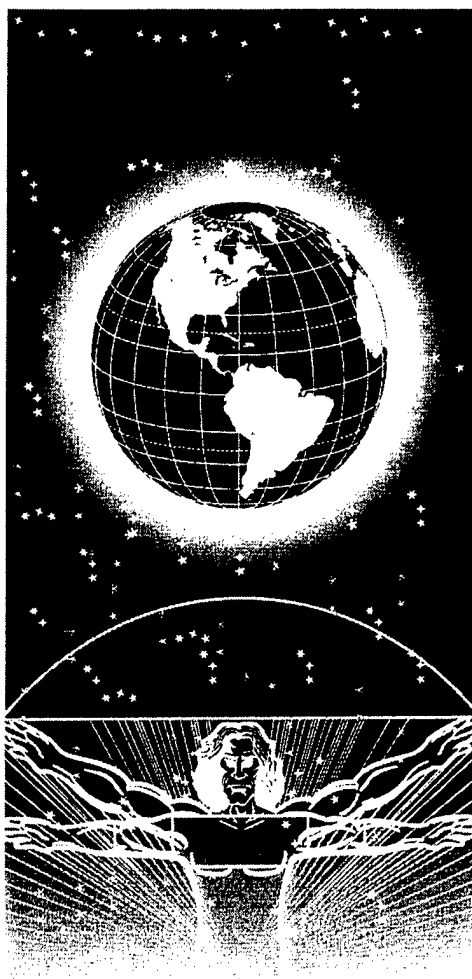




UNITED STATES AIR FORCE IERA

Characterization of Environmental and Health Exposures During a Composite Aircraft Fire and Simulated Aircraft Recovery Operations

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TABLE OF CONTENTS

LIST OF FIGURES.....	v
LIST OF TABLES.....	vi
VIDEO CLIPS.....	vi
ACKNOWLEDGEMENTS.....	vii
I. BACKGROUND.....	1
A. Hammer IPT.....	1
B. Purpose of Study.....	1
C. Previous Carbon Fiber Studies and CORKER.....	1
D. Reported Cases of Post Crash Illnesses.....	2
II. TEST SETUP AND DESIGN.....	2
A. The Burn Facility.....	2
B. Ventilation System.....	3
C. Test Parameters.....	5
D. Mishap Scenario.....	9
E. The Composite Wing Box.....	10
III. SAMPLING LOCATIONS/PROTOCOL.....	
A. Active Burn Sampling.....	10
B. Post Burn Sampling.....	15
IV. SAMPLE TESTS DISCUSSION.....	15
A. Temperature and Heat Flux.....	15
B. Industrial Hygiene Samples.....	17
C. Environmental Air Samples.....	25
D. Hazardous Waste Analysis of Burnt Carbon Fiber Epoxy Composite.....	62
V. CONCLUSION.....	68
REFERENCES.....	69-70
APPENDIX.....	71
Graph 1: PM 2.5 Flow Rates in JP-8 Test #1.....	72
Graph 2: Impactor Flow Rates in JP-8 Test #1.....	73
Graph 3: Temperature 5 Feet above the Test Pan in JP-8 Test #1.....	74
Graph 4: Temperature 10 Feet above the Test Pan in JP-8 Test #1.....	75
Graph 5: Temperature 15 Feet above the Test Pan in JP-8 Test #1.....	76
Graph 6: Temperature 20 Feet above the Test Pan in JP-8 Test #1.....	77
Graph 7: Ceiling Temperatures at Ventilation Inputs in JP-8 Test #1.....	78
Graph 8: O2 and CO2 Measured at the Ceiling in JP-8 Test #1.....	79
Graph 9: PM2.5 Flow Rates in JP-8 Test #2.....	80

Graph 10: Impactor Flow Rates in JP-8 Test #2.....	81
Graph 11: Total Particulate, O ₂ , & CO ₂ Flow Rates in JP-8 Test #2.....	82
Graph 12: Temperature 5 Feet above the Test Pan in JP-8 Test #2.....	83
Graph 13: Temperature 10 Feet above the Test Pan in JP-8 Test #2.....	84
Graph 14: Temperature 15 Feet above the Test Pan in JP-8 Test #2.....	85
Graph 15: Temperature 20 Feet above the Test Pan in JP-8 Test 2.....	86
Graph 16: Ceiling Temperature in JP-8 Test #2.....	87
Graph 17: Heat Flux on Composite in JP-8 Test #2.....	88
Graph 18: Integrated Heat Flux on Composite in JP-8 Test #2.....	89
Graph 19: O ₂ and CO ₂ Measured at the Test Pan in JP-8 Test #2.....	90
Graph 20: PM _{2.5} Flow Rates in Composite Test #1.....	91
Graph 21: Impactor Flow Rates in Composite Test #1.....	92
Graph 22: Impactor Flow Rates	93
Graph 23: Temperature 5 Feet above the Test Pan in Composite Test #1.....	94
Graph 24: Temperature 10 Feet above the Test Pan in Composite Test #1.....	95
Graph 25: Temperature 15 Feet above the Test Pan in Composite Test #1.....	96
Graph 26: Temperature 20 Feet above the Test in Composite Test #1.....	97
Graph 27: Ceiling Temperature in Composite Test #1.....	98
Graph 28: Temperatures Below Composite Test #1.....	99
Graph 29: Temperatures Inside Composite Test #1.....	100
Graph 30: Temperatures Above Composite in Composite Test #1.....	101
Graph 31: Heat Flux on Composite in Composite Test #1.....	102
Graph 32: Integrated Heat Flux on Composite in Composite Test #1.....	103
Graph 33: O ₂ and CO ₂ Measured at the Test Pan in Composite Test #1.....	104
Graph 34: PM _{2.5} Flow Rates in Composite Test #2.....	105
Graph 35: Impactor Flow Rates in Composite Test #2.....	106
Graph 36: Total Particulate, O ₂ & CO ₂ Flow Rates in Composite Test #2.....	107
Graph 37: Temperature 5 Feet above the Test Pan in Composite Test #2.....	108
Graph 38: Temperature 10 Feet above the Test Pan in Composite Test #2.....	109
Graph 39: Temperature 15 Feet above the Test Pan in Composite Test #2.....	110
Graph 40: Temperature 20 Feet above the Test Pan in Composite Test #2.....	111
Graph 41: Ceiling Temperature in Composite Test #2.....	112
Graph 42: Temperatures Below Composite in Composite Test #2.....	113
Graph 43: Temperatures Inside Composite in Composite Test #2.....	114
Graph 44: Temperatures Above Composite in Composite Test #2.....	115
Graph 45: Heat Flux on Composite in Composite Test #2.....	116
Graph 46: Integrated Heat Flux on Composite in Composite Test #2.....	117
Graph 47: O ₂ and CO ₂ Measured at the Test Pan in Composite Test #2.....	118
Graph 48: PM _{2.5} Flow Rates in Composite Test #3.....	119
Graph 49: Impactor Flow Rates in Composite Test #3.....	120
Graph 50: Total Particulate, O ₂ , & CO ₂ Flow Rates in Composite Test #3.....	121
Graph 51: Temperature 5 Feet above the Test Pan in Composite Test #3.....	122
Graph 52: Temperature 10 Feet above the Test Pan in Composite Test #3.....	123
Graph 53: Temperature 15 Feet above the Test Pan in Composite Test #3.....	124
Graph 54: Temperature 20 Feet above the Test Pan in Composite Test #3.....	125
Graph 55: Ceiling Temperature in Composite Test #3.....	126
Graph 56: Temperatures Below Composite in Composite Test #3.....	127
Graph 57: Temperatures Inside Composite in Composite Test #3.....	128
Graph 58: Temperatures Above Composite in Composite Test #3.....	129
Graph 59: Heat Flux on Composite in Composite Test #3.....	130
Graph 60: Integrated Heat Flux on Composite in Composite Test #3.....	131
Graph 61: O ₂ and CO ₂ Measured at the Test Pan in Composite Test #3.....	132

LIST OF FIGURES

Figure 1. Burn Facility.....	3
Figure 2. Vent System.....	3
Figure 3. JP-8 Test #1 Setup.....	5
Figure 4. JP-8 Test #1-40s After Ignition.....	5
Figure 5. Damaged Composite Material.....	6
Figure 6. Composite Burn 1 Material Damaged.....	6
Figure 7. Wing Description.....	7
Figure 8. Composite Test #1 Setup.....	7
Figure 9. Composite Test #1-60s After Ignition.....	7
Figure 10. Composite Test #2 Setup.....	9
Figure 11. Composite Test #2-60s After Ignition.....	9
Figure 12. Composite Test #3 Setup.....	9
Figure 13. Composite Test #3 60s After Ignition.....	9
Figure 14. Location of Thermocouples, Total Particulate, Impactors, and PM 2.5.....	11
Figure 15. Approximate Thermocouple and Heat Flux Sensor Locations.....	12
Figure 16. Composite Test #3 IR Image.....	16
Figure 17. Composite Burn 18 Sep 2000.....	20
Figure 18. Composite Burn 19 Sep 2000.....	21
Figure 19. Particle Size Profile, 13 Sept 2000.....	40
Figure 20. Particle Size Profile, 15 Sept 2000.....	40
Figure 21. Particle Size Profile, Hot Fire, 18 Sept 2000.....	41
Figure 22. Particle Size Profile, Smoldering Period, 18 Sept 2000.....	41
Figure 23. Particle Size Profile, Hot Fire, 19 Sept 2000.....	42
Figure 24. Particle Size Profile, Smoldering Period, 19 Sept 2000.....	42
Figure 25. TIC SPME #1, 9 Sept 2000.....	48
Figure 26. TIC SPME #3, PDMS Filter, 9 Sept 2000.....	49
Figure 27. TIC SPME Sampler PDMS-H04, 15 Sept 2000.....	49
Figure 28. TIC SPME PDMS-H03, 15 September 2000.....	50
Figure 29. TIC SPME PDMS/DVB-H02, 15 September 2000.....	50
Figure 30. TIC SPME C0106, 18 September 2000.....	55
Figure 31. TIC SPME C0104, 18 September 2000.....	55
Figure 32. TIC SPME C0105, 18 September 2000.....	56
Figure 33. TIC SPME PDMS-H02, 18 September 2000.....	56
Figure 34. TIC SPME PDMS-H04, 18 September 2000.....	57
Figure 35. TIC SPME C0102, 19 September 2000.....	58
Figure 36. TIC SPME C0106, 19 September 2000.....	58
Figure 37. TIC SPME C0101, 19 September 2000.....	59
Figure 38. 15 September 2000 Pre-Burn sample.....	62
Figure 39. 18 September 2000 Post-Burn sample.....	62

LIST OF TABLES

Table 1. Exhaust System Capacity.....	4
Table 2. Make-Up Air Capacity.....	4
Table 3. Test Parameters.....	5
Table 4. Occupational Exposure Limits.....	19
Table 5. Chemical Task Exposure Concentrations During the IR/SIB Phase.....	21-22
Table 6. Fiber/Particulate Task Exposure Concentrations During the IR/SIB Phase.....	22
Table 7. PAH Task Exposure Concentrations During the IR/SIB Phase.....	23-24
Table 8. Fiber/Particulate Task Exposure Concentrations During the Recovery Phase.....	24
Table 9. Plate Parameters for Anderson Mark III Impactor.....	28
Table 10. Total Particulate Data for Large Scale Composite Burns.....	32
Table 11. Summary of Results from PM2.5 Sample Collections.....	35
Table 12. Postburn Respirable Particulate Results.....	36
Table 13. Results from Particle Sizing Cascade Impactor Samples, based on particle densities of 1 g/cm ³	43-44
Table 14. Particle Sizing cascade impactor results based on particle densities=1.8 g/cm ³	45-46
Table 15. Summary of Qualitative SPME Results from the test burn on 9 September 2000.....	48
Table 16. Summary of qualitative SPME/GC/MS results from 15 September 2000 test burn.....	52
Table 17. Summary of PDMS/Carboxen tentatively identified compounds for 18 September 2000.....	52-54
Table 18. Compounds tentatively identified from PDMS/Carboxen SPME fibers exposed during 19 September test burn.....	59-61
Table 19. Characteristics of Hazardous Waste.....	66-67
Table 20. PPE Decision Matrix	68

VIDEO CLIPS

Video Clip 1.....	8
Video Clip 2.....	8

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I Background

A. HAMMER IPT

As the result of a T-3 Class A mishap Safety Investigation Board finding, the Air Force Safety Center (AFSC) expressed concern over the absence of standardized Air Force policy, procedures, and training for handling composite materials following a mishap. The Industrial Hygiene Branch of the Air Force Institute for Environment, Safety, and Occupational Health Risk Analysis (AFIERA), the Air Force Civil Engineer Support Agency (AFCESA), and the Air Force Safety Center (AFSC) were tasked by SAF/MIQ to establish an Integrated Product Team (IPT) to address these concerns. The effort is being implemented under the acronym Hazardous Aerospace Material Mishap Emergency Response (HAMMER). The HAMMER IPT has expanded its scope beyond composite material to include all hazardous aerospace material (HAM) such as: radioactive material, fuels, metals, coating systems, etc. In order to characterize personnel exposures, the IPT decided to conduct a large scale burn study involving the combustion of composites. The study was conducted in September 2000 at Tyndall AFB, Florida.

B. Purpose of Study

The purpose of the study was to conduct an exposure assessment during operations that typically occur during an aircraft mishap. Several composite wing boxes were burned, using JP-8 as an ignition source, and post-crash mishap operations were simulated. Environmental samples were collected during the fire to identify and quantify combustion byproducts (gaseous and particulate). The data were used to identify any materials that may be present post-crash. Personal breathing zone air samples were collected while workers conducted mishap investigation and recovery operations. The results of this study will be used to make standardized recommendations to: (1) assess hazards at a crash site, (2) recommend task-specific personal protective equipment, and (3) estimate downwind particulate/fiber concentrations.

C. Previous Carbon Fiber Studies and CORKER

National Aeronautic and Space Administration (NASA) conducted composite burn studies more than 20 years ago. The purpose was to determine downwind post crash electrical hazards posed by millimeter size carbon fibers when released during an aircraft mishap involving fire. Within the Air Force, the studies were referred to as "CORKER." There were approximately 270 burns conducted that led to large scale outdoor burns at Dugway Proving Grounds, Utah.

A burn test conducted at the Naval Weapon Center revealed that airborne fibers size distribution trended towards the respirable range. The next large scale "CORKER" study included a collection of fibers in the respirable range (less than 80 micrometers in length, less than 3 micrometer in diameter, and with length-to-diameter ratios from 3:1 to 10:1) with the sole

purpose of explaining the origin of the smaller size fibers. It was determined that the fire could cause carbon fiber to fibrillate producing smaller size fibers even to the extent of ashing.

The collection of respirable range fibers raised exposure concerns downwind. The fiber data collected from the Naval Weapon Center burn were evaluated for approximate downwind concentrations. The computed concentration was compared to the NIOSH 10-hour work shift exposure limits for respirable-sized fibrous glass or other man-made fibers. The respirable size carbon fiber concentration was well below the NIOSH standards. The health concern for carbon fibers within the Air Force was dropped.

The recent surge in post crash exposure anxiety regarding "mishap" carbon fiber/epoxy composite exposures necessitated a complete review of historical scientific data to better understand the risks associated with aircraft mishaps involving fire. As a result, a review of previous carbon fiber burn studies was conducted. The review of NASA studies led to two conclusions: (1) the NASA work was not focused on "health issues"; therefore, health-based sampling methods were not employed (2) the test designs did not simulate conditions that we would expect at an aircraft crash site (i.e. fire duration, ignition source).

D. Reported Cases of Post Crash Illnesses

This issue also became important due to cited cases of crash site illnesses and injuries. Concerns about the potential hazards from exposure to composite fibers, particulates, and smoke generated from fires related to mishaps were raised. The sources of the cited incidents are often unsupported by formal documentation. However, referring to these cases is important since they provide actual incidents of exposure with reported health effects. In the late 1980s, a Navy F-18 fighter plane went down on Santa Catalina Island. Two search and rescue personnel were exposed to ash and debris and experienced persistent diminished labored breathing and heightened reactivity to histamine challenge. It is unclear as to the extent of personal protective equipment (PPE) worn by the search and rescue personnel. In 1990, a Royal Air Force (RAF) GR.5 Harrier mishap occurred in Denmark. The RAF recovery team reported sore throats and eye, respiratory and skin irritation. The firefighters did not report any health problems. However, it was reported that following this incident the RAF imposed more stringent PPE requirements. In 1997, after responding to a USAF F-117A mishap, 22 Baltimore area firefighters complained of labored breathing, eye and skin irritation, nausea, and headaches.

II Test Setup and Design

A. The Burn Facility

Large-scale tests were conducted on Tyndall AFB, FL at the AFRL Test Range II Burn Facility shown in **Figure 1**. The facility is an 80 foot by 75 foot quonset hut structure with a 32 foot maximum ceiling height. Estimated volume of the hangar is 154,000 ft³.

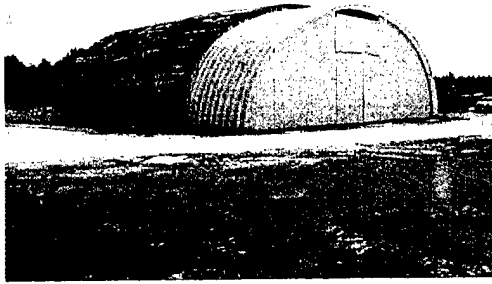


Figure 1. Burn Facility

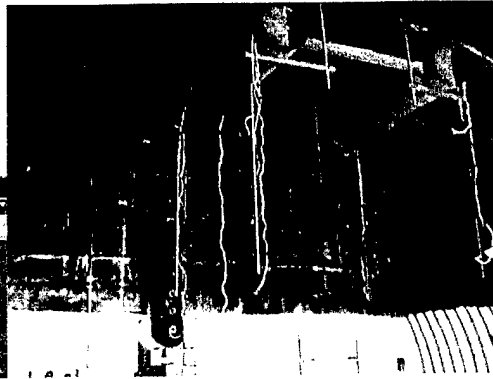


Figure 2. Vent System

B. Ventilation System

1. Physical Description

The facility was modified with the installation of a ventilation system, shown in **Figure 2**. The system has two 36-inch ducts that feed into a 48-inch duct. A series of spray nozzles in the 48-inch duct removed particulate matter from the air (scrubber). Semicircular openings were fitted with a shutter that can be moved to adjust the size of the opening or close the opening if necessary.

The plume enters the “scrubber” water mist generated by a series of 5 nozzle heads equal distance apart. The water captures the particulates and drains into a collection system. The water is re-circulated back to the nozzle heads after being filtered. A 48" duct exits the collection area where another set of five nozzle heads is positioned in the center of the pipe. The second set of nozzles is positioned at the same height as the first set to capture particulate matter that was not captured in the first. The duct proceeds up the backside of the building to the exhaust fan.

2. System Capacity

Face velocity measurements were taken to quantify volumetric airflow. A hot-wire anemometer was used. Six duct openings were measured (Table 1). The fan exhausted 20,881 cubic feet per minute (CFM) of air from the facility. The system purged the hangar air at 8 air changes per hour. Make-up air was supplied to prevent oxygen starvation of the fire (Table 2). One industrial blower and three axial fans were installed. The industrial blower was located outside the hangar and ducted close to the steel pan. The air movers provided a total of 21,878 CFM of make-up air to the hangar during the fire.

TABLE 1. Exhaust System Capacity

Duct	Area (ft ²)	AVG Face Velocity (fpm)	CFM
LFO-2	1.07	2292	2452
LFM-3	3.28	2102	6893
RFM-4	2.83	2258	6391
RFO-5	1.15	1960	2254
RBI-6	0.57	2317	1327
LBI-1	0.76	2043	1563
		TOTAL	20881

TABLE 2. Make-up Air Capacity

Air Mover	Area (ft ²)	AVG Face Velocity (fpm)	CFM
Blower #1	0.19	3425	672
Fan #1	3.14	3683	11564
Fan #2	1.48	3300	4884
Fan #3	1.48	3215	4758
		TOTAL	21878

C. Test Parameters

TABLE 3. Test Parameters

Test Name	JP-8 Quantity	Article	Total weight (lbs)	Est. comp weight (lbs)	Date
JP-8 Test #1	17 GPM Flowing	Fuel	N/A	N/A	9-Sep-00
JP-8 Test #2	10 Gallons	Fuel	N/A	N/A	13-Sep-00
Comp Test #1	10 Gallons	Strips	20	20 lbs	15-Sep-00
Comp Test #2	80 Gallons	Wing tip	287	155	18-Sep-00
Comp Test #3	80 Gallons	Wing tip	316	171	19-Sep00

N/A=not applicable

1. JP-8 Test #1

The fire pan size (15 feet by 15 feet) and fuel flow rate (17 GPM) were selected for this test based on the size/amount of the composite material planned to be subjected to a post-crash fuel fire. **Figure 3** shows the test setup. The fuel was ignited with a propane torch. **Figure 4** shows the fire size 40 seconds after ignition. This was a very intense fire and was determined to be destructive for the burn facility and the test equipment.

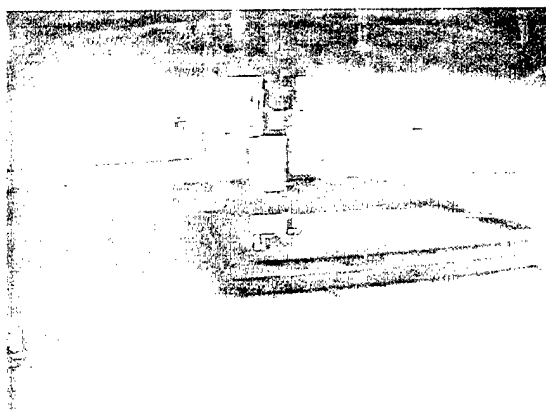


Figure 3. JP-8 Test #1 Setup



Figure 4. JP-8 Test #1 - 40s After Ignition

2. JP-8 Test #2

For the second test, the fire size was reduced to a 5 ft² pan (2.25 feet by 2.25 feet) with a fixed 10 gallons of JP-8 fuel. Fuel was not pumped into the pan for this fire or the remaining tests. The pan was placed in an eight-foot diameter pan. The fuel was ignited with a propane torch. No composite material was burned during this test. Both JP-8 trial tests were performed to

confirm/establish: (1) equipment set-up and operation, (2) data acquisition, (3) sampler sequence, and (4) fire size.

3. Wing Damage

A 12.5-ton bulldozer with caterpillar tracks repeatedly ran over the wing (**Figures 5,6, and 7**). The material was laid flat on the concrete and then it was placed on top of an angle iron to increase the weight/force being applied (to attempt to further damage). There was considerable damage to the exterior of the wing and probably internal damage. The wing was hollow thus vulnerable to crushing and general breaking of the composite material. The entire wing box was weighed intact prior to cutting and introducing damage. An Ohaus electronic industrial scale was used to obtain the pre- and post- weights. Weights were obtained with the materials placed in a wooden crate. Post-burn weights were obtained by placing burned composite sections and recovered pieces back into the crate prior to re-weighing the composite. Composite material percentage was estimated based upon the weight of the wing box.

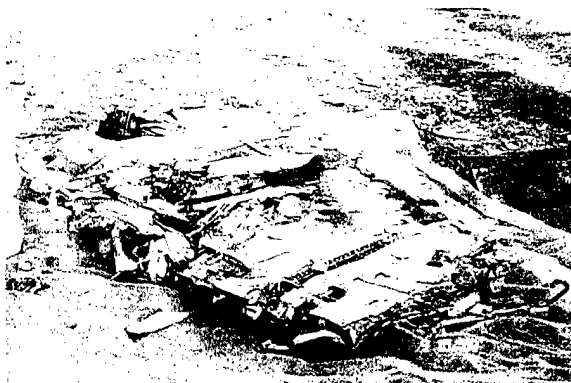


Figure 5. Damaged Composite Material



Figure 6. Composite Burn 1 Material Damaged

4. Composite Burn 1

Twenty pounds of composite material was cut out of the wing box for this test (**Figure 6**). In addition to the JP-8, the composite material sample was placed above the fuel surface. The fire size for the first composite burn was a 5 ft² pan (2.25 feet by 2.25 feet) with 10 gallons of JP-8 fuel. The 5 ft² pan was placed inside an eight-foot diameter pan. The composite material was placed on a grate supported by two custom-made steel horses. **Figure 8** shows the test setup. The fuel was ignited with a propane torch. **Figure 9** shows the fire one minute after ignition.

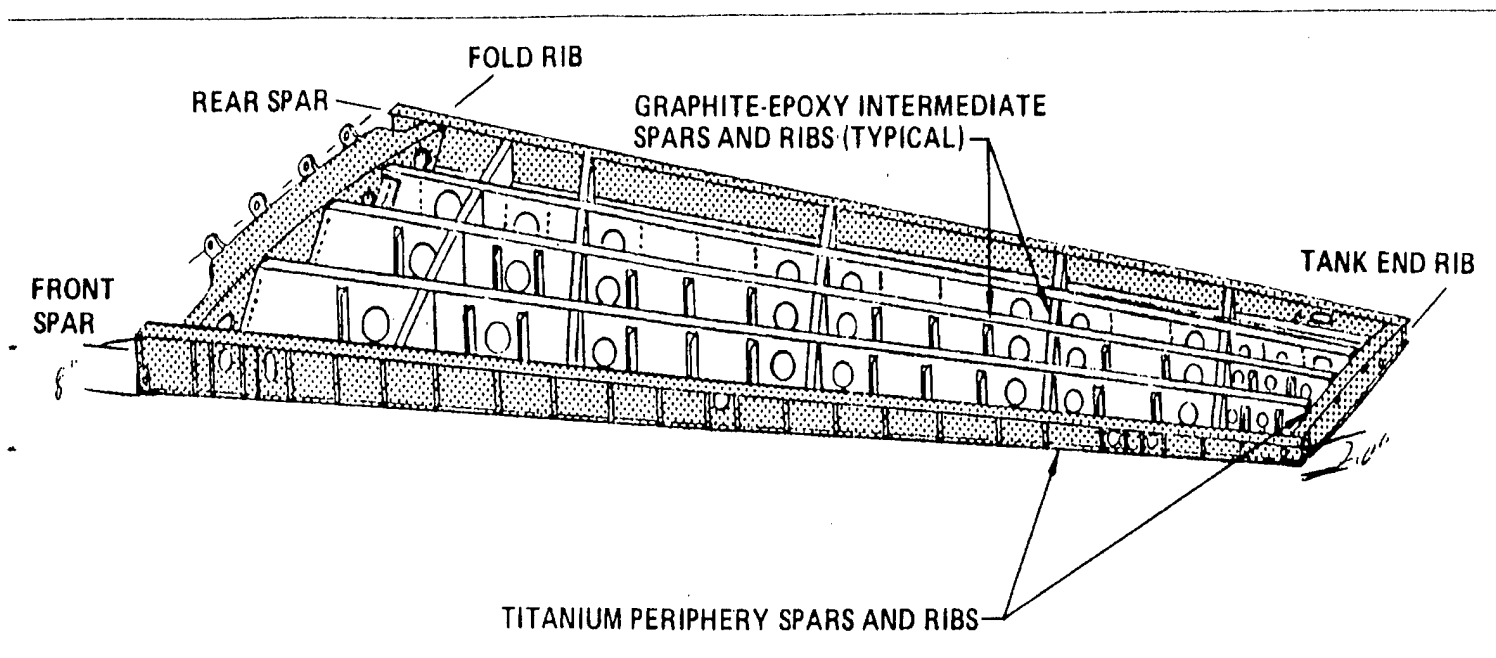


Figure 7. Wing Diagram

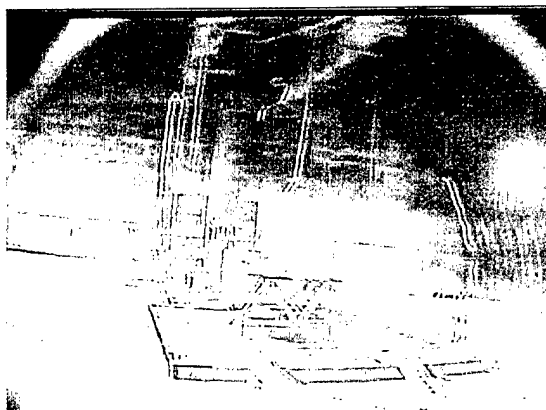


Figure 8: Composite Test #1 Setup



Figure 9: Composite Test #1 - 60s After Ignition

5. Composite Burn 2

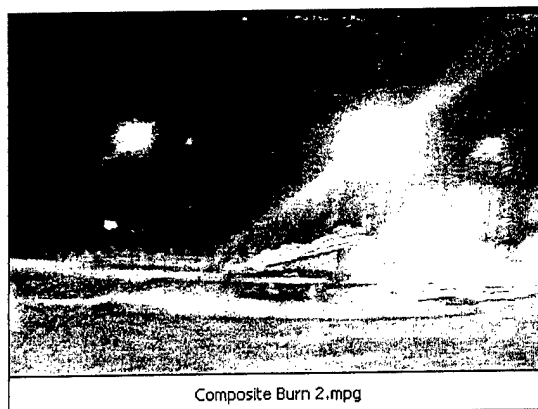
The fire size for the second composite burn was a 50ft² pan (8ft diameter) with 80 gallons of JP-8 fuel. Immediately before ignition, an additional 5 gallons of JP-8 was poured on the composite material with the excess flowing into the pan. The composite material was positioned on the metal grate in the pan at an angle with one side resting on the steel horse. This was done to place the composite material in the hottest part of the flame, based on predictions of the fire size. Video Clip 1 shows the placement of the composite above the test pan and **Figure 10** shows the final test setup. The fuel was ignited with a propane torch. **Figure 11** shows the flame one minute after ignition. Video Clip 2: shows the addition of the final 5 gallons of JP-8, the ignition, and early fire development.

6. Composite Burn 3

The fire size for the third composite burn was a 50ft² pan (8ft diameter) with 80 gallons of JP-8 fuel. The material was damaged as described in paragraph 3. Immediately before ignition, an additional five gallons of JP-8 was poured on the wing box with the excess flowing into the pan. The composite material sample was placed on a grate above the fuel surface. **Figure 12** shows the test setup. The fuel was ignited with a propane torch. **Figure 13** shows the flame one minute after ignition. Due to intermittent problems with thermocouples positioned to measure temperatures near the composite, sheathed thermocouples were installed to replace thermocouples 9, 10, and 12. These temperatures are plotted in **Graph 56-58**.



**Video Clip 1: Loading Composite Sample
For Testing (double click to play)**



**Video Clip 2: Adding Fuel and Igniting
(double click to play)**

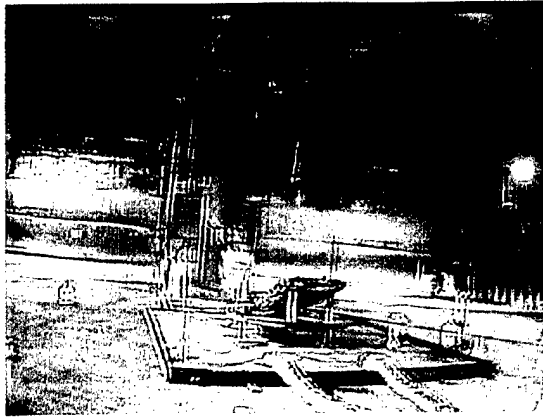


Figure 10. Composite Test #2 Setup

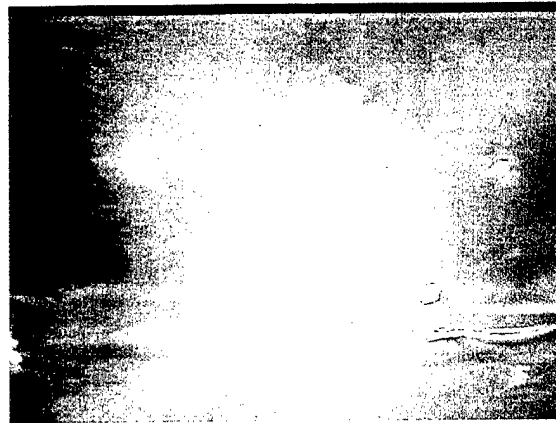


Figure 11. Composite Test #2 - 60s After Ignition



Figure 12: Composite Test #3 Setup

Figure 13: Composite Test #3
60s After Ignition

D. Mishap Scenario

The objective of the study design was to create a realistic aircraft mishap scenario. The scenario included response to a crashed and burning an aircraft that was constructed with composite materials. There were 3 phases:

Initial response (IR). This phase of a response would include Explosive Ordnance Disposal (EOD), Security, and Medical personnel. This phase was intended to simulate that timeframe at a mishap that immediately follows the scene being declared safe for entry by the Fire Chief. Operations may include: removal of fatalities, establishment of a cordon, inspection of any ordnance, etc. During this phase, light to moderate disturbance of the composite materials would be expected. Workers intentionally disturbed the material to simulate these operations.

Safety Investigation Board (SIB). Personnel involved with this team would displace the burned material as necessary to conduct the investigation. Similar to the previous phase, light to moderate disturbance of the composite material would be expected. For purposes of distinguishing between exposures that may occur between this phase and the previous, an attempt to sample during discrete times (the day of the burn and the day after) was made. During the day of the burn increased chemical exposures to the initial responders due to the composite material resin and jet fuel off gassing were expected. However, these phases were combined into one exposure assessment event due to time constraints. This phase was simulated after the fire was out for each of the 3 composite burns. When the IR/SIB simulation team entered the hangar, make-up air fans were turned off, but the exhaust system remained on.

Crash Recovery. During this phase the workers would normally be aggressively handling and manipulating the crash debris. Operations may include: cutting, wrapping, shoveling, sweeping, fixant application, etc. This phase was simulated on only 1 day (20 Sep 00), after the third composite box burn. Neither fixant nor fire fighting foam was used during any tests. The workers cut the material up with a circular saw equipped with a 12-inch titanium carbide blade. The cut material was then wrapped in plastic and placed inside a wooden box for disposition. When the recovery simulation team entered the hangar, make-up air fans were off, but the exhaust system was turned on.

E. The Composite Wing Box

The Hercules Corporation, now known as Hexcel, originally manufactured composite material. The primary material utilized unidirectional tape and quasi-isotropic laminate, with an unknown orientation. The resin identifier number was 3501-6, a 5-component system with a tetraglycidyl-diamino-diphenyl-methane (TGETPM) base, 2 other unknown epoxies, diaminodiphenylsulfone (DDS) curing agent and unknown accelerator. The fiber component was carbon IM6 with a nominal fiber diameter of 5 μm . The secondary material was a plain weave, single ply outer layer believed to be composed of 3501-6 epoxy. The primary material is also interspersed with a plain weave of secondary material formed with 3501-5 resin and IM6 carbon fiber.

III Sampling Locations/Protocol

A. Active Burn Sampling

1. Fire Progression Sampling

a) Temperature: Temperatures were measured with Type-K thermocouples positioned at various points around the fire, in the ductwork, and within the composite material. The position of the duct sensors is shown in **Figure 14**. **Figure 15** shows the approximate position of the thermocouples near the floor and within the composite wing box. Instrumentation for tests in the burn facility included temperature measurements in the test pan, around the test pan, above the test pan and in the ceiling. The ceiling measurement locations are shown in

Figure 14. Temperatures were measured at each of the ventilation system ducts shown in **Figure 14** and are identified in the test data as UV1 – UV7.

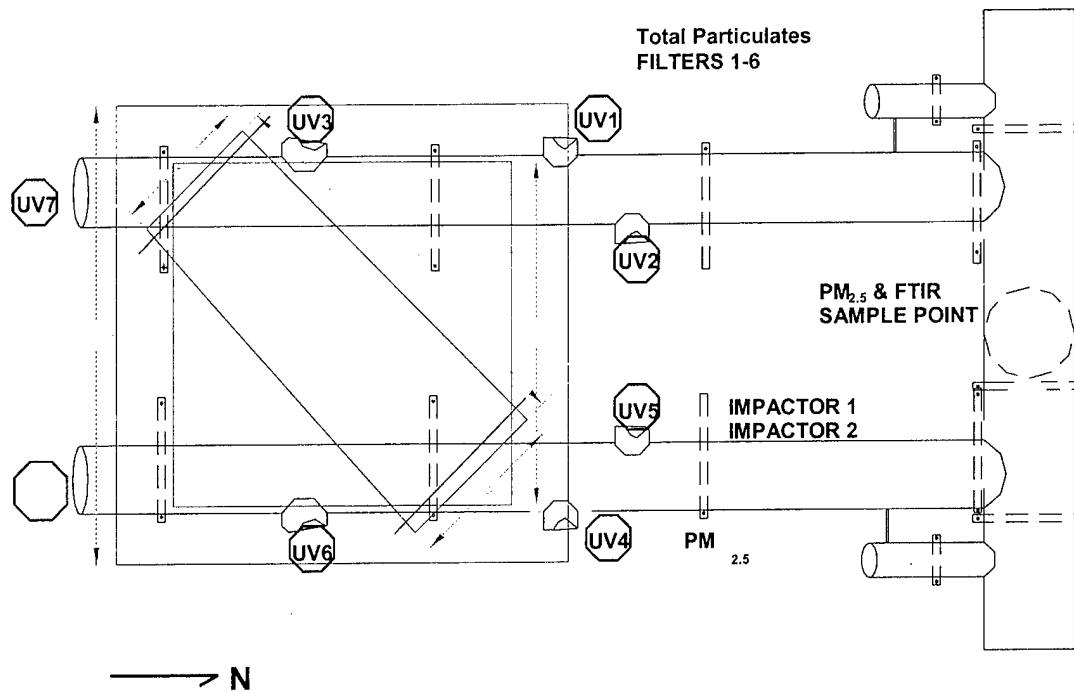


Figure 14. Location of Thermocouples,
Total Particulate, Impactors, and PM_{2.5} Samplers

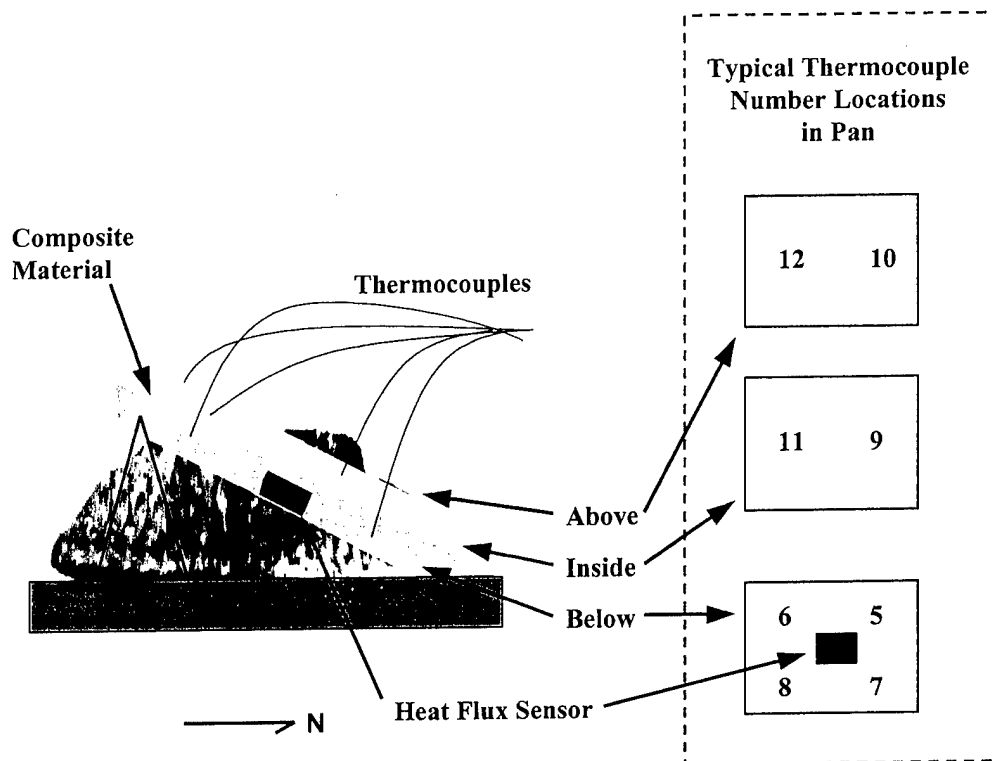


Figure 15. Approximate Thermocouple and Heat Flux Sensor Locations

b) Heat Flux: Directional Flame Thermometers (DFT) were located in the flame zone to measure hot wall heat flux or radiating temperatures. These sensors are a type of thin-skin calorimeter developed by M. H. Burgess and C. J. Fry.² They are constructed by attaching a thermocouple to a metal plate of known thickness (L), specific heat (C_p), and density (ρ). Heat flux (q_{plate}) is calculated by measuring the temperature change of the metal plate (dT_{plate}/dt) and applying the following formula:

$$q_{plate} = \rho C_p L (dT_{plate}/dt) \quad \text{Equation 1}$$

Two sensors on the DFT calorimeter 10 feet above the fuel spill measured the heat flux to determine fire intensity. These sensors were positioned facing north and south for all tests. In addition, two thin-skin calorimeters were positioned outside of the flame zone facing south into the fire, one 15 feet from the fire, one 25 feet from the fire. Radiant heat flux data was collected from these sensors as plate temperatures and converted to kW/m^2 units. The approximate positions of the heat flux sensors are shown in **Figure 15**.

c) Carbon Monoxide (CO) and Carbon Dioxide (CO₂): Two Horiba PIR 2000 gas analyzers were used to continuously measure CO₂ and CO. Data from these monitors was recorded by the data acquisition system. Gas from the fire facility was withdrawn through the total particulate sampling system (see section D 2 a)), and directed through these sensors using 3/8-inch copper tubing and a diaphragm pump.

d) Oxygen (O₂): A Servomex 540A paramagnetic oxygen analyzer was used to measure the oxygen concentration during the test. This sensor was fed with gas pumped from the burn facility through a common sampling line with the CO and CO₂ analyzers. Data was continuously collected by the data acquisition system.

2. Industrial Hygiene Sampling

An ambient air quality meter (AQ-502) and the PM_{2.5} unit were installed in a heat-shielded and thermally insulated box on the floor. The AQ- 502 measured CO, NO, NO₂, SO₂, and HCN using electrochemical sensors. Data were stored in an internal data logger that was downloaded at the end of each test burn.

3. Environmental Air Sampling

Air samples were collected from the burn facility, during each burn, to gather data on environmental and occupational hazards arising from burning composites. Fiber and particulates were studied by collecting total particulates, respirable particulates (PM_{2.5}), and particulates separated according to aerodynamic size. Volatile organic compounds released by the burning fuel and composites were collected by sorption onto solid phase microextraction (SPME) fibers.

a) Fiber and Particulate Samples: Total particulate sampling filters were mounted on a common sampling manifold that drew air from the burn facility. The air passed through the filters, a pump, and additional gas monitoring equipment. The total particulate sampling point was located in the burn facility, above and to one side of the fire pan, as shown in **Figure 14**. Respirable fibers were collected at two points during each burn, one from the ambient air near the fire pit, approximately 5 ft above the floor, and lastly, one from the exhaust duct as shown in **Figure 14**. The particle size distributions were measured with Andersen Mark III Cascade Impactors that sampled air from the exhaust duct, also as shown in **Figure 14**. Pumps and flow control equipment for the duct sampling equipment were located in the instrumentation room behind the burn facility.

b) SPME Samples: Solid phase microextraction (SPME) field samplers were hung from wires strung across the corners of the burn facility. These samplers are passive devices resembling gas chromatographic injection syringes. Although originally designed to extract organic compounds from aqueous environmental samples, these devices have proven useful for collecting organic compounds from ambient air.

B. Post Burn Sampling

1. Industrial Hygiene

Samples were collected by placing cassettes and tubes in the worker's breathing zone during simulation operations. Contaminants that were gathered included: respirable particulates, fibers, hydrogen cyanide, aromatic amines, cresols, phenol, and polynuclear aromatic hydrocarbons.

2. Environmental Air Sampling

Air samples were collected from the burn facility, after the fire extinguished, to obtain data on environmental and occupational hazards arising from the burning composite. Fiber and particulates were studied by collecting total particulates, respirable, (i.e. PM_{2.5}), particulates, and particulates separated according to aerodynamic size. Volatile organic compounds released by the burning fuel and composites were retrieved by sorption onto solid phase microextraction (SPME) fibers.

3. Hazardous Waste Sampling

Bulk samples of materials were collected for characterization to determine appropriate disposal classification. Bulk samples of the burnt composite material were submitted for Toxicity Characteristic Leaching Procedure (TCLP) analysis for organics and inorganics.

IV. Sample Tests Discussion

[**Note:** Not all samplers were deployed for all 5 tests. Results from each method that was successfully collected has data reported. However, data from composite burns 2 and 3 will be used as a basis for recommendations and decision-making]

A. Temperature and Heat Flux

1. JP-8 Test #1

Graphs 1-8 illustrate JP-8 Test #1 parameters (refer to appendix). **Graph 3-Graph 7** show the temperatures on the thermocouple trees and at the ventilation ducts for JP-8 Test #1. Fire plume temperatures were measured in excess of 1700° F at ten and twenty feet above the test pan in the early stages of the fire. These initial temperatures decreased significantly due to oxygen starvation within the closed building. In subsequent tests, decisions were made to reduce the fire size, size of the composite material sample, and to increase oxygen levels in the burn facility by adding outside air during the test using a blower and three fans. During this test, temperatures at the ceiling were measured above 400° F at all ventilation ducts for a 21-minute period during the test.

2. JP-8 Test #2

Graphs 9-20 illustrate JP-8 Test #2 parameters (refer to appendix). **Graphs 12-18** show air and ceiling temperatures measured in the burn facility during the test. Another heat flux sensor was added for this test. This sensor was placed directly above the fire where the composite material was to be placed in later tests. This sensor measured the impinging heat flux on the lower surface of the composite material. This measurement gave an indication of the effect of the fuel fire on the lower composite surface. **Graph 17** shows the calculated heat flux and the plate temperature of the sensor. The heat flux was above 10 kW/m^2 during the first two minutes of the test and averaged 10 kW/m^2 for the next minute before falling off to below 10 kW/m^2 . **Graph 18** shows the integrated heat flux or the total heat exposed to the underside of the composite material from the JP-8 fire measured in kJ/m^2 . This plot shows that during the first 11 minutes of the test, the sensor was absorbing heat for a total of 2700 kJ/m^2 indicating that heat was being transferred to the composite material for this time period. Around 17 minutes into the test, the plot then shows a decrease in the total heat absorbed that represents the sensor dissipating heat as the fire intensity decreased.

3. Composite Burn #1

Graphs 21-33 illustrate Composite Burn #1 parameters (refer to appendix). Air temperatures around and above the test pan and in the ceiling were measured and plotted in **Graph 23-Graph 27**. Temperatures and heat fluxes were measured on the lower side of the composite material and temperatures were measured inside and on the upper surface of the composite material. Temperatures measured directly below, inside and directly above the composite are plotted in **Graph 28-Graph 30**. The heat flux measured at the lower composite material surface is shown in **Graph 31**. The heat flux averaged 20 kW/m^2 during the first 2 minutes of the test and 10 kW/m^2 for the next minute before falling off to below 10 kW/m^2 . **Graph 32** plots the integrated heat flux on the lower surface of the composite measured in kJ/m^2 . This plot shows that during the first 10 minutes of the test, the sensor was absorbing heat for a total of 2500 kJ/m^2 indicating that heat was being transferred to the composite material for this time period. Around 17 minutes into the test, the plot begins to show heat dissipating from the sensor. These results follow close with JP-8 test #2, which had the same size fuel fire. It was determined that a larger JP-8 fuel fire in the 8ft diameter pan would allow for a larger composite burn and would be acceptable for the sampling equipment. The last 2 composite tests used this size fire.

4. Composite Burn #2

Graphs 34-47 illustrate Composite Burn #2 parameters (refer to appendix). Air temperatures around and above the test pan and in the ceiling were measured and plotted in **Graph 37-Graph 41**. Temperatures and heat fluxes were measured on the lower side of the composite material and temperatures were measured inside and on the upper surface of the composite material. Temperatures measured directly below, inside and directly above the composite are plotted in **Graph 42-Graph 44**. Thermocouple number 10 in **Graph 44** was measuring 600°F , 7 minutes into the test. The first responders to the test facility noticed a "hot"

spot in the composite material glowing approximately 120 minutes after ignition. They moved thermocouple 10 to this location and the temperature immediately measured 1200°F. This example illustrates that the temperature data were recorded at discrete points and mostly represented air temperatures. The solid composite material remaining after the fire burned out held heat longer than the air temperatures depicted in the graphs.

The heat flux measured at the lower composite material surface is shown in **Graph 45**. The heat flux averaged 10 kW/m² during the first 4.5 minutes of the test. **Graph 46** plots the integrated heat flux on the lower surface of the composite measured in kJ/m². This plot shows that during the first 10 minutes of the test, the sensor was absorbing heat for a total of 3000 kJ/m² indicating that heat was being transferred to the composite material for this time period. Equilibrium of the sensor and the flame temperature occurred at 1200°F for 40 minutes before temperatures began to drop, then heat began to dissipate from the sensor and the composite material.

5. Composite Burn #3

Graphs 48-61 illustrate Composite Burn #3 parameters (refer to appendix). Air temperatures around and above the test pan and in the ceiling were measured and plotted in **Graphs 51-55**. Temperatures and heat fluxes were measured on the lower side of the composite material and temperatures were measured inside and on the upper surface of the composite material. Temperatures measured directly below, inside and directly above the composite are plotted in **Graph 56-Graph 58**. Thermocouples 11 and 12 show much higher temperatures than other thermocouples in and around the composite material. They were positioned on the South side, inside and above the composite material. The flame during this test was leaning towards the Southeast part of the test pan thus resulting in higher temperatures on these thermocouples. The IR image taken from the South in **Figure 16** shows the flame leaning towards the East. The flame can also be seen leaning toward the South in **Figure 13**, a picture taken from the West side of the room.



Figure 16: Composite Test #3 IR Image

The heat flux measured at the lower composite material surface is shown in **Graph 59**. The heat flux fluctuated between 10 and 30 kW/m² during the first 2 minutes of the test as the fire developed. After 3.5 minutes the flux dropped below 10. **Graph 60** plots the integrated heat

flux on the lower surface of the composite measured in kJ/m^2 . This plot shows that during the first 5 minutes of the test, the sensor was absorbing heat for a total of 3000 kJ/m^2 indicating that heat was being transferred to the composite material during this time period.

B. Industrial Hygiene Samples

1. Sample preparation

During the simulation exercises, a team of 3 crewmembers entered the hangar in 2 teams. The teams were only allowed to stay in the hangar for approximately 25 minutes, due to heat stress concerns. Each team entered the hangar twice for each scenario. The workers wore a harness that held air-sampling pumps. These harnesses were swapped when the teams rotated. The sampling time of 100 minutes was based on the minimum sampling volume required for the PAH sampling {200 liters collected @ 2.0 liters per minute (lpm)}. Sampling media was attached within the breathing zones of the workers. Personal breathing zone samples were collected using SKC Universal Sample Pump, Model 224-PCXR8. Pump calibrators were BIOS DryCal and the DC Lite Calibrator. Each pump was pre- and post-calibrated with the appropriate media in-line. An SKC quad multiple-tube holder, model 224-26-04, was used allowing collection of several chemicals during the simulated aircraft mishap exercises. The holder was connected to an SKC pump that was calibrated to 2.0 lpm. The flow rate of the pump must be greater than the sum of the individual flow rates. Each sorbent tube was calibrated at the respective flow rate while the other tubes were in place (with the ends broken off). The three chemical groups sampled for in this configuration were hydrogen cyanide, aromatic amines, and phenols. A capped sorbent tube was placed in the fourth position. PVC and PTFE filters were conditioned in an environmentally controlled chamber at least 24 hours prior to sampling. The chamber was an Envirotronics model WPH175-1-1.5 walk-in chamber controlled at 50% humidity and 70°F . Filters were weighed on a Mettler UMT-2 microbalance. Other details on the filter weighing are given in section D2d Gravimetric Analysis.

2. Methods

a) Fibers: Fibers were collected using 0.8- μm , 25-mm mixed cellulose ester filter loaded in an anti-static cowl. NIOSH Method 7402 was followed, however, the asbestos counting rules were not used. Any fiber that had an aspect ratio greater than 3 was reported. Transmission Electron Microscopy (TEM) by the Yamate EPA Level II Method was followed for redeposit of the fibers. Portions of sample filters were placed in 100ml glass bottles, then rinsed with water five times, and finally with two rinses including ultra-sonication. An aliquot of the sample was deposited on 0.45- μm , MCE filters. The filters were dried and transferred to a glass slide with a drop of dimethyl formamide/acetic acid clearing solution. After clearing, the filters are etched in a plasma asher for five minutes to remove the top 10% of the MCE filter. The filters were then coated in a vacuum evaporator. Portions of the cleared/etched/coated filters were excised and placed on a 200-mesh copper TEM grid in a wick type solutional washer containing 100% dimethyl formamide. Two grids were placed consecutively in the TEM for examination. Five openings were examined on each grid at 15,000X magnification. Carbon fibers that had an aspect ratio of at least 3.0 were identified using morphology, selected area electron diffraction, and energy dispersive x-ray spectroscopy. Standard reference materials

were used to characterize carbon or composite fibers. Fiber length and width were determined. Results were reported as total fibers (structures) per square millimeter of filter and fibers per cubic centimeter of air (f/cc). The following calculations were used for airborne fiber concentrations and filter concentrations:

$$\begin{aligned} \text{grid size} &= 0.01 \text{ mm}^2 \\ \text{\# of grids examined/filter} &= 10 \\ \text{area of filter} &= 385 \text{ mm}^2 \end{aligned}$$

$$\frac{\text{\# fibers}}{\text{grid size} \times \text{\# grids}} \times \frac{385 \text{ mm}^2}{\text{filter}} \times \frac{\text{filter}}{\text{volume collected (L)}} \times \frac{1 \text{ L}}{1000 \text{ cc}} = \text{f/cc} \quad \text{Equation 2}$$

b) Respirable particulates: A Gilian cyclone with cassette holder assembly kit was used to collect respirable particulates following NIOSH Method 0600. The media used was a 5-um, 37-mm PVC filter and the pump was calibrated at 1.7 lpm. The 50% cut point is 10 um. The filters were weighed as previously described (section 4.3)

c) Total particulates: Total particulates were sampled using a 5-um, 37-mm PVC filter and a closed face cassette per NIOSH Method 0500. Both the blanks and sample filters were pre- and post-weighed to determine collected particulate mass as previously described. Sampling pumps were calibrated at 2.0 lpm

d) Hydrogen cyanide: Breathing zone samples for hydrogen cyanide were collected following NIOSH Method 6010. The media used was a soda lime 600mg/200mg solid sorbent tube. The pre-calibration flow rate was set to 0.20 lpm.

e) Aromatic amines: NIOSH Method 2002 includes sampling and analysis of: aniline, o-toluidine, 2,4-xyldine, N,N-Dimethyl-p-toluidine, and N,N-Dimethylaniline. A silica gel 150mg/ 75mg solid sorbent tube was used. The tube was placed in the multiple-tube holder and calibrated to 0.20 lpm.

f) Phenols: NIOSH Method 2546 includes sampling and analysis for: o-cresol, m-cresol, p-cresol, and phenol. The media used was an XAD-7 100mg/50mg solid sorbent tube. The tube was placed in the multiple-tube holder and calibrated to 0.10 lpm.

g) Polynuclear aromatic hydrocarbons: NIOSH Method 5515 requires a 2-um, 37-mm PTFE (Teflon®) filter and a XAD-2 tube sampling train. The Teflon® filters must be pre-weighed and allowed to equilibrate for at least 24 hours prior to sampling. This method also required eight area replicate samples in addition to the personal breathing zone samples. The area samples only require the Teflon® filters. Area samples are needed to determine the optimum extraction solvent. The sampling pumps were calibrated to 2.0 lpm.

3. Results and Discussion

Workers wore Tyvek coveralls, nitrile rubber gloves under leather gloves, steel-toed boots, and a full-face air-purifying respirator with an organic vapor/HEPA cartridge. All task chemical concentrations were below the occupational exposure limits listed in Table 4. Only two of the PAHs have OELs published. Tables 5-8 show the results of the personal air sampling. Task concentrations are the average personal exposure during the activity being performed. The time-weighted average (TWA) is the concentration averaged over an 8-hour workday. Most occupational exposure limits (OELs) are expressed as 8-hour TWA. There are also some ceiling limit concentrations established for some contaminants. A ceiling concentration should never be exceeded during a task. Air Force OELs are the most restrictive standard published by the Occupational Safety and Health Administration (OSHA), NIOSH, or the American Conference of Governmental Industrial Hygienists (ACGIH). The task exposure concentrations are the more appropriate results to use for analysis and recommendations since the task times will be different during each mishap.

TABLE 4. Occupational Exposure Limits Summary

Analyte	OELs (mg/m ³)	
	8 hr TWA	Ceiling
Aniline	7.6	None
Dimethylaniline,n,n	25	50
Dimethyl-p-toluidine	None	None
Toluidine, o-	8.8	None
Xylidine,2,4	2.4	None
Hydrogen cyanide	None	5
Phenol	19	60
Chrysene	0.2	None
Benzo(a)pyrene	0.2	None
Cresol	22	None
Respirable dust	3	None
Total dust	10	10
Fiber	1 f/cc	1 f/cc

The low concentrations of the chemicals monitored are not surprising. Peak HCN concentrations measured by the AQ-502 during the fire reached 100 ppm; however, the concentrations decreased quickly once the fire was out. Seventy minutes after the fire on 18 Sep 00 the HCN decreased to less than 5 ppm (see **Figures 17 & 18**). The IR/SIB team did not enter the hangar until 85 minutes and 66 minutes after the fire began on 18 and 19 Sep 00, respectively. This quick decrease was due to the exhaust system and make-up air purging the hangar and the source generation rate was significantly reduced. The other chemicals would have similarly decreased. Theoretical calculations predict that, on average, the airborne chemical concentrations would decrease by a factor of 8,000 before the workers ever entered the hangar.

Only during the Recovery Phase operations were fiber concentrations significant (close to the action level). Workers aggressively handled (cut) the composite material during this phase. The fiber and particulate exposure concentrations were similar to those measured during actual mishap operations. The USAF and the USN have sampled workers during mishap operations of fighter aircraft.³⁻⁸ NIOSH Method 7402 was used during this study to document fiber sizes. Although there were fibers reported with diameters less than 5µm (original diameter), no conclusive explanation can be made. The fiber diameters could have been reduced during the burn or during the TEM preparation (ashing/etching). There may also have been loss of fibers during TEM preparation; therefore, the numbers may underestimate the fiber exposure potential. During actual crash site sampling, NIOSH Method 7400 must be followed.

It should be noted that this was a small composite burn (compared to a full aircraft) and the exposures could be greater during real-world recovery operations. This is especially the case for aircraft such as the F-22, C-17, or B-2. To simulate worst-case scenario, fixant was not used. The PPE worn by the workers and the work-rest cycles were representative of actual recovery operations.

Figure 17. Composite Burn 18 Sep 00

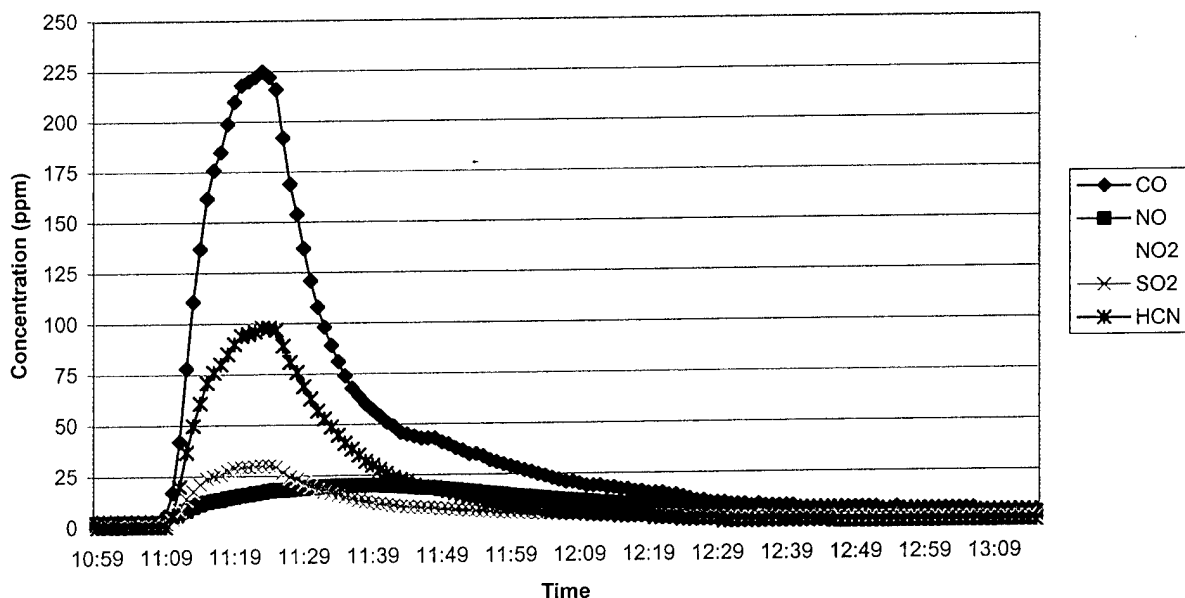


Figure 18. Composite Burn 19 Sep 00

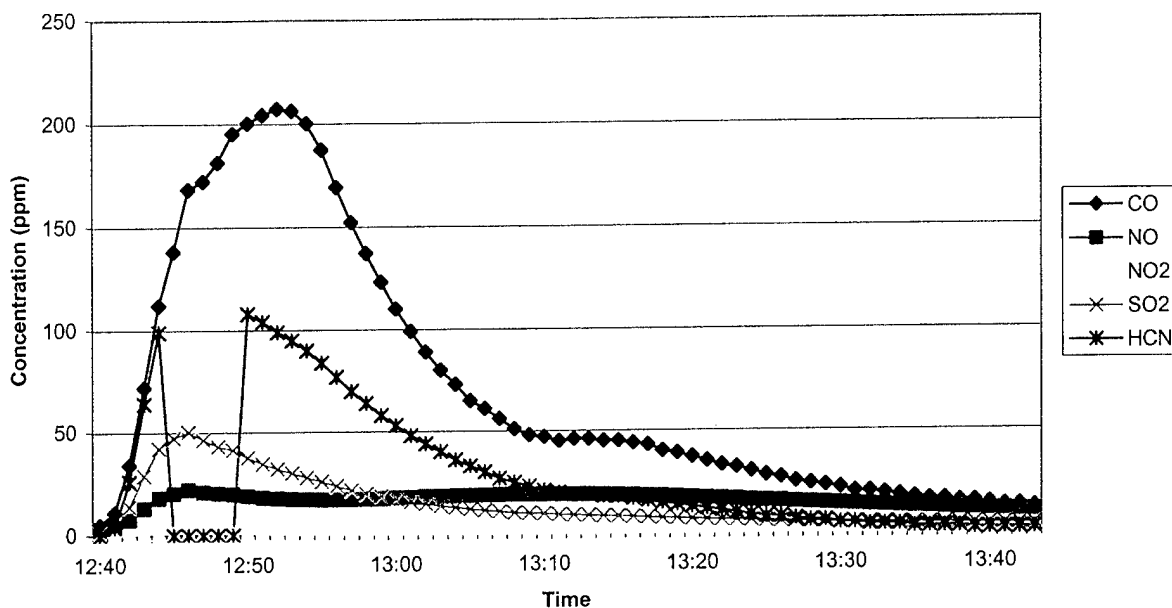


TABLE 5. Chemical Task Exposure Concentrations During the IR/SIB Phase

Team	Analyte	Composite Burns (mg/m ³)		
		15 Sept 00	18 Sept 00	19 Sept 00
Team 1	Analine	<0.013	<0.012	<0.013
	Dimethylaniline,n,n	<0.013	<0.012	<0.013
	Dimethyl-p-toluidine	<0.013	<0.012	<0.013
	Toluidine,o-	<0.013	<0.012	<0.013
	Xylidine,2,4	<0.026	<0.025	<0.027
	Hydrogen Cyanide	<0.065	<0.062	<0.067
	Phenol	<0.052	<0.05	<0.053
	Cresol	<0.078	<0.075	<0.08
Team 2	Analine	<0.0014	<0.013	<0.015
	Dimethylaniline,n,n	<0.0014	<0.013	<0.015
	Dimethyl-p-toluidine	<0.0014	<0.013	<0.015
	Toluidine,o-	<0.0014	<0.013	<0.015
	Xylidine,2,4	<0.028	<0.027	<0.031
	Hydrogen Cyanide	N/A	<0.067	<0.078
	Phenol	<0.178	<0.053	<0.062
	Cresol	<0.267	<0.08	<0.093

Team	Analyte	Composite Burns (mg/m ³)		
		15 Sept 00	18 Sept 00	19 Sept 00
Team 3	Analine	<0.013	<0.013	<0.023
	Dimethylaniline,n,n	<0.013	<0.013	<0.023
	Dimethyl-p-toluidine	<0.013	<0.013	<0.023
	Toluidine,o-	<0.013	<0.013	<0.023
	Xylidine,2,4	<0.026	<0.026	<0.046
	Hydrogen Cyanide	<0.083	<0.066	<0.16
	Phenol	<0.053	<0.053	<0.138
	Cresol	<0.079	<0.079	<0.207

TABLE 6. Fiber/Particulate Task Exposure Concentrations During the IR/SIB Phase

Team	Analyte	Composite Burns		
		15-Sep-00	18-Sep-00	19-Sep-00
Team 1	Fiber	NC	0.071 f/cc	0.038 f/cc
	Respirable dust	<0.037mg/m ³	<0.036mg/m ³	<0.038mg/m ³
	Total dust	0.032mg/m ³	<0.030mg/m ³	0.196mg/m ³
Team 2	Fiber	0.013f/cc	0.038f/cc	0.039f/cc
	Respirable dust	0.039mg/m ³	<0.038mg/m ³	<0.046mg/m ³
	Total dust	0.662mg/m ³	<0.097mg/m ³	0.116mg/m ³
Team 3	Fiber	0.014f/cc	<0.012f/cc	0.031f/cc
	Respirable dust	0.079mg/m ³	<0.039mg/m ³	<0.095mg/m ³
	Total dust	0.169mg/m ³	<0.095mg/m ³	<0.078mg/m ³

NC=not collected

TABLE 7. PAH Task Exposure Concentrations During the IR/SIB Phase

Team	Analyte	Composite Burns (mg/m ³)		
		15-Sep-00	18-Sep-00	19-Sep-00
Team 1	Naphthalene	<0.003	<0.002	<0.003
	Acenaphthene	<0.003	<0.004	<0.003
	Aceaphthylene	<0.003	<0.002	<0.003
	Anthracene	<0.003	<0.002	<0.003
	Benz(a)anthracene	<0.003	<0.002	<0.003
	Benzo(b)fluoranthene	<0.003	<0.002	<0.003
	Benzo(k)fluoranthene	<0.003	<0.002	<0.003
	Benzo(ghi)perylene	<0.003	<0.002	<0.003
	Benso(a)pyrene	<0.003	<0.002	<0.003
	Benzo(e)pyrene	<0.003	<0.002	<0.003
	Chrysene	<0.003	<0.002	<0.003
	Dibenz(a,h)anthracene	<0.003	<0.002	<0.003
	Fluoranthene	<0.003	<0.002	<0.003
	Fluorene	<0.022	<0.002	<0.003
	Indeno (1,2,3-cd) pyrene	<0.003	<0.002	<0.003
	Phenanthrene	<0.003	<0.002	<0.003
	Pyrene	<0.003	<0.002	<0.003
Team 2	Naphthalene	<0.003	<0.003	<0.003
	Acenaphthene	<0.003	<0.004	<0.003
	Aceaphthylene	<0.003	<0.003	<0.003
	Anthracene	<0.003	<0.003	<0.003
	Benz(a)anthracene	<0.003	<0.003	<0.003
	Benzo(b)fluoranthene	<0.003	<0.003	<0.003
	Benzo(k)fluoranthene	<0.003	<0.003	<0.003
	Benzo(ghi)perylene	<0.003	<0.003	<0.003
	Benso(a)pyrene	<0.003	<0.003	<0.003
	Benzo(e)pyrene	<0.003	<0.003	<0.003
	Chrysene	<0.003	<0.003	<0.003
	Dibenz(a,h)anthracene	<0.003	<0.003	<0.003
	Fluoranthene	<0.003	<0.003	<0.003
	Fluorene	<0.003	<0.009	<0.006
	Indeno (1,2,3-cd) pyrene	<0.003	<0.003	<0.003
	Phenanthrene	<0.003	<0.003	<0.003
	Pyrene	<0.003	<0.003	<0.003

TABLE 7. PAH Task Exposure Concentrations During IR/SIB Phase (cont.)

Team	Analyte	Composite Burns (mg/m ³)		
		15 Sept 00	18 Sept 00	19 Sept 00
Team 3	Naphthalene	<0.003	<0.003	<0.007
	Acenaphthene	<0.003	<0.003	<0.007
	Aceaphthylene	<0.003	<0.003	<0.007
	Anthracene	<0.003	<0.003	<0.007
	Benz(a)anthracene	<0.003	<0.003	<0.007
	Benzo(b)fluoranthene	<0.003	<0.003	<0.007
	Benzo(k)fluoranthene	<0.003	<0.003	<0.007
	Benzo(ghi)perylene	<0.003	<0.003	<0.007
	Benzo(a)pyrene	<0.003	<0.003	<0.007
	Benzo(e)pyrene	<0.003	<0.003	<0.007
	Chrysene	<0.003	<0.003	<0.007
	Dibenz (a,h)anthracene	<0.003	<0.003	<0.007
	Fluoranthene	<0.003	<0.003	<0.007
	Fluorene	<0.003	<0.003	<0.007
	Indeno (1,2,3-cd) pyrene	<0.003	<0.003	<0.007
	Phenanthrene	<0.003	<0.003	<0.007
	Pyrene	<0.003	<0.003	<0.007

TABLE 8. Fiber/Particulate Task Exposure Concentrations During the Recovery Phase

Team	Analyte	Recovery
		20-Sep-00
Team 1	Fiber	0.41 f/cc
	Respirable dust	0.001 mg/m ³
	Total dust	0.0035 mg/m ³
Team 2	Fiber	0.26 f/cc
	Respirable dust	0.0004 mg/m ³
	Total dust	0.004 mg/m ³
Team 3	Fiber	0.38 f/cc
	Respirable dust	0.0005 mg/m ³
	Total dust	0.003 mg/m ³

C. Environmental Air Samples

1. Purpose

The purpose of the total particulate and floor level PM_{2.5} sampling was to quantify ambient airborne concentrations that may be expected proximal to a mishap site. This information would be important to anyone working at the site and to the general public if the mishap occurred in a residential area. A PM_{2.5} and two cascade impactor samplers were also placed in the duct to estimate potential downwind concentrations.

2. Methodology

a) Total Particulates: The EPA recommended ambient air particulate matter collection method is the EPA IP-10A. This method is size-selective using an aerodynamic diameter cutoff of 2.5 μm or 105 μm . The decision was made not to use this traditional equipment because it would not withstand the expected temperature conditions. Also, the particulate matter concentrations were expected to be much higher than a typical community environment may present. Therefore, a low-flow total particulate collector was designed for this study. The sampler was designed to allow discrete collection of total PM_{2.5} during and after the fire.

The sampling probe for the total particulates drew air and particles from a point behind and above the fire from the burn facility. While the air was not still, the flow rates were low and irregular enough that traditional isokinetic stack sampling methods, such as EPA Method 5, were not applicable.⁹

In order to collect total particulates, gases were drawn from the air of the Fire Test Facility through a micro-porous filter, then through an electronic mass flow controller, and through a sampling pump. Six filter holders were dedicated to this collection, but only the single sampling pump and flow controller were available. All six filters were connected to the pump and controller through a manifold and solenoid valves were used to direct the flow through the filters at selected intervals. All six total particulate samples were thus collected from a single point above the fire, but they represented six distinct sampling periods. Total particulate catches were to be weighed before and after exposure to determine total particulate concentrations.

Stainless steel filter holders (Pall Gelman, Inc) and supports to hold 47-mm filters were chosen for the total particulate filters. The uncertainties regarding temperature and flow conditions that would be experienced by the sampling equipment produced corresponding indecision regarding the filter media to be used for the total particulate filters. EPA stack sampling methods, such as EPA Method 5, recommend combustion particulates to be collected on glass fiber filters.⁹ However, glass fiber media were not recommended for use in conjunction with SEM, as the glass fibers would clutter the image and obscure particulates and fibers derived from the fire.¹⁰ Teflon[®] filter media were initially considered, but initial modeling estimates projected that filters would be subjected to hot gas temperatures in excess of 700°F which would exceed the maximum recommended temperature for Teflon[®]. A search of available commercial filter media revealed an aluminum oxide-based 47-mm filter media (Annopore, SPI Inc.). The Annopore filters were specified to have a polypropylene support ring, which would have limited the filter

temperatures even more severely than the Teflon[®] media. Initial attempts to collect total particulates used 47-mm Annopore filters that had been annealed at 500°F to remove the polypropylene support ring. Annopore filters without the support ring proved to be too fragile for the various filter weighing, installation, collection, removal, and reweighing operations. Temperature readings from initial JP-8 fires revealed that the duct temperatures rarely exceeded 400°F, so later total particulate samples were collected on 47-mm Teflon[®] media with 1- μ m pores and a Teflon[®] support ring (Gelman Sciences, R2PL047).

b) PM_{2.5} Sampling: Respirable particulates were collected from the general fire area and from the exhaust duct according to protocols described in EPA Method IO 4.2. Following doctrine of the EPA, special emphasis was placed on particulates that were 2.5-microns in effective diameter or smaller. Following Method IO 4.2, exhaust gas was drawn into a pre-separator cyclone at a prescribed flow rate, and then passed through a collection filter, flow measurement and control equipment, and a pump. Components of commercially available PM_{2.5} ambient air samplers (URG-3000, University Research Glassware, Inc.) were modified in effort to enhance their tolerance to high temperatures and used to collect these particulates.¹¹

In order to measure particles with aerodynamic diameters smaller than 2.5-microns, the samplers must be equipped with a pre-separator cyclone that directs the sampled air in a roughly circular path and precipitates out particles using centrifugal principals. A statistical distribution of particles is obtained, and the cyclone is rated by the diameter corresponding to half, or 50%, of the particles passed through the separator. The PM_{2.5} samplers were equipped with cyclones (URG-3000-EH, University Research Glassware, Inc.) that produced a 2.5-micron particle cutoff when operated at a flowrate of 16.7 L/min. Varying the flowrate through the cyclone would vary the 50% cutoff particle diameter.

Upstream of the particle discriminating cyclones, the particles which passed through the cyclones were deposited on a series of two or three 47-mm Teflon[®] membrane filters with 1- μ m pores and a Teflon[®] support ring (Gelman Sciences, R2PL047). This arrangement allowed the chance of collecting particles that broke through the first filter on subsequent ones. Initially two three-stage filter holders were used, but one of these was destroyed in the initial burn test, and only two-stage filter holders were immediately available as replacements.

To study PM_{2.5} emissions in the fire test facility, the optional annular denuders designed to trap reactive gases and the PUF samplers designed to trap organic compounds on polyurethane foam were removed from the sampler setup. The short, curved probes normally used on URG-3000 samplers were replaced by longer, straight metal tubing probes, approximately 18-in long and 1/2-inch in diameter. Normal URG-3000 samplers include temperature-controlling cases that maintain the samplers slightly above ambient temperature in order to prevent condensation.

The expectation of high temperatures eliminated the need for heating the samplers. Rather, steps had to be taken to protect the samplers from the high heat within the test facility. A sampler on the floor level of the fire test facility was placed in a defunct refrigerator, with additional heat shielding. The digitally controlled sampling pump for the floor level sampler was also placed in the shielded refrigerator. Power supply cords and remote control and signal lines passed into the refrigerator to control the pump's on-off state and transmit the pump's flow signal to the test control and data acquisition computer. A blower located behind the fire test facility blew cool, ambient air into the refrigerator to cool the instrumentation inside.

A second sampler was placed in an insulated box welded to an arm of the exhaust duct. A length of ¼-inch tubing connected the filter holder, through the back wall of the facility, to the dry gas meter and sampling pump placed near the back wall, on the roof of the instrumentation shack. A straight probe, 18-inches long and ½-inch in diameter, extended from the cyclone through a hole in the wall of the exhaust duct into the exhaust stream.

c) Size Differentiated Particulates: Andersen Mark III Particle Sizing Cascade Impactor (PSCI) stack samplers were used to examine the particle size distributions of the particles emitted in the fire tests. These samplers featured eight stages of sample collection stacked in a sampling device suitable for use in regular smokestacks. A cyclonic preseparator could optionally attach to the impactor sampler to prevent large particles from clogging the system. The flow holes of each sampling stage were offset from those of the previous and following stage so that air flow through the stages had to follow a deflecting path. Two configurations of impactor media were loaded covering alternating stages such that the flow holes in each stage were left uncovered. The flow rate and the radii of curvature in the flow paths allowed some particulates to land or impact on the stages, according to their effective aerodynamic diameters. Particles landed and were collected by collection media on the surface of the stages between the rows of flow holes. Successive impactor stages caught successively smaller particulates, and a glass fiber final filter trapped extremely fine particles. Impactor stages were covered with media for trapping the particles. Available sampling media included glass fiber media and stainless steel foils.¹²

The size of particles trapped on each stage of the PSCI is controlled by a complicated relationship of flow rate, temperature, gas pressure, various physical gas parameters, and parameters such as the size and number of holes in the previous stage. The particle diameter (D_p) in cm, collected with 50% efficiency, collected at each stage of the impactor is given in Equation 3. In Equation 3, μ represents the air viscosity, in poise, D_c represents the diameter of the jet holes in the impactor stage, Ψ represents a dimensionless impaction parameter=0.14, N represents the number of holes in the impactor stage, ρ represents the particle density, in g/cm³, and Q_a represents the actual flow rate at the conditions of the impactor. The number and diameter of holes for each stage of the Andersen Mark III Particle Sizing Stack Sampler are listed in Table 9. The Cunningham slip correction factor, C , is calculated as shown in Equation 4. The mean free path for the gas molecules, λ , is calculated as shown in Equation 5. The gas viscosity, μ , in poise is calculated from Equation 6. Other parameters in these equations include the gas constant, R , absolute temperature, T , particle density, ρ , and gas molecular weight, (M).^{12,13} For these calculations the equivalent molecular weight of air, 29 g/mole, was used for the molecular weight.

$$D_p = \sqrt{\frac{18\mu\Psi N\pi D_c^3}{4\rho C Q_a}} \quad \text{Equation 3}$$

$$C = 1 + \frac{2\lambda}{D_p} \left(1.23 + 0.41e^{-.44D_p/10^{-4}/\lambda} \right) 10^4 \cong 1 + .16 \times \frac{10^{-4}}{D_p} \quad \text{Equation 4}$$

$$\lambda = \frac{\mu(82.057)T}{.499PM\sqrt{\frac{8RT}{\pi M}}} \quad \text{Equation 5}$$

$$\mu = (63 + 0.40T)10^{-6} \quad \text{Equation 6}$$

TABLE 9. Plate parameters for Andersen Mark III Impactor.

Plate No.	No. of Holes	Hole Diameter (cm)
0	264	0.1613
1	264	0.1181
2	264	0.0914
3	264	0.0711
4	264	0.0533
5	264	0.0343
6	264	0.0254
7	156	0.0254

Calculation of the particle diameter from Equation 3 is complicated by the dependence of the Cunningham slip correction factor on the particle diameter. To resolve this, computer programs can iteratively plug in diameters from the expected range of particle diameters, calculate the Cunningham slip correction, and then calculating the particle diameter. The calculated particle diameters that is self consistent with diameter estimate used to calculate the Cunningham slip factor is taken as the particle diameter for the impactor stage.¹³

Andersen Mark III Cascade Impactors were used to sample particulates from the facility exhaust duct. These stack sampling PSCIs were used with cyclonic pre-separators to collect larger particles and prevent their plugging the particle sizing cascade. These pre-separators exhibited particle size cutoffs that overlapped with the first two impactor stages. Metal probes of ¼-inch stainless steel tubing, approximately 18-inches long drew particulate laden air from the exhaust duct. The probe ends were ground to produce a 45-degree bevel and the impactors were rotated at installation to face the bevels upstream and promote collection. This probe arrangement allowed the use of duct holes approximately ½-inch in diameter. Two holes were placed in the exhaust duct to accommodate two PSCIs approximately 18-inches apart. The PSCIs were installed on a shelf, welded to the duct in a position to allow the impactors to connect to the probes, extending into the duct as described. The PSCIs were manifolded into a common sampling line, composed of 3/8-inch copper tubing, extending from the PSCI sampling site on the duct, through the back wall of the fire test facility, to the instrumentation shack. A sampling

pump and mass flow controller, controlled by the test control computer, drew air through the impactors. The line divided near the PSCI installation, into two lines with solenoid on-off valves and fittings appropriate to the PSCI hardware. The sample pump drew air from the exhaust duct, through one PSCI device at a time, with the flow rate being controlled by the mass flow controller. The solenoid valves on the manifold selected which PSCI received sample at a given time. This allowed one impactor to be exposed during the intense period of the burn, and one to be exposed later, during the smoldering period.

d) Gravimetric Measurements: Measurements of Total Particulates, $PM_{2.5}$, and Size Differentiated Particulates involved precise weight determinations of empty and loaded filters and impactor media. These determinations were made using a Metler UMT-2 microbalance, capable of weighing samples up to 2 grams to an indicated accuracy of the nearest 0.1 μ g. The microbalance provided separate housings for power supply, printer, and the weighing module. The weighing module provided an automatic draft shield to protect the samples from weighing errors due to air currents. The entire balance was installed in a secondary draft shield, situated on top of a marble balance table to minimize effects due to vibrations. The balance, with its auxiliary draft shielding and marble weighing table, was housed in an environmentally controlled chamber (Envirotronics, Model WPH175-1-1.5) that was maintained at 22°C and 50% relative humidity. Small filters, exposed in 47-mm housings, and impactor media were weighed with this equipment. Five or more weight readings were taken and averaged to determine critical filter weights. Samples were equilibrated in the environmental chamber for a minimum of 16 hours before being weighed, with 24-hour minimum equilibrations being preferable.

Cyclone catches proved to be a more difficult challenge. Initial attempts were made to obtain cyclone catch weights by discharging the cyclones into tarred beakers or glass petri dishes. These weighing accessories exceeded the allowable weight limits of the UMT-2 microbalance and they were weighed to the nearest 0.01mg using a Metler AT-201 balance. Although the AT-201 balance featured a motorized draft shield, it was situated in an ordinary laboratory room with conventional climate controls. In addition to the extra degrees of uncertainty from the full-sized balance and the conventional air conditioning system, weights of cyclone catches and other supplemental catches measured with this balance suffered from inaccuracies produced by the high electrostatic charges present on many of the particulate samples. The electrostatic charges often caused particulates to fly away from a cyclone and away from the tarred collection vessel, producing a loss of sample content. Gradually a technique was developed in which the cyclone particulates could be drawn from the collecting cyclone under vacuum for re-deposition on a small Teflon[®] filter held in a 25-mm syringe filter holder. The loaded filter would be weighed immediately before and after the transfer so that the captured particulates were weighed by difference between before and after weights.

e) Solid Phase Microextraction (SPME) Sampling: SPME was originally developed as a technique for extracting organics from water samples for injection into gas chromatographic analysis systems. The extractive media is a 1-cm length of fused silica fiber, coated with an organic phase that usually is similar to a gas chromatographic stationary phase. The extractive fibers are installed in syringe-like devices such that by depressing a plunger on the fiber holder, the fiber is extended from a septum-piercing needle.

Extending the extraction fiber from the needle places it into contact with the media to be sampled or it exposes a loaded fiber to heated carrier gas in a gas chromatographic injection port. The technique was originally developed as a simple, rapid, and sensitive means of sampling organic pollutants from water samples. It can also be used to sample organic compounds from air.^{14,15}

In conducting an SPME extraction, an SPME extraction device is inserted into a sample through a septum and the extractive fiber is extended to contact the sample for a controlled period of time. At the end of the extraction period, the extractive fiber is retracted and the SPME device is removed from the sample and inserted into a gas chromatographic injection port. Extracted volatile compounds are exposed to the injection port's carrier gas by extending the extractive fiber. The gas chromatographic injection port can be operated at elevated temperature, which promotes desorption of sorbed volatile compounds from the extractive fiber into the carrier gas, which in turn sweeps the volatile components into the gas chromatographic column for separation and analysis.¹⁶

SPME was used as a monitoring technique during the experimental burns. Preconditioned SPME field sampling holders were fitted with wire hangers and were hung from a series of four wires arranged in the corners of the experimental burn facility. The four sampling positions were numbered for easier reference; position 1 was a wire hung across the northwest corner of the burn facility, position 2 across the southwest, position 3 across the southeast, and position 4 across the northeast. Field sampler fiber holders featured internal septa through which the needle was extended for sampling and desorption. After sampling, the needle was withdrawn into a space provided in the field sampling holder. The sampling was conducted by first hanging the samplers during the preparation period, and then extending the sampling fibers shortly before the test fire was to be ignited.

Samples collected by SPME were analyzed with a Viking portable GC/MS system, operated in a laboratory setting. The SPME samplers were desorbed in a split/splitless injection port, operated in splitless mode for a desorption period of three minutes at a temperature of 250°C. The chromatographic separations were accomplished with a fused silica capillary column, 30m long with an inner diameter of 0.28mm, and coated with 3.0 µm of a bonded polymethylsiloxane stationary phase (MXT-1, Restek, Inc.). The column oven was programmed from 40°C to 270°C at a program rate of 10°C/min, with an initial isothermal hold time of 5 minutes at 40°C and a final isothermal hold time of six minutes at 270°C. The quadrupole mass spectrometer was scanned from 35 – 450 daltons at a rate of 1.4 scans/second. The mass spectrometer was set to reject ions with less than 150 abundance counts, and the electron multiplier operated at a voltage of 2965 volts during these analyses.

3. Results and Discussion

a) Total Particulates: Total particulates were collected successfully for the large JP-8/composite burns that took place on 18-19 September. Previous collection attempts failed. During the initial large JP-8 burn, made on 9 September, a power failure in the solenoid valve control system prevented the solenoid valves of the total particulate sampler from opening when directed. The high temperatures generated by the 9 September fire burned off insulation from the power wires of several of the control solenoids, causing a fuse to blow when one of the un-insulated circuits was energized. The solenoid valves in the fire test facility were repaired and the low-temperature insulation was protected by additional aluminum foil heat shielding prior to the 13 September burn. Total particulate filter holders prepared for the 13 September burn were loaded with Annopore filters whose polyethylene support rings had been burned off with an annealing oven. These filters crumbled when attempts were made to remove and re-weigh them. The total particulate filter holders were loaded with 47-mm Teflon® membrane filters prior to the 15 September burn. When these filters were recovered, visual examination showed they had collected very little if any particulate, despite visual evidence that the fire had produced ample amounts of smoke. This prompted a large-scale examination of the total particulate sampling equipment and associated gas flow lines to eliminate all possible leaks. This re-examination and repair was completed prior to the 18 September burn. Total particulate data from the burns conducted on 18 and 19 September are listed in Table 10.

Both total particulate distributions are similar. Total particulates appear to have developed more rapidly on 19 September and to have built up to a much larger total concentration. The sampler flowrate during all total particulate collection on 18 and 19 September was set to 1.0 lpm except for the final filter collected on 18 September, which was collected at 3.0 lpm. The minor differences in the collection profile between the two days of sample collection do not appear to be flowrate related. Both total particulate distributions exhibit an increase in total particulates in the 5th filter, opened approximately 40 to 50 min into the burns. We have no explanation for this phenomenon. Bias or slipping in one of the filters might account for this, but we were not able to confirm any problems with filter holder number five.

Two factors may account for the higher total particulate concentrations measured on 19 September. Differences in the composite samples may have influenced the generation of particulates. The composite wing box burned on 19 September weighed 29 pounds more than the sample burned on 18 September. The sample burned on 19 September had been subjected to more damage than the one burned on 18 September. The 19 September sample had been subjected to deliberate crushing, breaking the sample into two pieces and small samples had been cut from the wing box for use on 15 September. The additional damage to the wing box on 19 September could have allowed greater access of the flames to the composite material. Also, the burn facility was not decontaminated following the experiment on 18 September. Small airborne particulates could persist from one day to the next.

The high particulate concentration forced experimenters to open sampling filters for brief times during the intense moments of the fire to prevent overloading of the filters. This produced a number of data gaps for each day in which no samples or particulate data were collected. The use of a continuous particulate measuring device such as a TEOM might have produced a more complete picture of particulates versus time, but the available devices were judged to be too delicate for use with these experiments.

TABLE 10. Total Particulate Data for Large Scale Composite Burns

18 Sept 2000						
	Filter 1	Filter 2	Filter 3	Filter 4	Filter 5	Filter 6
Sample On-Time (minutes)	1.03	10.07	25.02	36.40	50.25	55.02
Sample Off-Time (minutes)	3.82	14.00	29.02	43.42	55.00	100.08
Volumes, L at 25 C, 1 atm	7.9	7.9	8.0	14.1	9.6	255.9
Volumes, m ³ at 25 C, 1 atm	0.0079	0.0079	0.0080	0.0141	0.0096	0.2559
Catch weights (mg)	1.3606	1.5638	0.8541	0.5528	1.1723	1.9341
Total particulate Conc (mg/m ³)	172	198	106	39.3	122	7.56
19 Sept 2000	Filter 1	Filter 2	Filter 3	Filter 4	Filter 5	Filter 6
Sample On-Time (seconds)	61	603	960	1561	2403	3304
Sample Off-Time (seconds)	197	735	1081	1979	2821	6003
Sample On-Time (minutes)	1.02	10.05	16.00	26.02	40.05	55.07
Sample Off-Time (minutes)	3.28	12.25	18.02	32.98	47.02	100.05
Volumes, L at 25 C, 1 atm	4.2	4.4	4.1	14.0	14.1	90.7
Volumes, m ³ at 25 C, 1 atm	0.0042	0.0044	0.0041	0.0140	0.0141	0.0907
Catch weights (mg)	4.1575	4.4534	4.0841	14.0470	14.1588	90.796
Total particulate Conc (mg/m ³)	1177.1	434.5	369.5	108.3	249.2	12.3

b) PM_{2.5} Results: Discrimination among the airborne particles depended upon cyclonic pre-separators attached upstream of the filters in the PM_{2.5} samplers. Cyclones for the URG-3000 samplers were designed to operate at specific volume flow rates, 16.7 lpm being the flow intended for the cyclones used for the September 2000 HAMMER tests. The intended flow rate is adjusted on the sampler's pump box prior to the collection of a sample. The actual flow rate is measured by a mass flow controller/sensor in the sampler's pump box and is reported as a voltage signal to the data collection computer. The flow rate signal varied from 0 to 5 volts, DC, corresponding in a linear fashion to flow rates of 0.0 to 20.0 lpm (see Appendix). Flow rates from both PM_{2.5} pump boxes were monitored by the data collection computer, with the flow rate being recorded in a log file once each second. The data collection computer also recorded the state of the remote operation switch that turned the PM_{2.5} sampling on and off.

As the PM_{2.5} filters loaded, it was common for the PM_{2.5} sampling flow to fall off from the set value of 16.7 lpm. When possible, the sampling event was terminated if the flow rate fell below 12.0 lpm. In some events, even the minimum flow was never achieved, indicating plugging had occurred before the sampling started. Usually a plugged flow condition could be explained upon examination of the equipment for sample flow lines that collapsed due to heat or improper placement of the equipment. The restricted space of the refrigerator sampling box at the floor

level was especially conducive to having the sampler's DGM placed on top of some of the sample flow lines, collapsing them. After the initial burn on 9 September, the flow lines were inspected before the burn event to ensure the lines were open, but collapses still occurred on occasion. PM_{2.5} samplings made during such blockages were invalid as PM_{2.5} measurements, but where the flow rate was low enough to prevent any separation in the cyclones, the measurements could provide additional data on total particulate loads. On 19 September, the flow line for the Duct PM_{2.5} sampler melted off, so that the volume and flow readings no longer reflected sample flowing through the filter and cyclone, and as a result neither PM_{2.5} nor total particulate result from that collection is valid.

The aerodynamic diameter versus flow rate data, provided by the sampler manufacturer, was fitted to a series of curve families and were found to fit an exponential curve as in Equation 7. This equation was then used to calculate the aerodynamic diameter being cut off by the sampling cyclone at various times during the sampling. From this, the minimum and maximum aerodynamic diameter could easily be determined. A weighted average aerodynamic diameter was also calculated, using the flow rate through the cyclone as the weighting factor, as shown in Equation 8. These calculations were made for each PM_{2.5} trial and the results are listed in Table 11. Table 11 also summarizes the filter weights, sample volumes, and particulate concentrations obtained.

$$D = 24.847Q^{-0.8172} \quad \text{Equation 7}$$

D = Aerodynamic Diameter in microns

Q = Sampling Flowrate in L/min

$$R^2 = 1$$

$$D_{avg} = \frac{\sum_{t=ti}^{t=tf} D_t Q_t}{\sum_{t=ti}^{t=tf} Q_t} \quad \text{Equation 8}$$

ti = initial sampling time

tf = final sampling time

The filter loading occurred sufficiently fast that the flowrate needed to sample 2.5-micron particles could not be maintained in any of the trials. In most cases the weighted average aerodynamic diameter of the particles was between the 2.5-micron figure preferred by US EPA and the 4-micron figure preferred by OSHA. The 16.7 lpm cyclone had been chosen to allow the maximum sample volume within a potentially brief sampling event, since sampling periods during a live fire experiment had to be shortened to a few minutes. Lower flow rate sampling cyclones are available from the sampler manufacturer, and these may be indicated for future samplings of this nature, since the pumps could probably maintain the required sampling flow rate for a longer period using lower flow cyclones. Cyclones designed to sample at 10.0 lpm would probably have worked for these conditions.

On 18 and 19 September, the PM_{2.5} filters in the floor-level, refrigerator sampler were replaced during the sample recovery period, and additional respirable particulate samples were collected while the recovery team worked and for an extended period of time after. During the post-burn samples collected on 18 and 19 September, the flow rates and some additional data from the facility sensors were collected in special, supplementary data files. During the final post burn sample of 19 September, the equipment was operated in an unmanned mode, with the Lab View data collection program specially modified to shut down sampling when the flowrate fell below 12.0 lpm. The recovery period samples were loaded to a much lower degree than during the burn samples, so that sampling could be carried out over an extended period. The results from the recovery period sampling are given in Table 12.

Current EPA ambient air quality standards allow 24-hour exposures of up to 65 $\mu\text{g}/\text{m}^3$ or yearly exposures averaging 15 $\mu\text{g}/\text{m}^3$. All of the during burn samples indicated concentrations far above the 24-hour allowable value, and they were collected in a few minutes. Clearly, respiratory protection was indicated during the burn events. The post-burn samples collected during the sample recovery periods of 18 and 19 September were substantially cleaner in terms of respirable particulates and total particulates. The first post-burn sample collected on 19 September may be in error, but the remaining post-burn collections yield more consistent post burn concentrations that are still within allowable limits.

TABLE 11. Summary of Results from PM2.5 Sample Collections

	9-Sep-00		13-Sep-00		15-Sep-00		18-Sep-00		19-Sep-00	
	Duct Sample	Floor Level Sample	Duct Sample	Floor Level Sample	Duct Sample	Floor Level Sample	Duct Sample	Floor Level Sample	Duct Sample	Floor Level Sample
Sample Start Time (Min)	1.43	1.43	2.33	2.33	4.02	40.00	4.02	25.15	4.02	25.00
Sample End Time (Min)	5.88	5.92	10.57	10.57	8.00	50.38	8.00	65.10	4.95	40.00
Sample Volume (m ³)	134.2	122	210.3	19.3	101.2	84	7.2	787.9	NA	80.6
Weighted Average Diameter (μm)	5.06	3.96	3.50	42.7	3.49	14.2	10.4	3.28	3.14	9.91
Total Filter Catch (mg)	81.278	58.87	15.2563	7.2453	20.0	2.5027	2.6164	11.2955	21.2841	1.8837
Respirable Particulate (mg/m ³)	0.606	0.483	0.0725	NA	0.20	NA	NA	0.014	NA	0.023
Total Particulate (mg/m ³)	0.615	0.489	0.4315	0.3754	0.21	0.03	0.363	0.016	NA	0.024

TABLE 12. Postburn Respirable Particulate Results

	18-Sep-00	19-Sep-00	19-Sep-00	Post Decon
	Post-Burn	Post Burn-1	Post Burn-2	
Sample Volume (m ³)	1071.6	1686.2	3972.4	14696.8
Maximum Flow (l/min)	15.84	17.24	15.44	16.7
Minimum Flow (l/min)	4.76	13.24	12	12
Minimum Particle Diameter (µm)	2.5992	2.4254	2.4254	
Maximum Particle Diameter (µm)	6.9428	3.0093	3.2611	
Weighted Average Diameter (µm)	3.5241	2.8654	2.9579	
Total Filter Catch (mg)	0.1105	0.0551	0.494	0.3345
Cyclone Catch (mg)	0.00447	0.0354	0.01764	0.0663
Respirable Particulate (mg/m ³)	1.031E-04	3.268E-05	1.244E-04	2.276E-05
Total Particulate (mg/m ³)	1.073E-04	5.367E-05	1.289E-04	2.727E-05

c) Particle Size Distribution Results: The impactors prepared for the 9 September burn were uniquely prepared, with one impactor loaded with glass fiber impactor media and with the other loaded with stainless steel foil media. The particle size distribution experiment did not proceed successfully during the 9 September burn. During this experiment heat levels were high enough to burn insulation off of some of the solenoid valve connection wires, causing shorts in the power supply wiring for some of the solenoid valves, and in turn blowing the circuit breaker of the solenoid valve power supply. As a result, the solenoid valves controlling flow selection to the impactors never opened. When the impactors were recovered, a brief examination of the preseparator and initial media plates showed that the prepared impactors were unexposed. They were used again for the 13 September burn.

Following the 13 September burn, Impactor #1, which had been loaded with the stainless steel media, was found to be mis-loaded. The alternating media configurations had been placed on Impactor #1, in the wrong order, so that the flow holes in the impactor stages were obstructed and no effective flow passed through the impactor. The error was traced to the stainless steel impactor media that was labeled in the opposite numerical convention to that used for the glass fiber media. The remaining stainless steel media were relabeled to conform to the manufacturer's impactor assembly instructions.

During each burn the temperature of the thermocouple nearest the Particle Size Cascade Impactor (PSCI) sampling position was monitored in real time in search of a time period when the temperature would be approximately stable. The aim was to adjust the flowrate setting for the PSCI experiment to produce 10.0 lpm of flow through the impactors. Another challenge was to calculate the flow to be measured at the flow controller, which indicated flow in standard liters per minute, to correspond to 10.0 lpm under the conditions of the duct. Attempts were made to collect two PSCI samples for each burn. When the temperature of the duct was judged to be approaching a stable condition, the temperature was used to calculate the desired flowrate setting, which was then placed on the PSCI experiment's flow controller and the sampler #1 valve was opened. Similar temperature versus flow calculations were made before opening PSCI sampler #2's valve later during the fire.

Some instability was noted when the sampling valve is first opened, but the flowrate exhibits less falloff than is noted for the $PM_{2.5}$ samplers. The Dry Gas Meter (DGM) intended to measure total flow through the PSCI samplers failed early in the experiment series, and due to the experimental arrangements, it was not possible in any case to read the volumes from the DGM at the beginning and the end of each sampling event. So, the total flow volume through each PSCI sampler was obtained by numerically integrating the flowrate profile over the duration of the sampling, as shown in Equation 9. The numerical integration was performed in MATLAB using a Trapezoidal Rule numerical integration routine.

$$V = \int_{ti}^{tf} Q(t) dt \quad \text{Equation 9}$$

V = sample volume

$Q(t)$ = Time dependent flowrate

ti = initial time of sampling

tf = final time of sampling

Despite the attempts to start PSCI sampling after the duct temperature stabilized, the duct temperature did not remain stable for extended periods, and the sampling temperature thus exhibited considerable variation. A typical temperature profile during sampling is shown in the Graph 7. This temperature variation would have the effect of smearing the particle size distribution obtained in the PSCI. The cut-point diameters obtained from Equations 3-6 are 50% probability values rather than firm cut-off limits, this smearing is an additional experimental source of variation. Equations 3-6 were used to estimate the diameter cutoff for each stage of the PSCI during each collection run, using the arithmetic average temperature during the time of the sampling event as the temperature for the calculations. Particle densities for use in Equation 3 were assumed to be 1 g/cm³. The resulting particle diameter cutoffs for each stage and for each sample collection are listed in Table 13.

After sample collection, the exposed PSCIs were transported to the laboratory and stored overnight in the temperature and humidity controlled sample-weighing facility. After equilibrating for approximately 24 hours, the PSCI samplers were disassembled and the particulates collected at each stage were weighed. The results from the PSCI collections are summarized in Table 13. Bar graphs of the particle distributions from these six collections are shown in **Figures 19-24**. Several of the collections, 13 Sept. 2000, 15 Sept. 2000, and the hot fire samples collected on 18 and 19 Sept. 2000 show large concentrations of fine particulates in the size category of "fines", i.e. particles less than 1 micron in diameter. It should be noted that there is some probability for such fine particles to settle onto earlier stages, so the true distributions may be even more skewed toward fine particles. The only samples not dominated by fines were the smoldering phase samples collected on 18 and 19 Sept. 2000. The final filters from these samples showed some staining by fine particles, but the staining was much lighter than that of the final filters collected during active fires. Also, despite equilibration in the weighing chamber these filters exhibited a loss of weight so that their catch weights were much lower than the other stages and lower than the other fine particulate collections. The lack of fines during the smoldering samples may be due to successful exchanging of the air within the burn facility by the exhaust system. Fine particles would be expected to respond to the airflow

near the duct vents more efficiently than larger particles, so that they may have been pumped out of the burn facility more efficiently.

Use of the particle size profiles in air quality models, such as the HPAC model, required calculation of a number density of the particles at each PSCI stage. This was done by assuming the particles behaved as spherically equivalent particles with densities of 1 g/cm^3 . Thus the volume, V_p , was related to the particle radius, r , and diameter, D , according to the well-known geometric relationship in Equation 10. The volume of sample, V_s , could be calculated from the assumed density, ρ , as shown in Equation 11. The number of particles was then estimated by dividing the sample volume by the particle volume as shown in Equation 12. The numerical densities of particles collected in the particle size distribution experiment are also included in Table 13.

$$V_p = \frac{4}{3} \pi r^3 = \frac{4}{3} \pi \left(\frac{D}{2} \right)^3 \quad \text{Equation 10}$$

$$V_s = \frac{m}{\rho} \quad \text{Equation 11}$$

$$N_p = \frac{V_s}{V_p} \quad \text{Equation 12}$$

The PSCI results could also be used to estimate respirable particle concentrations, accepting that particles 3.5 microns in diameter and smaller should fall within the ranges of 4 microns, used by NIOSH, and 2.5 microns, as accepted by the USEPA. The $\text{PM}_{2.5}$ concentration could be estimated by summing the concentrations measured by stages 5 – 8 and the final stage of each PSCI collection. These concentrations are also listed in Table 13.

Analysis of total particulate filter catches by TEM indicated that the primary element present in the bulk of the particulate matter was carbon. This knowledge prompted a reevaluation of the cascade impactor data, using the density of carbon as the expected particulate density. Because of the sensitivity of the particle diameter calculations to the particle density and also the further dependence of the particle number calculations on density, this new density figure produces substantially different results, which are listed in Table 14.

Figure 19 Particle Size Profile, 13 Sept 2000

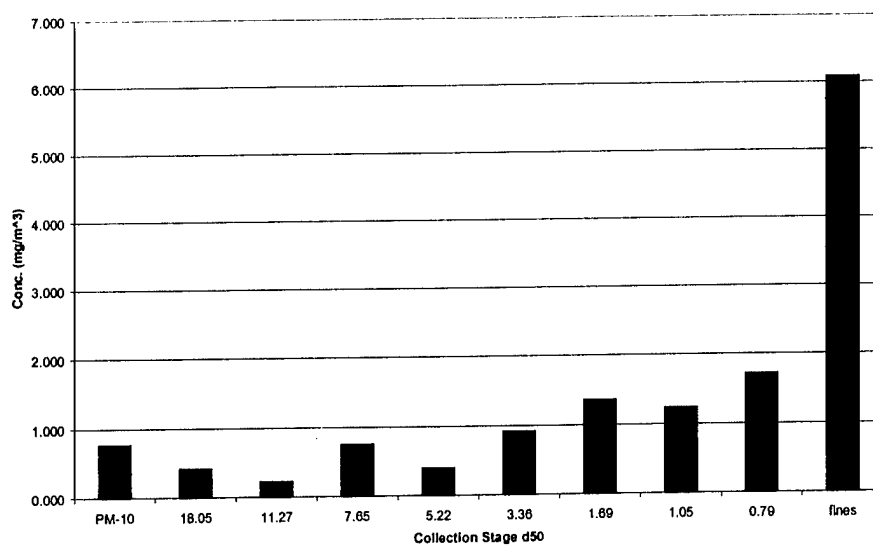


Figure 20. Particle Size Profile, 15 Sept. 2000

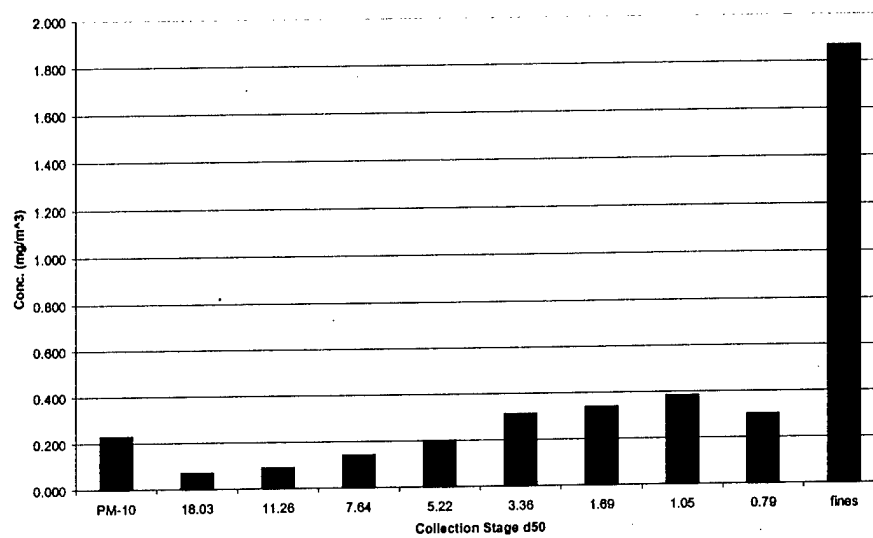


Figure 21. Particle Size Profile, Hot Fire, 18 Sept. 2000

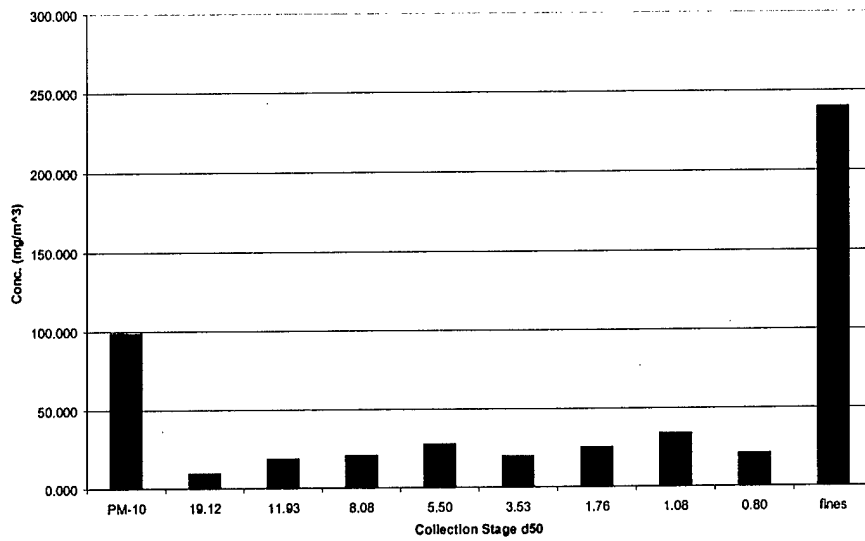


Figure 22. Particle Size Profile, Smoldering Period, 18 Sept. 2000

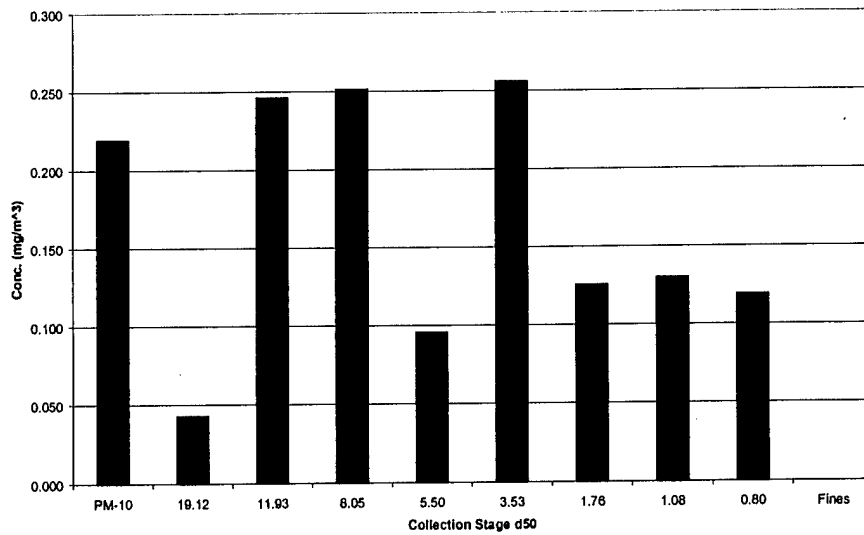


Figure 23. Particle Size Profile, Hot Fire, 19 Sept. 2000

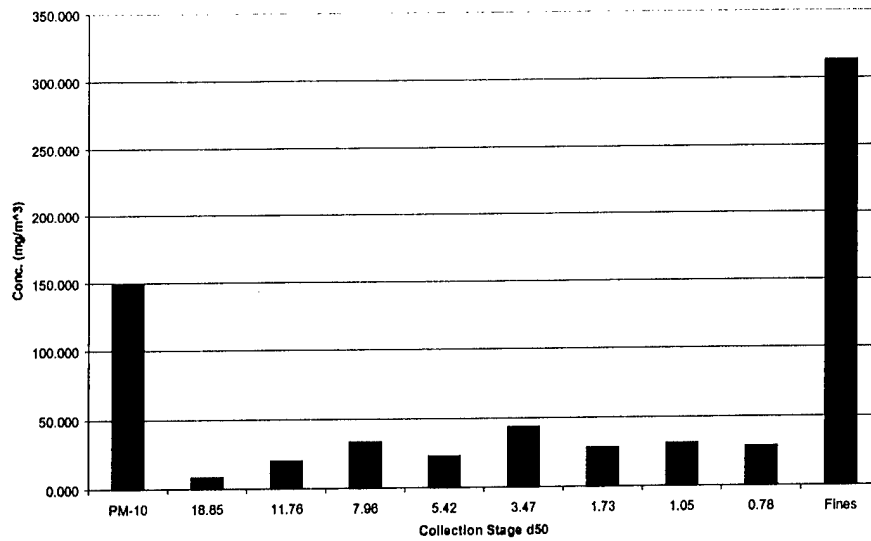


Figure 24. Particle Size Profile, Smoldering Period, 19 Sept. 2000

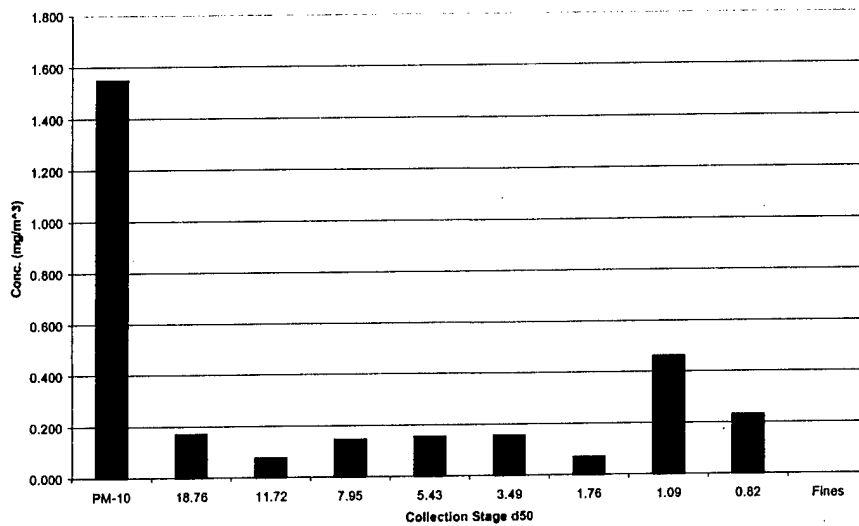


TABLE 13. Results from Particle Sizing Cascade Impactor Samples, based on particle densities of 1 g/cm³.

	13-Sep-00				15-Sep-00				18-Sep-00			
	Impactor #2				Impactor #1				Impactor #3			
Sample Start Time (sec)	296				272				601			
Sample End Time (sec)	5084				7045				2400			
Volume: (l, stp)	570				812				177			
Volume, stp (m ³):	0.570				0.812				0.177			
Tavg: (deg-F)	109.5				101.1				341.5			
Qs-avg (l/min)	7.15				7.20				5.73			
Qa-avg (l/min)	7.58				7.52				8.55			
	Diameter Cut-off (Microns)	Stage Weight (mg)	Stage Conc. (mg/m ³)	Particle Count Conc (/m ³)	Diameter Cut-off (Microns)	Stage Weight (mg)	Stage Conc. (mg/m ³)	Particle Count Conc (/m ³)	Diameter Cut-off (Microns)	Stage Weight (mg)	Stage Conc. (mg/m ³)	Particle Count Conc (/m ³)
Cyclone Preseparator	PM-10	0.44286	0.776		PM-10	1.65072	0.229		PM-10	17.42754	98.528	
Stage 1	18.05	0.24292	0.426	3.03E+05	18.03	0.51364	0.071	1.53E+07	19.12	1.67804	9.487	6.02E+03
Stage 2	11.27	0.12934	0.227	6.62E+05	11.26	0.66470	0.092	2.77E+07	11.93	3.32130	18.777	4.91E+04
Stage 3	7.65	0.43361	0.760	3.24E+06	7.64	1.03068	0.143	1.28E+08	8.08	3.67674	20.787	3.90E+04
Stage 4	5.22	0.23166	0.406	5.45E+06	5.22	1.44460	0.201	2.75E+08	5.50	4.92264	27.831	1.65E+05
Stage 5	3.36	0.52606	0.922	4.64E+07	3.36	2.26216	0.314	2.01E+09	3.53	3.51894	19.895	4.47E+05
Stage 6	1.69	0.77854	1.365	5.40E+08	1.69	2.45240	0.341	1.04E+10	1.76	4.48890	25.378	4.60E+06
Stage 7	1.05	0.70680	1.239	2.04E+09	1.05	2.78518	0.387	5.16E+10	1.08	6.03746	34.133	2.68E+07
Stage 8	0.79	0.98288	1.723	6.67E+09	0.79	2.17544	0.302	1.15E+11	0.80	3.73556	21.119	4.08E+07
Final GFF	finest	3.47414	6.090	1.16E+13	finest	13.44780	1.869	5.99E+14	finest	42.42812	239.870	2.37E+11
PM-3.5			11.34				28.46				1924	

TABLE 13. Results from Particle Sizing Cascade Impactor Samples, based on particle densities of 1 gm/cm³. (Cont.)

	18-Sep-00				19-Sep-00			
	Impactor #1				Impactor #2			
Sample Start Time (sec)	3000				600			
Sample End Time (sec)	6000				1800			
Volume: (l, stp)	335				117			
Volume, stp (m ³):	0.335				0.117			
Tavg: (deg-F)	115.6				372.1			
Qs-avg (l/min)	6.69				5.84			
Qa-avg (l/min)	7.18				9.05			
	Diameter Cut-off (Microns)	Stage Weight (mg)	Stage Conc. (mg/m ³)	Particle Count Conc (/m ³)	Diameter Cut-off (Microns)	Stage Weight (mg)	Stage Conc. (mg/m ³)	Particle Count Conc (/m ³)
Cyclone Preseparator	PM-10	0.03883	0.220		PM-10	17.42328	149.2	
Stage 1	19.12	0.00760	0.043	1.09E+04	18.85	1.01908	8.727	1.53E+07
Stage 2	11.93	0.04357	0.246	2.57E+05	11.76	2.37286	20.32	2.77E+07
Stage 3	8.05	0.04446	0.251	4.86E+05	7.96	3.95700	33.89	1.28E+08
Stage 4	5.50	0.01692	0.096	5.80E+05	5.42	2.68003	22.95	2.75E+08
Stage 5	3.53	0.04532	0.256	5.88E+06	3.47	5.12190	43.86	2.01E+09
Stage 6	1.76	0.02222	0.126	2.33E+07	1.73	3.29914	28.25	1.04E+10
Stage 7	1.08	0.02300	0.130	1.04E+08	1.05	3.65098	31.27	5.16E+10
Stage 8	0.80	0.02112	0.119	2.35E+08	0.78	3.33630	28.57	1.15E+11
Final GFF	Fines				Fines	36.61285	313.5	5.99E+14
PM-3.5			0.334				445.5	
								0.919

TABLE 14. Particle Sizing Cascade Impactor Results Based on Particle Densities=1.8 g/cm³.

	13-Sep-00				15-Sep-00				18-Sep-00			
	Impactor #2				Impactor #1				Impactor #3			
Sample Start Time (sec)	296				272				601			
Sample End Time (sec)	5084				7045				2400			
Volume: (l, stp)	570				812				177			
Volume, stp (m ³):	0.570				0.812				0.177			
Tavg: (deg-F)	109.5				101.1				341.5			
Qs-avg (l/min)	7.15				7.20				5.73			
Qa-avg (l/min)	7.58				7.52				8.55			
	Diameter Cut-off (Microns)	Stage Weight (mg)	Stage Conc. (mg/m ³)	Particle Count Conc (/m ³)	Diameter Cut-off (Microns)	Stage Weight (mg)	Stage Conc. (mg/m ³)	Particle Count Conc (/m ³)	Diameter Cut-off (Microns)	Stage Weight (mg)	Stage Conc. (mg/m ³)	Particle Count Conc (/m ³)
Cyclone Preseparator	8	0.44286	0.776		8	1.65072	0.229		8	17.42754	98.528	
Stage 1	13.43	0.24292	0.426	4.08E+05	13.42	0.51364	0.071	5.35E+03	14.22	1.67804	9.487	8.13E+03
Stage 2	8.38	0.12934	0.227	8.95E+05	8.37	0.66470	0.092	2.86E+04	8.86	3.32130	18.777	6.66E+04
Stage 3	5.68	0.43361	0.760	4.40E+06	5.67	1.03068	0.143	5.93E+04	5.99	3.67674	20.787	5.31E+04
Stage 4	3.87	0.23166	0.406	7.43E+06	3.87	1.44460	0.201	2.61E+05	4.07	4.92264	27.831	2.27E+05
Stage 5	2.48	0.52606	0.922	6.42E+07	2.48	2.26216	0.314	1.56E+06	2.60	3.51894	19.895	6.22E+05
Stage 6	1.24	0.77854	1.365	7.60E+08	1.24	2.45240	0.341	1.35E+07	1.28	4.48890	25.378	6.65E+06
Stage 7	0.76	0.70680	1.239	2.99E+09	0.76	2.78518	0.387	6.66E+07	0.77	6.03746	34.133	4.11E+07
Stage 8	0.57	0.98288	1.723	9.87E+09	0.57	2.17544	0.302	1.23E+08	0.57	3.73556	21.119	6.27E+07
Final GFF	finest	3.47414	6.090	6.46E+12	finest	13.44780	1.869	1.41E+11	finest	42.42812	239.870	1.32E+11
PM-3.5			11.34				28.46				1924	

TABLE 14. Particle Sizing Cascade Impactor Results Based on Particle Densities=1.8 g/cm³. (Cont.)

	18-Sep-00				19-Sep-00							
	Impactor #1				Impactor #2				Impactor #4			
Sample Start Time (sec)	3000				600				2402			
Sample End Time (sec)	6000				1800				4800			
Volume: (l, stp)	335				117				261			
Volume, stp (m ³):	0.335				0.117				0.261			
Tavg: (deg-F)	115.6				372.1				131.5			
Qs-avg (l/min)	6.69				5.84				6.53			
Qa-avg (l/min)	7.18				9.05				7.19			
	Diameter Cut-off (Microns)	Stage Weight (mg)	Stage Conc. (mg/m ³)	Particle Count Conc (/m ³)	Diameter Cut-off (Microns)	Stage Weight (mg)	Stage Conc. (mg/m ³)	Particle Count Conc (/m ³)	Diameter Cut-off (Microns)	Stage Weight (mg)	Stage Conc. (mg/m ³)	Particle Count Conc (/m ³)
Cyclone Preseparator	8.00	0.03883	0.220		8	17.42328	149.2		8	0.40446	1.550	
Stage 1	14.22	0.00760	0.043	1.47E+04	14.01	1.01908	8.727	2.07E+07	14.01	0.04462	0.171	4.81E+05
Stage 2	8.86	0.04357	0.246	3.49E+05	8.72	2.37286	20.32	3.78E+07	8.72	0.01974	0.076	8.82E+05
Stage 3	5.99	0.04446	0.251	6.56E+05	5.90	3.95700	33.89	1.75E+08	5.90	0.03840	0.147	7.60E+05
Stage 4	4.07	0.01692	0.096	7.95E+05	4.00	2.68003	22.95	3.81E+08	4.00	0.04044	0.155	2.57E+06
Stage 5	2.60	0.04532	0.256	8.17E+06	2.55	5.12190	43.86	2.81E+09	2.55	0.04070	0.156	9.98E+06
Stage 6	1.28	0.02222	0.126	3.36E+07	1.25	3.29914	28.25	1.53E+10	1.25	0.01822	0.070	3.79E+07
Stage 7	0.77	0.02300	0.130	1.60E+08	0.75	3.65098	31.27	7.86E+10	0.75	0.12038	0.461	1.16E+09
Stage 8	0.57	0.02112	0.119	3.61E+08	0.55	3.33630	28.57	1.82E+11	0.55	0.06036	0.231	1.48E+09
Final GFF	Fines			0	Fines	36.61285	313.5	3.33E+14	Fines			0
PM-3.5			0.334				445.5				0.919	

d) SPME Samples: SPME samples were analyzed with a Viking portable GC/MS operated in a laboratory setting, using its split/splitless injection port. The built-in data system of this instrument used software closely related to Mass Spectral Chemstation (Hewlett-Packard, Inc.) data systems. Result files from the GC/MS analyses were transferred to a Chemstation data system to more easily permit library searches using a mass spectral library (John Wiley & Sons, Inc.)¹⁷ and to more easily allow printed records from the results.

Blank analyses of conditioned SPME sampling fibers and from the Viking system frequently showed a contaminant that was tentatively identified as an isomer of diethylphthalate. The peak for this compound also was detected in many of the burn samples, but due to the presence in the blanks, this does not provide strong evidence for this compound in the indoor burn facility.

SPME samplers were utilized with several different extractive phases, including fibers coated with 100 μm polydimethylsiloxane (PDMS, Supelco, PN 504823), 65 μm of mixed extractive phase of polymethylsiloxane and divinylbenzene (PDMS/DVB, Supelco, PN 57359-U), and 75 μm of mixed extractive phase of polydimethylsiloxane and carboxen (PDMS/Carboxen, Supelco, PN 504831). The PDMS fibers were considered to be good fibers for general organic compound sampling, including volatile and semivolatile compounds. The PDMS/DVB fibers were also considered to be good general-purpose fibers, but they are often considered to be better than PDMS for volatile and polar analytes. The PDMS/Carboxen fibers are considered to be highly useful for sampling volatile compounds at trace concentrations.

For the 9 September burn event, two SPME fibers coated with 100 μm PDMS were hung from wires at SPME sampling positions 1 and 3. A SPME fiber coated with 65 μm PDMS/DVB was hung in position 2. The total ion chromatogram (TIC) from the SPME device hung in position 1 is shown in **Figure 25**. Few peaks are evident in the early portion of the chromatogram, where volatile components would be expected to elute. Some peaks are evident in the later portion of the chromatogram, although baseline drifting, presumably due to column bleed, obscures some of the less abundant substances. The high column bleed also contributed to chemical noise in the mass spectrometer, forcing extensive use of background subtraction to be able to identify some of the larger peaks. The peaks identified are listed in Table 15. The TIC from the PDMS sampling fiber hung in position 3 is shown in **Figure 26**. The early portion of this chromatogram is dominated by a baseline distortion that is largely due to excess air in the carrier gas. This is probably an artifact produced by the Viking GC/MS, which switches carrier gas off between runs and re-establishes carrier gas flow only in time for the next run. A number of peaks did appear in the later part of the chromatogram, and once again these required background subtraction to obtain identifiable mass spectra. The tentative identities of these peaks are listed in Table 15. The analysis of the PDMS/DVB SPME device failed due to an injection error.

Figure 25. TIC from position 1 SPME Sampler, PDMS Fiber, 9 Sept 2000

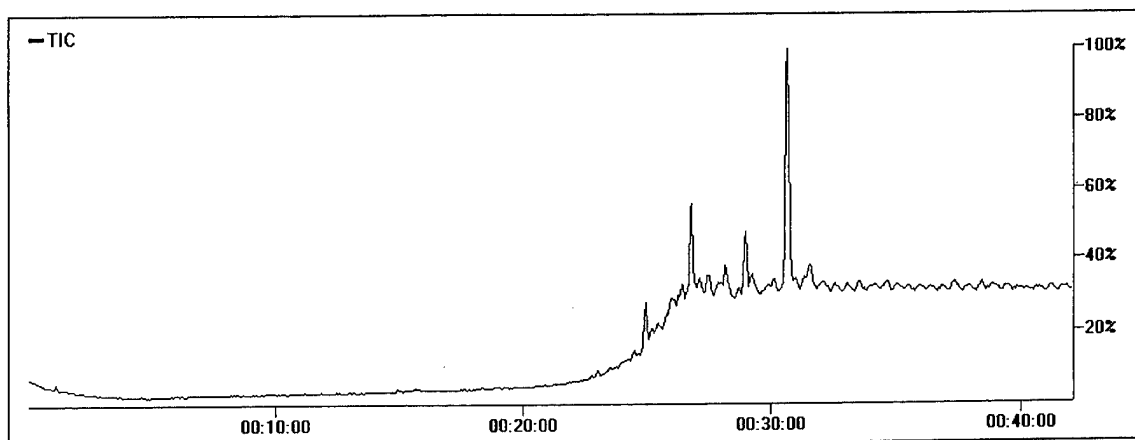


TABLE 15. Summary of Qualitative SPME Results from the test burn on 9 September 2000.

Peak	Position 1 TIC		Position 3 TIC	
	Retention Time	Peak Area	Retention Time	Peak Area
Tridecane	24.92	454236	25.61	309886
Tetradecane	26.74	778558	27.44	743227
Pentadecane	28.94	849803	29.71	887432
Diethylphthalate	30.60	3589002	31.44	8678010
2,3-epoxy-2-methyl-4-octanone	31.49	250676		

Figure 26. TIC from Position 3 SPME Sampler, PDMS Fiber, 9 Sept 2000

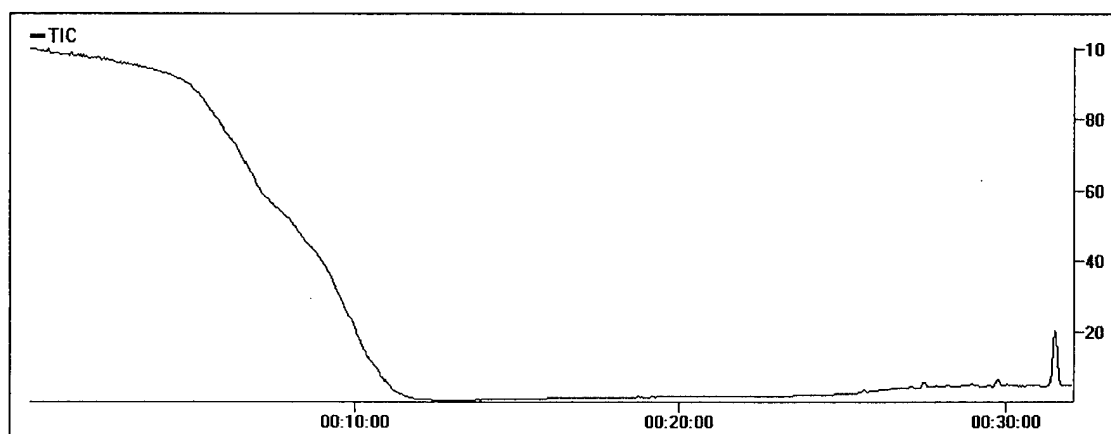


Figure 27. TIC from SPME Sampler PDMS-H04, Sample Collected 15 Sept 2000

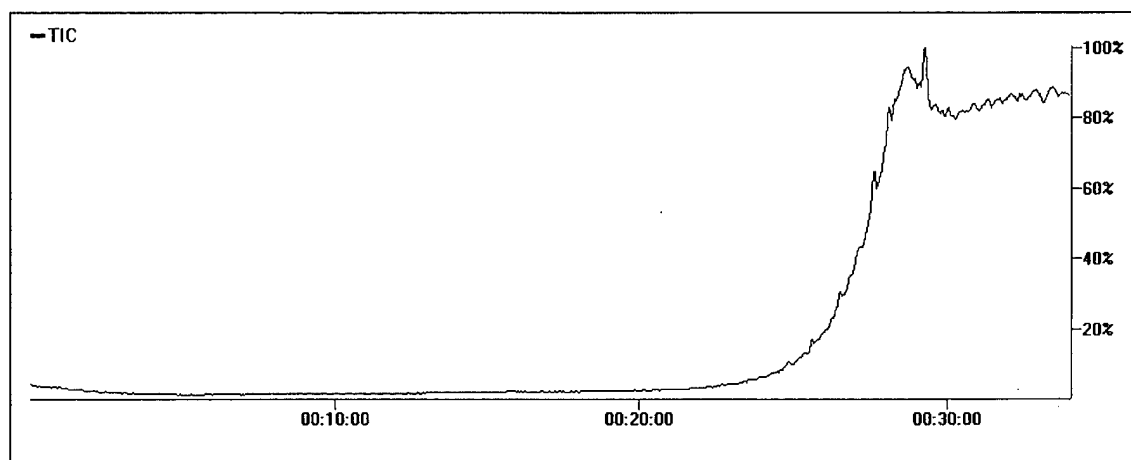


Figure 28. TIC from SPME sampler PDMS-H03, 15 Sept 2000

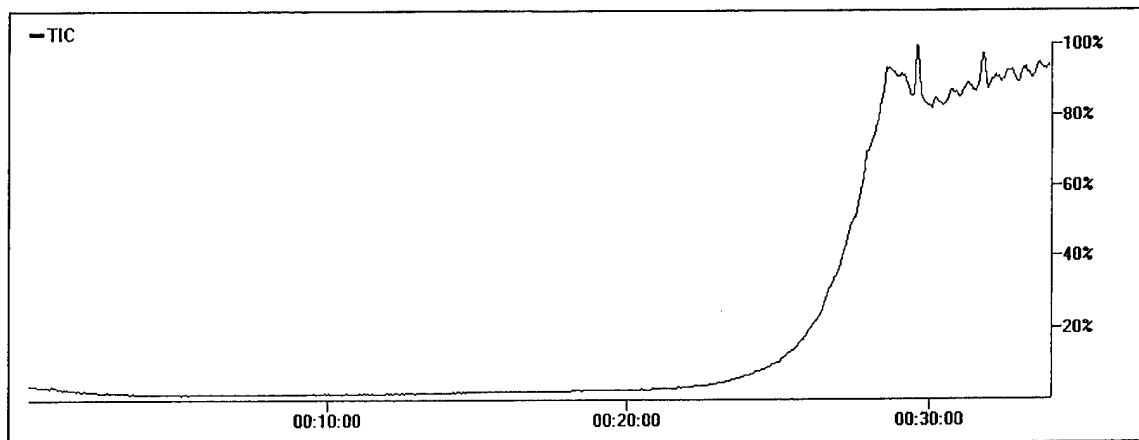
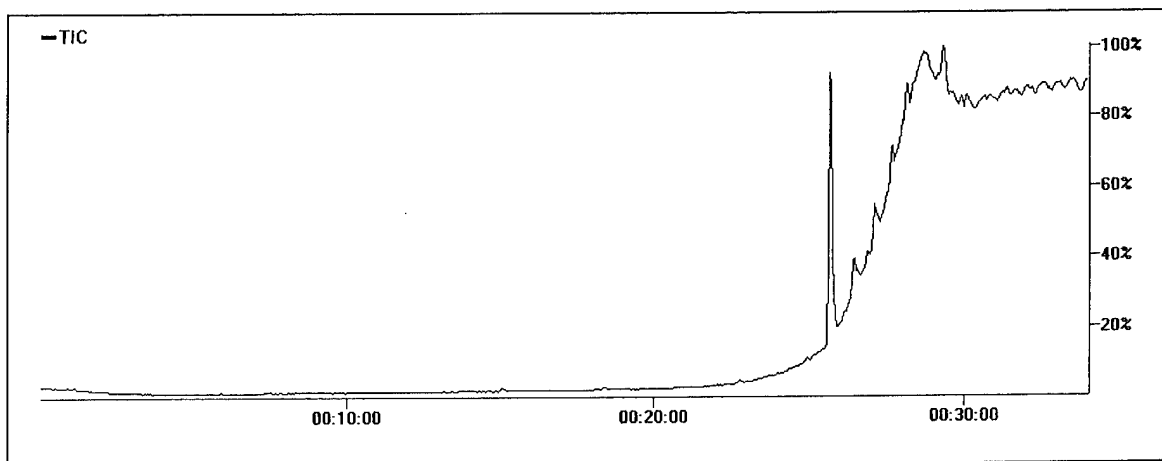


Figure 29. TIC from SPME sampler PDMS/DVB-H02, 15 Sept 2000



The positions of the 3 SPME sampling devices used for the 15 September burn were not recorded. These SPME devices consisted of 2 fibers coated with 100 μm PDMS and 1 coated with 65 μm PDMS/DVB mixed phase. The TIC from one PDMS sampling fiber, designated PDMS-H04, is shown in **Figure 27**. Three small peaks were noted, and they all required background subtraction in order to isolate the unknown compound's mass spectrum from the column bleed. The peak eluting at 27.59 min produces a background subtracted mass spectrum consistent with biphenylene or acenaphthalene, either compound of which produces virtually identical spectra. The peak eluting at 28.08 min is due to an alkane, and the details of the mass spectrum and the retention time appear consistent with pentadecane. The peak at 29.245 min appears to be diethylphthalate. The results of the background subtracted library searches are summarized in Table 16.

The TIC from the analysis of the second PDMS fiber, designated PDMS-H03, is shown in **Figure 28**. Aside from baseline variations this displays two readily discernable peaks, and these mass spectra must be isolated from the column bleed by background subtraction. The peak eluting at 29.59 min appears to be diethylphthalate. The peak eluting at 31.76 min displayed a base peak of 100 daltons and its best library match was 2 (5H)-Thiophenone. These results are also summarized in Table 16.

The TIC from the PDMS/DVB fiber, designated PDMS/DVB-H02, is shown in **Figure 29**. The peaks discernable in this chromatogram also required background subtraction to eliminate spectral components due to column bleed. The large peak eluting at 25.66 min produced a background subtracted spectrum whose best library match was 2,4-diisocyanato-1-methylbenzene. The background subtracted spectrum from the peak at 26.445 min resembled 1,3-dihydro-5-methyl-2H-Benzimidazol-2-one. No library search match for the peak at 27.10 min actually accounted for the peaks of the spectrum, so this substance remains unidentified. The peak eluting at 27.65 min was consistent with biphenylene or acenaphthylene. The peak at 28.13 min was an alkane whose spectrum resembled that of pentadecane. The peak eluting at 29.31 min appeared to be diethylphthalate. These are summarized in Table 16. The sulfur compound tentatively identified, 2(5H)-thiophenone, is puzzling if it is an accurate identification, since sulfur is not abundant in jet fuel. However sulfur is present in the composite resin due to the use of diaminodiphenylsulphone (DDS) as the composite curing agent during manufacture.

TABLE 16. Summary of qualitative SPME/GC/MS results from 15 September 2000 test burn.

Peak	PDMS-H04		PDMS-H03		PDMS/DVB-H02	
	Retention Time	Area	Retention Time	Area	Retention Time	Area
2,4-diisocyanato-1-methylbenzene					25.66	5604392
1,3-dihydro-5-methyl-2H-benzimidazol-2-one					26.45	1013705
Unidentified					27.10	990934
Biphenylene or acenaphthalene	27.59	509852			27.65	771681
Pentadecane	28.08	481029			28.13	483310
Diethylphthalate	29.25	1136604	29.59	1280612	29.31	1137973
2 (5H)-Thiophenone			31.76	1328666		

For the 18 September 2000 large scale test fire with JP-8 fuel and a large composite sample, three SPME fibers with 75 μ m PDMS/Carboxen coatings were hung in the corner sampling positions, but the specific positions of the three samplers were not recorded. One sampler's TIC exhibited a large initial signal of air, probably due to inadequate purging of the Viking GC/MS flow system prior to the first run of a series, following a period of inactivity. This TIC is for the sampler designated C0106, and it is shown in **Figure 30**. Several peaks are discernable in this chromatogram. Mass spectra from the peaks located by automatic integration of the peaks were submitted to the library search routine. The tentatively identified peaks and their peak areas are summarized in Table 17. The TIC for the PDMS/Carboxen fiber designated C0104 is shown in **Figure 31**, and its tentatively identified compounds are also summarized in Table 17. The final PDMS/Carboxen fiber exposed on 18 September 2000 was designated C0105, and its TIC is shown in **Figure 32**. Tentatively identified compounds from this sample are summarized in Table 17. Most of the compounds detected using the PDMS/Carboxen fibers were aromatic in nature, although several siloxane peaks were exhibited with greater intensities than were accounted for in the fiber cleanup blanks.

TABLE 17. Summary of PDMS/Carboxen tentatively identified compounds for 18 September 2000.

Compound	Retention Time	C0106		C0104		C0105	
		Peak Areas	% Area	Peak Areas	% Area	Peak Areas	% Area
unidentified	.98					98272	0.38
benzene	8.71			418845.00	1.96	809415	3.17
heptane	9.42			70969.00	0.33		
unidentified	10.36	93104	0.78	0	0.00	82096	0.32
unidentified	10.97						
methylbenzene	12.31			368798	1.73	375994	1.47

TABLE 17. Summary of PDMS/Carboxen tentatively identified compounds for 18 Sept 2000

Compound	Retention Time	C0106		C0104		C0105	
		Peak Areas	% Area	Peak Areas	% Area	Peak Areas	% Area
unidentified	12.55			57382	0.27		
branched octane isomer	13.60			139636	0.65	117730	0.46
Hexamethylcyclotri-siloxane	14.22			1428122	6.69	4195023	16.42
ethylbenzene	15.49	1360866	11.34	180532	0.85	114242	0.45
m&p-xylene	16.16	417561	3.48	1272979	5.96	907920	3.55
3-methyloctane	15.74			149142	0.70		
styrene	16.00			103932	0.49	97035	0.38
o-xylene	16.16			569911	2.67	379326	1.48
nonane	16.50	1166020	9.71	1005464	4.71		
2-methyl-3-heptanone or 2,5-dimethyl-3-hexanone	16.55					864042	3.38
2-methylheptanone	16.72						
unidentified or C3-benzene + 3-(1,1-dimethylethyl)-1,1'-biphenyl-2-ol	16.85			54038	0.25	185716	0.73
C3-benzene	16.98						
(1-methylethyl)-benzene + unidentified hydrocarbon	17.02			145998	0.68	93827	0.37
unidentified	17.24			106065	0.50		
propylcyclohexane or (1-methylethyl)-cyclohexane	17.45			354147	1.66	267035	1.05
benzaldehyde	17.56			354147	1.66	130108	0.51
propylbenzene	17.76						
phenol + C3-benzene	17.85	1117125	9.31	1851600	8.67	1726371	6.76
C3-benzene	18.00		0.00		0.00		
C3-benzene	18.17			596763	2.79	535246	2.09
1-ethyl-4-methylbenzene or isomer	18.48			239109	1.12		
1,2,4-trimethylbenzene or isomer+octamethylcyclotetrasiloxane	18.83	2335000	19.45	3231412	15.13	6280534	24.58
decane	19.03	1222684	10.19	969864	4.54		
unidentified or C4-benzene	19.46			67304	0.32		
1,2,3-trimethylbenzene or isomer	19.55			669007	3.13	276125	1.08
2,3-dihydroindene	19.90			82727	0.39		

TABLE 17. Summary of PDMS/Carboxen tentatively identified compounds for 18 Sept 2000

Compound	Retention Time	C0106		C0104		C0105	
		Peak Areas	% Area	Peak Areas	% Area	Peak Areas	% Area
butylcyclohexane	20.00						
1H-indene	20.00			97035	0.45	140936	0.55
(1-methylpropyl)-benzene or isomer	20.14			95212	0.45		
1-ethyl-3,5-dimethylbenzene or isomer	20.29		0.00	214364	1.00	360499	1.41
C4-benzene	20.50						
C4-benzene	20.80					163235	0.64
C4-benzene	20.98					126322	0.49
undecane	21.25	823903	6.86	878868	4.11	610516	2.39
1-ethyl-3,5-dimethylbenzene or isomer	21.69			153777	0.72	113613	0.44
tetramethylbenzene or similar isomer	21.88						
C4-benzene	21.96						
methyl-2,3-dihydro-1H-indene (isomer uncertain)	22.15						
C4-benzene	22.22						
Octamethylcyclotetra-siloxane	22.41						
methyl-2,3,-dihydro-1H-indene (isomer uncertain)	22.45						
Decamethylcyclopenta-siloxane	22.56					1219919	4.77
Diethylmethylbenzene or isomer	22.66			164936	0.77		
1,2,3,4-tetrahydronaphthalene	22.95						
Naphthalene	23.12	3467127	28.88	4567329	21.38	4790183	18.75
Dodecane	23.26		0.00	698297	3.27	586993	2.30
Unidentified	24.11						
Methylnaphthalene (isomer uncertain)	25.12						
Methylnaphthalene (isomer uncertain)	25.42						
Tetradecane	26.52						
Total Peak Area		12003390		21357711		25550001	

Retention Times were adjusted between runs based on time variations of easily recognized "marker" compounds.

Figure 30. TIC from SPME sampler C0106, 18 Sept 2000

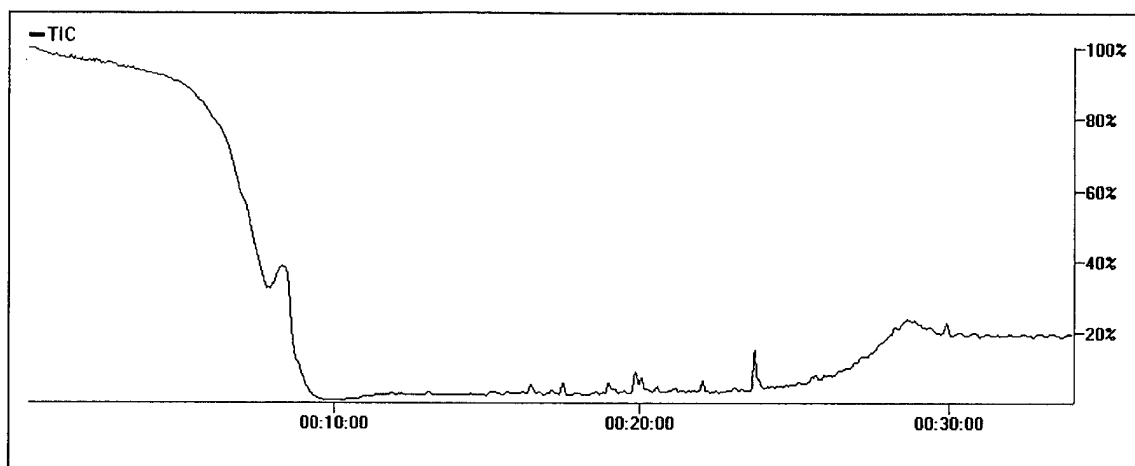


Figure 31. TIC from SPME sampler C0104, 18 Sept 2000

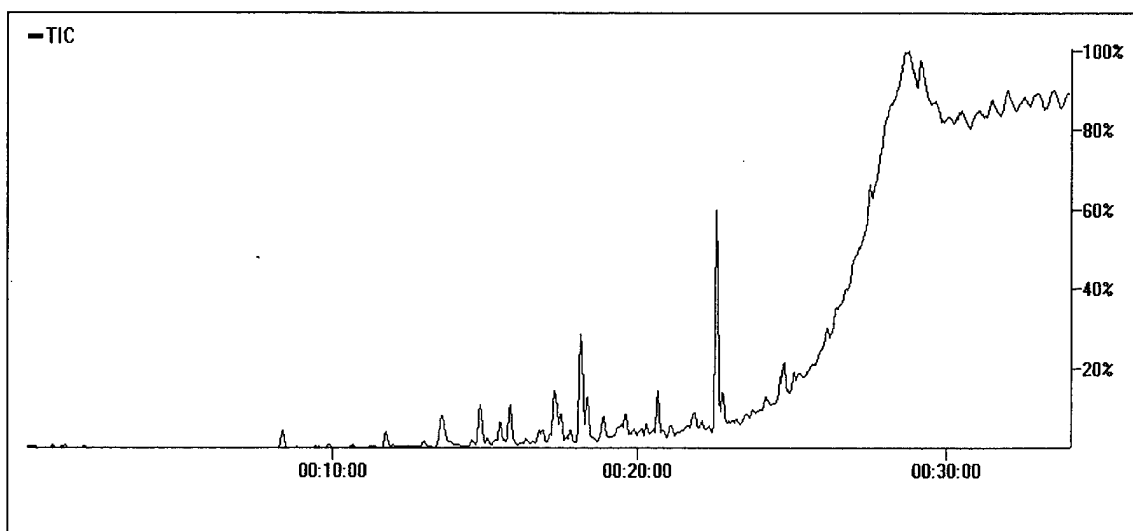


Figure 32. TIC from SPME sampler C0105, 18 Sept 2000

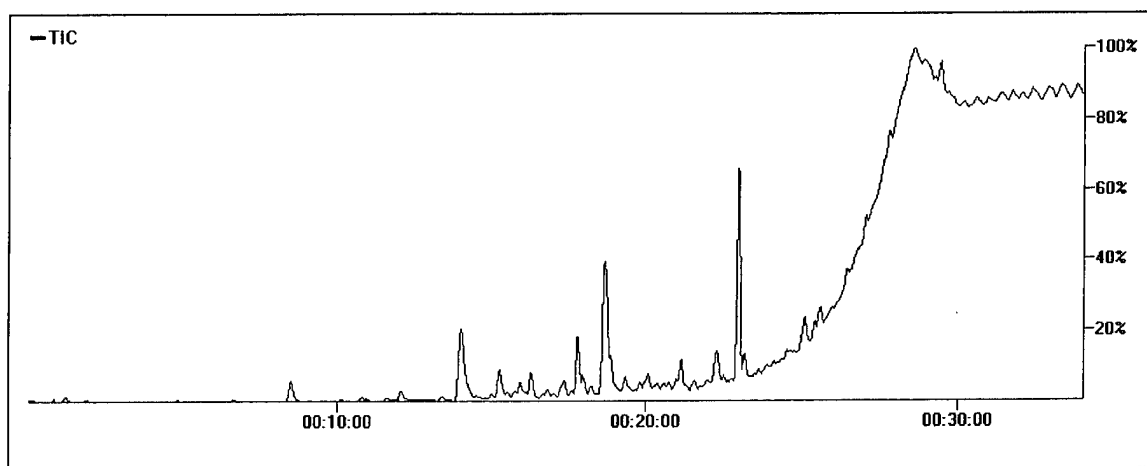


Figure 33. TIC from SPME sampler PDMS-HO2, 18 Sept 2000

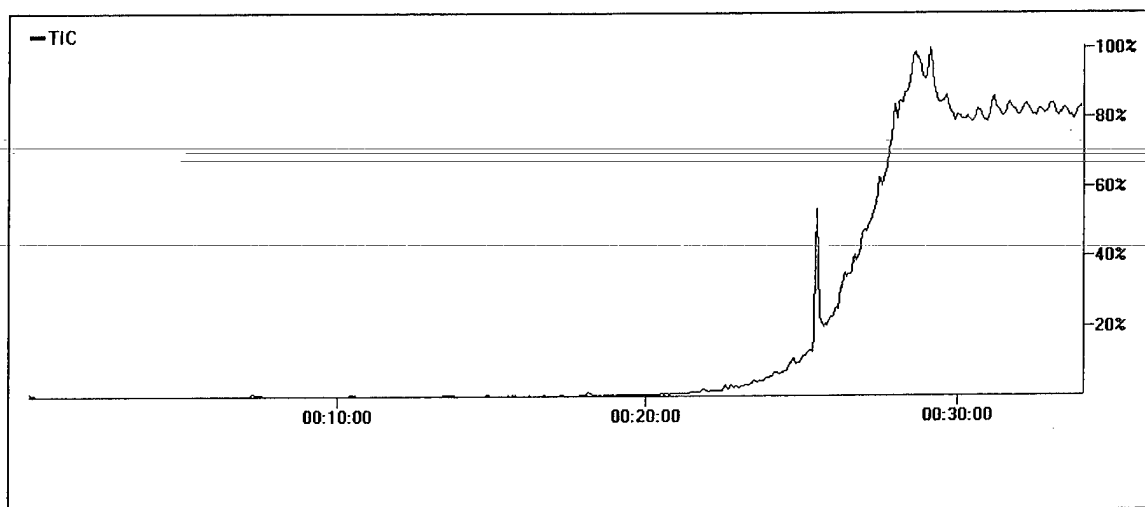
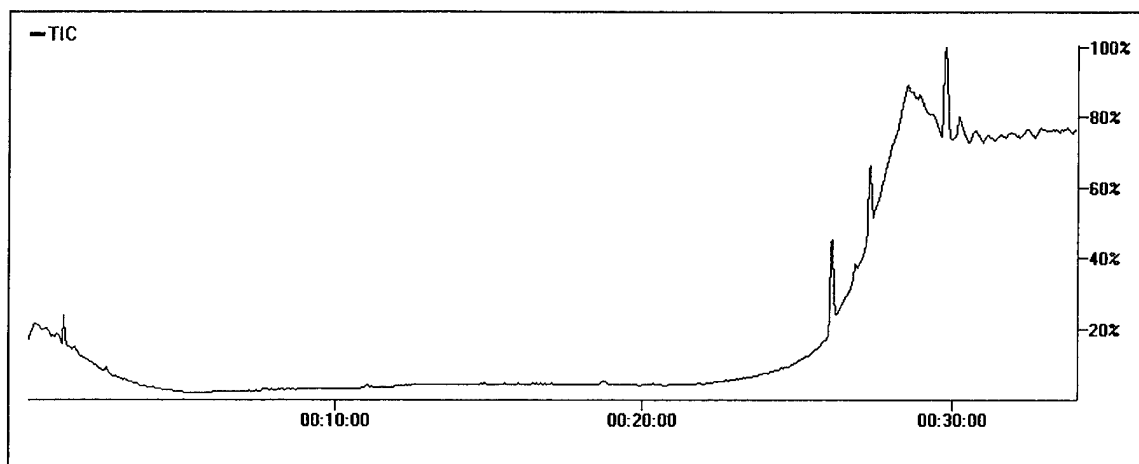


Figure 34. TIC from SPME sampler PDMS-HO4, 18 Sept 2000



A PDMS sampling fiber, PDMS-H02 was also hung on 18 September 2000. Its TIC is shown in **Figure 33**. The prominent peaks are tentatively identified as 2,4-diisocyanato-1-methylbenzene and diethylphthalate. A second PDMS sampling fiber, PDMS-H04 was also hung. Its TIC is shown in **Figure 34** and displays three significant peaks, which are tentatively identified as 2,4-diisocyanato-1-methylbenzene, the methyl ester of 4-hydroxybenzoic acid, and diethylphthalate.

On 19 September greater care was taken to record the positions of the SPME fibers hung on the sampling wires in the corners of the burn facility. The PDMS/Carboxen fiber C0102 was hung in sampling position 1, in the northwest corner of the burn facility. Its TIC is shown in **Figure 35** and the tentatively identified compounds are listed in Table 18. The PDMS/Carboxen fiber C0106 was hung in position 3, in the southeast corner of the facility. Its TIC is shown in **Figure 36** and its peaks are also summarized in Table 18. PDMS/Carboxen fiber C0101 was hung in position 4, in the northeast corner of the burn facility, and its TIC is shown in **Figure 37**, with the tentatively identified compounds listed in Table 18.

Figure 35. TIC from SPME sampler CO102, position 1, 19 Sept 2000

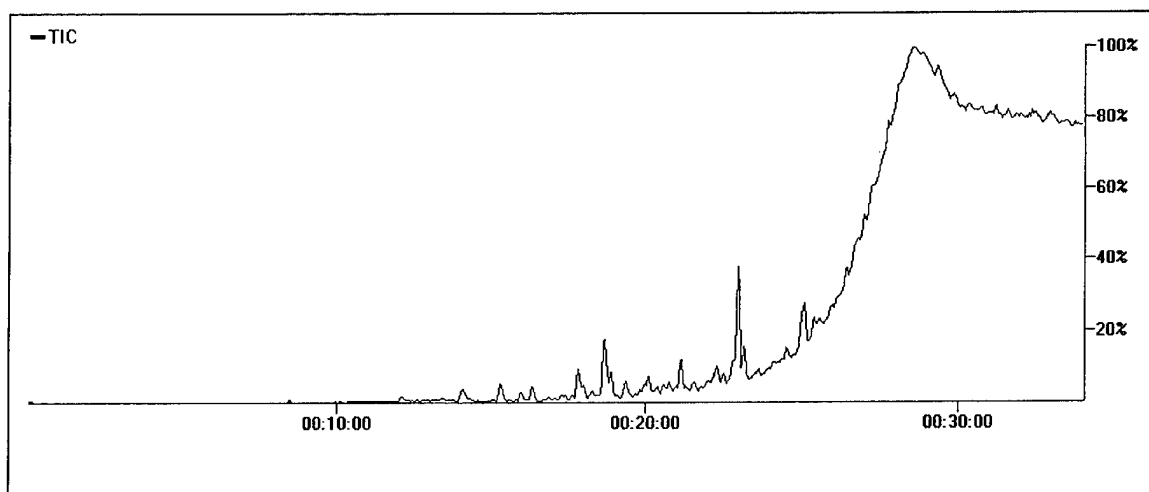


Figure 36. TIC from SPME sampler CO106, position 3, 19 Sept 2000

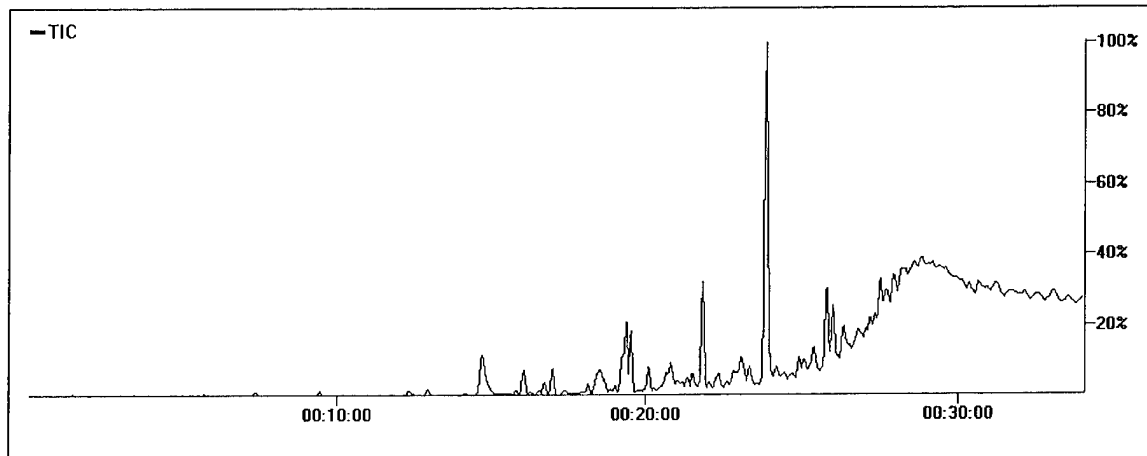
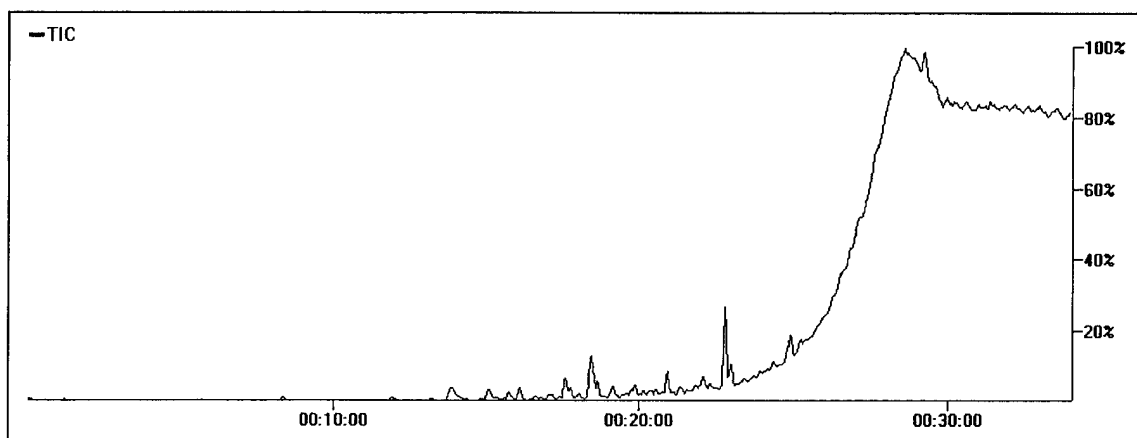


Figure 37. TIC from SPME sampler C0101, position 4, 19 Sept 2000



In a number of cases the SPME sampling devices were found to be coated in soot when they were recovered. Closing the fiber after the sampling tended to rub off most or all particles that had collected on the fiber during the burn. Although the soot was easily removed it might have competed for sorption of some of the organics with the SPME phase. It was a convenient qualitative sampling technique, but as it was used in this series of experiments, quantitation is not practical.

TABLE 18. Compounds tentatively identified from PDMS/Carboxen SPME fibers exposed during 19 September test burn.

		C0101		C0106		C0102	
Compound	Retention Time ⁺	Peak Areas	% Area	Peak Areas	% Area	Peak Areas	% Area
Unidentified	.98						
Benzene	8.71	85357	1.15	277898	0.42	53661	0.69
Heptane	9.42						
Unidentified	10.36						
Unidentified	10.97						
Methylbenzene	12.31	47013	0.64	403504	0.61	87864	1.12
Unidentified	12.55						
Branched octane isomer	13.60	15176	0.20				

⁺ Retention times were adjusted between runs based on retention time variations of "marker" compounds.

TABLE 18. Compounds tentatively identified from PDMS/Carboxen SPME fibers exposed during 19 Sept 2000 test burn.

Compound	Retention Time ⁺	C0101		C0106		C0102	
		Peak Areas	% Area	Peak Areas	% Area	Peak Areas	% Area
Hexamethylcyclotri-siloxane	14.22	532300	7.19	6372136	9.64	222225	2.84
Ethylbenzene	15.49	32572	0.44			50401	0.64
m&p-xylene	16.16	141802	1.92	1874527	2.83	437099	5.59
3-methyloctane	15.74	34578	0.47			34740	0.44
Styrene	16.00						
o-xylene	16.16	174551	2.36	759317	1.15	192271	2.46
Nonane	16.50	246907	3.34				
2-methyl-3-heptanone or 2,5-dimethyl-3-hexanone	16.55					304120	3.89
2-methylheptanone	16.72			1586473	2.40		
unidentified or C3-benzene + 3-(1,1-dimethylethyl)-1,1'-biphenyl-2-ol	16.85						
C3-benzene	16.98					18207	0.23
(1-methylethyl)-benzene + unidentified hydrocarbon	17.02	45516	0.61				
unidentified	17.24			386752	0.58		
propylcyclohexane or (1-methylethyl)-cyclohexane	17.45	65959	0.89			69102	0.88
benzaldehyde	17.56			555140	0.84	52982	0.68
propylbenzene	17.76	55924	0.76			39997	0.51
phenol + C3-benzene	17.85	546571	7.38	1465981	2.22		
C3-benzene	18.00					640212	8.19
C3-benzene	18.17	206857	2.79			229352	2.93
1-ethyl-4-methylbenzene or isomer	18.48	110904	1.50	292958	0.44	147613	1.89
1,2,4-trimethylbenzene or isomer+octamethyl-cyclotetrasiloxane	18.83	1393079	18.82	3147999	4.76	1311009	16.77
decane	19.03	308325	4.16	3560830	5.39	359487	4.60
unidentified or C4-benzene	19.46	35294	0.48			29272	0.37
1,2,3-trimethylbenzene or isomer	19.55	228400	3.09	1496175	2.26	207498	2.65
2,3-dihydroindene	19.90	36905	0.50			29204	0.37

⁺ Retention times were adjusted between runs based on retention time variations of "marker" compounds.

TABLE 18. Compounds tentatively identified from PDMS/Carboxen SPME fibers exposed during 19 Sept 2000 test burn.

Compound	Retention Time ⁺	C0101		C0106		C0102	
		Peak Areas	% Area	Peak Areas	% Area	Peak Areas	% Area
butylcyclohexane	20.00					37806	0.48
1H-indene	20.00						
(1-methylpropyl)-benzene or isomer	20.14	70372	0.95			127219	1.63
1-ethyl-3,5-dimethylbenzene or isomer	20.29	208767	2.82	1151564	1.74	257601	3.30
C4-benzene	20.50	105035	1.42	1560883	2.36		
C4-benzene	20.80	115936	1.57			177743	2.27
C4-benzene	20.98	93113	1.26	715340	1.08	190134	2.43
undecane	21.25	380746	5.14	6027021	9.11	467823	5.99
1-ethyl-3,5-dimethylbenzene or isomer	21.69	95660	1.29			71203	0.91
tetramethylbenzene or similar isomer	21.88			701280	1.06		
C4-benzene	21.96			610019	0.92		
methyl-2,3-dihydro-1H-indene (isomer uncertain)	22.15	74274	1.00				
C4-benzene	22.22			381298	0.58		
Octamethylcyclotetra-siloxane	22.41	173300	2.34				
methyl-2,3,-dihydro-1H-indene (isomer uncertain)	22.45			414232	0.63		
Decamethylcyclopenta-siloxane	22.56						
diethylmethylbenzene or isomer	22.66	24880	0.34				
1,2,3,4-tetrahydronaphthalene	22.95			947371	1.43	138230	1.77
naphthalene	23.12	1405496	18.99	24316261	36.77	1368230	17.51
dodecane	23.26	396884	5.36			463846	5.93
unidentified	24.11			1279605	1.94		
methylnaphthalene (isomer uncertain)	25.12			3118652	4.72		
methylnaphthalene (isomer uncertain)	25.42			1314646	1.99		
tetradecane	26.52			1404385	2.12		
Total Peak Area		7403096		66122247		7816151	

D. Hazardous Waste Analysis of Burnt Carbon Fiber Epoxy Composite

Knowledge of the hazardous characteristics of the burnt composite is needed when making disposal decisions (40 CFR Part 268). To characterize this waste, a defined set of analytical tests is performed. If the results are below the regulatory limit then the waste is considered as a solid waste and not a hazardous waste.

Randomly chosen pieces of burnt composite were analyzed for two of the four characteristics identifying hazardous waste. Ignitibility, corrosivity, reactivity, and toxicity are the four characteristics.¹⁸ Toxicity and corrosivity were the two characteristics that were tested. The selected characteristics were based on knowledge of the process that generated the composite waste and knowledge of the burnt composite material properties. Following is the methodology and results of the testing.

1. Methodology

a) Toxicity: The laboratory received two bulk burnt pieces of composite wrapped in plastic from the September 15th and September 18th burn. The September 15th burn samples were strips of composite cut from the wing box (Figures 6 and 38). A randomly chosen piece was sent for testing. The September 18th burn was the first large scale composite wing box burn (Figure 39). The sample was taken from the top surface of the wing box. The wing box experienced flaming conditions long enough to cause severe burn damage (see Graphs 30 and 44).

Figure 38. September 15th pre-burn samples

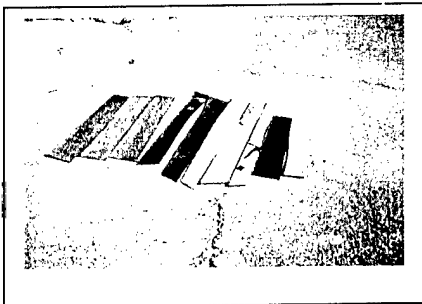


Figure 39. September 18th, post burn sample



Guidance was given to the laboratory for safe handling of the fibrous composite waste when performing the preliminary steps of the procedure. The analytical method requires a specific sample amount and size. To meet this requirement the bulk pieces sent to the laboratory would have to be reduced. Cutting of burnt composite to the size requirements of the method could release burnt particulate and fibers.

Liquid leachates were generated from the burnt composites. The leachates were produced following the Toxic Characteristic Leaching Procedure (TCLP) in the Environmental Protection Agency publication SW-846, Method 1311¹⁹. The leachates were then prepared and analyzed for the toxic waste constituents. The volatile and semivolatile organics were analyzed by SW-846, Methods 8260B and 8270C, respectively. The metals were analyzed following SW-846, Methods 6010B and 7470A. The target list requested was volatile, semivolatile and metals hazardous waste characteristics (EPA Hazardous Waste No. D).

b) Corrosivity: Corrosive materials pose potential hazards to the environment and to human health. There are two methods for corrosivity. The method choice depends on what the hazardous situation is. Burning polymer resins can create acidic or basic gases or liquid vapor that can collect on surfaces. If collection were to occur on the burnt composite, the composite may be corrosive to touch. For burnt composite material the corrosive property to test is pH.

Section 7 of SW-846 requires Method 9045 for pH determination of a solid. Since pH determination is part of the TCLP, the pH value obtained during that procedure was used to make a corrosivity determination for this burn study. It is noted method deviations are not allowed for compliance purposes.

2. Discussion and Results

a) Toxicity Characteristics: Table 19 below lists the results for each analysis. The results of the two characteristics would categorize the burnt material as a solid waste and not as a hazardous waste.

(1) The reporting limits for the organic results were the hazardous waste regulatory limits. The results were non-detect for all organic compounds. There were no detectable organic compounds in the composite leachable at the regulatory limit.

(2) The reporting limits for the metal results are limits used for water evaluation and not for hazardous waste toxicity evaluations. The water limits are in the parts per billion (ppb) range and are much lower than the hazardous waste regulatory limits, which are in the parts per million range (ppm).

(3) The September 15th burn metal results were non-detect at the regulatory limit. Three metals were reported for the September 18th burn. The amounts reported were lower than the hazardous waste toxicity limits.

(4) The results for the corrosive characteristic test determined that the material condition produced from this particular burn was non-corrosive.

The condition of the burnt composite, the sample preparation method, and the regulatory limits will be used to discuss the results.

b) Volatile: From the list of target compounds in Table 19, benzene is the most likely compound to be detected. While burning, the matrix²⁰ and the JP8 fuel could be a source of benzene. The regulatory limits of concern are in the parts per million range (ppm). The TCLP leaching mixture is a 20:1 ratio, liquid to solid which introduces a dilution factor of 20. To have detected benzene using the TCLP, high ppm levels of benzene would have to be present on the burnt composite. The volatility of benzene at fire temperatures would suggest that most of what is released would be carried away with the plume and what is possibly remaining may not be detectable using the prescribed analytical methods.

c) Semivolatile: The non-detect results obtained are not unreasonable. The major constituents of JP8 do not provide sources for the semivolatile target compounds in Table 1 (JP8 additive information is unknown). Then, sources for the semivolatiles target compounds would have to come from the resin. Since the resin formulation 3501-6 is proprietary, knowing what specific combustion compounds could exist is difficult. Most of the target compounds listed are solvents and/or are used in organic synthesis. Chlorinated combustion products were not identified on the material safety data sheet (MSDS) for the resin, which indicates that chlorinated hydrocarbons are not part of the resin formulation. This eliminates the possibility of detecting the chlorinated compounds on the target list. Methyl phenols or cresols and nitrobenzene could be a possible combustion product of epoxies. Pyridine is not so likely. The fire conditions were such that most of the resin combustion products were carried away with the plume and any remaining may not be detectable by the prescribed analytical methods.

d) Metals: The metal results were non-detect at the regulatory limit for the September 15th burn. September 18th results reported cadmium, chromium and silver. The amounts are less than the regulatory limit of concern, see Table 20. Fire temperatures were above the volatilization point of the coating's organic material. Metals dispersed within the coatings are now fully exposed to the flame. Cadmium's boiling point is 1413°F. Chromium and silver's boiling point is around 4000°F. There were no coatings visible on the surface of the burnt composite sample sent to the laboratory for analysis. The composite wing box ply configuration did not contain a lightening strike layer, which would introduce a metal source. Macroscopically, the test specimen was just burnt composite material, carbon/epoxy. Resin formulations can contain some metals but at very minute amounts not measurable by the method employed. Sources of metal contamination are the non-composite material of the wingbox. Material sources to consider for metal contamination of composites are: coatings, paint, solder, electronic components, fasteners and conductive adhesives.

e) Corrosivity: The pH measurements for both burnt composite pieces were not within a characteristic corrosive range. Interestingly, varying pH values were obtained. The values differed by two pH units. This indicates that varying fire conditions produce varying pH properties. Recommendation would be to take measurements in more than 1 sample location, especially if the values are approaching the corrosive ranges. The MSDS for the resin can be used as a guide in determining what possible corrosive gases are generated during a fire.

Table 19. Characteristic of Hazardous Waste, 40 CFR Part 261.24.
Analytical Methods are within EPA Publication SW 846.

Toxicity target compounds	Regulatory Limit (mg/L)	Amount Detected (mg/L) <u>Sept. 15th</u>	Amount Detected (mg/L) <u>Sept. 18th</u>
Volatile			
1,1-dichloroethene	0.7	<R.L.	<R.L.
1,2-dichloroethane	0.5	<R.L.	<R.L.
1,4-dichlorobenzene	7.5	<R.L.	<R.L.
benzene	0.5	<R.L.	<R.L.
carbon tetrachloride	0.5	<R.L.	<R.L.
chlorobenzene	100.	<R.L.	<R.L.
chloroform	6.0	<R.L.	<R.L.
methyl ethyl ketone	200.	<R.L.	<R.L.
tetrachloroethene	0.7	<R.L.	<R.L.
trichloroethylene	0.5	<R.L.	<R.L.
Semivolatile			
2,4,5-trichlorophenol	400.	<R.L.	<R.L.
2,4,6-trichlorophenol	2.0	<R.L.	<R.L.
2,4-dinitrotoluene	0.13	<R.L.	<R.L.
2-methylphenol	200.	<R.L.	<R.L.
3-methylphenol	200.	<R.L.	<R.L.
4-methylphenol	200.	<R.L.	<R.L.
hexachlorobenzene	0.13	<R.L.	<R.L.
hexachlorobutadiene	0.5	<R.L.	<R.L.
hexachloroethane	3.0	<R.L.	<R.L.
nitrobenzene	2.0	<R.L.	<R.L.
pentachlorophenol	100.	<R.L.	<R.L.
pyridine	5.0	<R.L.	<R.L.
Metals			
Arsenic	5.0	<R.L.	<R.L.
Barium	100.	<R.L.	<R.L.
Cadmium	1.0	<R.L.	(.676) <R.L.
Chromium	5.0	<R.L.	(.062) <R.L.
Lead	5.0	<R.L.	<R.L.
Mercury	0.2	<R.L.	<R.L.
Selenium	1.0	<R.L.	<R.L.
Silver	5.0	<R.L.	(.012) <R.L.
Herbicide	Not Tested		
Pesticide	Not Tested		

Table 19. Characteristic of Hazardous Waste, Continued

Ignitability Solid ¹	Regulatory Limit	Amount Detected
	Causing fire through friction	Not tested
Corrosivity Solid	pH < 2. or >12.5	6.55 – Sept. 15th 8.03 – Sept. 18th
Reactivity		
Readily undergoes chemical change? ²	yes / no	no
React violently when mixed with water? ²	yes / no	no
Forms explosive mixture mixed with water? ²	yes / no	no
Capable of detonation with an ignition source? ²	yes / no	no
Hydrogen cyanide or Hydrogen sulfide bearing waste when exposed to mild acidic or basic conditions generates toxic gases? ³	HCN - 250mgHCN/kg H ₂ S - 500mg H ₂ S/kg	Not tested Not tested

R.L.=regulatory limit

¹ Not a commonly conducted or requested method. Ignition of composite could occur if the piece tested contained JP8.

² Answered by having knowledge of the waste material properties.

² Answered by having knowledge of the waste material properties.

² Answered by having knowledge of the waste material properties.

³ Formation is possible in a fire but HCN and H₂S are very reactive.

V. Conclusion

The primary focus of this study was to quantify exposures to gases and particulates during post-crash operations with an emphasis on composite materials. The measured concentrations to workers during this study and other previous assessments during actual crash responses can be used to determine personal protective equipment and necessary work practice controls. The crash site is an inherently dangerous work environment with many hazards including: hydrazine, munitions, damaged aircraft parts with sharp, jagged edges, fuels, oils, pressurized tanks, etc. Any risk assessment at a crash site needs to consider all of these hazards. Early in the response phase, these hazards should be assumed to be present until a hazard assessment shows otherwise. Specific to composite materials the following factors should be considered: aircraft type (quantity of composites), extent of fire and physical damage, terrain, and environmental conditions. The worst-case scenario for composite hazard is a mishap that involves fire and physical damage. The composite hazard assessment should categorize the site as presenting a high or low risk. Coupled with this categorization should be the task being performed. Tasks can also be grouped into either a no/light movement of materials or aggressive handling of materials. PPE decisions can then be made using a 2 x 2 matrix.

TABLE 20. PPE Decision Matrix

Task	Composite Hazard	
	<i>Low</i>	<i>High</i>
No/light movement	Level 1	Level 2
Aggressive handling	Level 2/3	Level 3

Level 1 – Long-sleeve, leather gloves (outer) with nitrile rubber (inner)

Level 2 – Coveralls, leather gloves (outer) with nitrile rubber (inner), dust mask (filtering facepiece device)

Level 3 – Coveralls, leather gloves (outer) with nitrile rubber (inner), full-face air purifying respirator with organic vapor/HEPA cartridge

REFERENCES

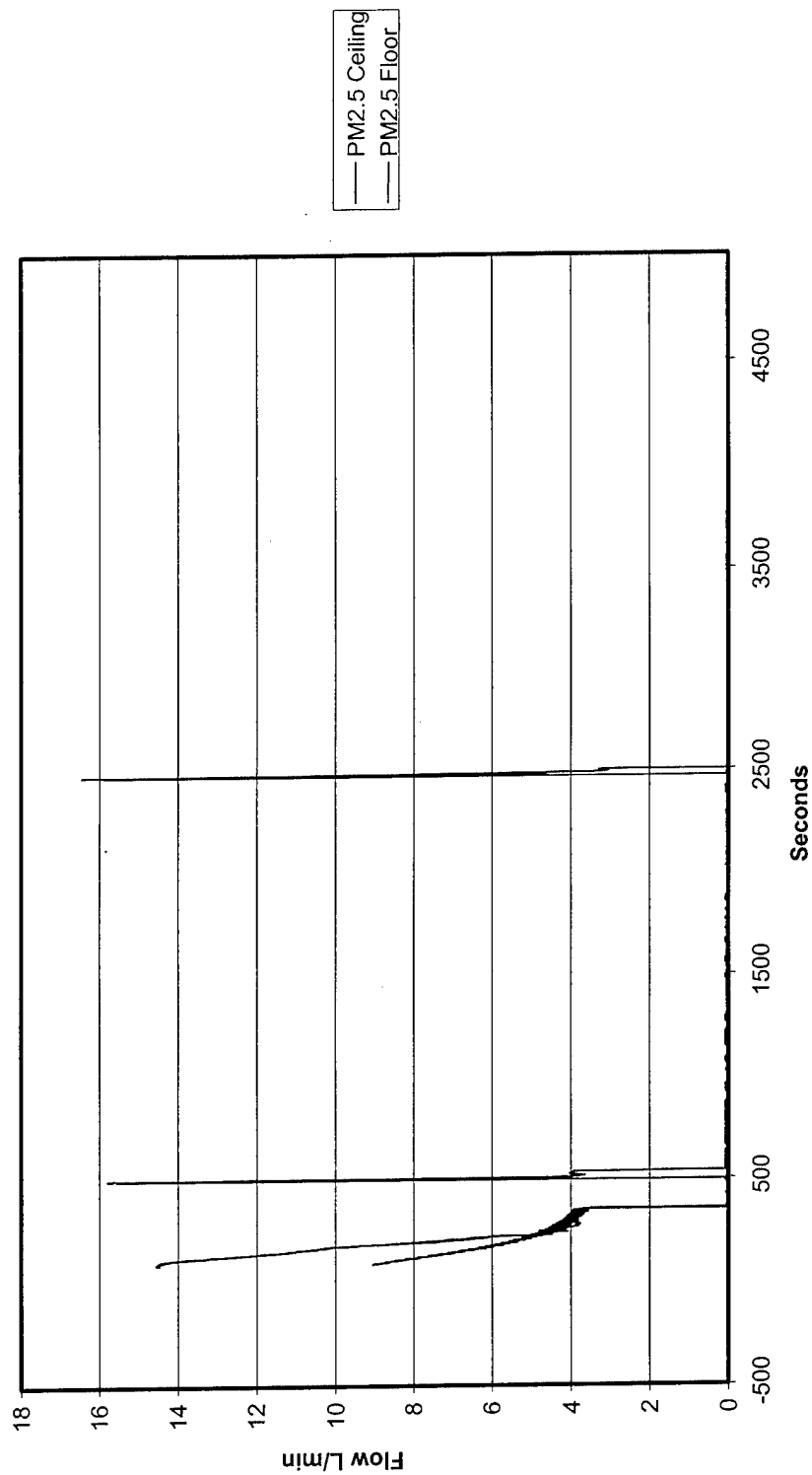
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APPENDIX
GRAPHS 1 – 61

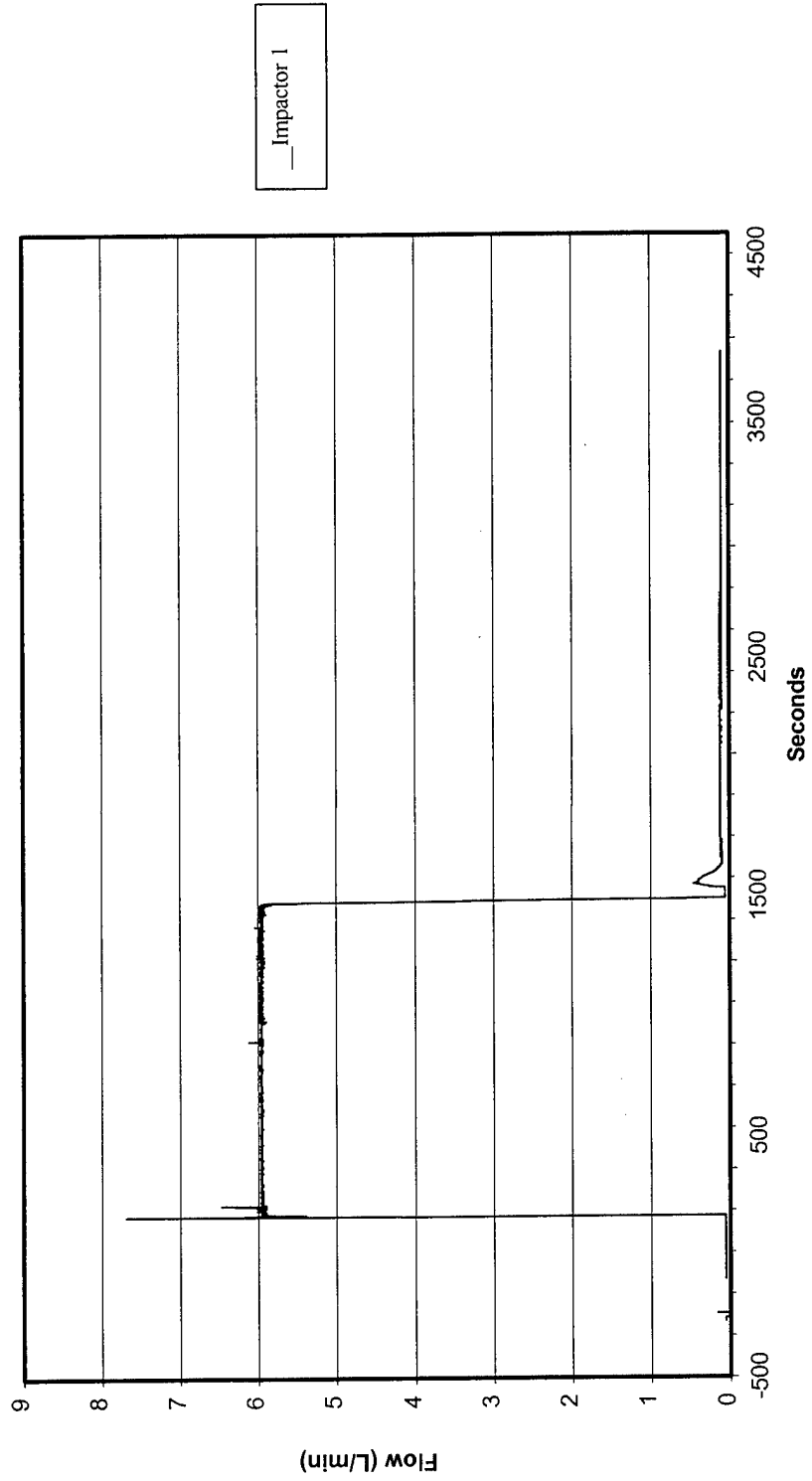
Graph 1

PM 2.5 Flow Rates
JP-8 Test #1
9 September 2000

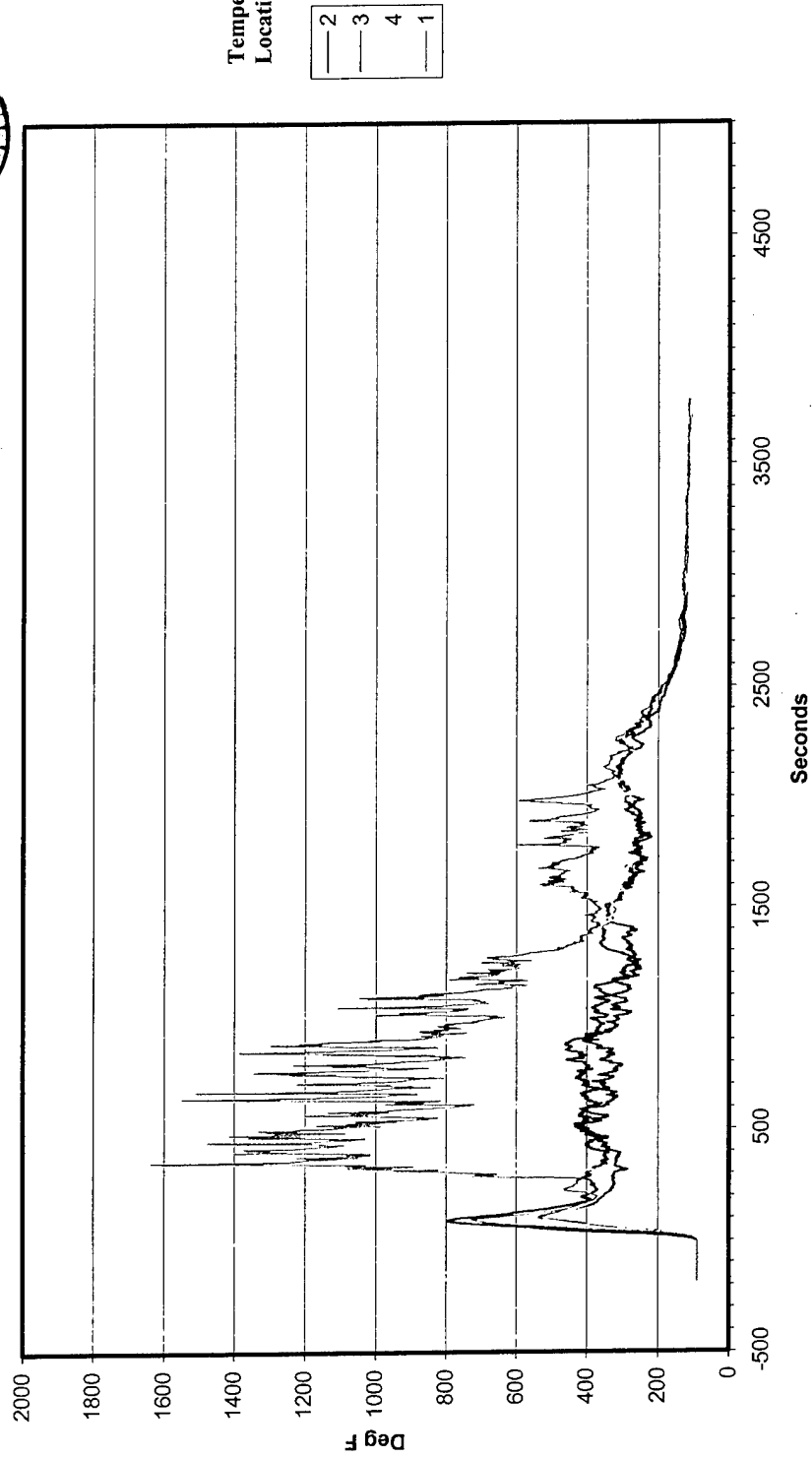


Graph 2

Impactor Flow Rates
JP-8 Test #1
9 September 2000

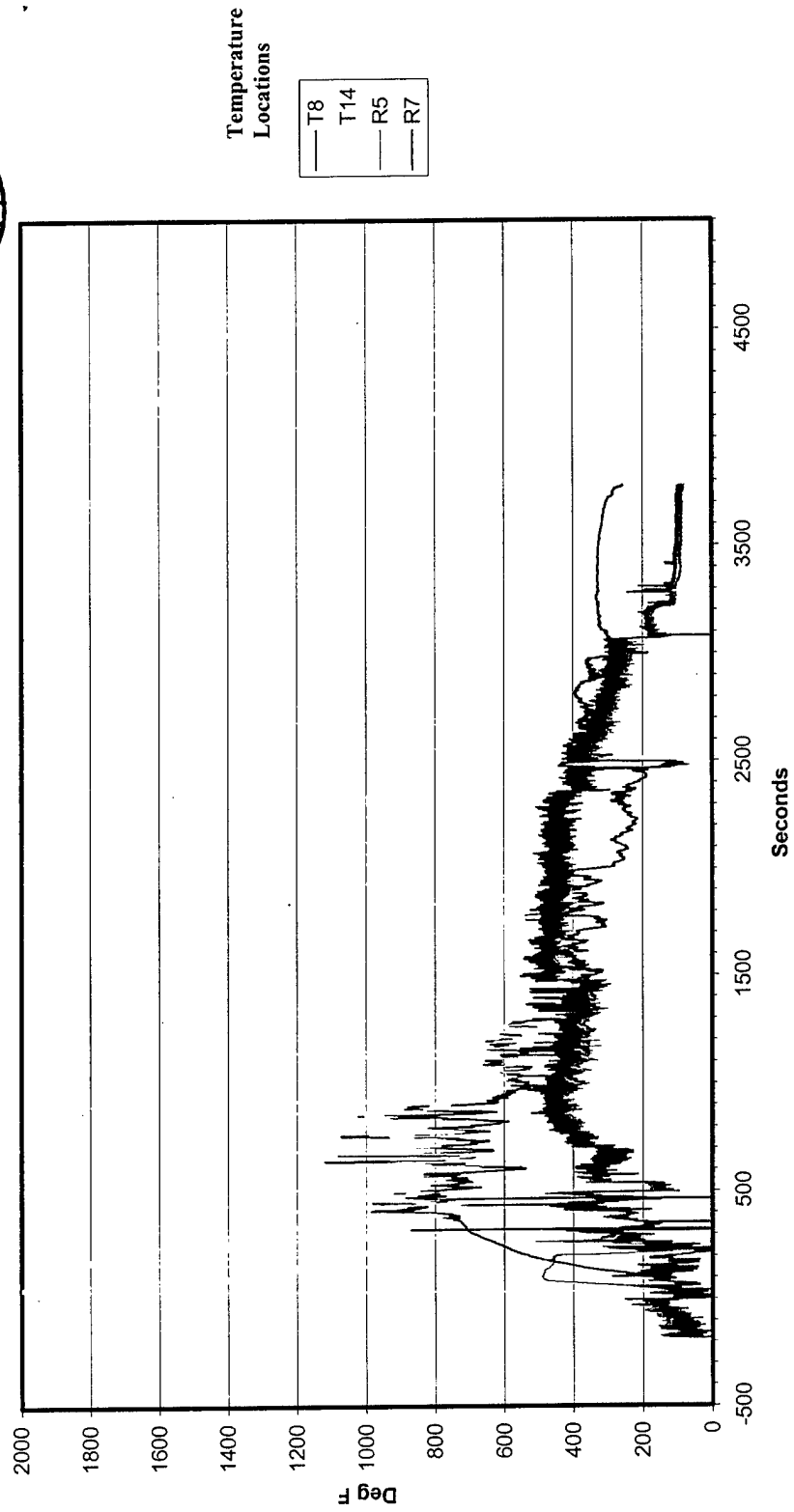


Temperature
Locations



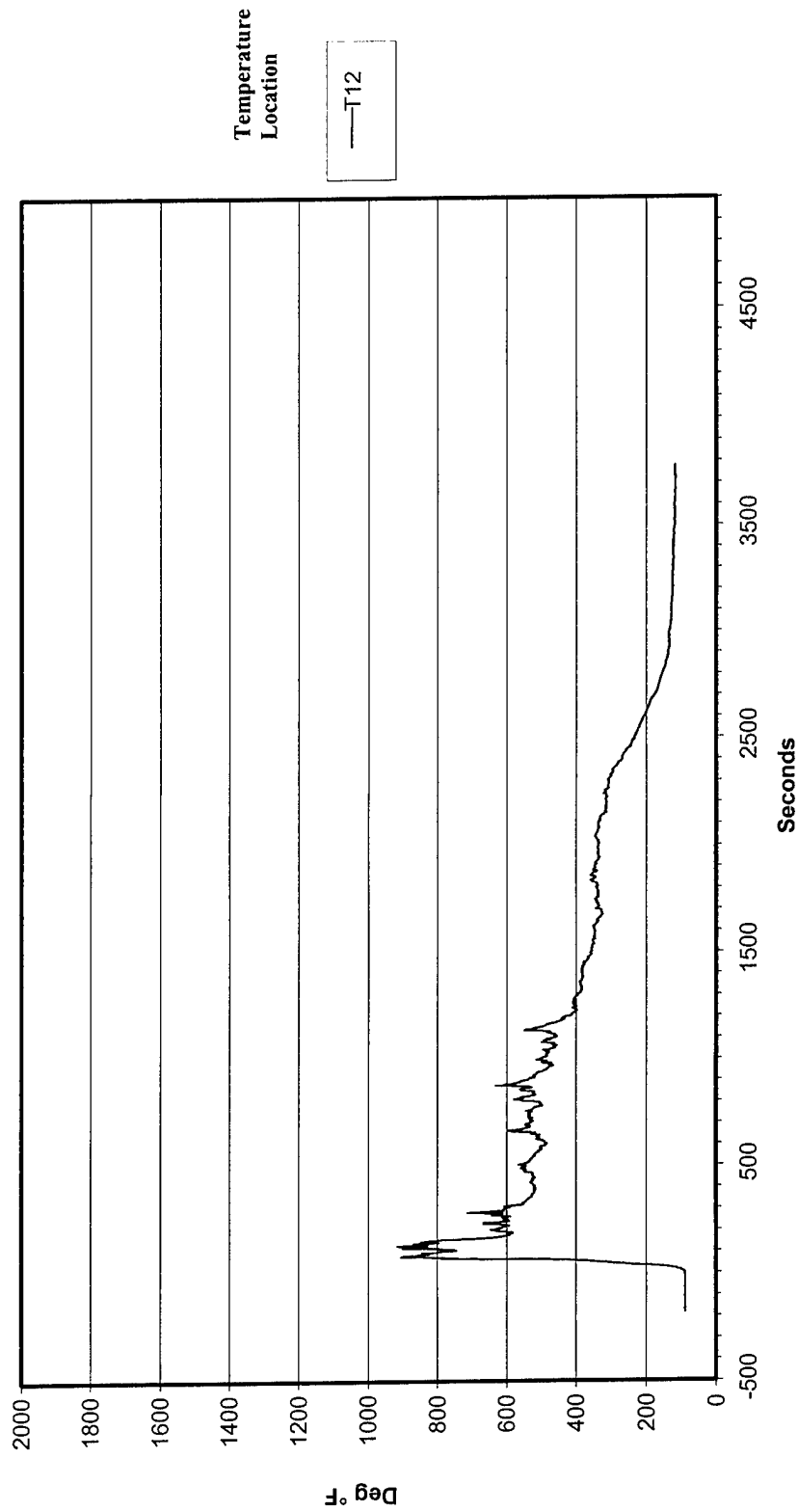
Graph 4

10 Ft. Temperatures
JP-8 Test #1
9 September 2000



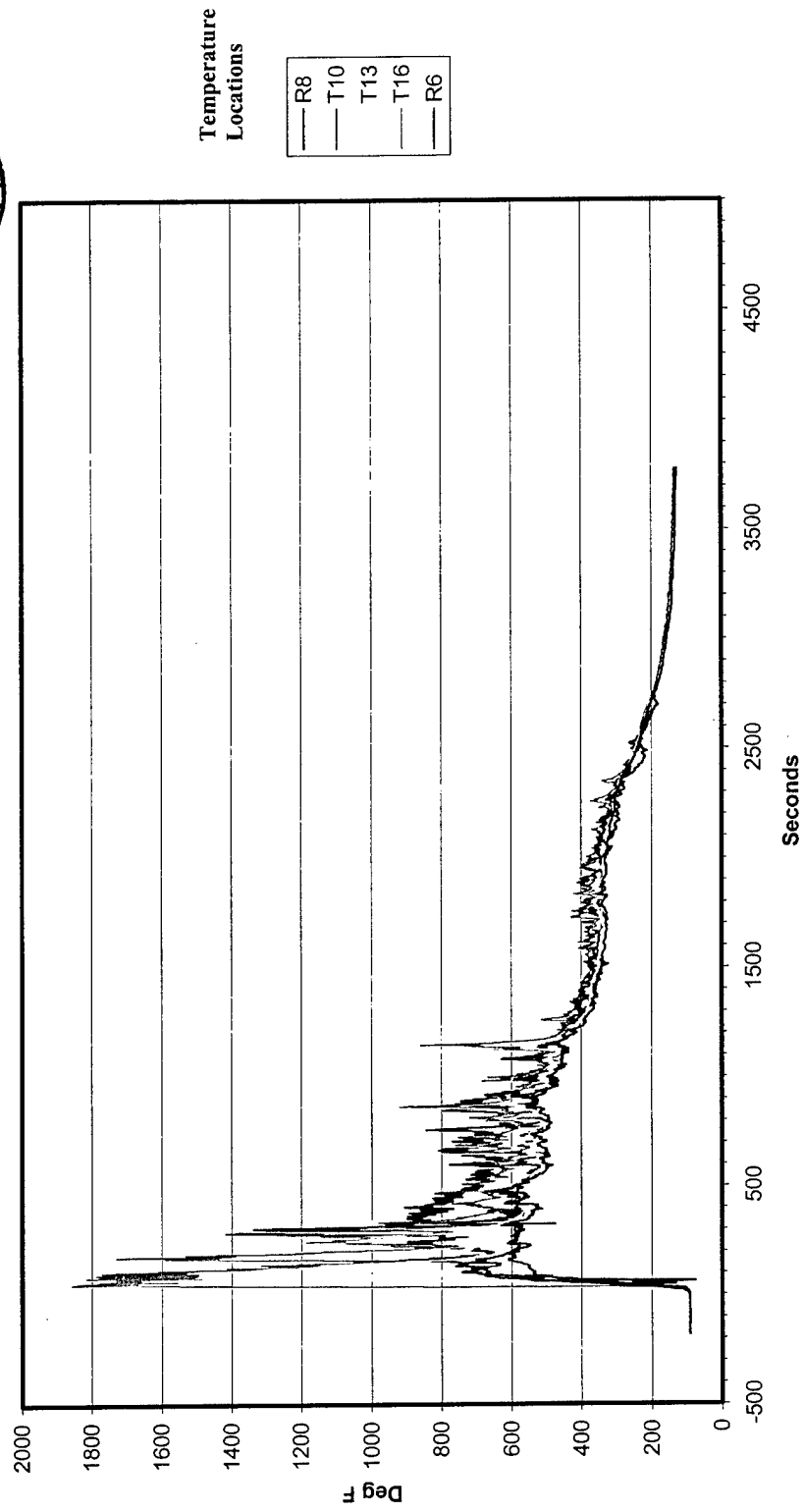
Graph 5

15 Ft. Temperatures
JP-8 Test #1
9 September 2000

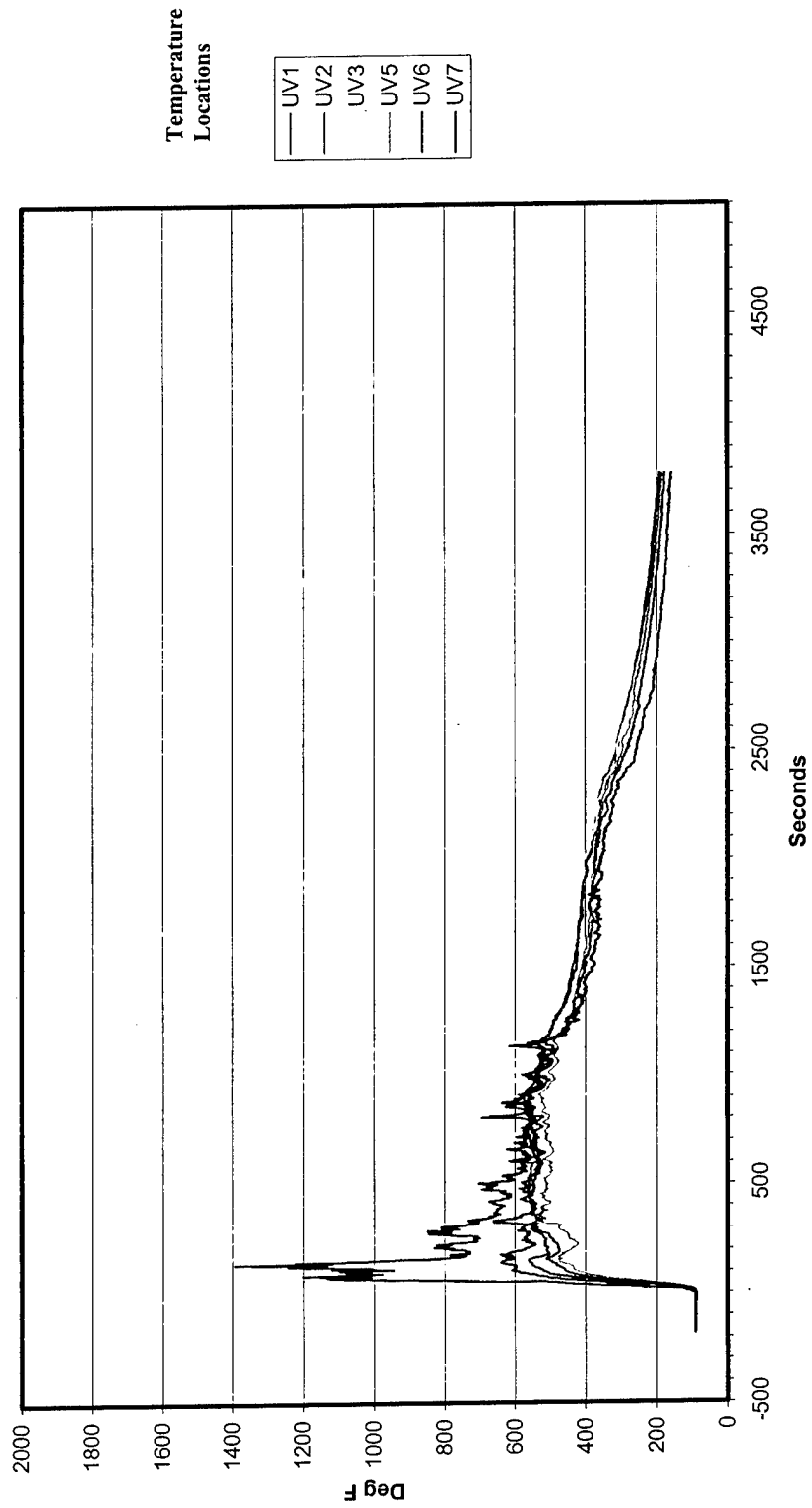


Graph 6

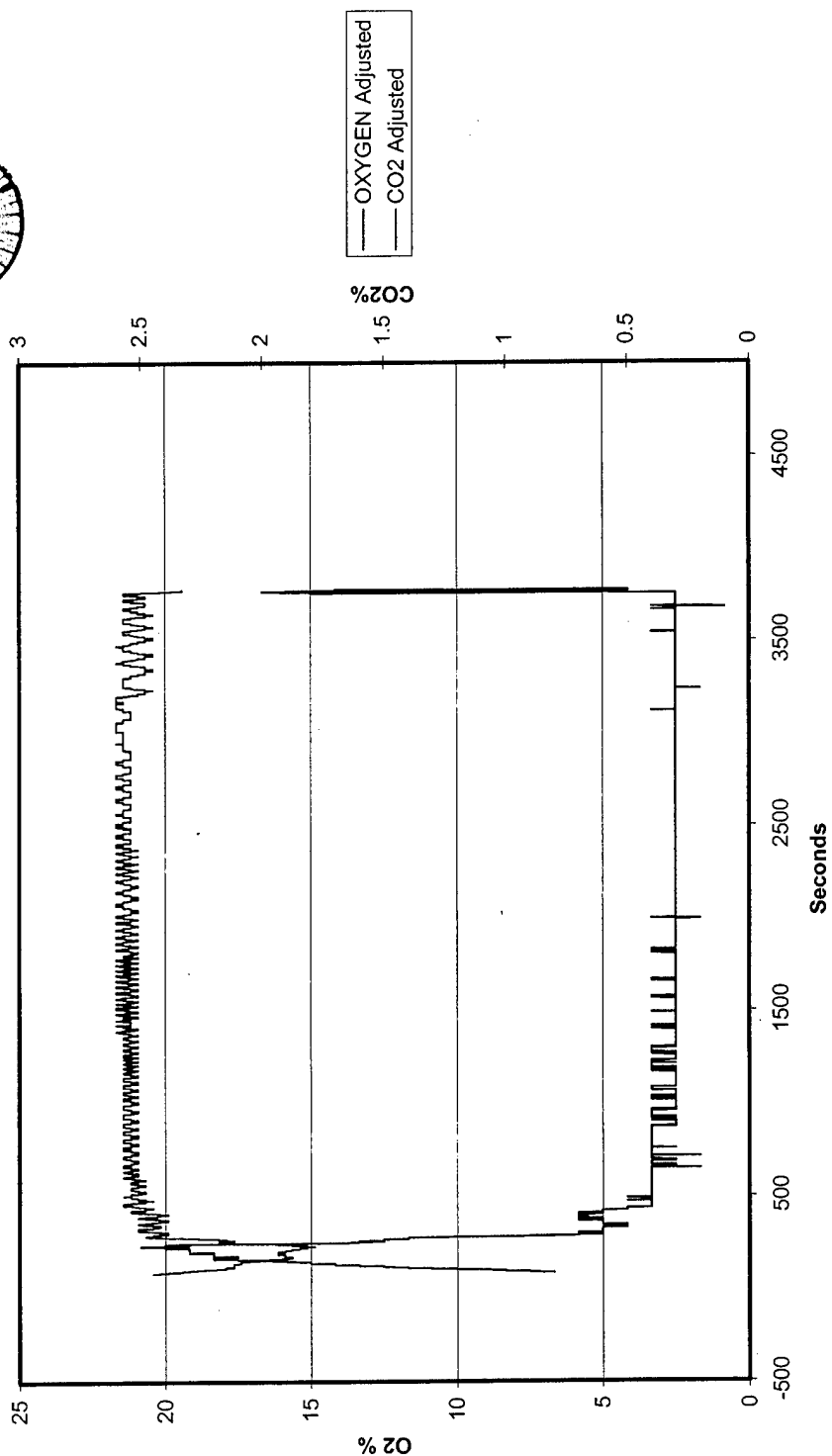
20 Ft. Temperatures
JP-8 Test #1
9 September 2000



Graph 7
Ceiling Temperatures
JP-8 Test #1
9 September 2000

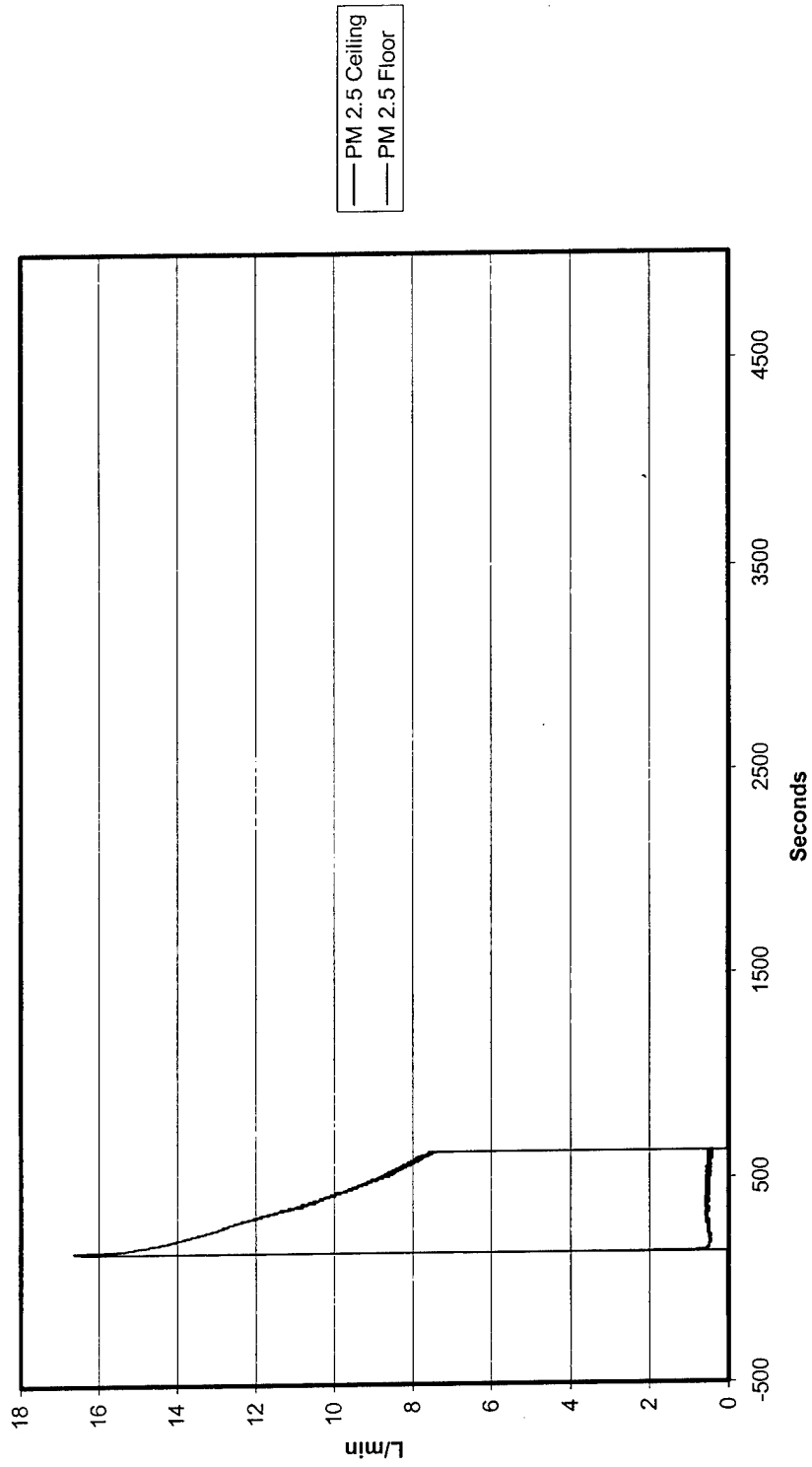


Graph 8
Oxygen & CO2
JP-8 Test #1
9 September 2000



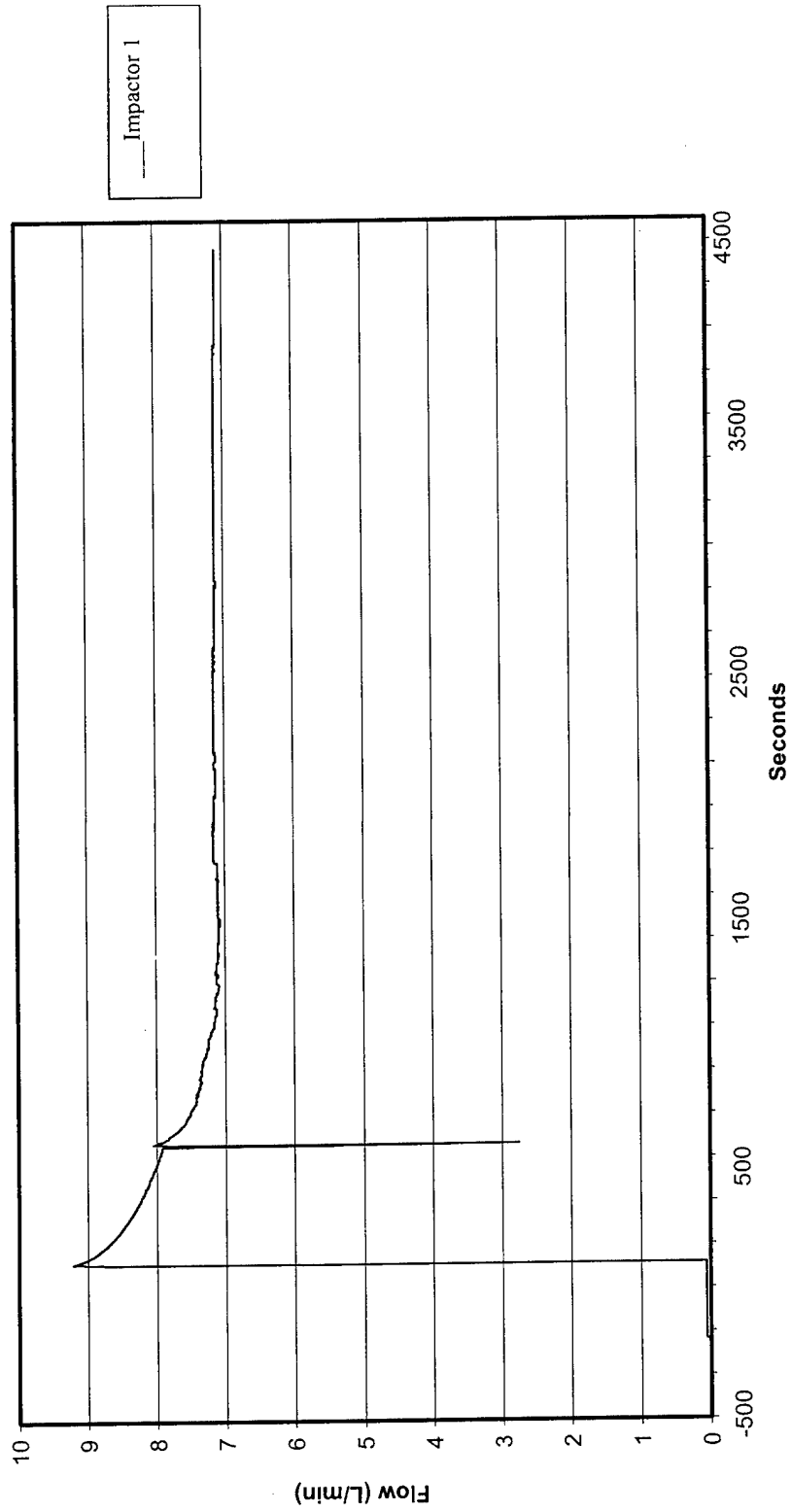
Graph 9

PM 2.5 Flow Rates
JP-8 Test #2
13 September 2000

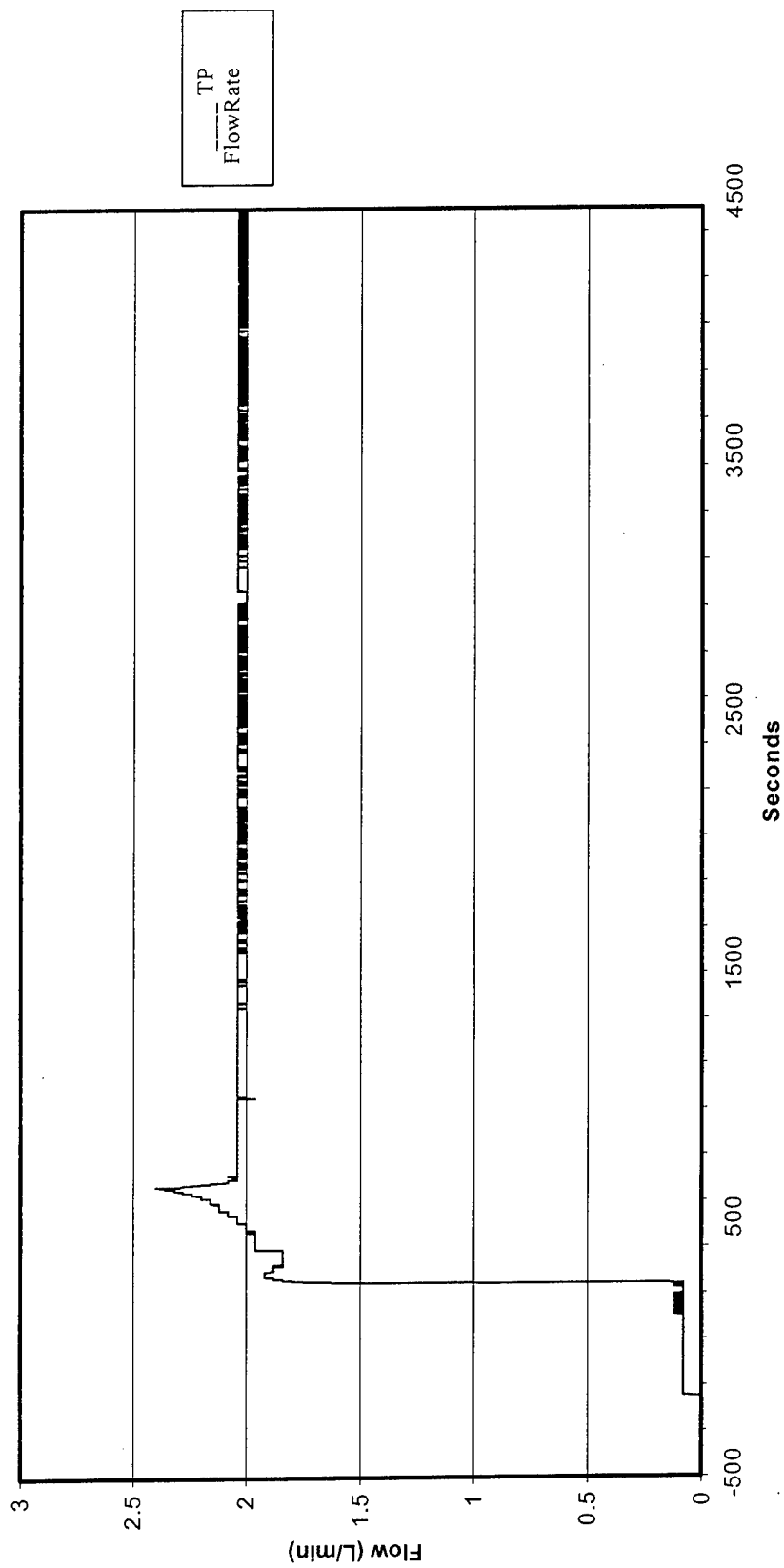


Graph 10

Impactor Flow
JP-8 Test
13 September 2000

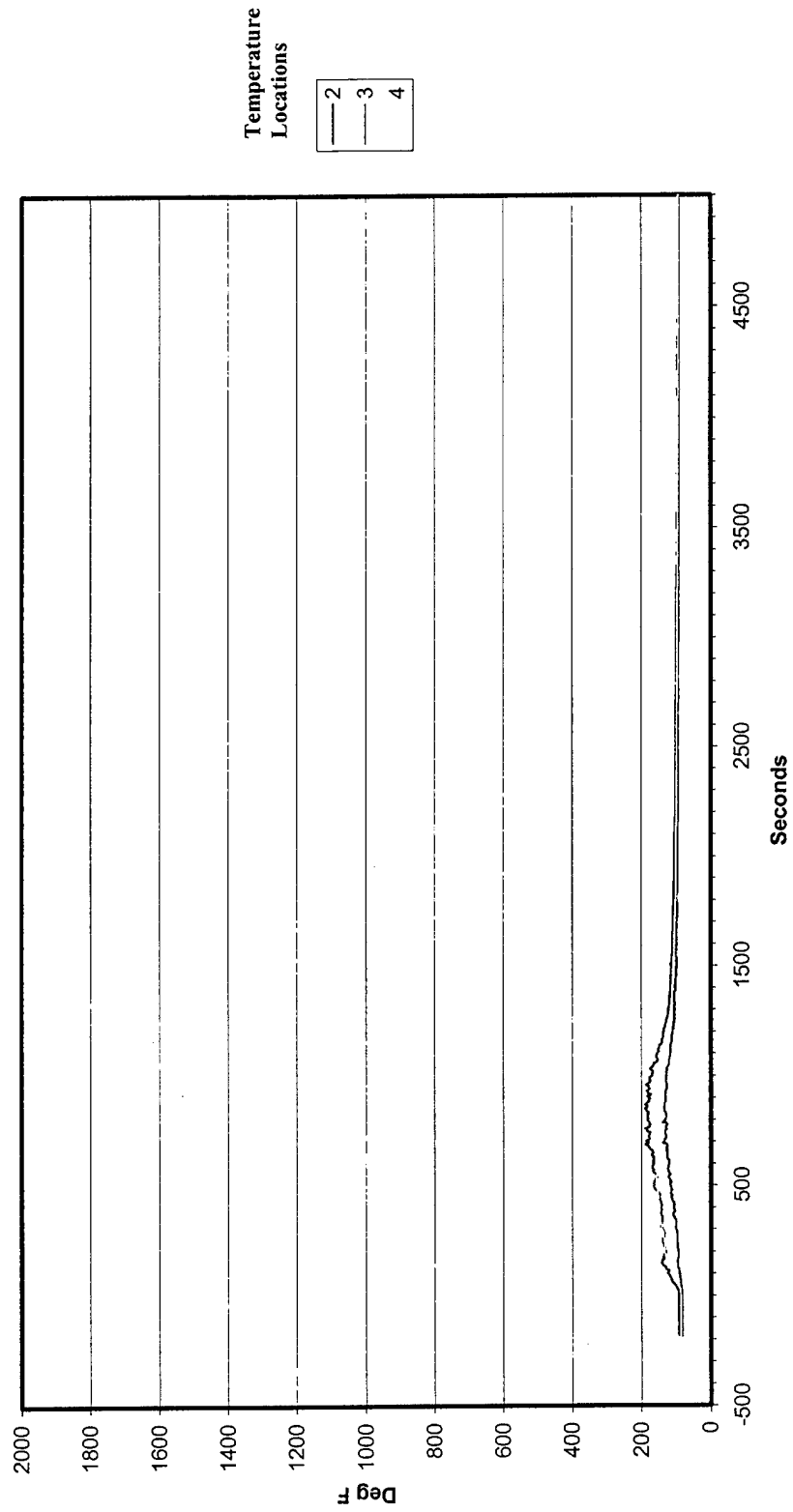


Total Particulate (TP), O₂, and CO₂ Flow Rates
JP-8 Test
13 September 00



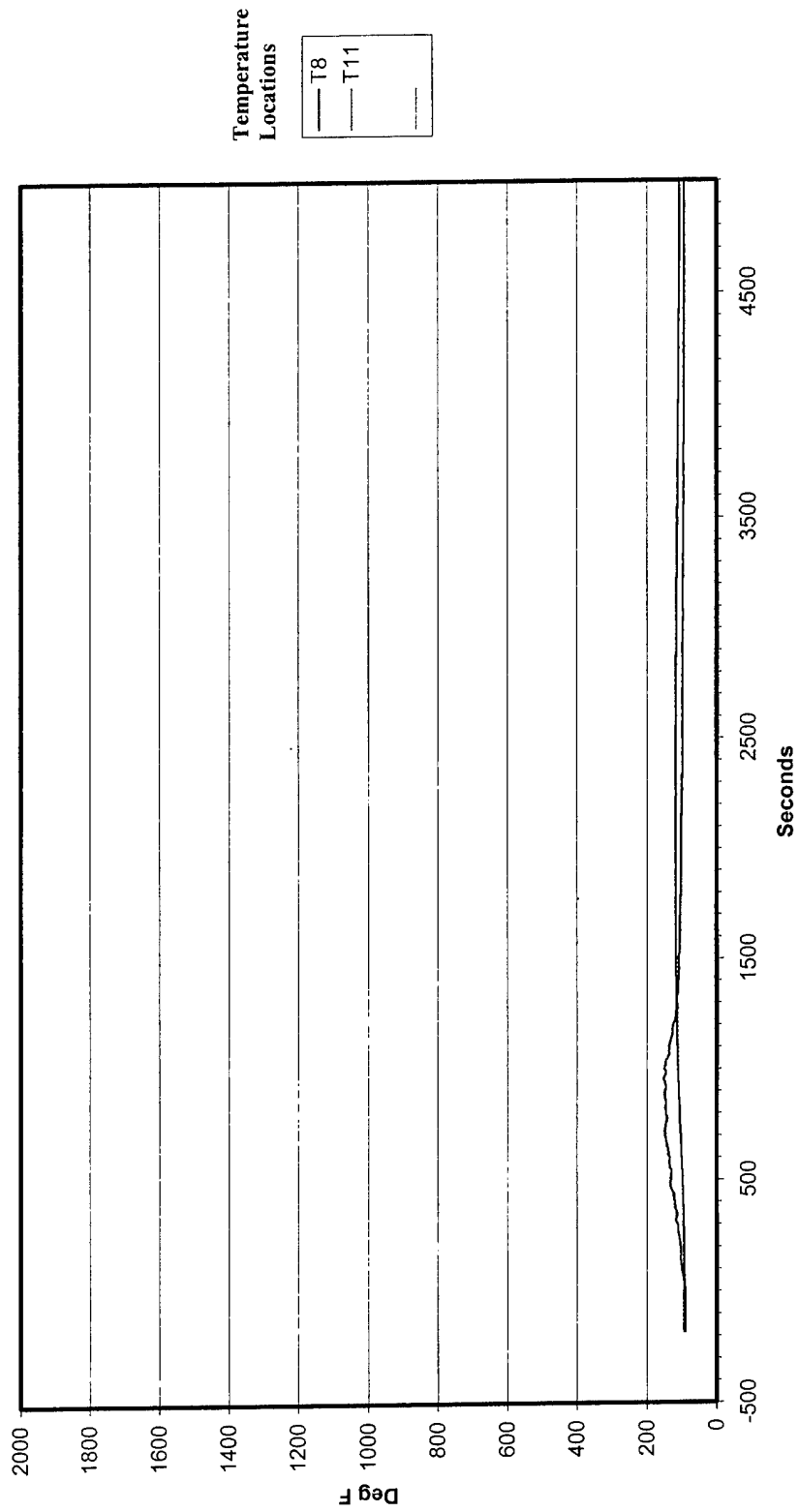
Graph 12

5 Ft. Temperatures
JP-8 Test #2
13 September 2000



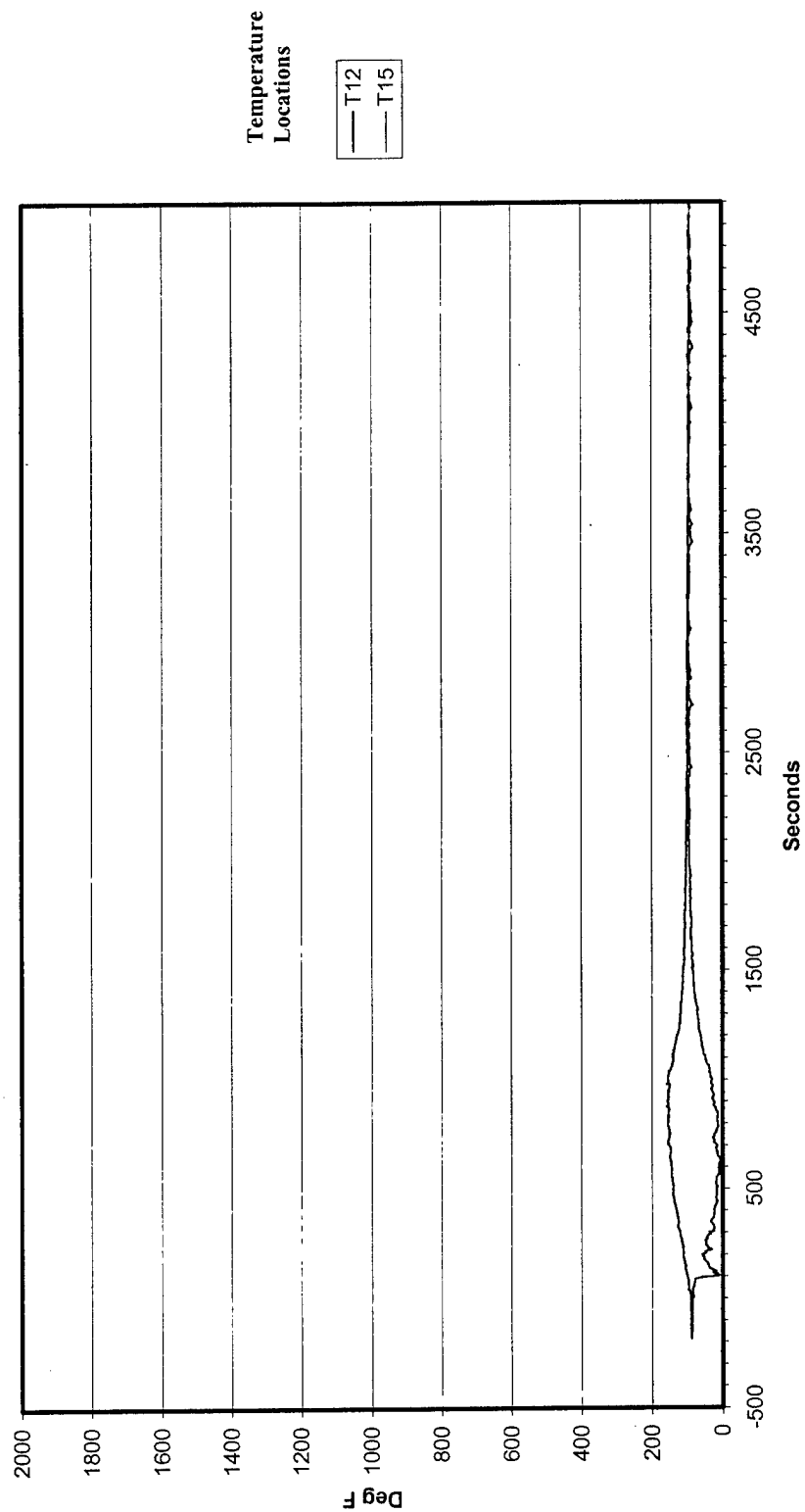
Graph 13

10 Ft. Temperatures
JP-8 Test #2
13 September 2000



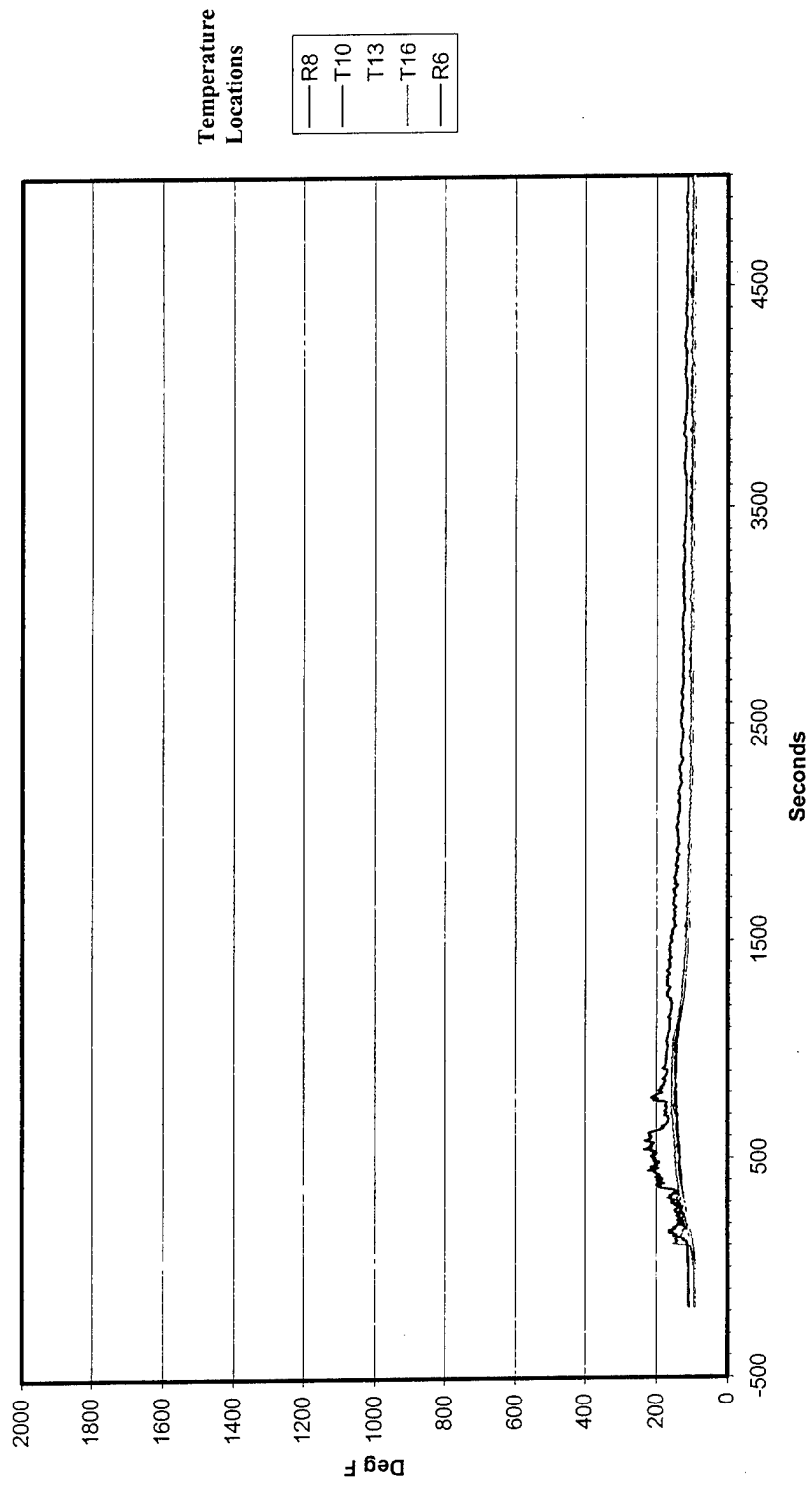
Graph 14

15 Ft. Temperatures
JP-8 Test #2
13 September 2000

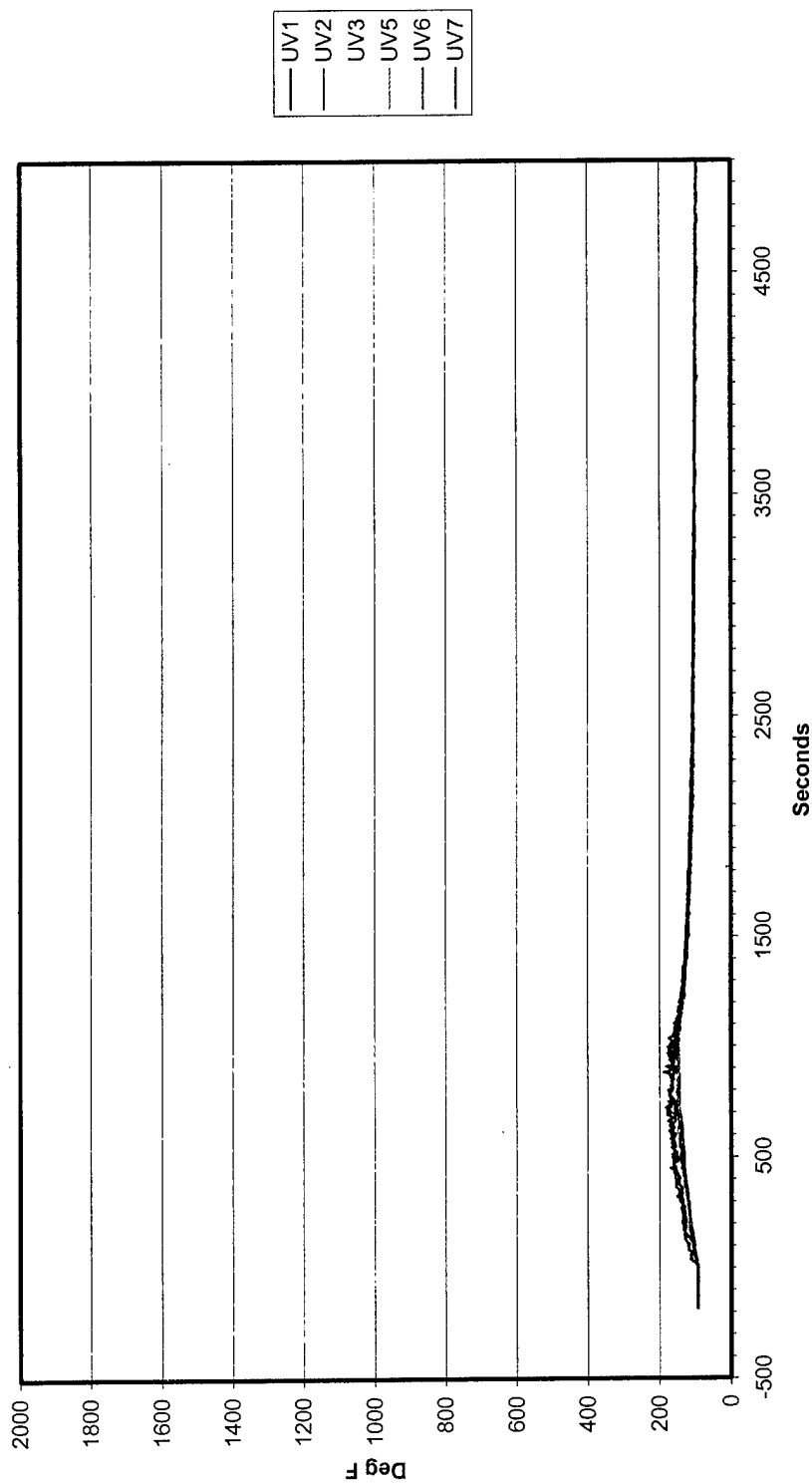


Graph 15

20 Ft. Temperatures
JP-8 Test #2
13 September 2000



Graph 16
Ceiling Temperatures
JP-8 Test #2
13 September 2000

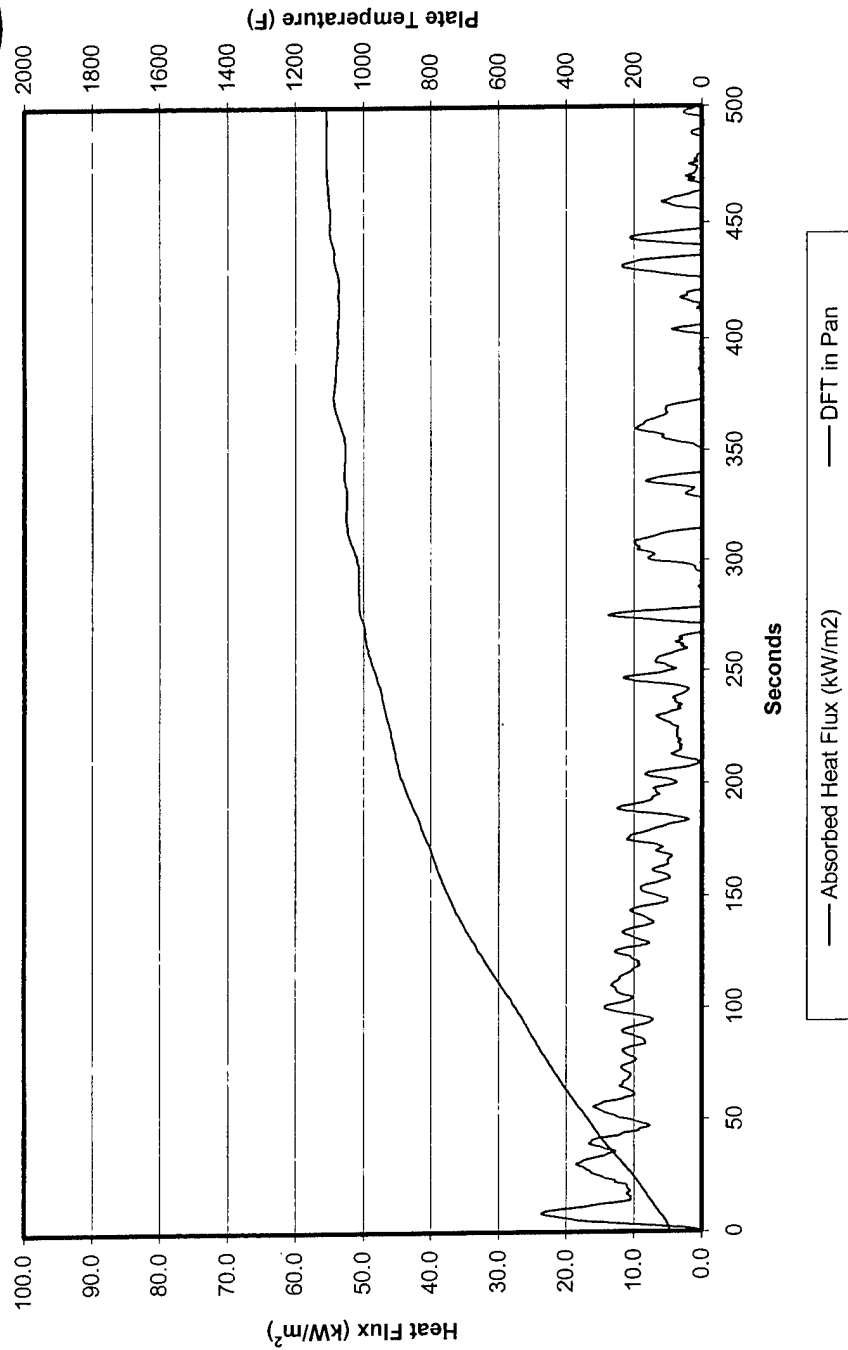


Graph 17

Flux on Composite - DFT in Pan

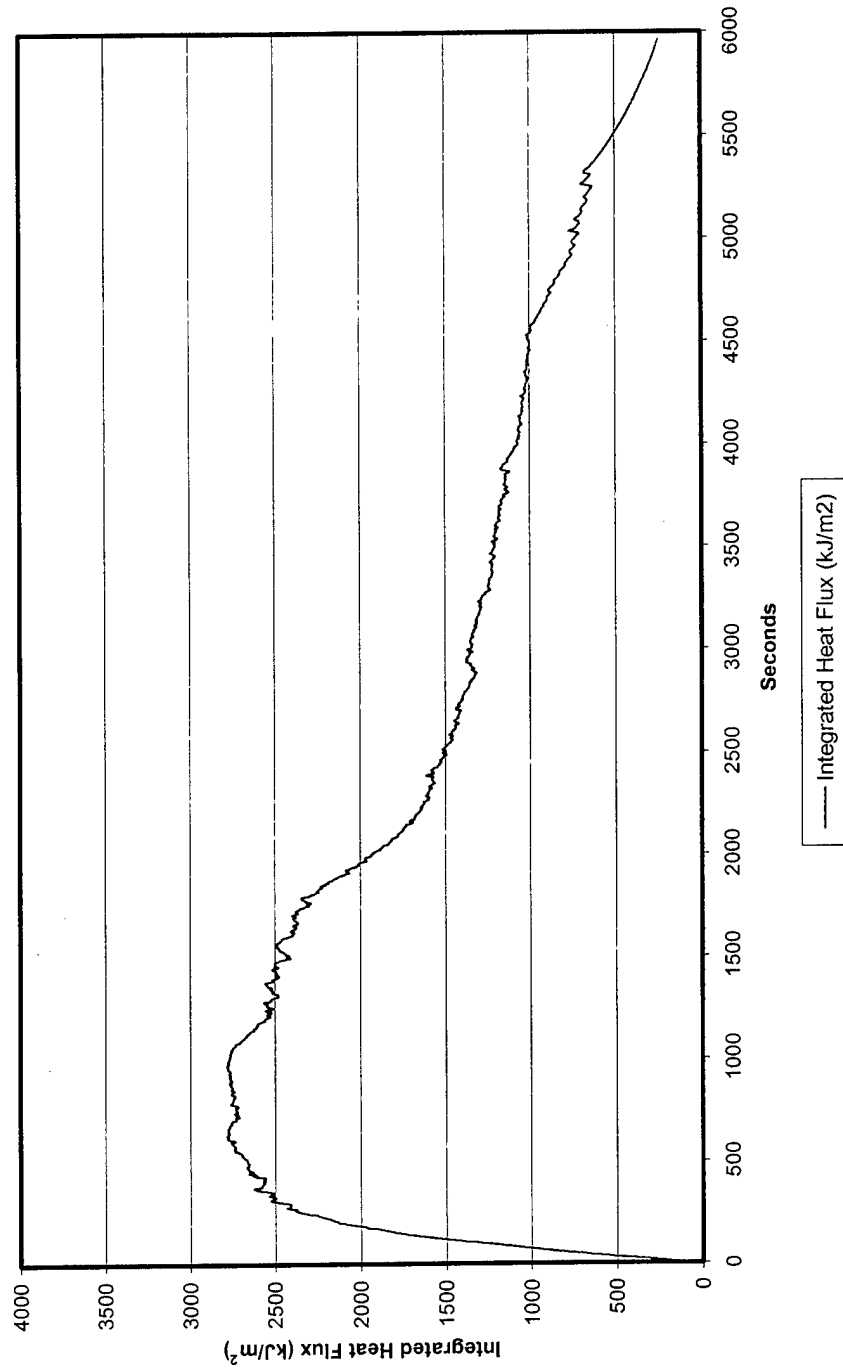
JP-8 Test #2

13 September 2000

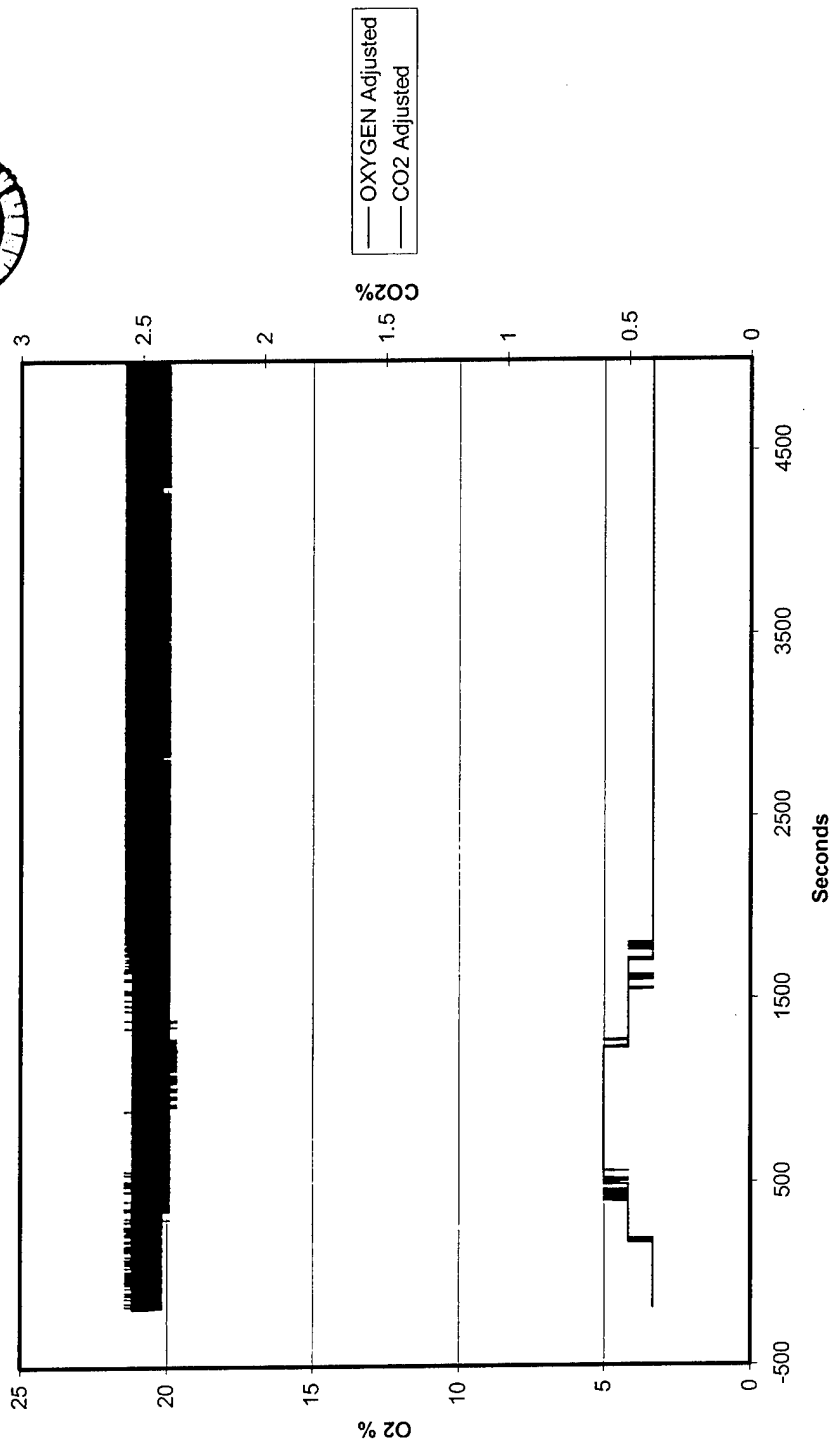


Graph 18

Integrated Flux on Composite - DFT in Pan
JP-8 Test #2
13 September 2000



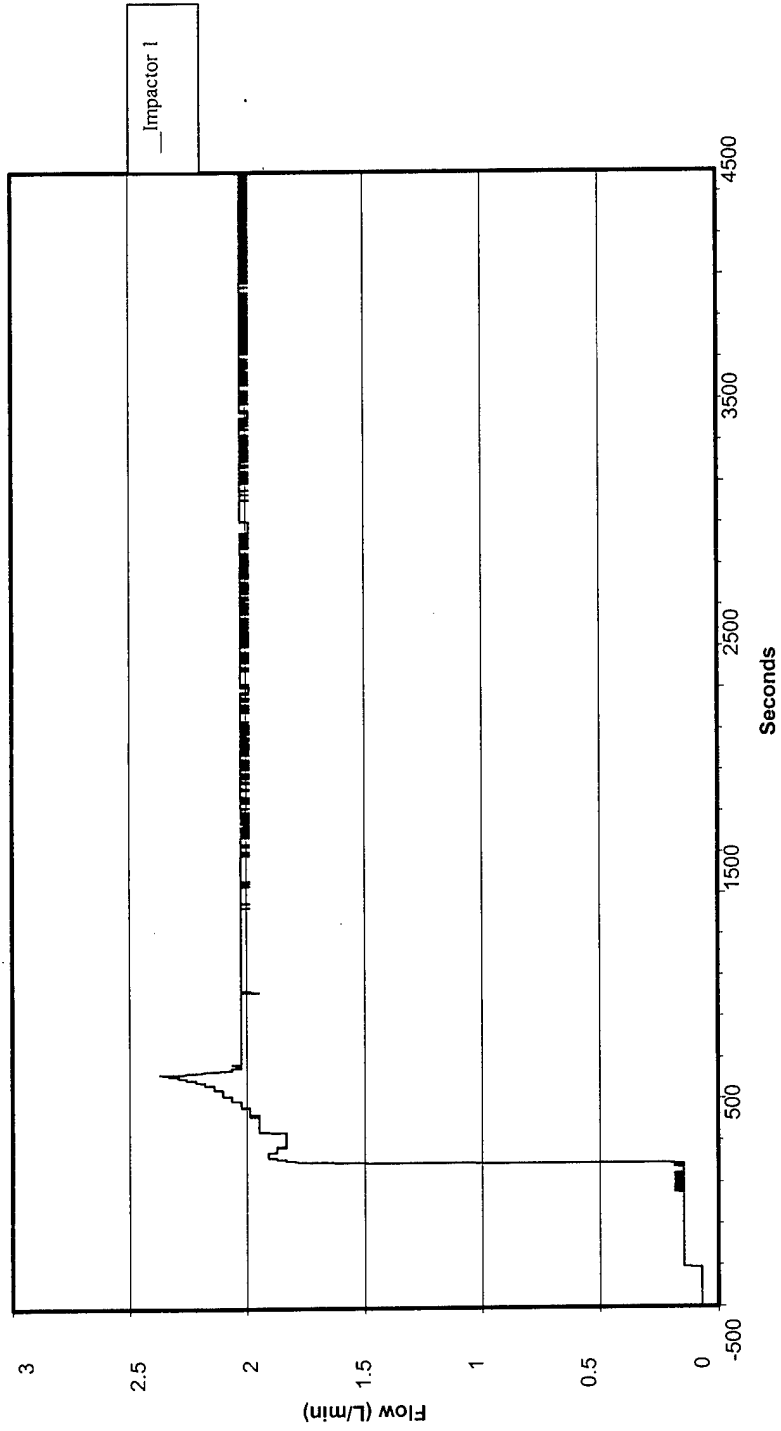
Graph 19
Oxygen & CO₂
JP-8 Test #2
13 September 2000



GRAPH 20



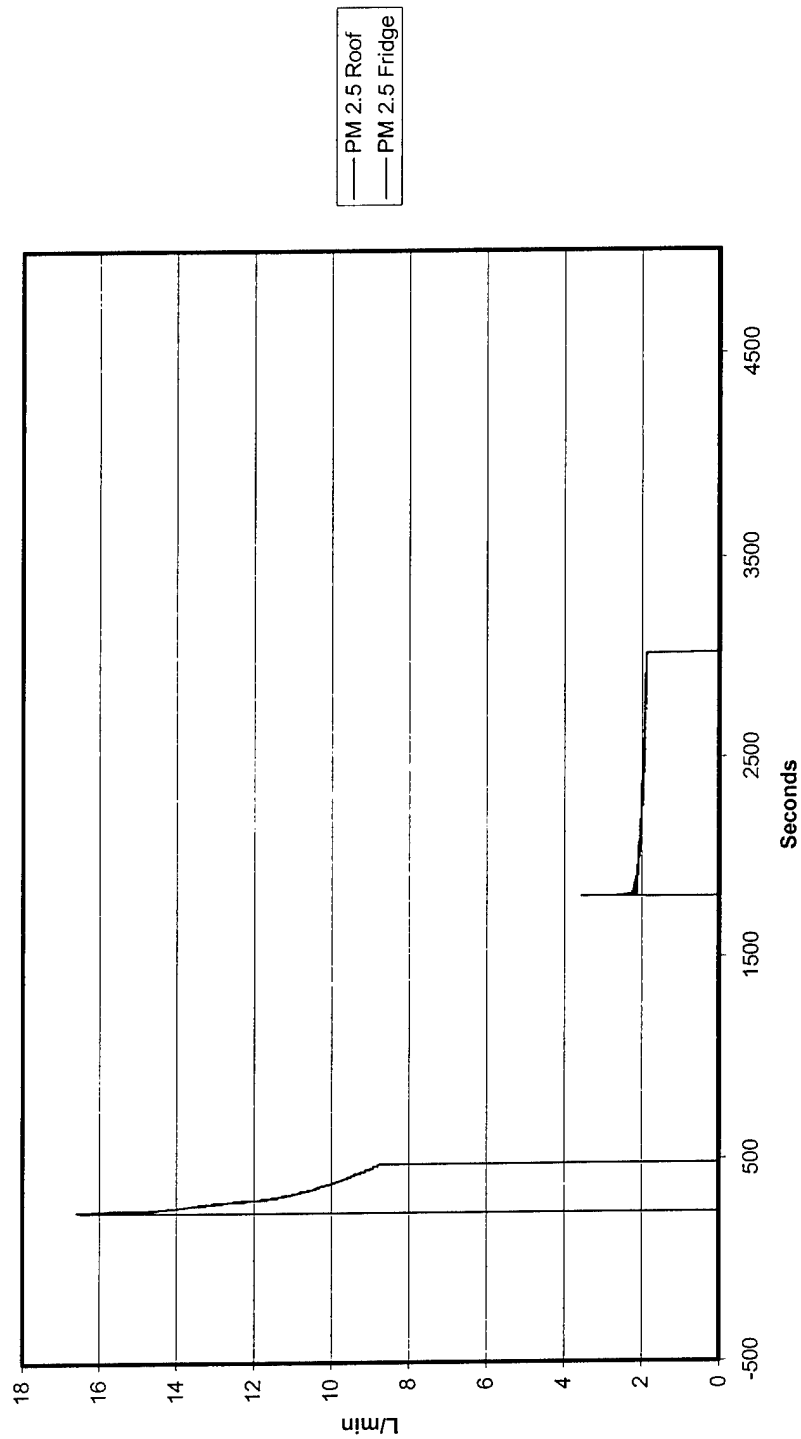
Impactor Flow Rates
Composite #1
13 September 00



Graph 20

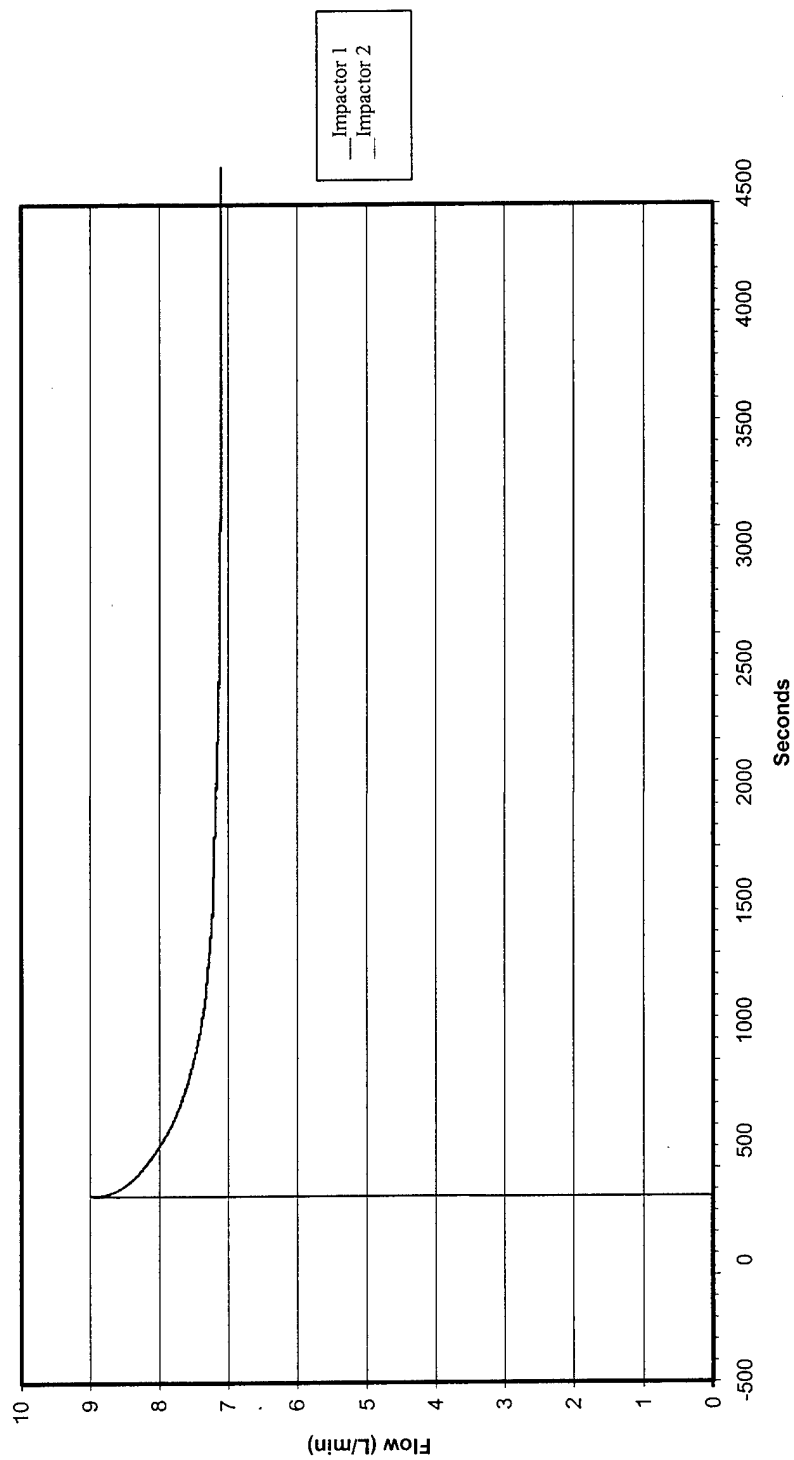
Graph 21

PM 2.5 Flow Rates
Composite Test #1
15 September 2000



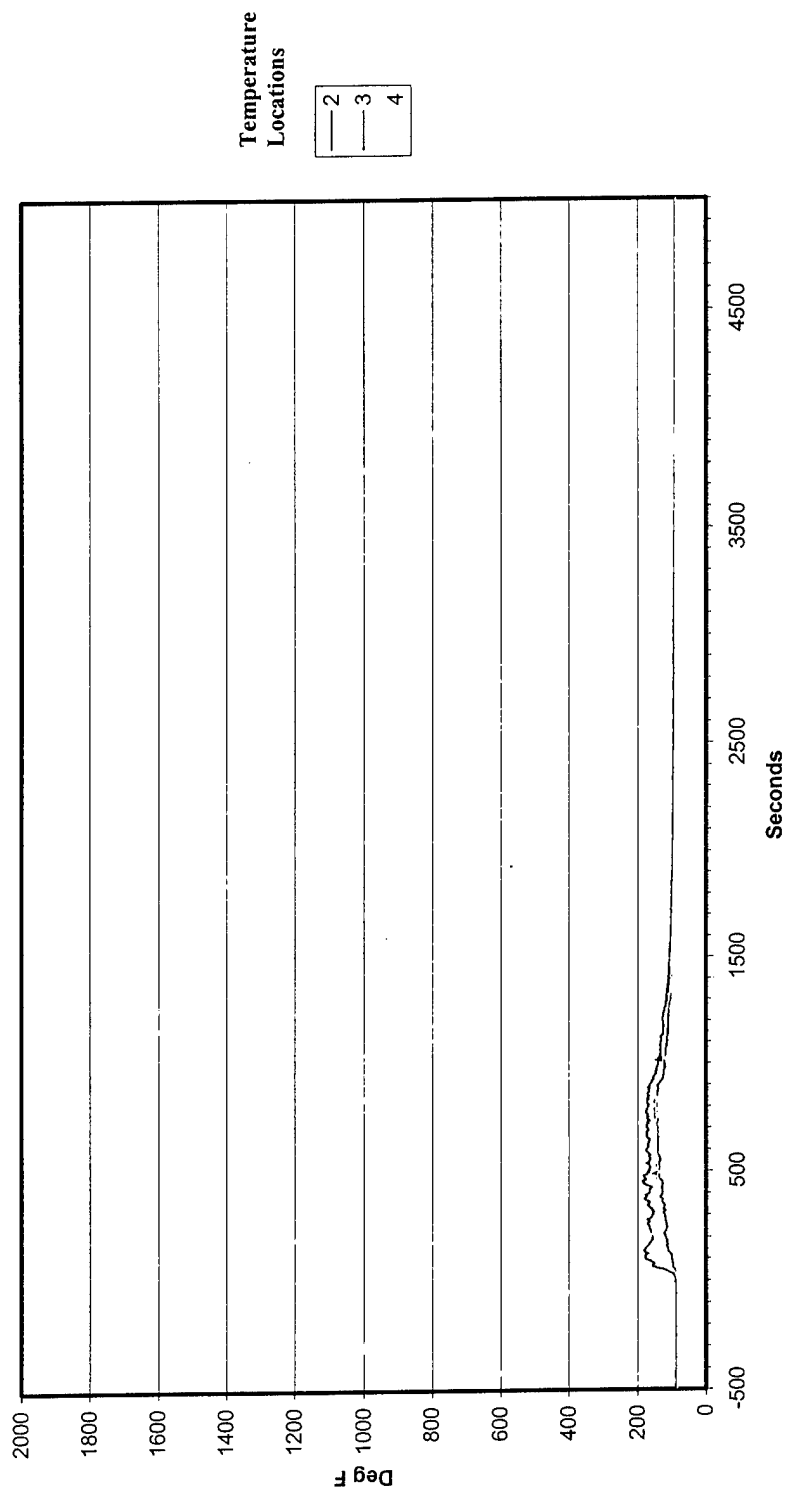
Graph 22

Impactor Flow
Composite Test
15 September



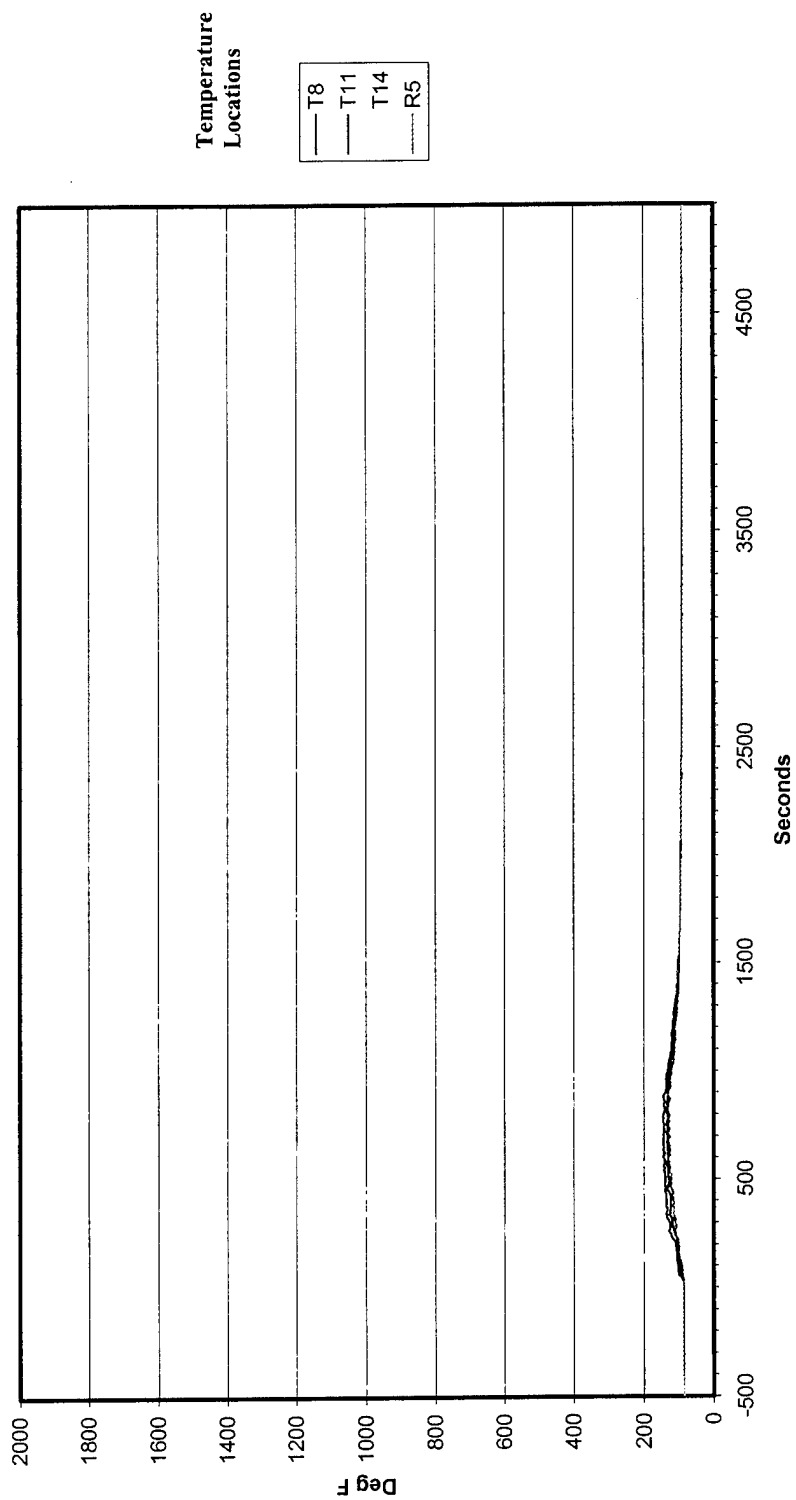
Graph 23

5 Ft. Temperatures
Composite Test #1
15 September 2000

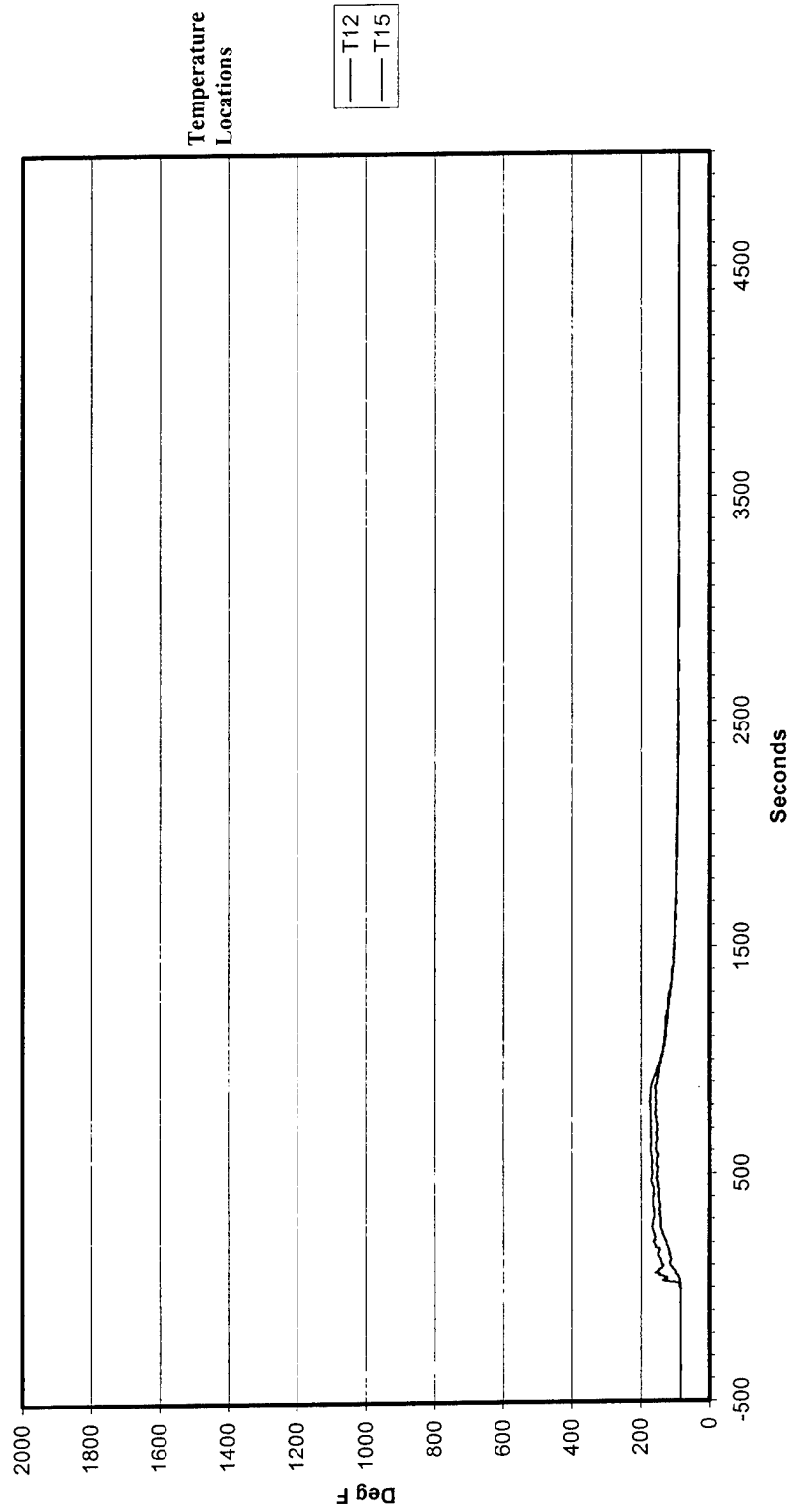


Graph 24

10 Ft. Temperatures
Composite Test #1
15 September 2000

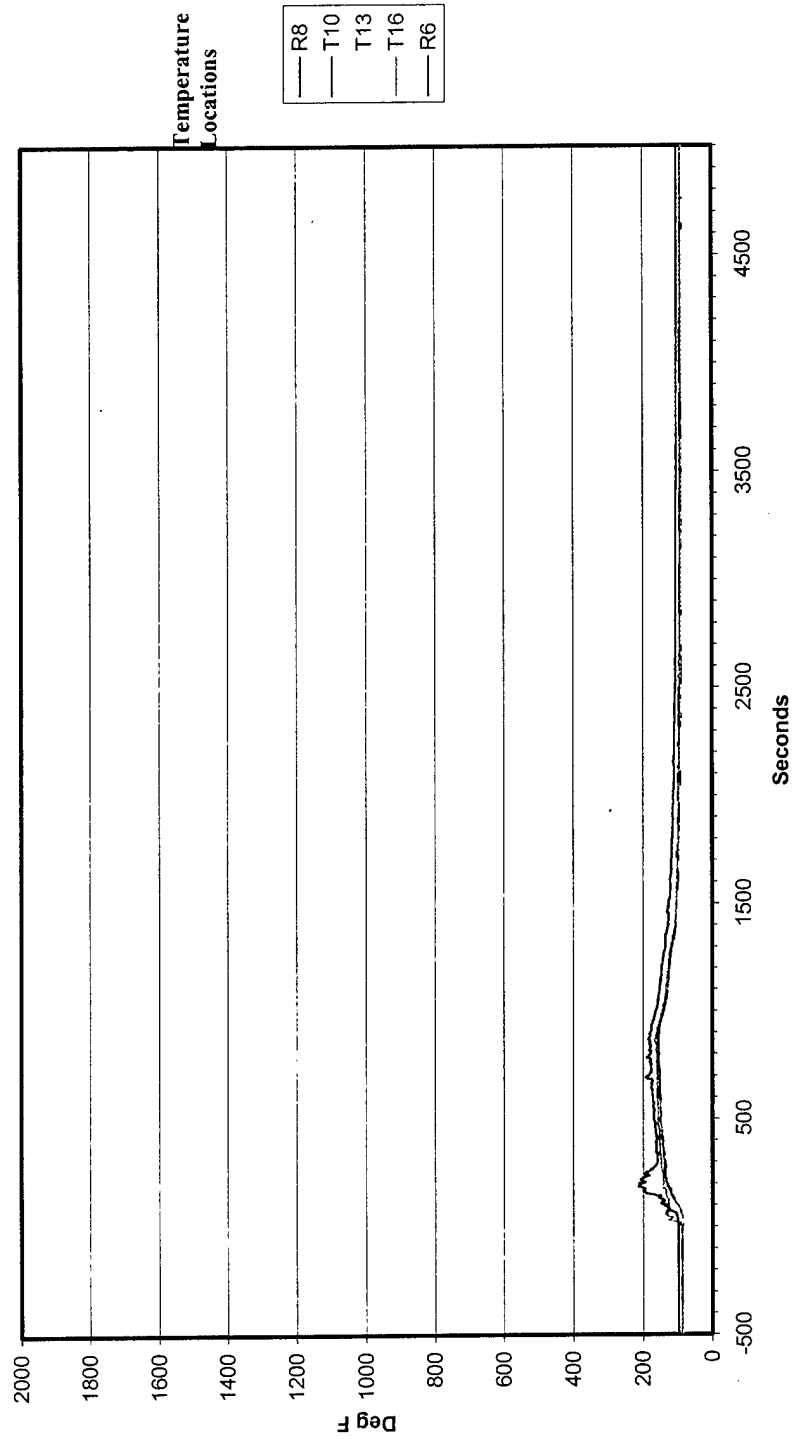


Graph 25
15 Ft. Temperatures
Composite Test #1
15 September 2000



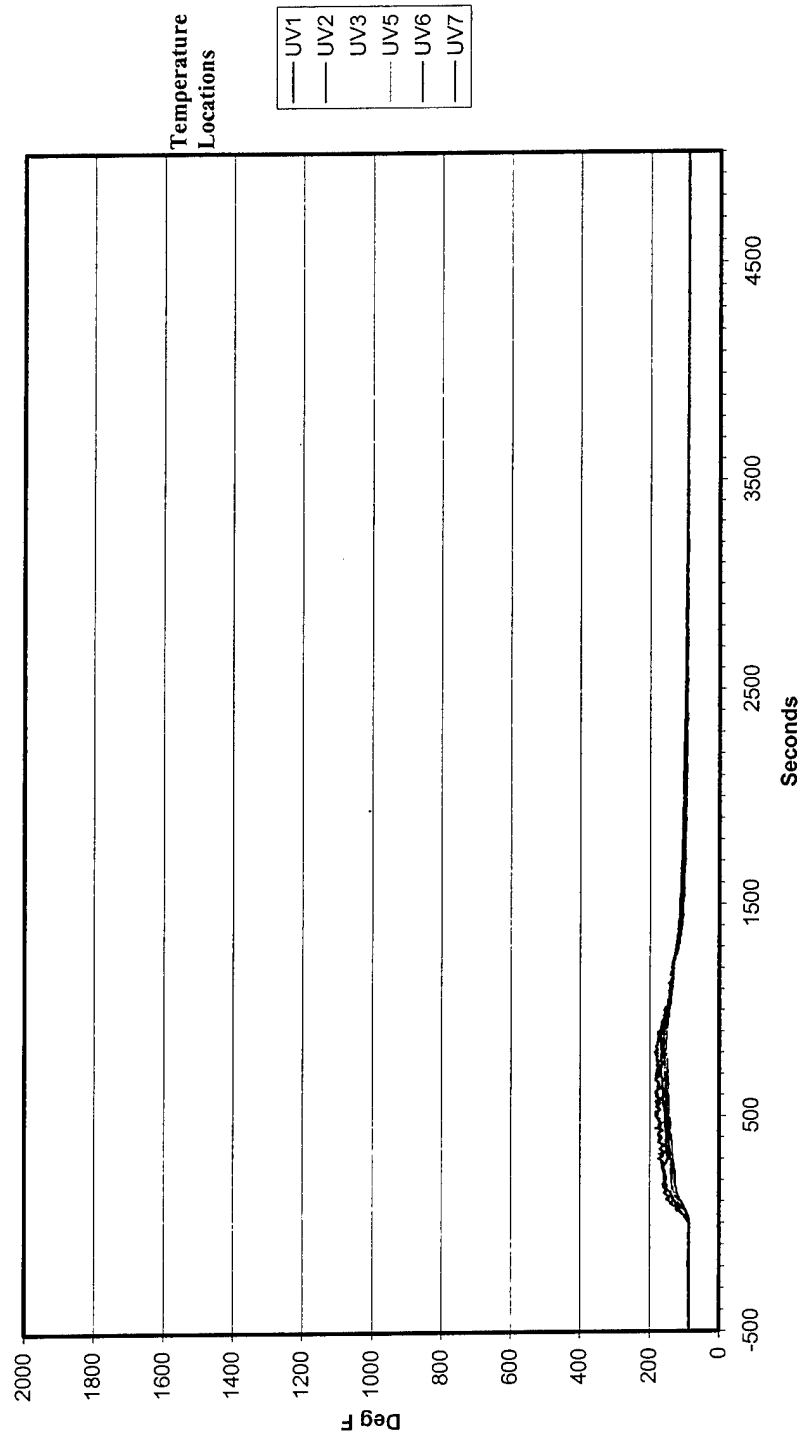
Graph 26

20 Ft. Temperatures
Composite Test #1
15 September 2000



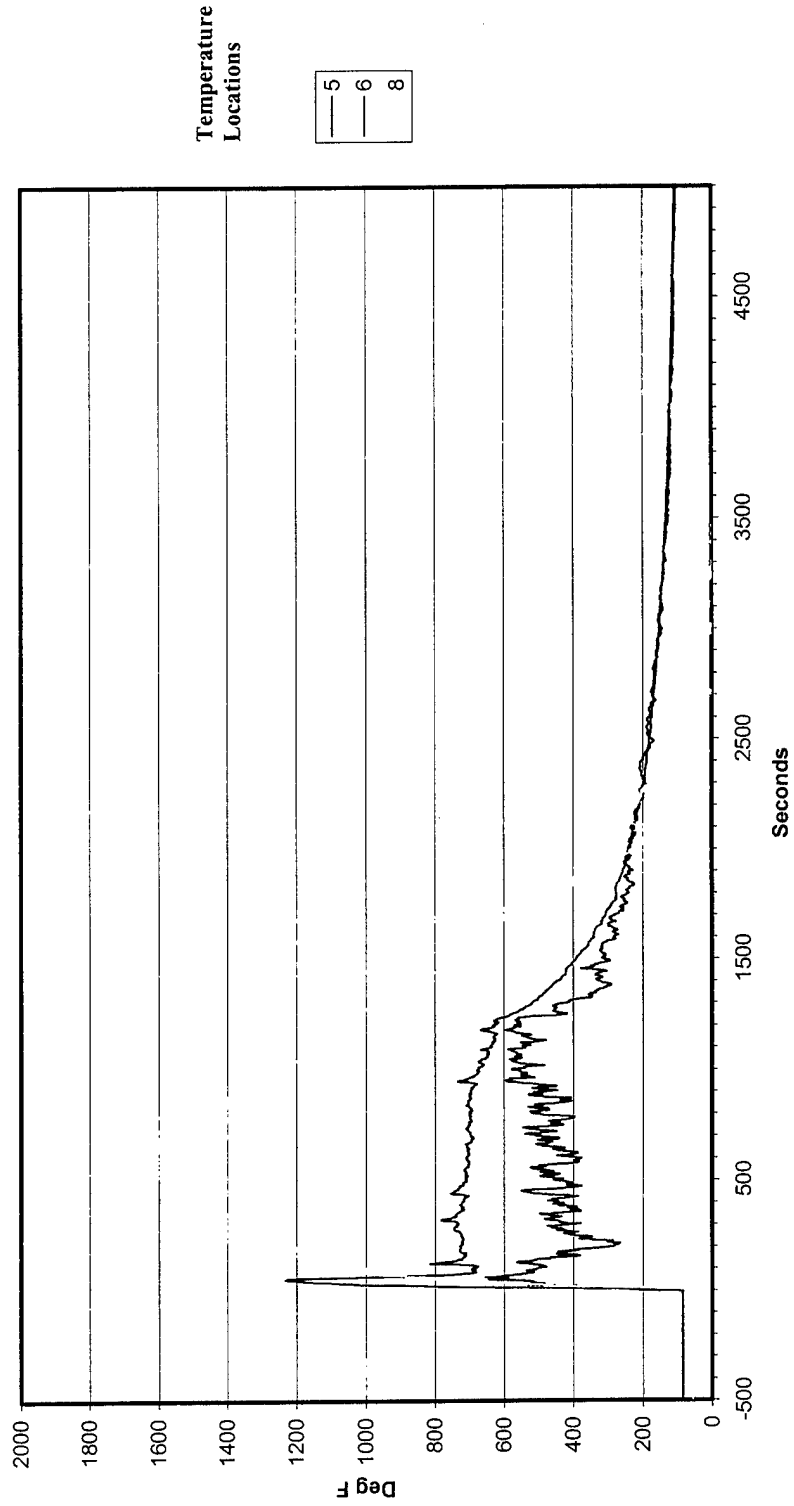
Graph 27

Ceiling Temperatures
Composite Test #1
15 September 2000



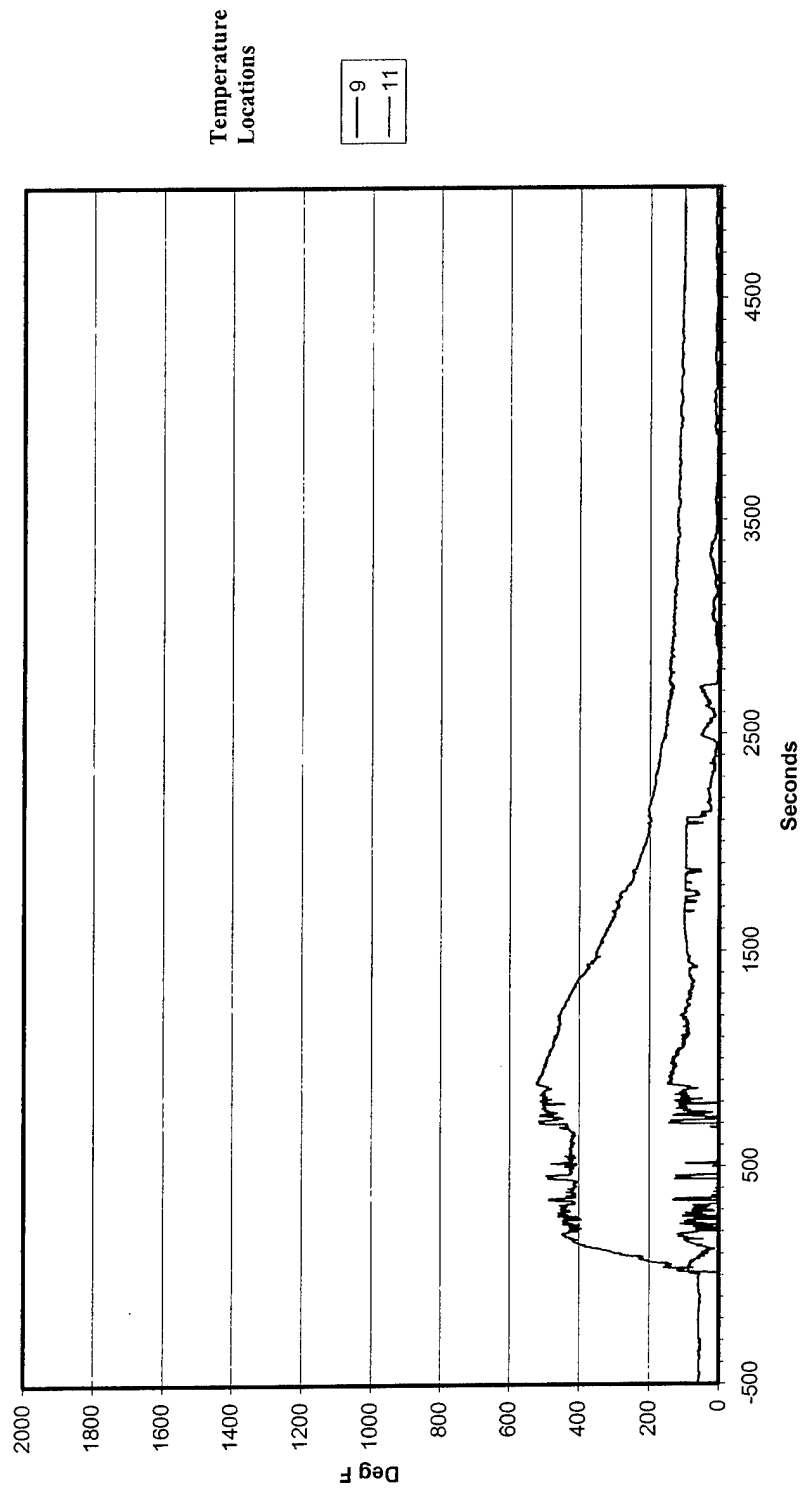
Graph 28

Below Composite Temperatures
Composite Test #1
15 September 2000

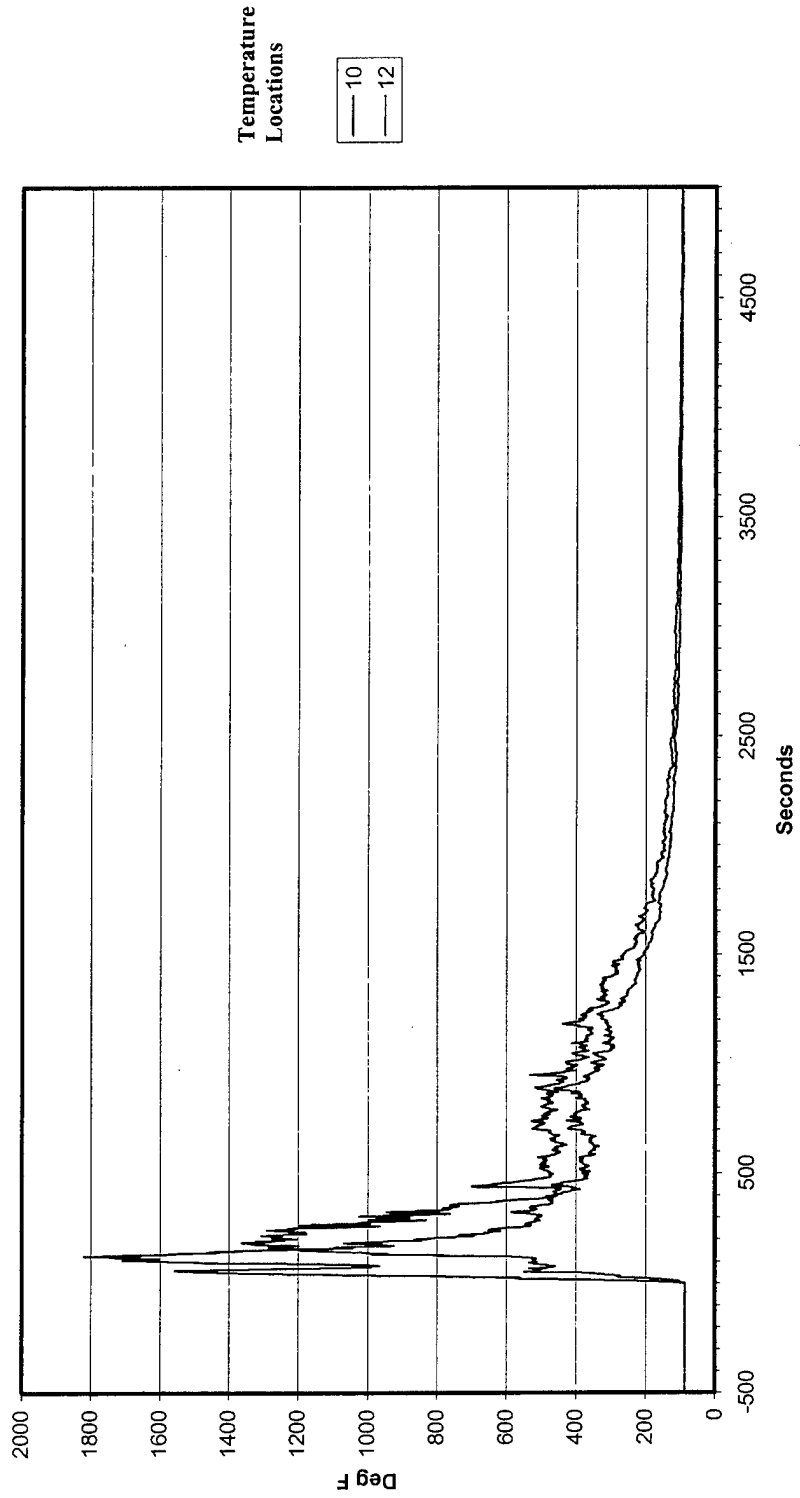


Graph 29

Inside Composite Temperatures
Composite Test #1
15 September 2000

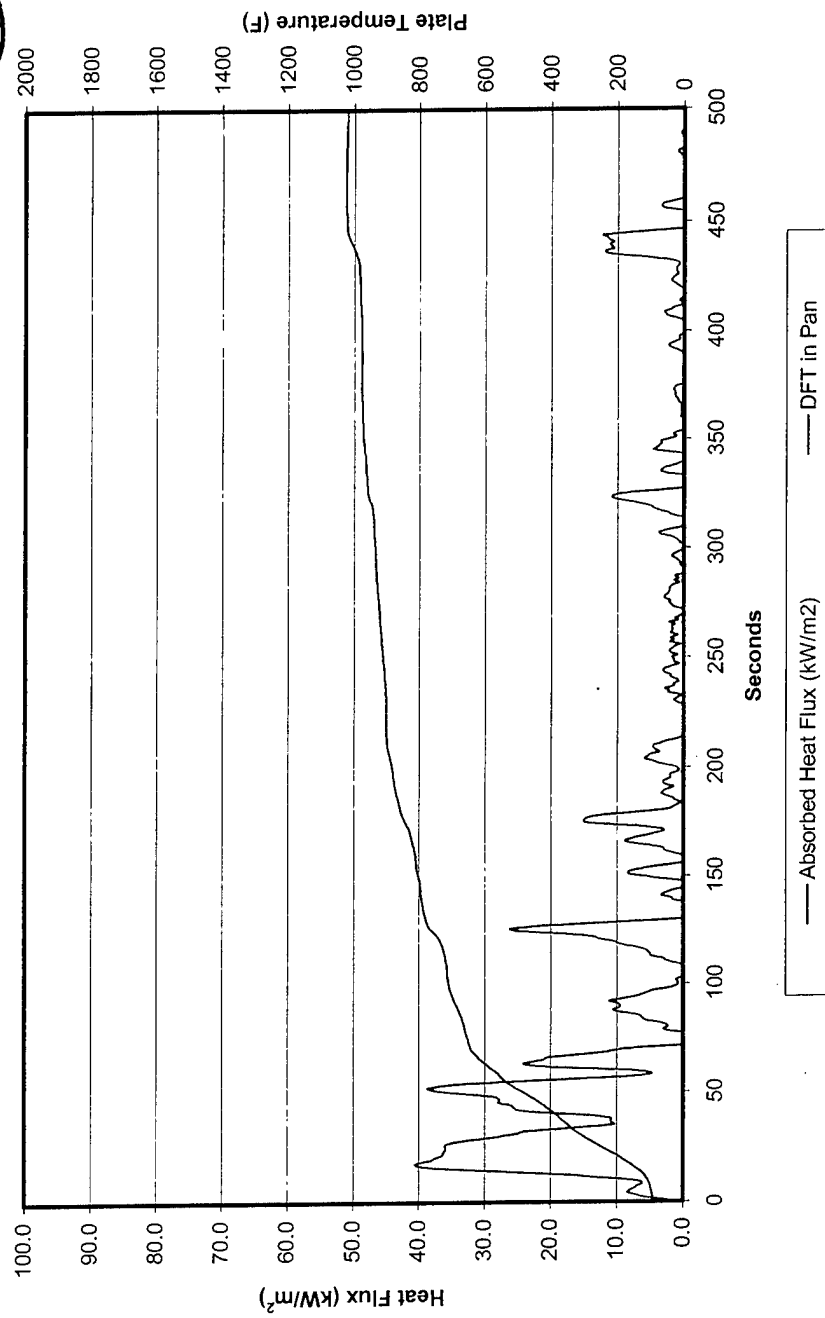


Graph 30
Above Composite Temperatures
Composite Test #1
15 September 2000



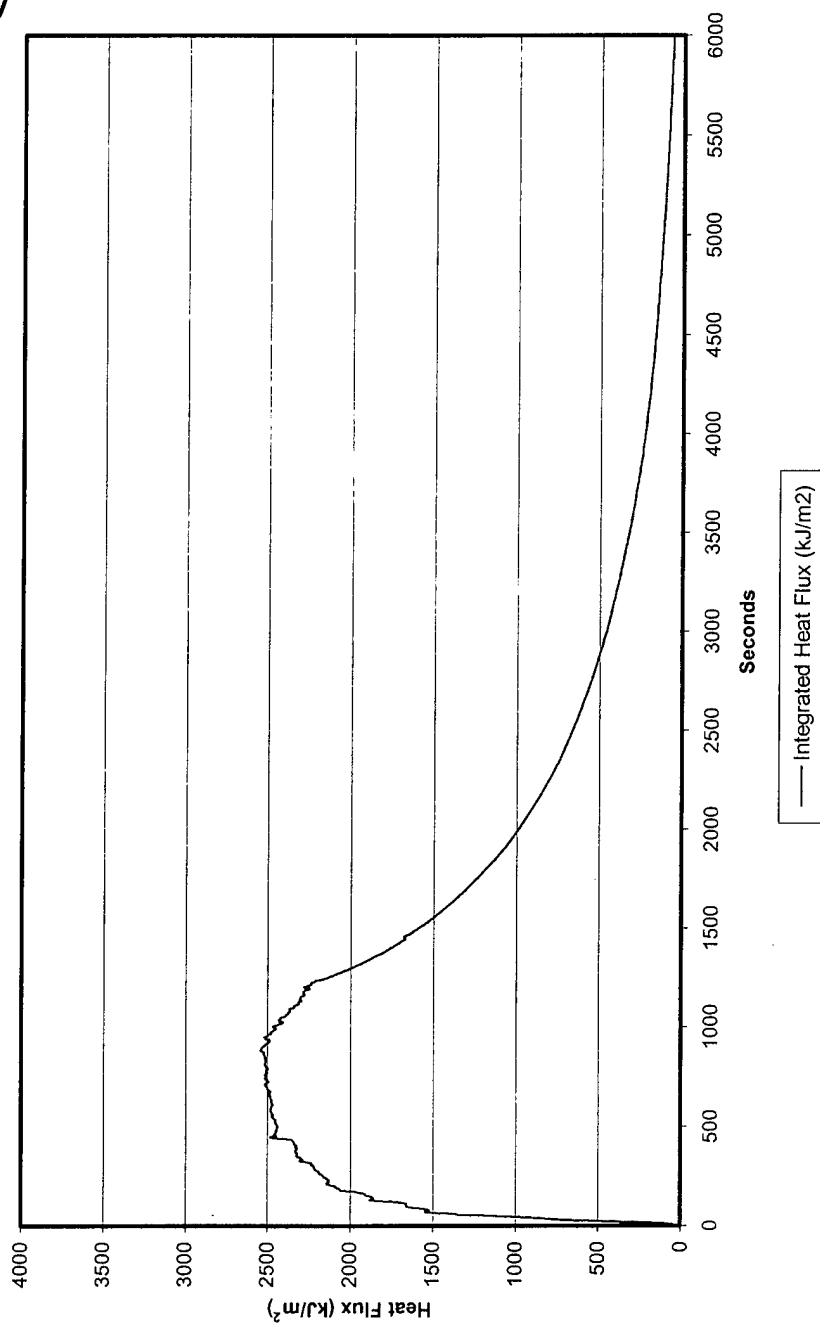
Graph 31

Flux on Composite - DFT in Pan
Composite Test #1
15 September 2000



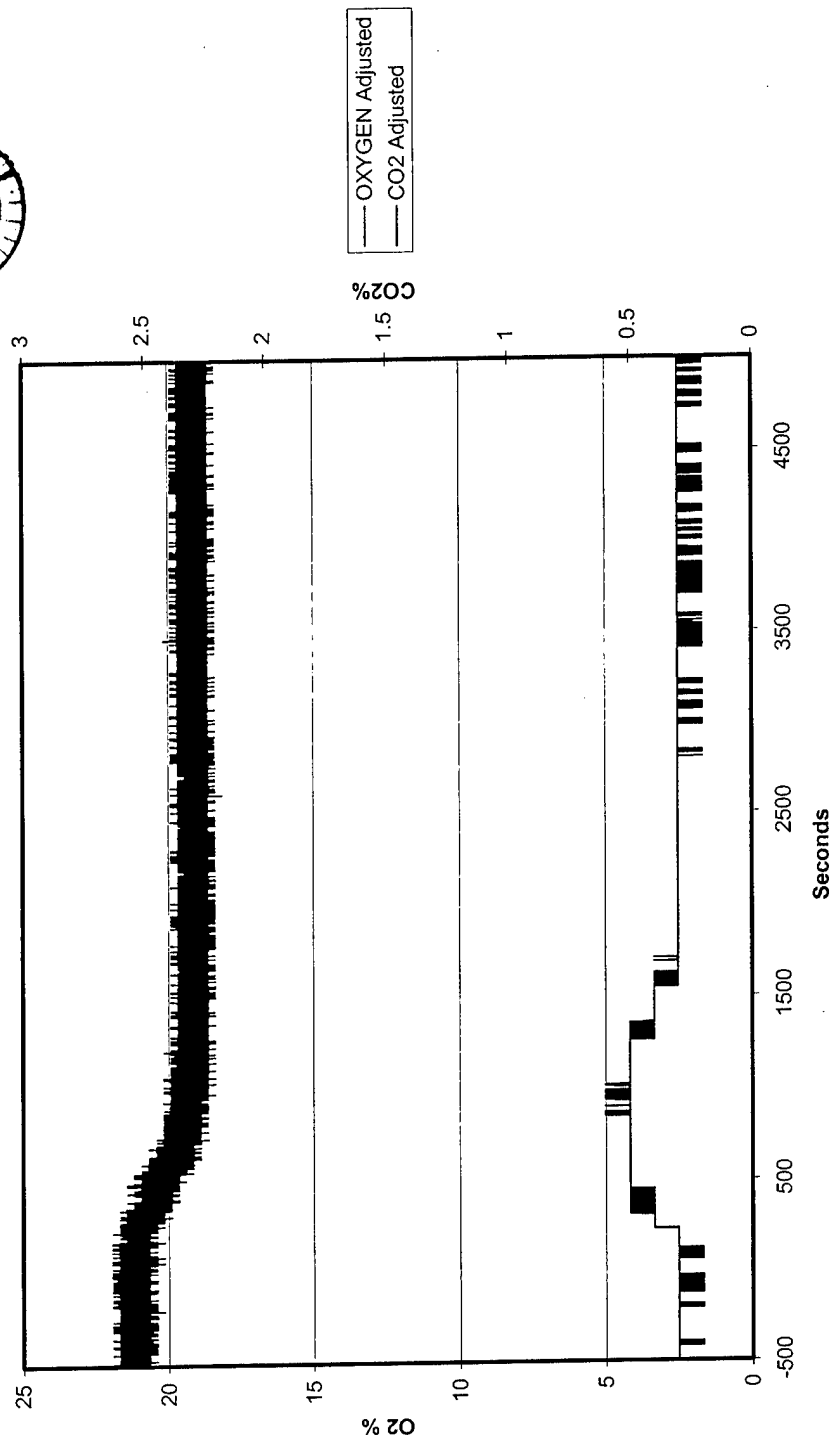
Graph 32

Integrated Flux on Composite - DFT in Pan
Composite Test #1
15 September 2000



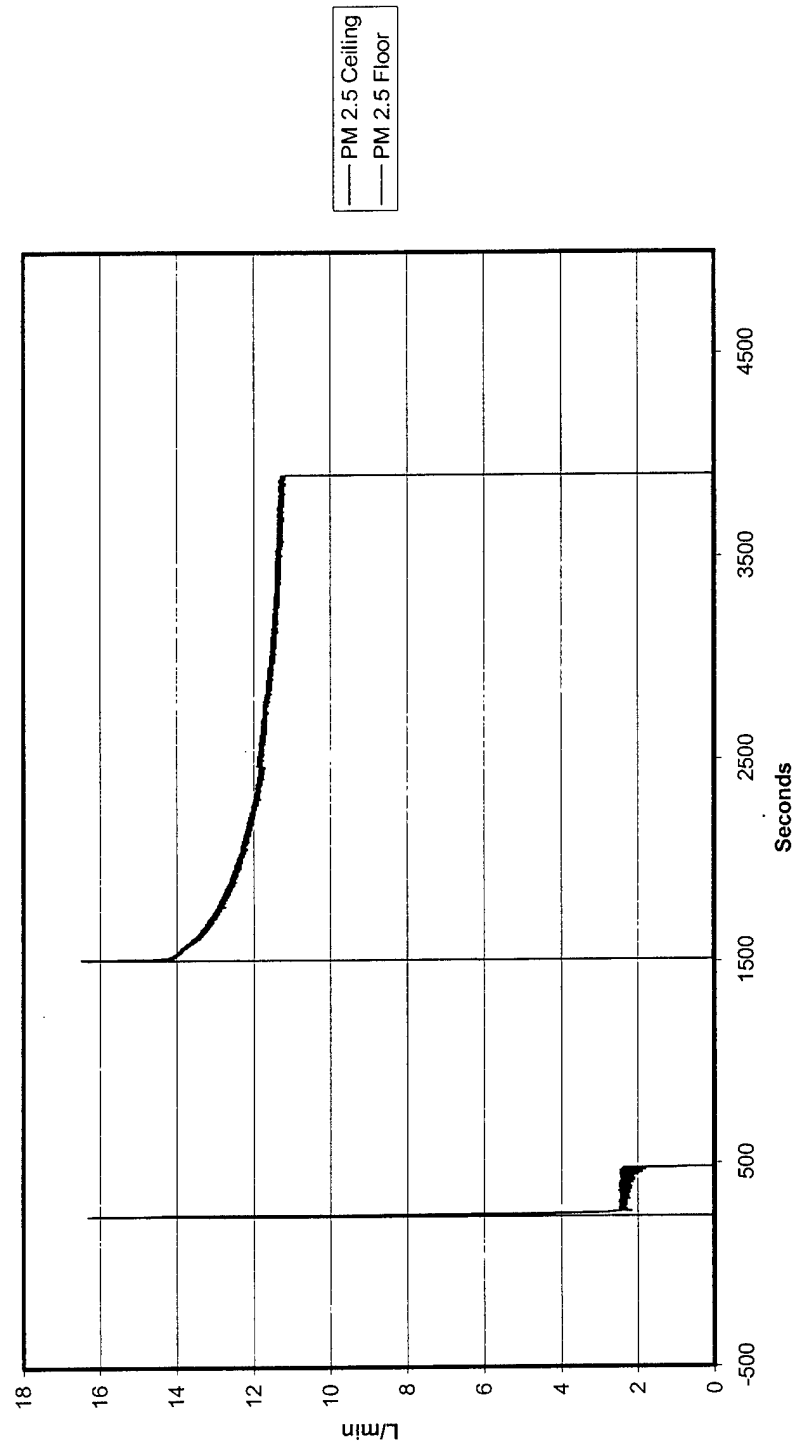
Graph 33

Oxygen & CO₂
Composite Test #1
15 September 2000



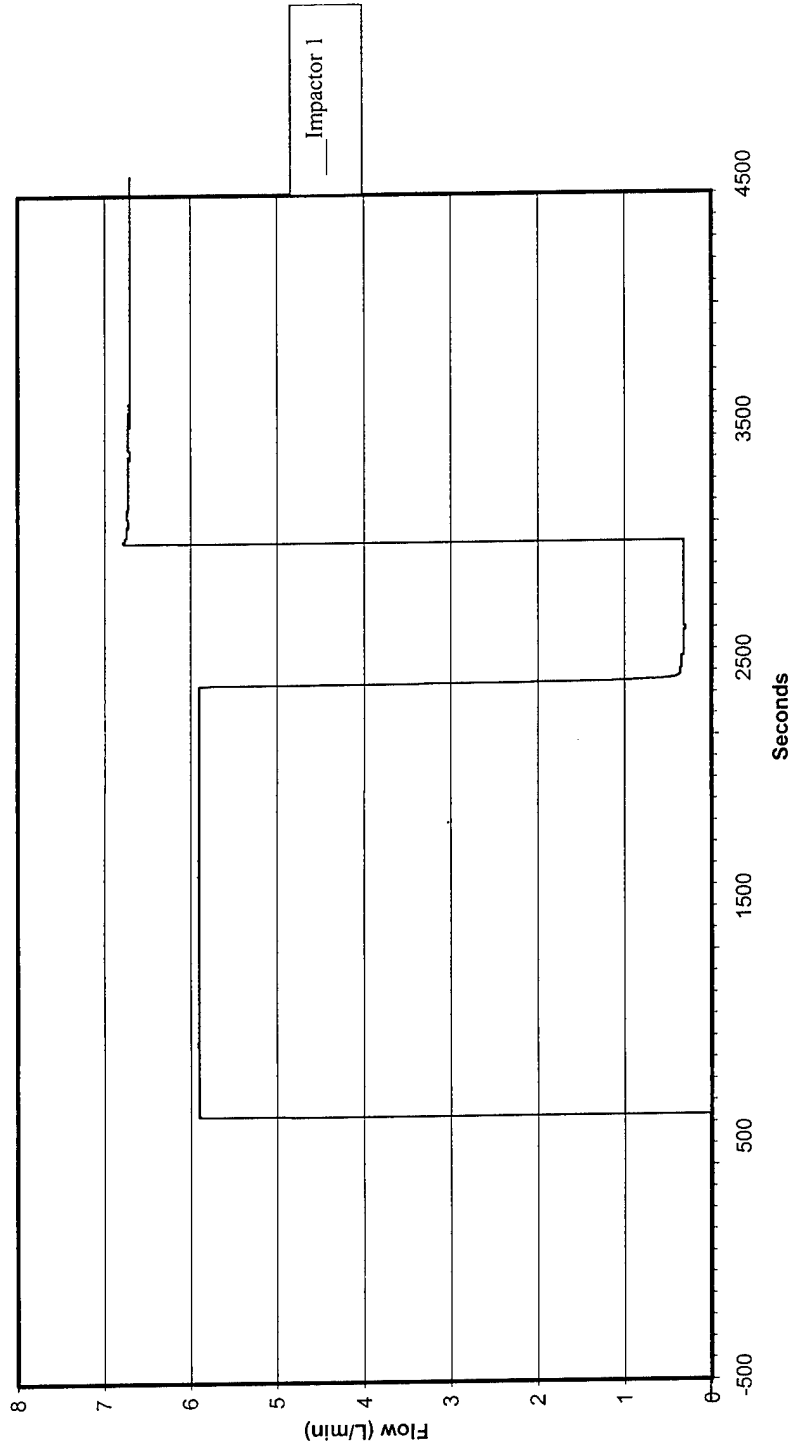
Graph 34

PM 2.5 Flow Rates
Composite Test #2
18 September 2000



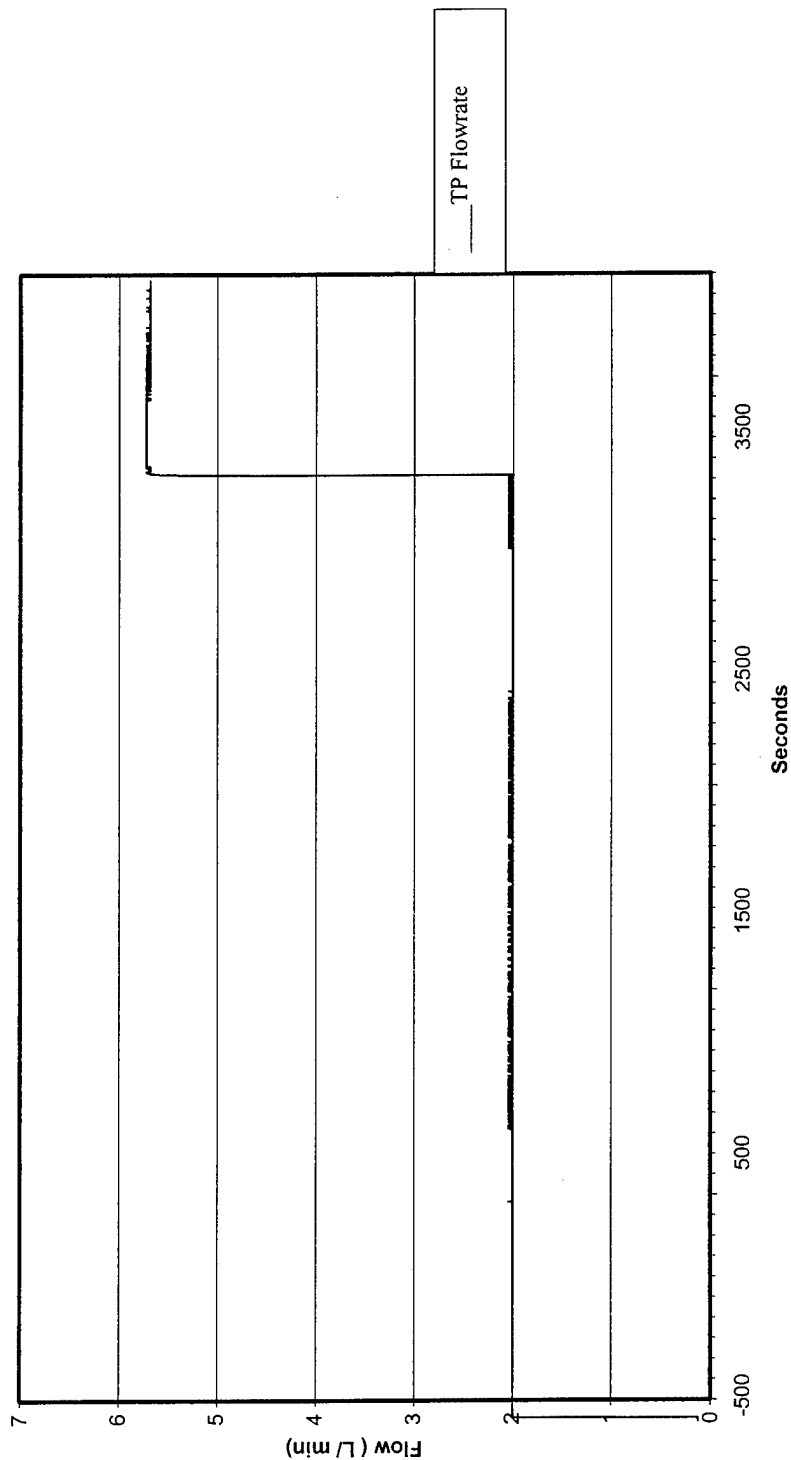
Graph 35

Impactor Flow
Composite Test
18 September



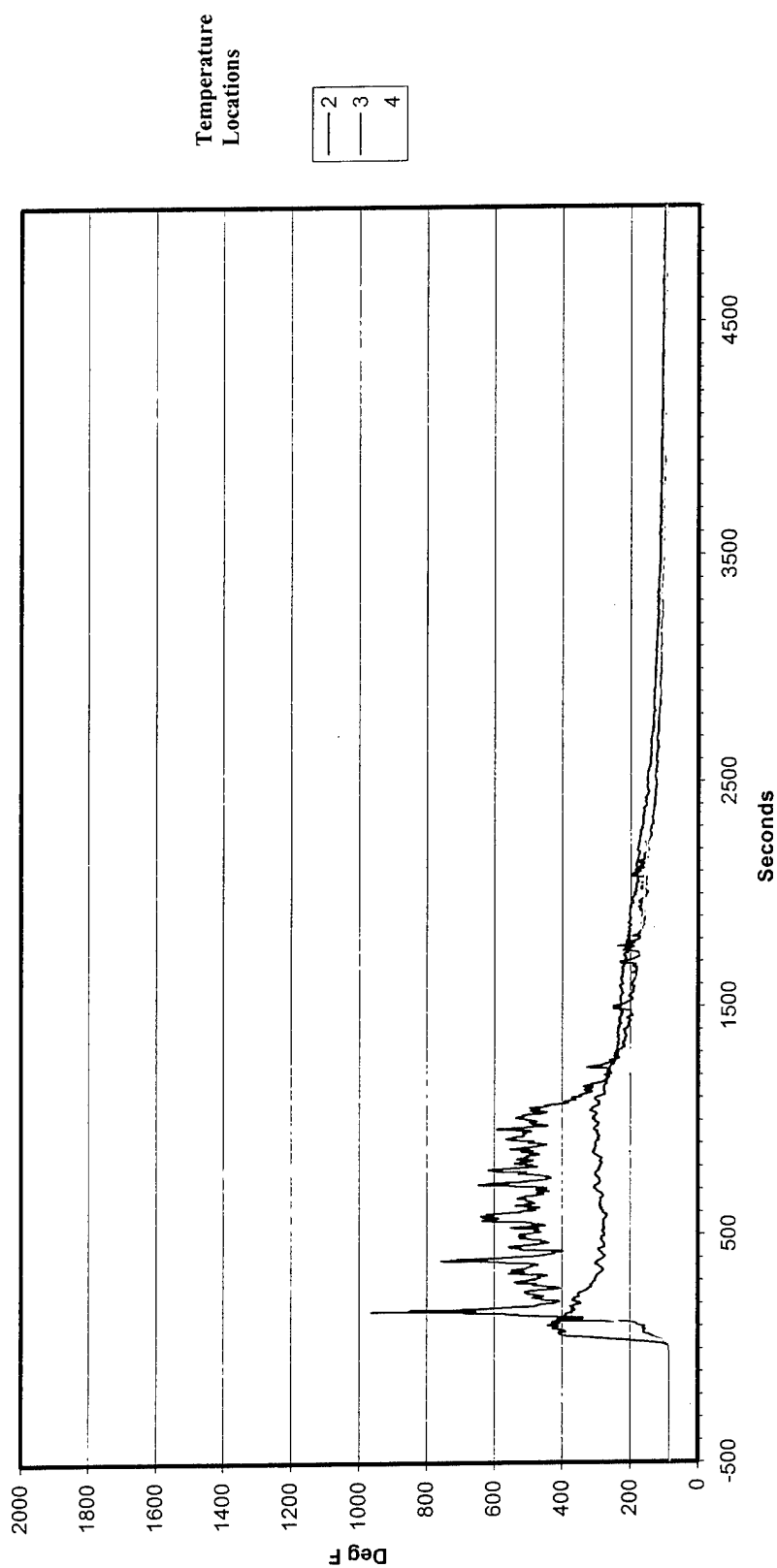
Graph 36

Total Particulate (TP), O₂, and CO₂ Flow Rates
Composite Test
18 September 2000



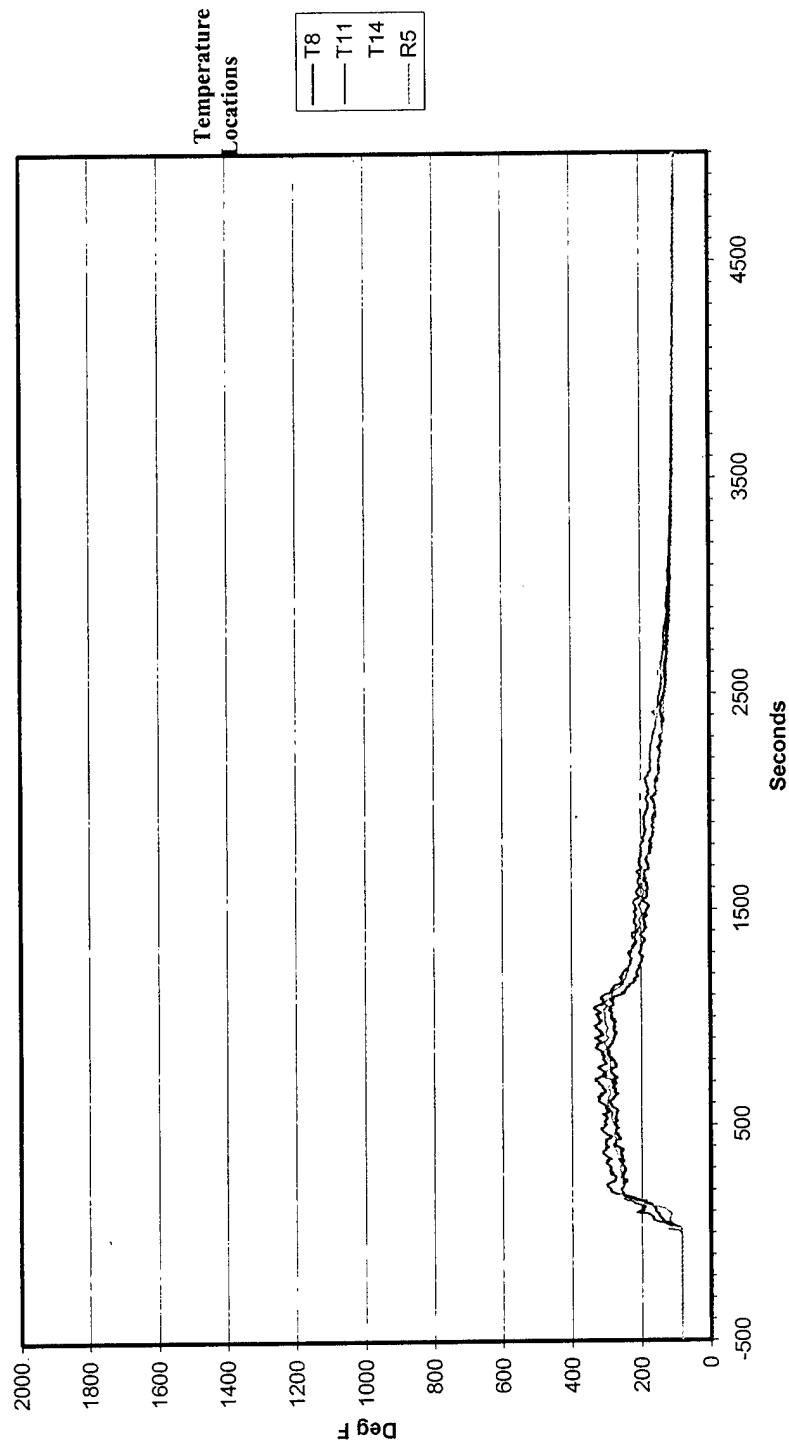
Graph 37

5 Ft. Temperatures
Composite Test #2
18 September 2000



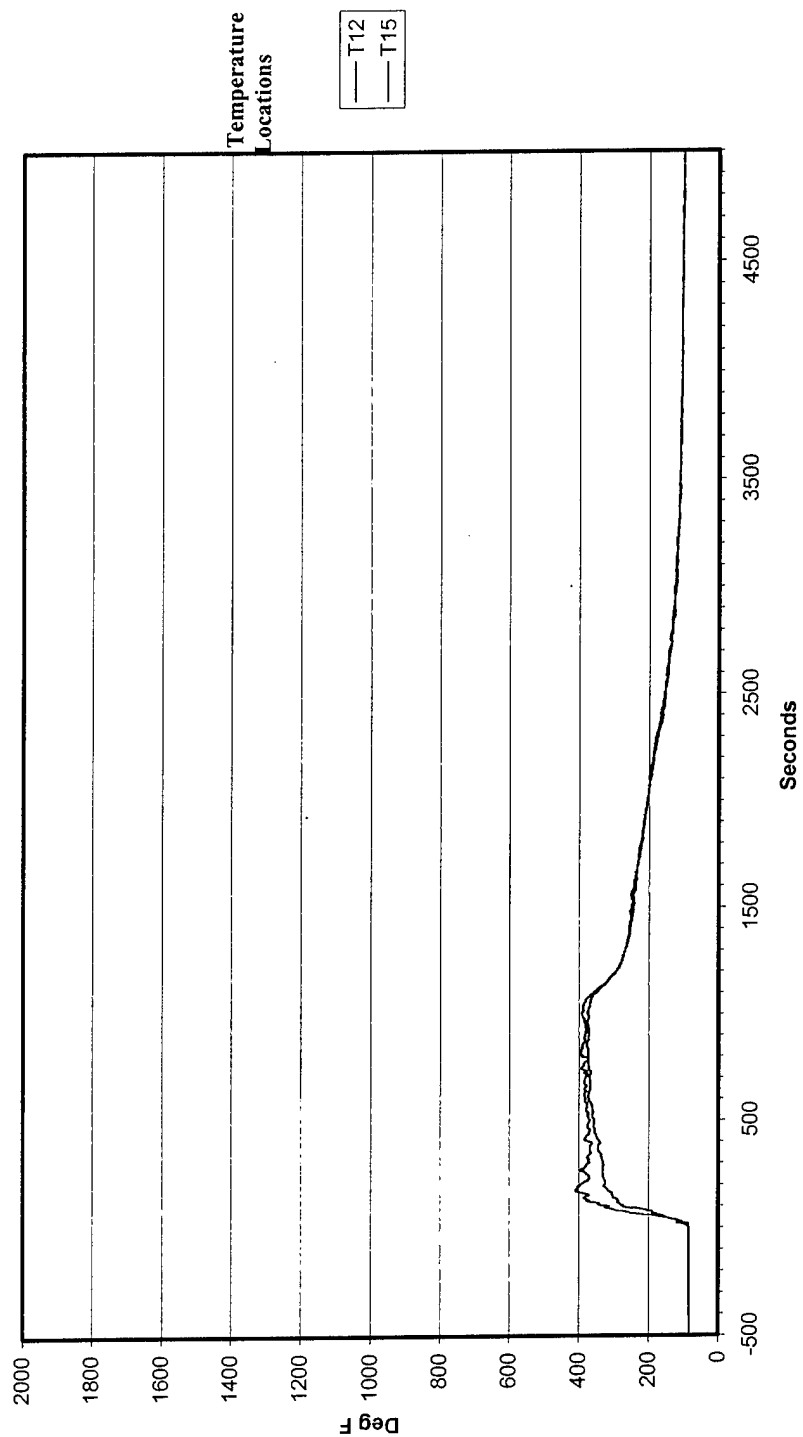
Graph 38

10 Ft. Temperatures
Composite Test #2
18 September 2000



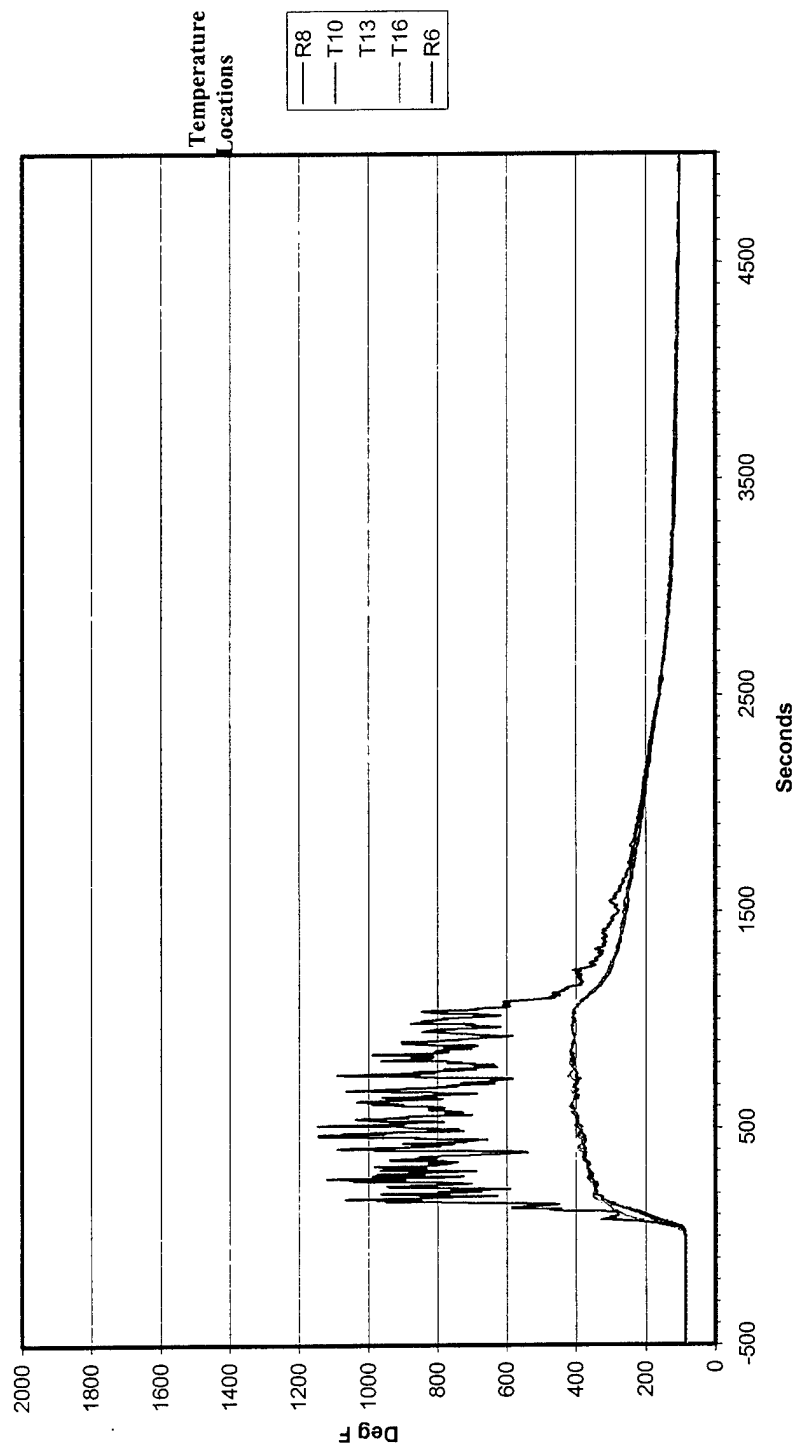
Graph 39

15 Ft. Temperatures
Composite Test #2
18 September 2000



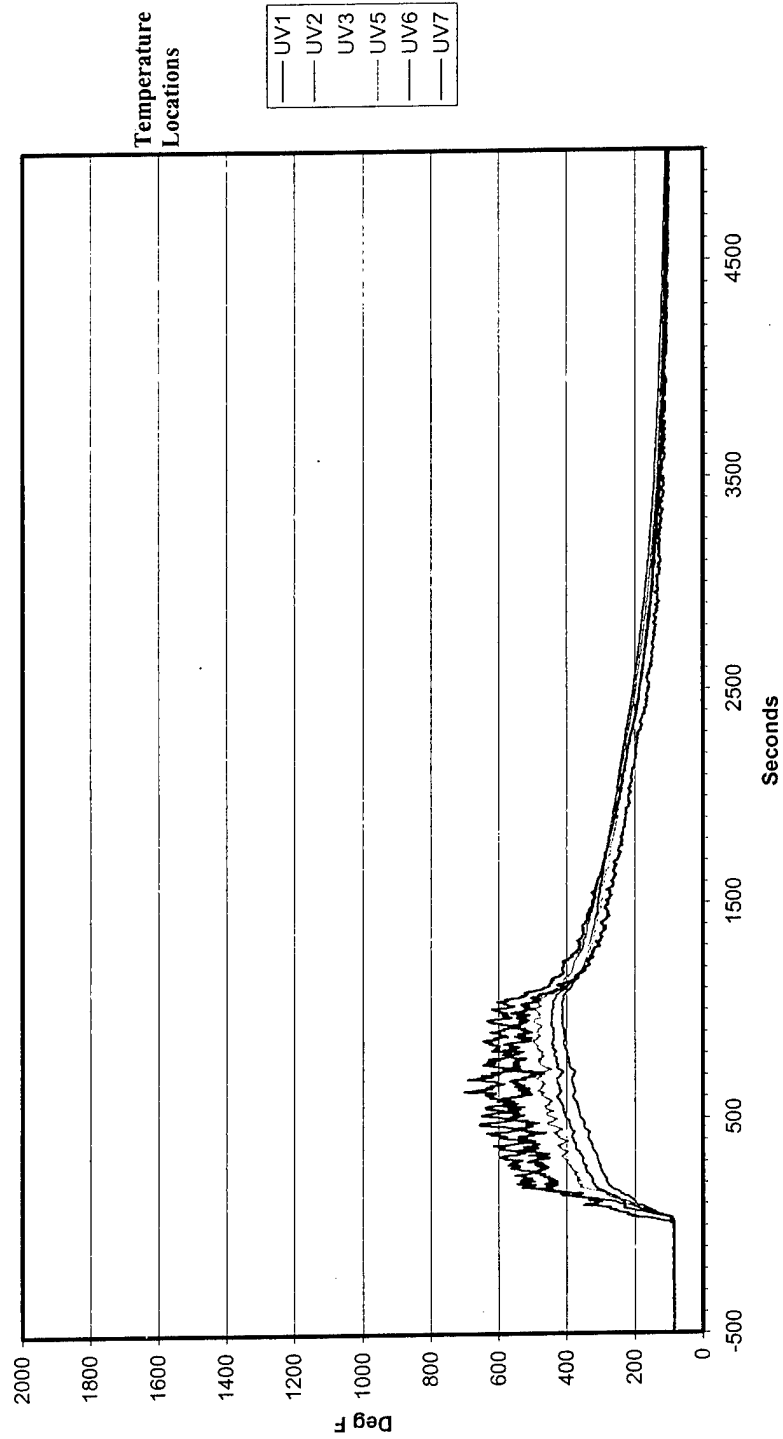
Graph 40

20 Ft. Temperatures
Composite Test #2
18 September 2000



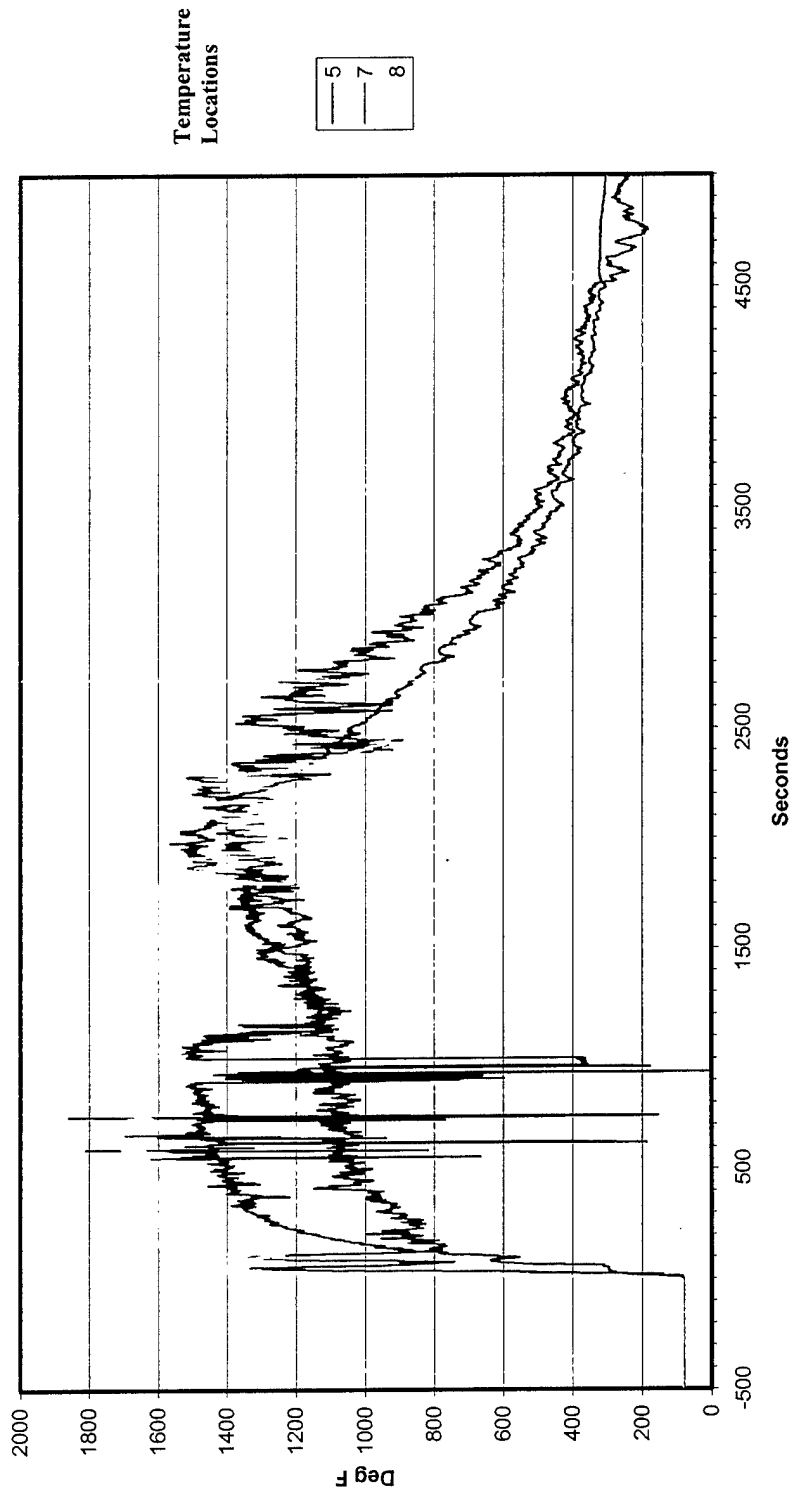
Graph 41

Ceiling Temperatures
Composite Test #2
18 September 2000



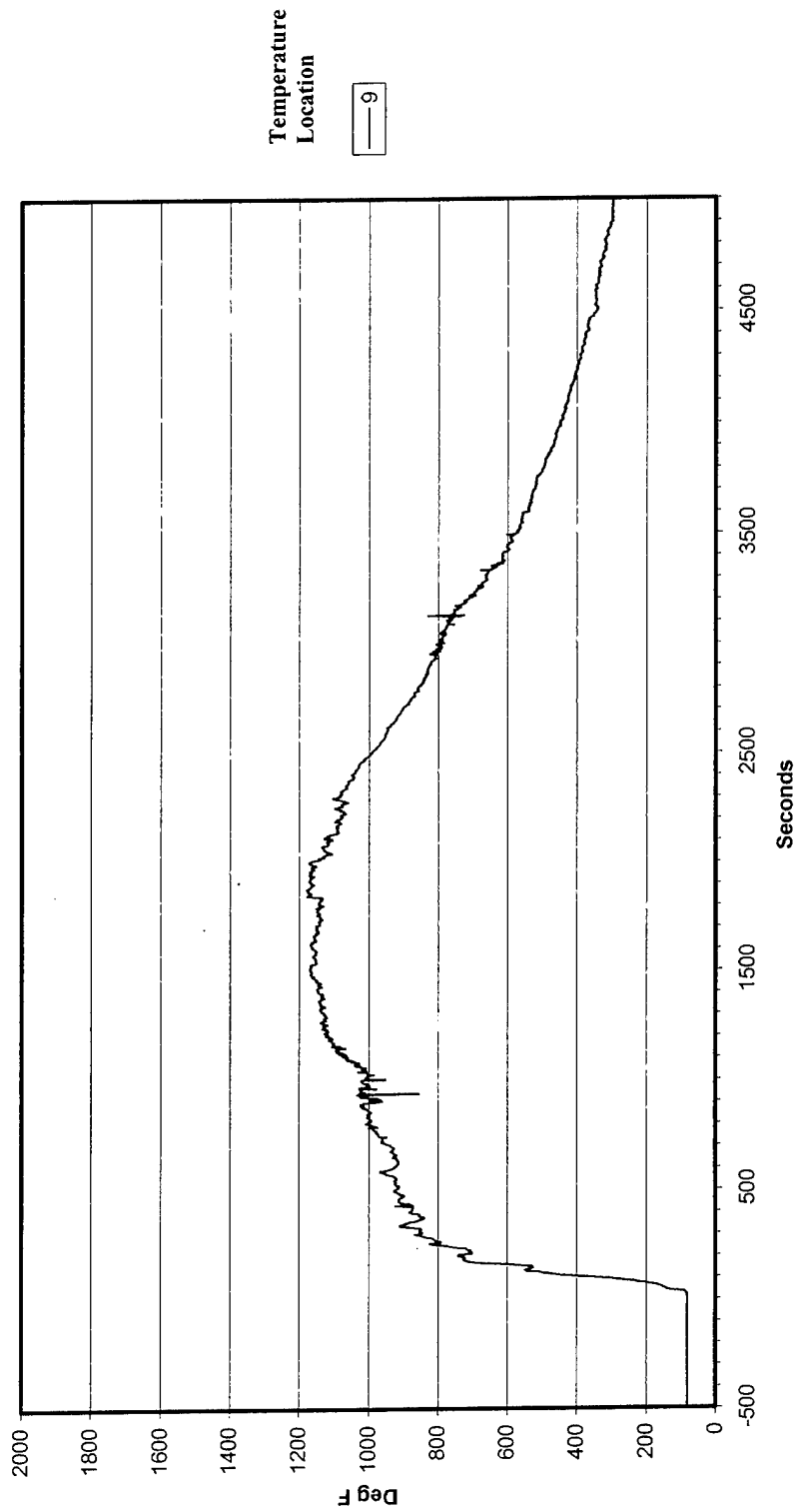
Graph 42

Below Composite Temperatures
Composite Test #2
18 September 2000



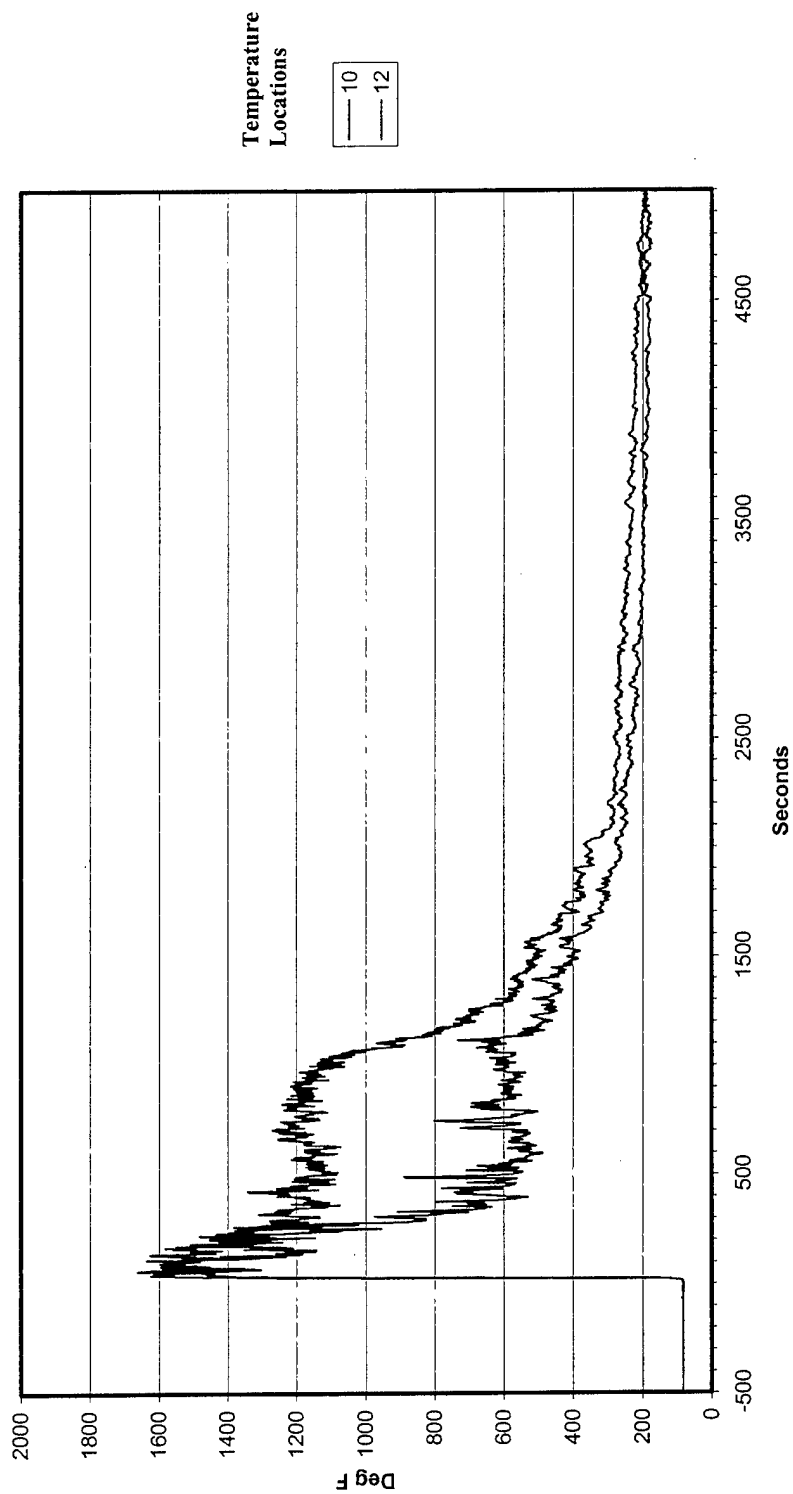
Graph 43

Inside Composite Temperatures
Composite Test #2
18 September 2000



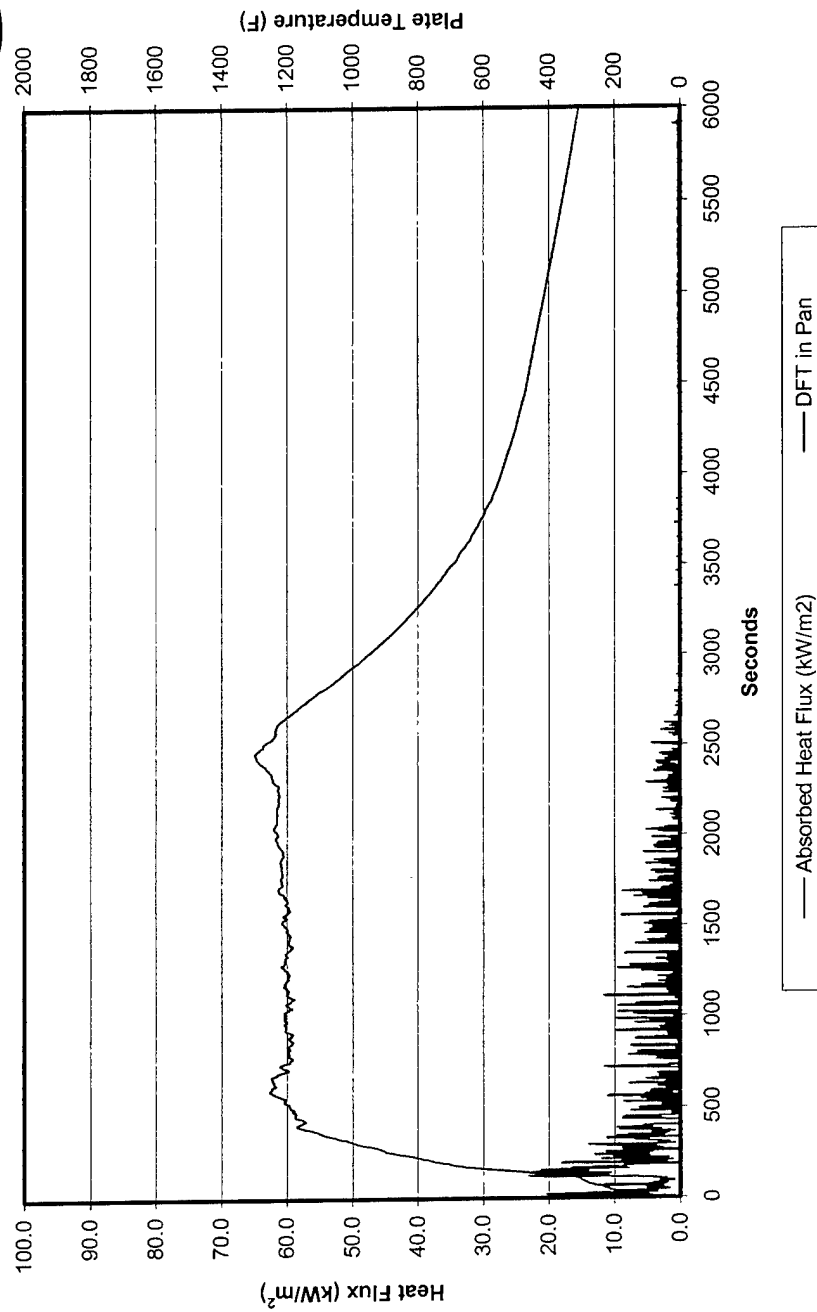
Graph 44

Above Composite Temperatures
Composite Test #2
18 September 2000



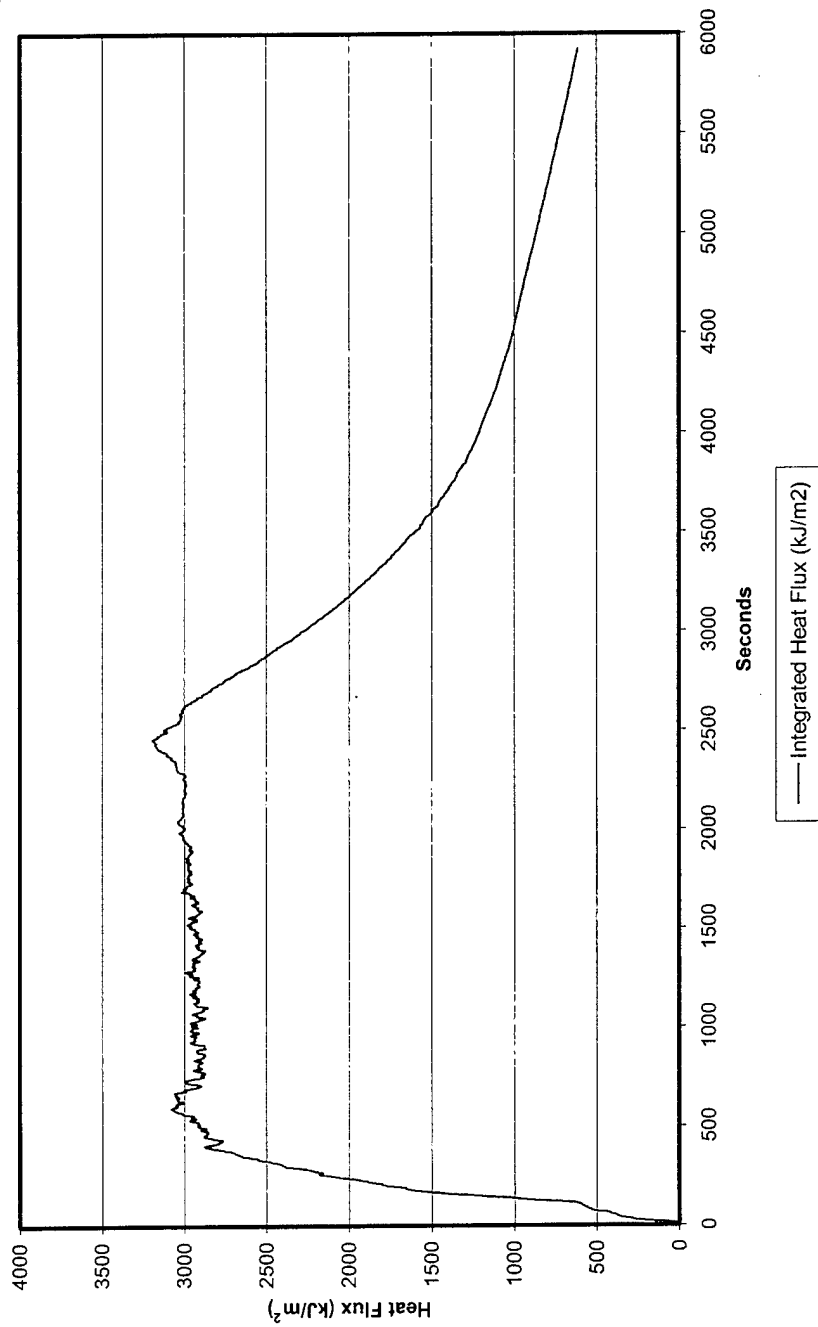
Graph 45

Flux on Composite - DFT in Pan
Composite Test #2
18 September 2000

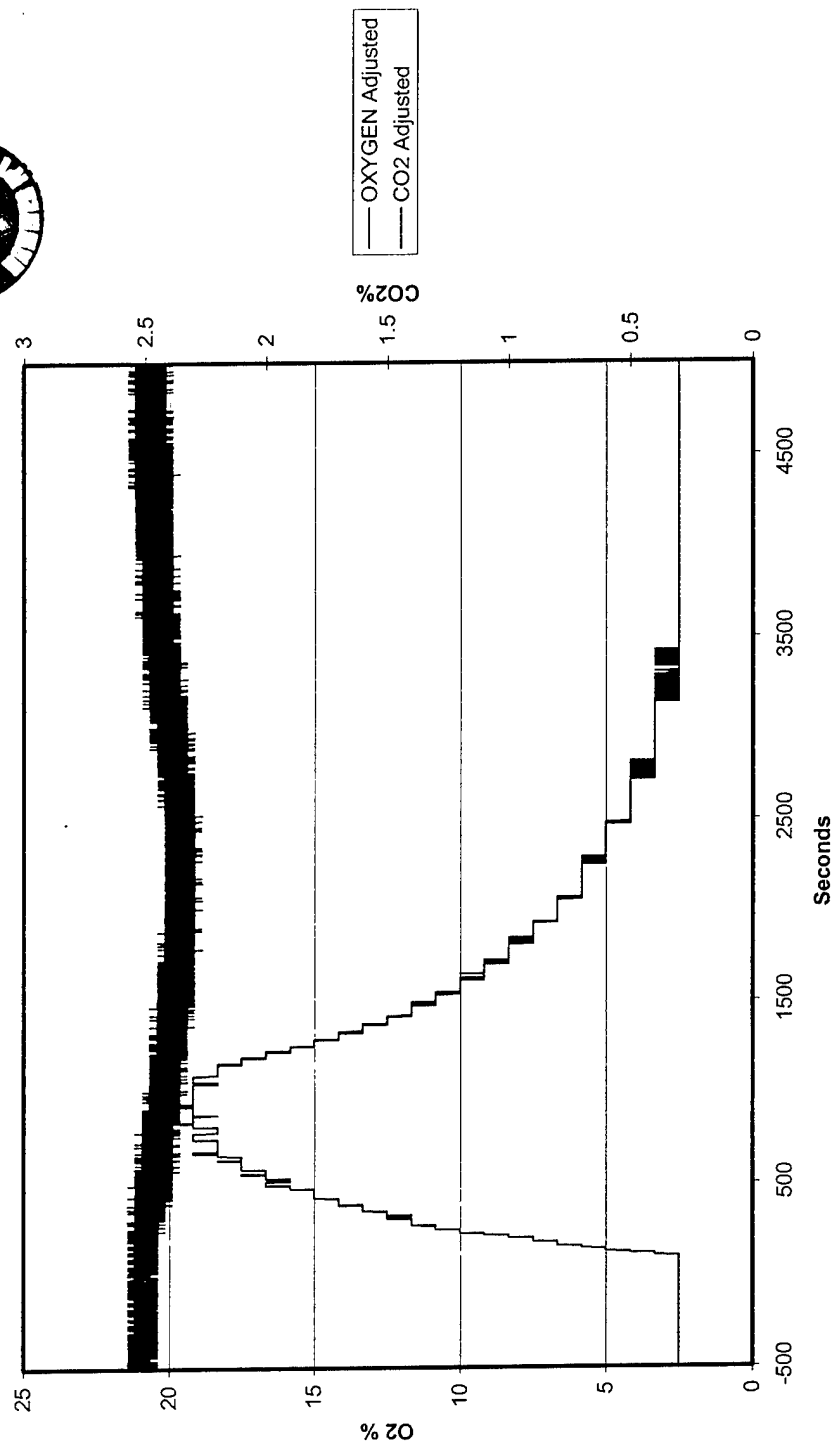


Graph 46

Integrated Flux on Composite - DFT in Pan
Composite Test #2
18 September 2000

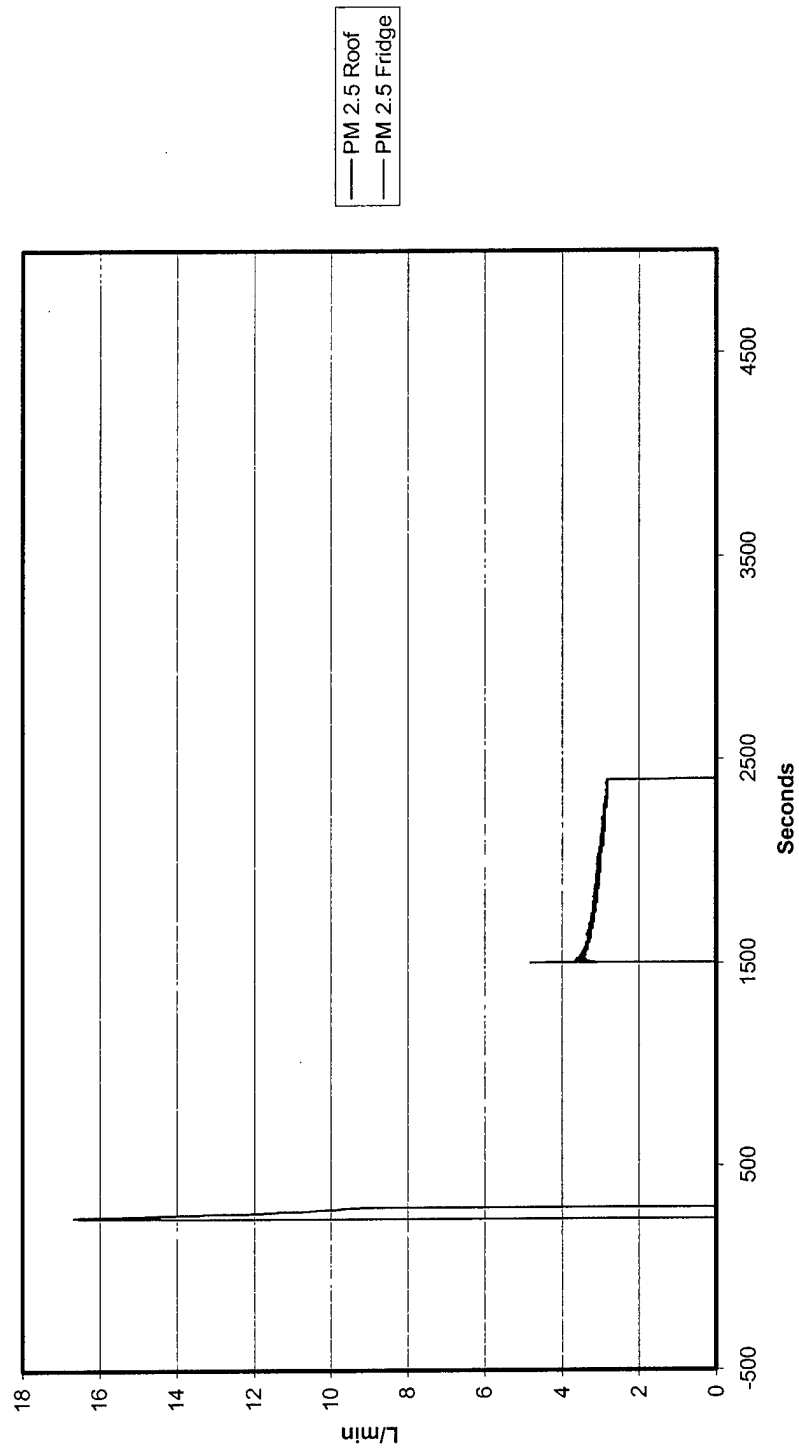


Graph 47
Oxygen & CO₂
Composite Test #2
18 September 2000



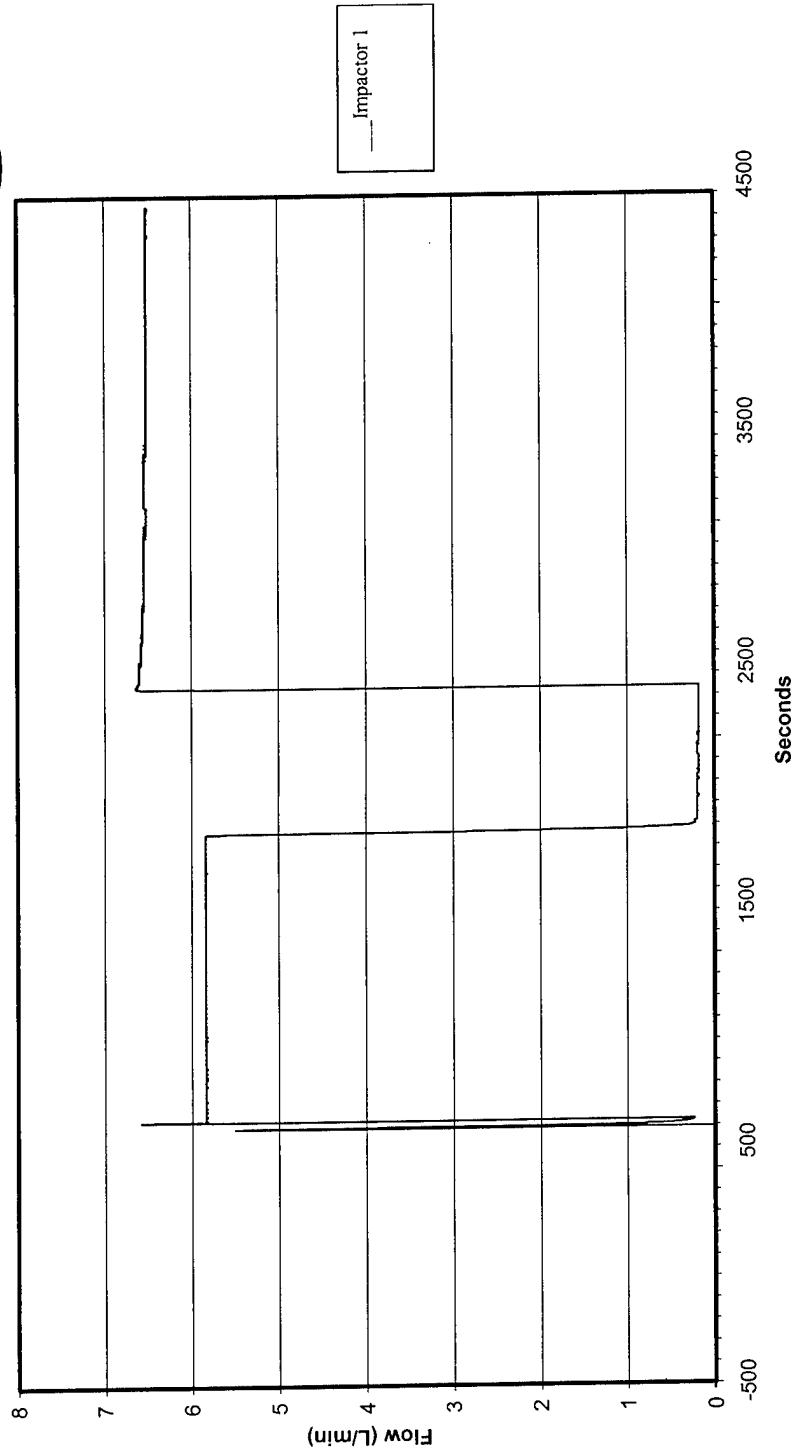
Graph 48

PM 2.5 Flow Rates
Composite Test #3
19 September 2000



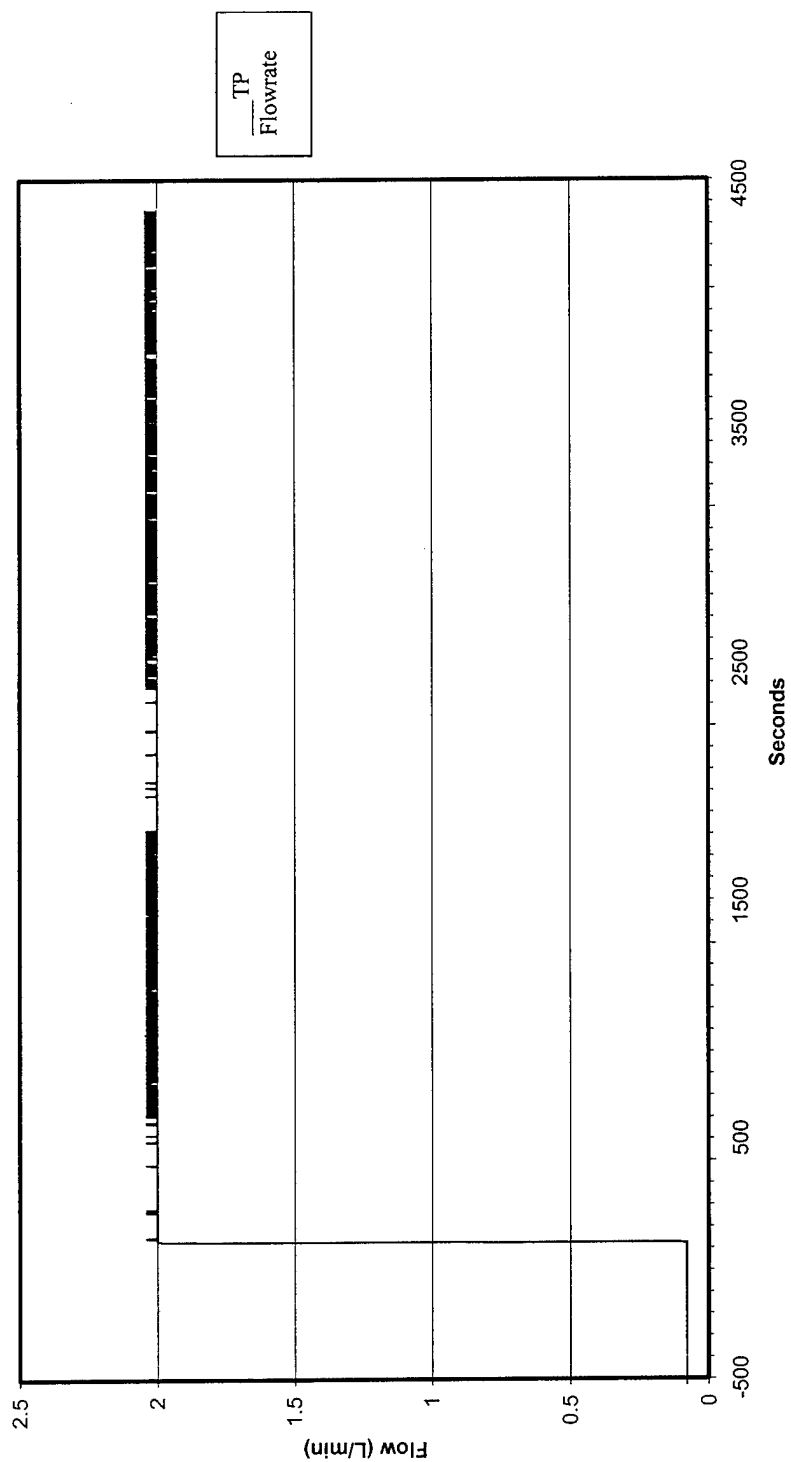
Graph 49

Impactor Flow
Composite Test
19 September



Graph 50

Total Particulate (TP), O₂, and CO₂ Flow Rates
Composite Test
19 September



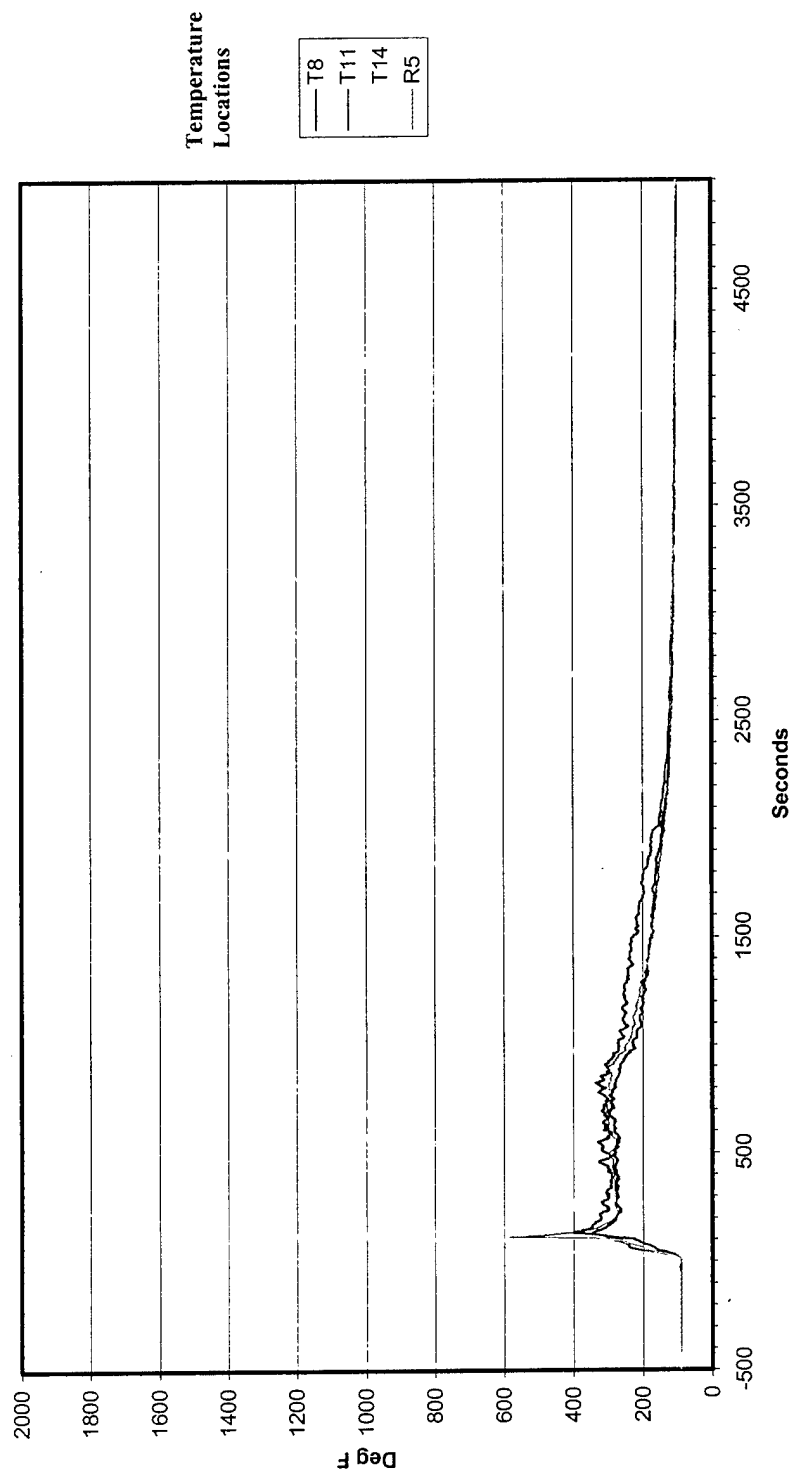
Graph 51

5 Ft. Temperatures
Composite Test #3
19 September 2000



Graph 52

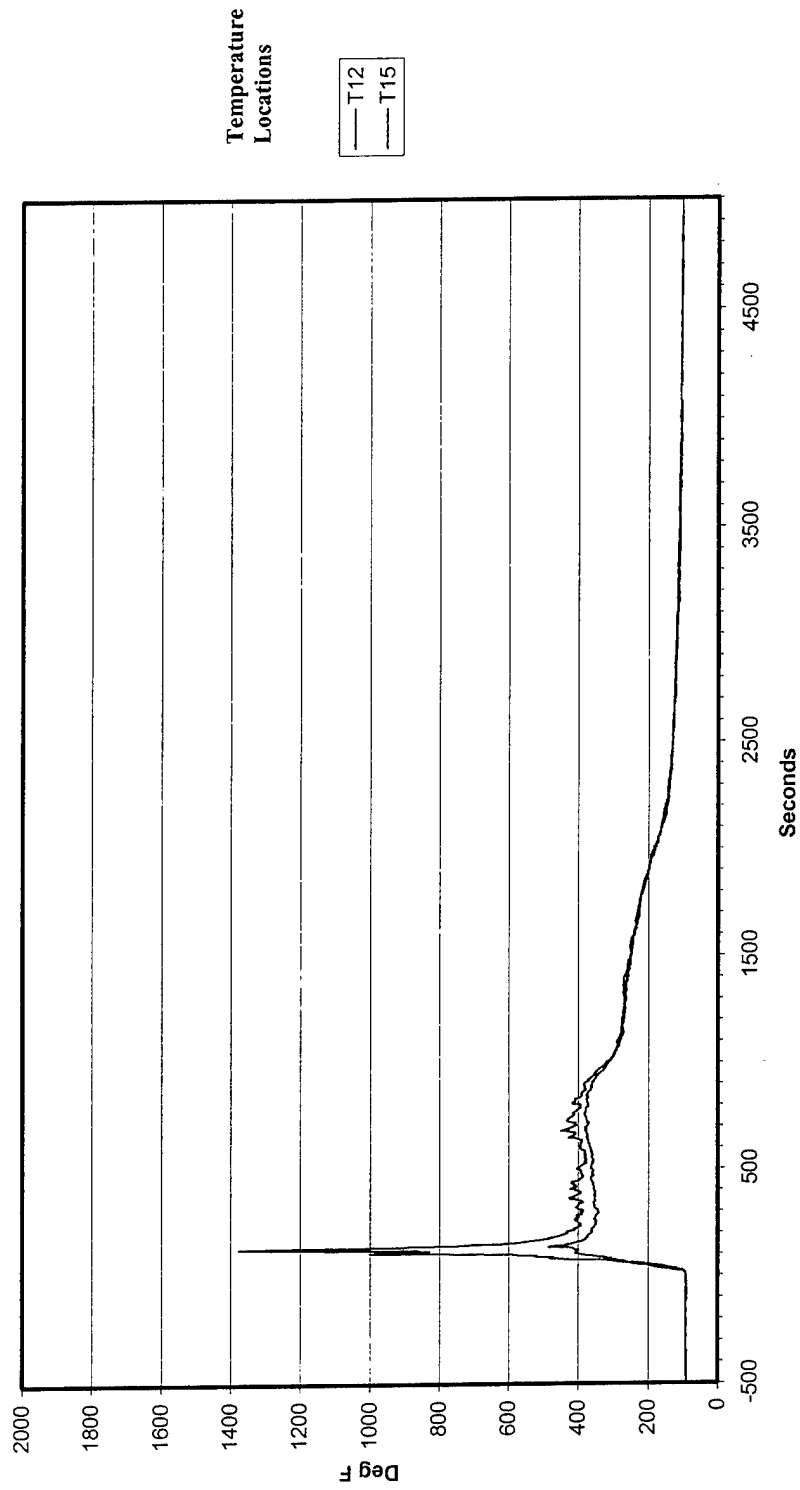
10 Ft. Temperatures
Composite Test #3
19 September 2000



Graph 53

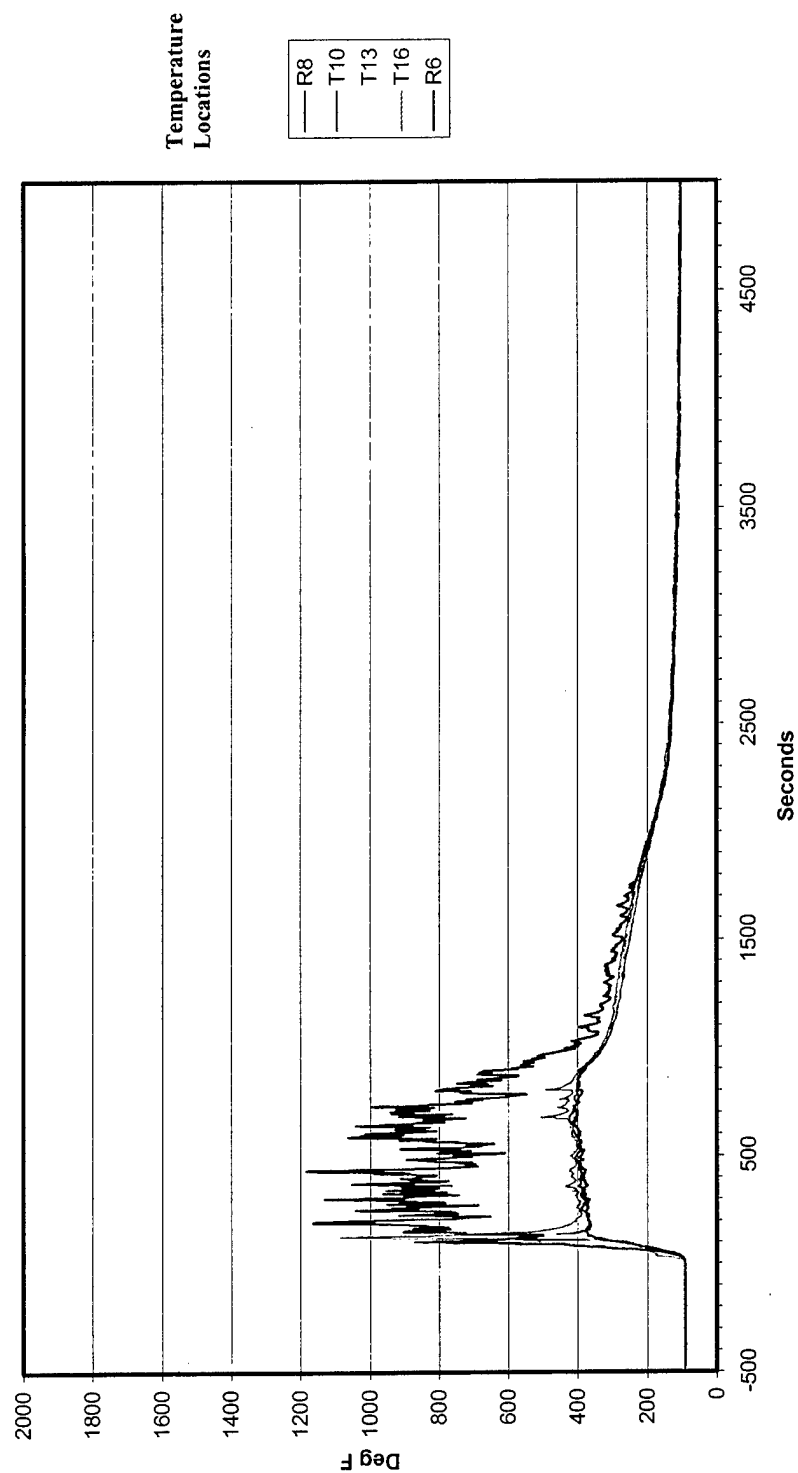


15 Ft. Temperatures
Composite Test #3
19 September 2000



Graph 54

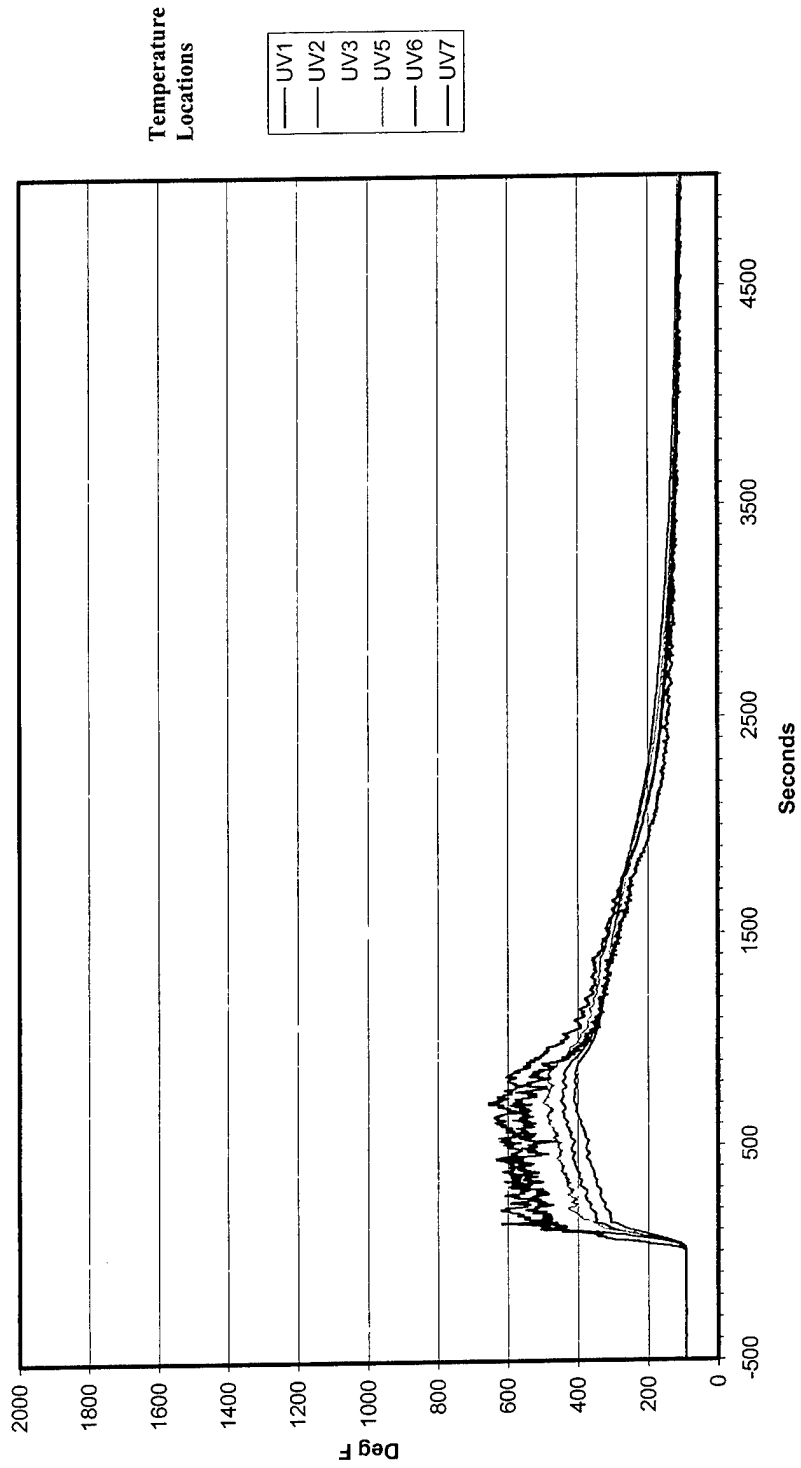
20 Ft. Temperatures
Composite Test #3
19 September 2000



Graph 55

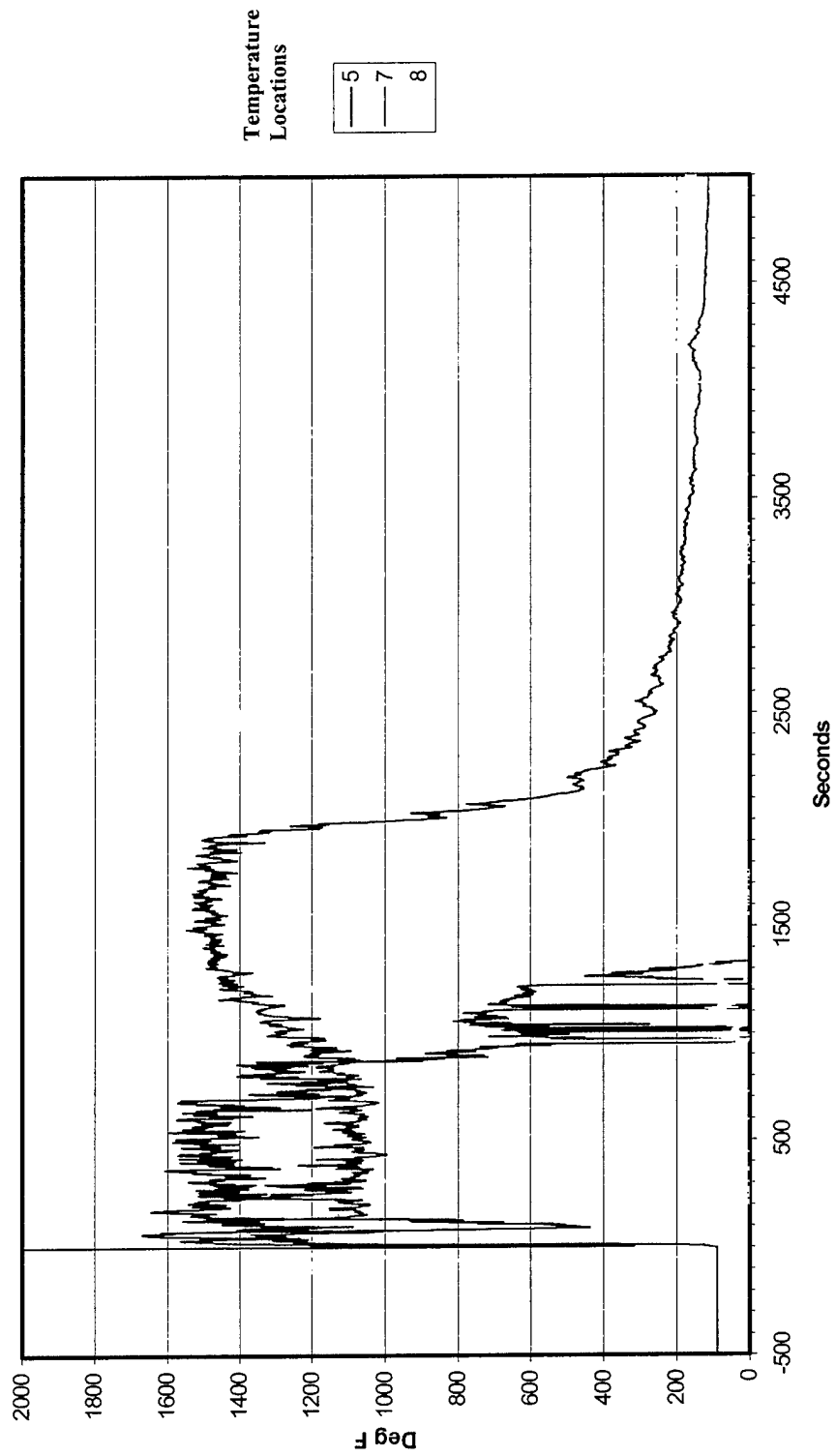


Ceiling Temperatures
Composite Test #3
19 September 2000



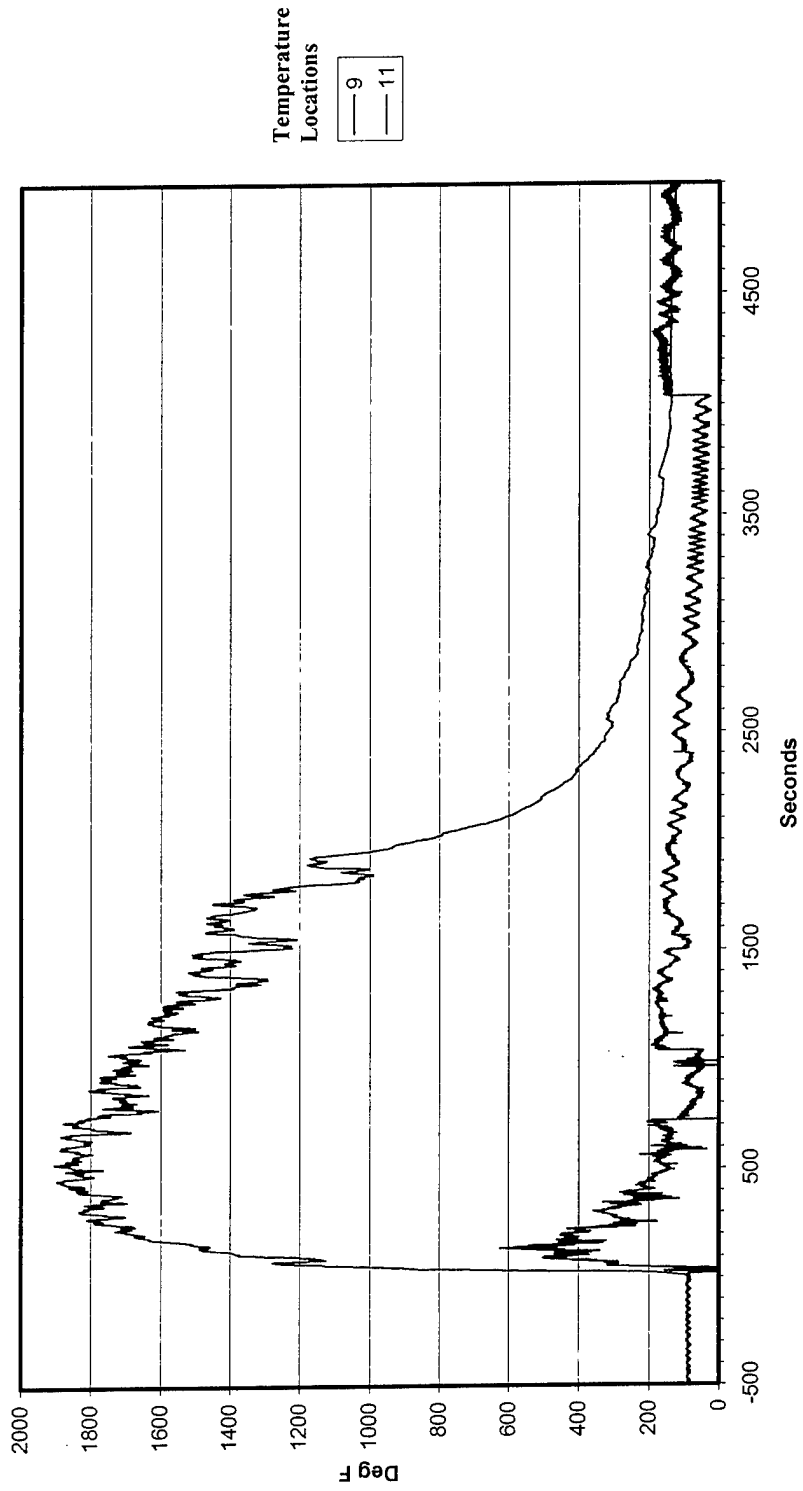
Graph 56

Below Composite Temperatures
Composite Test #3
19 September 2000



Graph 57

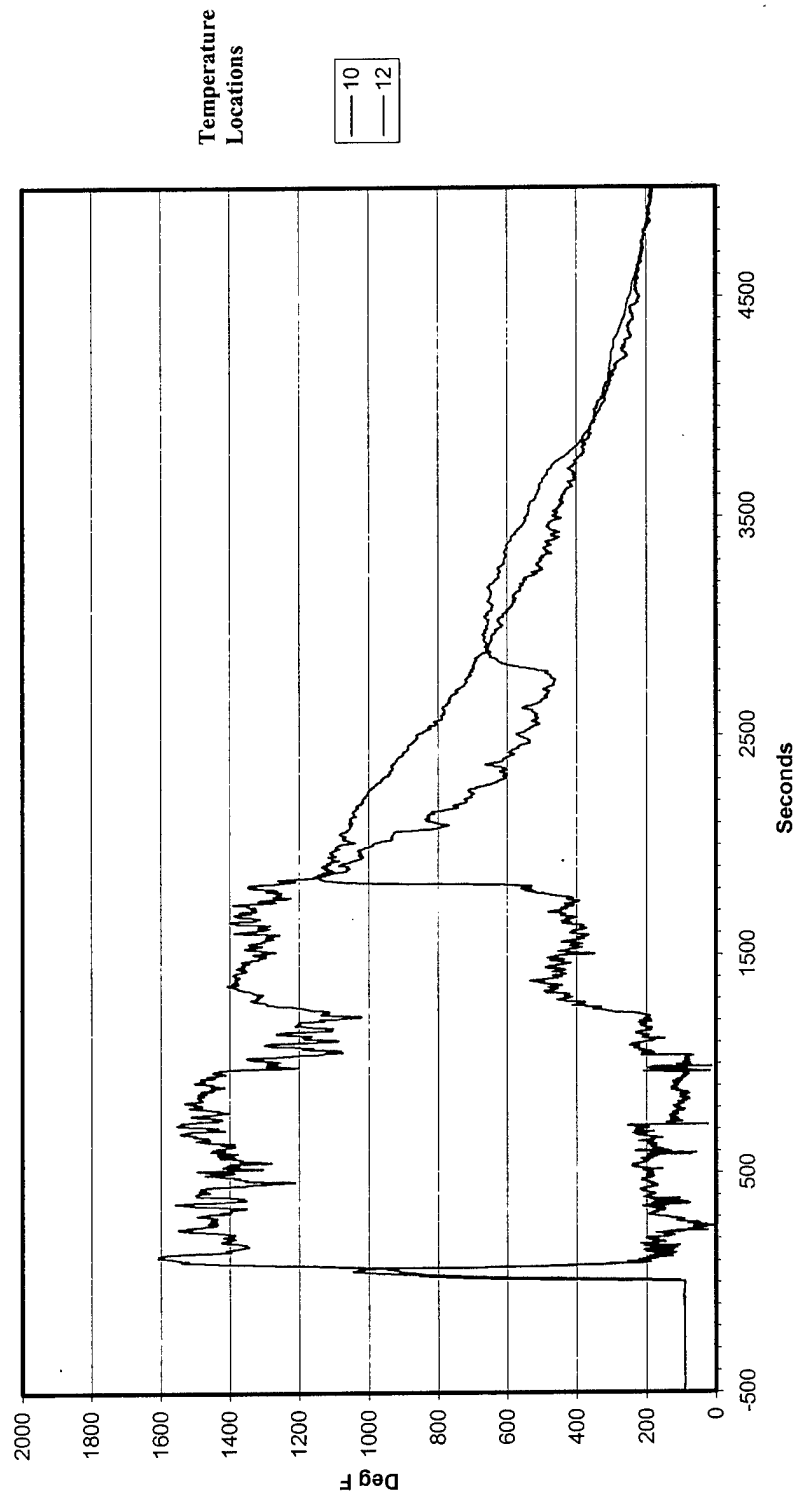
Inside Composite Temperatures
Composite Test #3
19 September 2000



Graph 58

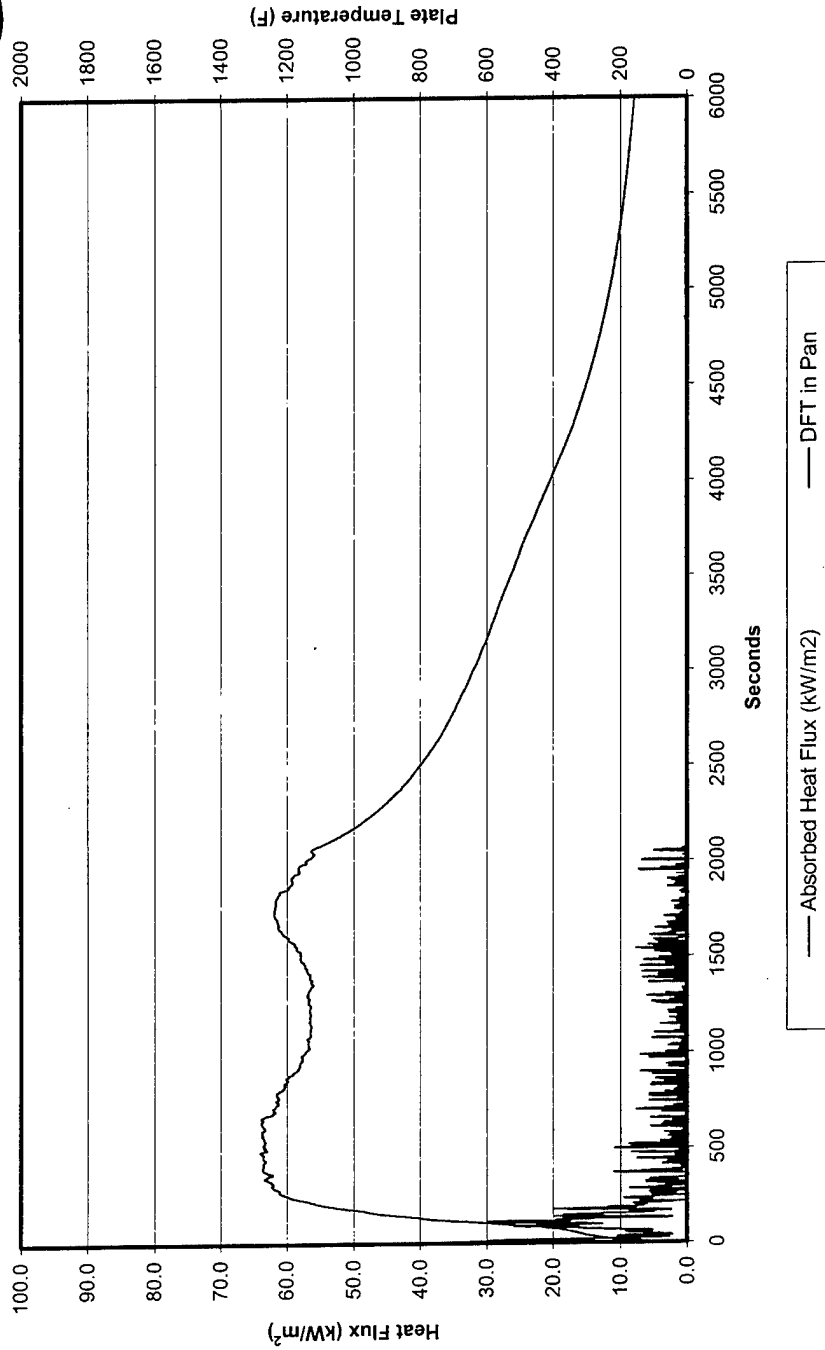


Above Composite Temperatures Composite Test #3 19 September 2000



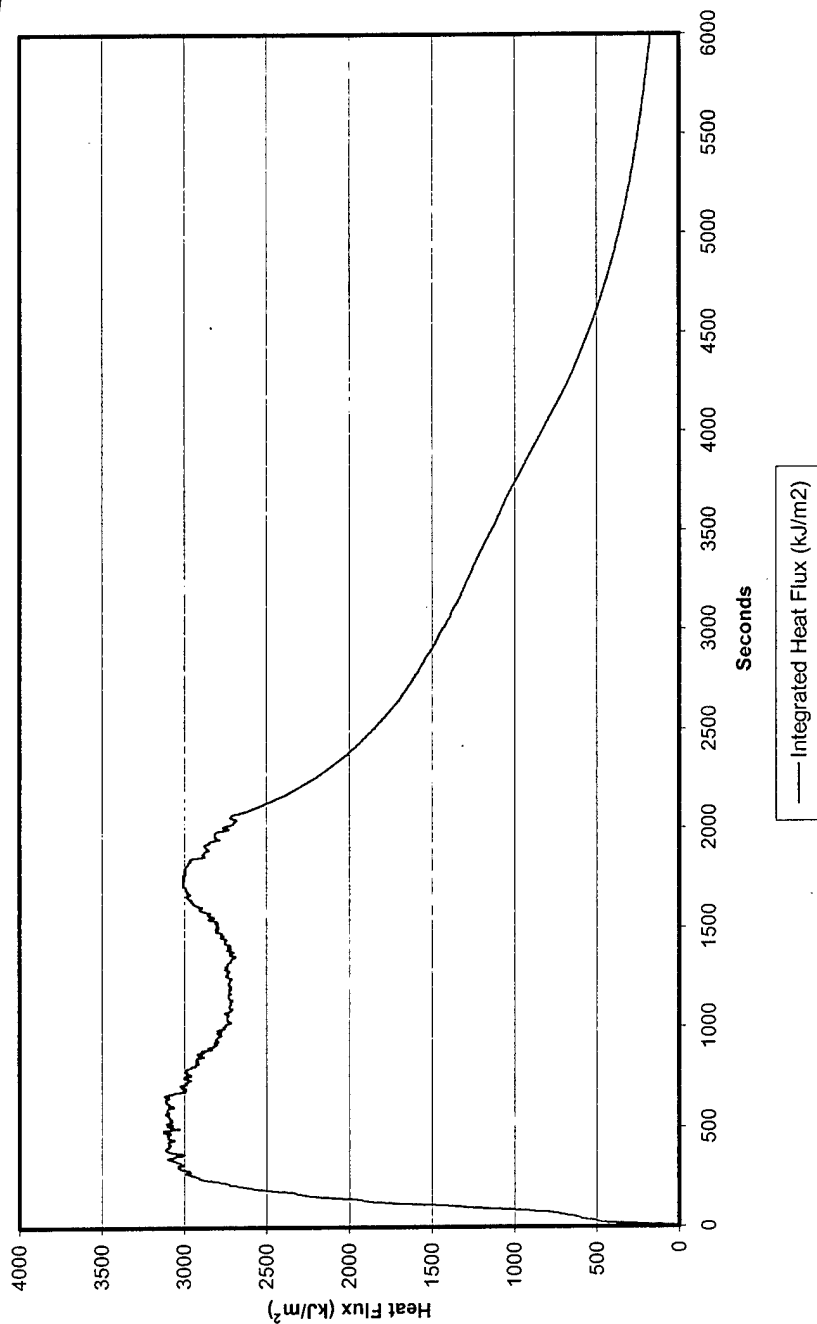
Graph 59

Flux on Composite - DFT in Pan
Composite Test #3
19 September 2000

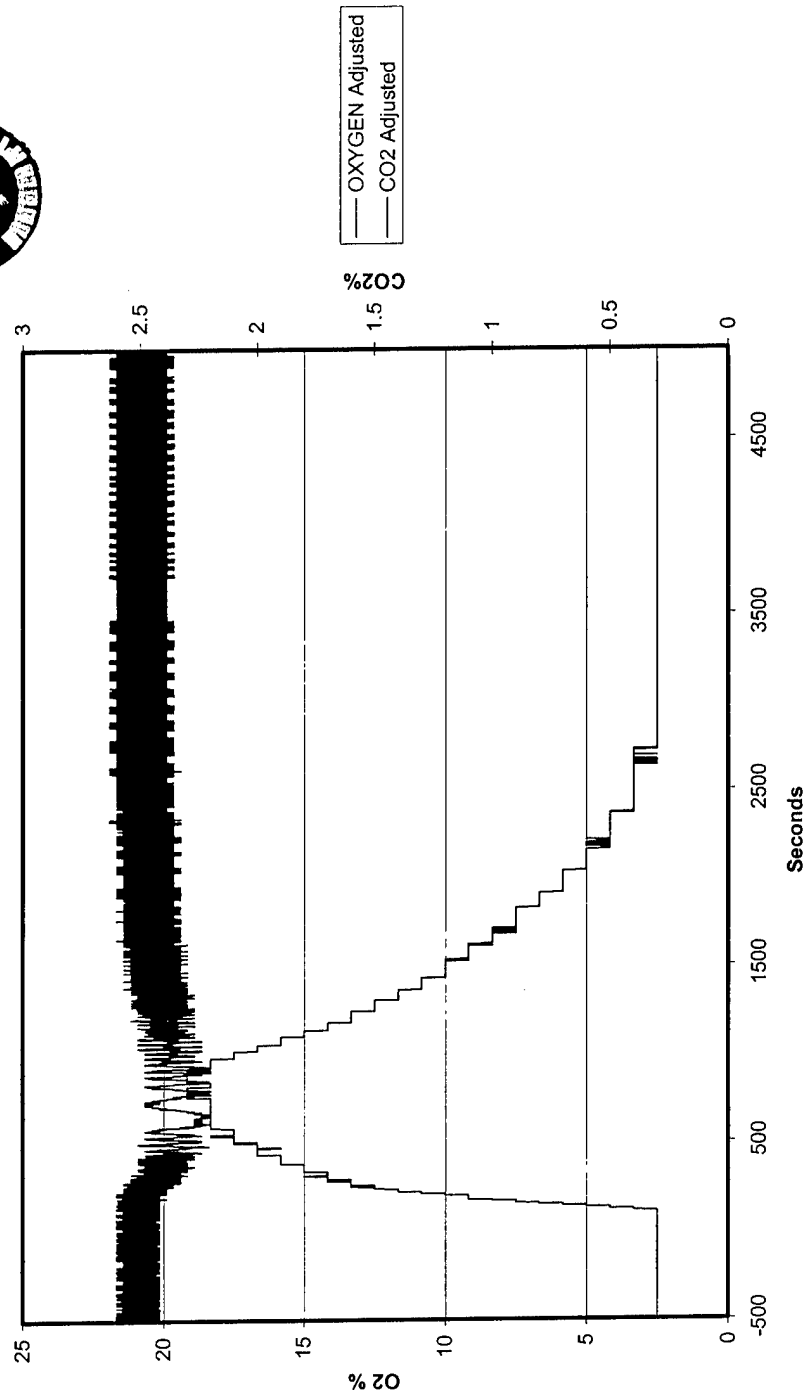


GRAPH 60

Integrated Flux on Composite - DFT in Pan
Composite Test #3
19 September 2000



Graph 61
Oxygen & CO₂
Composite Test #3
19 September 2000



AFIERA/DOBP (STINFO)
2513 KENNEDY CIRCLE
BROOKS AFB TX 78235-5116

OFFICIAL BUSINESS