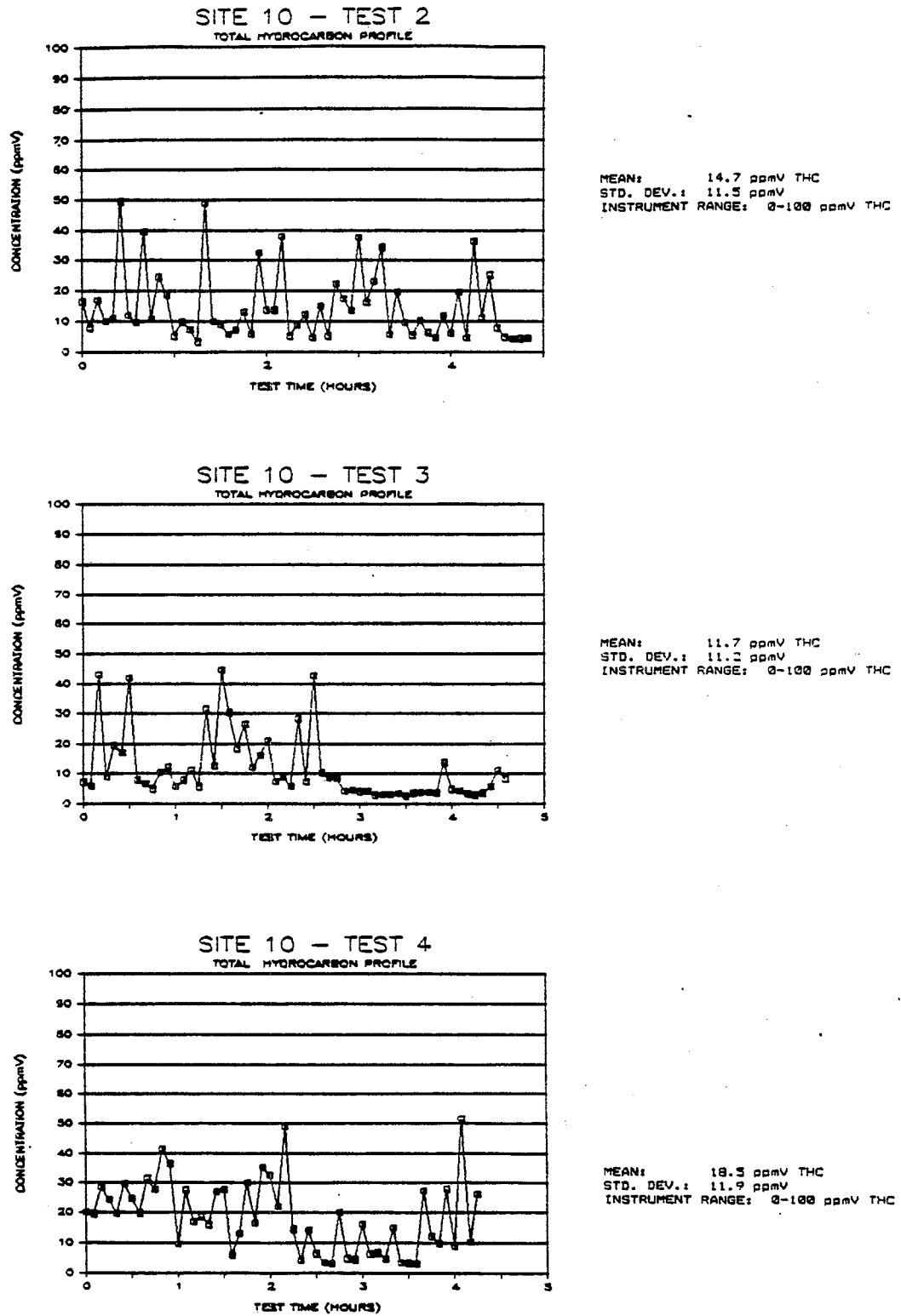


Figure 5-5. Total Hydrocarbon Concentration Data
at the Stack Breaching Location (as-measured values)

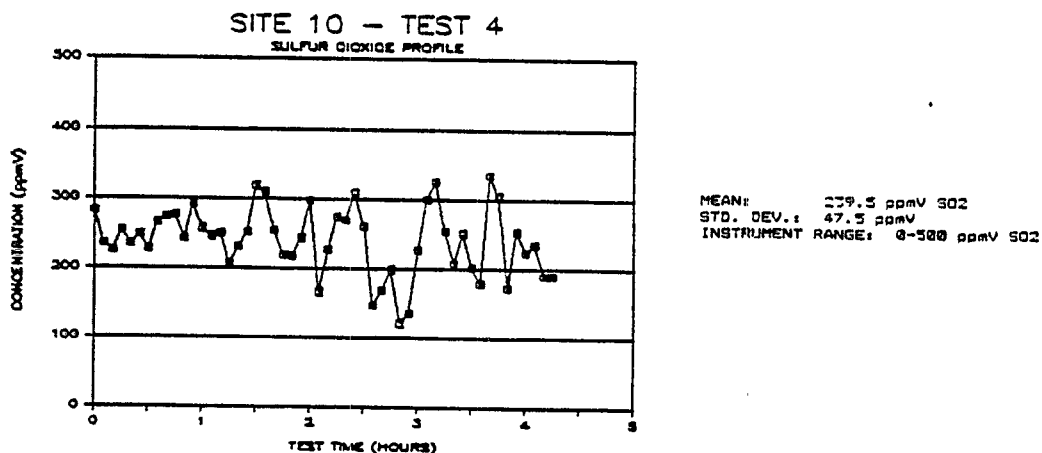
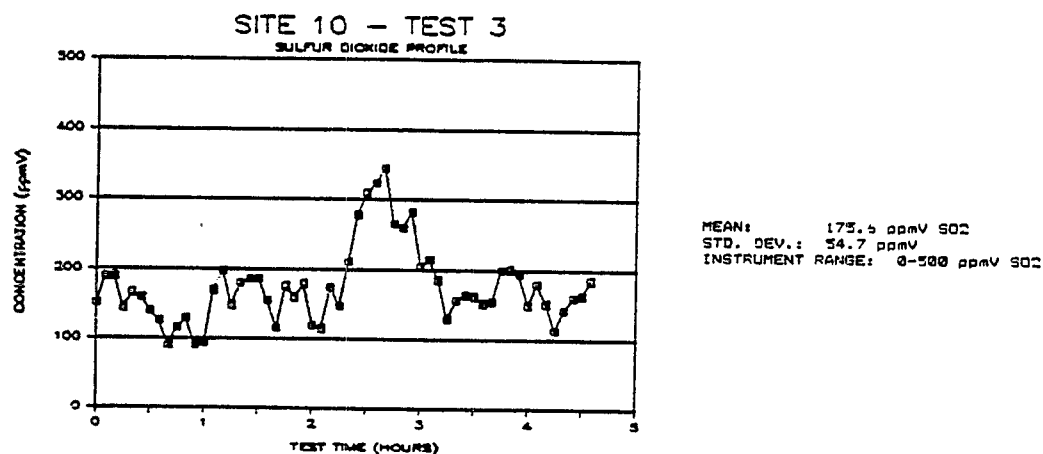
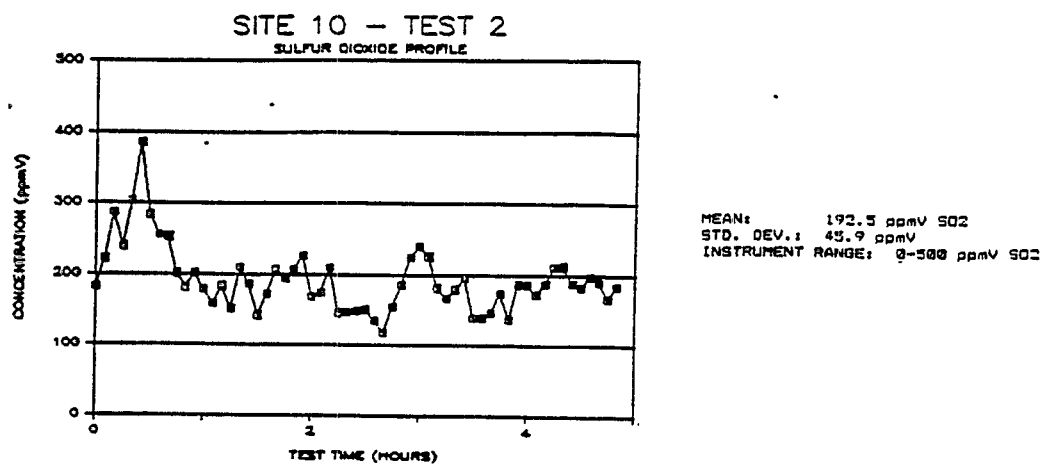
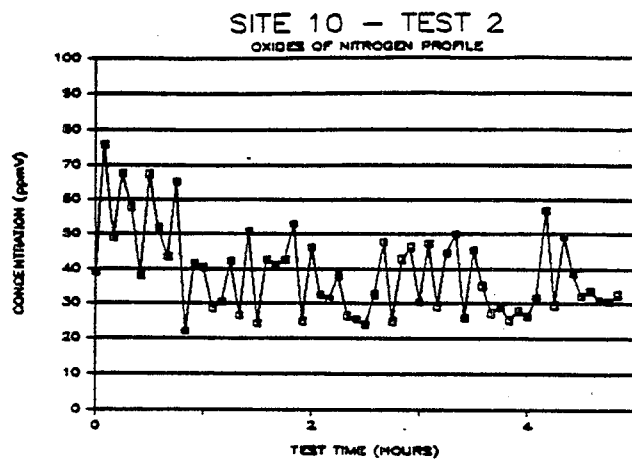
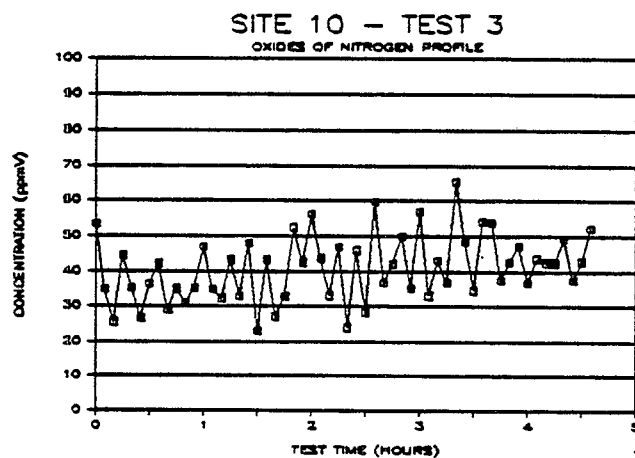


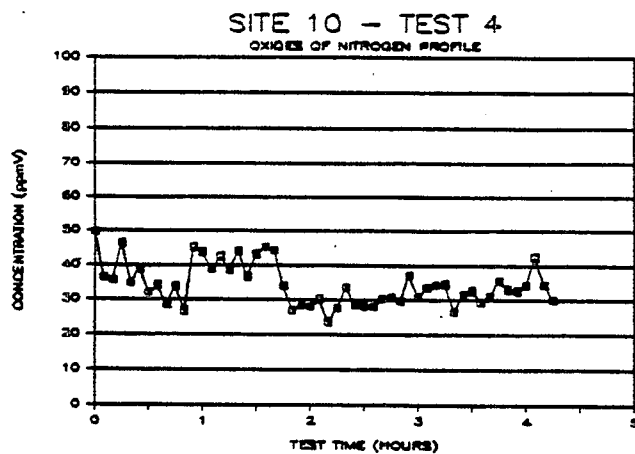
Figure 5-6. Sulfur Dioxide Concentration Data at the Stack Breaching Location (as-measured values)



MEAN: 38.9 ppmV NOx
 STD. DEV.: 12.3 ppmV
 INSTRUMENT RANGE: 0-100 ppmV NOx



MEAN: 40.9 ppmV NOx
 STD. DEV.: 9.4 ppmV
 INSTRUMENT RANGE: 0-100 ppmV NOx



MEAN: 34.8 ppmV NOx
 STD. DEV.: 6.1 ppmV
 INSTRUMENT RANGE: 0-100 ppmV NOx

Figure 5-7. Nitrogen Oxides Concentration Data at the Stack Breaching Location (as-measured values)

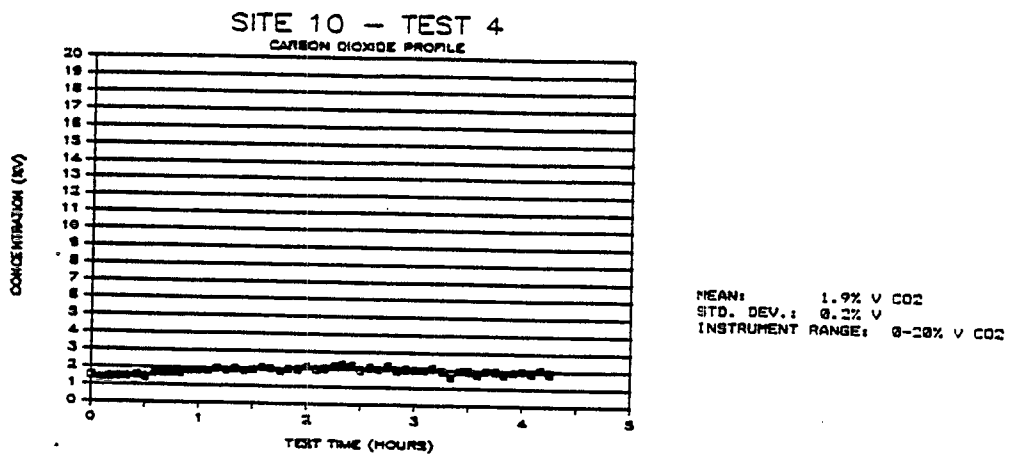
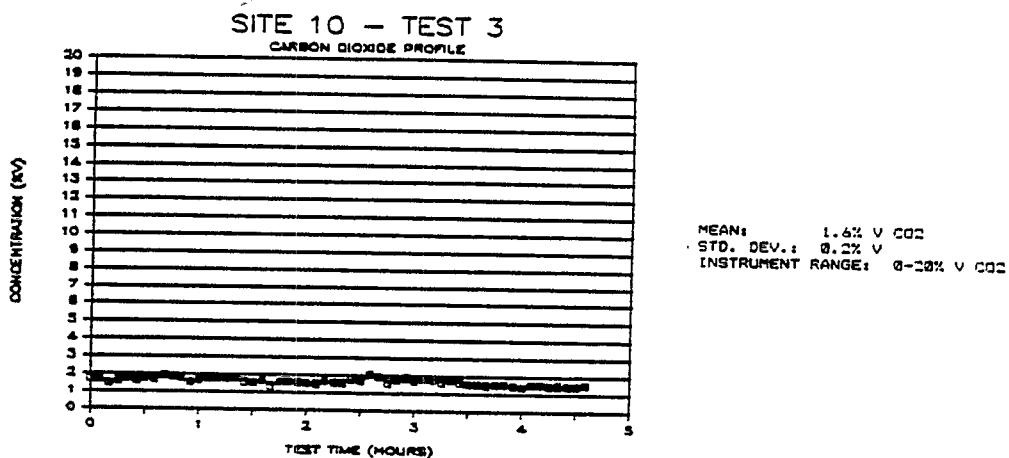
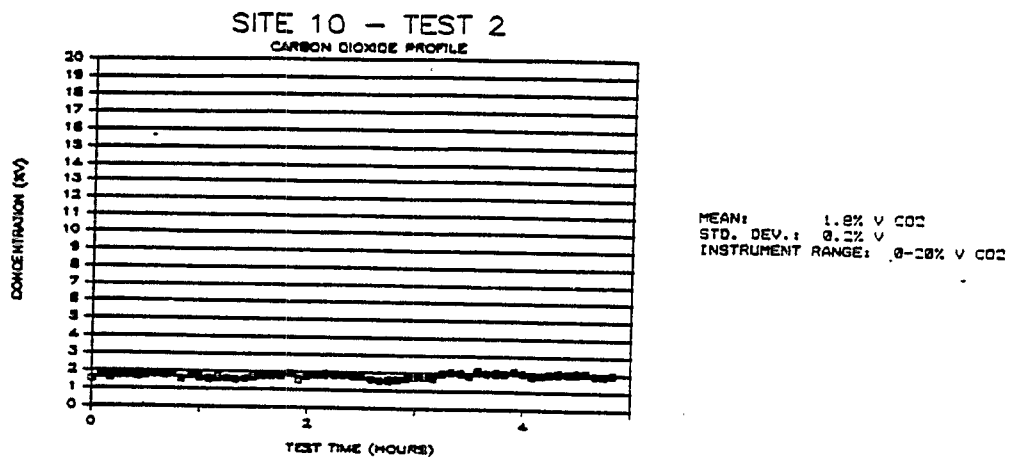


Figure 5-8. Carbon Dioxide Concentration Data at the Stack Breaching Location (as-measured values)

5.4 DIOXIN/FURAN EMISSIONS DATA

Emissions concentration and emissions rate data measured at the exhaust stack sampling location are shown in Tables 5-10 and 5-11 for the 2378 TCDD, total PCDD, and total PCDF species. The data include dioxin and furan captured by the entire MM5 train, including the filter, primary XAD sorbent trap, back-up XAD sorbent trap, impingers, and sample train clean-up rinses.

Average* as-measured emissions concentrations of the 2378 TCDD, total PCDD, and PCDF species were 10.6 ng/dscm 2378 TCDD, 558 ng/dscm total PCDD, and 2,820 ng/dscm total PCDF. When corrected to 3% O₂ using the Radian CEM oxygen concentration data, these values correspond to 232 ng/dscm @ 3% O₂, 11,900 ng/dscm @ 3% O₂, and 60,700 ng/dscm @ 3% O₂, respectively. Average emission rates for the three species were 0.005 g/hr 2378 TCDD, 0.28 g/hr total PCDD, and 1.42 g/hr total PCDF. Emissions of 2378 TCDD varied by about a factor of 3 between runs, while total PCDD and total PCDF emissions showed less variability. The maximum deviations of the total PCDD and total PCDF emission concentrations for any individual run from the average values for all runs were 40 percent and 22 percent, respectively.

Isomer- and homologue-specific emission concentration data are summarized in Tables 5-12 and 5-13 for the three test runs. Run-specific data tables showing homologue emission concentrations in both ng/dscm and part-per-trillion units and homologue emission rates in ug/hr units are included in Appendix D. Detectable quantities of each targeted dioxin and furan species were found in the flue gas samples.

Figure 5-9 is a histogram that shows the relative distributions of the 2378 TCDD/TCDF isomers and the tetra-through octa PCDD/PCDF homologues in the exhaust stack emissions (mole basis). The distribution of dioxin species was relatively uniform among the various homologues. The 2378 TCDD isomer accounted for 1 to 4 percent of the total dioxins analyzed for, which corresponded to roughly 10 to 20 percent of the tetra-homologue total for

* Surrogate recoveries could not be determined for Runs 02 and 04 dioxin/furan samples because of the large quantities of native CDD and CDF species present; therefore, no measure of extraction method efficiency was available. All three runs gave similar results, tending to lend credibility to the validity of the estimated values for the Runs 02 and 04 samples. See Section 8.3.1.2 for more details.

TABLE 5-10. OVERVIEW OF DIOXIN AND FURAN EMISSIONS CONCENTRATION DATA FOR SITE MET-A (STACK LOCATION)

Run Number	Emissions Concentration, ng/dscm		
	2378 TCDD	Total PCDD	Total PCDF
<u>ng/dscm (as-measured)</u>			
Run 02	17.5	436	2,190
Run 03	8.5	781	3,270
Run 04	5.8	456	3,000
Average ^b	10.6	558	2,820
<u>ng/dscm @ 3% O₂^a</u>			
Run 02	395	9,800	49,200
Run 03	170	15,600	65,300
Run 04	130	10,300	67,400
Average ^b	232	11,900	60,700

^aFlue gas concentration data corrected to 3% O₂ using the average Radian CEM data in Table 5-8.

^bSurrogate recoveries could not be determined for Runs 02 and 04 dioxin/furan samples because of the large quantities of native CDD and CDF species present; therefore, no measure of extraction method efficiency was available. All three runs gave similar results, tending to lend credibility to the validity of the estimated values for the Runs 02 and 04 samples. See Section 8.3.1.2 for more details.

TABLE 5-11. SUMMARY OF DIOXIN AND FURAN EMISSION RATE
DATA FOR SITE MET-A (STACK LOCATION)

Run Number	Dioxin/Furan Emission Rate, ug/hr		
	2378 TCDD	Total PCDD	Total PCDF
Run 01	8,830	219,000	1,110,000
Run 02	4,430	408,000	1,700,000
Run 03	2,810	222,000	1,460,000
Average ^a	5,360	283,000	1,420,000

^aSurrogate recoveries could not be determined for Runs 02 and 04 dioxin/furan samples because of the large quantities of native CDD and CDF species present; therefore, no measure of extraction method efficiency was available. All three runs gave similar results, tending to lend credibility to the validity of the estimated values for the Runs 02 and 04 samples. See Section 8.3.1.2 for more details.

TABLE 5-12 SUMMARY OF DIOXIN/FURAN EMISSIONS CONCENTRATION
DATA FOR SITE MET-A (AS-MEASURED CONCENTRATIONS)

Dioxin/Furan Isomer	Isomer Concentration in Flue Gas (ng/dscm)			
	Run 02	Run 03	Run 04	Avg. ^b
DIOXINS				
2378 TCDD	1.75E+01	8.50E+00	5.77E+00	1.06E+01
Other TCDD	3.53E+01	7.01E+01	5.40E+01	5.31E+01
Penta-CDD	6.28E+01	1.16E+02	7.45E+01	8.46E+01
Hexa-CDD	1.45E+02	1.08E+02	6.76E+01	1.07E+02
Hepta-CDD	1.09E+02	2.93E+02	1.48E+02	1.84E+02
Octa-CDD	6.51E+01	1.85E+02	1.06E+02	1.19E+02
Total PCDD	4.36E+02	7.81E+02	4.56E+02	5.58E+02
FURANS				
2378 TCDF	1.86E+02	2.53E+02	2.65E+02	2.35E+02
Other TCDF	6.28E+02	8.90E+02	1.33E+03	9.48E+02
Penta-CDF	5.59E+02	9.27E+02	7.65E+02	7.50E+02
Hexa-CDF	5.10E+02	3.04E+02	2.58E+02	3.57E+02
Hepta-CDF	1.81E+02	5.32E+02	1.97E+02	3.03E+02
Octa-CDF	1.23E+02	3.60E+02	1.85E+02	2.22E+02
Total PCDF	2.19E+03	3.27E+03	3.00E+03	2.82E+03

- a. Data reported in this table represent lower bounds on the actual dioxin/furan emissions from Site MET-A. See Section 8.3.1.2 for discussion of analytical surrogate recovery results.
- b. Surrogate recoveries could not be determined for Runs 02 and 04 dioxin/furan samples because of the large quantities of native CDD and CDF species present; therefore, no measure of extraction method efficiency was available. All three runs gave similar results, tending to lend credibility to the validity of the estimated values for the Runs 02 and 04 samples. See Section 8.3.1.2 for more details.

NOTE: Concentrations shown are at as-measured oxygen conditions.
ng = 1.0E-09g

TABLE 5-13 SUMMARY OF DIOXIN/FURAN EMISSIONS CONCENTRATION
DATA FOR SITE MET-A
(CONCENTRATIONS CORRECTED TO 3% OXYGEN)

Dioxin/Furan Isomer	Isomer Concentration in Flue Gas (ng/dscm @ 3% oxygen)			
	Run 02	Run 03	Run 04	Avg. ^b
DIOXINS				
2378 TCDD	3.95E+02	1.70E+02	1.30E+02	2.32E+02
Other TCDD	7.93E+02	1.40E+03	1.22E+03	1.14E+03
Penta-CDD	1.41E+03	2.33E+03	1.68E+03	1.81E+03
Hexa-CDD	3.27E+03	2.15E+03	1.52E+03	2.32E+03
Hepta-CDD	2.46E+03	5.86E+03	3.34E+03	3.89E+03
Octa-CDD	1.47E+03	3.70E+03	2.39E+03	2.52E+03
Total PCDD	9.80E+03	1.56E+04	1.03E+04	1.19E+04
FURANS				
2378 TCDF	4.18E+03	5.06E+03	5.97E+03	5.07E+03
Other TCDF	1.41E+04	1.78E+04	2.99E+04	2.06E+04
Penta-CDF	1.26E+04	1.85E+04	1.72E+04	1.61E+04
Hexa-CDF	1.15E+04	6.08E+03	5.81E+03	7.79E+03
Hepta-CDF	4.06E+03	1.06E+04	4.44E+03	6.38E+03
Octa-CDF	2.76E+03	7.20E+03	4.15E+03	4.70E+03
Total PCDF	4.92E+04	6.53E+04	6.74E+04	6.07E+04

- a. Data reported in this table represent lower bounds on the actual dioxin/furan emissions from Site MET-A. See Section 8.3.1.2 for discussion of analytical surrogate recovery results.
- b. Surrogate recoveries could not be determined for Runs 02 and 04 dioxin/furan samples because of the large quantities of native CDD and CDF species present; therefore, no measure of extraction method efficiency was available. All three runs gave similar results, tending to lend credibility to the validity of the estimated values for the Runs 02 and 04 samples. See Section 8.3.1.2 for more details.

NOTE: Concentrations shown are corrected to 3% oxygen using the Radian CEM data.
ng = 1.0 E-09g

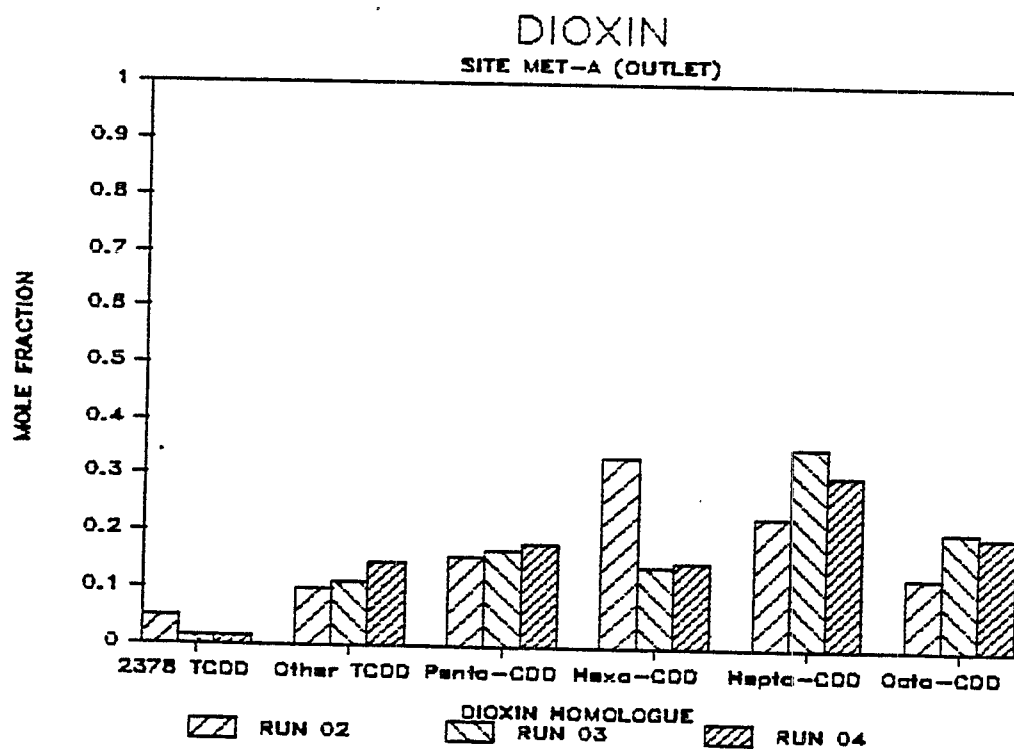
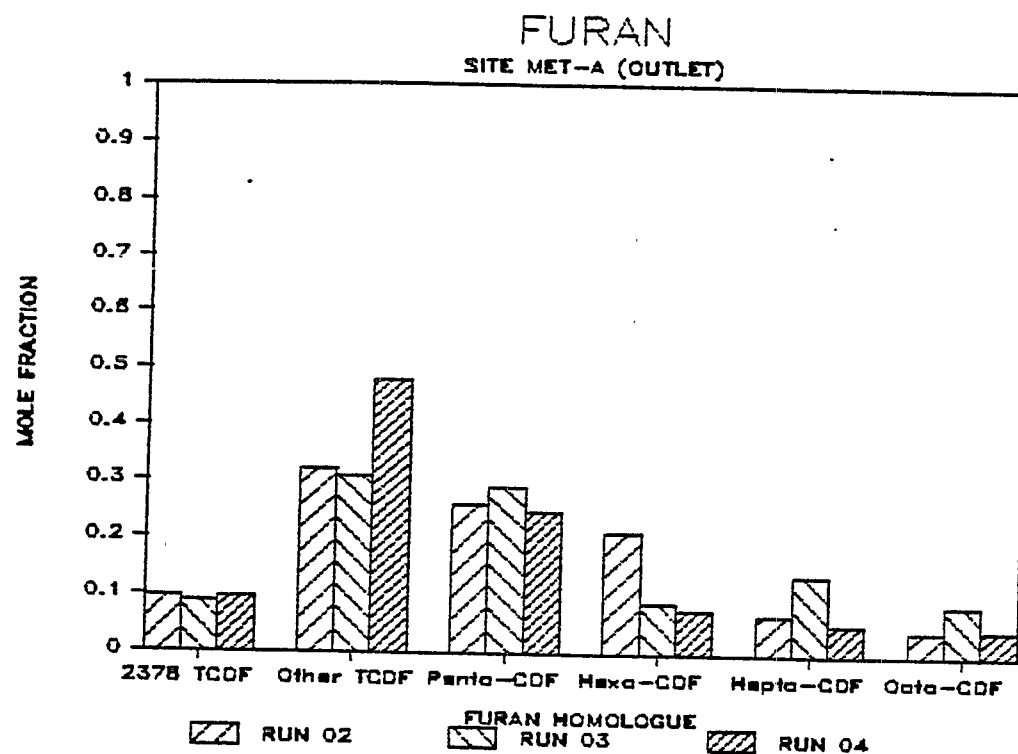


Figure 5-9. DIOXIN/FURAN HOMOLOGUE DISTRIBUTION
FOR SITE MET-A OUTLET EMISSIONS

individual test runs. The contributions of the tetra- through octa-chlorinated dioxin homologues to the total PCDD emissions were: tetra, 13-16%; penta, 12-18%; hexa, 21-23%; hepta, 29-32%; and octa, 17-23%. The furan species were less uniformly distributed than the dioxin species, with the tetrachlorinated homologue being the largest single contributor to the total PCDF emissions. The contributions of the tetra- through octa-chlorinated furan homologues to the total PCDF were: tetra, 45-52%; penta, 21-23%; hexa, 7-13%; hepta, 5-9%; and octa, 4-6%.

Emission factors for the various dioxin and furan homologues were reasonably consistent between test runs. Emission factors based on the coke-free cupola furnace feed rates are shown in Table 5-14. Average* emission factors for 2378 TCDD, total PCDD, and total PCDF were 0.13 ug 2378 TCDD emitted per kg coke-free feed; 6.4 ug total PCDD emitted per kg coke-free feed; and 32.5 ug total PCDF emitted per kg coke-free feed. The coke-free feed rate basis was chosen for the emission factors because it is the basis used by the host plant to determine the cupola furnace feed rate.

5.5 ADDITIONAL DIOXIN/FURAN EMISSIONS DATA FROM SITE MET-A

Approximately one year after Site MET-A was sampled for dioxin/furans under the Tier 4 study, Radian Corporation, under contract to Site MET-A, performed additional dioxin/furan emission testing. Flue gas samples at the outlet stack were collected during four 60-minute test runs performed on April 15, 1986 and April 18, 1986 (two on each day). For the four tests, an average of 445 ng/dscm of PCDD and 3968 ng/dscm of PCDF were detected in the flue gas. On an emission rate basis, 274 mg/hr of PCDD and 2450 mg/hr of PCDF were measured. (These results are not blank or surrogate-corrected.) The concentration of each target dioxin and furan homologue are summarized in Table 5-15. The homologue distribution for the April 1986 test is shown in

* Surrogate recoveries could not be determined for Runs 02 and 04 dioxin/furan samples because of the large quantities of native CDD and CDF species present; therefore, no measure of extraction method efficiency was available. All three runs gave similar results, tending to lend credibility to the validity of the estimated values for the Runs 02 and 04 samples. See Section 8.3.1.2 for more details.

TABLE 5-14 DIOXIN/FURAN EMISSION FACTORS FOR SITE MET-A

Dioxin/Furan Isomer	Dioxin/Furan Emission Factors (ug/kg)			
	Run 02	Run 03	Run 04	Avg. ^b
DIOXINS				
2378 TCDD	2.22E-01	9.05E-02	6.76E-02	1.27E-01
Other TCDD	4.46E-01	7.47E-01	6.33E-01	6.09E-01
Penta-CDD	7.94E-01	1.24E+00	8.73E-01	9.70E-01
Hexa-CDD	1.84E+00	1.15E+00	7.92E-01	1.26E+00
Hepta-CDD	1.38E+00	3.12E+00	1.74E+00	2.08E+00
Octa-CDD	8.23E-01	1.97E+00	1.24E+00	1.35E+00
Total PCDD	5.51E+00	8.32E+00	5.35E+00	6.39E+00
FURANS				
2378 TCDF	2.35E+00	2.70E+00	3.11E+00	2.72E+00
Other TCDF	7.94E+00	9.48E+00	1.56E+01	1.10E+01
Penta-CDF	7.07E+00	9.88E+00	8.96E+00	8.64E+00
Hexa-CDF	6.45E+00	3.24E+00	3.03E+00	4.24E+00
Hepta-CDF	2.28E+00	5.67E+00	2.31E+00	3.42E+00
Octa-CDF	1.55E+00	3.83E+00	2.16E+00	2.52E+00
Total PCDF	2.76E+01	3.48E+01	3.51E+01	3.25E+01

- a. Data reported in this table represent lower bounds on the actual dioxin/furan emissions from Site MET-A. See Section 8.3.1.2 for discussion of analytical surrogate recovery results.
- b. Surrogate recoveries could not be determined for Runs 02 and 04 dioxin/furan samples because of the large quantities of native CDD and CDF species present; therefore, no measure of extraction method efficiency was available. All three runs gave similar results, tending to lend credibility to the validity of the estimated values for the Runs 02 and 04 samples. See Section 8.3.1.2 for more details.

NOTE: Emission factors are defined as the ug of dioxin/furan emitted per kg of coke-free feed to the cupola furnace.

ug = 1.0E-06g

kg = 1.0E+03g

TABLE 5-15. DIOXIN/FURAN HOMOLOGUE RESULTS FOR APRIL 1986 TEST

Homologue	Run 01	Concentration (ng/dscm, as-measured)			Average
		Run 02	Run 03	Run 04	
<u>Dioxins</u>					
2378-TCDD ^a	ND (0.004)	ND (0.008)	2.48	1.50	1.0
Other TCDD	39.9	51.0	29.6	25.4	36.5
Penta-CDD	61.8	85.7	31.2	43.2	55.5
Hexa-CDD	77.3	28.9	82.1	74.3	65.7
Hepta-CDD	71.9	116	154	116	114
Octa-CDD	131	132	242	182	172
Total PCDD	382	413	542	442	445
<u>Furans</u>					
2378-TCDF	174	227	85.5	71.6	140
Other TCDF	631	637	393	277	485
Penta-CDF	410	504	439	331	421
Hexa-CDF	307	501	806	539	538
Hepta-CDF	561	828	1260	631	820
Octa-CDF	1100	1490	2090	1570	1563
Total PCDF	3180	4190	5080	3420	4000

^aMinimum detection limit indicated in parenthesis.

Figure 5-10. The higher chlorinated homologues appear to be more prevalent compared to the Tier 4 test (Figure 5-9).

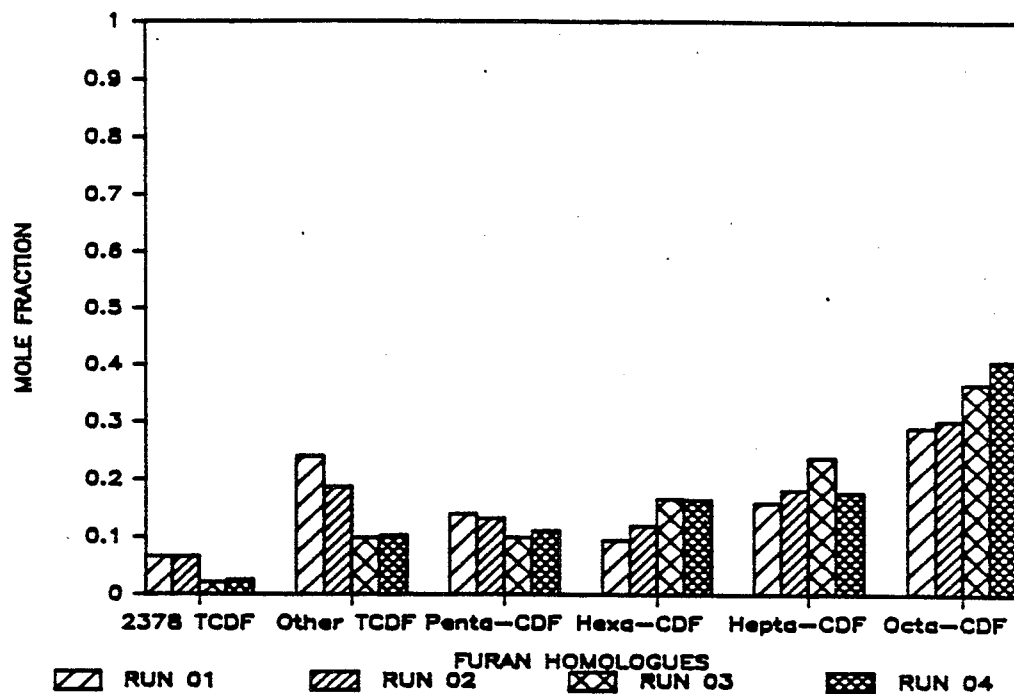
For comparison, the average mass emission rates and the average concentration measured during the Tier 4 test (May 1985) and the April 1986 test are presented in Table 5-16. The CEM results for each test are included in Table 5-17. During the April 1986 test, oxygen and carbon monoxide were lower than during the Tier 4 test. Carbon monoxide was higher. Total hydrocarbons are not comparable since the Tier 4 results were measured on a wet basis, and the April 1986 results were measured on a non-condensable (less than 40°F) basis. The emission rates for 2378-TCDD and 2378-TCDF were lower during the April 1986 test. However, considering that the analytical results are precise to ± 50 percent, total PCDD and PCDF emissions for both tests are not significantly different.

5.6 HCl TRAIN CHLORIDE EMISSIONS DATA

Table 5-18 summarizes HCl train chloride emissions data measured at the exhaust stack sampling location. The data are reported as "front-half," "back-half", and "train-total" chloride emissions. The front-half emissions represent chlorides captured in the probe rinse/filter fraction of the HCl train, which may include metal chlorides contained in the particulate matter. The back-half emissions represent chlorides captured in the HCl sample train impingers, which would include HCl and any metal chlorides that pass through the sample train filter. The train-total emissions represent the sum of the front-half and back-half emissions.

As shown in Table 5-18, the average as-measured train-total chloride emissions concentration was approximately 2.4 mg/dscm (0.001 gr/dscf). Corrected to 3% O₂ using the Radian CEM data, this corresponds to approximately 60 mg/dscm @ 3% O₂ (0.026 gr/dscf @ 3% O₂). The train-total chloride mass emission rate from the baghouse exhaust stack was about 1.2 kg/hr (2.6 lb/hr). Chloride emissions were approximately equally distributed between the front-half and back-half of the HCl sample train.

FURAN HOMOLOGUES



DIOXIN HOMOLOGUES

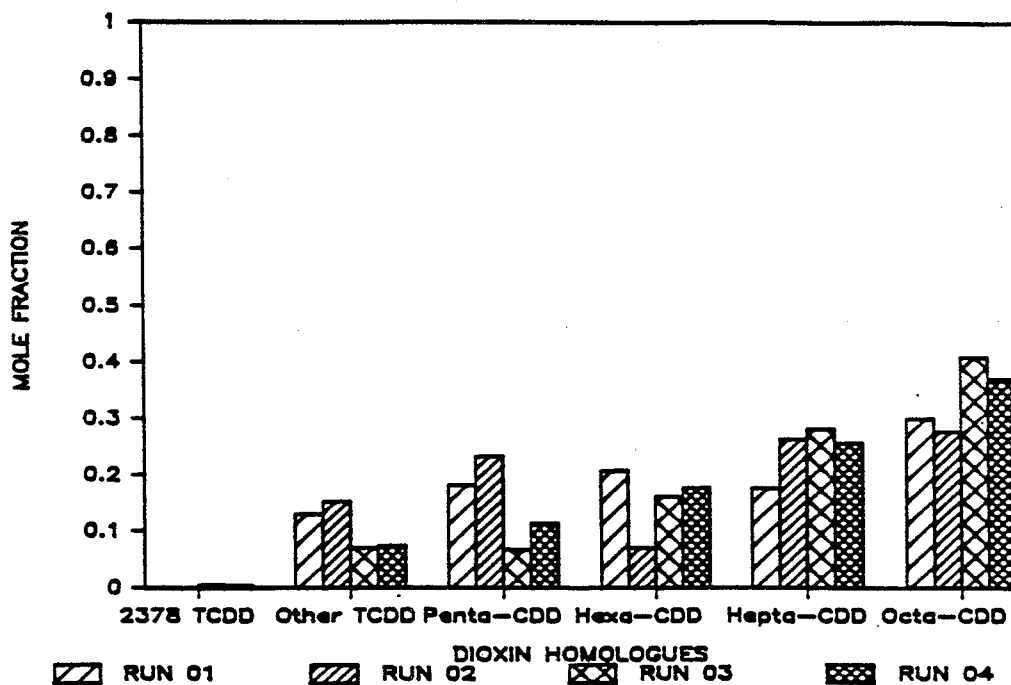


Figure 5-10. Dioxin/furan homologue distribution for Site MET-A outlet emissions, April 1986 Test

TABLE 5-16. COMPARISON OF DIOXIN/FURAN RESULTS FROM
APRIL 1986 TEST TO TIER 4 (MAY 1985) RESULTS

Dioxin/furan Homologues	Average Emissions Rate (mg/hr)		Average Concentration ng/dscm @ 3% O ₂		Percent Change
	Tier 4		Tier 4		
	May 1985	April 1986	May 1985	April 1986	
<u>Dioxins</u>					
2378-TCDD	5.36	0.59	232	13	-94
Other TCDD	26.9	22.9	1140	399	-65
Penta-TCDD	42.9	35.0	1810	591	-67
Hexa-CDD	54.1	40.3	2320	744	-68
Hepta-CDD	93.4	70.1	3890	1337	-66
Octa-CDD	60.3	105	2520	2010	-20
Total PCDD	283	274	11900	5093	-57
<u>Furans</u>					
2378-TCDF	118	88	5070	1489	-71
Other TCDF	475	306	20600	5273	-74
Penta-TCDF	379	262	16100	4730	-71
Hexa-CDF	181	328	7790	6388	-18
Hepta-CDF	155	504	6380	9758	+53
Octa-CDF	113	1277	4700	18205	+287
Total PCDF	1420	2450	60700	46850	-23

TABLE 5-17. COMPARISON OF APRIL 1986 TEST CEM RESULTS
TO TIER 4 (MAY 1985) RESULTS

Parameter	Average Concentrations	
	Tier 4 May 1985	April 1986
O ₂ (% vol) ^a	20.2	19.1
CO (ppmv) ^a	1220	1060
CO ₂ (% vol) ^a	1.8	2.3
THC (ppmv) as propane	15.0 ^b	7.5 ^c

^aConcentrations are on a dry basis.

^bMeasured on a wet basis.

^cOnly non-condensable hydrocarbons.

TABLE 5-18. HCl TRAIN CHLORIDE EMISSIONS DATA FOR SITE MET-A

Sample Component	Test Run	Emissions Concentration			Emissions Rate (kg/hr)
		mg/dscm	ppmv ^a	mg/dscm _b @ 3% O ₂	
Train Total	Run 02	3.05	2.1	78.1	1.53
	Run 03	2.38	1.6	53.3	1.24
	Run 04	1.86	1.3	47.6	0.90
	Average	2.43	1.6	59.7	1.22
Front Half	Run 02	1.70	1.2	43.5	0.86
	Run 03	1.49	1.0	33.4	0.78
	Run 04	0.93	0.6	23.8	0.45
	Average	1.37	0.9	33.6	0.70
Back Half	Run 02	1.35	0.9	34.6	0.68
	Run 03	0.89	0.6	19.9	0.46
	Run 04	0.93	0.6	23.8	0.45
	Average	1.06	0.7	26.1	0.53

^a ppmv = parts per million chloride by volume, dry basis at actual stack O₂ concentration

^b Concentration corrected to 3% O₂ using the equation:

$[Cl^-] @ 3\% O_2 = [Cl^-], \text{ as measured } \times (20.9 - 3)/(20.9 - \% O_2)$
 where: % O₂ = oxygen concentration in stack gas as measured by the Radian CEM system (See Table 5-8)

5.7 DIOXIN/FURAN ANALYSIS OF BAGHOUSE DUST SAMPLES

Table 5-19 shows the mean dioxin/furan contents of Baghouse No. 1 and Baghouse No. 2 dust catch samples for the three test runs, and Table 5-20 shows the run-specific data.

The No. 1 Baghouse dust samples contained higher levels of each of the dioxin and furan homologues than the No. 2 Baghouse dust samples. The analytical values for the No. 1 Baghouse dust were consistently about 50 percent higher than those for the No. 2 Baghouse dust. There is no simple explanation for this fact, although the No. 1 Baghouse does handle exhaust gases from sources other than the cupola furnace, while the No. 2 baghouse does not. As discussed in Section 3.3, ventilation gases from the arc furnace ladles, settler tap holes, settler ladles, and silo bin vent account for about 18 vol% of the No. 1 Baghouse gas, with cupola furnace exhaust (20 vol%), cupola furnace charge floor ventilation gas (14%) and ambient dilution air (48 vol%) accounting for the remainder. Another difference between the two baghouses was that the mean inlet gas temperature to the No. 1 Baghouse during the test runs was 142°C (288°F), while the mean inlet temperature to the No. 2 Baghouse was 130°C (266°F). Also, there are physical differences, (e.g. length, diameter) in the ductwork leading to the two baghouses.

The distribution of tetra through octa dioxin and furan homologues in the baghouse dust samples does not mirror that of the baghouse emissions. On a relative basis, the higher chlorinated species tend to be more prevalent in the baghouse dust samples than in the emissions. This may be due to a condensation phenomenon that preferentially concentrates the less volatile, more highly chlorinated species in the baghouse dusts.

5.8 CUPOLA FURNACE FEED SAMPLE ANALYSES

As discussed in Section 6.2.1, four cupola furnace feed material categories were sampled at Site MET-A. These were: (1) electronic switching gear internals and associated light gauge coated wire; (2) circuit boards; (3) miscellaneous plastic parts, heavy gauge wire, and telephone receiver parts; and (4) coke. These samples were analyzed for chlorinated benzenes,

TABLE 5-19. AVERAGE DIOXIN/FURAN CONTENT OF BAGHOUSE
DUST SAMPLES FROM SITE MET-A

Isomer/Homologue	Average Dioxin/Furan Homologue Contents, Parts per Billion (ppb)		
	No. 1 Baghouse Dust	No. 2 Baghouse Dust	Overall Average
<u>Dioxins</u>			
2378 TCDD	0.17	0.12	0.15
Other TCDD	2.8	1.8	2.3
Penta CDD	5.6	4.4	5.0
Hexa CDD	20.7	11.3	16.0
Hepta CDD	44.3	27.7	36.0
Octa CDD	53.5	40.4	47.0
Total PCDD	127.1	85.7	106.4
<u>Furans</u>			
2378 TCDF	10.8	6.9	8.8
Other TCDF	92.1	58.1	75.1
Penta CDF	96.1	55.0	75.5
Hexa CDF	140.8	52.3	96.5
Hepta CDF	154.2	94.7	124.5
Octa CDF	207.2	158.8	183.0
Total PCDF	700.0	425.7	562.9

TABLE 5-20. DIOXIN/FURAN CONTENTS OF INDIVIDUAL
BAGHOUSE DUST SAMPLES FROM SITE MET-A

Isomer/ Homologue	Dioxin/Furan Homologue Content, Parts per Billion						Detection Limit
	No. 1 Baghouse Dust			No. 2 Baghouse Dust			
	Run 02	Run 03	Run 04	Run 02	Run 03	Run 04	
<u>Dioxins</u>							
2378 TCDD	0.20	0.10	0.20	0.13	0.04	0.20	0.01
Other TCDD	3.1	2.5	2.7	1.9	1.7	1.8	0.02
Penta CDD	9.5	5.1	2.2	5.0	4.5	3.6	0.02
Hexa CDD	20.4	18.8	23.0	11.5	10.4	12.0	0.01
Hepta CDD	47.7	46.6	38.6	36.8	27.2	19.0	0.01
Octa CDD	66.8	49.8	44.0	55.4	34.4	31.4	0.01
Total PCDD	147.7	122.9	110.7	110.7	78.2	68.0	NA ^a
<u>Furans</u>							
2378 TCDF	10.9	9.6	11.8	6.4	4.1	10.1	0.03
Other TCDF	102.8	84.0	89.5	63.1	39.9	71.2	0.01
Penta CDF	154.4	105.4	28.6	67.3	47.8	49.8	0.02
Hexa CDF	156.7	139.2	126.4	40.0	52.0	64.8	0.01
Hepta CDF	159.0	175.0	128.6	120.0	88.8	75.4	0.01
Octa CDF	228.6	226.8	166.2	205.2	139.4	131.8	0.01
Total PCDF	812.4	740.0	547.5	502.0	372.0	403.1	NA ^a

^aDetection limits are not applicable to Total PCDD and Total PCDF concentrations because these values are obtained by addition of the homologue-specific values.

chlorinated biphenyls, and chlorinated phenols. In addition, a composite of the circuit board samples and the electrical switching gear samples was analyzed for total organic halide (TOX).

Table 5-21 summarizes the results of the compound-specific precursor analyses. The electronic switching gear sample and the miscellaneous plastic parts/heavy gauge wire/telephone receiver parts sample were found to contain small quantities (<300 ppb) of chlorinated biphenyls, but chlorinated benzenes and chlorinated phenols were not detected. None of the precursor compounds analyzed for were found in the coke and circuit board samples.

A composite of the circuit board sample and the electrical switching gear samples from Site MET-A was analyzed using the TOX procedures. The circuit board/electrical switching gear composite sample contained approximately 4,300 ppm total TOX. Thus, although the specific precursors analyzed for (i.e., chlorobenzenes, chlorinated biphenyls, and chlorophenols) were either not detected or were found in only small quantities, there were significant quantities of halogenated species present. This suggests that either (1) the specific precursors analyzed for were present in the samples but were not easily detected using the GC/MS procedure due to the complexity of the sample matrix, or (2) halogenated species other than the specific precursors analyzed for were present in the samples. Potential sources of these "other" halogenated species include polyvinyl chloride, halogenated plasticizers, etc., that may have been present in the plastic-bearing feed components.

5.9 AMBIENT XAD TRAIN DATA

Dioxin and furan concentration data for ambient air samples taken near the baghouse dilution air intake point are shown in Table 5-22. Small but detectable quantities were found of all species analyzed for except 2378-TCDD and penta-CDD, which were not detected. Measured ambient air concentrations of total PCDD and total PCDF were 0.15 ng/dscm and 1.1 ng/dscm, respectively.

5.10 SOIL SAMPLING DATA

The soil sample was archived pending evaluation of analytical data.

TABLE 5-21. SUMMARY OF DIOXIN PRECURSOR DATA FOR SITE MET-A FEED SAMPLES

Precursor Categories	Precursor Concentration, ug/g (ppm)			
	Coke	Telephone Parts, Wire	Circuit Boards	Electronic Switching Gear
Total Chlorinated Benzenes	ND	ND	ND ^b	ND
Total Chlorinated Biphenyls	ND	0.004 ^a	ND ^b	0.26 ^c
Total Chlorinated Phenols	ND	ND	ND	ND
Total Organic Halide (TOX)	NA	NA	4,300 ^d	4,300 ^d

- a. Pentachlorobiphenyl was the only polychlorinated biphenyl homologue detected in the telephone parts and wire sample.
- b. Base neutral surrogate recoveries were very low for the circuit board samples (See Table 8-8), which may indicate low method efficiencies for the chlorinated benzenes and biphenyls.
- c. Penta-, Hexa-, Hepta-, and Octa- polychlorinated biphenyls were all detected in the electronic switching gear samples.
- d. TOX analysis was performed on a composite circuit board/electronic switching gear sample only.

ND = not detected
NA = not analyzed

TABLE 5-22. DIOXIN/FURAN AMBIENT CONCENTRATION DATA FOR SITE MET-A

Isomer/Homologue	Concentration (ng/dscm)
<u>Dioxins</u>	
2378 TCDD	ND
Other TCDD	3.9×10^{-2}
Penta CDD	ND
Hexa CDD	3.1×10^{-2}
Hepta CDD	3.1×10^{-2}
Octa CDD	5.4×10^{-2}
Total PCDD	1.5×10^{-1}
<u>Furans</u>	
2378 TCDF	4.6×10^{-2}
Other TCDF	4.6×10^{-1}
Penta CDF	1.1×10^{-1}
Hexa CDF	2.3×10^{-1}
Hepta CDF	1.3×10^{-1}
Octa CDF	1.2×10^{-1}
Total PCDF	1.1×10^0

ND = Not detected.

6.0 SAMPLING LOCATIONS AND PROCEDURES

This section details the sampling locations and procedures listed in Table 4.1 of Section 4.0. Gaseous sampling is considered in section 6.1, and solids sampling is considered in Section 6.2.

6.1 GASEOUS SAMPLING

Four types of gaseous samples were taken during this test program: Modified Method 5 dioxin/furan (MM5), Modified Method 5 HCl (HCl), EPA Method 3, and continuous emissions monitoring (CEM). The sampling locations and methods are listed in Table 6-1 and are further discussed in this section.

6.1.1 Gaseous Sampling Locations

6.1.1.1 Cupola furnace baghouse system exhaust stack. The exhaust stack sampling location of the cupola furnace baghouse system is shown as Point A in Figure 4-1. This location was used for dioxin/furan sampling and HCl sampling, according to MM5 procedures described in section 6.2.2. EPA Methods 2, 3, and 4 were performed to determine the volumetric flowrate, molecular weight and moisture content of the exhaust gas, respectively.

The sample port locations and dimensions are shown in Figure 6-1. The outside diameter of the stack is 12 feet. Four MM5 sample ports are located approximately 160 feet from the base of the stack. The MM5 sample ports have 3 inch diameters and are spaced 90° apart. The MM5 sample ports are 80 ft (6-7 equivalent duct diameters) downstream of the breeching where the baghouse exhaust gases enter the stack and 90 ft (7-8 equivalent duct diameters) upstream of the top of the stack. According to EPA Method 1, a total of 12 traverse points are required. A layout of the traverse points is shown in Figure 6-2. the railings of the platform limit the effective length of the sample probe to four feet, which requires the use of all four ports to complete a sampling traverse.

TABLE 6-1. SUMMARY OF GAS SAMPLING METHODS FOR SITE MET-A

Sample Location	Sample Type or Parameter	Sample Collection Method
Blast Furnace Baghouse System Exhaust Stack	Dioxin/furan	Modified EPA Method 5
	Volumetric flow	EPA Method 2
	Molecular weight	EPA Method 3
	Moisture	EPA Method 4
	HCl	HCl train
Breeching toe Exhaust Stack	CO, CO ₂ , O ₂ , NO _x , SO ₂ , and THC monitoring.	Continuous Monitors
Ambient Dilution Air Sampling	Dioxin/furan	Ambient XAD train
	Dioxin precursors	Ambient XAD train

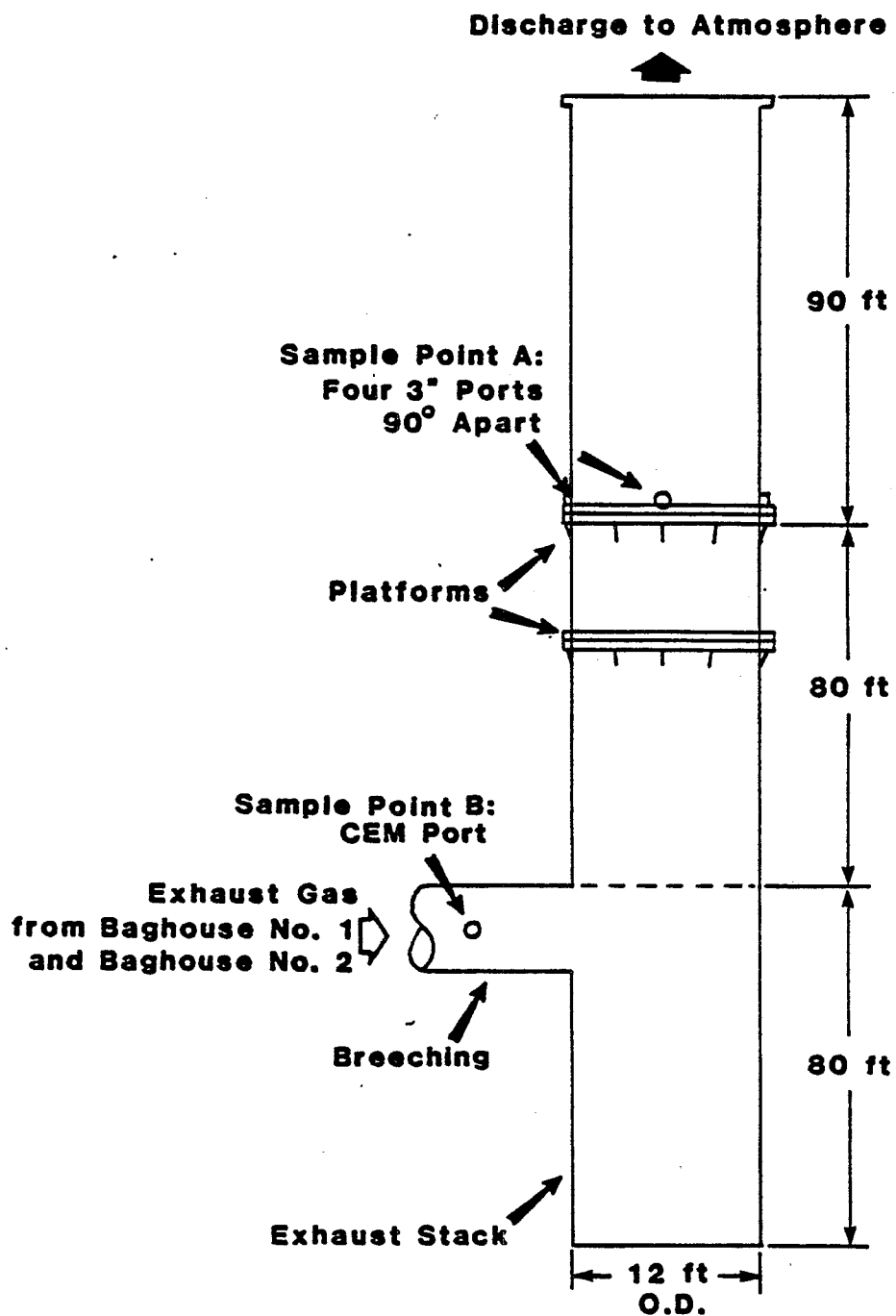


Figure 6-1. Sample port locations and flow dimensions.

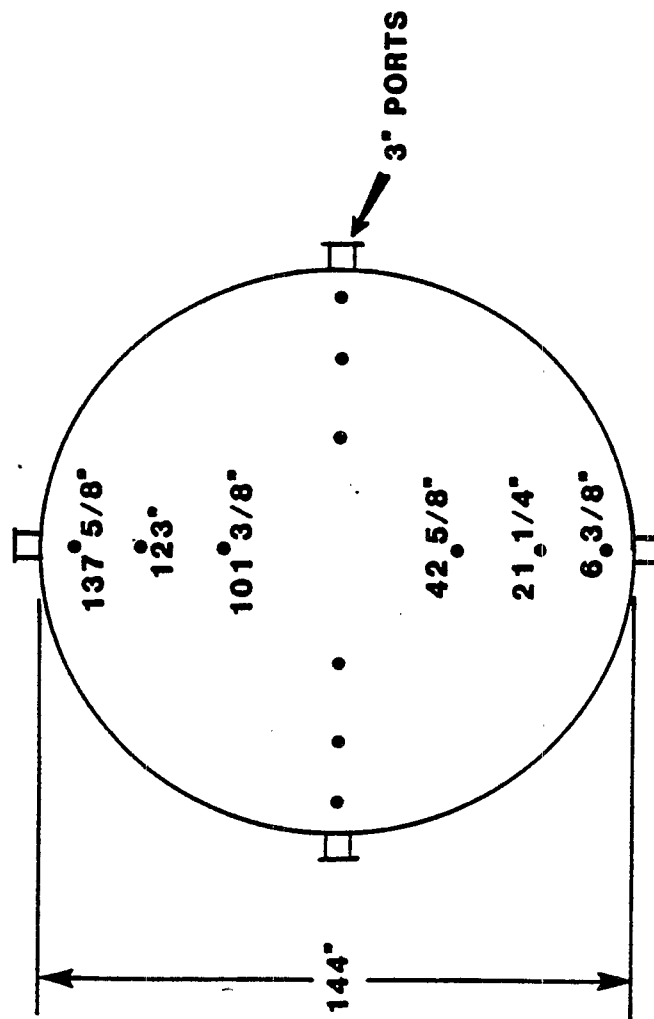


Figure 6-2. Traverse point layout for Sample Point A.

6.1.1.2 Cupola furnace baghouse system breeching to exhaust stack. The sample ports used by Radian and the host plant for continuous monitoring are located in the breeching to the exhaust stack, as shown in Figure 6-1. The exhaust gases from baghouse No. 1 and baghouse No. 2 are combined before they reach the sampling location.

6.1.1.3 Ambient dilution air sampling. The baghouse ambient dilution air was sampled for dioxin/furan and dioxin precursors near the air dilution intake point, which is shown as Point C in Figure 4-1. Samples were collected using the ambient XAD train, which is described in Section 6.2.2.3.

Two separate ambient XAD trains were run simultaneously during the time periods that the MM5 samples were collected. The same two ambient XAD trains were used during all three MM5 test runs, providing composite dilution air samples for the site. One ambient XAD train was analyzed for dioxin/furan and the other for dioxin/furan precursors.

6.1.2 Gaseous Sampling Procedures

Gaseous sampling procedures used during this program are discussed in detail in the Tier 4 QAPP.⁽¹⁾ A brief description of each method is provided in the following sections.

6.1.2.1 Modified Method 5 (MM5). Gas sampling for dioxins and furans was based on the October 1984 draft of the ASME chlorinated organic compound sampling protocol. This sampling method is a modified version of EPA Method 5 that includes a solid sorbent module (i.e., XAD-2 resin) for trapping vapor phase organics. The only differences in the sampling protocol which were not discussed in the Tier 4 QAPP are as follows:

- (1) Benzene was substituted for hexane or toluene as both the cleanup and extractant solvent for the MM5 filters and the XAD-2 resin. This was caused by a discrepancy between the draft ASME sampling protocol and the draft ASME analytical protocol. (November 16, 1985)
- (2) Methylene chloride was substituted for hexane as the final field rinse solvent for the MM5 train. Methylene chloride was also substituted for hexane in the glassware cleaning procedure. This

substitution was instituted to improve the field recovery of dioxins and furans from the MM5 train.

- (3) A backup XAD sorbent module was used at this test site to ensure high capture efficiencies for dioxins and furans.

The MM5 samples were collected isokinetically over a 4 hour sampling period at the exhaust stack location. The minimum sample volume for any test run was 3.3 dscm (116 dscf). The MM5 sampling rate was approximately 0.016 dscmm (0.56 dscfm).

Following sample recovery, the various components of the sample (filter, solvent rinses, XAD module, etc.) were sent to the EPA's Troika laboratories to quantify 2378 TCDD, the tetra- through octa-PCDD homologues, and the tetra-through octa-PCDF homologues present in the samples.

A schematic diagram of the MM5 sampling train used at Site MET-A is shown in Figure 6-3. Flue gas is pulled from the stack through a nozzle and a glass-lined probe. Particulate matter is removed from the gas stream by means of a glass fiber filter housed in a teflon-sealed glass filter holder maintained at $248 \pm 25^{\circ}\text{F}$. The gas passes through a sorbent trap similar to that illustrated in Figure 6-4 for removal of organic constituents. The trap consists of separate sections for (1) cooling the gas stream, and (2) adsorbing the organic compounds on Amberlite XAD-2^R resin (XAD). A backup XAD resin trap was used at this test site to ensure high capture efficiencies for dioxins and furans. A chilled impinger train following the sorbent trap is used to remove water from the flue gas, and a dry gas meter is used to measure the sample gas flow.

6.1.2.2 HCl Determination. HCl concentrations in the outlet exhaust stack were determined using another modification of EPA Method 5. The sample train components and operation are identical to those of Method 5 with the following exceptions:

1. Water in the first two impingers was replaced with 0.1 m NaOH.
2. Sampling was single point isokinetic, with the nozzle placed at points in the stack with approximate average velocity.
3. The moisture/NaOH in the impingers was saved for laboratory analysis by ion chromatography.

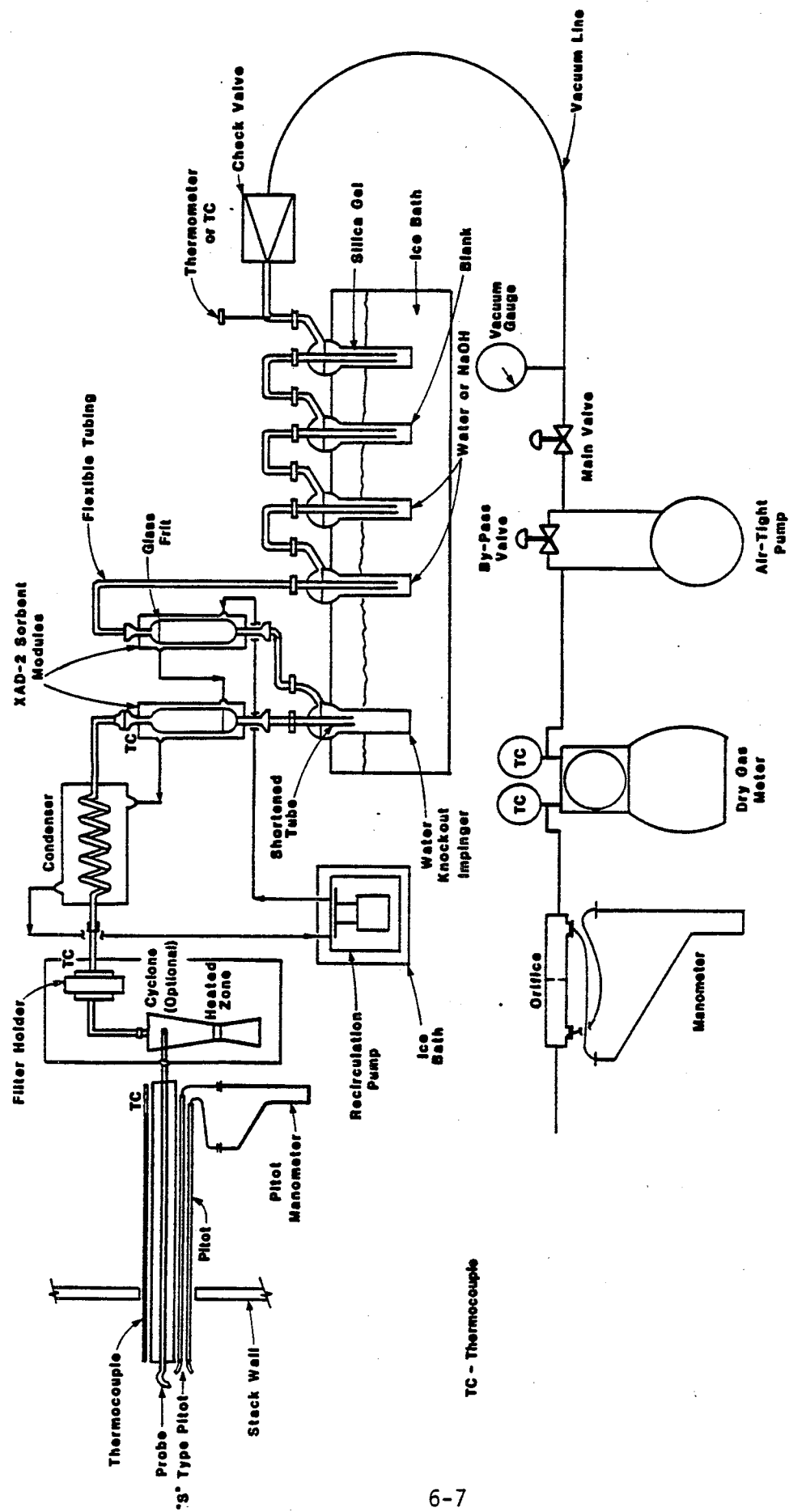


Figure 6-3. Modified Method 5 Train With Backup Sorbent Module

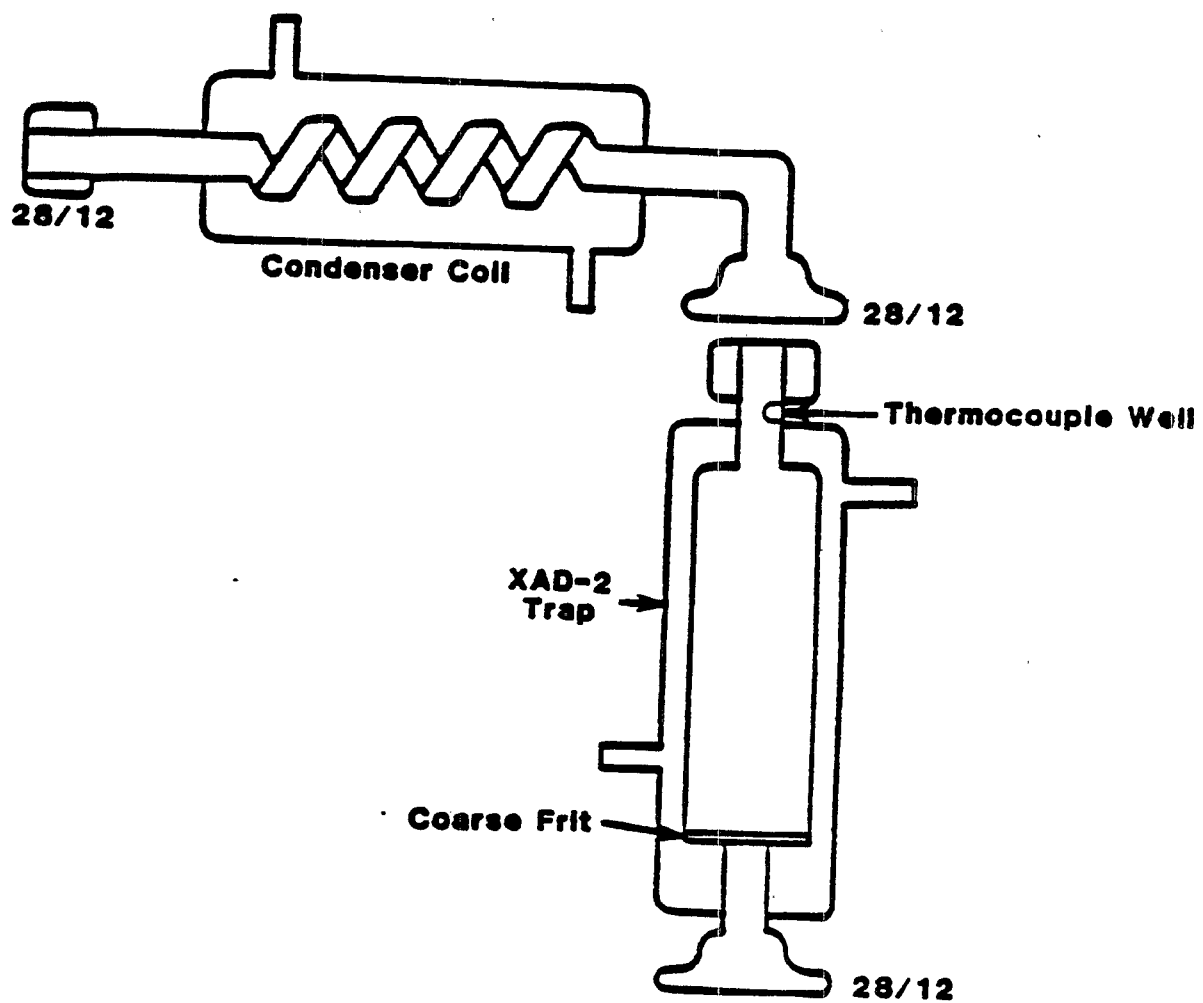


Figure 6-4. Condenser Coil and XAD-2 Resin Trap

Recovery of the HCl train provided a sample consisting of three components: probe rinse, filter, and back-half rinse/impinger catch. These components were shipped from the field to Radian's Austin, Texas laboratory for analysis by ion chromatography.

6.1.2.3 Ambient Air Sampling. A schematic diagram of the ambient XAD sample train is shown in Figure 6-5. The ambient train consists of a short glass probe, sorbent tube, knockout impinger (optional), silica gel impinger, umbilical line, pump, and dry gas meter. Ambient air is drawn into the sorbent module, where it is cooled to 20°C (68°F) or lower, and the organic constituents are adsorbed by the XAD resin. The gas is then dried with the silica gel, and the sample volume is measured by the dry gas meter.

The entire ambient XAD sample train is leak tested before and after each test run at 10 inches H₂O to ensure that the leak rate is less than 0.02 cfm. Dry gas meter readings are recorded twice daily (i.e., at the beginning and end of each test period). The dry gas meter temperature, ice bath temperatures, pressure, and volume are recorded once per hour during the sampling periods.

Recovery of the ambient XAD sample train is similar to that of the MM5 train. The probe is rinsed with acetone and methylene chloride three times each, and this rinse is stored in a single sample container. The XAD sorbent module is capped with ground glass caps. If the optional knockout impinger is used, the impinger is rinsed with acetone and methylene chloride, and the condensate and rinse are combined in a single container.

6.1.2.4 Volumetric Gas Flow Rate Determination. The volumetric gas flow rate was determined using EPA Method 2. Based on this method, the volumetric gas flow rate is determined by measuring the average velocity of the flue gas and the cross-sectional area of the duct. The average flue gas velocity is calculated from the average gas velocity pressure (ΔP) across an S-type pitot tube, the average flue gas temperature, the wet molecular weight, and the absolute static pressure.

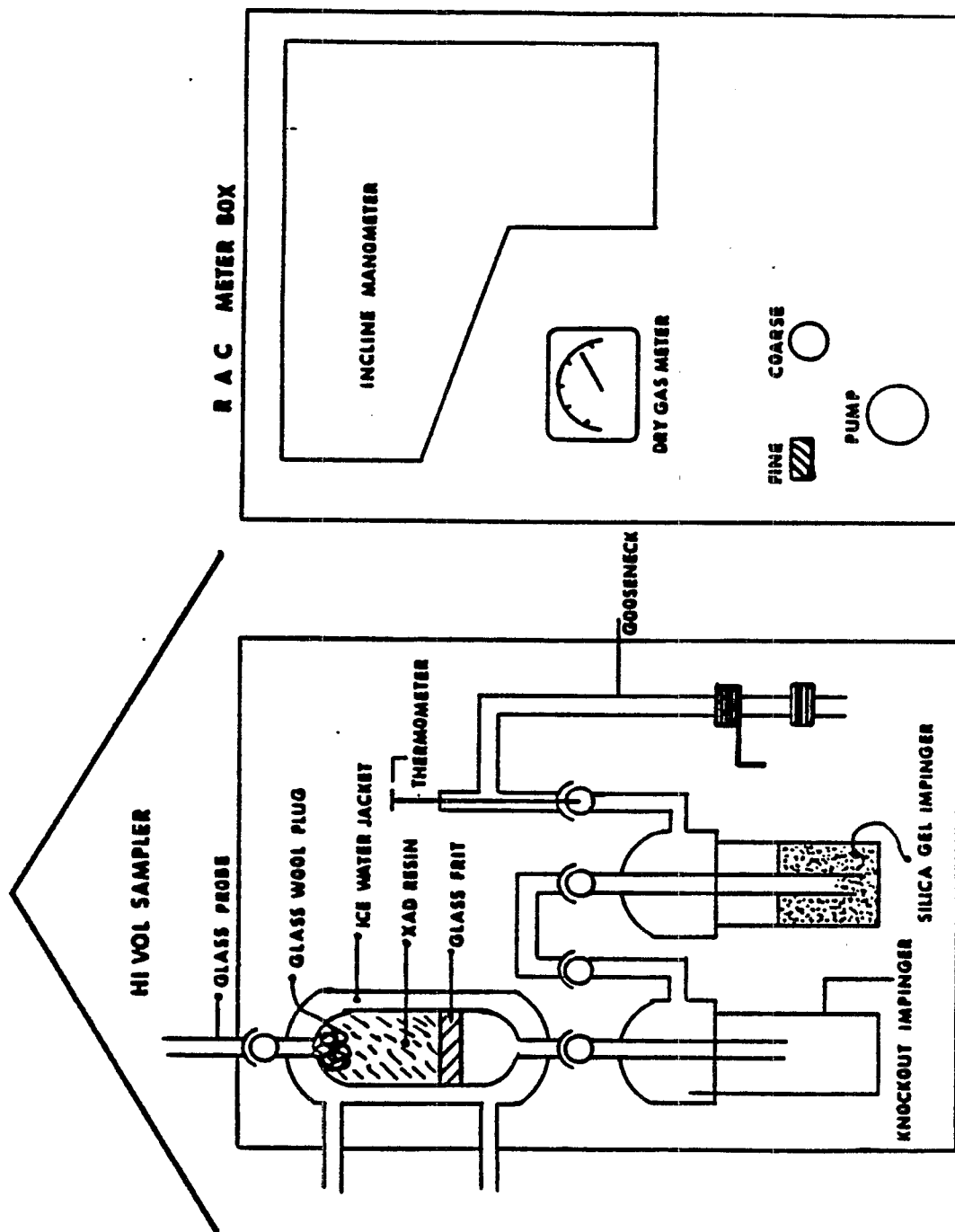


Figure 6-5. Components of ambient XAD sampling train.

6.1.2.5 Flue Gas Moisture Determination. The moisture content of the flue gas was determined using EPA Method 4. Based on this method, a known volume of particulate-free gas is pulled through a chilled impinger train. The quantity of condensed water is determined gravimetrically and then related to the volume of gas sampled to determine the moisture content.

6.1.2.6 Flue Gas Molecular Weight Determination. The integrated sampling technique described in EPA Method 3 was used to obtain a composite flue gas sample for fixed gas analysis (O_2 , CO_2 , N_2). The fixed gas analysis was used to determine the molecular weight of the gas stream. A small diaphragm pump and a stainless steel probe were used to extract single point flue gas samples. The samples were collected at the MM5 sampling ports using Tedlar^R bags. Moisture was removed from the gas sample by a water-cooled condenser so that the fixed gas analysis is on a dry basis.

The composition of the gas sample was determined using a Shimadzu Model 3BT analyzer instead of the Fyrite or Orsat analyzer prescribed in Method 3. The Shimadzu instrument employs a gas chromatograph and a thermal conductivity detector to determine the fixed gas composition of the sample.

6.1.2.7 Continuous Emissions Monitoring. Continuous emissions monitoring was performed in the breeching leading to the exhaust stack for O_2 , CO_2 , CO , NO_x , SO_2 , and THC throughout the 3 to 5-hour period that dioxin sampling was conducted each test day. Sample acquisition was accomplished using an in-stack filter probe and a Teflon^R sample line connected to a mobile laboratory. The heat-traced sample line was maintained at a temperature of at least $120^{\circ}C$ ($248^{\circ}F$) to prevent condensation in the sample line. The stack gas sample was drawn through the filter and sample line using pumps located in the mobile laboratory. Sample gas to be analyzed for CO , CO_2 , O_2 , SO_2 , and NO_x was pumped through a sample gas conditioner, which consists of an ice bath and knockout trap. The sample gas conditioner removes moisture and thus provides a dry gas stream for analysis. A separate unconditioned gas stream was supplied to the THC analyzer for analysis on a wet basis.

An Anarad Model 412 nondispersive infrared analyzer was used to measure CO and CO_2 ; a Beckman Model 755 paramagnetic analyzer was used to measure O_2 ; and a Beckman Model 402 flame ionization analyzer was used to measure THC.

6.2 SOLID SAMPLES

Samples of the cupola furnace feed materials, the No. 1 and No. 2 baghouse dusts, and plant soils were taken at Site MET-A. The sampling locations and methods are discussed in the following sections.

6.2.1 Cupola Furnace Feed Samples

The telephone scrap component of the charge bed and the metallurgical coke used to fire the blast furnace were the only feed materials with the potential to contain dioxin/furan precursors. These materials were sampled once during the test program and analyzed by the Radian/RTP laboratory for dioxin/furan precursor content.

Telephone scrap sampling consisted of taking grab samples of one or more large pieces of each clearly distinguishable plastic-bearing telephone scrap material in the charge bed. The large grab samples so obtained were size reduced, composited and analyzed by the Radian/RTP laboratory. Due to the heterogeneity of the charge bed, it was beyond the scope of the Tier 4 project to obtain truly representative samples. The feed sampling effort was considered representative only in the sense that each major plastic-bearing material was sampled.

For the purpose of the Tier 4 project, the telephone scrap was considered to consist of the following materials: (i) switching gear internals and associated narrow gauge coated wire; (ii) circuit boards; and (iii) miscellaneous plastic parts, heavy gauge wire, and telephone receiver parts. No attempt was made to estimate the relative contributions of these types of materials to the telephone scrap category.

6.2.2 Baghouse Dust Samples

Separate samples of the No. 1 and No. 2 baghouse dusts were taken twice per MM5 test run, once at the beginning and once at the end of each run. The individual samples were taken from a capped spout installed by plant personnel on the baghouse screw conveyors. A composite sample of dust from each baghouse was prepared at the end of each run and sent to Troika for dioxin/furan analysis.

6.2.3 Soil Sampling

A single composite soil sample comprised of 10 individual soil core samples was prepared for Site MET-A. Soil sampling protocol for Tiers 3, 5, 6, and 7 of the National Dioxin Study are specified in the documents, "Sampling Guidance Manual for the National Dioxin Study." A similar protocol was used for soil sampling at Site MET-A. Soil samples were collected by forcing a bulb planter into the soil to a depth of 3 inches. The soil samples were composited in a clean stainless steel bucket. A portion of the composite was shipped to Troika for potential dioxin/furan analysis.

A total of 10 soil sampling locations were selected around the periphery of the plant site. These locations are shown in Figure 6-6. It should be noted that the plant site consists mainly of fill dirt; thus, natural soils for the area were not available.

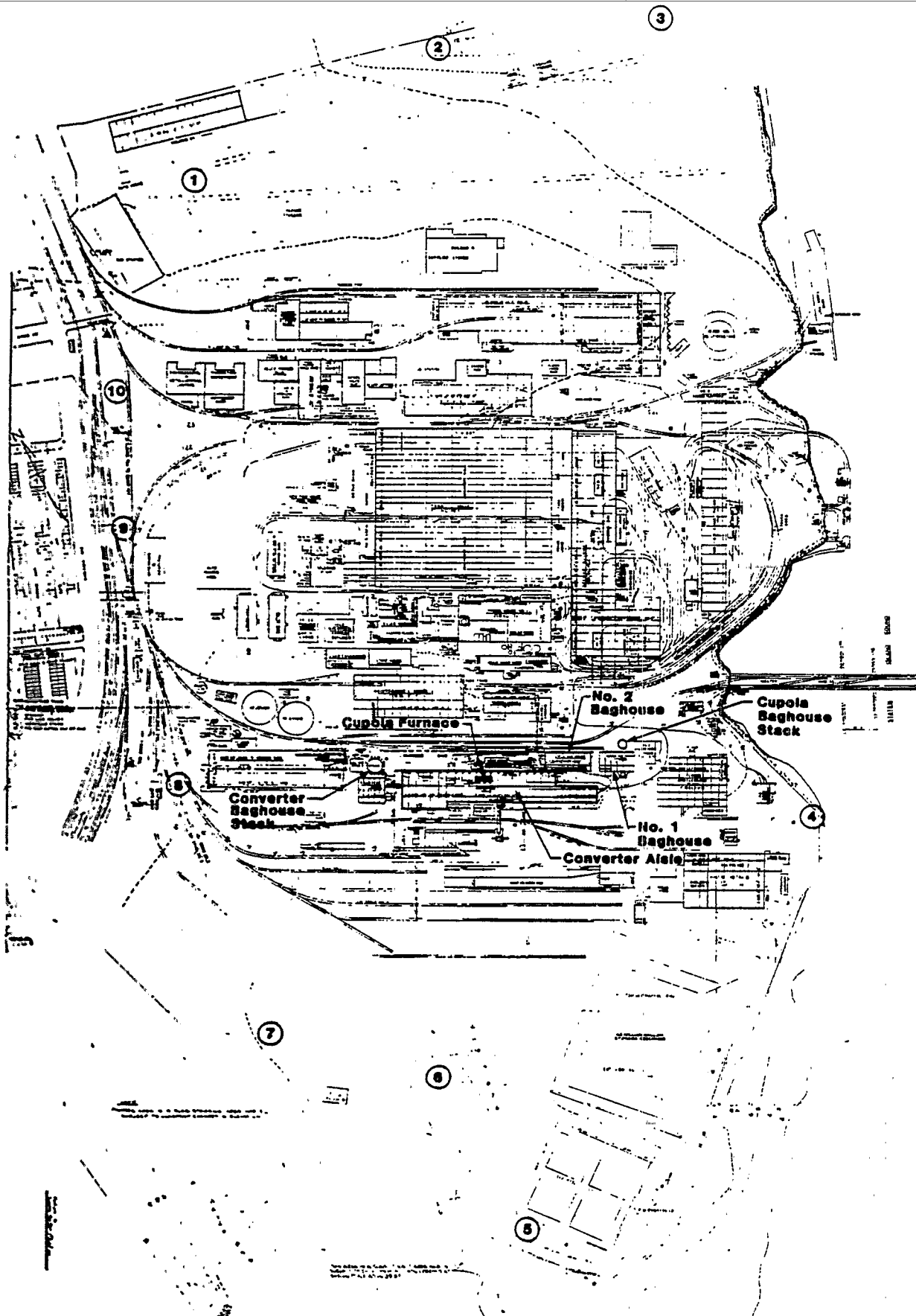


Figure 6-6. Soil Sampling Locations for Site MET-A

7.0 ANALYTICAL PROCEDURES

Laboratory procedures used to quantify dioxins/furans and dioxin/furan precursors in the Tier 4 samples are described in this section. Samples analyzed by EPA's Troika laboratories for dioxin/furan content included MM5 train samples, back-up XAD traps, baghouse dust samples, and ambient XAD train samples. Procedures used for the dioxin/furan analyses are described in detail in the Analytical Procedures and QA Plan for the Analysis of Tetra through Octa CDD's and CDF's in Samples from Tier 4 Combustion and Incineration Processes. These procedures are summarized in Section 7.1. Cupola furnace feed samples were analyzed by Radian to determine concentrations of chlorinated phenols (CP), chlorobenzenes (CB), polychlorinated biphenyls (PCBs), and total organic halogen (TOX). Procedures used for these analyses are detailed in Section 7.2.

7.1 DIOXINS/FURANS

The analytical procedures summarized in this section were used by Troika for dioxin/furan analysis of MM5 train samples, back-up XAD traps, baghouse dust samples, and ambient XAD train samples from Site MET-A. A separate document detailing these procedures has been prepared.¹

Samples consisting of organic solvents, aqueous solutions, and solids were prepared for analysis using slightly different procedures. The organic solvent samples consisted of rinses from the MM5 probe, nozzle, filter housing and condenser coil. Aqueous samples consisted of impinger catch solutions, and solid samples included filters, XAD resin, and baghouse dust. Isotopically-labeled surrogate compounds were added to all samples prior to extraction to allow determination of method efficiency and for quantification purposes.

Organic liquid samples (e.g., acetone and methylene chloride-based MM5 train rinses) were concentrated using a nitrogen blowdown apparatus. The

1. Analytical Procedures and Quality Assurance Plan for the Analysis of Tetra Through Octa Chlorinated Dibenzo-p-Dioxins and Dibenzofurans in Samples from Tier 4 Incineration Processes. Addendum to: "Analytical Procedures and Quality Assurance Plan for the Analysis of 2378-TCDD in Tier 3-7 Samples of the U.S. Environmental Protection Agency National Dioxin Strategy." EPA/600/3-85-019, April 1985.

residue, which contained particulate matter from the MM5 train probe and nozzle, was combined with the filter and handled as a solid sample. Solid samples were extracted with benzene in a Soxhlet apparatus for a period of at least 16 hours. The extract was concentrated by nitrogen blowdown and subjected to chromatographic cleanup procedures.

Aqueous solutions (e.g., MM5 train impinger samples) were extracted with hexane by vigorous shaking for a three hour period. This extraction procedure was repeated three times, with the organic fractions ultimately being combined and concentrated for chromatographic cleanup.

The cleanup procedure involved using liquid chromatographic columns to separate the compounds of interest from other compounds present in the samples. Four different types of columns were used: a combination acid and base modified silica gel column, a basic alumina column, a PX-21 carbon/celite 545 column and a silica/diol micro column. These were used in successive steps, with the last two being used only if necessary.

The cleaned samples were analyzed using high resolution gas chromatography/high resolution mass spectrometry (GC/MS). Conditions for the analyses were as follows:

Gas Chromatograph - Injector configured for capillary column, splitless injection; injector temperature 280°C; helium carrier gas at 1.2 ml/min; initial column temperature 100°C; final column temperature 240°C; interface temperature 270°C.

Mass Spectrometer - Varian/MAT Model 311A; electron energy 70ev; filament emission 1mA; mass resolution 8000 to 10,000; ion source temperature 270°C.

7.2 DIOXIN/FURAN PRECURSORS

Feed samples for Site MET-A were analyzed by Radian/RTP for chlorophenols (CP), chlorobenzenes (CB) and polychlorinated biphenyls (PCBs) by GC/MS; total organic halides (TOX) by GC/Hall detector. Analytical procedures are discussed in the following sections.

7.2.1 GC/MS Analyses

The analytical procedures used for determining CP, CB, and PCB concentrations in feed samples are modified versions of procedures typically used for the analysis of MM5 train components. These procedures involve initial extraction of the sample with an appropriate solvent, preliminary separation of the compounds of interest by solvent partitioning and liquid chromatography, and analysis of the processed fractions. Solutions containing CB and PCB are injected directly into the GC/MS, and solutions containing CP are derivatized prior to injection. Details on the procedures used for Site MET-A samples are provided in the sections below.

7.2.1.1 Sample Preparation

A flow chart for the sample preparation procedure used for Site MET-A feed samples is shown in Figure 7-1. The first step in the procedure involved adding labeled surrogate compounds to provide a measure of extraction method efficiency. The next step involved adding a mixture of 0.5 N NaOH and MeCl_2 to the sample and sonicating the sample for 30 minutes. The NaOH and MeCl_2 mixture converts the acid compounds to their salts and collects base/neutrals in the organic solvent. The sonicated sample was filtered and rinsed with 0.5 N NaOH. The filtrate was extracted three times in a separatory funnel with MeCl_2 and the aqueous and organic fractions were saved for derivatization and/or further cleanup. The aqueous fraction (or acids portion) was acidified to pH2 with HCl and then extracted three times with MeCl_2 . The MeCl_2 from this extraction was dried with anhydrous Na_2SO_4 , exchanged to benzene, and concentrated using a nitrogen blowdown apparatus. Acetylation of any CP present in the sample involved the following steps:

1. 2.0 mL isooctane, 2.0 mL acetonitrile, 50 μL pyridine, and 20 μL acetic anhydride were added to the extract. The test tube containing the extract was placed in a 60°C water bath for 15 minutes and was shaken 30 seconds every 2 minutes.

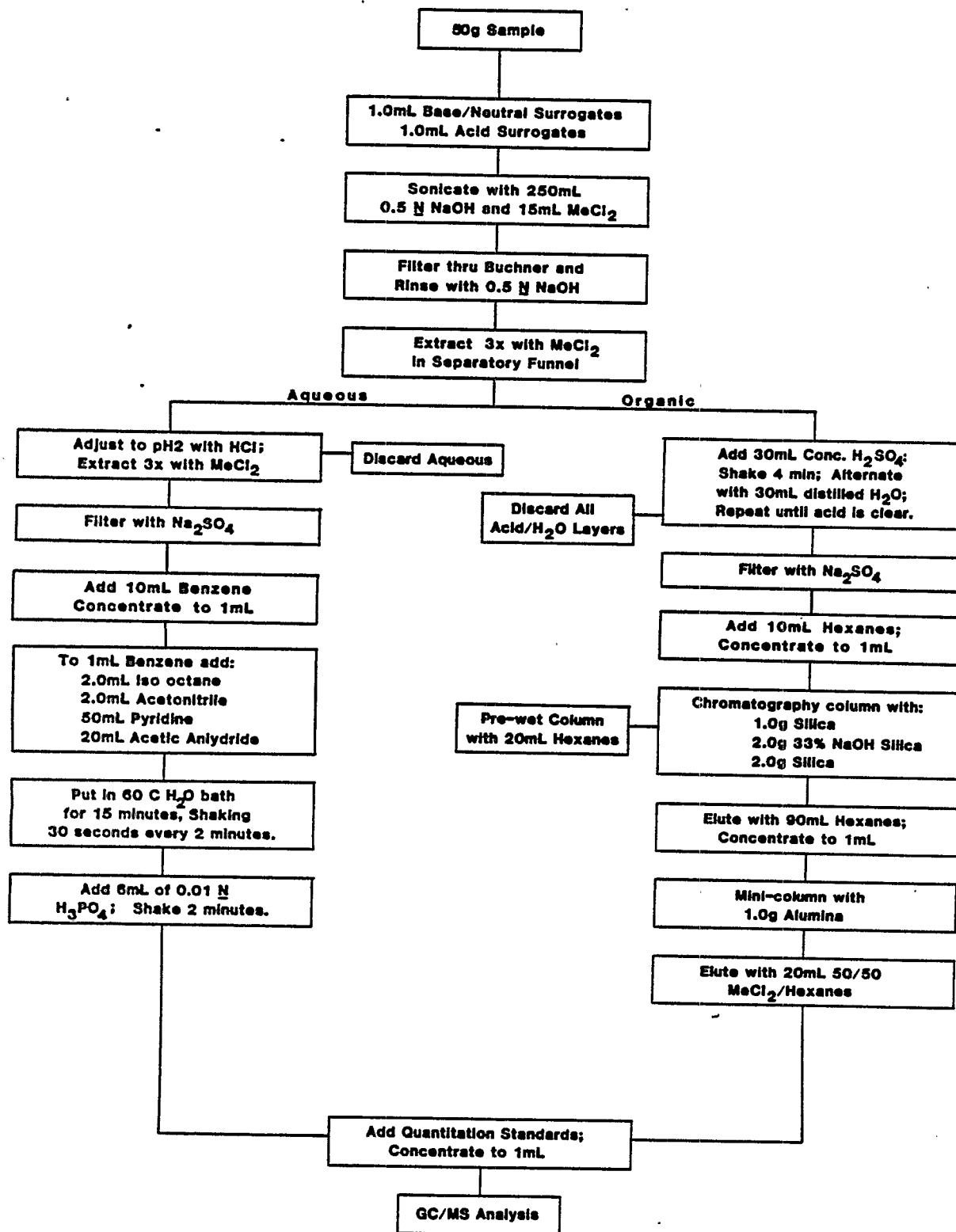


Figure 7-1. Sample Preparation Flow Diagram for Site MET-A Precursor Analyses.

2. 6 mL of 0.01 N H_3PO_4 were added to the test tube, and the sample was agitated for 2 minutes on a wrist action shaker.
3. The organic layer was removed and the quantitation standard was added. The sample was concentrated in a Reacti-Vial at room temperature (using prepurified N_2) to 1 mL prior to GC/MS analysis.

Cleanup of the organic (or base/neutrals) layer from the first MeCl_2 extraction involved successively washing the extract with concentrated H_2SO_4 and double-distilled water. The acid or water was added in a 30 mL portion and the sample was shaken for two minutes. After the aqueous (or acid) and organic layers were completely separated, the aqueous (or acid) layer was discarded. The acid washing procedure was repeated until the acid layer was colorless. The organic fraction from the final wash was dried with anhydrous Na_2SO_4 , exchanged to hexane and concentrated. Final cleanup of the sample by column chromatography involved the following procedure.

A glass macro-column, 20 mm o.d. x 230 mm in length, tapered to 6 mm o.d. on one end was prepared. The column was packed with a plug of silanized glass wool, followed successively by 1.0 g silica, 2.0 g silica containing 33% (w/w) 1 N NaOH , and 2.0 g silica. The concentrated extract was quantitatively transferred to the column and eluted with 90 mL hexane. The entire eluate was collected and concentrated to a volume of 1 mL in a centrifuge tube.

A disposable liquid chromatography mini-column was constructed by cutting off a 5-mL Pyrex disposable pipette at the 2.0 mL mark and packing the lower portion of the tube with a small plug of silanized glass wool, followed by 1 g of Woehlm basic alumina. The alumina had been previously activated for at least 16 hours at 600°C in a muffle furnace and cooled in a desiccator for 30 minutes just before use. The concentrated eluate from above was quantitatively transferred onto the liquid chromatography column. The centrifuge tube was rinsed consecutively with two 0.3-mL portions of a 3 percent MeCl_2 : hexane solution, and the rinses were transferred to the liquid chromatography column.

The liquid chromatography column was eluted with 20 mL of a 50 percent (v/v) MeCl_2 :hexane solution, and the eluate was concentrated to a volume of approximately 1 mL by heating the tubes in a water bath while passing a stream

of prepurified N₂ over the solutions. The quantitation standard was added and the final volume was adjusted to 1.0 mL prior to GC/MS analysis.

7.2.1.2 Analysis

Analyses for CP, CB and PCBs present in the feed sample extracts were performed with a Finnigan Model 5100 mass spectrometer using selected ion monitoring. A fused silica capillary column was used for chromatographic separation of the compounds of interest. Analytical conditions for the GC/MS analysis are shown in Table 7-1.

Tuning of the GC/MS was performed daily as specified in the Tier 4 QA Project Plan. An internal-standard calibration procedure was used for sample quantitation. Compounds of interest were calibrated against a fixed concentration of either d₁₂-chrysene (for CP) or d₈-naphthalene (for CB, PCB). Components of the calibration solution are shown in Table 7-2. For multi-point calibrations, this solution was injected at levels of 10, 50, 100, and 150 ng/mL.

Compound identification was confirmed by comparison of chromatographic retention times and mass spectra of unknowns with retention times and mass spectra of reference compounds. Since the selected ion monitoring technique was necessary for the samples analyzed, care was taken to monitor a sufficiently wide mass region to avoid the potential for reporting false positives.

The instrument detection limit for the analytes of interest (i.e., CP, CB, and PCB) was estimated to be approximately 500 pg on column. For a 50 g sample and 100 percent recovery of the analyte, this corresponds to a feed sample detection limit of 10 ppb.

7.3 TOX ANALYSIS

Cupola furnace feed samples were analyzed for total organic halide (TOX) by short-column GC and a Hall detector (GC/Hall). Solid samples were extracted with benzene for at least 16 hours in a Soxhlet apparatus. The

TABLE 7-1. INSTRUMENT CONDITIONS FOR GC/MS PRECURSOR ANALYSES

	Chlorobenzenes/ Polychlorinated biphenyls	Chlorophenols
Column	30 m WB DB-5 (1.0 u film thickness) fused silica capillary	
Injector Temperature	290°C	290°C
Separator Oven Temperature	290°C	290°C
Column Head Pressure	9 psi	9 psi
He flow rate	1 mL/min	1 mL/min
GC program	40(4)-290°C, 10°/min & hold	40(1)-290°C, 12°/min & hold
Emission Current	0.50 ma	0.50 ma
Electron Energy	70 ev	70 ev
Injection Mode	Splitless 0.6 min, then 10:1 split	
Mode	Electron ionization, Selected Ion Monitoring	

TABLE 7-2. COMPONENTS OF THE CALIBRATION SOLUTION

Base/Neutrals

4-chlorobiphenyl
 3,3'-dichlorobiphenyl
 2,4',5-trichlorobiphenyl
 3,3',4,4'-tetrachlorobiphenyl
 2,2',6,6'-tetrachlorobiphenyl
 2,2,4,5,6-pentachlorobiphenyl
 2,2',4,4',5,5'-hexachlorobiphenyl
 2,2',3,4,4',5',6-heptachlorobiphenyl
 2,2',3,3',4,4',5,5'-octachlorobiphenyl
 2,2',3,3',4,4',5,6,6'-nonachlorobiphenyl
 decachlorobiphenyl
 p-dichlorobenzene
 1,2,4-trichlorobenzene
 1,2,3,5-tetrachlorobenzene
 pentachlorobenzene
 hexachlorobenzene
 d₄-1,4-dichlorobenzene (SS)¹
 3-bromobiphenyl (SS)
 2,2',5,5'-tetrabromobiphenyl (SS)
 2,2',4,4',6,6'-hexabromobiphenyl (SS)
 octachloronaphthalene (QS)²
 d₁₀-phenanthrene (QS)
 d₁₂-chrysene (QS)

Acids

2,5-dichlorophenol
 2,3-dichlorophenol
 2,6-dichlorophenol
 3,5-dichlorophenol
 3,4-dichlorophenol
 2,3,5-trichlorophenol
 2,3,6-trichlorophenol
 3,4,5-trichlorophenol
 2,4,5-trichlorophenol
 2,3,4-trichlorophenol
 2,3,5,6-tetrachlorophenol
 pentachlorophenol
 d₆-phenol (SS)
 d₄-2-chlorophenol (SS)
¹³C₆-pentachlorophenol (SS)
 d₈-naphthalene (QS)
 2,4,6-tribromophenol (QS)
 d₁₀-phenanthrene (QS)
 d₁₂chrysene (QS)

¹Surrogate standard.

²Quantitation standard.

extracts were washed three times with 100 mL portions of reagent-grade water concentrated to 10 mL.

An attempt to use a fused silica capillary column to separate surrogates from target compounds was unsuccessful due to the complexity of the sample constituents. Determinations for TOX were therefore performed on samples without surrogates and no measure of extraction efficiency is available.

Instrument conditions are shown in Table 7-3. Sample quantitation was based on an average response factor developed from a mixture of chlorinated benzenes and brominated biphenyls. Individual CP, CB and PCBs were also injected at various concentrations to develop a calibration curve for comparison to the mixture response factors.

TABLE 7-3. ANALYTICAL CONDITIONS FOR TOX ANALYSIS

Hall Detector Conditions

Reactor temperature - 850°C

Solvent - n-propanol

Hydrogen flow rate - 35 mL/min

GC Conditions (Varian 3700)

Injection volume (1 - 5 uL)

Helium carrier gas flow rate - 60 mL/min

Column - 3-ft packed column with 1 in 10% OV 101

Column temperature - 200°C isothermal

8.0 QUALITY ASSURANCE/QUALITY CONTROL (QA/QC)

This section summarizes the results of the quality assurance and quality control (QA/QC) activities for Site MET-A. The flue gas dioxin/furan surrogate recovery data for Run 03 was within the QC specifications presented in the Tier 4 QAPP. The surrogate recoveries for Runs 02 and 04 were not within the specifications. The surrogate recoveries could not be determined because of the large amounts of native CDDs and CDFs which were present in the samples. The surrogate recoveries for the back-up XAD modules ranged from 82 to 96 percent. The surrogate recoveries for the baghouse dust samples and ambient XAD train samples were all within the specifications designated in the QAPP. The results of the analysis of the fortified laboratory QC sample were all within 32 percent of true value except for 2378 TCDF, which was 100 percent higher than the true value. This should not affect the data quality since the true value was so near the detection limit. The specifications for the fortified sample were ± 50 percent. The laboratory fortified QC sample for baghouse dust was also within 32 percent of the true value. Generally, the reported analytical results for the flue gas samples should be considered lower bounds on the true values while the baghouse dust and ambient results should be considered reasonable estimates.

The dioxin/furan precursor analysis of the feed samples was not as accurate as the dioxin/furan homologue analysis. Surrogate recoveries of the base neutrals fractions were generally within the specified QC limits of ± 50 percent; however, the surrogate acid fractions were generally below the specified limits. In spite of the low recoveries of the acid fraction, the dioxin/furan precursor results are considered a reasonable approximation of the true precursor concentration in the feed samples.

The following sections summarize the results of all Site MET-A QA/QC activities. Manual gas sampling methods are considered in Section 8.1 and continuous emission monitoring and molecular weight determinations are considered in Section 8.2. The laboratory analyses QA/QC activities are summarized in Section 8.3.

8.1 MANUAL GAS SAMPLING

Manual gas sampling methods at Site MET-A included Modified Method 5 (MM5), EPA Methods 1 through 4, and HCl train sampling. These methods are discussed in Section 6.0. Quality assurance and quality control (QA/QC) activities for the manual sampling methods centered around (1) equipment calibration, (2) glassware pre-cleaning, (3) procedural QC checks, and (4) sample custody procedures. Key activities and QC results in each of these areas are discussed in this section. Also discussed are problems encountered that may have affected data quality.

8.1.1 Equipment Calibration and Glassware Preparation

Pre-test calibrations or inspections were conducted on pitot tubes, sampling nozzles, temperature sensors and analytical balances. Both pre-test and post-test calibrations were performed on the dry gas meters. All of the field test equipment met the calibration criteria specified in the Tier 4 Quality Assurance Project Plan (QAPP). Differences in the pre-test and post-test dry gas meter calibrations were less than 2 percent (%).

An extensive pre-cleaning procedure was used for all sample train glassware and sample containers. This cleaning procedure, which is outlined in Table 8-1, was implemented to minimize the potential for sample contamination with substances that could interfere with the dioxin/furan analysis. A blank MM5 train that had been pre-cleaned using this procedure (i.e., proof train blank) was recovered with acetone and methylene chloride rinses according to the usual MM5 recovery procedure. The rinses and other MM5 train components of the proof train blank (i.e., filter, XAD trap, and impinger solution) were submitted to Troika for dioxin/furan analysis.

To minimize the potential for contamination in the field, all sample train glassware was capped with foil prior to use. Sample train field recovery was performed in an industrial hygiene laboratory at the host plant. This laboratory was performing low-level metals analysis using nitric, sulfuric, and hydrochloric acids. No organic solvents were in use. A blank MM5 train that had been previously used and field-recovered at least once at

Table 8-1. GLASSWARE PRECLEANING PROCEDURE

NOTE: USE DISPOSABLE GLOVES AND ADEQUATE VENTILATION

1. Soak all glassware in hot soapy water (Alconox^R) 50°C or higher.
2. Distilled/deionized H₂O rinse (X3).^a
3. Chromerge^R rinse if glass, otherwise skip to 6.
4. High purity liquid chromatography grade H₂O rinse (X3).
5. Acetone rinse (X3), (pesticide grade).
6. Methylene chloride rinse (X3), (pesticide grade).
7. Cap glassware with clean glass plugs or methylene chloride rinsed aluminum foils.

^a(X3) = three times.

Site MET-A (i.e., field recovery train blank) was assembled and recovered according to the usual MM5 recovery procedures. The rinses and other components of the field recovery train blank (i.e., filter, XAD trap, and impinger solution) were submitted to Troika for dioxin/furan analysis. Analytical results for the proof train blank and field recovery train blank are presented in section 8.3.1.3.

8.1.2 Procedural QC Activities/Manual Gas Sampling

Procedural QC activities during the manual gas sampling for dioxin/furan and HCl focused on:

- visual equipment inspections,
- utilization of sample train blanks,
- ensuring the proper location and number of traverse points,
- conducting pre-test and post-test sample train leak checks,
- maintaining proper temperatures at the filter housing, sorbent trap and impinger train,
- maintaining isokinetic sampling rates, and
- recording all data on preformatted field data sheets.

Unusual circumstances noted while carrying out the procedural QC activities are discussed below.

As noted earlier, the first test run, Run 01, (5/21/85) was aborted after about 30 minutes of on-line sampling because the MM5 sample train filter housing was incorrectly assembled. Insufficient time and inclement weather prohibited the sampling team from beginning another test run on 5/21/85. As a result, two test runs (Runs 02 and 03) were performed on 5/22/85. The final test run (Run 04) was performed on 5/23/85. Both the MM5/dioxin and MM5/HCl sampling proceeded without incident during Runs 02, 03, and 04.

Results of the average isokinetics calculations for the three valid MM5 test runs are shown in Table 8-2. The QA objective of 100 ± 10 percent was met for all test runs. Initial, final, and port change leak checks for the MM5 and HCl sample trains also achieved the QA objectives for all test runs. The leak check data are noted on the MM5 field data sheets.

TABLE 8-2. SUMMARY OF ISOKINETIC RESULTS FOR MM5 AND HCl SAMPLING
AT SITE MET-A

Run	<u>MM5 Outlet</u>		<u>HCl Outlet</u>	
	Isokinetics	Meets QC Objective?	Isokinetics	Meets QC Objective?
02	107.1	YES	97.5	YES
03	102.2	YES	104.8	YES
04	105.7	YES	103.2	YES

The quality assurance objective for MM5 and HCl sampling was isokinetics of 100 \pm 10 percent.

8.1.3 Sample Custody

Sample custody procedures used during this program emphasized careful documentation of the samples collected and the use of chain-of-custody records for samples transported to the laboratory for analysis. Steps taken to identify and document samples collected included labeling each sample with a unique alphanumeric code and logging the sample in a master logbook. All samples shipped to Troika or returned to Radian-RTP were also logged on chain-of-custody records that were signed by the field sample custodian upon shipment and also signed upon receipt at the laboratory. Each sample container lid was individually sealed to ensure that samples were not tampered with. No evidence of loss of sample integrity was reported for samples collected at this site.

8.2 CONTINUOUS MONITORING/MOLECULAR WEIGHT DETERMINATION

Flue gas concentrations measured continuously at the stack breeching location included O_2 , CO, CO_2 , THC, NO_x , and SO_2 . Concentrations of O_2 , CO_2 and N_2 were also determined for integrated bag samples of the flue gas. Quality control results for these analyses are discussed in this section.

Drift check results for the continuously monitored flue gas parameters are summarized in Table 8-3. Data reduction was performed by assuming a linear drift of the instrument response over the test day based on drift checks at the beginning and end of the day. The drift check results met the QC criteria of ± 10 percent daily drift for all species except for SO_2 , which showed nearly 32 percent drift during Run 04.

The quality control gases for this program consisted of mid-range concentration standards different than those used for daily calibration. The QC gases were analyzed immediately after calibration each day to provide data on instrument variability. The acceptance criteria for the analysis of each QC standard was agreement within ± 10 percent (%) of the running mean value. Since there were only two test days, this consisted of a comparison of QC output data from 5/22/85 (Runs 02, 03) and 5/23/85 (Run 04). The QC output data for O_2 , CO, CO_2 , NO_x , and THC each agreed within less than 4 percent,

TABLE 8-3. SUMMARY OF DRIFT CHECK AND CONTROL STANDARD RESULTS

Test Date	Test Run	Parameter	Drift Check			Meets QC? ^b	Input Conc.	QC Standard Output Conc.	Difference from Running Mean, %	Meets QC? ^c
			Input Conc.	Instrument Drift, % ^a	Input Conc.					
5/22/85	02,03	O ₂	21.0% V	-2.30	9.3% V	Yes	9.3% V	9.67	--	Yes
5/23/85	04	O ₂	21.0% V	-0.10	9.3% V	Yes	9.3% V	9.42	-1.26	Yes
5/22/85	02,03	CO	5580 ppmv	1.81	2006 ppmv	Yes	2006 ppmv	2182	--	Yes
5/23/85	04	CO	5580 ppmv	-0.06	2006 ppmv	Yes	2006 ppmv	2148	-0.78	Yes
5/22/85	02,03	CO ₂	18.0% V	0.52	13.0% V	Yes	13.0% V	13.00	--	Yes
5/23/85	04	CO ₂	18.0% V	3.69	13.0% V	Yes	13.0% V	12.58	-1.64	Yes
5/22/85	02,03	SO ₂	83.1 ppmv	3.00	d	Yes	d	d	d	d
5/23/85	02	SO ₂	83.1 ppmv	31.55	d	No	d	d	d	d
5/22/85	02,03	NO _x	84.6 ppmv	-9.92	21.0 ppmv	Yes	21.0 ppmv	22.47	--	Yes
5/23/85	04	NO _x	84.6 ppmv	-0.69	21.0 ppmv	Yes	21.0 ppmv	21.55	-2.09	--
5/22/85	02,03	THC	90 ppmv	0.54	19.7 ppmv	Yes	19.7 ppmv	21.6	--	Yes
5/23/85	04	THC	90 ppmv	0.62	19.7 ppmv	Yes	19.7 ppmv	19.94	-4.00	--

^aInstrument drift is defined as the percent difference between the instrument response to the input concentration at the beginning and end of the test run.

^bQC criteria was daily instrument drift within +/-10 percent.

^cQC criteria was output concentration within +/-10 percent of the running mean concentration for this test site.

^dNot available. SO₂ gas cylinder originally intended for QC purposes was used for instrument calibration.

thus achieving the QC objective. There is no QC output data for SO₂ because the SO₂ gas cylinder originally intended for QC purposes was used for instrument calibration.

8.3 LABORATORY ANALYSES

QA/QC activities were carried out for dioxin/furan, precursor, and total chloride analyses performed on Site MET-A samples. The dioxin/furan analyses of MM5 train samples, baghouse dust samples and ambient XAD train samples performed by Troika are considered in Section 8.3.1; the precursor analyses of cupola furnace feed samples performed by Radian/RTP are considered in Section 8.3.2; and the total chloride analyses of HCl train samples performed by Radian/Austin are considered in Section 8.3.3.

8.3.1 Dioxin/Furan Analyses

Three individual topics related to the dioxin/furan analyses at Site MET-A are discussed in this section. The contribution of the back-up XAD trap to the train-total MM5 dioxin/furan catch is presented in Section 8.3.1.1. Analytical recoveries of labeled surrogate compounds spiked onto MM5 train samples, baghouse dust samples, and ambient XAD train samples prior to extraction are reported in Section 8.3.1.2. Sample blank data are reported in Section 8.3.1.3.

8.3.1.1 Back-Up XAD Trap Data

As noted in Section 6.1.2.1, a back-up XAD trap was added to the MM5 trains used at Site MET-A (See Figure 6-3). The back-up traps were analyzed separately from the "primary" MM5 train samples. Table 8-4 summarizes the contribution of the back-up XAD trap to the total amount of each dioxin and furan species measured on the entire train (i.e., primary MM5 train plus back-up XAD trap). In general, the back-up XAD trap accounted for a fairly small portion of the train-total catch. As a rule, the higher the degree of chlorination for both dioxin and furan species, the lower was the amount of

TABLE 8-4. PERCENTAGE CONTRIBUTION OF BACK-UP XAD MODULE TO
TOTAL MM5 TRAIN CATCH OF DIOXIN/FURAN HOMOLOGUES

Isomer/Homologue	Range of Back-up XAD Module Percentage Contribution to Total MM5 Train Catch ^a
Dioxins	
2378 TCDD	0 - 0.8
Other TCDD	0.5 - 13.5
Penta CDD	0 - 1.9
Hexa CDD	0 - 0.4
Hepta CDD	0 - 0.2
Octa CDD	0.03 - 0.1
<u>Furans</u>	
2378 TCDF	0.3 - 3.2
Other TCDF	1.1 - 11.5
Penta CDF	0.1 - 1.8
Hexa CDF	0 - 0.6
Hepta CDF	0 - 0.5
Octa CDF	0 - 0.3

- a. Run 02 showed the highest percentage back-up XAD module contribution for all isomers/homologues except Octa CDD. Run 04 showed the highest percentage back-up XAD contribution for Octa CDD.

the species that escaped capture by the first XAD trap. The maximum percentage contributions of the back-up trap to the train-total catch ranged from 0.1 percent for the octa-CDDs to 13.5 percent for other-TCDDs.

8.3.1.2 Surrogate Recoveries of the Test Samples

Table 8-5 presents the analytical recovery data reported by Troika for four isotopically labeled surrogate compounds spiked onto the primary MM5 train samples, back-up XAD trap samples, baghouse dust, and ambient XAD train samples. Those samples consisting solely of solid components (i.e., back-up XAD traps, baghouse dusts, and ambient train XAD traps) were spiked with the $^{13}\text{C}_{12}$ -TCDD and $^{13}\text{C}_{12}$ -Octa CDD surrogates. Samples consisting solely of liquid components (i.e., the aqueous portion of the ambient train samples) were spiked with the $^{37}\text{Cl}_4$ -TCDD and $^{37}\text{Cl}_4$ -Hepta CDD surrogates. Samples that consisted of both solid and liquid components (i.e., the primary MM5 train samples) were spiked with all four of the surrogates.

Surrogate recoveries for the back-up XAD trap samples, baghouse dust samples, and ambient XAD train samples were all within the target ranges of 50 to 120 percent for the labeled TCDDs and 40 to 120 percent for the labeled hepta- and octa- CDDs. Recoveries for the primary MM5 train samples could not be determined for all four surrogate compounds because of the relatively large quantities of native CDD and CDF species present in the samples. Since no measure of extraction method efficiency is available for the MM5 samples, it should be noted that the reported analytical results for native compounds may actually represent lower bounds on the true values.

8.3.1.3 Sample Blanks

Table 8-6 summarizes the analytical results reported by Troika for internal laboratory blanks, laboratory fortified quality control (QC) samples, proof blank MM5 train samples, and field recovery blank MM5 train samples. In general, the data show good surrogate recoveries, with values ranging from 80 to 100 percent. Comparison of the measured and spiked values for the

TABLE 8-5. PERCENT SURROGATE RECOVERIES FOR
SITE MET-A DIOXIN/FURAN ANALYSES

Sample	$^{37}\text{Cl}_4$ TCDD	$^{13}\text{C}_{12}$ TCDD	$^{37}\text{Cl}_4$ Hepta-CDD	$^{13}\text{C}_{12}$ Octa CDD
<u>MM5 Train Samples</u>				
Run 02 Primary MM5	NR	NR	NR	NR
Run 02 Back-up XAD	-	96	-	82
Run 03 Primary MM5	NR	120	NR	58
Run 03 Back-up XAD	-	96	-	93
Run 04 Primary MM5	NR	NR	NR	33
Run 04 Back-up XAD	-	94	-	87
<u>Baghouse Dust Samples</u>				
Run 02 #1 BH Dust	-	100	-	73
Run 02 #2 BH Dust	-	102	-	56
Run 03 #1 BH Dust	-	104	-	63
Run 03 #2 BH Dust	-	90	-	64
Run 04 #1 BH Dust	-	96	-	64
Run 04 #2 BH Dust	-	68	-	45
<u>Ambient XAD Train Samples</u>				
Ambient XAD	-	86	-	87
Ambient Aqueous	88	-	112	-

Note: NR indicates that surrogate recovery data were not reported for this compound. In some cases, valid surrogate recoveries could not be determined for the primary MM5 train because of the large amounts of native CDDs and CDFs present in the samples.

Dash (-) indicates that the surrogate compound of interest was not spiked onto this sample.

TABLE A-6. ANALYSIS RESULTS FOR QUALITY CONTROL SAMPLES

Compound	Flue Gas Quality Control Samples				Baghouse Dust Quality Control Samples				
	Laboratory Blank	Laboratory Fortified		Proof Blank #15 Train	Field Blank #15 Train		Laboratory Blank	Laboratory Fortified	
		Measured Value	True Value ^{a,b}		Measured Value	True Value ^{a,b}			
								AMOUNT DETECTED, (Nanograms Per Sample)	
Dioxins									
2378 TCDD	ND	0.5	0.4 (+25)	NR	0.1	ND	0.04	0.04 (0)	
Other TCDD	ND	ND	ND (0)	0.2	1.9	ND	ND	ND (0)	
Penta CDD	ND	ND	ND (0)	ND	0.3	ND	ND	ND (0)	
Hexa CDD	ND	1.1	1.6 (-32)	ND	7.5	ND	0.11	0.16 (-32)	
Hepta CDD	ND	1.9	2.4 (-21)	ND	7.3	ND	0.30	0.24 (-21)	
Octa CDD	ND	2.8	3.2 (-13)	1.3	6.3	ND	0.29	0.32 (-9)	
Furans									
2378 TCDF	ND	0.8	0.4 (+100)	NR	2.6	ND	0.09	0.04 (+125)	
Other TCDF	ND	ND	ND (0)	1.6	26.6	0.16	ND	ND (0)	
Penta CDF	ND	1.0	0.8 (+25)	ND	21.0	ND	0.09	0.08 (+13)	
Hexa CDF	ND	1.3	1.6 (-19)	0.3	40.0	ND	0.12	0.16 (-25)	
Hepta CDF	ND	1.9	2.4 (-21)	0.5	16.1	ND	0.29	0.24 (+21)	
Octa CDF	ND	2.8	3.2 (-13)	0.4	43.1	ND	0.30	0.32 (-6)	
SURROGATE RECOVERIES, Percent									
³⁷ Cl ₄ - TCDD	96	94	NA	82	80	NR	NR	NA	
¹³ C ₁₂ - TCDD	94	84	NA	82	90	96	92	NA	
³⁷ Cl ₄ - H7CDD	92	80	NA	108	90	88	88	NA	
¹³ C ₁₂ - OCDD	89	84	NA	93	65	61	57	NA	

a. True values represent the amounts of each homologue spiked into the laboratory fortified QC samples.

b. Value shown in parenthesis is the percentage difference between the measured value and the true value, i.e., % difference = (measured value - true value)/true value x 100%.

ND = not detected

NR = not reported by Troika

NA = not applicable

H7CDD = hepta-chlorinated dibenzo-p-dioxin

laboratory fortified QC samples showed agreement to within ± 30 percent for all target species except the 2378 TCDF isomer. The measured values for the 2378 TCDF isomer were about twice as high as the spiked values. Small but detectable quantities of several dioxin and furan species were found in the proof blank MM5 train samples, and detectable quantities of all targeted dioxin and furan species were found in the field blank MM5 train. Table 8-7 gives a comparison of the dioxin/furan analytical results for the field blank MM5 train and the test run MM5 trains. In no case did the field blank value correspond to more than 10 percent of the minimum test run value, which indicates that there were no significant blanking problems at Site MET-A. Thus, the field clean-up procedures were found to be adequate for this test site. Emissions data reported in Section 5.4 are not blank-corrected.

8.3.2 Precursor Analyses

Table 8-8 presents analytical recovery efficiencies for six isotopically labeled compounds used as surrogates for the target precursor analytes in the Site MET-A feed samples. The surrogate recovery values in Table 8-8 vary considerably by sample type and by specific surrogate species. The overall ranges of surrogate recoveries for the different types of feed samples were: 7 to 84% for coke, 28 to 89% for telephone parts and wire, 0 to 15% for circuit boards and 11 to 64% for electronic switching gear. These values are below the 50 percent objective stated in the Tier 4 QA Project Plan and are below those generally considered achievable when analyzing for similar compounds in water or from MM5 train components. There are no directly comparable surrogate recovery values reported in the literature for samples similar to the Site MET-A feed materials.

There are several reasons for the comparatively low surrogate recoveries reported in the Tier 4 study for samples such as the Site MET-A circuit boards. First, the complex nature of the samples required extensive clean-up procedures prior to GC/MS analysis, which increased the potential for losses of the surrogate compounds (and analytes) during sample preparation. Second, large sample sizes (25 to 50 g) were required to increase method sensitivity for the target analytes and to ensure that representative portions of the

TABLE 8-7. FIELD BLANK DIOXIN/FURAN DATA
FOR SITE MET-A MM5 SAMPLES

Amount Detected, Nanograms per Train			
Isomer/Homologue	Field Blank Value	Minimum Test Run Value	Percentage ^a
<u>Dioxins</u>			
2378 TCDD	0.1	19	0.5
Other TCDD	2.0	134	1.5
Penta CDD	0.3	238	0.1
Hexa CDD	7.5	223	3.4
Hepta CDD	7.3	415	1.8
Octa CDD	6.3	247	2.6
<u>Furans</u>			
2378 TCDF	2.6	705	0.4
Other TCDF	29.2	2380	1.2
Penta CDF	21.0	2119	1.0
Hexa CDF	40.0	852	4.7
Hepta CDF	16.1	652	2.5
Octa CDF	43.1	465	9.3

a. Percentage shown is the ratio of the field blank value to the minimum test run value, expressed as a percentage.

TABLE 8-8. PERCENT SURROGATE RECOVERIES FOR SITE MET-A FEED SAMPLES

Surrogate Compound	Feed Materials			
	Coke ^a	Telephone Parts, Wire	Circuit Boards ^a	Electronic Switching Gear
o d ₄ -dichlorobenzene	26, 31	51	3, trace	11
o bromobiphenyl	80, 68	89	5,1	21
o 2', 5, 5' tetra bromobiphenyl	84, 78	67	3, ND	20
o d ₄ -2-chlorophenol	49, 45	28	3, 2	50
o ¹³ C ₆ -pentachlorophenol	24, 7	72	14,15	64
o d ₆ -phenol	22, 18	22	ND, 1	43

a. Duplicate analyses were run on the coke and circuit board samples.

samples were analyzed. Due to the high cost of labeled surrogates, it was not desirable to spike the large sample sizes with surrogates in proportion to that normally used for smaller samples. Supplemental in-house laboratory studies showed that when sample size was restricted to 1 g and the amount of surrogate spiked was held fixed, surrogate recoveries improved and were directly comparable to those reported in previous studies.¹ Surrogate recoveries for Tier 4 samples and the results for small sample sizes are further discussed in the Tier 4 Engineering Analysis Report.

In spite of the relatively low surrogate recovery values for some of the feed samples, the resulting analytical sensitivity for the target analytes was considered acceptable for the purpose of this study. The instrumental detection limit ranged from about 100 to 500 picograms on-column for the 1 microliter of final extract injected into the GC/MS. At a method recovery efficiency of 100 percent for a 50 gram solid sample cleaned up to a final extract volume of 1 milliliter, the overall analytical sensitivity would be approximately 2 to 10 ppb in the solid sample. For samples such as the circuit boards with surrogate recoveries as low as 1 percent, the overall analytical sensitivity of the method would still be 200 to 1000 ppb, or 0.2 to 1.0 ppm. Thus, even in a worst-case situation the analytical procedures used provide information on the precursor content of the feed samples down to the ppm level.

8.3.3 Total Chloride Analysis

Total chloride analyses were performed by Radian/Austin on the HCl train samples. QA/QC activities included total chloride analysis of field recovery blank HCl train samples, total chloride analysis of an aliquot of the NaOH solution used in the sample train impingers, and duplicate total chloride

¹M.L. Taylor, T.O. Tiernan, J.H. Garrett, G.F. Van Ness, J.G. Solch. Assessments of Incineration Processes as Sources of Supertoxic Chlorinated Hydrocarbons: Concentrations of Polychlorinated Dibenzo-p-dioxins/Dibenzofurans and Possible Precursor Compounds in Incinerator Effluents in Chlorinated Dioxins and Dibenzofurans in the Total Environment, G. Choudhary, L.H. Keith, and C. Rappe, eds., Butterworth Publishers, Boston, Massachusetts, 1983.

analyses of two individual samples. Chlorides were not detected in either the field recovery blank train samples or the aliquot of NaOH solution analyzed. Duplicate ion chromatograph analyses of the probe rinse/filter fraction of the HCl train from Run 03 were in exact agreement. Duplicate analyses of the impinger fraction of the HCl train from Run 03 showed non-detectable levels of total chlorides in both cases.

APPENDIX A

FIELD SAMPLING DATA

- A-1 Modified Method 5 and EPA Methods 1-4
Field Results
- A-2 Continuous Emissions Monitoring Results
- A-3 HCl Train Results
- A-4 Ambient XAD Train Results
- A-5 Modified Method 5 Sample Calculations

APPENDIX A-1

Modified Method 5 and EPA Methods 1-4
Field Results

R A D I A N S O U R C E T E S T
E P A M E T H O D 2 - 5
(R A W D A T A)

PLANT : DIOXIN SITE #10
PLANT SITE :
SAMPLING LOCATION : BAGHOUSE EXHAUST
TEST # : 10-MM5-02
DATE : 5/22/85
TEST PERIOD : 0750-1240

PARAMETER -----	VALUE -----
Sampling time (min.)	240
Barometric Pressure (in.Hg)	29.87
Sampling nozzle diameter (in.)	.183
Meter Volume (cu.ft.)	137.566
Meter Pressure (in.H2O)	.95
Meter Temperature (F)	82.15
Stack dimension (sq.in.)	14957.16
Stack Static Pressure (in.H2O)	-.26
Stack Moisture Collected (gm)	195.1
Absolute stack pressure(in Hg)	29.85088
Average stack temperature (F)	214
Percent CO2	1.98
Percent O2	20.4
Percent N2	77.6
Delp's Subroutine result	26.352
DGM Factor	.9978
Pitot Constant	.84

R A D I A N S O U R C E T E S T
 E P A M E T H O D S 2 - 5
 F I N A L R E S U L T S
 PLANT : DIOXIN SITE #10
 PLANT SITE :
 SAMPLING LOCATION : BAGHOUSE EXHAUST
 TEST # : 10-MM5-02
 DATE : 5/22/85
 TEST PERIOD : 0750-1240

PARAMETER -----	RESULT -----
Vm(dscf)	133.7695
Vm(dscm)	3.788352
Vw gas(scF)	9.198965
Vw gas (scm)	.2605147
% moisture	6.434263
Md	.9356573
MWd	29.1272
MW	28.41125
Vs(fpm)	3898.842
Vs (mpm)	1188.671
Flow(acfm)	404969.5
Flow(acmm)	11468.74
Flow(dscfm)	296148
Flow(dscmm)	8386.91
% I	107.0902
% EA	23611.36

Program Revision:1/16/84

R A D I A N S O U R C E T E S T
E P A M E T H O D 2 - 5
(R A W D A T A)

PLANT : DIOXIN SITE #10
PLANT SITE :
SAMPLING LOCATION : BAGHOUSE EXHAUST
TEST # : 10-MM5-03
DATE : 5/22/85
TEST PERIOD : 1440-1910

PARAMETER -----	VALUE -----
Sampling time (min.)	240
Barometric Pressure (in.Hg)	29.87
Sampling nozzle diameter (in.)	.184
Meter Volume (cu.ft.)	140.937
Meter Pressure (in.H2O)	1.02
Meter Temperature (F)	95.2
Stack dimension (sq.in.)	14957.16
Stack Static Pressure (in.H2O)	-.26
Stack Moisture Collected (gm)	190.4
Absolute stack pressure(in Hg)	29.85088
Average stack temperature (F)	221.5
Percent CO2	1.78
Percent O2	20.4
Percent N2	77.8
Delps Subroutine result	27.5893
DGM Factor	.9978
Pitot Constant	.84

R A D I A N S O U R C E T E S T
 E P A M E T H O D S 2 - 5
 F I N A L R E S U L T S
 PLANT : DIOXIN SITE #10
 PLANT SITE :
 SAMPLING LOCATION : BAGHOUSE EXHAUST
 TEST # : 10-MM5-03
 DATE : 5/22/85
 TEST PERIOD : 1440-1910

PARAMETER -----	RESULT -----
Vm(dscf)	133.8492
Vm(dscm)	3.790609
Vw gas(scF)	8.97736
Vw gas (scm)	.2542388
% moisture	6.285499
Md	.937145
MWd	29.0952
MW	28.39781
Vs(fpm)	4082.87
Vs (mpm)	1244.777
Flow(acfm)	424084.3
Flow(acmm)	12010.07
Flow(dscfm)	307201
Flow(dscmm)	8699.932
% I	102.1788
% EA	14655.15

Program Revision:1/16/84

R A D I A N S O U R C E T E S T
E P A M E T H O D 2 - 5
(R A W D A T A)

PLANT : DIOXIN SITE #10
PLANT SITE :
SAMPLING LOCATION : BAGHOUSE EXHAUST
TEST # : 10-MM5-04
DATE : 05/23/85
TEST PERIOD : 1215-1646

PARAMETER -----	VALUE -----
Sampling time (min.)	240
Barometric Pressure (in.Hg)	29.87
Sampling nozzle diameter (in.)	.175
Meter Volume (cu.ft.)	120.014
Meter Pressure (in.H2O)	.72
Meter Temperature (F)	82.1
Stack dimension (sq.in.)	14957.16
Stack Static Pressure (in.H2O)	-.26
Stack Moisture Collected (gm)	167.6
Absolute stack pressure(in Hg)	29.85088
Average stack temperature (F)	213.4
Percent CO2	1.48
Percent O2	20.7
Percent N2	77.8
Delp's Subroutine result	25.3921
DGM Factor	.9978
Pitot Constant	.84

R A D I A N S O U R C E T E S T
 E P A M E T H O D S 2 - 5
 F I N A L R E S U L T S
 PLANT : DIOXIN.SITE #10
 PLANT SITE :
 SAMPLING LOCATION : BAGHOUSE EXHAUST
 TEST # : 10-MM5-04
 DATE : 05/23/85
 TEST PERIOD : 1215-1646

PARAMETER -----	RESULT -----
Vm(dscf)	116.6468
Vm(dscm)	3.303436
Vw gas(scF)	7.902341
Vw gas (scm)	.2237943
% moisture	6.34476
Md	.9365524
MWd	29.0592
MW	28.35752
Vs(fpm)	3760.38
Vs (mpm)	1146.457
Flow(acfm)	390587.6
Flow(acmm)	11061.44
Flow(dscfm)	286158.7
Flow(dscmm)	8104.013
% I	105.6801
% EA	-12873.06

Program Revision:1/16/84

APPENDIX A-2
Continuous Emissions Monitoring Results

CEMS DATA - SITE 10 - TEST 2

TIME	O2 (%V)	CO (PPMV)	CO2 (%V)	SO2 (PPMV)	NOX (PPMV)	THC (PPMV)
=====	=====	=====	=====	=====	=====	=====
750	21.1	1302.6	1.5	182.7	39.2	16.4
755	20.1	455.3	1.8	221.7	75.7	7.9
800	19.9	1564.3	1.6	286.6	48.9	17.0
805	21.1	654.8	1.8	239.4	67.4	10.0
810	19.9	766.2	1.7	304.0	57.9	11.2
815	20.0	3035.6	1.7	386.3	38.1	49.4
820	20.9	904.2	1.8	284.3	67.3	11.8
825	19.8	873.1	1.8	255.8	51.7	9.5
830	20.0	2377.1	1.7	252.7	43.4	39.5
835	21.1	809.7	1.8	200.5	65.2	10.8
840	20.1	2066.4	1.5	181.3	22.0	24.5
845	20.2	1210.0	1.7	201.2	41.3	18.7
850	21.0	430.6	1.7	178.1	40.4	5.2
855	20.0	913.7	1.6	158.8	28.9	9.8
900	20.2	1025.8	1.6	182.8	30.6	7.2
905	21.0	53.0	1.6	150.4	42.2	3.2
910	20.0	3575.1	1.5	209.2	26.6	48.9
915	19.8	191.6	1.6	185.5	50.9	10.0
920	20.8	1480.9	1.7	141.7	24.4	9.0
925	19.9	580.5	1.8	172.7	42.6	5.6
930	19.9	1088.7	1.8	206.2	41.1	7.3
935	21.1	1190.6	1.8	193.5	42.5	13.0
940	19.8	635.9	1.9	206.5	53.0	5.7
945	19.7	3713.4	1.6	226.4	25.0	32.6
955	19.7	2256.3	1.8	173.7	32.5	13.6
1000	19.9	3409.9	1.9	208.8	31.2	38.0
1005	21.0	136.1	1.9	146.1	38.2	5.2
1010	19.8	1257.0	1.9	146.9	26.5	8.8
1015	19.8	1139.1	1.8	149.6	25.5	12.1
1020	20.9	393.0	1.8	151.1	23.9	4.6
1025	19.9	1447.0	1.6	135.8	32.7	15.0
1030	20.1	110.7	1.5	117.8	47.7	5.1
1035	21.2	2512.4	1.6	154.4	24.9	22.4
1040	20.0	1684.7	1.6	186.2	42.8	17.3
1045	19.9	1248.1	1.7	224.3	46.3	13.4
1050	21.1	3254.1	1.8	240.5	30.7	37.5
1055	19.9	1663.9	1.8	225.7	47.2	16.0
1100	19.9	3718.0	1.7	180.8	29.2	23.2
1105	21.1	1853.8	2.0	165.9	44.7	34.3
1110	19.7	497.6	2.1	178.8	50.1	5.8
1115	19.7	2987.2	2.0	195.7	25.8	19.6
1120	20.9	551.2	1.9	139.4	45.4	9.6
1125	19.5	580.4	2.1	139.5	35.0	5.4
1130	19.4	1439.3	2.0	147.5	27.3	10.4
1135	21.2	557.3	2.0	174.3	29.0	6.2
1140	19.6	198.4	2.0	137.8	25.4	4.4
1145	19.6	1649.8	2.1	187.1	28.0	11.9
1150	21.0	712.3	2.0	185.9	26.4	5.9

CEMS DATA - SITE 10 - TEST 2

1155	19.8	2054.0	1.9	172.9	31.7	19.7
1200	19.8	248.0	1.9	187.5	57.1	4.6
1205	21.1	4218.2	2.0	210.9	29.6	36.4
1210	19.4	547.1	2.0	211.9	49.3	11.0
1215	19.5	2568.5	2.0	188.0	38.7	25.3
1220	20.8	377.0	2.0	182.5	32.0	7.9
1225	19.5	133.9	2.1	197.2	33.6	4.8
1230	19.6	71.6	1.9	189.5	30.9	4.1
1235	21.2	68.1	1.9	166.2	30.6	4.3
1240	19.8	239.6	2.0	183.7	32.7	4.5
1245	19.6					
1250	21.0					

NO. PTS.	61	58	59	59	59	59
MEAN	20.2	1322.1	1.8	192.5	38.9	14.7
STD. DEV.	0.6	1089.9	0.2	45.9	12.3	11.5

CEMS DATA - SITE 10 - TEST 3

TIME	O2 (%V)	CO (PPMV)	CO2 (%V)	SO2 (PPMV)	NOX (PPMV)	THC (PPMV)
=====	=====	=====	=====	=====	=====	=====
1440	21.3	685.9	1.7	150.2	53.4	7.1
1445	19.9	463.4	1.7	188.5	34.8	5.7
1450	20.0	3347.8	1.4	188.4	25.7	43.0
1455	19.7	848.9	1.6	144.5	44.4	8.7
1500	20.1	1856.8	1.8	165.2	35.1	19.5
1505	19.8	1447.8	1.6	159.0	26.7	16.9
1510	19.9	2938.5	1.8	159.0	36.5	41.9
1515	19.7	369.4	1.7	126.0	42.1	7.8
1520	19.9	487.2	1.9	90.6	29.1	6.5
1525	19.6	146.8	1.8	115.5	35.0	4.8
1530	19.7	1211.3	1.8	130.1	30.9	10.3
1535	19.9	905.7	1.5	91.3	35.1	12.1
1540	20.3	702.4	1.7	95.3	46.9	5.8
1545	19.9	995.8	1.8	169.8	34.7	7.8
1550	19.9	1177.8	1.7	196.9	32.3	11.2
1555	19.7	587.4	1.8	148.1	43.2	5.5
1600	19.8	2450.6	1.7	180.2	32.8	31.5
1605	19.9	795.1	1.6	186.0	48.2	12.5
1610	20.0	3626.2	1.5	185.4	23.1	44.4
1615	20.1	1499.8	1.7	154.1	43.3	30.3
1620	20.0	1289.4	1.3	115.4	27.2	18.4
1625	20.0	1868.4	1.6	174.9	32.8	26.6
1630	20.0	915.5	1.6	159.9	52.5	11.8
1635	20.0	1073.2	1.6	179.0	42.4	16.2
1640	20.5	927.4	1.5	120.2	56.3	21.2
1645	20.2	204.3	1.5	115.2	43.6	7.3
1650	20.2	594.0	1.7	174.3	33.2	8.8
1655	20.0	453.0	1.6	147.1	46.9	5.8
1700	20.3	2227.1	1.6	211.6	34.1	28.5
1705	20.0	427.5	1.8	278.4	45.9	7.2
1710	20.0	3072.9	1.7	309.1	28.4	42.6
1715	19.5	292.1	2.1	323.3	59.8	10.1
1720	19.6	1048.2	1.9	345.5	36.8	8.4
1725	19.8	426.9	1.6	265.2	42.1	8.5
1730	19.9	98.9	1.8	260.1	50.1	4.1
1735	20.0	346.9	1.9	283.5	35.1	4.5
1740	20.5	24.5	1.7	205.9	57.1	4.0
1745	20.0	146.7	1.8	215.2	33.2	4.2
1750	19.8	55.7	1.8	184.8	42.9	2.8
1755	20.1	92.5	1.6	130.3	36.9	2.9
1800	20.0	51.1	1.8	156.7	65.3	2.9
1805	20.1	100.2	1.6	163.6	48.5	3.3
1810	20.1	36.4	1.6	161.5	34.7	2.4
1815	20.2	164.5	1.5	151.8	54.1	3.6
1820	20.4	156.4	1.5	155.0	53.8	3.8
1825	20.3	243.9	1.5	198.7	37.6	3.7
1830	20.3	337.2	1.5	200.4	42.6	3.5
1835	20.4	1436.7	1.5	193.5	47.3	13.7

CEMS DATA - SITE 10 - TEST 3

1840	20.6	251.3	1.4	149.8	36.9	4.6
1845	20.2	206.4	1.6	180.0	43.6	4.2
1850	20.2	111.5	1.6	151.6	42.5	3.2
1855	20.3	166.2	1.5	114.3	42.4	2.8
1900	20.2	135.5	1.5	142.6	49.1	3.6
1905	20.5	391.3	1.4	160.8	37.5	5.7
1910	20.4	851.5	1.5	163.5	42.7	11.2
1915	20.3	371.8	1.6	185.0	52.4	8.2
1920	21.2					
=====						
NO. PTS.	57	56	56	56	56	56
MEAN	20.1	843.6	1.6	175.6	40.9	11.7
STD. DEV.	0.3	890.3	0.2	54.7	9.4	11.2

CEMS DATA - SITE 10 - TEST 4

TIME	O2 (%V)	CO (PPMV)	CO2 (%V)	SO2 (PPMV)	NOX (PPMV)	THC (PPMV)
=====	=====	=====	=====	=====	=====	=====
1215		685.7	1.5	215.4	39.7	8.1
1220		1206.0	1.5	231.1	46.7	12.5
1225	20.5	1303.4	1.5	282.7	49.6	20.1
1230	20.3	1348.2	1.4	233.9	36.5	19.4
1235	20.2	2073.4	1.4	225.2	35.6	28.5
1240	21.1	1729.9	1.5	254.0	46.3	24.4
1245	20.3	2030.3	1.5	235.0	34.9	19.7
1250	20.2	1616.4	1.6	248.2	39.0	29.9
1255	21.1	1438.2	1.4	226.0	32.1	24.7
1300	20.0	1281.4	1.7	266.9	34.2	19.9
1305	20.1	2664.2	1.7	275.2	28.5	31.5
1310	21.2	2099.4	1.7	276.9	33.9	27.7
1315	20.0	3425.0	1.7	241.9	26.8	41.3
1320	19.8	2530.2	1.8	292.2	45.1	36.4
1325	20.5	728.8	1.8	257.1	43.5	9.6
1330	19.8	2521.2	1.8	245.0	38.8	27.6
1335	19.8	866.3	2.0	250.5	42.4	16.9
1340	21.2	2118.3	1.8	206.1	38.4	18.7
1345	19.6	1091.4	2.0	229.9	44.0	16.0
1350	20.0	2688.9	1.8	252.0	36.6	27.0
1355	21.1	2478.0	1.9	319.1	43.2	27.8
1400	19.8	624.7	2.1	309.1	45.4	5.9
1405	19.8	1154.7	2.0	254.2	44.1	13.1
1410	21.1	2885.9	1.9	219.4	34.2	30.1
1415	19.9	1435.7	2.0	217.4	27.2	16.5
1420	19.8	3631.5	2.0	243.4	28.6	35.2
1425	20.5	2568.8	2.2	298.2	28.3	32.5
1430	19.8	1499.5	2.0	165.3	30.4	21.9
1435	19.8	3072.2	2.0	226.8	23.8	48.8
1440	21.2	843.0	2.2	275.9	27.8	14.4
1445	19.8	376.6	2.3	270.0	33.7	4.1
1450	19.4	1854.0	2.2	309.0	28.6	14.2
1455	21.1	566.8	2.0	260.1	28.4	6.3
1500	19.5	131.9	2.1	147.0	28.2	3.4
1505	19.5	534.9	2.0	168.7	30.5	2.8
1510	21.1	1811.0	2.2	198.3	30.9	19.9
1515	19.4	1006.5	1.9	121.1	29.7	4.8
1520	19.4	729.4	2.0	135.9	37.3	4.3
1525	20.4	1536.7	2.0	226.3	30.9	16.1
1530	19.8	854.5	2.0	301.1	33.6	6.2
1535	19.6	821.6	2.1	326.2	34.5	6.7
1540	21.1	646.8	1.9	253.6	34.6	4.5
1545	19.5	1276.4	1.6	207.1	26.6	15.1
1550	19.7	443.3	2.0	250.8	31.7	3.4
1555	21.0	295.1	2.0	201.6	32.7	3.2
1600	19.7	620.7	1.8	177.4	29.5	3.0
1605	19.8	1887.3	2.0	335.5	31.2	27.4
1610	21.1	1484.1	2.0	305.3	35.7	12.1

CEMS DATA - SITE 10 - TEST 4

1615	19.7	714.1	1.8	172.9	33.1	9.7
1620	19.7	1633.9	1.9	253.0	32.7	28.0
1625	20.4	753.5	2.0	223.0	34.5	8.8
1630	19.8	1662.7	1.9	234.4	42.4	51.5
1635	19.8	436.0	2.1	189.9	34.5	10.3
1640	21.1	3266.5	1.9	189.3	30.1	26.2
1645	19.5					
1650	19.9					

NO. PTS.	54	54	54	54	54	54
MEAN	20.2	1499.7	1.9	239.5	34.8	18.5
STD. DEV.	0.6	871.3	0.2	47.5	6.1	11.9

APPENDIX A-3
HCl Train Results

R A D I A N S O U R C E T E S T
E P A M E T H O D 2 - 5
(R A W D A T A)

PLANT : DIOXIN SITE #10
PLANT SITE :
SAMPLING LOCATION : BAGHOUSE EXHAUST
TEST # : 10-HCL-02
DATE : 5/22/85
TEST PERIOD : 0753-0953

PARAMETER -----	VALUE -----
Sampling time (min.)	120
Barometric Pressure (in.Hg)	29.87
Sampling nozzle diameter (in.)	.189
Meter Volume (cu.ft.)	61.288
Meter Pressure (in.H2O)	.8
Meter Temperature (F)	81
Stack dimension (sq.in.)	14957.16
Stack Static Pressure (in.H2O)	-.26
Stack Moisture Collected (gm)	91.6
Absolute stack pressure(in Hg)	29.85088
Average stack temperature (F)	207.4
Percent CO2	1.98
Percent O2	20.4
Percent N2	77.6
Delp's Subroutine result	24.2253
DGM Factor	1.0053
Pitot Constant	.84

R A D I A N S O U R C E T E S T
 E P A M E T H O D S 2 - 5
 F I N A L R E S U L T S
 PLANT : DIOXIN SITE #10
 PLANT SITE :
 SAMPLING LOCATION : BAGHOUSE EXHAUST
 TEST # : 10-HCL-02
 DATE : 5/22/85
 TEST PERIOD : 0753-0953

PARAMETER -----	RESULT -----
Vm(dscf)	60.15003
Vm(dscm)	1.703449
Vw gas(scf)	4.31894
Vw gas (scm)	.1223124
% moisture	6.699254
Md	.9330074
MWd	29.1272
MW	28.38176
Vs(fpm)	3586.054
Vs (mpm)	1093.309
Flow(acfm)	372480.5
Flow(acmm)	10548.65
Flow(dscfm)	274303.9
Flow(dscmm)	7768.285
% I	97.47961
% EA	23611.36

Program Revision:1/16/84

R A D I A N S O U R C E T E S T
E P A M E T H O D 2 - 5
(R A W D A T A)

PLANT : DIOXIN SITE #10
PLANT SITE :
SAMPLING LOCATION : BAGHOUSE EXHAUST
TEST # : 10-HCL-03
DATE : 05/22/85
TEST PERIOD : 1452-1652

PARAMETER -----	VALUE -----
Sampling time (min.)	120
Barometric Pressure (in.Hg)	29.87
Sampling nozzle diameter (in.)	.185
Meter Volume (cu.ft.)	62.935
Meter Pressure (in.H2O)	.78
Meter Temperature (F)	104.2
Stack dimension (sq.in.)	14957.16
Stack Static Pressure (in.H2O)	-.26
Stack Moisture Collected (gm)	87.7
Absolute stack pressure(in Hg)	29.85088
Average stack temperature (F)	220.7
Percent CO2	1.78
Percent O2	20.4
Percent N2	77.8
Delp's Subroutine result	23.5768
DGM Factor	1.0053
Pitot Constant	.84

R A D I A N S O U R C E T E S T
 E P A M E T H O D S 2 - 5
 F I N A L R E S U L T S
 PLANT : DIOXIN SITE #10
 PLANT SITE :
 SAMPLING LOCATION : BAGHOUSE EXHAUST
 TEST # : 10-HCL-03
 DATE : 05/22/85
 TEST PERIOD : 1452-1652

PARAMETER -----	RESULT -----
Vm(dscf)	59.2237
Vm(dscm)	1.677215
Vw gas(scF)	4.135055
Vw gas (scm)	.1171048
% moisture	6.526415
Md	.9347359
MWd	29.0952
MW	28.37108
Vs(fpm)	3490.714
Vs (mpm)	1064.242
Flow(acfm)	362577.6
Flow(acmm)	10268.2
Flow(dscfm)	262279.1
Flow(dscmm)	7427.743
% I	104.7663
% EA	14655.15

Program Revision:1/16/84

R A D I A N S O U R C E T E S T
 E P A M E T H O D 2 - 5
 (R A W D A T A)

PLANT : DIOXIN SITE #10
 PLANT SITE :
 SAMPLING LOCATION : BAGHOUSE EXHAUST
 TEST # : 10-HCL-04
 DATE : 05/23/85
 TEST PERIOD : 1218-1418

PARAMETER -----	VALUE -----
Sampling time (min.)	120
Barometric Pressure (in.Hg)	29.87
Sampling nozzle diameter (in.)	.185
Meter Volume (cu.ft.)	58.644
Meter Pressure (in.H2O)	.73
Meter Temperature (F)	87.8
Stack dimension (sq.in.)	14957.16
Stack Static Pressure (in.H2O)	-.26
Stack Moisture Collected (gm)	85.4
Absolute stack pressure(in Hg)	29.85088
Average stack temperature (F)	208.3
Percent CO2	1.48
Percent O2	20.7
Percent N2	77.8
Delp's Subroutine result	22.5451
DGM Factor	1.0053
Pitot Constant	.84

R A D I A N S O U R C E T E S T
 E P A M E T H O D S 2 - 5
 F I N A L R E S U L T S
 PLANT : DIOXIN SITE #10
 PLANT SITE :
 SAMPLING LOCATION : BAGHOUSE EXHAUST
 TEST # : 10-HCL-04
 DATE : 05/23/85
 TEST PERIOD : 1218-1418

PARAMETER -----	RESULT -----
Vm(dscf)	56.83091
Vm(dscm)	1.609451
Vw gas(scf)	4.02661
Vw gas (scm)	.1140336
% moisture	6.616455
Md	.9338354
MWd	29.0592
MW	28.32747
Vs(fpm)	3340.53
Vs (mpm)	1018.454
Flow(acfm)	346978.1
Flow(acmm)	9826.42
Flow(dscfm)	255405.7
Flow(dscmm)	7233.088
% I	103.2391
% EA	-12873.06

Program Revision:1/16/84

APPENDIX A-4
Ambient XAD Train Results

R A D I A N S O U R C E T E S T
E P A M E T H O D 2 - 5
(R A W D A T A)

PLANT : DIOXIN SITE #10
PLANT SITE :
SAMPLING LOCATION : AMBIENT SAMPLING LOCATION
TEST # : AMBIENT "A" TRAIN
DATE : 05/21-23/85
TEST PERIOD : (1350-1352) (0755-1900) (1235-1740)

PARAMETER -----	VALUE -----
Sampling time (min.)	972
Barometric Pressure (in.Hg)	30
Sampling nozzle diameter (in.)	0
Meter Volume (cu.ft.)	496.45
Meter Pressure (in.H2O)	.85
Meter Temperature (F)	116.4
Stack dimension (sq.in.)	0
Stack Static Pressure (in.H2O)	0
Stack Moisture Collected (gm)	65.5
Absolute stack pressure(in Hg)	30
Average stack temperature (F)	0
Percent CO2	.001
Percent O2	21
Percent N2	79
Delps Subroutine result	0
DGM Factor	1.003
Pitot Constant	0

R A D I A N S O U R C E T E S T
 E P A M E T H O D S 2 - 5
 F I N A L R E S U L T S
 PLANT : DIOXIN SITE #10
 PLANT SITE :
 SAMPLING LOCATION : AMBIENT SAMPLING LOCATION
 TEST # : AMBIENT "A" TRAIN
 DATE : 05/21-23/85
 TEST PERIOD : (1350-1352) (0755-1900) (1235-1740)

PARAMETER -----	RESULT -----
Vm(dscf)	458.3001
Vm(dscm)	12.97906
Vw gas(scf)	3.088325
Vw gas (scm)	8.746136E-02
% moisture	.6693547
Md	.9933064
MWd	28.84044
MW	28.76788
Vs(fpm)	0
Vs (mpm)	0
Flow(acfm)	0
Flow(acmm)	0
Flow(dscfm)	0
Flow(dscmm)	0
% I	0
% EA	0

Program Revision:1/16/84

R A D I A N S O U R C E T E S T
E P A M E T H O D 2 - 5
(R A W D A T A)

PLANT : DIOXIN SITE #10
PLANT SITE :
SAMPLING LOCATION : AMBIENT SAMPLING LOCATION
TEST # : AMBIENT "B" TRAIN
DATE : 05/21-23/85
TEST PERIOD : (1345-1350) (0800-1900) (1238-1740)

PARAMETER -----	VALUE -----
Sampling time (min.)	967
Barometric Pressure (in.Hg)	30
Sampling nozzle diameter (in.)	0
Meter Volume (cu.ft.)	508.53
Meter Pressure (in.H2O)	.85
Meter Temperature (F)	109.2
Stack dimension (sq.in.)	0
Stack Static Pressure (in.H2O)	0
Stack Moisture Collected (gm)	63.7
Absolute stack pressure(in Hg)	30
Average stack temperature (F)	0
Percent CO2	.001
Percent O2	21
Percent N2	79
Delps Subroutine result	0
DGM Factor	1.004
Pitot Constant	0

R A D I A N S O U R C E T E S T
 E P A M E T H O D S 2 - 5
 F I N A L R E S U L T S
 PLANT : DIOXIN SITE #10
 PLANT SITE :
 SAMPLING LOCATION : AMBIENT SAMPLING LOCATION
 TEST # : AMBIENT "B" TRAIN
 DATE : 05/21-23/85
 TEST PERIOD : (1345-1350) (0800-1900) (1238-1740)

PARAMETER -----	RESULT -----
Vm(dscf)	475.8639
Vm(dscm)	13.47647
Vw gas(scF)	3.003455
Vw gas (scm)	8.505785E-02
% moisture	.6271998
Md	.9937281
MWd	28.84044
MW	28.77245
Vs(fpm)	0
Vs (mpm)	0
Flow(acfm)	0
Flow(acmm)	0
Flow(dscfm)	0
Flow(dscmm)	0
% I	0
% EA	0

Program Revision:1/16/84

R A D I A N S O U R C E T E S T
 E P A M E T H O D 2 - 5
 S A M P L E C A L C U L A T I O N
 PLANT : DIOXIN SITE #10
 PLANT SITE :
 SAMPLING LOCATION : AMBIENT SAMPLING LOCATION
 TEST # : AMBIENT "B" TRAIN
 DATE : 05/21-23/85
 TEST PERIOD : (1345-1350) (0800-1900) (1238-1740)

1) Volume of dry gas sampled at standard conditions (68 deg-F ,29.92 in. Hg).

$$V_m(\text{std}) = \frac{Y \times V_m \times [T(\text{std}) + 460] \times [P_b + (P_m/13.6)]}{P(\text{std}) \times (T_m + 460)}$$

$$V_m(\text{std}) = \frac{1.004 \times 508.53 \times 528 \times [30 + (.85/13.6)]}{29.92 \times (109.2 + 460)}$$

$$V_m(\text{std}) = 475.864 \text{ dscf}$$

2) Volume of water vapor at standard conditions:

$$V_w(\text{gas}) = 0.04715 \text{ cf/gm} \times W(1) \text{ gm}$$

$$V_w(\text{gas}) = 0.04715 \times 63.7 = 3.003 \text{ scf}$$

3) Percent Moisture in stack gas :

$$\%M = \frac{100 \times V_w(\text{gas})}{V_m(\text{std}) + V_w(\text{gas})}$$

$$\%M = \frac{100 \times 3.003}{475.864 + 3.003} = 0.63 \%$$

4) Mole fraction of dry stack gas :

$$M_d = \frac{100 - \%M}{100} = \frac{100 - 0.63}{100} = .9937281$$

APPENDIX A-5
Modified Method 5 Sample Calculations

R A D I A N S O U R C E T E S - T
E P A M E T H O D S 2 - 5
D E F I N I T I O N O F T E R M S

PARAMETER -----	DEFINITION -----
Tt(min.)	TOTAL SAMPLING TIME
Dn(in.)	SAMPLING NOZZLE DIAMETER
Ps(in.H2O)	ABSOLUTE STACK STATIC GAS PRESSURE
Vm(cu.ft.)	ABSOLUTE VOLUME OF GAS SAMPLE MEASURED BY DGM
Vw(gm.)	TOTAL STACK MOISTURE COLLECTED
Pm(in.H2O)	AVERAGE STATIC PRESSURE OF DGM
Tm(F)	AVERAGE TEMPERATURE OF DGM
Pb(in.Hg.)	BAROMETRIC PRESSURE
% CO2	CARBON DIOXIDE CONTENT OF STACK GAS
% O2	OXYGEN CONTENT OF STACK GAS
% N2	NITROGEN CONTENT OF STACK GAS
SQR(DELPs)	AVE. SQ. ROOT OF S-PITOT DIFF. PRESSURE-TEMP. PRODUCTS
As(sq.in.)	CROSS-SECTIONAL AREA OF STACK(DUCT)
Ts(F)	TEMPERATURE OF STACK
Vm(dscf)	STANDARD VOLUME OF GAS SAMPLED ,Vm(std),AS DRY STD. CF
Vm(dscm)	STANDARD VOLUME OF GAS SAMPLED,Vm(std),AS DRY STD. CM
Vw gas(scf)	VOLUME OF WATER VAPOR IN GAS SAMPLE,STD
% moisture	WATER VAPOR COMPOSITION OF STACK GAS
Md	PROPORTION, BY VOLUME,OF DRY GAS IN GAS SAMPLE
MWd	MOLECULAR WEIGHT OF STACK GAS,DRY BASIS LB/LB-MOLE
MW	MOLECULAR WEIGHT OF STACK GAS,WET BASIC LB/LB-MOLE
Vs(fpm)	AVERAGE STACK GAS VELOCITY
Flow(acfm)	AVERAGE STACK GAS FLOW RATE(ACTUAL STACK COND.)
Flow(acmm)	AVERAGE STACK GAS FLOW RATE(ACTUAL STACK COND.)
Flow(dscfm)	AVERAGE STACK GAS VOLUMETRIC FLOW RATE(DRY BASIS)
Flow(dscmm)	AVERAGE STACK GAS VOLUMETRIC FLOW RATE(DRY BASIS)
% I	PERCENT ISOKINETIC
% EA	PERCENT EXCESS AIR IN STACK GAS
DGM	DRY GAS METER
Y	DRY GAS METER CORRECTION FACTOR
Pg	STACK STATIC GAS PRESSURE
Cp	PITOT COEFFICIENT
dH	ORIFICE PLATE DIFF. PRESS. VALUE
dP	PITOT DIFF. PRESS. VALUE
*** EPA STANDARD CONDITIONS	Temperature = 68 deg-F (528 deg-R) Pressure = 29.92 in. Hg.

R A D I A N S O U R C E T E S T
 E P A M E T H O D 2 - 5
 S A M P L E C A L C U L A T I O N

PLANT : DIOXIN SITE #10
 PLANT SITE :
 SAMPLING LOCATION : BAGHOUSE EXHAUST
 TEST # : 10-MM5-02
 DATE : 5/22/85
 TEST PERIOD : 0750-1240

1) Volume of dry gas sampled at standard conditions (68 deg-F ,29.92 in. Hg).

$$V_m(\text{std}) = \frac{Y \times V_m \times [T(\text{std}) + 460] \times [P_b + (P_m/13.6)]}{P(\text{std}) \times (T_m + 460)}$$

$$V_m(\text{std}) = \frac{.9978 \times 137.566 \times 528 \times [29.87 + (.95/13.6)]}{29.92 \times (82.15 + 460)}$$

$$V_m(\text{std}) = 133.769 \text{ dscf}$$

2) Volume of water vapor at standard conditions:

$$V_w(\text{gas}) = 0.04715 \text{ cf/gm} \times W(1) \text{ gm}$$

$$V_w(\text{gas}) = 0.04715 \times 195.1 = 9.199 \text{ scf}$$

3) Percent Moisture in stack gas :

$$\%M = \frac{100 \times V_w(\text{gas})}{V_m(\text{std}) + V_w(\text{gas})}$$

$$\%M = \frac{100 \times 9.199}{133.769 + 9.199} = 6.43 \%$$

4) Mole fraction of dry stack gas :

$$M_d = \frac{100 - \%M}{100} = \frac{100 - 6.43}{100} = .9356573$$

S A M P L E C A L C U L A T I O N
P A G E T W O

5) Average Molecular Weight of DRY stack gas :

$$MWd = (.44 \times \%CO_2) + (.32 \times \%O_2) + (.28 \times \%N_2)$$

$$MWd = (.44 \times 1.98) + (.32 \times 20.4) + (.28 \times 77.6) = 29.1272$$

6) Average Molecular Weight of wet stack gas :

$$MW = MWd \times Md + 18(1 - Md)$$

$$MW = 29.1272 \times .9356573 + 18(1 - .9356573) = 28.41125$$

7) Stack gas velocity in feet-per-minute (fpm) at stack conditions :

$$Vs = Kp \times Cp \times [SQRT(dP)] \times \text{favef} \times SQRT[Ts \times \text{favgf}] \times SQRT[1/(Ps \times MW)] \times 60 \text{sec/min}$$

$$Vs = 85.49 \times .84 \times 60 \times 26.352 \times SQRT[1/(29.85088 \times 28.41125)]$$

$$Vs = 3898.842 \text{ FPM}$$

8) Average stack gas dry volumetric flow rate (DSCFM) :

$$Qsd = \frac{Vs \times As \times Md \times T(std) \times Ps}{144 \text{ cu.in./cu.ft.} \times (Ts + 460) \times P(std)}$$

$$Qsd = \frac{3898.842 \times 14957.16 \times .9356573 \times 528 \times 29.85088}{144 \times 674 \times 29.92}$$

$$Qsd = 296148 \text{ dscfm}$$

S A M P L E C A L C U L A T I O N
P A G E T H R E E

9) Isokinetic sampling rate (%) :

Dimensional Constant C = $K_4 \times 60 \times 144 \times [1 / (P_i / 4)]$
 $K_4 = .0945$ FOR ENGLISH UNITS

$$I\% = \frac{C \times V_m(\text{std}) \times (T_s + 460)}{V_s \times T_t \times P_s \times M_d \times (D_n)^{.2}}$$

$$I\% = \frac{1039.574 \times 133.7695 \times 674}{3898.842 \times 240 \times 29.85088 \times .9356573 \times (.183)^{.2}}$$

$$I\% = 107.0902$$

10) Excess air (%) :

$$EA = \frac{100 \times \%O_2}{(.264 \times \%N_2) - \%O_2} = \frac{100 \times 20.4}{(.264 \times 77.6) - 20.4}$$

$$EA = 23611.36$$

11) Particulate Concentration :

$$C_s = (\text{grams part.}) / V_m(\text{std}) = 0 / 133.7695$$

$$C_s = 0.0000000 \text{ Grams/DSCF}$$

$$C_a = \frac{T(\text{std}) \times M_d \times P_s \times C_s}{P(\text{std}) \times T_s}$$

$$C_a = \frac{528 \times .9356573 \times 29.85088 \times 0.0000000}{29.92 \times 674}$$

$$C_a = 0.0000000 \text{ Grams/ACF}$$

$$\text{LBS/HR} = C_s \times 0.002205 \times Q_{sd} \times 60$$

$$\text{LBS/HR} = 0.0000000 \times 0.002205 \times 296148.0 \times 60$$

$$\text{LBS/HR} = 0$$

Program Revision: 1/16/84

APPENDIX B
Sample Shipment Letters

May 24, 1985

U.S. EPA ECC Toxicant Analysis Center
Building 1105
Bay St. Louis, MS 39529

Attention: Danny McDaniel

Subject: Tier 4 - Analysis Instructions

Dear Sir:

The objective of this letter is to clarify instructions and priorities for individual samples from specific Tier 4 combustion sites. This instruction letter is No. 12 and pertains to EPA Site No. 10 (MET-A).

The Episode No. is 2646, and SCC numbers assigned to this site were numbers DQ002000 through DQ002099.

SCC numbers DQ002001 through DQ002006 have been assigned to Troika for QA/QC purposes. SCC numbers DQ002007 through DQ002025 have been assigned to samples included in this shipment. SCC numbers DQ002026 through DQ002028 have been assigned to samples being archived at Radian. All remaining SCC numbers are unused.

The sample shipment for EPA Site No. 10 (MET-A) consists of 3 boxes containing 42 samples in 43 containers. The boxes were shipped under Federal Express, Airbill Nos. 769751765, 769751776 and 769751780.

Instructions for extraction and analysis follow.

1. Priority #1 samples include the sample train components, the baghouse dust, the lab proof blank, and the reagent blanks. These samples require immediate extraction and analysis.

MMS TRAIN SAMPLES

Radian Run # 10-MMS-01 was an aborted run with no samples.

Radian Run # 10-MMS-02 (Total of 6 train components)

SCC_No.	Component	Fraction
DQ002008	1	Filter
DQ002008	2	Probe Rinse
DQ002008	3	Back Half/Coil Rinse
DQ002008	4	Condensate
DQ002008	5	Impinger Solution
DQ002008	6	XAD Module

Radian Run # 10-MMS-03 (Total of 6 train components)

<u>SCC_No.</u>	<u>Component</u>	<u>Fraction</u>
DQ002012	1	Filter
DQ002012	2 *	Probe Rinse
DQ002012	3	Back Half/Coil Rinse
DQ002012	4	Condensate
DQ002012	5	Impinger Solution
DQ002012	6	XAD Module

* indicates two containers

Radian Run # 10-MMS-04 (Total of 6 train components)

DQ002021	1	Filter
DQ002021	2	Probe Rinse
DQ002021	3	Back Half/Coil Rinse
DQ002021	4	Condensate
DQ002021	5	Impinger Solution
DQ002021	6	XAD Module

Radian Run # 10-MMS-FBL (Total of 6 train components)

DQ002023	1	Filter
DQ002023	2	Probe Rinse
DQ002023	3	Back Half/Coil Rinse
DQ002023	4	Condensate
DQ002023	5	Impinger Solution
DQ002023	6	XAD Module

BACK UP XAD*

<u>SCC_No.</u>	<u>SAMPLE</u>
DQ002009	MMS Run 10-MMS-02
DQ002013	MMS Run 10-MMS-03
DQ002022	MMS Run 10-MMS-04
DQ002016	Blank XAD

*Back up XAD used at Site 10 to verify organic collection.

AMBIENT XAD TRAIN

Radian Run # 10-AMB-A (Total of 2 train components)

<u>SCC_No.</u>	<u>Container</u>	<u>Fraction</u>
DQ002020	1	XAD Module
DQ002020	2	Probe Rinse

LABORATORY PROOF BLANK

<u>SCC_No.</u>	<u>Component</u>	<u>Fraction</u>
DQ002007	1	Filter
DQ002007	2	Probe Rinse, Back Half/Coil Rinse, and Impinger Solution
DQ002007	3	XAD Module

REAGENT BLANKS

<u>SCC_No.</u>	<u>Sample</u>
DQ002017	HPLC grade water blank
DQ002018	Acetone blank
DQ002019	Methylene chloride blank

NO. 1 BAGHOUSE DUST

<u>SCC_No.</u>	<u>Sample</u>
DQ002010	Baghouse Dust, Run 02
DQ002014	Baghouse Dust, Run 03
DQ002024	Baghouse Dust, Run 04

NO. 2 BAGHOUSE DUST

<u>SCC_No.</u>	<u>Sample</u>
DQ002011	Baghouse Dust, Run 02
DQ002015	Baghouse Dust, Run 03
DQ002025	Baghouse Dust, Run 04

2. The priority #2 samples are the plastic bearing furnace feed samples and the coke samples. These samples will be held at Radian for analysis pending the results of Priority #1 samples analysis.

COKE - PROCESS SAMPLE

SCC # DQ002026 Sample: composite of coke for entire test.

U. S. EPA ECC Toxicant Analysis Center
Page four
May 24, 1985

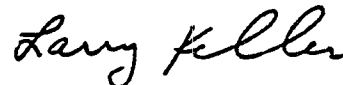
PLASTIC-BEARING FEED MATERIALS - PROCESS SAMPLE

SCC # DQ002028 Sample: 10-Scrap

3. The soil sample is the only Priority #3 sample. It will be held at Radian for analysis pending the results of Priority #1 and Priority #2 samples. The SCC number for the soil sample is DQ002027.

If any questions arise concerning this sample shipment, please contact either Larry Keller or James McReynolds at Radian Corporation at (919) 541-9100.

Sincerely,



TEST TEAM LEADER

cc: E. Hanks/EPA/AMTB
A. Miles/Radian
Radian Field File - RTP/PPK

RADIAN

CORPORATION

November 11, 1985

U.S. EPA ECC Toxicant Analysis Center
Building 1105
Bay St. Louis, MS 39529

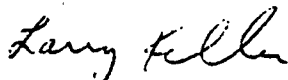
Attention: Danny McDaniel
Subject: Tier 4-Analysis Instructions

Dear Sir:

Enclosed is the soil sample for Tier 4 Site No. 10 (MET-A) that has been archived at Radian. The Episode No. is 2646, and the SCC number of the sample is DQ-002027. This sample is to be extracted for dioxin / furan analysis.

If any questions arise concerning this sample shipment, please contact Larry Keller or Andrew Miles at Radian Corporation at (919) 541-9100.

Sincerely,



Larry Keller
Staff Chemical Engineer

cc: E. Hanks/EPA/AMTB
A. Miles/Radian
Radian Field File-RTP/PPK

APPENDIX C

DIOXIN/FURAN ANALYTICAL DATA
FOR GASEOUS SAMPLES

- C-1 Modified Method 5 Trains
- C-2 Ambient XAD Train

TABLE C-1. DIOXIN/FURAN ANALYTICAL DATA FOR MM5 TRAINS

Isomer/Homologue	Amount Detected, Picograms Per Sample Train ^a		
	Run 02	Run 03	Run 04
<u>Dioxins</u>			
2378 TCDD	66,500	32,200	19,050
Other TCDD	133,600	265,700	178,350
Penta CDD	238,100	441,500	246,000
Hexa CDD	551,200	408,300	223,000
Hepta CDD	415,000	1,111,300	489,800
Octa CDD	246,800	701,000	350,200
Total PCDD	1,651,200	2,960,000	1,506,400
<u>Furans</u>			
2378 TCDF	704,900	959,100	875,100
Other TCDF	2,380,300	3,372,400	4,380,300
Penta CDF	2,119,000	3,513,400	2,524,300
Hexa CDF	1,933,500	1,151,500	852,000
Hepta CDF	684,100	2,018,030	651,700
Octa CDF	464,600	1,364,000	609,000
Total PCDF	8,286,400	12,378,430	9,892,400

a. Includes back-up XAD trap. See Section 8.3.2 for a discussion of quality assurance/quality control results for these analyses.

TABLE C-2. DIOXIN/FURAN ANALYTICAL DATA FOR AMBIENT XAD TRAIN

Isomer/Homologue	Amount Detected Picograms per Train
<u>Dioxins</u>	
2378 TCDD	ND(40)
Other TCDD	500
Penta CDD	ND(200)
Hexa CDD	400
Hepta CDD	400
Octa CDD	700
Total PCDD	2,000
<u>Furans</u>	
2378 TCDF	600
Other TCDF	6,000
Penta CDF	1,400
Hexa CDF	3,000
Hepta CDF	1,700
Octa CDF	1,600
Total PCDF	14,300

ND = not detected

See Section 8.3.2 for a discussion of quality assurance/quality control results for these analyses.

APPENDIX D

RUN-SPECIFIC DIOXIN/FURAN EMISSIONS DATA

- D-1 Run-Specific Dioxin/Furan Emissions Data
(As-Measured Concentrations)
- D-2 Run-Specific Dioxin/Furan Emissions Data
(Concentrations Corrected to 3 Percent Oxygen)

APPENDIX D-1

Run-Specific Dioxin/Furan Emissions Data
(As-Measured Concentrations)

TABLE D-1. DIOXIN/FURAN EMISSIONS DATA FOR RUN 2, SITE MET-A^a
(AS-MEASURED CONCENTRATIONS)

Dioxin/Furan Isomer	Isomer Concentration In Flue Gas (ng/dscm)	Isomer Concentration In Flue Gas (ppt)	Isomer Hourly Emissions Rate (ug/hr)
DIOXINS			
2378 TCDD	1.75E+01(N/A)	1.31E+00(N/A)	8.83E+03
Other TCDD	3.53E+01(N/A)	2.63E+00(N/A)	1.77E+04
Penta-CDD	6.28E+01(N/A)	4.25E+00(N/A)	3.16E+04
Hexa-CDD	1.45E+02(N/A)	8.95E+00(N/A)	7.32E+04
Hepta-CDD	1.09E+02(N/A)	6.20E+00(N/A)	5.51E+04
Octa-CDD	6.51E+01(N/A)	3.41E+00(N/A)	3.28E+04
Total PCDD	4.36E+02	2.67E+01	2.19E+05
FURANS			
2378 TCDF	1.86E+02(N/A)	1.46E+01(N/A)	9.36E+04
Other TCDF	6.28E+02(N/A)	4.94E+01(N/A)	3.16E+05
Penta-CDF	5.59E+02(N/A)	3.96E+01(N/A)	2.81E+05
Hexa-CDF	5.10E+02(N/A)	3.27E+01(N/A)	2.57E+05
Hepta-CDF	1.81E+02(N/A)	1.06E+01(N/A)	9.08E+04
Octa-CDF	1.23E+02(N/A)	6.64E+00(N/A)	6.17E+04
Total PCDF	2.19E+03	1.54E+02	1.10E+06

a. Data reported in this table represent lower bounds on the actual dioxin/furan emissions from Site MET-A. See Section 8.3.1.2 for discussion of analytical surrogate recovery results.

NOTE: Isomer concentrations shown are at as-measured oxygen conditions.
N/A = Not applicable. QA samples indicate the method capabilities and minimum limits of detection when values are positive.
ng = 1.0E-09g
ug = 1.0E-06g
ppt = parts per trillion, dry volume basis

TABLE D-2. DIOXIN/FURAN EMISSIONS DATA FOR RUN 3, SITE MET-A^a
(AS-MEASURED CONCENTRATIONS)

Dioxin/Furan Isomer	Isomer Concentration In Flue Gas (ng/dscm)	Isomer Concentration In Flue Gas (ppt)	Isomer Hourly Emissions Rate (ug/hr)
DIOXINS			
2378 TCDD	8.50E+00(N/A)	6.35E-01(N/A)	4.43E+03
Other TCDD	7.01E+01(N/A)	5.24E+00(N/A)	3.66E+04
Penta-CDD	1.16E+02(N/A)	7.87E+00(N/A)	6.08E+04
Hexa-CDD	1.08E+02(N/A)	6.63E+00(N/A)	5.62E+04
Hepta-CDD	2.93E+02(N/A)	1.66E+01(N/A)	1.53E+05
Octa-CDD	1.85E+02(N/A)	9.67E+00(N/A)	9.65E+04
Total PCDD	7.81E+02	4.66E+01	4.08E+05
FURANS			
2378 TCDF	2.53E+02(N/A)	1.99E+01(N/A)	1.32E+05
Other TCDF	8.90E+02(N/A)	7.00E+01(N/A)	4.64E+05
Penta-CDF	9.27E+02(N/A)	6.56E+01(N/A)	4.84E+05
Hexa-CDF	3.04E+02(N/A)	1.95E+01(N/A)	1.59E+05
Hepta-CDF	5.32E+02(N/A)	3.13E+01(N/A)	2.78E+05
Octa-CDF	3.60E+02(N/A)	1.95E+01(N/A)	1.88E+05
Total PCDF	3.27E+03	2.26E+02	1.70E+06

a. Data reported in this table represent lower bounds on the actual dioxin/furan emissions from Site MET-A. See Section 8.3.1.2 for discussion of analytical surrogate recovery results.

NOTE: Isomer concentrations shown are at as-measured oxygen conditions.
N/A = Not applicable. QA samples indicate the method capabilities and minimum limits of detection when values are positive.
ng = 1.0E-09g
ug = 1.0E-06g
ppt = parts per trillion, dry volume basis

TABLE D-3. DIOXIN/FURAN EMISSIONS DATA FOR RUN 4, SITE MET-A^a
(AS-MEASURED CONCENTRATIONS)

Dioxin/Furan Isomer	Isomer Concentration In Flue Gas (ng/dscm)	Isomer Concentration In Flue Gas (ppt)	Isomer Hourly Emissions Rate (ug/hr)
DIOXINS			
2378 TCDD	5.77E+00(N/A)	4.31E-01(N/A)	2.81E+03
Other TCDD	5.40E+01(N/A)	4.04E+00(N/A)	2.63E+04
Penta-CDD	7.45E+01(N/A)	5.04E+00(N/A)	3.62E+04
Hexa-CDD	6.76E+01(N/A)	4.16E+00(N/A)	3.29E+04
Hepta-CDD	1.48E+02(N/A)	8.40E+00(N/A)	7.22E+04
Octa-CDD	1.06E+02(N/A)	5.55E+00(N/A)	5.16E+04
Total PCDD	4.56E+02	2.76E+01	2.22E+05
FURANS			
2378 TCDF	2.65E+02(N/A)	2.08E+01(N/A)	1.29E+05
Other TCDF	1.33E+03(N/A)	1.04E+02(N/A)	6.45E+05
Penta-CDF	7.65E+02(N/A)	5.41E+01(N/A)	3.72E+05
Hexa-CDF	2.58E+02(N/A)	1.66E+01(N/A)	1.26E+05
Hepta-CDF	1.97E+02(N/A)	1.16E+01(N/A)	9.60E+04
Octa-CDF	1.85E+02(N/A)	1.00E+01(N/A)	8.97E+04
Total PCDF	3.00E+03	2.17E+02	1.46E+06

a. Data reported in this table represent lower bounds on the actual dioxin/furan emissions from Site MET-A. See Section 8.3.1.2 for discussion of analytical surrogate recovery results.

NOTE: Isomer concentrations shown are at as-measured oxygen conditions.
N/A = Not applicable. QA samples indicate the method capabilities and minimum limits of detection when values are positive.

ng = 1.0E-09g

ug = 1.0E-06g

ppt = parts per trillion, dry volume basis

APPENDIX D-2

Run-Specific Dioxin/Furan Emissions Data
(Concentrations Corrected to 3 Percent Oxygen)

TABLE D-4 DIOXIN/FURAN EMISSIONS DATA FOR RUN 2, SITE MET-A^a
(CONCENTRATIONS CORRECTED TO 3% OXYGEN)

Dioxin/Furan Isomer	Isomer Concentration In Flue Gas (ng/dscm @ 3% oxygen)	Isomer Concentration In Flue Gas (ppt @ 3% oxygen)	Isomer Hourly Emissions Rate (ug/hr)
DIOXINS			
2378 TCDD	3.95E+02(N/A)	2.95E+01(N/A)	8.83E+03
Other TCDD	7.93E+02(N/A)	5.93E+01(N/A)	1.77E+04
Penta-CDD	1.41E+03(N/A)	9.55E+01(N/A)	3.16E+04
Hexa-CDD	3.27E+03(N/A)	2.01E+02(N/A)	7.32E+04
Hepta-CDD	2.46E+03(N/A)	1.39E+02(N/A)	5.51E+04
Octa-CDD	1.47E+03(N/A)	7.66E+01(N/A)	3.28E+04
Total PCDD	9.80E+03	6.02E+02	2.19E+05
FURANS			
2378 TCDF	4.18E+03(N/A)	3.29E+02(N/A)	9.36E+04
Other TCDF	1.41E+04(N/A)	1.11E+03(N/A)	3.16E+05
Penta-CDF	1.26E+04(N/A)	8.90E+02(N/A)	2.81E+05
Hexa-CDF	1.15E+04(N/A)	7.36E+02(N/A)	2.57E+05
Hepta-CDF	4.06E+03(N/A)	2.39E+02(N/A)	9.08E+04
Octa-CDF	2.76E+03(N/A)	1.49E+02(N/A)	6.17E+04
Total PCDF	4.92E+04	3.45E+03	1.10E+06

a. Data reported in this table represent lower bounds on the actual dioxin/furan emissions from Site MET-A. See Section 8.3.1.2 for discussion of analytical surrogate recovery results.

NOTE: Isomer concentrations shown are corrected to 3% oxygen.

N/A = Not applicable. QA samples indicate the method capabilities and minimum limits of detection when values are positive.

ng = 1.0E-09g

ug = 1.0E-06g

ppt = parts per trillion, dry volume basis

TABLE D-5 DIOXIN/FURAN EMISSIONS DATA FOR RUN 3, SITE MET-A^a
(CONCENTRATIONS CORRECTED TO 3% OXYGEN)

Dioxin/Furan Isomer	Isomer Concentration In Flue Gas (ng/dscm @ 3% oxygen)	Isomer Concentration In Flue Gas (ppt @ 3% oxygen)	Isomer Hourly Emissions Rate (ug/hr)
DIOXINS			
2378 TCDD	1.70E+02(N/A)	1.27E+01(N/A)	4.43E+03
Other TCDD	1.40E+03(N/A)	1.05E+02(N/A)	3.66E+04
Penta-CDD	2.33E+03(N/A)	1.57E+02(N/A)	6.08E+04
Hexa-CDD	2.15E+03(N/A)	1.33E+02(N/A)	5.62E+04
Hepta-CDD	5.86E+03(N/A)	3.32E+02(N/A)	1.53E+05
Octa-CDD	3.70E+03(N/A)	1.93E+02(N/A)	9.65E+04
Total PCDD	1.56E+04	9.33E+02	4.08E+05
FURANS			
2378 TCDF	5.06E+03(N/A)	3.98E+02(N/A)	1.32E+05
Other TCDF	1.78E+04(N/A)	1.40E+03(N/A)	4.64E+05
Penta-CDF	1.85E+04(N/A)	1.31E+03(N/A)	4.84E+05
Hexa-CDF	6.08E+03(N/A)	3.90E+02(N/A)	1.59E+05
Hepta-CDF	1.06E+04(N/A)	6.26E+02(N/A)	2.78E+05
Octa-CDF	7.20E+03(N/A)	3.90E+02(N/A)	1.88E+05
Total PCDF	6.53E+04	4.51E+03	1.70E+06

a. Data reported in this table represent lower bounds on the actual dioxin/furan emissions from Site MET-A. See Section 8.3.1.2 for discussion of analytical surrogate recovery results.

NOTE: Isomer concentrations shown are corrected to 3% oxygen.

N/A = Not applicable. QA samples indicate the method capabilities and minimum limits of detection when values are positive.

ng = 1.0E-09g

ug = 1.0E-06g

ppt = parts per trillion, dry volume basis

TABLE D-6 DIOXIN/FURAN EMISSIONS DATA FOR RUN 4, SITE MET-A^a
(CONCENTRATIONS CORRECTED TO 3% OXYGEN)

Dioxin/Furan Isomer	Isomer Concentration In Flue Gas (ng/dscm @ 3% oxygen)	Isomer Concentration In Flue Gas (ppt @ 3% oxygen)	Isomer Hourly Emissions Rate (ug/hr)
DIOXINS			
2378 TCDD	1.30E+02(N/A)	9.70E+00(N/A)	2.81E+03
Other TCDD	1.22E+03(N/A)	9.08E+01(N/A)	2.63E+04
Penta-CDD	1.68E+03(N/A)	1.13E+02(N/A)	3.62E+04
Hexa-CDD	1.52E+03(N/A)	9.35E+01(N/A)	3.29E+04
Hepta-CDD	3.34E+03(N/A)	1.89E+02(N/A)	7.22E+04
Octa-CDD	2.39E+03(N/A)	1.25E+02(N/A)	5.16E+04
Total PCDD	1.03E+04	6.21E+02	2.22E+05
FURANS			
2378 TCDF	5.97E+03(N/A)	4.69E+02(N/A)	1.29E+05
Other TCDF	2.99E+04(N/A)	2.35E+03(N/A)	6.45E+05
Penta-CDF	1.72E+04(N/A)	1.22E+03(N/A)	3.72E+05
Hexa-CDF	5.81E+03(N/A)	3.73E+02(N/A)	1.26E+05
Hepta-CDF	4.44E+03(N/A)	2.61E+02(N/A)	9.60E+04
Octa-CDF	4.15E+03(N/A)	2.25E+02(N/A)	8.97E+04
Total PCDF	6.74E+04	4.89E+03	1.46E+06

a. Data reported in this table represent lower bounds on the actual dioxin/furan emissions from Site MET-A. See Section 8.3.1.2 for discussion of analytical surrogate recovery results.

NOTE: Isomer concentrations shown are corrected to 3% oxygen.

N/A = Not applicable. QA samples indicate the method capabilities and minimum limits of detection when values are positive.

ng = 1.0E-09g

ug = 1.0E-06g

ppt = parts per trillion, dry volume basis

APPENDIX E

RUN-SPECIFIC RISK MODELING INPUT DATA

TABLE E-1. RISK MODELING PARAMETERS FOR RUN 2, SITE MET-A^a

Latitude = 40 Degrees , 33 Minutes , 48 Seconds
 Longitude = 74 Degrees , 13 Minutes , 05 Seconds
 Stack Height (From Grade Level) = 76.2 m
 Stack Diameter (ID) = 3.5 m
 Flue Gas Flow Rate (Dry Standard) = 8386.9 dscmm
 Flue Gas Exit Temperature = 374.3 Degrees K
 Flue Gas Exit Velocity (Actual) = 19.8 mps

Dioxin/Furan Isomer	Isomer Concentration In Flue Gas (ng/dscm)	Isomer Hourly Emissions Rate (ug/hr)	Relative Potency Factor	2,3,7,8 - TCDD Equivalent Emissions (mg/yr)
2378 TCDD	1.75E+01	8.83E+03	1.000	7.20E+04
Other TCDD	3.53E+01	1.77E+04	.010	1.45E+03
2378 TCDF	1.86E+02	9.36E+04	.100	7.64E+04
Other TCDF	6.28E+02	3.16E+05	.001	2.58E+03
Penta-CDD	6.28E+01	3.16E+04	.500	1.29E+05
Penta-CDF	5.59E+02	2.81E+05	.100	2.30E+05
Hexa-CDD	1.45E+02	7.32E+04	.040	2.39E+04
Hexa-CDF	5.10E+02	2.57E+05	.010	2.09E+04
Hepta-CDD	1.09E+02	5.51E+04	.001	4.50E+02
Hepta-CDF	1.81E+02	9.08E+04	.001	7.41E+02
Octa-CDD	6.51E+01	3.28E+04	.000	.00E+00
Octa-CDF	1.23E+02	6.17E+04	.000	.00E+00

Net 2378 TCDD Equivalent Atmospheric Loading 5.57E+05

- a. Data reported in this table represent lower bounds on the actual dioxin/furan emissions from Site MET-A. See Section 8.3.1.2 for discussion of analytical surrogate recovery results.

ng = 1.0E-09g

ug = 1.0E-06g

mg = 1.0E-03g

Standard conditions: 293 K (20 C) temperature and 1 atmosphere pressure.
8160 operating hours per year

TABLE E-2. RISK MODELING PARAMETERS FOR RUN 3, SITE MET-A^a

Latitude = 40 Degrees , 33 Minutes , 48 Seconds
 Longitude = 74 Degrees , 13 Minutes , 05 Seconds
 Stack Height (From Grade Level) = 76.2 m
 Stack Diameter (ID) = 3.5 m
 Flue Gas Flow Rate (Dry Standard) = 8699.9 dscmm
 Flue Gas Exit Temperature = 378.4 Degrees K
 Flue Gas Exit Velocity (Actual) = 20.7 mps

Dioxin/Furan Isomer	Isomer Concentration In Flue Gas (ng/dscm)	Isomer Hourly Emissions Rate (ug/hr)	Relative Potency Factor	2,3,7,8 - TCDD Equivalent Emissions (mg/yr)
2378 TCDD	8.50E+00	4.43E+03	1.000	3.62E+04
Other TCDD	7.01E+01	3.66E+04	.010	2.99E+03
2378 TCDF	2.53E+02	1.32E+05	.100	1.08E+05
Other TCDF	8.90E+02	4.64E+05	.001	3.79E+03
Penta-CDD	1.16E+02	6.08E+04	.500	2.48E+05
Penta-CDF	9.27E+02	4.84E+05	.100	3.95E+05
Hexa-CDD	1.08E+02	5.62E+04	.040	1.84E+04
Hexa-CDF	3.04E+02	1.59E+05	.010	1.29E+04
Hepta-CDD	2.93E+02	1.53E+05	.001	1.25E+03
Hepta-CDF	5.32E+02	2.78E+05	.001	2.27E+03
Octa-CDD	1.85E+02	9.65E+04	.000	.00E+00
Octa-CDF	3.60E+02	1.88E+05	.000	.00E+00
Net 2378 TCDD Equivalent Atmospheric Loading				8.29E+05

a. Data reported in this table represent lower bounds on the actual dioxin/furan emissions from Site MET-A. See Section 8.3.1.2 for discussion of analytical surrogate recovery results.

ng = 1.0E-09g

ug = 1.0E-06g

mg = 1.0E-03g

Standard conditions: 293 K (20 C) temperature and 1 atmosphere pressure.
 8160 operating hours per year

TABLE E-3. RISK MODELING PARAMETERS FOR RUN 4, SITE MET-A^a

Latitude = 40 Degrees , 33 Minutes , 48 Seconds
 Longitude = 74 Degrees , 13 Minutes , 05 Seconds
 Stack Height (From Grade Level) = 76.2 m
 Stack Diameter (ID) = 3.5 m
 Flue Gas Flow Rate (Dry Standard) = 8104.0 dscmm
 Flue Gas Exit Temperature = 373.9 Degrees K
 Flue Gas Exit Velocity (Actual) = 19.1 mps

Dioxin/Furan Isomer	Isomer Concentration In Flue Gas (ng/dscm)	Isomer Hourly Emissions Rate (ug/hr)	Relative Potency Factor	2,3,7,8 - TCDD Equivalent Emissions (mg/yr)
2378 TCDD	5.77E+00	2.81E+03	1.000	2.29E+04
Other TCDD	5.40E+01	2.63E+04	.010	2.14E+03
2378 TCDF	2.65E+02	1.29E+05	.100	1.05E+05
Other TCDF	1.33E+03	6.45E+05	.001	5.27E+03
Penta-CDD	7.45E+01	3.62E+04	.500	1.48E+05
Penta-CDF	7.65E+02	3.72E+05	.100	3.04E+05
Hexa-CDD	6.76E+01	3.29E+04	.040	1.07E+04
Hexa-CDF	2.58E+02	1.26E+05	.010	1.02E+04
Hepta-CDD	1.48E+02	7.22E+04	.001	5.89E+02
Hepta-CDF	1.97E+02	9.60E+04	.001	7.84E+02
Octa-CDD	1.06E+02	5.16E+04	.000	.00E+00
Octa-CDF	1.85E+02	8.97E+04	.000	.00E+00
Net 2378 TCDD Equivalent Atmospheric Loading				6.09E+05

a. Data reported in this table represent lower bounds on the actual dioxin/furan emissions from Site MET-A. See Section 8.3.1.2 for discussion of analytical surrogate recovery results.

ng = 1.0E-09g

ug = 1.0E-06g

mg = 1.0E-03g

Standard conditions: 293 K (20 C) temperature and 1 atmosphere pressure.
 8160 operating hours per year

APPENDIX F
COMPOUND-SPECIFIC PRECURSOR RESULTS

TABLE F-1. COMPOUND-SPECIFIC DIOXIN PRECURSOR CONCENTRATIONS
FOR SITE MET-A FEED SAMPLES

Precursor Compounds	Precursor Concentration, ug/g (ppm)			
	Coke	Telephone Parts, Wire	Circuit Boards	Electronic Switching Gear
<u>Base Neutrals Fraction</u>				
<u>Chlorinated Benzenes:</u>				
Dichlorobenzenes	ND, ND	ND	ND, ND	ND
Trichlorobenzenes	ND, ND	ND	ND, ND	ND
Tetrachlorobenzenes	ND, ND	ND	ND, ND	ND
Pentachlorobenzenes	ND, ND	ND	ND, ND	ND
Hexachlorobenzenes	ND, ND	ND	ND, ND	ND
Total Chlorinated Benzenes	ND ND	ND	ND ND	ND
<u>Chlorinated Biphenyls:</u>				
Chlorobiphenyls	ND, ND	ND	ND, ND	ND
Dichlorobiphenyls	ND, ND	ND	ND, ND	ND
Trichlorobiphenyls	ND, ND	ND	ND, ND	ND
Tetrachlorobiphenyls	ND, ND	ND	ND, ND	ND
Pentachlorobiphenyls	ND, ND	0.004	ND, ND	0.003
Hexachlorobiphenyls	ND, ND	ND	ND, ND	0.100
Heptachlorobiphenyls	ND, ND	ND	ND, ND	0.140
Octachlorobiphenyls	ND, ND	ND	ND, ND	0.016
Nonachlorobiphenyls	ND, ND	ND	ND, ND	ND
Decachlorobiphenyls	ND, ND	ND	ND, ND	ND
Total Chlorinated Biphenyls	ND, ND	0.004	ND, ND	0.26
<u>Acids Fraction</u>				
<u>Chlorinated Phenols:</u>				
Dichlorophenols	ND, ND	ND	ND ND	ND
Trichlorophenols	ND, ND	ND	ND ND	ND
Tetrachlorophenols	ND, ND	ND	ND ND	ND
Pentachlorophenols	ND, ND	ND	ND ND	ND
Total Chlorinated Phenols	ND, ND	ND	ND ND	ND

ND = not detected

See Section 8.3.2 for a discussion of quality assurance/quality control results for these analyses.

APPENDIX G
RESEARCH TRIANGLE INSTITUTE (RTI)
SYSTEMS AUDIT



RESEARCH TRIANGLE INSTITUTE

QUALITY ASSURANCE AUDIT FOR TIER 4 OF THE NATIONAL DIOXIN STUDY:
SECONDARY COPPER RECOVERY BLAST FURNACE. SITE MET-A

By

Richard V. Crume
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EPA Contract No. 68-02-3149
Work Assignment 10-1

RTI Project No. 472U-2500-48

EPA Technical Project Monitor
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1.0 INTRODUCTION

On May 30, 1985, Research Triangle Institute (RTI) performed a quality assurance (QA) audit of an emission test program underway at a secondary copper recovery blast furnace (Site MET-A). The emission test program was one of a series of tests performed by Radian Corporation for the U.S. Environmental Protection Agency (EPA). The data collected during these tests will be added to the data base supporting Tier 4 of EPA's National Dioxin Study. The primary objective of Tier 4 is to determine if various combustion facilities are sources of dioxin emissions. If any of the combustion facilities are found to emit dioxins, the secondary objectives of Tier 4 are to quantify these dioxin emissions and, if possible, to relate the emissions to combustion device operating conditions. The audit was performed by RTI's Richard V. Crume and Robert S. Wright. The EPA Project Officer was William B. Kuykendal of the Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina. A list of persons present during the audit, including a number of observers from the States of New York and New Jersey, is presented in Table 1.

At EPA's request, RTI's audit focused on the continuous emission monitoring system and on modifications made to the Modified Method 5 sampling train. Additionally, RTI examined other sampling systems and reviewed in-house audit data provided by Radian. In preparing for the audit, RTI reviewed the following two documents:

- o Site Specific Test Plan, Secondary Copper Recovery Blast Furnace, Test Number Ten, Site MET-A. Radian Corporation. April 8, 1985.
- o Radian Corporation's Response to Comments Submitted by the State of New York. No Date.

TABLE 1. LIST OF PERSONS PRESENT DURING
THE SITE MET-A AUDIT

U.S. Environmental Protection Agency

William Lamason

Radian Corporation

Deborah Benson, Assistant
Lee Garcia, MMS Operator
Gary Henry, MMS Operator
Larry Keller, Engineer
Jill Myerson, Assistant
Jim Reynolds, Sample Team Leader
Dave Savia, CEM Operator

Research Triangle Institute

Richard Crume
Robert Wright

State of New York

Michael Bryce
Al Columbus
Louise Halper
Steven Ohrwaschel
Michael Osual
Michael Surgan

State of New Jersey

Ezikpe Akuma
Edward Chromaiski
Scott Hawthorne
David Lowie, Jr.
Rich Oaniak
Frank Papp
Bryon Sullivan

The results of this audit are also reported in a letter to the EPA Project Officer, William B. Kuykendal¹.

¹ Crume, R.V. Letter to William B. Kuykendal discussing results of Site MET-A audit. Research Triangle Institute, Research Triangle Park, North Carolina. August 1, 1985.

2.0 AUDIT RESULTS

2.1 Continuous Emission Monitoring System

The continuous emission monitoring system was of particular interest to EPA because a new set-up, which had not been used during previous Tier 4 tests, was in use during the MET-A tests. Although the new set-up consisted of the same equipment that had previously been used, the equipment had been moved to a newly outfitted truck. The auditors carefully examined the new set-up and concluded that it was satisfactory, although several minor problems were detected. It is recommended that these problems, which are summarized below, be addressed prior to any future testing.

- o O₂ Monitor. Although the O₂ monitor was operating correctly, a problem with the signal conditioning box prevented the signal from reaching the data acquisition system. Instead, 5-minute averages were taken by hand.
- o SO₂ Calibration and QC Gases. The SO₂ concentrations found in the stack (about 250 ppm) were much higher than expected. As a consequence, the concentrations of the calibration and QC gases (83.5 and 19.6 ppm, respectively) were too low to be effective. (The instrument scale was 500 ppm rather than the 100 ppm scale anticipated prior to the testing.)
- o Verification of Calibration Gas. The calibration gas certifications had not been verified. However, Radian felt that the \pm 20% accuracy QA objective would cover any possible certification inaccuracy. (Nevertheless, prior RTI audits of commercial "certified" calibration standards found that their certified values could be in error by greater than 20 percent. Errors of this magnitude would leave little room for other instrumental errors).
- o Calibration Gas Certification. Several of the calibration standards had not been analyzed or re-analyzed within 6 months of the test. (It should be noted, however, that Radian's QA project plan does not call for periodic re-analysis of the calibration standards.)

- o Calibrations Standards vs. Certificates. The gas producers' calibration standards on-hand in the Radian mobile facility did not match producers' certificates on-hand. This problem is illustrated in Tables 2 and 3.
- o NO_x Monitor. The NO_x monitor drift, at + 5 to 10%, exceeded that observed for the other monitors. Although at this time the drift is still within the acceptance limit of + 20% for the single point response factor test, the monitor should be closely watched to prevent a worsening of drift during future tests.

In addition to evaluating Radian's on-site continuous emission monitoring system, RTI asked Radian to provide the results of any in-house continuous monitor performance auditing relevant to the Tier 4 tests. The materials Radian provided are contained in the Appendix. Note that although most performance test data for the continuous emission monitors fall within the $\pm 20\%$ objectives, the relative errors for the CO and NO_x instruments exceeded this objective in several cases.

2.2 Modified Method 5 Sampling Train

The Modified Method 5 sampling train in use at Test Site MET-A was unique in that a second XAD resin cartridge was added to the system just after the first impinger, as illustrated in Figure 1. This configuration, which was requested by EPA, was designed to mitigate concerns regarding the horizontal position of the XAD condenser. (Although the horizontal mounting of the condenser had been approved by EPA during previous Tier 4 tests, officials from the State of New York remained concerned about an increased potential for organic compounds breaking through the resin.)

The set-up and operation of the second XAD resin cartridge appeared to be acceptable. Furthermore, with one exception, operation of the entire train appeared normal. The one exception involved the formation of a yellow precipitate in the condenser, between the filter and the first XAD resin cartridge. The nature of this precipitate is unknown, although its color suggests that it may be chloride. Radian reported that the precipitate was easily removed with acetone.

TABLE 2. RADIAN CALIBRATION STANDARDS

Cylinder I.D.	Contents	Concentrations	Cylinder Analysis Date	Comments
CC-18556	Propane Air	19.7 ppm ----	10/84	None.
CC-541	Propane Air	90.0 ppm ----	10/84	None.
CC-1904	CO CO ₂ O ₂ N ₂	5580 ppm 18.0% 21.1% ----	4/85	None.
CC-18428	CO CO ₂ O ₂ N ₂	2000 ppm 13.0% 9.3% ----	Not Found	None.
CC-17628	NO N ₂	84.6 ppm ----	4/85	No tag. Value read from cylinder wall.
CC-9688	NO N ₂	20.8 ppm ----	9/84	None.
CC-18595	SO ₂ N ₂	83.1 ppm ----	Not Found	No tag. Value read from cylinder wall.
CC-16903	SO ₂ N ₂	19.5 ppm ----	Not Found	No tag. Value read from cylinder wall.

TABLE 3. ON-HAND CYLINDER CERTIFICATES (AIRCO)

Cylinder I.D.	Contents	Concentrations
N-249706	H ₂ N ₂	40.1% -----
C-18428	CO CO ₂ O ₂ N ₂	2000 ppm 13.0% 9.3% -----
CC-16600	SO ₂ N ₂	2005 ppm -----
CC-17350	O ₂ N ₂	10.2% -----
CC-2320	CO CO ₂ O ₂ N ₂	5175 ppm 18.5% 21.0% -----
CC-15819	NO NO ₂ N ₂	285 ppm < 2 ppm -----
CC-18059	NO NO ₂ N ₂	1042 < 10 ppm -----
CC-180064	O ₂ N ₂	17.8% -----
CC-17673	NO NO ₂ N ₂	155 ppm < 2.0 ppm -----

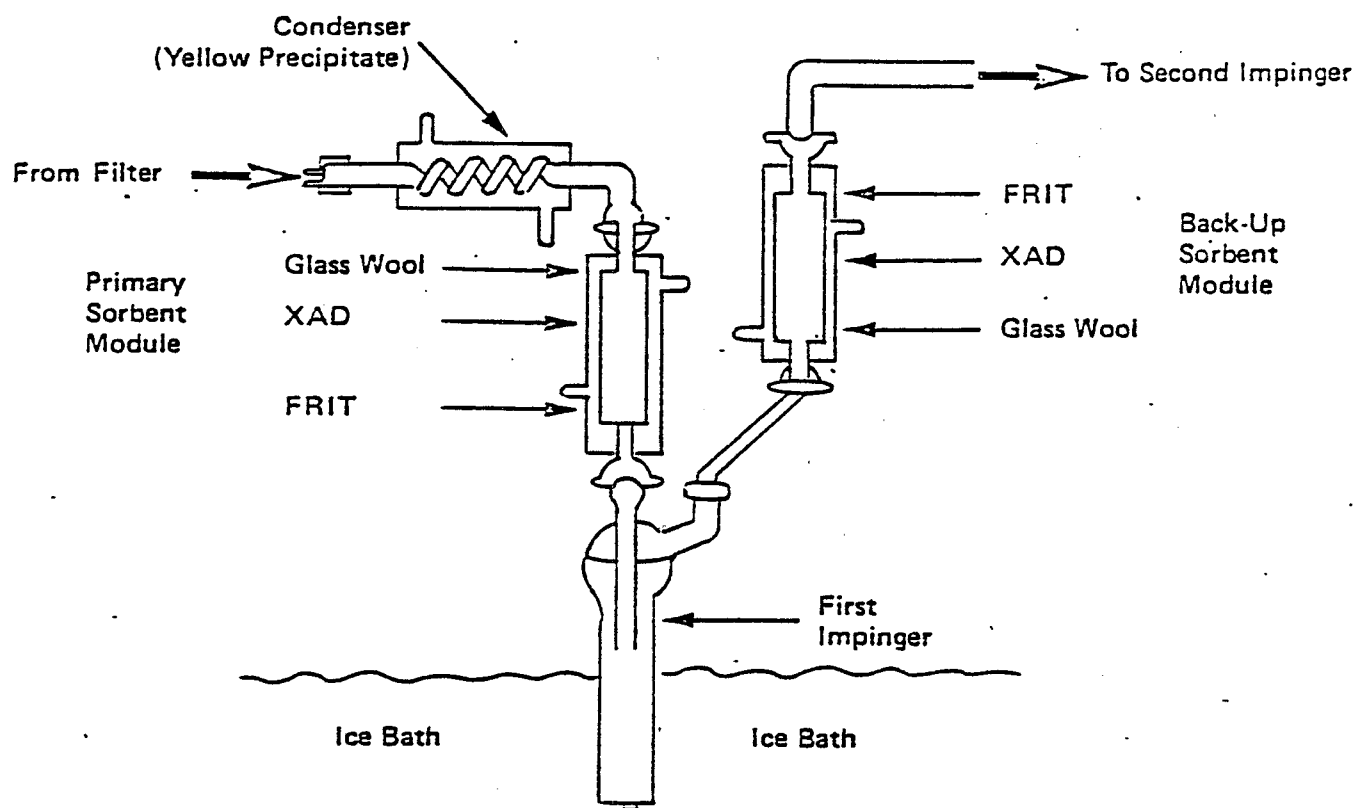


Figure 1. Configuration of primary and back-up sorbent modules in modified Method 5 sampling train.

2.3 Additional Observations

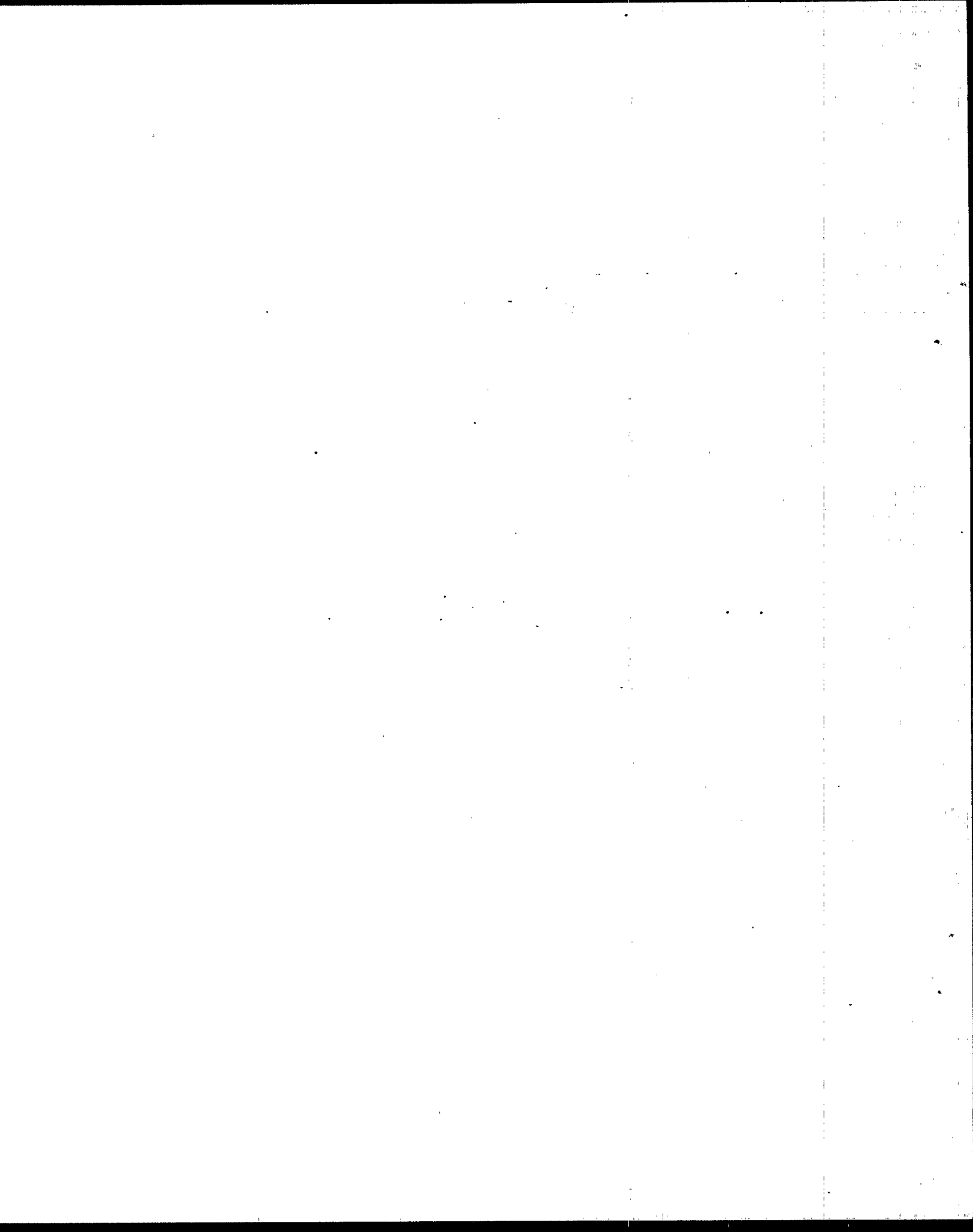
Several other problems occurred during the test program, as summarized below:

- o Analytical Laboratory. Radian's mobile analytical laboratory was damaged en route to the test site and had to be left behind. Most of the laboratory equipment was salvaged and transferred to a temporary laboratory set-up at the plant. The temporary laboratory was inspected by RTI and appeared to be satisfactory.
- o Filter Placement. On the first day of testing the Modified Method 5 sample train filters were placed backwards, thereby invalidating the test results. These tests were consequently repeated.
- o Electrical Problems. Power supply problems forced testing to be delayed during the morning of the second day. However, these problems were solved by noon and did not seriously interfere with the test schedule.

3.0 CONCLUSIONS

Operation of the continuous emission monitoring system and the Modified Method 5 sampling train was found to be satisfactory. Although several problems with the monitoring system were detected, these problems did not appear to significantly interfere with testing or to compromise test results. Nevertheless, if these problems are not corrected, more serious problems could develop during any future testing. In particular, it is recommended that the following actions be taken:

- o Repair the signal conditioning box so that the O₂ signals can reach the data acquisition system.
- o Calibration and QC gas concentrations should be selected to fall within the operating range of the continuous emission monitors.
- o Calibration and QC gases for the most critical measurements should be verified.
- o Gas cylinder calibrations should be kept up to date.
- o Calibration standards should match the gas producers' certificates on-hand.
- o The NO_x monitor drift problem should be corrected.
- o The relative errors associated with the CO and NO_x monitors should be examined.



4.0 APPENDIX

4.1 Section From Internal Radian Audit Report Describing Audit of Continuous Emission Monitoring System

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-450/4-84-014s		2.		3. RECIPIENT'S ACCESSION NO.	
4. TITLE AND SUBTITLE National Dioxin Study Tier 4 - Combustion Sources Final Test Report - Site 10 Secondary Copper Recovery Cupola Furnace MET - A				5. REPORT DATE April 1987	
				6. PERFORMING ORGANIZATION CODE	
7. AUTHOR(S) Lawrence E. Keller, James R. McReynolds Deborah J. Benson				8. PERFORMING ORGANIZATION REPORT NO. 87-231-056-12-44	
9. PERFORMING ORGANIZATION NAME AND ADDRESS Radian Corporation Post Office Box 13000 Research Triangle Park, NC 27709				10. PROGRAM ELEMENT NO.	
				11. CONTRACT/GRANT NO. 68-03-3148	
12. SPONSORING AGENCY NAME AND ADDRESS U.S. Environmental Protection Agency, OAQPS Research Triangle Park, NC 27711 Office of Research and Development Washington, DC 20460				13. TYPE OF REPORT AND PERIOD COVERED Final	
				14. SPONSORING AGENCY CODE	
15. SUPPLEMENTARY NOTES EPA Project Officers: Donald Oberacker, ORD William B. Kuykendal, OAQPS					
16. ABSTRACT <p>This report summarizes the results of a dioxin/furan emissions test of a secondary copper recovery cupola furnace equipped with an afterburner for hydrocarbon emissions control and two baghouses for particulate emissions control. The cupola furnace is used for recovery of copper from telephone scrap and other copper-bearing materials. The test was the 10 in a series of dioxin/furan emissions tests conducted under Tier 4 of the National Dioxin Study. The primary objective of Tier 4 is to determine if various combustion sources are sources of dioxin/or furan emissions. If any of the combustion sources are found to emit dioxin or furan, the secondary objective of Tier 4 is to quantify these emissions.</p> <p>Secondary copper recovery cupola furnaces are one of 8 combustion source categories that have been tested in the Tier 4 program. The tested cupola furnace, hereafter referred to as cupola furnace MET-A, was selected for this test after an initial information screening and a one-day pretest survey visit. Cupola furnace MET-A is a large secondary copper recovery cupola furnace relative to others in the United States. The furnace feed includes plastic-bearing materials of various types, some of which may contain chlorinated organic compounds.</p> <p>Data presented in the report include dioxin (tera through octa homologue +2378 TCDD) and furan (tetra through octa homologue +2378 TCDF) results for both stack samples and ash samples. In addition, process data collected during sampling are also presented.</p>					
KEY WORDS AND DOCUMENT ANALYSIS					
a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS		c. COSATI Field/Group	
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