

NATIONAL DIOXIN STUDY TIER 4 — COMBUSTION SOURCES

Final Test Report — Site 13 Residential Wood Stove WS — A

By

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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 residential woodstove conducted by Radian Corporation. The stove is a freestanding noncatalytic model manufactured by Atlanta Stove Works and offered for sale in the Sears Catalog (#42G84156N). During testing oak and pine were burned at low burn rates, which is representative of normal residential use. The test was the thirteenth 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.

Residential woodstoves are among 8 combustion source categories that have been tested in the Tier 4 program. The tested woodstove, hereafter referred to as Woodstove WS-A, is a test unit located at an EPA contractor facility. This stove was selected for inclusion in the Tier 4 program due to its location in the Research Triangle Park area and because simultaneous testing of the stove was already being conducted for another EPA program (Integrated Air Cancer Project). The woodstove tested is considered representative of woodstoves built in the last 5 to 10 years.

This test report is organized as follows. A summary of test results and conclusions is provided in Section 2.0, followed by a process description in Section 3.0. The source sampling and analysis plan is outlined in Section 4.0, and the dioxin test data are presented in Section 5.0. Sections 6.0 through 8.0 present various testing details. These include descriptions of the

^aThe term "dioxin/furan" and the acronyms PCDD and PCDF as used in this report refer to the polychlorinated dibenzo-p-dioxin and dibenzofuran isomers with four or more chlorine atoms.

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.

2.0 SUMMARY AND CONCLUSIONS

2.1 SOURCE SAMPLING AND ANALYSIS OVERVIEW

A simplified diagram of Woodstove WS-A is shown in Figure 2-1. The stove is considered to be a typical residential wood stove. The fuel was oak and pine aged approximately 1 year. The stove was operated at low burn rates and low operating temperatures for maximum wood use efficiency, which is typical of residential operation.

Sampling for dioxin/furan emissions was performed by Radian at the outlet exhaust stack in each of a series of three test runs conducted on May 10, 17, and 24, 1985. 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. Modifications to the draft ASME protocol used at this test site are discussed in Section 6.1.2. MM5 train components and train rinses were analyzed for dioxins and furans by ECL-Bay St. Louis and EMSL-RTP, two of three EPA laboratories collectively known as Troika. The dioxin/furan analysis attempted to quantify the 2378 TCDD/TCDF isomers and the tetra-through octa- dioxin/furan homologues present in the samples.

Dioxin/furan precursor analyses were performed by Radian on samples of the wood fed to the stove. The specific dioxin precursors analyzed for were chlorophenols, chlorobenzenes, polychlorinated biphenyls, and total chlorides. Woodstove ash and flue wipe samples were also taken and analyzed by Troika for dioxin/furan content.

In addition to the above sampling and analysis efforts conducted specifically for the Tier 4 program, simultaneous testing of the woodstove was

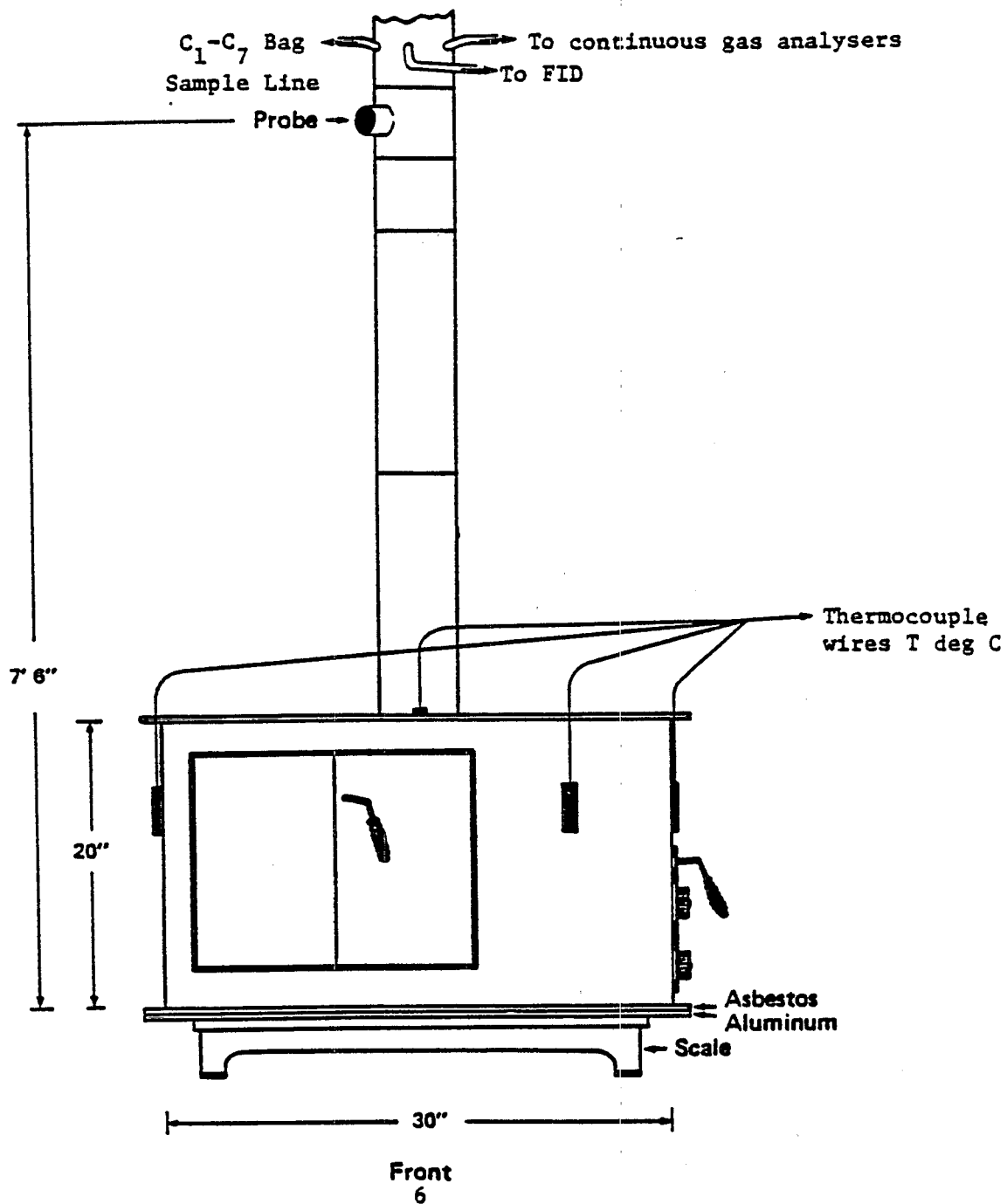


Figure 2-1. Simplified Diagram of Woodstove WS-A

TABLE 2-1. SOURCE SAMPLING AND ANALYSIS OVERVIEW

Item	Item Description
1. Number of test runs	- Three test runs (Runs 01, 02, 03)
2. Gaseous Sampling	<ul style="list-style-type: none"> - MM5 sampling at woodstove outlet (Runs 01, 02, 03). Dioxin/furan analysis. - EPA Reference Methods 2 and 4 at woodstove outlet exhaust stack (Runs 01, 02, 03). Gas velocity and moisture. - Continuous monitoring of CO, CO₂, O₂, and total hydrocarbons at woodstove² outlet (Runs 01, 02, 03).
3. Solids Sampling	<ul style="list-style-type: none"> - Oak feed sampling (Runs 01, 02). Dioxin/furan precursor analysis. - Pine feed sampling (Run 03). Dioxin/furan precursor analysis. - Bottom ash sampling (Runs 01, 02, 03) Dioxin/furan analysis. - Stack wipe sampling at outlet exhaust stack (Runs 02, 03)

performed by Research Triangle Institute (RTI) as part of the Integrated Air Cancer Project. Continuous emissions monitoring (CEM) was performed by RTI personnel at the stove exhaust location for CO, CO₂, THC, and O₂. RTI also conducted Modified Method 5 sampling tests for polycyclic aromatic hydrocarbons (PAH)(GC-FID with GC-MS confirmation), gravimetric and total chromatographable hydrocarbons sampling, spot dilution tests for PAH concentration, and retene analysis. Manual recordings included wood weight, burn time, stack flow, room temperature and humidity, inlet flows through the dampers and general operating conditions, and occurrences. Continuous measurements of stack temperature and stove temperature were also recorded. The data from these tests are reported in reference 1.

2.2 SUMMARY OF RESULTS

No valid flue gas dioxin/furan emissions data were obtained for Woodstove WS-A. Labelled internal standards spiked onto the MM5 sample train components were not recoverable due to the large amounts of hydrocarbons present.

Analyses of woodstove ash and flue wipe samples from this test site showed minimal dioxin/furan content. Octa-CDD was the only dioxin/furan homologue detected in the three ash samples analyzed, and the values reported were near the analytical detection limit. The maximum octa-CDD content of the ash samples was 0.09 parts-per-billion (ppb). Small quantities of octa-CDD were found in each of the two flue wipe samples analyzed, with hepta-CDD also being detected in one of the two samples. The maximum octa-CDD content of the flue wipe samples was 0.6 ppb, and the measured hepta-CDD content was 0.04 ppb.

The woodstove was operated at low burn rates for all test runs, which is representative of normal consumer operation. Burn rates for individual test runs ranged from 1.3 kg/hr (Run 01) to 3.5 kg/hr (Run 02). Average

-
1. Leese, K. E., and S. M. Harkins, RTI. Integrated Air Cancer Project-Source Measurement. Draft Final Report. RTI/3065-07. March 1986.

as-measured emission concentrations of CO and THC during the test runs were 8,000 ppmv and 10,800 ppmv, respectively. The average oxygen content of the flue gas was 17.0 vol %.

Chlorobenzenes, chlorophenols, and polychlorinated biphenyls were not detected in the oak and pine samples analyzed. The total chloride contents of the oak and pine samples were 125 ppm and 49 ppm, respectively.

3.0 PROCESS DESCRIPTION¹

Woodstove WS-A is a Sears Catalog No. 42G84156N free-standing radiant woodstove. The stove is rectangular with a set of hinged interlocking doors on the front and one hinged door on the right side which houses three screw-down air dampers. The air dampers are each three inches in diameter and form a triangle on the door. These dampers are used to control the amount of air entering the stove, and thus, the burn rate. The upper damper was sealed shut with silicone high temperature sealant to allow better control of the burn rate. A steel grate is normally located on the front of the stove just inside the two interlocking front doors, but it was removed to facilitate loading of kindling before each run and removal of ash after each run. The interior of the stove is lined with firebrick. The stove is baffled and the flue exit is in the rear, opposite the hinged interlocking front doors. The legs of the stove were removed, and the stove and flue sections were mounted on a Detecto 5850 scale which was calibrated to 1000 pounds just prior to this study. Before the stove and flue were mounted, the scale was leveled and a 3' x 3' x 1/2" sheet of aluminum was placed on top of the platform along with an asbestos board of the same approximate dimensions. The flue exit from the rear of the stove is 6 inches in diameter and the inside diameter of the flue is 8 inches. A single-walled 6-inch/8-inch adaptor was used to connect the stove exit to an 8-inch inside diameter double-walled Metalbestos^R insulated tee. All sections of the flue from the tee upward consisted of the same type of double-walled insulated flue. Two 30-inch and two 9-inch vertical flue sections were mounted above the tee.

1. Leese, K.E., and S. M. Harkins, RTI. Integrated Air Cancer Project-Source Measurement. Draft Final Report. RTI/3065-07. March 1986.

4.0 TEST DESCRIPTION

This section describes the Tier 4 field sampling, process monitoring, and analytical activities that were performed for test Site WS-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. Specific testing details (sampling locations and procedures) will be presented later, 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 WS-A. Three dioxin/furan emissions tests (Runs 01, 02, 03) were performed at the woodstove outlet exhaust stack. Dioxin/furan sampling was based on the MM5 sampling protocol developed by ASME for measuring emissions of chlorinated organic compounds. Testing was performed at the woodstove exhaust stack for a period corresponding to 240 minutes of on-line sampling. The ASME protocol was modified for woodstove use by the addition of a second XAD-2^R resin trap due to the high total hydrocarbon concentration in the exhaust gas. The protocol was also modified to allow for velocity readings taken by a vane anemometer every 15 minutes rather than with a pitot tube. The extremely low velocity of the woodstove exhaust gas precluded normal flow measurement and isokinetic sampling. Additional details on sampling procedures and deviations from the ASME protocol are contained in Section 6.2.1.

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

Sample Location	Sample Type or Parameter	Sampling Method	Analytical Method	Number of Samples/ Sample Frequency
1. Woodstove Outlet Exhaust Stack	Dioxin/furan emissions	Modified EPA Method 5 with back-up XAD trap	Gas Chromatography/ Mass Spectrometer	Three test runs (Runs 01, 02, 03); one proof blank; one field recovery blank
	Volumetric gas flow rate	Vane anemometer	Not applicable	Once per MW5 test run
	Molecular Weight	EPA Method 3	Continuous monitors	Average value determined for each MW5 test run
	Moisture	EPA Method 4	Gravimetric Balance	Once per MW5 test run
	CO, CO ₂ concentration	In-stack filter probe and heat-traced Teflon sample line	Non-dispersive infrared analyzer	Continuously during MW5 test runs
	O ₂ concentration	Same as CO/CO ₂	Paramagnetic analyzer	Continuously during MW5 test runs
	THC concentration	Same as CO/CO ₂	Flame ionization detector	Continuously during MW5 test runs
	Dioxin/furan content of woodstove ash samples	Grab samples	Gas chromatography/ Mass Spectrometer	Once per MW5 test run
	Dioxin/furan content of flue wipe samples	Flue wipe with glass wool	Gas chromatography/ Mass Spectrometer	Once for each wood type
	Precursor content of wood feed samples	Grab samples	Gas chromatography/ Mass Spectrometer	One of each wood type
2. Woodstove Ash				
3. Flue Wipe				
4. Oak Pine				

Continuous emissions monitoring of O_2 , CO, CO_2 , and THC was performed by RTI during the three MM5 test runs. These data were obtained to assess variations in combustion conditions during the sampling periods. Instantaneous concentration values for each species monitored were determined every five minutes by the CEM system.

Three types of process samples were taken at Site WS-A: the wood feed, the bottom ash after the burn and the stack flue creosote deposits. The wood samples were taken from a representative log of each type of wood selected at random after the test period. Three identical portions of each wood sample were prepared: one for potential dioxin/furan analysis by Troika, one for dioxin/furan precursor analysis by Radian/RTP, and one for total chlorides analysis by RTI. The ash samples were taken from the woodstove after each test burn and were sent to Troika for dioxin/furan analysis. The flue deposits were taken after the oak and pine tests by wiping the inside of the flue with precleaned glass wool. These samples were sent to Troika for dioxin/furan analysis.

4.2 LABORATORY ANALYSES

Laboratory analyses performed on samples from test Site WS-A included dioxin/furan analyses, dioxin/furan precursor analyses and chloride analyses. Samples analyzed for dioxin/furan are discussed in Section 4.3.1 and samples analyzed for dioxin precursors are discussed in Section 4.3.2. Samples analyzed for chloride are discussed in Section 4.3.3.

4.2.1 Dioxin/Furan Analyses

All dioxin/furan analyses for Site WS-A samples were performed by Troika. Field samples requiring dioxin/furan analysis were prioritized by Tier 4 based on their relative importance to the program objectives. The priority levels, in order of decreasing importance, were designated Priority 1 through Priority 3; however, during this test all samples were designated Priority 1.

Priority 1 samples were sent to Troika with instructions to perform immediate extraction and analysis. These included the MM5 train components for the outlet sampling locations, the ash and flue wipe samples, and an MM5 train field blank.

4.2.2 Dioxin/Furan Precursor Analysis

Dioxin/furan precursor analyses of wood feed samples were performed by Radian/RTP. The specific dioxin/furan precursors analyzed for included chlorophenols, chlorobenzenes, and PCB's. Total chlorine analyses of the wood feed samples were performed by RTI.

5.0 TEST RESULTS

The results of the Tier 4 dioxin/furan emissions tests of Woodstove WS-A are presented in this section. The individual test runs are designated as Runs 01-03 in this report and as Runs 2, 3, and 5 in the RTI report.

Process data obtained during the test runs are presented in Section 5.1, and continuous monitoring results for O_2 , CO, CO_2 , and THC are presented in Section 5.2. Dioxin/furan emissions data are contained in Section 5.3. Ash and flue wipe sample analyses are presented in Section 5.4, and precursor analyses of the wood feed samples are presented in Section 5.5.

5.1 PROCESS DATA

An overview of the woodstove operating data obtained during the Tier 4 test runs is presented in Table 5-1. Additional operating data (e.g., stove temperatures, detailed wood analyses, inlet air flow rates, etc.) are contained in the RTI report.

The feed during all test runs was split cord wood. Oak was burned during Runs 01 and 02, and pine was burned during Run 03. Cured wood was burned during Runs 01 and 03, and uncured wood was burned during Run 02. Burn rates were low for all test runs, ranging from 1.25 kg/hr to 3.5 kg/hr. Low burn rate test runs were purposely selected for the Tier 4 program to maximize the potential for dioxin/furan formation. The wood load ranged from 8.8 kg of initial charge to 20.3 kg of initial charge, which is close to the capacity of the stove. Flue gas flow rates were consistent between test runs, ranging from 19.6 to 27.5 dscfm. These flow rates were typical for this stove at low burn rates.

TABLE 5.1 SUMMARY OF WOODSTOVE OPERATING PARAMETERS DURING
THE TIER 4 TEST RUNS

Run Number	Fuel Type	Wood Moisture (wt %)	Wood Load (kg)	Burn Rate (kg/hr)	Flue Gas Flow (dscfm)
1	Oak	18.7 (cured)	8.8	1.25	19.6
2	Oak	34.9 (uncured)	20.3	3.53	25.1
3	Pine	15.1 (cured)	12.0	1.87	27.5

5.2 CONTINUOUS EMISSIONS MONITORING DATA

Mean values and standard deviations of the continuously monitored combustion gases at the stack location (O_2 , CO, CO_2 , and THC) are shown for each MM5 test run in Table 5-2. The data show that most of the runs have similar mean concentration values for the individual gases. The overall mean values for the three test runs are as follows: oxygen, 17.0 percent by volume (dry); carbon monoxide, 3.7 percent by volume (dry @ 3% O_2); carbon dioxide, 15.8 percent by volume (dry @ 3% O_2); and total hydrocarbons, 4.9 percent by volume (wet @ 3% O_2 , as propane).

Instantaneous concentration values obtained at 5-minute intervals for each of the continuously monitored combustion gases are tabulated in Appendix A-2 and are shown graphically as functions of time in Figures 5-1 through Figures 5-4. These graphs show that in general the measured O_2 values were fairly constant within runs and between runs. During all three runs conducted on the woodstove, the hydrocarbon analyzer was in the maximum reading position. The THC values are to be considered lower bound values, since the instrument's upper limit on the highest range is 10,000 ppmv as methane.

5.3 MM5 DIOXIN/FURAN EMISSIONS DATA

No valid flue gas dioxin/furan emissions data were obtained for the woodstove. The four labelled internal standards spiked in the MM5 train samples could not be recovered. This indicates that both the aqueous and XAD-2 portions of the samples caused serious sample preparation problems. The sample extracts were reported to be yellow in color, and exhibited evidence of significant hydrocarbon contamination. This resulted in peak broadening and overloading of the alumina and carbon GC/MS columns. The Troika laboratory report concluded that the analytical results did not yield any valid indication of whether dioxins/furans were present in the MM5 samples.

TABLE 5-2. MEAN VALUES AND STANDARD DEVIATIONS OF CONTINUOUSLY MONITORED COMBUSTION GASES AT THE OUTLET LOCATION

Parameter (a,b,c)	Run 01	Run 02	Run 03	Average
O ₂ (% vol)	16.8	17.5	16.6	17.0
Standard deviation	(0.4)	(0.3)	(0.5)	
CO (ppmv @ 3% O ₂)	32464.6	41730.2	36419.9	37000
Standard deviation	(5366.3)	(5592.3)	(7050.0)	
CO ₂ (% vol @ 3% O ₂)	14.3	16.9	16.3	15.8
Standard deviation	(2.0)	(1.2)	(1.8)	
THC (ppmv @ 3% O ₂)	40965.2	46577.9	60879.2	49000
Standard deviation	(4057.0)	(10620.4)	(8385.1)	

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

^aGas sampling for the continuous monitors was performed at the outlet location.

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

^cTotal hydrocarbon data are expressed in units of ppmv (wet) as methane.

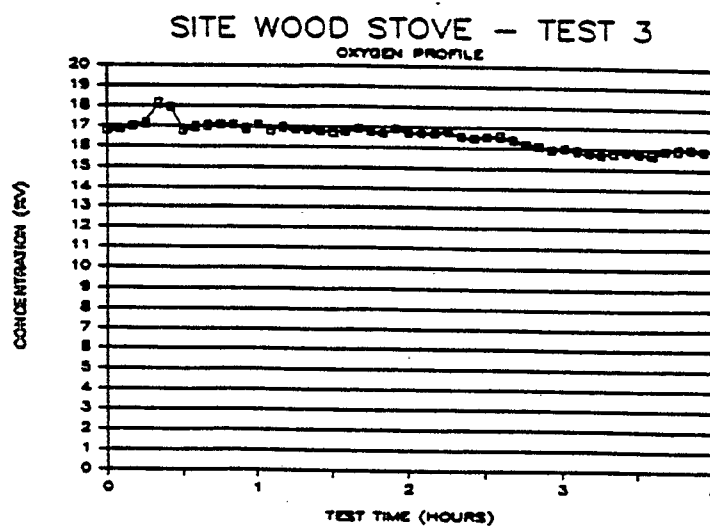
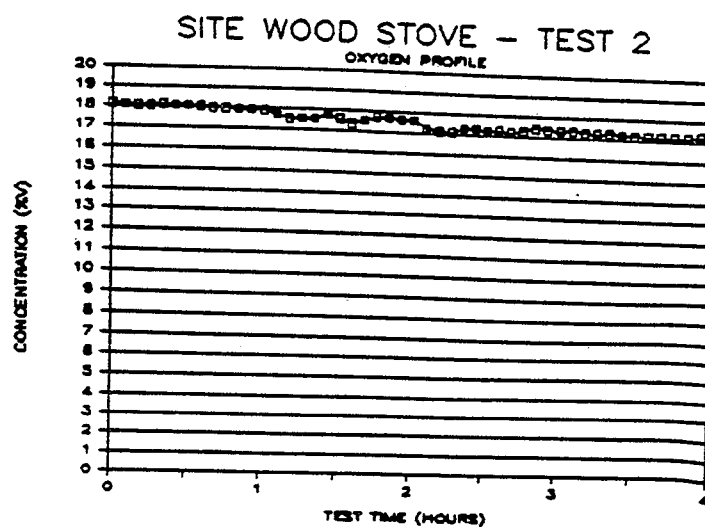
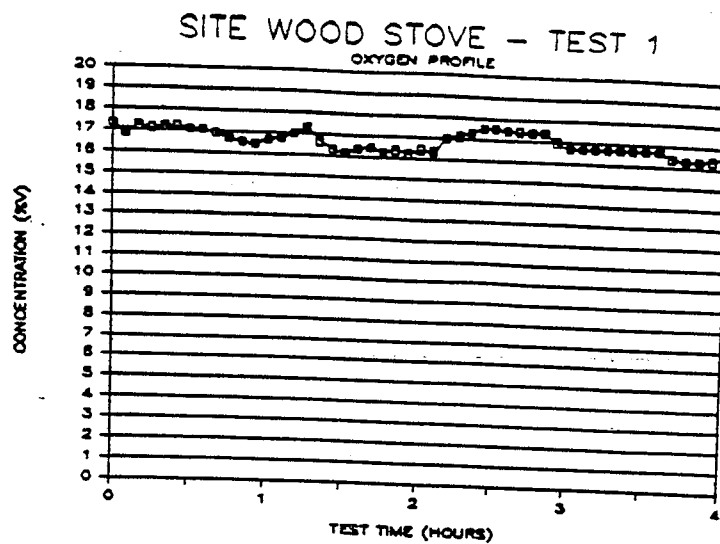


Figure 5-1. Oxygen Concentration Data

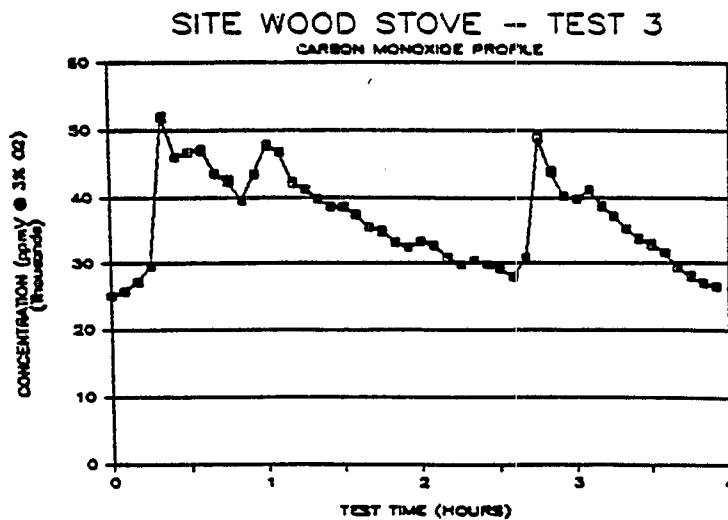
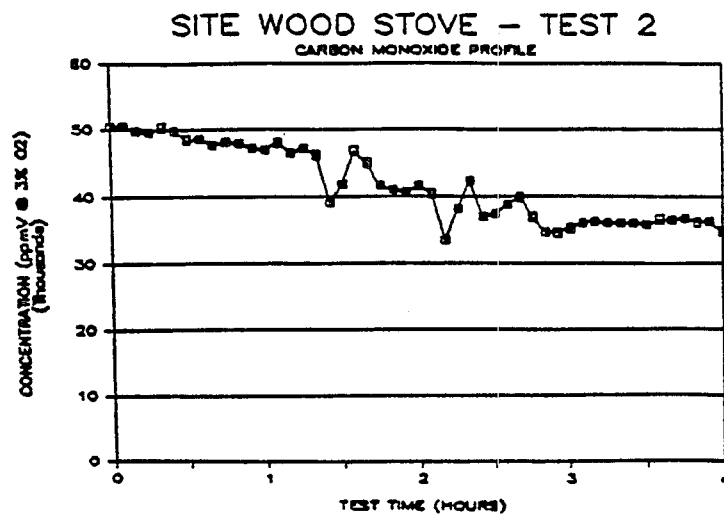
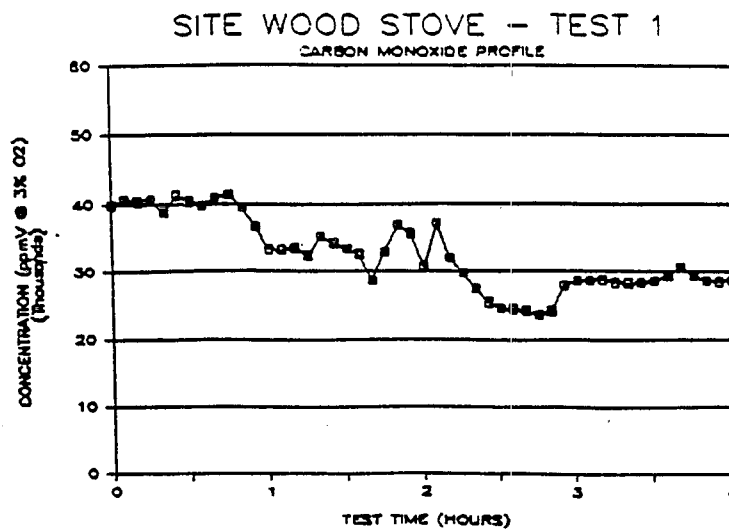


Figure 5-2. Carbon Monoxide Concentration Data
(corrected to 3% O₂)

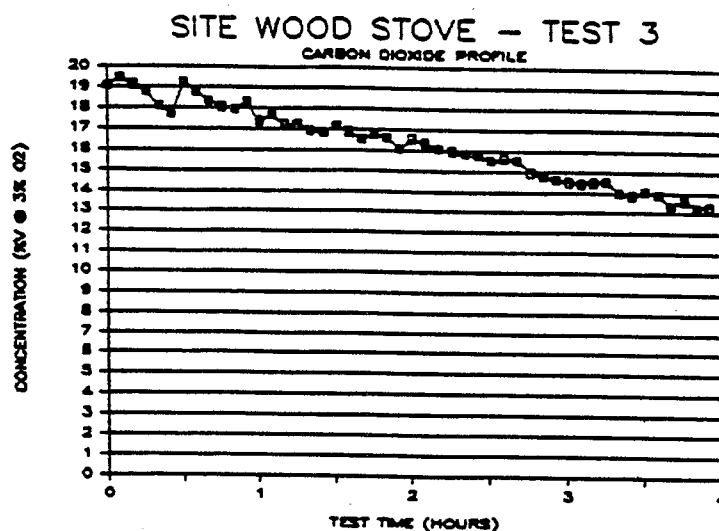
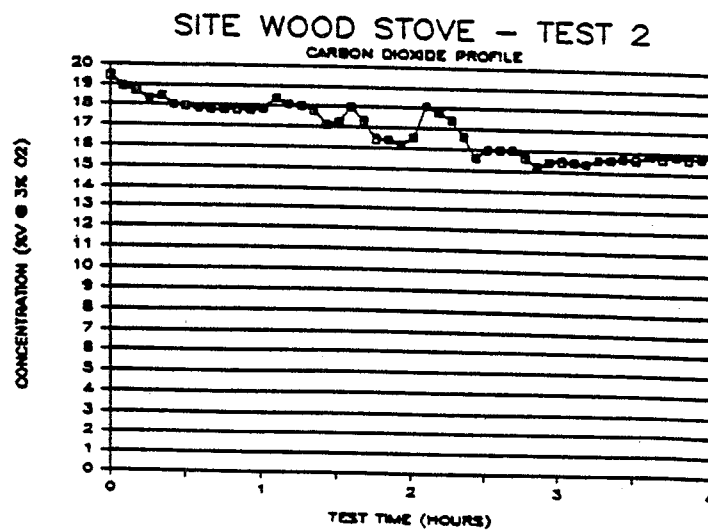
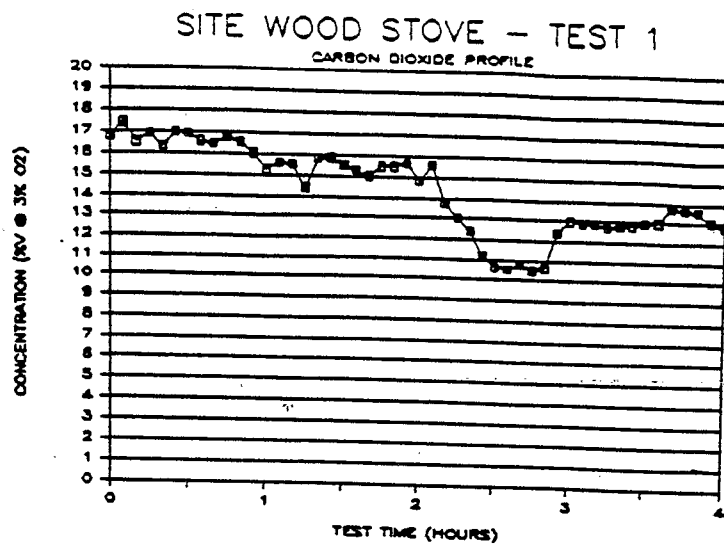


Figure 5-3. Carbon Dioxide Concentration Data
(corrected to 3% O₂)

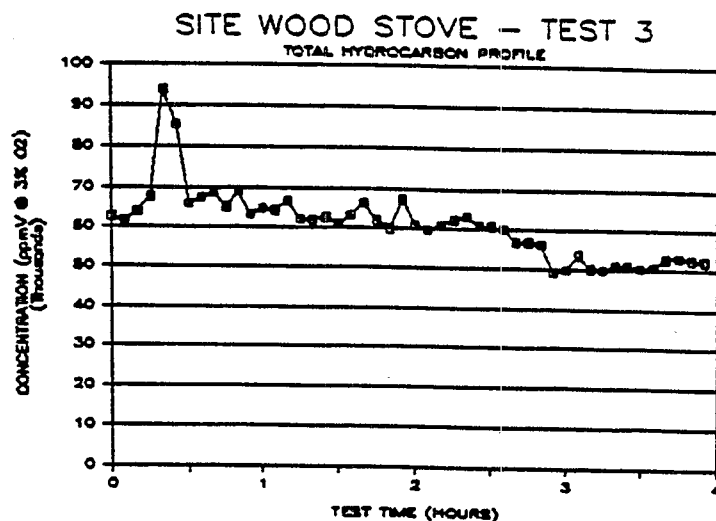
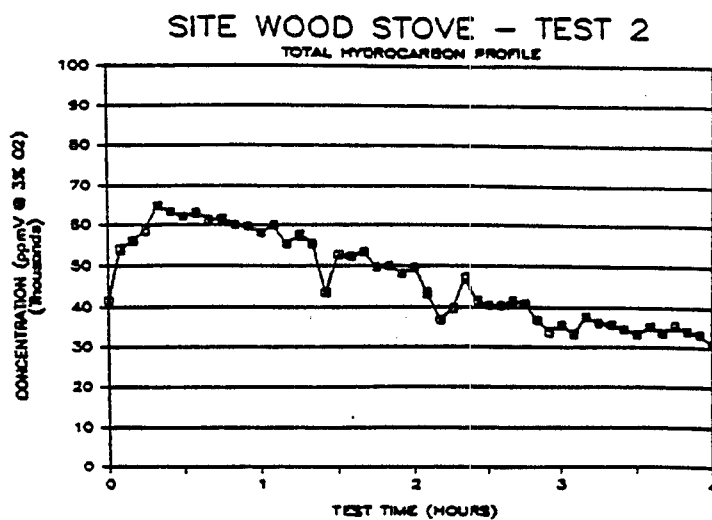
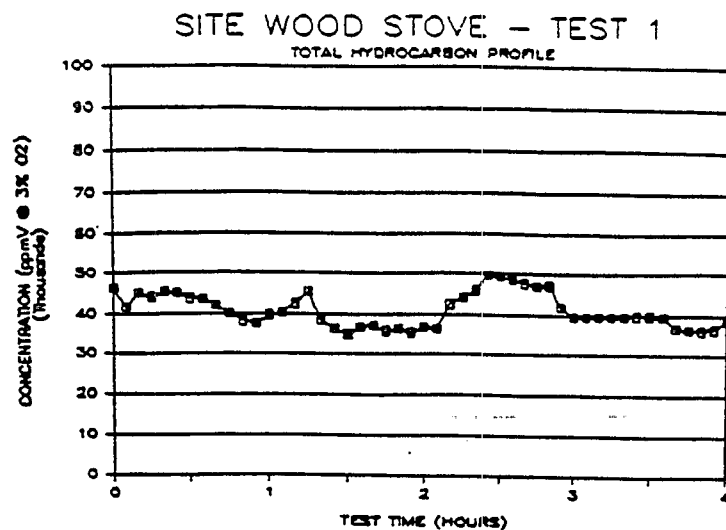


Figure 5-4. Total Hydrocarbon Concentration Data
(corrected to 3% O₂)

5.4 WOODSTOVE ASH AND FLUE WIPE SAMPLE DIOXIN/FURAN DATA

Table 5-3 summarizes the results of dioxin/furan analyses of woodstove ash samples from Runs 01-03 and flue wipe samples from Runs 02 and 03. Octa-CDD was the only dioxin/furan homologue detected in the woodstove ash samples, with the maximum value for any test run being 0.09 ppb octa-CDD. Both hepta-CDD and octa-CDD were detected in the flue wipe samples, with the maximum values for any test run being 0.04 ppb hepta-CDD and 0.3 ppb octa-CDD.

5.5 WOOD FEED PRECURSOR DATA

Table 5-4 summarizes the dioxin/furan precursor data for Site WS-A feed samples. Chlorobenzenes, chlorophenols, and polychlorinated biphenyls were not detected in the oak and pine samples analyzed. The total chloride contents of the oak and pine samples were 125 ppm and 49 ppm, respectively.

TABLE 5-3. DIOXIN/FURAN CONTENT OF WOODSTOVE ASH
AND FLUE WIPE SAMPLES

Dioxin/Furan Homologue	Dioxin/Furan Content, ppb				
	Woodstove Ash Samples			Flue Wipe Samples	
	Run 01	Run 02	Run 03	Run 02	Run 03
<u>Dioxins</u>					
2378 TCDD	a	a	a	a	a
all tetra CDD	ND(0.03)	ND(0.01)	ND(0.04)	ND(0.01)	ND(0.08)
penta CDD	ND(0.02)	ND(0.03)	ND(0.02)	ND(0.02)	ND(0.02)
hexa CDD	ND(0.03)	ND(0.04)	ND(0.03)	ND(0.01)	ND(0.02)
hepta CDD	ND(0.03)	ND(0.03)	ND(0.2)	ND(0.02)	0.04
octa CDD	0.01	0.01	0.09	0.06	0.3
total PCDF	0.01	0.01	0.09	0.06	0.34
<u>Furans</u>					
2378 TCDF	a	a	a	a	a
all tetra CDF	ND(0.03)	ND(0.02)	ND(0.09)	ND(0.02)	ND(0.02)
penta CDF	ND(0.01)	ND(0.01)	ND(0.03)	ND(0.02)	ND(0.03)
hexa CDF	ND(0.01)	ND(0.02)	ND(0.04)	ND(0.03)	ND(0.01)
hepta CDF	ND(0.01)	ND(0.02)	ND(0.08)	ND(0.02)	ND(0.04)
octa CDF	ND(0.01)	ND(0.01)	ND(0.02)	ND(0.006)	ND(0.03)
total PCDF	ND(0.07)	ND(0.08)	ND(0.26)	ND(0.10)	ND(0.13)

ND=species not detected (detection limit in parenthesis)

^aAnalytical detection limit for the 2378 isomers is estimated to be less than half of the detection limits shown for all tetra CDDs and all tetra CDFs.

TABLE 5-4. SUMMARY OF DIOXIN/FURAN PRECURSOR DATA
FOR SITE WS-A FEED SAMPLES

Precursor Category	Oak	Pine
Total Chlorinated Benzenes	ND	ND
Total Chlorinated Biphenyls	ND	ND
Total Chlorinated Phenols	ND	ND
Total Chloride	125 ug/g	49 ug/g

ND = not detected

6.0 SAMPLING LOCATIONS AND PROCEDURES

Details on the sampling locations and methods at Site WS-A are discussed in Sections 6.1 through 6.3. Analytical procedures for continuous monitoring of CO, CO₂, O₂, and THC are included in Section 6.1. All other analytical procedures are discussed in Section 7.0.

6.1 GASEOUS SAMPLING

Two types of gaseous samples were taken during this test program: Modified Method 5 (MM5) and continuous emission monitoring (CEM). The sampling locations and methods are further discussed in this section.

6.1.1. Gaseous Sampling Locations

The Tier 4 MM5 samples were taken at a single point in the center of the 8-inch diameter stack. The sampling location was approximately 14 feet (21 duct diameters) downstream of the stove/stack coupling and 2 feet (3 duct diameters) upstream of the stack discharge. The RTI continuous monitoring probe, which was the nearest upstream flow disturbance, was located 6 feet (9 duct diameters) from the Tier 4 MM5 probe.

6.1.2 Gaseous Sampling Procedures

Gaseous sampling procedures used during the testing are listed in Table 6-1. These procedures are discussed in detail in the Tier 4 Quality Assurance Project Plan (QAPP). A brief description of each method and any necessary deviations from the procedures outlined in the QAPP are provided in the following section.

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

Sample Location	Sample Type or Parameter	Sample Collection Method
Woodstove outlet exhaust stack	Dioxin/Furan	Modified EPA Method 5
	Volumetric Flow	Vane Anemometer
	Molecular Weight	Obtained from CEM Analysis
	Moisture	EPA Method 4

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. Minor deviations from the ASME protocol are discussed later in this section. This sampling method is a modified version of EPA Method 5 that includes a solid sorbent module for trapping vapor phase organics. The MM5 sampling train was used to collect samples at the wood stove outlet exhaust stack sampling location. Following sample recovery, the various parts of the sample (filter, solvent rinses, sorbent traps, etc.) were sent to the EPA's Troika laboratories to quantify 2,3,7,8-TCDD, tetra- through octa- dioxin homologues, and tetra- through octa- furan homologues. A total of three MM5 test runs was conducted at the sampling location, with one test run being conducted at each location per test day. The MM5 samples were collected at a constant rate over a 240-minute on-line sampling period outlet with a sample flow rate of approximately 0.5 scfm.

A schematic diagram of the MM5 sampling train is shown in Figure 6-1. Flue gas is pulled from the stack through a nozzle and a heated glass 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 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. During the woodstove testing the THC level was extremely high and a backup XAD module was inserted to collect any compounds that might have broken through the first module. A chilled impinger train following the sorbent trap is used to remove water from the flue gas, and a dry gas meter was used to measure the sample gas flow.

Modifications to the ASME protocol that were instituted for this test site include the following:

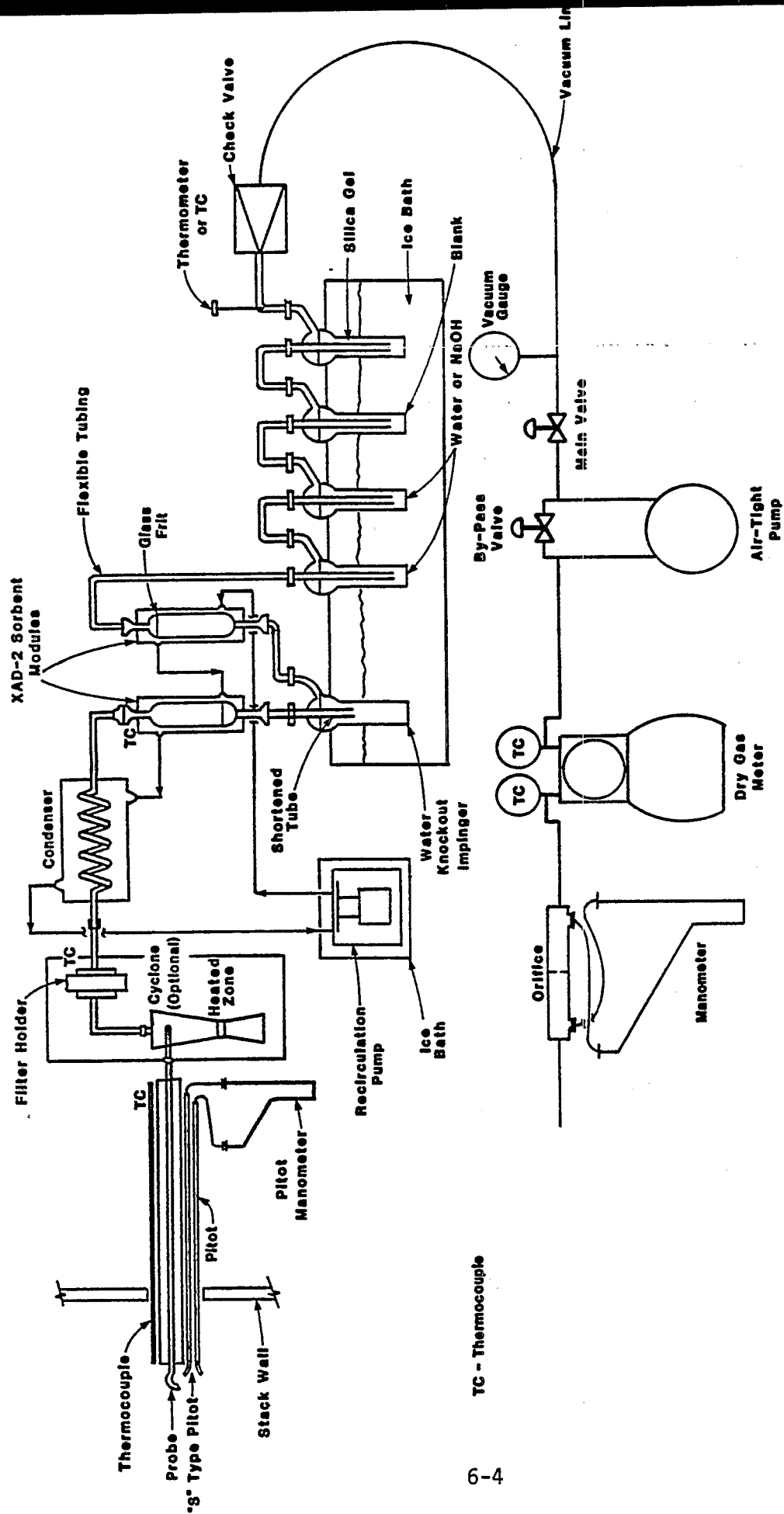


Figure 6-1. Modified Method 5 Train with Back-Up Sorbent Module

1. Sample recovery was modified to include water in the sample train rinsing scheme. Water, acetone, and methylene chloride were used in series to recover the probe, back half/coil, and first impinger samples.
2. A back-up XAD trap was placed between the first and second impingers.
3. Traversing was not performed since the flow rate on a woodstove is approximately 30 ACFM, making measurement by a pitot tube impossible. The flows were taken by a four-inch vane anemometer located in the center of the eight-inch diameter duct. This was the only point of representative flow.
4. The MM5 train condenser was oriented horizontally.
5. The volume sampled was maintained at 0.5 CFM through the meter in order to ensure sufficient sample to analyze, which resulted in high isokinetics.
6. The probe brush specified in the ASME protocol is inert material with a stainless steel handle. To ensure cleanliness, a separate nylon bristle brush attachable to a stainless steel handle was used for each probe cleaning.

6.1.2.2 Volumetric Gas Flow Rate Determination. The average flue gas flow rate was calculated from the average gas velocity as directly measured by the vane anemometer, the average flue gas temperature, the wet molecular weight, and the absolute static pressure. Anemometer readings were taken every 20 minutes during the test.

6.1.2.3 Flue Gas Moisture Determination. The moisture content of the flue gas was determined at the outlet sampling locations using EPA Method 4.

Based on this method, a measured volume of particulate-free gas was pulled through a chilled impinger train. The quantity of condensed water was determined gravimetrically and then related to the volume of gas sampled to determine the moisture content.

6.2 WOOD SAMPLING

Samples were taken of both types of wood burned (oak and pine). Oak was burned during tests one and two and an oak sample was taken from a randomly selected log in the woodpile. Chips were prepared from the sample using a precleaned circular data saw. Two identical oak samples were obtained from tests one and two: a one-liter container was sent to RTI for total chlorine analysis and a one-liter composite was retained at Radian/RTP for precursor analysis. A pine sample for test three was treated similarly.

6.3 ASH SAMPLING

After each test run, samples were obtained of the bottom ash or wood residue left in the firebox. This sample was collected and sent to Troika for dioxin analysis.

6.4 STACK WIPE SAMPLING

After the oak burn and the pine burn, the exhaust stack was wiped with a precleaned portion of glass wool to remove the creosote buildup from the stack wall. This material is thought to contain the heavier organic compounds which condense out on the stack lining. The glass wool containing the creosote was placed in a wide mouth amber jar (precleaned) and sent to Troika for dioxin analysis.

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 the EPA's Troika laboratories for dioxin/furan content included MM5 train samples and the woodstove ash and flue wipe 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 Chlorinated Dibenzo-p-dioxins and Dibenzofurans in Samples from Tier 4 Combustion and Incineration Processes Addendum to EPA 600/3-85/019, May 1986. These procedures are summarized in Section 7.1. Wood feed samples were analyzed by Radian to determine concentrations of chlorinated phenols (CP), chlorobenzenes (CB), and polychlorinated biphenyls (PCB's). Total chlorine analyses of the wood feed samples were performed by RTI. Procedures used for these analyses are detailed in Section 7.2.

7.1 DIOXINS/FURANS

The analytical procedures described in this section were used by Troika for dioxin/furan analysis of MM5 train samples and the woodstove ash and flue wipe samples from Site WS-A. 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; solid samples included filters, XAD resin, woodstove ash samples, and flue wipe samples. Isotopically-labeled surrogate compounds were added to all samples prior to extraction to allow determination of method efficiency.

Organic liquid samples (e.g., acetone and methylene chloride-based MM5 train rinses) were concentrated using a nitrogen blowdown apparatus. The 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 toluene 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 such as the MM5 train impinger samples were extracted with hexane by vigorous shaking for a 3-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/mass spectrometry (GC/MS). The 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 8,000 to 10,000, ion source temperature 270°C.

7.2 DIOXIN/FURAN PRECURSORS

Feed samples for Site WS-A were analyzed by Radian/RTP for CP, CB, and PCB's by GC/MS. 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 WS-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 WS-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.
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.

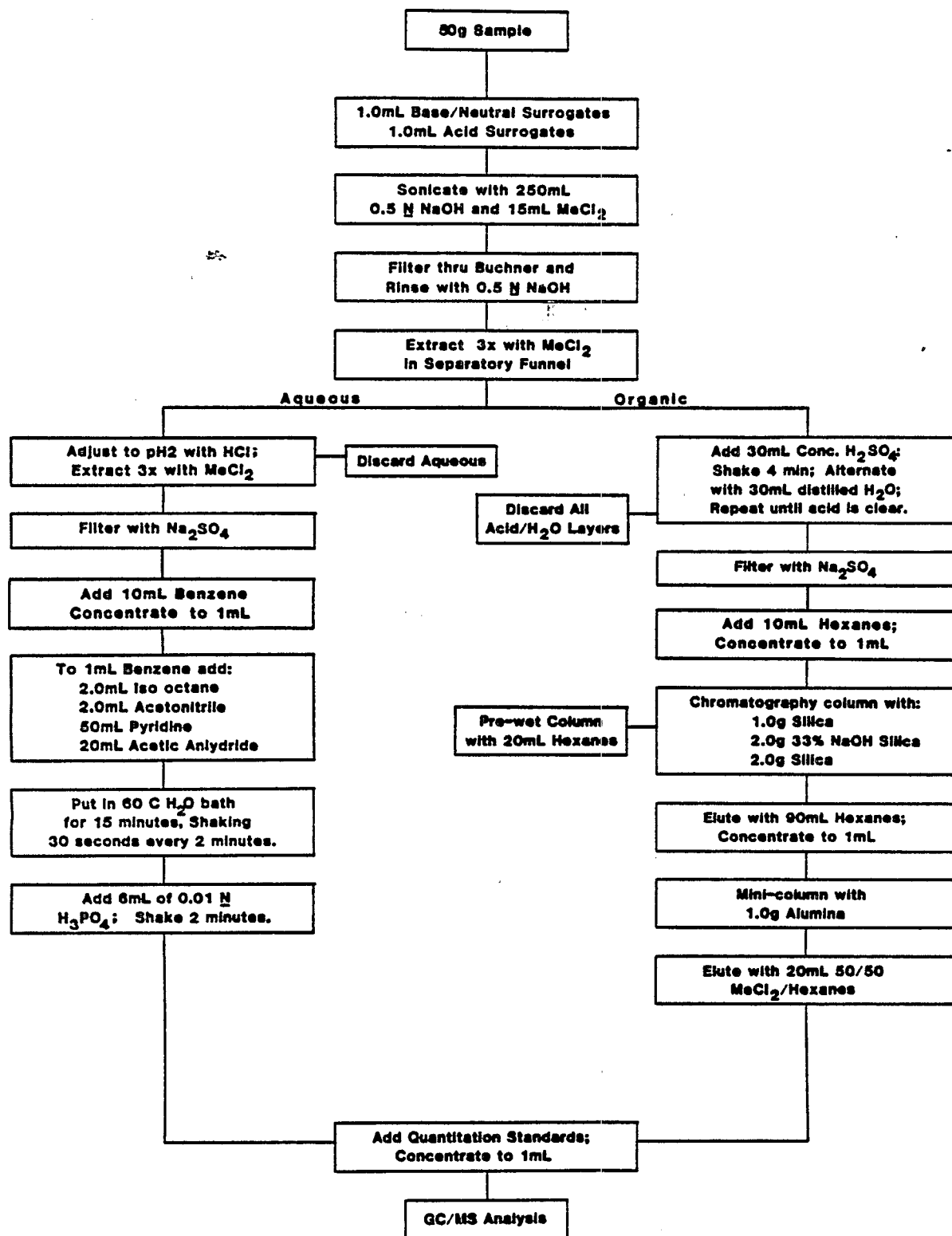


Figure 7-1. Sample Preparation Flow Diagram for Site WS-A Precursor Analyses.

Cleanup of the organic (or base/neutrals) layers 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 2 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 micro-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 percent (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 min-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 N_2 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 Analyses. Analyses for CP, CB, and PCB's 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 Quality Assurance Project Plan. An internal-standard calibration procedure was used for sample quantitation. Compounds of interest were calibrated against a fixed concentration of either d_{12} -chrysene (for CO) or d_8 -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.

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 TOTAL CHLORINE ANALYSIS

Total chlorine concentrations in feed samples were determined by Parr Bomb combustion followed by ion chromatography (IC). An 0.5 g sample was placed in the Parr Bomb with 10 mL of a 50 g/L Na_2CO_3 solution. After combustion of the samples according to standard procedures (ASTM 2015), the contents of the bomb were rinsed into a 100 mL flask and diluted to 100 mL. The resulting solution was analyzed for chloride concentration (Cl^-) by IC using standard anion conditions.

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

Parameter	Chlorobenzenes/ Polychlorinated biphenyls	Chlorophenols
Column	30 m WB DB-5 (1.0 μ 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

<u>Base/Neutrals</u>	<u>Acids</u>
4-chlorobiphenyl	2,5-dichlorophenol
3,3'-dichlorobiphenyl	2,3-dichlorophenol
2,4',5-trichlorobiphenyl	2,6-dichlorophenol
3,3',4,4'-tetrachlorobiphenyl	3,5-dichlorophenol
2,2',6,6'-tetrachlorobiphenyl	3,4-dichlorophenol
2,2,4,5,6-pentachlorobiphenyl	2,3,5-trichlorophenol
2,2',4,4',5,5'-hexachlorobiphenyl	2,3,6-trichlorophenol
2,2',3,4,4',5',6-heptachlorobiphenyl	3,4,5-trichlorophenol
2,2',3,3',4,4',5,5'-octachlorobiphenyl	2,4,5-trichlorophenol
2,2',3,3',4,4',5,6,6'-nonachlorobiphenyl	2,3,4-trichlorophenol
decachlorobiphenyl	2,3,5,6-tetrachlorophenol
p-dichlorobenzene	pentachlorophenol
1,2,4-trichlorobenzene	d ₆ -phenol (SS)
1,2,3,5-tetrachlorobenzene	d ₄ -2-chlorophenol (SS)
pentachlorobenzene	¹³ C ₆ -pentachlorophenol (SS)
hexachlorobenzene	d ₈ -naphthalene (QS)
d ₄ -1,4-dichlorobenzene (SS) ¹	2,4,6-tribromophenol (QS)
3-bromobiphenyl (SS)	d ₁₀ -phenanthrene (QS)
2,2',5,5'-tetrabromobiphenyl (SS)	d ₁₂ chrysene (QS)
2,2',4,4',6,6'-hexabromobiphenyl (SS)	
octachloronaphthalene (QS) ²	
d ₁₀ -phenanthrene (QS)	
d ₁₂ -chrysene (QS)	

¹Surrogate standard.²Quantitation standard.

8.0 QUALITY ASSURANCE/ QUALITY CONTROL (QA/QC)

This section summarizes the results of quality assurance and quality control (QA/QC) activities for WS-A. No valid flue gas dioxin/furan emissions data were obtained for this site. The sample extracts exhibited evidence of significant hydrocarbon contamination. The ash dioxin/furan data for this site were generally within the QC specifications presented in the Tier 4 QAPP. All of the surrogate recoveries for labeled TCDD's were within the specified limits of 50 to 120 percent. The surrogate recoveries for the octa-CDD species from the Run 03 sample was the only run not within the QC limits of 40 to 120 percent for hepta- and octa-CDD's. The results of the analysis of the fortified laboratory QC sample were all within the Tier 4 objective of ± 50 percent. These data indicate that the dioxin/furan results are within accuracy criteria specified for Tier 4.

The dioxin/furan precursor analysis of the feed samples was not as accurate as the dioxin/furan homologue analysis. Surrogate recoveries of the six isotopically labeled compounds used as surrogates varied considerably by specific surrogate species and by wood type. The surrogate recoveries were generally below the specified 50 percent objective. In spite of the low recoveries of the surrogates for some feed samples, the resulting analytical sensitivity for the target analytes was considered acceptable for the purpose of this study.

The following sections summarize the results of all WS-A QA/QC activities. Manual gas sampling methods are considered in Section 8.1 and the laboratory analyses QA/QC activities are summarized in Section 8.2.

8.1 MANUAL GAS SAMPLING

Manual gas sampling methods used at WS-A included Modified Method 5 (MM5), and EPA Methods 1 through 4. These methods are discussed in Section 6.0. Quality assurance and quality control (QA/QC) activities for the manual methods centered around 1) equipment calibration, 2) glassware precleaning, 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.

Pre-test calibrations or inspections were conducted on the anemometer, sampling nozzles, temperature sensors and analytical balances. Both pre-test and post-test calibrations were also performed on dry gas meters. All of this equipment met the calibration criteria specified in the QAPP. Differences in pre- and post-test dry gas meter calibrations were less than 3.0 percent.

An extensive precleaning procedure was implemented 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 potentially interfere with the analysis for dioxins and furans. To minimize the potential for contamination in the field, all sample train glassware was kept capped until use and a controlled environment was maintained in the recovery trailer during sample train assembly and recovery.

Procedural QC activities during manual gas sampling focused on:

- . inspecting equipment visually,
- . collecting sampling train blanks,
- . conducting pre-test, port change, and post-test sample train leak checks,
- . maintaining proper temperatures at the filter housing, sorbent trap and impinger train,
- . maintaining sampling rates, and
- . recording all data on preformatted data sheets.

TABLE 8-1. GLASSWARE PRECLEANING PROCEDURE

NOTE: USE DISPOSABLE GLOVES AND ADEQUATE VENTILATION

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

^a (X3) = three times.

Sample custody procedures used during this program emphasized careful documentation of the samples collected and the use of chain-of-custody records for samples to be transported. Steps taken to identify and document samples collected included labeling each sample with a unique alphanumeric code and logging the sample in a master sample logbook. All samples shipped to Troika or returned to Radian were also logged on chain-of-custody records that were signed by the sampler at shipment and then by the receiving laboratory when the samples arrived. Each sample container was also sealed with chain-of-custody seal so that the container could not be opened without tearing the seal.

8.2 LABORATORY ANALYSIS

QA/QC activities were carried out for dioxin/furan and precursor analyses performed on Site WS-A samples. The dioxin/furan analyses are considered in Section 8.2.1, and the precursor analyses are considered in Section 8.2.2.

8.2.1 Dioxin/Furan Analysis

8.2.1.1 Recovery of Labelled Surrogate Compounds. No valid flue gas dioxin/furan emissions data were obtained for the woodstove. The four labelled internal standards spiked in the MM5 train samples could not be recovered. This indicates that both the aqueous and XAD-2 portions of the samples caused serious sample preparation problems. The sample extracts were reported to be yellow in color, and exhibited evidence of significant hydrocarbon contamination. This resulted in peak broadening and overloading of the alumina and carbon columns. The Troika laboratory report submitted for this test site concluded that the analytical results did not yield any valid indication of whether dioxins/furans were present in the MM5 samples.

Analytical recovery values for the labelled TCDD and octa-CDD species spiked onto woodstove ash and creosote flue wipe samples are shown in Table 8-2. In general, the surrogate recoveries for these samples are within the Tier 4 QA objectives of 50 to 120 percent for the TCDD species and 40 to

TABLE 8-2. PERCENT SURROGATE RECOVERIES FOR SITE WS-A
ASH AND FLUE WIPE DIOXIN/FURAN ANALYSES

Sample	$^{13}\text{C}_{12}$ TCDD	$^{13}\text{C}_{12}$ OCDD
<u>Woodstove Ash Samples</u>		
Run 01	94	68
Run 02	93	72
Run 03	99	25
<u>Creosote Flue Wipe Samples</u>		
Run 02	61	92
Run 03	45	52

120 percent for the octa-CDD species. The only exception was the 25 percent recovery value for the octa-CDD species for the woodstove ash sample from Run 03.

8.2.1.2 Sample Blanks. Table 8-3 summarizes the analytical results reported by Troika for internal laboratory blanks, laboratory fortified QC samples, and field recovery blank MM5 train samples. In general, these data showed good surrogate recoveries, with values within the Tier 4 QA objectives of 50 to 120 percent for the tetra-CDD surrogates and 40 to 120 percent for the hepta- and octa-CDD surrogates. Comparisons of the measured and spiked values for the laboratory fortified QC samples were all within the Tier 4 QA objectives of \pm 50 percent. The field blank MM5 sample was clean except for very small quantities of hepta-CDD and octa-CDD. The analytical results for the QA samples at Site WS-A indicate that the sample preparation procedures and GC/MS detection technique were performing in a satisfactory manner, and that no significant MM5 train blanking problems occurred.

8.2.2 Precursor Analyses

Table 8-4 presents analytical recovery efficiencies for six isotopically labeled compounds used as surrogates for the target precursor analytes in the Site WS-A feed samples. The surrogate recovery values in Table 8-4 vary considerably by specific surrogate species and by wood type. Several of the recoveries 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. 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.

TABLE 8-3. ANALYSIS RESULTS FOR QUALITY CONTROL SAMPLES

Flue Gas Quality Control Samples				
Compound	Laboratory Blank	Fortified Laboratory QC Sample		Field Blank MM5 Train Outlet
		Measured Value	True Value ^{a,b}	
Amount Detected (Nanograms per Sample)				
<u>Dioxins</u>				
2378 TCDD	ND	0.3	0.4 (-25)	ND
Other TCDD	ND	ND	ND (0)	ND
Penta CDD	ND	ND	ND (0)	ND
Hexa CDD	ND	1.0	1.6 (-37)	ND
Hepta CDD	ND	2.6	2.4 (8)	0.2
Octa CDD	0.1	3.0	3.2 (-6)	0.4
<u>Furans</u>				
2378 TCDF	ND	0.4	0.4 (0)	ND
Other TCDF	ND	ND	ND (0)	ND
Penta CDF	ND	0.6	0.8 (-25)	ND
Hexa CDF	ND	0.9	1.6 (-44)	ND
Hepta CDF	ND	2.6	2.4 (8)	ND
Octa CDF	ND	3.0	3.2 (-6)	ND
Surrogate Recoveries (Percent)				
³⁷ C ₁₄ -TCDD	100	84	NA	80
¹³ C ₁₂ -TCDD	96	104	NA	74
³⁷ C ₁₄ -Hepta CDD	41	44	NA	83
¹³ C ₁₂ -Octa CDD	42	49	NA	90

^aTrue values represent the amounts of each homologue spiked into the laboratory fortified QC samples.

^bValue shown in parenthesis is the percentage difference between the measured and the true value:

$$\% = \frac{\text{Measured Value} - \text{True Value}}{\text{True Value}} \times 100$$

NR = Not reported by Troika.

ND = Not detected.

NA = Not applicable.

TABLE 8-4. PERCENT SURROGATE RECOVERIES FOR SITE WS-A FEED SAMPLES

Surrogate Compound	Percent Surrogate Recovery	
	Oak ^a	Pine
<u>Base Neutrals Fraction</u>		
d ₄ -dichlorobenzene	34, 25	18
2', 5, 5' tetra bromobiphenyl	93, 94	45
2', 4, 4', 6, 6' hexabromobiphenyl	50, 35	1
<u>Acids Fraction</u>		
d ₆ -phenol	14, 13	6
d ₄ -2-chlorophenol	30, 28	21
¹³ C ₆ -pentachlorophenol	26, 20	26

^aDuplicate analyses were performed on the oak sample .

APPENDIX A
FIELD SAMPLING DATA

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 : WOOD STOVE TEST FOR DIOXIN PROJECT
PLANT SITE : RTI//DURHAM , NORTH CAROLINA
SAMPLING LOCATION : WOOD STOVE EXHAUST
TEST # : WS-MM5-01
DATE : 04/11/85
TEST PERIOD : 1353-1753

PARAMETER -----	VALUE -----
Sampling time (min.)	240
Barometric Pressure (in.Hg)	29.9
Sampling nozzle diameter (in.)	.5
Meter Volume (cu.ft.)	132.02
Meter Pressure (in.H2O)	.91
Meter Temperature (F)	104.04
Stack dimension (sq.in.)	50.2656
Stack Static Pressure (in.H2O)	-.00001
Stack Moisture Collected (gm)	133.7
Absolute stack pressure(in Hg)	29.9
Average stack temperature (F)	124.0833
Percent CO2	3.28
Percent O2	16.8
Percent N2	79.92
Delps Subroutine result	.3771501
DGM Factor	.997
Pitot Constant	.99

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 : WOOD STOVE TEST FOR DIOXIN PROJECT
 PLANT SITE : RTI//DURHAM , NORTH CAROLINA
 SAMPLING LOCATION : WOOD STOVE EXHAUST
 TEST # : WS-MM5-01
 DATE : 04/11/85
 TEST PERIOD : 1353-1753

PARAMETER -----	RESULT -----
Vm(dscf)	123.4069
Vm(dscm)	3.494882
Vw gas(scf)	6.303955
Vw gas (scm)	.178528
% moisture	4.860008
Md	.9513999
MWd	29.1968
MW	28.65264
Vs(fpm)	65.4332
Vs (mpm)	19.94915
Flow(acfm)	22.84055
Flow(acmm)	.6468443
Flow(dscfm)	19.63082
Flow(dscmm)	.5559447
% I	670.9438
% EA	390.7995

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 : WOOD STOVE TEST FOR DIOXIN PROJECT
PLANT SITE : RTI//DURHAM , NORTH CAROLINA
SAMPLING LOCATION : WOOD STOVE EXHAUST
TEST # : WS-MM5-02
DATE : 04/17/85
TEST PERIOD : 1515-1915

PARAMETER -----	VALUE -----
Sampling time (min.)	240
Barometric Pressure (in.Hg)	29.9
Sampling nozzle diameter (in.)	.5
Meter Volume (cu.ft.)	122.452
Meter Pressure (in.H2O)	.71
Meter Temperature (F)	113.6
Stack dimension (sq.in.)	50.2656
Stack Static Pressure (in.H2O)	-.00001
Stack Moisture Collected (gm)	203.4
Absolute stack pressure(in Hg)	29.9
Average stack temperature (F)	150.8958
Percent CO2	3.15
Percent O2	17.54
Percent N2	79.31
Delps Subroutine result	.5180025
DGM Factor	.997
Pitot Constant	.99

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 : WOOD STOVE TEST FOR DIOXIN PROJECT
 PLANT SITE : RTI//DURHAM , NORTH CAROLINA
 SAMPLING LOCATION : WOOD STOVE EXHAUST
 TEST # : WS-MM5-02
 DATE : 04/17/85
 TEST PERIOD : 1515-1915

PARAMETER -----	RESULT -----
Vm(dscf)	112.5001
Vm(dscm)	3.186004
Vw gas(scf)	9.59031
Vw gas (scm)	.2715976
% moisture	7.855087
Md	.9214491
MWd	29.2056
MW	28.32539
Vs(fpm)	90.38786
Vs (mpm)	27.55728
Flow(acfm)	31.55139
Flow(acmm)	.8935352
Flow(dscfm)	25.11113
Flow(dscmm)	.7111472
% I	478.1586
% EA	516.2106

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 : WOOD STOVE TEST FOR DIOXIN PROJECT
PLANT SITE : RTI//DURHAM , NORTH CAROLINA
SAMPLING LOCATION : WOOD STOVE EXHAUST
TEST # : WS-MM5-03
DATE : 05/01/85
TEST PERIOD : 1220-1620

PARAMETER -----	VALUE -----
Sampling time (min.)	240
Barometric Pressure (in.Hg)	29.9
Sampling nozzle diameter (in.)	.5
Meter Volume (cu.ft.)	123.18
Meter Pressure (in.H2O)	.73
Meter Temperature (F)	107.5
Stack dimension (sq.in.)	50.2656
Stack Static Pressure (in.H2O)	-.00001
Stack Moisture Collected (gm)	140.8
Absolute stack pressure(in Hg)	29.9
Average stack temperature (F)	169.2041
Percent CO2	3.88
Percent O2	16.56
Percent N2	79.56
Delp's Subroutine result	.5723236
DGM Factor	.997
Pitot Constant	.99

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 : WOOD STOVE TEST FOR DIOXIN PROJECT
 PLANT SITE : RTI//DURHAM , NORTH CAROLINA
 SAMPLING LOCATION : WOOD STOVE EXHAUST
 TEST # : WS-MM5-03
 DATE : 05/01/85
 TEST PERIOD : 1220-1620

PARAMETER -----	RESULT -----
Vm(dscf)	114.391
Vm(dscm)	3.239554
Vw gas(scf)	6.638721
Vw gas (scm)	.1880086
% moisture	5.485198
Md	.945148
MWd	29.2832
MW	28.66429
Vs(fpm)	99.27441
Vs (mpm)	30.26659
Flow(acfm)	34.65339
Flow(acmm)	.981384
Flow(dscfm)	27.46613
Flow(dscmm)	.7778408
% I	444.5079
% EA	372.6507

Program Revision:1/16/84

APPENDIX A-2
CONTINUOUS EMISSION MONITORING RESULTS

CEMS DATA - SITE WS - TEST 1

**	FACTOR	**	NORMALIZED / CORRECTED DATA - WITH				
**	FOR 3% O2	**	ACTUAL O2 *				
**	NORMALIZATION	**					
**	OF	**					
**	OTHER PROCESS	**	TIME	O2	CO	CO2	THC
**	GASES	**		(%V)	(PPMV)	(%V)	(PPMV)
**		**			@ 3% O2	@ 3% O2	@ 3% O2
**	=====	**	=====	=====	=====	=====	=====
**		**					
**	4.9571	**	1355	17.3	39909.4	16.8	46151.9
**	4.4450	**	1400	16.9	40733.9	17.4	41384.2
**	4.8365	**	1405	17.2	40389.9	16.5	45029.6
**	4.7217	**	1410	17.1	40748.4	16.9	43960.5
**	4.8588	**	1415	17.2	38846.5	16.3	45237.3
**	4.8222	**	1420	17.2	41292.5	17.0	44896.1
**	4.6871	**	1425	17.1	40398.0	16.9	43638.2
**	4.6663	**	1430	17.1	39799.0	16.6	43444.8
**	4.4952	**	1435	16.9	40893.1	16.5	41851.9
**	4.2731	**	1440	16.7	41346.5	16.8	39783.8
**	4.1027	**	1445	16.5	39607.3	16.5	38197.2
**	4.0297	**	1450	16.5	36751.0	16.0	37517.9
**	4.2619	**	1455	16.7	33409.1	15.3	39679.6
**	4.3247	**	1500	16.8	33373.8	15.6	40264.4
**	4.5921	**	1505	17.0	33646.3	15.5	42489.3
**	5.0112	**	1510	17.3	32417.4	14.4	45282.7
**	4.2167	**	1515	16.7	35357.2	15.8	38472.6
**	3.9066	**	1520	16.3	34276.4	15.9	36371.5
**	3.7597	**	1525	16.1	33491.5	15.5	34986.8
**	3.9646	**	1530	16.4	32668.0	15.3	36911.3
**	4.0352	**	1535	16.5	28621.4	15.0	37243.4
**	3.8412	**	1540	16.2	32976.7	15.5	35762.7
**	3.9211	**	1545	16.3	37027.3	15.5	36507.0
**	3.8045	**	1550	16.2	35712.5	15.7	35420.7
**	3.9849	**	1555	16.4	30795.0	14.8	36852.4
**	3.9117	**	1600	16.3	37196.5	15.6	36419.2
**	4.5593	**	1605	17.0	32134.3	13.7	42448.9
**	4.7354	**	1610	17.1	29842.8	13.0	44088.5
**	4.9571	**	1615	17.3	27487.0	12.4	45889.1
**	5.3561	**	1620	17.6	25468.1	11.2	49533.5
**	5.3290	**	1625	17.5	24689.1	10.7	49148.0
**	5.2416	**	1630	17.5	24514.9	10.5	48534.9
**	5.1319	**	1635	17.4	24284.1	10.8	47531.5
**	5.0751	**	1640	17.4	23619.7	10.5	46783.6
**	5.0823	**	1645	17.4	24278.3	10.7	47142.8
**	4.5408	**	1650	17.0	27908.0	12.4	41962.8
**	4.2337	**	1655	16.7	28662.0	13.0	39416.8
**	4.2337	**	1700	16.7	28662.0	12.9	39416.8
**	4.2277	**	1705	16.7	28714.4	12.9	39361.0
**	4.2277	**	1710	16.7	28291.6	12.7	39361.0
**	4.2447	**	1715	16.7	28218.9	12.8	39519.7
**	4.2670	**	1720	16.7	28413.8	12.8	39726.9
**	4.2619	**	1725	16.7	28614.4	13.0	39679.6
**	4.2337	**	1730	16.7	29322.5	13.0	39416.8
**	3.9401	**	1735	16.4	30713.3	13.8	36683.8
**	3.9066	**	1740	16.3	29319.0	13.6	36371.5
**	3.8922	**	1745	16.3	28646.2	13.6	36237.1
**	3.9358	**	1750	16.4	28530.6	13.1	36643.4
**	4.1502	**	1755	16.6	28744.6	12.8	38640.0

CEMS DATA - SITE WS - TEST 1

NO. PTS. 49
 MEAN 4.4121
 STD. DEV. 0.4

NO. PTS. 49 49 49 49
 MEAN 16.8 32464.6 14.3 40965.2
 STD. DEV. 0.4 5366.3 2.0 4057.0

* CO, CO2, NOX and THC values are corrected to 3% O2.
 To obtain actual measured values, divide values in the
 table by the corresponding normalization factor.

CEMS DATA - SITE WS - TEST 2

			NORMALIZED / CORRECTED DATA - WITH ACTUAL O2 *				
FACTOR FOR 3% O2 NORMALIZATION OF OTHER PROCESS GASES			TIME	O2 (%V)	CO (PPMV) @ 3% O2	CO2 (%V) @ 3% O2	THC (PPMV) @ 3% O2
=====			=====	=====	=====	=====	=====
** 6.4388 **			1514	18.1	50545.0	19.4	41414.7
** 6.3229 **			1519	18.1	50538.6	19.0	54111.0
** 6.2478 **			1524	18.0	49870.1	18.7	56311.6
** 6.2984 **			1529	18.1	49511.6	18.3	58757.6
** 6.4112 **			1534	18.1	50398.2	18.5	64663.1
** 6.3860 **			1539	18.1	49849.2	18.0	63266.3
** 6.3611 **			1544	18.1	48528.5	17.9	61975.7
** 6.2741 **			1549	18.0	48624.3	17.9	63054.7
** 6.1176 **			1554	18.0	47753.7	17.8	61261.3
** 6.1176 **			1559	18.0	48157.5	17.8	61579.4
** 6.0596 **			1604	17.9	48034.3	17.8	60123.2
** 5.9906 **			1609	17.9	47224.1	17.8	59744.5
** 5.9567 **			1614	17.9	47088.0	17.9	58221.2
** 5.6008 **			1619	17.7	48110.5	18.4	60208.1
** 5.2771 **			1624	17.5	46491.5	18.1	55573.4
** 5.3385 **			1629	17.5	47208.4	18.0	57581.1
** 5.2865 **			1634	17.5	46166.8	17.8	55534.4
** 5.6916 **			1639	17.8	39146.6	17.1	43386.9
** 5.3851 **			1644	17.6	41976.7	17.2	52795.3
** 5.0437 **			1649	17.4	46886.0	18.0	52363.4
** 5.2959 **			1654	17.5	45020.1	17.3	53467.0
** 5.6413 **			1659	17.7	41667.0	16.4	49717.2
** 5.5729 **			1704	17.7	41038.5	16.4	49999.6
** 5.4857 **			1709	17.6	40759.1	16.1	48011.3
** 5.4774 **			1714	17.6	41606.0	16.5	49728.9
** 4.8974 **			1719	17.2	40335.0	18.1	43160.8
** 4.7367 **			1724	17.1	33573.7	17.8	36737.9
** 4.7155 **			1729	17.1	38110.6	17.4	39704.4
** 4.9722 **			1734	17.3	42432.9	16.6	47072.0
** 4.9722 **			1739	17.3	37053.0	15.6	41358.9
** 4.8974 **			1744	17.2	37470.0	16.0	40232.1
** 4.9122 **			1749	17.3	38830.8	16.0	40279.9
** 4.8235 **			1754	17.2	39938.6	16.0	41477.3
** 4.9352 **			1759	17.3	36885.7	15.6	40745.1
** 5.1585 **			1804	17.4	34629.0	15.2	36873.0
** 5.0594 **			1809	17.4	34575.6	15.4	33912.9
** 5.0281 **			1814	17.3	35251.9	15.5	35709.5
** 5.0594 **			1819	17.4	36083.3	15.4	33265.3
** 4.9352 **			1824	17.3	36342.9	15.3	37492.8
** 4.9122 **			1829	17.3	36011.2	15.6	35937.5
** 4.9271 **			1834	17.3	36120.3	15.6	35494.5
** 4.8509 **			1839	17.2	35989.2	15.7	34499.9
** 4.8378 **			1844	17.2	35891.9	15.6	33221.4
** 4.8300 **			1849	17.2	36635.6	15.8	35090.0
** 4.8235 **			1854	17.2	36533.2	15.7	33687.3
** 4.8235 **			1859	17.2	36692.3	15.8	35365.9
** 4.8235 **			1904	17.2	36210.0	15.7	34058.7
** 4.9189 **			1909	17.3	36223.0	15.7	33222.5
** 4.9041 **			1914	17.3	34760.3	16.0	30866.5

CEMS DATA - SITE WS - TEST 2

NO. PTS. 49
 MEAN 5.3843
 STD. DEV. 0.6

NO. PTS. 49 49 49 49
 MEAN 17.5 41730.2 16.9 46577.9
 STD. DEV. 0.3 3592.3 1.2 10620.4

* CO, CO2 and THC values are corrected to 3% O2.
 To obtain actual measured values, divide values in the
 table by the corresponding normalization factor.

CEMS DATA - SITE WS - TEST 3

FACTOR FOR 3% O2 NORMALIZATION OF OTHER PROCESS GASES			NORMALIZED / CORRECTED DATA - WITH ACTUAL O2 *				
			TIME	O2 (%V)	CO (PPMV) @ 3% O2	CO2 (%V) @ 3% O2	THC (PPMV) @ 3% O2
=====			=====	=====	=====	=====	=====
**	4.3153	**	1220	16.8	25050.5	19.1	62589.6
**	4.4002	**	1225	16.8	25833.6	19.5	61611.6
**	4.6182	**	1230	17.0	27265.6	19.1	64007.7
**	4.7367	**	1235	17.1	29528.6	18.8	67673.3
**	6.4365	**	1240	18.1	52084.4	18.1	93799.6
**	5.9966	**	1245	17.9	46150.2	17.7	85404.3
**	4.3510	**	1250	16.8	46834.1	19.3	65935.0
**	4.5328	**	1255	17.0	47145.6	18.8	67398.1
**	4.6457	**	1300	17.0	43567.7	18.3	68654.6
**	4.6530	**	1305	17.1	42458.4	18.1	64941.6
**	4.7006	**	1310	17.1	39640.4	18.0	68958.2
**	4.4494	**	1315	16.9	43537.5	18.3	63315.2
**	4.6871	**	1320	17.1	47873.9	17.3	64799.0
**	4.3755	**	1325	16.8	46856.8	17.7	64236.1
**	4.5328	**	1330	17.0	42259.2	17.2	66650.2
**	4.4002	**	1335	16.8	41265.0	17.2	61990.0
**	4.4307	**	1340	16.9	39845.2	16.9	61914.5
**	4.3341	**	1345	16.8	38547.8	16.8	62715.0
**	4.2936	**	1350	16.7	38565.1	17.1	60951.9
**	4.3510	**	1355	16.8	37501.2	16.9	63280.9
**	4.4941	**	1400	16.9	35624.7	16.5	66413.8
**	4.3574	**	1405	16.8	35020.0	16.8	61931.0
**	4.2457	**	1410	16.7	33329.0	16.6	59932.7
**	4.5134	**	1415	16.9	32550.4	16.1	67289.7
**	4.2347	**	1420	16.7	33568.3	16.6	60767.7
**	4.2751	**	1425	16.7	32807.4	16.3	59787.8
**	4.2751	**	1430	16.7	30832.3	16.1	61031.9
**	4.3101	**	1435	16.7	29804.6	15.9	62242.7
**	4.1131	**	1440	16.5	30523.0	15.8	63102.4
**	4.0297	**	1445	16.5	29815.9	15.8	60768.1
**	4.0868	**	1450	16.5	29024.2	15.5	60696.5
**	4.1244	**	1455	16.6	27885.2	15.6	60031.0
**	3.9427	**	1500	16.4	30907.1	15.5	56779.3
**	3.7653	**	1505	16.1	48974.6	14.9	56866.6
**	3.7160	**	1510	16.1	43837.7	14.8	56312.4
**	3.6060	**	1515	15.9	40321.9	14.6	49091.6
**	3.6479	**	1520	16.0	39827.2	14.5	50099.6
**	3.5572	**	1525	15.9	41224.8	14.4	53643.1
**	3.4710	**	1530	15.7	38774.7	14.5	50204.7
**	3.4258	**	1535	15.7	37214.9	14.5	50120.0
**	3.5057	**	1540	15.8	35305.7	14.0	51186.4
**	3.5139	**	1545	15.8	33842.7	13.8	51208.6
**	3.4636	**	1550	15.7	32939.0	14.0	50475.4
**	3.4489	**	1555	15.7	31661.3	13.9	50713.2
**	3.5736	**	1600	15.9	29310.4	13.3	52910.2
**	3.6227	**	1605	16.0	28000.2	13.6	53062.4
**	3.6643	**	1610	16.0	26991.1	13.3	52582.4
**	3.5980	**	1615	15.9	26423.6	13.3	52124.1

CEMS DATA - SITE WS - TEST 3

NO. PTS. 48
MEAN 4.2047
STD. DEV. 0.6

NO. PTS. 48 48 48 48
MEAN 16.6 36419.9 16.3 60879.2
STD. DEV. 0.5 7050.0 1.8 8385.1

* CO, CO2 and THC values are corrected to 3% O2.
To obtain actual measured values, divide values in the
table by the corresponding normalization factor.

TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-450/4-84-014v		2.	3. RECIPIENT'S ACCESSION NO.	
4. TITLE AND SUBTITLE National Dioxin Study Tier 4 - Combustion Sources Final Test Report - Site 13 Residential Wood Stove WS - A			5. REPORT DATE April 1987	
			6. PERFORMING ORGANIZATION CODE	
7. AUTHOR(S) Michael W. Hartman, Deborah J. Benson Lawrence E. Keller			8. PERFORMING ORGANIZATION REPORT NO. 87-222-109-02-25	
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	
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			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 residential woodstove conducted by Radian Corporation. The stove is a freestanding noncatalytic model manufactured by Atlanta Stove Works and offered for sale in the Sears Catalog (#42G84156N). During testing oak and pine were burned at low burn rates, which is representative of normal residential use. The test was the 13th in a series of dioxin/furan emissions tests conducted under Tier 4 of the National Dioxin Study. The primary objective 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.</p> <p>Residential woodstoves are among 8 combustion source categories that have been tested in the Tier 4 program. The tested woodstove, hereafter referred to as Woodstove WS-A, is a test unit located at an EPA contractor facility. This stove was selected for inclusion in the Tier 4 program due to its location in the RTP area and because simultaneous testing of the stove was already being conducted for another EPA program (Integrated Air Cancer Project). The woodstove tested is considered representative of woodstoves built in the last 5 to 10 years.</p> <p>No dioxin/furan stack data were obtained from this source. Labelled internal standards used to determine analytical recovery efficiency were not detected because of the very high levels of hydrocarbons present in the stack gas. Dioxin/furan ash data are presented.</p>				
KEY WORDS AND DOCUMENT ANALYSIS				
a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS		c. COSATI Field/Group
Air Emissions Combustion Sources Dioxin Furans 2,3,7,8 Tetrachlorodibenzo-p-dioxin Woodstoves		Air Pollution Emissions Data		
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