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EVALUATION OF EMISSIONS
TEST RESULTS FROM
AN MSW INCINERATOR

CSC 110.J811

Prepared for
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Prepared by
Concord Scientific Corporation
2 Tippett Road
Downsview, Ontario, Canada
M3H 2V2

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DO NOT CITE OR QUOTE



ABSTRACT

TO BE PREPARED 200 words maximum

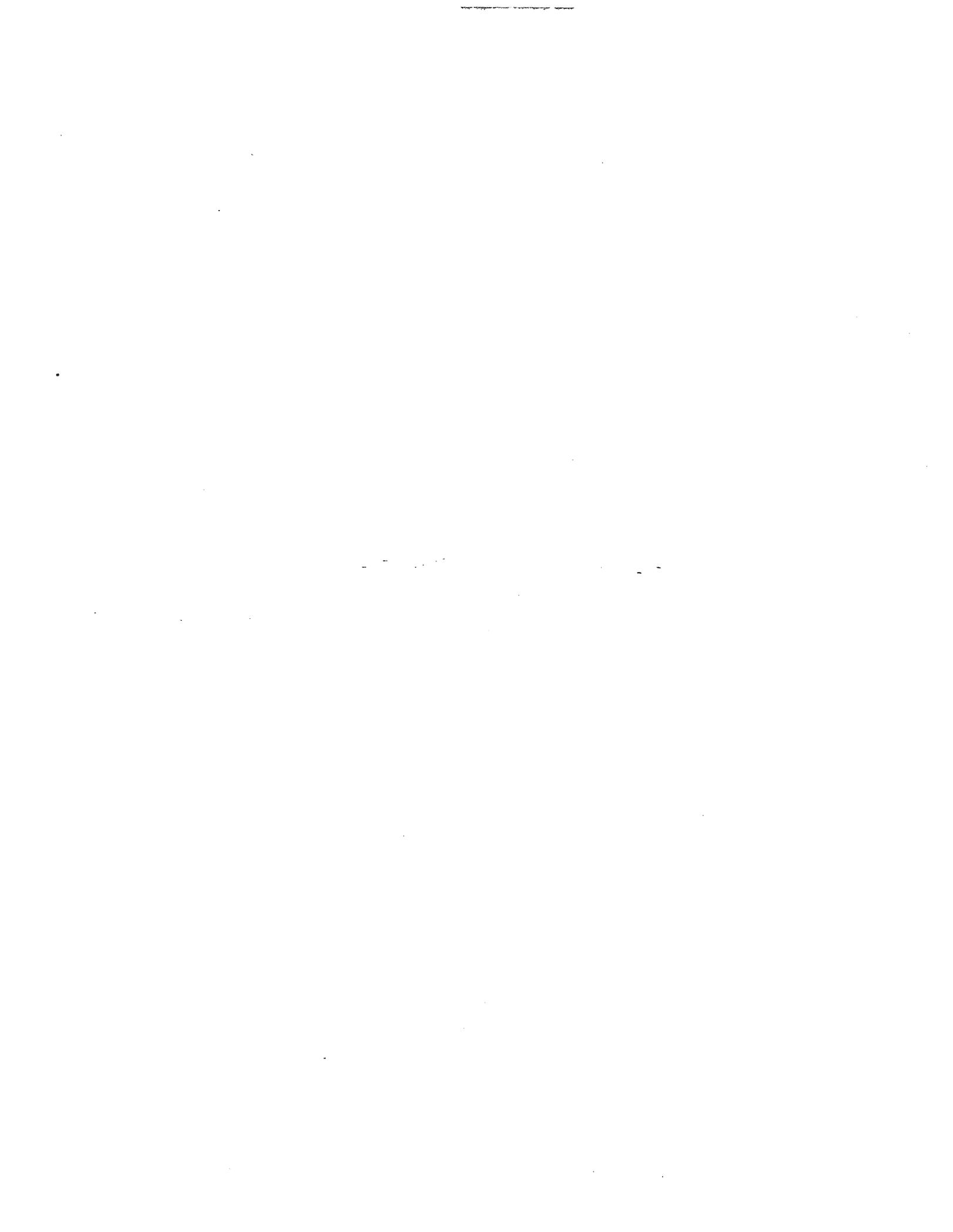


ACKNOWLEDGEMENTS

To follow.

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SUMMARY AND CONCLUSIONS

In October 1983 several government agencies funded the testing of an advanced air pollution control system on a municipal solid waste incinerator in Japan. The objectives of that work were:

- to assess the performance of various elements in the system with respect to the control of air emissions; and,
- to develop emission factors for facilities of this sort.

Testing for the most part was successful and much of the work was reported by Cooper (1985) in their report to the initial funding agency. The test data, however, did show some unexpected results particularly with respect to emissions of trace organics (polychlorinated dibenzo-p-dioxins, PCDDs and polychlorinated dibenzofurans PCDFs). Thus, these data were withheld from publication until the implications of the results could be more thoroughly examined. Such an examination was undertaken in the preparation of this report.

In October 1985 the California Air Resources Board issued a request for proposals to undertake an outside review of the 1983 test results. The objective of the review was to provide a third party scientific review of the sampling, analytical, and quality control aspects of the trace organic sampling portions of the Japanese test program. Since other work had been completed in the period since the tests were finished, the data were to be compared to other information and the appropriateness of the Japanese data for emission factor determination was to be established.

The review included evaluation of test locations and protocols, examination of laboratory procedures and a rework of all data calculations. Data from Swedish and Canadian tests on similar air pollution control systems were examined along with other published emissions and PCDD/PCDF related information. Utilizing much of the information from Cooper

(1985) a new report of the 1983 test program has been produced and this report incorporates comments on QA/QC issues as well as the appropriate data from the literature.

In examining the procedures utilized for the testing program it was determined that:

- sample sites were as good as could be expected considering the physical limitations of the facility's arrangements;
- the sampling protocol was satisfactory with the exception of sample time duration and documentation of procedures particularly sample train preparation and leak checks;
- analytical procedures, including all sample handling issues, were satisfactorily addressed however some legitimate concern can be raised about the procedures utilized for sample splitting of resins and impinger contents; and,
- no reason exists to reject the results of the two trace organic sampling runs on the second sampling day.

There are some reservations about the particle sizing data both in terms of the representative nature of the sample location and also in terms of sample size limitations. This latter data is of more use in determining system performance than in establishing data on the nature of emissions from such facilities.

The report discusses improvements to test procedures for future work but considers these to be positive refinements rather than limiting criticisms of the existing program.

The data generated during the test program can be considered, for the most part, to be representative of the operation of the Japanese facility. This facility, which does not include a provision for steam generation, cannot be considered to be totally representative of proposed North American facilities where EFW will be the norm. Thus the results

are only of limited use in developing emission factors for proposed facilities in California or other parts of North America. This aside, the results do provide valuable information on system performance and illustrate the range of upset condition emissions that may be expected.

The following observations of system performance are useful in developing an understanding of the mechanisms governing PCDD/PCDF emissions from the Japanese facility:

- the nature of the PCDD/PCDF material collected in the samplers is the same for all locations except location D. (Much more PCDF than PCDD was present in the samples at locations A, B and C whereas at D the ratio was different. In addition, tetra homologues dominate at all locations except D for test 2);
- higher particulate matter concentrations were measured at all locations during the second test;
- performance of the fabric filter during all tests was highly variable ranging from 94.5% to 98.8% removal and did not meet the anticipated performance level of 99.9%;
- fine particulate matter made up the majority of the material escaping from the fabric filter. (This material was caught in the back-half of the sampling train);
- the pressure drop across the fabric filter was lower than would have been anticipated;
- uncontrolled emissions (sample location A) were generally at the low end of values reported for incinerator facilities without boiler installations; and,
- performance of various parts of the system in removing PCDDs/PCDFs from the gas stream are similar to those shown in the Canadian tests, with the exception of after the fabric filter.

The data favours the argument that the high PCDD/PCDF emissions from the Japanese incinerator were the result of two contributing factors:

- measurements being taken after upsets in the operating conditions; and,
- poor fabric filter removal efficiencies.

The former situation may have been ruled out with better sampling timing, i.e. testing both during periods of relatively stable operation and over longer periods. The latter situation may also have been compensated for by longer sampling runs.

The data suggests that the Japanese data is not appropriate for determining emission factors from MSW facilities even if they are equipped with similar pollution control systems.

RECOMMENDATIONS

Based upon the Japanese test protocols and sampling results several recommendations can be made.

With respect to future test programs:

- test procedures should follow more closely those defined in the ASME protocol;
- leak checks should be undertaken at the recommended times and all checks must be thoroughly documented;
- only facilities with appropriate ductwork arrangements should be utilized for "in-system" testing purposes;
- stable operating conditions should be a major criteria for test commencement;
- no sample splitting should be undertaken.

In addition to these procedural issues the work has shown the limitations of conventional sampling methods when used to determine both particle size distributions and emissions from fabric filter systems. This suggests that there is a need to:

- undertake detailed testing to determine particle size distributions from well operated filter systems on MSW incinerators using more advanced equipment; and,
- clearly define test protocols for fabric filter outlet testing.

Furthermore, this work should only be undertaken after a thorough review of the work of EPRI and others on the performance of fabric filters on coal-fired electrical power generating stations.

With respect to the use of the Japanese test data:

- it should be released with a clearly worded statement that it is not an appropriate data set for determination of potential emissions from EFW/MSW incinerator facilities;
- the data is valid for the operating conditions during which it was collected but further work would be beneficial particularly for the plant operators.

Further work on the particular facility should include:

- a review of all real time data available for the test period to establish other data trends and complete the limited observations in the report;
- particulate emissions test work to establish fabric filter performance. This could possibly be optimized by reducing the amount of Tesisorb added at the dry venturi. This should also establish emissions related to cleaning cycle history for the system;
- a review of fabric filter bag history and pressure drop across the system to determine if the bags used during the test period were too "green";
- improvement in air distribution in the incinerator by employing the overfire air and testing the impact of this measure on particulate levels; and,
- having optimized both combustion and control efficiency, re-testing for PCDDs/PCDFs to determine a more representative emission level.

LIST OF SYMBOLS AND ABBREVIATIONS

SI Prefixes

Prefix	Symbol	Multiplication Factor	Exponent
mega	M	1 000 000	= 10^6
kilo	k	1 000	= 10^3
hecto	h	100	= 10^2
deca	da	10	= 10^1
unit	-	1	= 10^0
deci	d	0.1	= 10^{-1}
centi	c	0.01	= 10^{-2}
milli	m	0.001	= 10^{-3}
micro	μ	0.000 001	= 10^{-6}
nano	n	0.000 000 001	= 10^{-9}
pico	p	0.000 000 000 001	= 10^{-12}

Units

Symbol	Unit	Comments
Mass/Weight		
g	gram	-
tonne	metric tonne	1 tonne = 1 Mg
lb	pound	1 pound = 453.592 g
gr	grain	7000 grains = 1 pound
Length		
m	metre	-
ft	foot	1 ft = 0.3048 m

LIST OF SYMBOLS AND ABBREVIATIONS (cont'd)

Symbol	Unit	Comments
Volume		
L	litre	-
m ³	cubic metre	1 m ³ = 1000 L
Nm ³	normal cubic metre	at standard conditions 0°C, 101.325 kPa
cm ³	cubic centimetre	
ft ³	cubic foot	1 ft ³ = 0.02832 m ³
SCF	Standard cubic foot	at 29.92" Hg and 68°F
SDCF	Standard dry cubic foot	SCF with moisture removed
ACF	Actual cubic foot	at stack conditions
Time		
s	second	-
m (min)	minute	1 min = 60 s
h (h)	hour	1 h = 3600 s
Temperature		
°C	degree Celsius	
°F	degree Fahrenheit	(1.8 x °C + 32)
Electricity		
V	volt	
Pressure		
bar	bar	-
Pa	Pascal	1 Pa = 10 ⁻⁵ bar
"H ₂ O	inches water	1" H ₂ O = 248.84 Pa
"Hg	inches mercury	13.6 inches H ₂ O
Energy		
J	Joule	
BTU	British Thermal Units	BTU = 1055J

LIST OF SYMBOLS AND ABBREVIATIONS (cont'd)

Acronyms

APC	Air Pollution Control	
ASTM	American Society for Testing and Materials	
NITEP	National Incinerator Testing and Evaluation Program	
PEI	Prince Edward Island	
<i>NITEP</i> QC	Quebec City <i>NITEP Tests on APC System</i>	
U.S. EPA	Environmental Protection Agency	United States of America
EPS	Environmental Protection Service	Environment Canada
ASME	American Society of Mechanical Engineers	
XAD-2	Resin Trap	
GC	Gas Chromatography	Analysis
MS	Mass Spectrometry	Analysis
EC	Electron Capture Detection	Analysis
MID	Multiple Ion Detection	Analysis
BAAQMD	Bay Area Air Quality Management District	
BACT	Best Available Control Technology (California definition, basically equivalent to the U.S. EPA LAER)	
CARB	California Air Resources Board	
CDOHS	California Department of Health Services	
CEM	Continuous Emissions Monitoring	
CWMB	California Waste Management Board	
MOE	Ministry of Environment; Ontario, Canada	

LIST OF SYMBOLS AND ABBREVIATIONS (cont'd)

MSW	Municipal Solid Waste
PM	Particulate Matter
QA	Quality Assurance
QC	Quality Control
SCAQMD	South Coast Air Quality Management District
SWRCB	State Water Resources Control Board
TESI	Teller Environmental Systems, Inc.
WCA	West County Agency of Contra Costa County
WCCSD	West Contra Costa Sanitary District
WSU	Wright State University, Dayton, Ohio

Compounds

PCDD	Polychlorinated - dibenzo-p-dioxins	e.g., TCDD = Tetrachlorinated dibenzo-p-dioxin
PCDF	Polychlorinated dibenzofurans	e.g., TCDF = Tetrachlorinated dibenzofurans
CO	Carbon Monoxide	
CO ₂	Carbon Dioxide	
O ₂	Oxygen	
NO _x	Nitrogen Oxide	
SO ₂	Sulphur Dioxide	
N ₂	Nitrogen	
HCl	Hydrogen Chloride	
TSP	Total Suspended Particulate or Particulate Matter	

LIST OF SYMBOLS AND ABBREVIATIONS (cont'd)

HF	Hydrogen Fluoride
NaOH	Sodium Hydroxide
KMnO ₄	Potassium Permanganate
H ₂ O	Water
H ₂ SO ₄	Sulphur Acid
HNO ₃	Nitric Acid
Na ₂ SO ₄	Sodium Sulphate
HClO ₄	Perchloric Acid

Miscellaneous

psi	pound force per square inch	lbf/in ²
Hi	high	
Lo	low	
ppm	parts per million	
ppmv	parts per million volume	
ppmdv	parts per million dry volume	
°	Degree	Angle or Temperature
±	plus or minus	
<	less than	
>	greater than	
=	equal	
x	Multiply	
HHV	Higher Heating Value	
ID	Induced Draft	Fan
BFW	Boiler Feed Water	
RSD	Relative standard deviation	

DISCLAIMER

The statements and conclusions in this report are those of the contractor and not necessarily those of the California Air Resources Board. The mention of commercial products, their source or their use in connection with material reported herein is not to be construed as either an actual or implied endorsement of such products.



1.0 INTRODUCTION

Since the late 1970s studies have been underway in western Contra Costa County, part of the San Francisco Bay Area, to determine the feasibility and costs associated with utilizing sewage sludge and municipal solid waste (MSW) as fuel for an energy from waste (EFW) plant. As Cooper (1985) reports, the West County Agency of Contra Costa County received funds from the California Waste Management Board to gather test data on MSW incinerator emissions in support of the study. With additional funding from the California Air Resources Board and the Ministry of Environment, Province of Ontario, Canada part of the testing was conducted in October, 1983.

The intent of the testing program was to investigate both criteria and non-criteria emissions from a municipal waste incineration facility equipped with air pollution control equipment similar to that being proposed for California facilities. Testing was carried out on an air pollution control (APC) system consisting of a dry scrubber (quench reactor), dry venturi and fabric filter in series following an MSW incinerator equipped with water quenching to reduce gas exit temperatures. This APC unit was located in Japan and was the first of its type available for testing. The emissions measured at this facility were sulfur dioxide (SO₂) hydrogen chloride (HCl), hydrogen fluoride (HF), particulate matter (PM), metals, and halogenated heterocyclic compounds (polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans PCDDs/PCDFs).

Between August and October of 1984, the results of the testing program were subjected to peer review by the funding agencies and 32 representatives from the industrial, governmental, and academic communities. The majority of the data obtained from the test program was determined to be valid. Following this review, these test results were released in a report authored by Cooper Engineers (Cooper, 1985). Not all the test

data were included in this report. During the course of the peer review, the PCDD/PCDF data were the subject of much discussion, and at the time the main report was issued, there were still several unresolved technical questions relating to the validity of the organic compounds data. Thus, those results were not included in that report.

In October, 1985 the California Air Resources Board issued a request for proposal (RFP) for an outside review of the 1983 PCDD/PCDF test results. This contract was subsequently awarded in March 1986 and the report that follows is the result of the work carried out for that review.

Considerable test work has been undertaken on MSW systems since October 1983. Results of the Japanese test program stimulated interest for investigations in several different directions. Some of these investigations provide additional benchmarks for comparison of the Japanese results and are utilized in the report that follows.

The objective of the work program was, as described in the RFP, "to provide a third-party scientific review of the sampling, analytical and quality control aspects of the PCDD and PCDF portions of the test program". The results of the review were anticipated to determine the degree to which the Japanese data could be used as typical emission factors for proposed facilities in California.

1.1 Scope of Work

To address the sampling, analytical and quality control issues surrounding the PCDD/PCDF data collected in Japan, the Contractor undertook the six tasks outlined in the RFP:

1. Review of Test Protocol
2. Review of Test Performance
3. Review of Analytical Procedure
4. Data Analysis

5. Report Preparation
6. Project Management/Meetings

In conducting this review the contractor utilized their experience in designing QA/QC programs and executing projects such as the National Incinerator Testing and Evaluation Program (NITEP) undertaken for Environment Canada.

1.1.1 Approach

It is important that quality control/assurance be stressed in all areas of sampling programs to ensure that all data are of the highest possible and documented quality. To meet this goal, a rigorous and comprehensive QA/QC program must be implemented from the outset of the study program to ensure that the data reported and analyzed in the study are complete, and that measures of its accuracy and precision are documented.

The development of appropriate QA/QC programs for PCDD/PCDF sampling and analysis protocols (ASME, 1984; Harris et al., 1984; Little, 1985; Concord, 1985; and Palazzolo et al., 1985). The reader is referred to these documents for an in-depth discussion of QA/QC issues surrounding:

- source sampling;
- sample identification;
- sample equipment proofing;
- sample equipment calibration;
- sample containers;
- adsorbents, filters and chemicals;
- sample shipping;
- laboratory procedures; and
- data recording and verification.

For this study the project team reviewed many of these issues with specific emphasis on the procedures used for PCDD/PCDF sampling and

analysis. Where possible information was obtained from the previous report (Cooper, 1985) or from direct discussions with members of the project team. Influences were drawn from the available data when it was not possible to ascertain the exact operations performed nor the sequence in which they were handled. These uncertainties are identified in the report.

The detailed work outline is provided in the following section.

1.1.2 Detailed Task Description

Task 1 - Test Protocol Review

The selection of sample methods and locations is often constrained by physical limitations in the facility. A preliminary review of the Cooper (1985) report shows some non-ideal sampling locations with respect to upstream/ downstream disturbances. Recognizing that physical constraints limit these locations, the review of the sample locations addresses the applicability of the trade-offs made to undertake the work and the changes incorporated to overcome the limitations (i.e., whether more sample points were used when differences in velocity between adjacent points were significant). Judging these changes and their adequacy was on the basis of experience and recommendations in various codes such as those published by the U.S. EPA, by EPS in Canada, by the Ontario Ministry of the Environment and by ASME. These protocols and the testing were be considered both in terms of the ideals and as comparative the results for the testing at various points in the system even if these points were not ideal.

PCDD/PCDF sampling equipment now consists of a modified EPA Method 5 train equipped with an XAD-2 resin cartridge, after the filter and a condenser, and before the impinger train. This arrangement has evolved with time. The Ontario MOE has utilized other procedures (1984) and the

method utilized by Cooper (1985) was compared to both the MOE protocol and the current ASME/EPA protocols.

Process data were reviewed both in terms of the variability found on other days and the furnace wall temperature data that provides an indication of performance. This data was further utilized in the interpretation of the results.

Task 2 - Test Performance Review

Accepted levels of performance for stack sampling are defined in EPA Method 5, the Environmental Protection Service of Environment Canada (EPS) (Canadian code), the Ontario sampling code and the recently issued ASME code. Some of the issues to be considered are outlined previously. One of the major areas that was reviewed was the occurrence of upsets in operating conditions.

The actual stack sampler collected data from the tests were initially spot checked to review calculations and transcription. All data were subsequently utilized in a computer-based processing system to redo all calculations subsequently.

Sample recovery procedures, along with labelling, packaging, storage and ultimate shipment of samples to the laboratory were reviewed. This evaluation involved consideration of the elements of sample custody outlined in the EPA QA manuals and those protocols laid out by ASME.

Task 3 - Analytical Procedure

Receipt of the samples at the laboratory was reviewed to ensure that any sample loss or breakage was noted. Laboratory notebooks were reviewed to test the continuity of the sample handling procedures.

Actual analysis procedures from extraction, to clean-up, to injection and interpretation were reviewed and compared to the procedures presently being utilized for NITEP studies and the ASME analytical protocol.

Issues such as:

- the establishment of the GC retention time windows, and data to back this up,
- components used for calibration standards and response factors,
- the use of internal standards added to the sample prior to extraction, and.
- development of recovery factors, were reviewed.

Most important in any organic analysis evaluation was the determination of the precision and accuracy of the data. One can question the significance of differences between various sampling levels purely on the basis of the range that the analytical data represent. Precision and accuracy were assessed on the basis of recovery factors calculated by the laboratory.

In addition to the contractors staff several knowledgeable chemists were asked to complete a review of the analytical procedures and results.

Task 4 - Data Analyses

At the completion of data analysis, the accuracy and validity of all data sets were identified. The valid data were then utilized in the discussion of the results. This discussion addresses the various results, their inter-relationship with other results in the system, and the similarity between these and other test results.

Task 5 - Report Preparation

As originally conceived, the report was to form an addendum to Cooper (1985). After project initiation it was determined that, as much as possible, this report should stand on its own. For this reason the authors have made use of the Cooper material, in some cases duplicating it directly, while in other cases they have edited the work to fit this study.

Some duplication of the description and the results of Cooper (1985) are thus evident in this report, however this was considered necessary to ensure that the PCDD/PCDF data were not utilized out of context. This also allowed an overall approach to data interpretation to be taken in the report. Consideration of the inter-relationships between operation, furnace emissions, fabric filter performance and stack emissions is key to developing an understanding of the test data.

An important section of the discussion includes the comparison of these test results to those of others. Attempts are made to present the data in a manner that is most useful, both for comparison to other data and for the determination of emission factors.

The report that follows describes the plant, and the testing methods used, reviews the QA/QC aspects of the project, and presents and discusses the data. A bibliography and a list of acronyms are included before the Appendices.

2 THE INCINERATOR FACILITY

2.1 Introduction

The incinerator facility burns locally collected MSW for the purpose of volume reduction. There is no steam or power production. The facility consists of two parallel trains each having the design capacity to burn 165 tons MSW per day. Unit operation is controlled from a central control room. As shown in Figure 2-1, each train consists of a waste receiving area and storage pit, a furnace with a Martin reverse reciprocating grate, and the Teller Environmental Systems Inc., Air Pollution Control (TESI APC) system.

2.2 Detailed Description

2.2.1 Waste Receiving and Storage Area

Trucks arrive at the plant and back-up to the waste receiving doors. Unless trucks are unloading, the doors are kept closed for odour control. Waste from the trucks falls into a storage pit, and a clamshell crane transfers the waste into the furnace feed chute.

To aid in odour control, combustion air is drawn from the storage area. Water drainage from the storage area is collected, treated, and used as incinerator flue gas quench water.

2.2.2 Incinerator and Incinerator Quench Reactor

Waste in the furnace feed chute flows by gravity into the ram feed system which pushes the waste onto the grates in the furnace cavity. The waste is burned as it is moved by the Martin reverse reciprocating grates down through the length of the inclined furnace. The ash falls from the end of the grate into a quench tank where it is removed to the ash pit by a hydraulic ram.

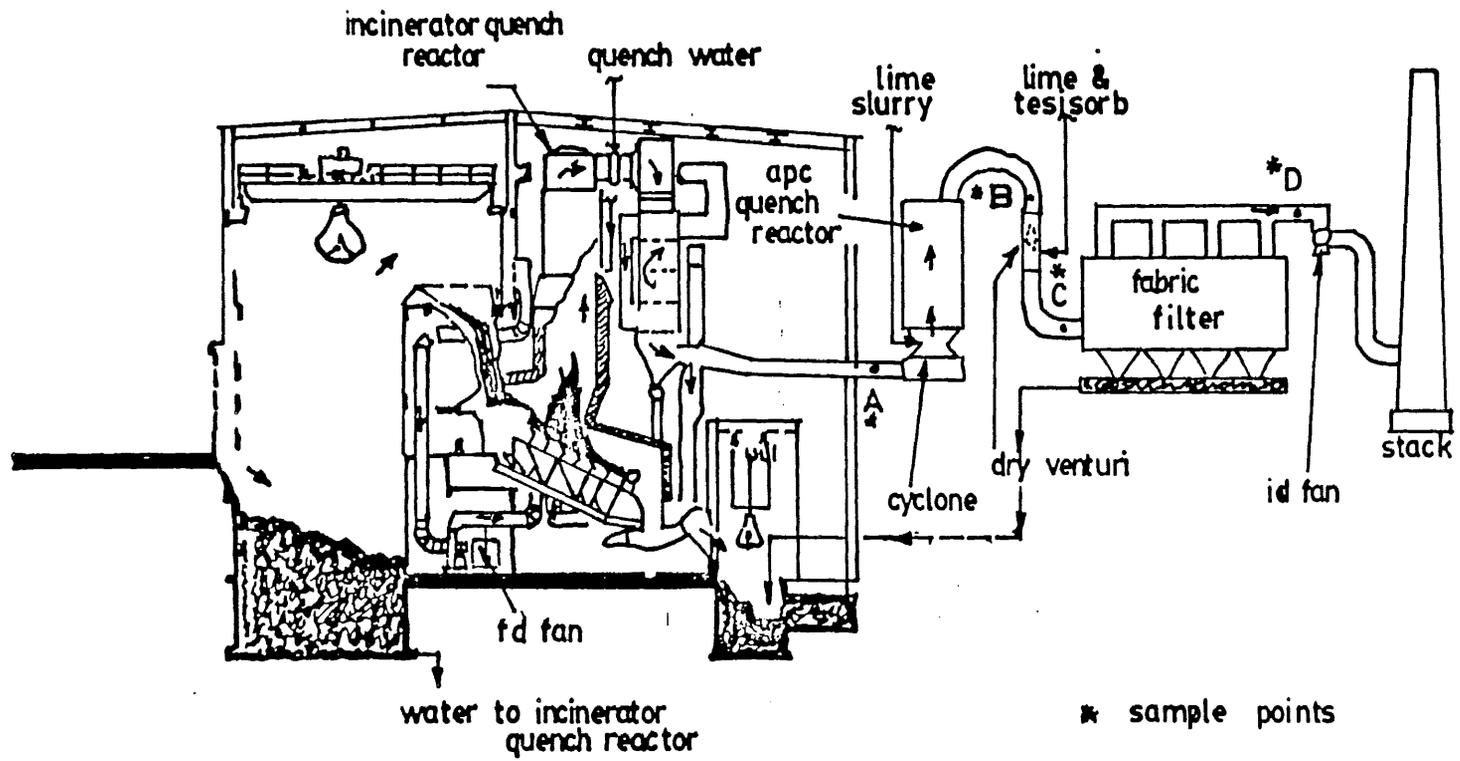


FIGURE 2-1 PLANT SCHEMATIC

The furnace is lined with uncooled refractory and is supplied with underfire air at a constant rate by the forced draft fan. The fan draws air from the waste receiving area and storage pit, through the air preheater, and discharges it, through manually operated dampers into the furnace. No overfire air was used during the test period. The amount of excess air can vary widely, but it is common to have over 100% excess air for this incinerator design.

Figure 2-2 shows the location of the thermocouple which is used for incinerator temperature control. The control loop adjusts the speed of the ram feed system to maintain approximately 1470°F at the thermocouple. This temperature signal also provides for feed forward control of the incinerator quench water spray and lime slurry feed in the APC quench reactor. Hot flue gas exits the furnace at approximately 1650°F and is contacted by quench water sprayed through nozzles in the incinerator quench reactor. During quenching the gas is cooled to approximately 840°F. Average flue gas residence time in the furnace up to the water spray level in the incinerator quench reactor is 2.5 seconds. After quenching the gas passes through the air preheater which heats the incoming combustion air from ambient to 390°F, while cooling the flue gas to 680°F. The flue gas then enters the APC system.

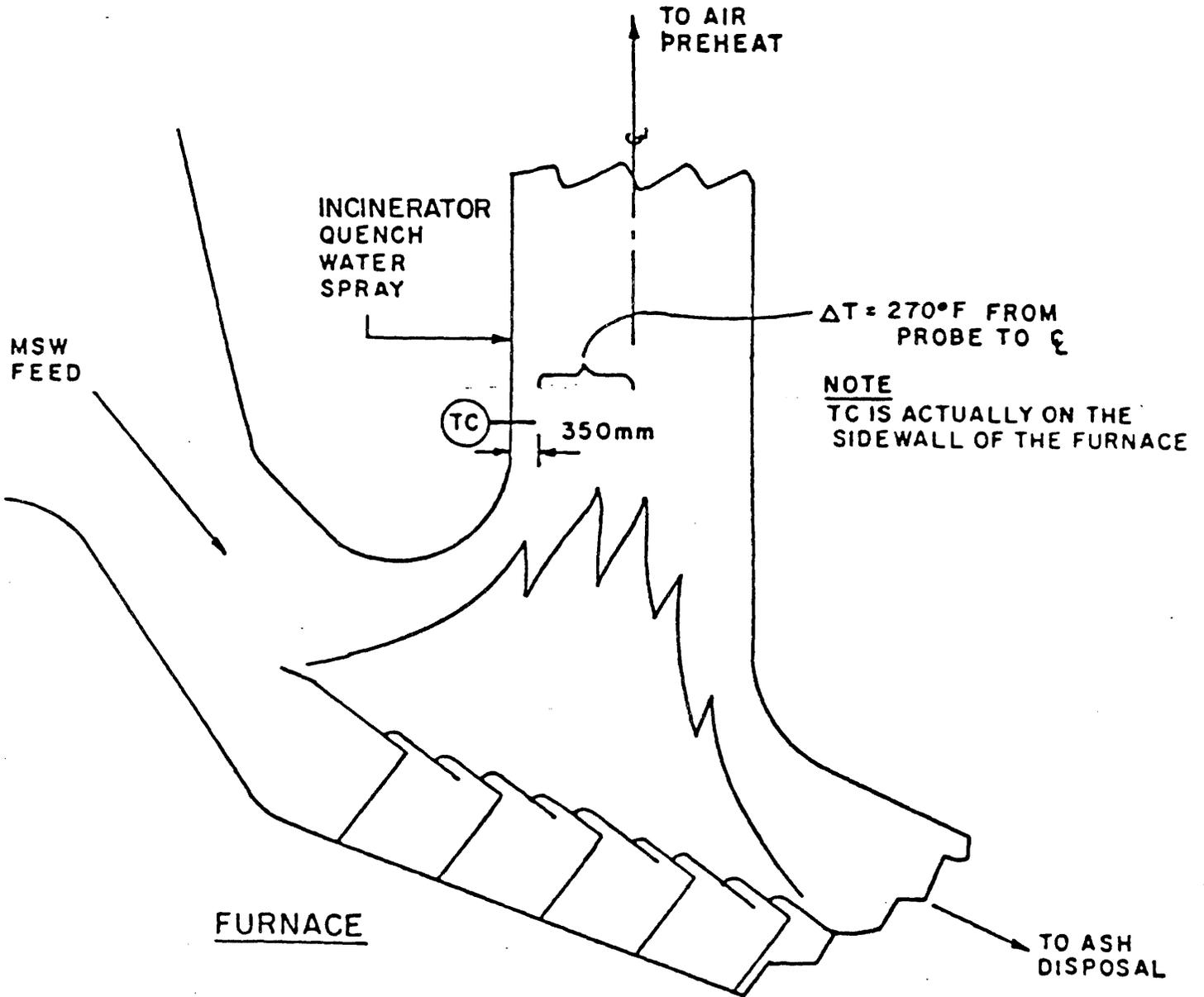
2.2.3 Air Pollution Control System

The major components of the APC system are the APC quench reactor, the dry venturi, and the fabric filter. The design provides for a certain degree of flexibility such that temporarily high levels of SO₂, HCl, and particulate, caused by incinerator excursions, can still be removed at relatively high efficiencies.

As shown in Figure 2-1, flue gas enters a cyclone separator at the base of the quench reactor where larger particles are removed. The flue gas is then passed upwards through the APC quench reactor where a two-fluid nozzle injects and atomizes the lime slurry upward with the flow of flue gas.

FIGURE 2-2

Furnace Thermocouple Location



The TESI upflow quench reactor was designed to ensure that a dry bottom is maintained and that the residence time of the spray droplets is increased. The two-fluid nozzle is a Panasonic atomizer designed to allow replacement without incinerator shutdown.

The lime slurry is very dilute (1.5-2.0% calcium hydroxide - Ca(OH)_2) and is prepared on-site from hydrated lime. No lime slaking is done at the facility. The slurry injection rate is controlled to provide an approximately 180°F temperature drop across the APC quench reactor, provided the inlet temperature is sufficiently high. During downward excursions in flue gas temperature, the slurry injection rate is reduced.

The flue gas leaves the top of the APC quench reactor at approximately 500°F and turns downward towards the dry venturi.

According to TESI, the primary purpose of the dry venturi is to aid in the collection of submicron particles by inertial impaction onto the larger (target) particles introduced in the dry venturi. The inert target particles (Tesisorb) are injected, with air, at a constant rate countercurrent to the flue gas flow. Dry hydrated lime is injected along with the Tesisorb to provide for further reduction of SO_2 and HCl levels. The lime and Tesisorb mixture, when collected on the fabric filter, not only provides sites for further reaction with SO_2 and HCl, but also improves fabric filter performance by improving the quality of the filter cake. Japanese Tesisorb was used as a filter aid on the fabric filter to keep the pressure drop across the filter low even with the high particle and lime loadings.

The injection of air in the dry venturi significantly increases the total flue gas volume and lowers its temperature to approximately 440°F before the gas enters the fabric filter.

The fabric filter consists of 8 cells, 96 bags per cell, complete with reverse air fans, hopper heaters, and a closed screw conveyor for fly ash removal. The filter bags are fiberglass with silicon-graphite/TFE coating, 8 inches in diameter by 20 feet long. The reverse air cleaning cycle is repeated every 2-3 hours using clean flue gas and no shaking. The gross actual air-to-cloth ratio is approximately $1.9 \text{ ft}^3/\text{ft}^2 \text{ min.}$ based on a maximum gas flow of 60,000 ACFM at 450°F.

The induced draft fan draws the clean flue gas from the fabric filter and discharges it to the 193 foot concrete stack.

The facility is equipped with a Fuji Electric continuous emissions monitoring system. Analyzers include a paramagnetic oxygen monitor, a dual cell infrared SO_2/NO_2 monitor (Fuji Electric Type ZRL AD241-6D24), and a wet electrode type HCl monitor. The stack outlet is also equipped with a TV monitor for observation of visible emissions.

2.3 Plant Operation During Test Period

During all periods of testing the plant personnel operated the incinerator as they normally did. The overfire air was shut-off since the operators were attempting to obtain low NO_x values with soft combustion development in the furnace. Lime feed to both the APC quench reactor and the dry venturi was manually set at a level corresponding to the design inlet HCl concentration. As a result, lime feed was excessive during the entire test period. Stoichiometric ratios in the APC quench reactor and the dry venturi ranged from 1.7 to 3.5 and from 4.7 to 6.4 respectively, with the overall stoichiometric ratio ranging from approximately 6 to 10. Stoichiometric ratio is the molar ratio of available reagent over that required to neutralize the inlet HCl and SO_2 .

A visible plume was observed twice during the test period. Both times this occurred were before sampling had started and the condition was related to an upset condition in the incinerator and the by-passing of the APC system. The visible plume lasted for a few minutes each time.

The waste being incinerated appeared to be made up largely of tree trimmings, paper products, and plastic products. A visual examination of the incinerator ash indicated that almost all non-combustibles had been removed from the incoming waste. Interviews with plant personnel revealed that the city has an extensive recycling program. This program includes plastics recycling. The waste appeared to be wet, a condition demonstrated by the water draining out of the waste in the storage area. This water was mixed with other water and injected as incinerator quench water.

It should be noted that during normal operation the furnace temperature can change rapidly. On several occasions during the testing, the furnace temperature dropped dramatically.

2.3.1 Process Data

Tables 2.3-1 and 2.3-2 show the process data for test days 2 and 3 when the PCDD/PCDF testing took place. These data are based mainly upon hourly readings taken from the plant instrumentation during testing. The MSW feed figures represent one or more discrete crane loads fed during the hour and as such are not hourly averages. However, taken together, the MSW feed figures yield an accurate figure for daily MSW feed. Table 2.3-3 shows the calculated MSW feed rates for each test run. The average MSW feed rate during PCDD/PCDF testing was 6.21 tons per hour.

Hourly furnace sidewall temperatures from Tables 2.3-1 and 2.3-2 are plotted versus time in Figure 2.3-1. Figures 2.3-2 show calculated furnace residence times versus time for test days 2 and 3 respectively. Figures 2.3-3 and 2.3-4, supplied by Josef Martin GmbH, are detailed drawings including the furnace dimensions upon which the residence time calculations are based. τ_{OFA} on the graphs represents the average time it takes for a unit volume of gas to pass from its point of entry to the level of the overfire air nozzles. The furnace volume for τ_{OFA} is the sum of zones A, B, and C. τ_{TOT} represents the average time

TABLE 2.3-1

Process Data-Day 2, 10/14/83

Time	MSW Feed (tons/hr)	Furnace Sidewall Temp. (°F)	Incinerator Quench Water Spray (GPM)	APC QUENCH REACTOR			LIME SLURRY FLOW ⁽³⁾ (tons/hr)	DRY VENTURI		FABRIC FILTER		
				Temp. (°F) ⁽²⁾ In	Out	ΔT		Tesisorb (lb/hr)	Lime ⁽¹⁾ (lb/hr)	Press., (in H ₂ O) In	Out	ΔP
1900	6.08	1472	32	680	500	180		106	86	6.3	12.6	6.3
2000	9.24	1472	32	680	500	180	1.54	106	86	6.3	14.1	7.8
2100	3.37	1454	32	680	500	180		106	86	6.7	12.6	5.9
2200	8.47	1148	5	662	500	162	0.99	106	86	3.9	10.2	6.3
2300	5.70	1472	33	680	500	180		106	86	6.3	11.8	5.5
0000	6.06	1472	32	680	500	180		106	86	6.7	11.8	5.1
0100	8.37	1490	33	680	500	180		106	86	6.3	14.2	7.9
0200	6.07	1472	30	680	500	180	1.54	106	86	6.3	13.0	6.7
0300	2.34	1121	0	662	500	162		106	86	4.7	9.4	4.7
0400	6.70	950	7	590	500	90	1.49	106	86	5.9	11.0	5.1
0500	5.00	1508	7	680	500	180		106	86	5.5	10.2	4.7
0600	4.58	1328		680	500	180	1.10	106	86	5.5	10.6	5.1
0700												
0800												

- (1) As 100% Ca(OH)₂
(2) Inlet Pressure (in. H₂O) -2.5 @ 2300 hrs. and 0400 hrs.
(3) % Ca(OH)₂ in lime slurry 1.6% @ 2200 hrs.
(4) Fabric Filter Temperatures @ 2300 hrs. In 441°F; Out, 410°F; @ 0400 hrs. In, 439°F Out, 391°F.

TABLE 2.3-2

Process Data Day 3, 10/15/83

Time	MSW Feed (tons/hr)	Furnace Sidewall Temp. (°F)	Incinerator Quench Water Spray (GPM)	APC QUENCH REACTOR			LIME SLURRY FLOW ⁽³⁾ (tons/hr)	DRY VENTURI		FABRIC FILTER		
				In	Out	ΔT		Tesisorb (lb/hr)	Lime ⁽¹⁾ (lb/hr)	In	Out	ΔP
1900	7.91	1571		680	500	180	1.38	106	86	5.9	12.6	6.7
2000	4.60	1571		680	500	180	1.82	106	86	7.9	16.1	8.2
2100	7.66	1499		680	500	180	1.65	106	86	7.1	13.8	6.7
2200	4.69	1589	30	680	500	180	1.76	106	86	7.5	16.9	9.4
2300	9.20	1544	30	680	500	180		106	86	7.5	15.7	8.2
0000	8.27	1562	30	680	500	180	1.71	106	86	9.0	15.7	6.7
0100	7.27	1499	26	680	500	180		106	86	7.9	15.7	7.8
0200	2.71	1625	26	680	500	180	1.82	55	86	9.0	16.5	7.5
0300	6.94	1553	21	680	500	180		55	86	9.0	17.3	8.3
0400	7.16	1607	32	680	500	180	1.87	55	86	8.7	16.5	7.8
0500	5.43	1607		671	500	171		55	86	9.0	16.5	7.5
0600	4.42	1580		680	500	180	1.76	55	86	9.2	15.7	6.5
0700	4.07	1553	28	680	500	180		55	86	8.8	15.7	6.9
0800	7.63	1454		680	500	180		55	86	8.8	15.8	7.5

- (1) As 100% Ca(OH)₂
(2) Inlet pressure not recorded.
(3) % Ca(OH)₂ in lime slurry - 1.6% @ 2200 hrs; 1.5% @ 0400 hrs.
(4) Fabric Filter Temperatures Inlet 450°F @ 2400 hrs., 0400 hrs., and 0700 hrs.
Outlet 410°F from 2100 hrs. to 0400 hrs.

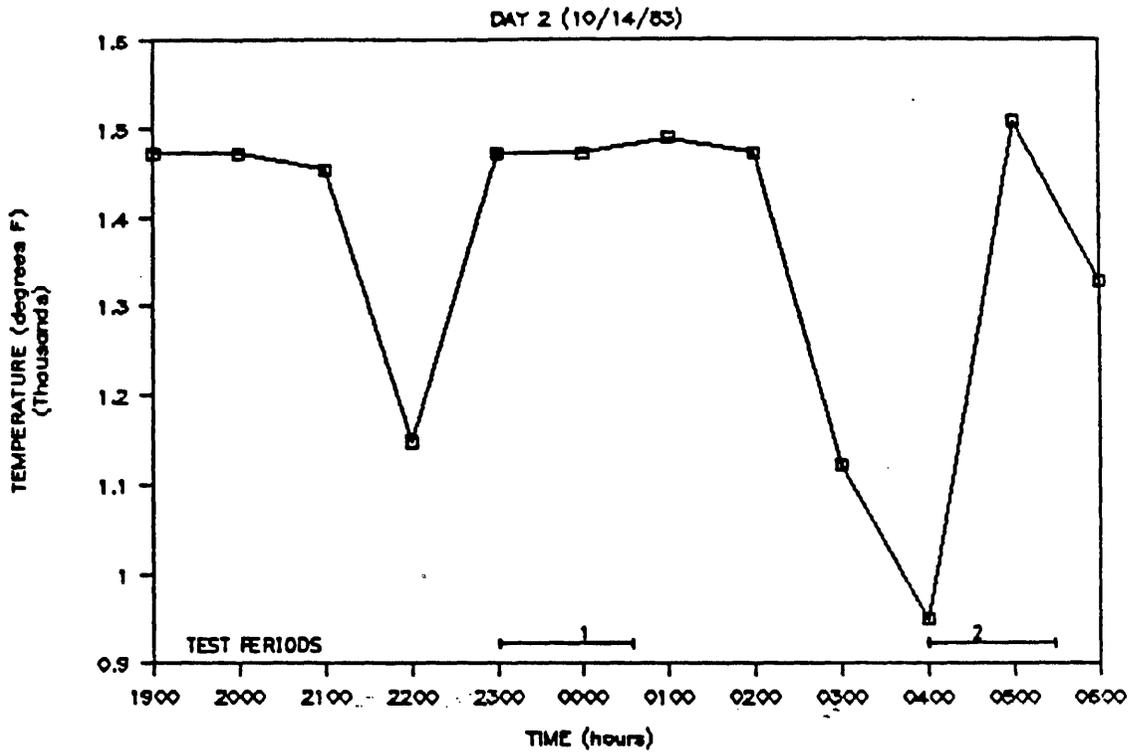
TABLE 2.3-3

MSW Feed Rates for Each Test Run

<u>Run</u> ⁽¹⁾	<u>Run Time</u>	<u>Time-Weighted MSW Feed Rate</u> <u>Tons Per Hour</u>
2A1	2300-0040	5.84
2A2	0350-0455	6.03
2B1	2301-0013	5.77
2B2	0357-0509	6.31
3B1M	0036-0106	8.07
3B2M	0352-0437	7.12
3B3M	0725-0755	4.07
2C1	2258-0041	5.90
2C2	0402-0526	6.17
3C1M	0036-0106	8.07
3C2M	0352-0437	7.12
3C3M	0722-0752	4.08
2D1	2301-0031	5.82
2D2	0353-0518	5.99
3D1M	2058-0458	<u>6.74</u>
Time-Weighted Average During PCDD/PCDF Testing		6.21

(1) Test Number 2A1 = day 2, test point A, test 1
M = Multiclone

FIGURE 2.3-1 FURNACE SIDEWALL TEMPERATURE VS TIME



FURNACE SIDEWALL TEMPERATURE VS TIME

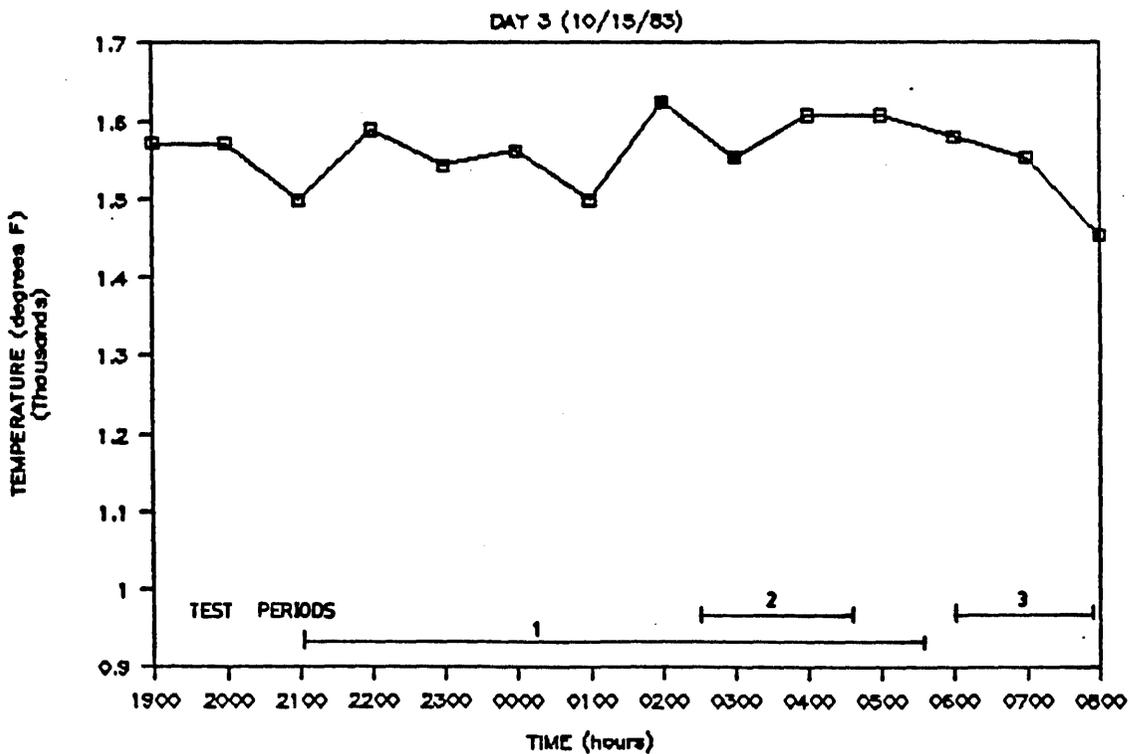
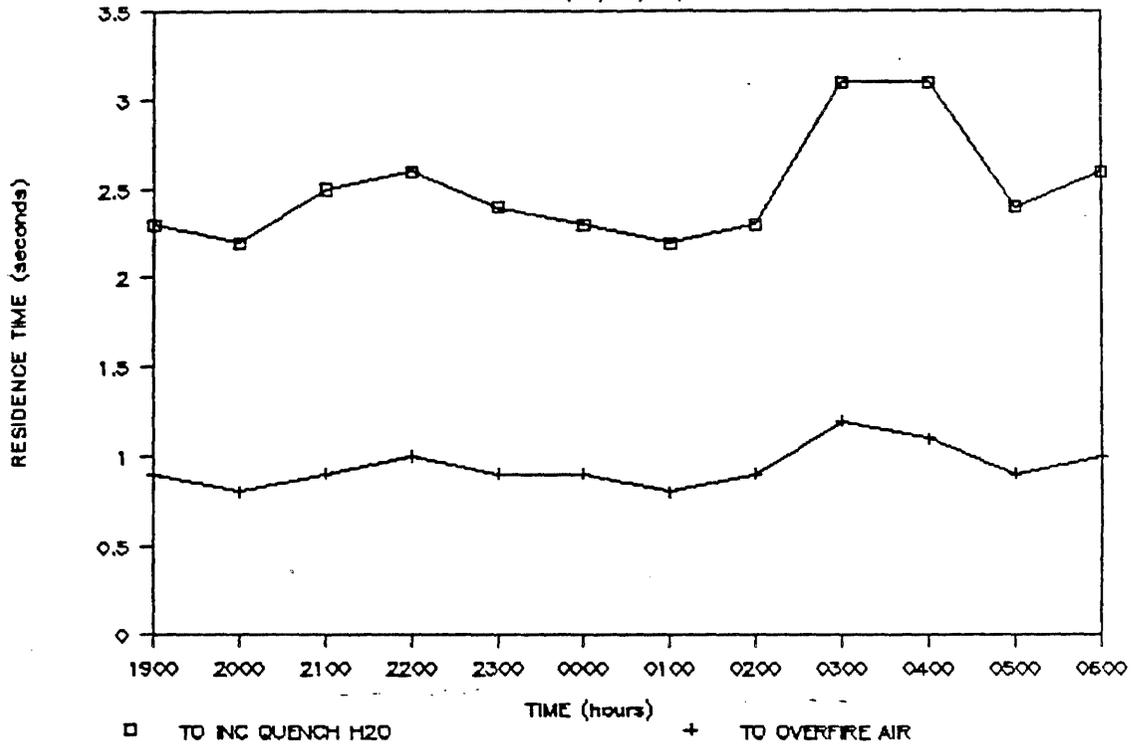


FIGURE 2.3-2 FURNACE RESIDENCE TIME VS TIME

DAY 2 (10/14/83)



FURNACE RESIDENCE TIME VS TIME

DAY 3 (10/15/83)

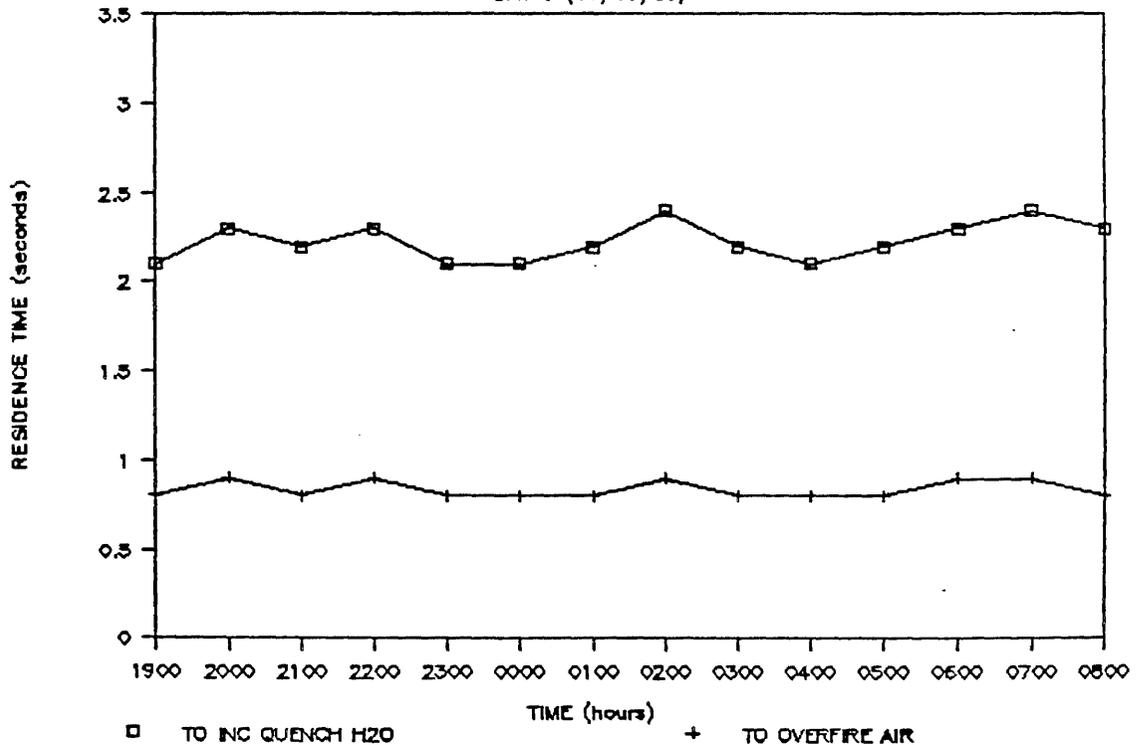


FIGURE 2.3-3

Furnace Dimensions - Side View

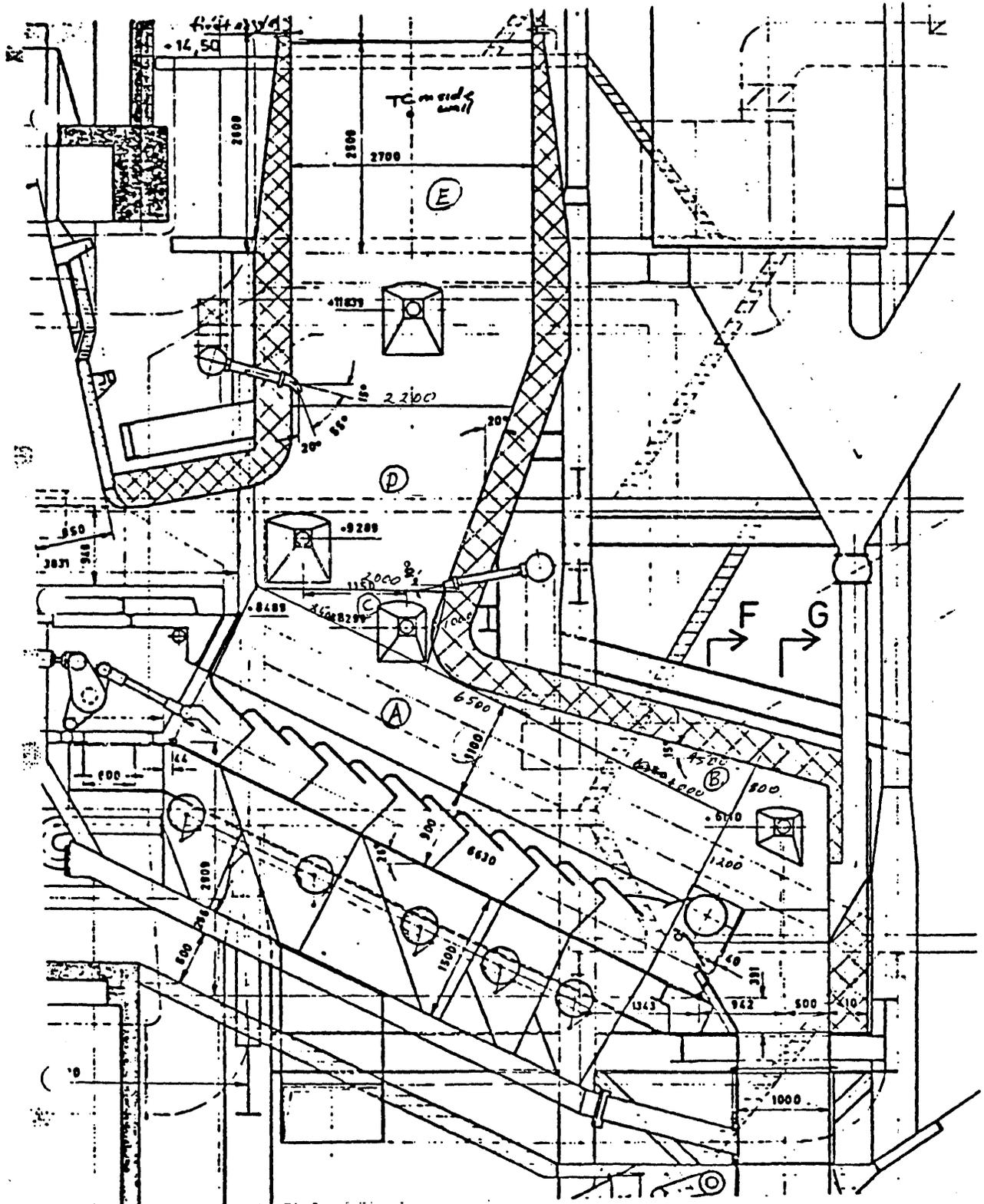
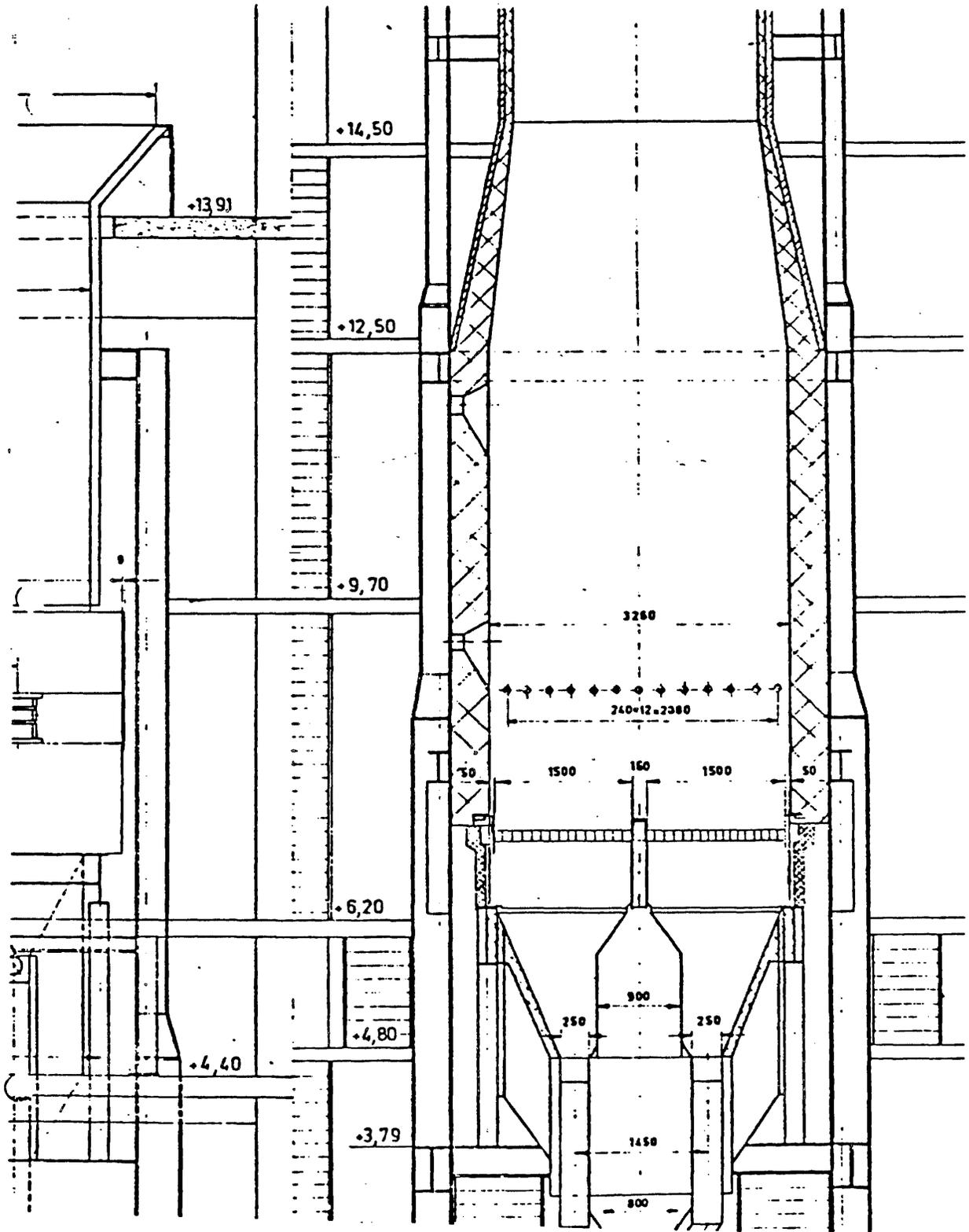


FIGURE 2.3-4

Furnace Dimensions - End View



for the unit volume of gas to pass from the point of entry to the level of the first incinerator quench water spray nozzles. The furnace volume for τ_{TOT} is the sum of all zones A through E. These values are as presented in Cooper (1985).

The calculation of furnace residence times based on hourly process data required the generation of hourly flue gas data. Since hourly MSW feed rate data were available, an equation was derived to correlate flue gas flow with MSW feed rate. This was done in the following manner:

- Since furnace air dampers are manually controlled, it was assumed that combustion air flow is roughly constant. Therefore, nitrogen (N_2) in the flue gas at the furnace would be constant.
- The average N_2 flow rate was calculated from available flow data at points A and B (Table 5.1-1) as $N_2 = \text{total flow} - O_2 - CO_2$. The result is SCFM $N_2 = 10,930$, neglecting CO.
- O_2 in flue gas was calculated as $O_{2,Air} + O_{2,Fuel} - O_{2,Combustion}$. 18% carbon and 2.5% hydrogen were assumed in the wet MSW to calculate $O_{2,Combustion}$. The result is SCFM $O_2 = 2905 + (209.5 \times \text{MSW tons/hr.})$.
- CO_2 in flue gas was calculated from $CO_{2,Combustion}$. Given 18% carbon, SCFM $CO_2 = 190 \times \text{MSW tons/hr.}$
- H_2O in flue gas was calculated as $H_{2O,Fuel} + H_{2O,Air} + H_{2O,combustion}$. 40% moisture was assumed for the MSW while 0.013 lb. H_2O /lb. dry air was assumed for the combustion air. The MSW moisture content is a critical assumption since a moisture balance was impossible (flue gas before the incinerator quench spray was not sampled and the moisture and hydrogen content of the MSW during the testing was not available). The result is SCFM $H_2O = 288 + (439.2 \times \text{MSW tons/hr.})$.

- The terms are summed to yield:
Total SCFM = 14,123 + (420 x MSW tons/hr.).
- The ACFM was calculated given hourly furnace sidewall temperatures. The temperature difference between the sidewall and the furnace centerline was estimated at 270°F. Therefore a mean furnace temperature equal to the sidewall temperature plus 135°F was used.

Table 2.3-4 compares measured flow data at point A to calculated flows using the above method.

Given the hourly flow data, residence time was calculated as actual flow rate divided into furnace volume minus the average fuel volume on the grate. Residence time calculations were included in Cooper (1985). The importance of the residence time and temperature graphs with respect to the test results is discussed in Chapter 6.

Mass balances for sampling runs 2-1 and 2-2 (on October 14, 1983) are shown in Figures 2.3-5 and 2.3-6.

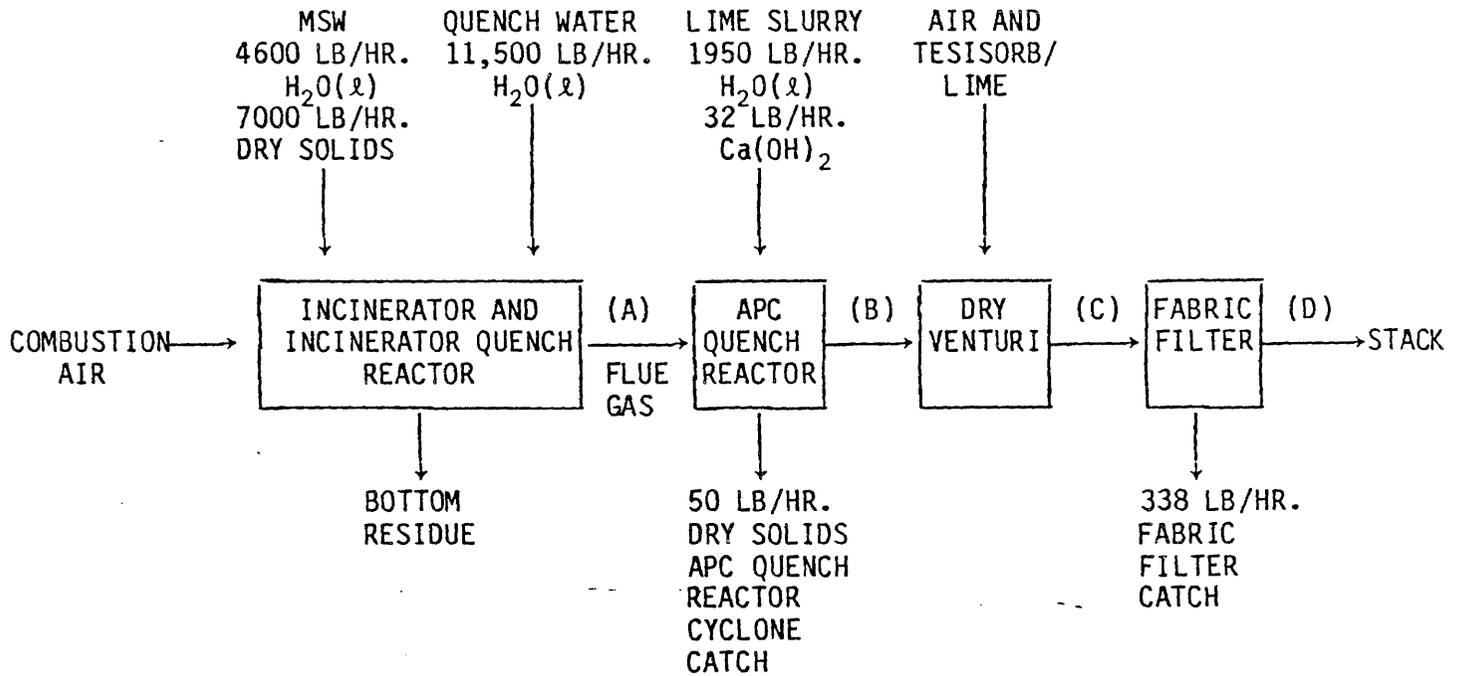
TABLE 2.3-4

**Measured vs Calculated Flue Gas Flows
(from Cooper 1985)**

Run	Fuel Feed (TPH)		Oxygen (SCFM)	Carbon Dioxide (SCFM)	Nitrogen (SCFM)	Total Flow (SDCFM)	Water (SCFM)	Total Flow (SCFM)
2A1	5.84	Measured	1414	1157	10286	12857	6843	19700
		Calculated	1681	1110	10930	13721	6370	20091
2A2	6.03	Measured	1526	1050	9931	12507	4816	17323
		Calculated	1642	1146	10930	13718	6453	20171

FIGURE 2.3-5

Mass Balance - Sampling Run 2-1



COMPONENT	COMB. AIR	A	B	DRY LIME & TESISORB	C	D
N ₂ , mol/hr.	1,627	1,627	1,683	651	2,334	2,334
O ₂ , mol/hr.	432	224	239	173	412	412
CO ₂ , mol/hr.	-	183	183		183	183
H ₂ O(g), mol/hr.	43	1,081	1,189	15	1,204	1,204
SDCFM(1)	13,000	13,000	13,000		NA	17,700
SCFM(1)	13,300	20,000	21,000		25,400	25,900
ACFM(1)	13,300	43,000	38,000		43,900	43,300
H ₂ O(l), lb/hr.						
Lime, lb/hr.				86		
Tesisorb, lb/hr.				106		
Temperature, °F	320-644(2)	680	500		440	410
Particulate, lb/hr (Front Half)		137	145		338 ⁽³⁾	0.9
HCl, lb/hr.		18	<1		<1	<1

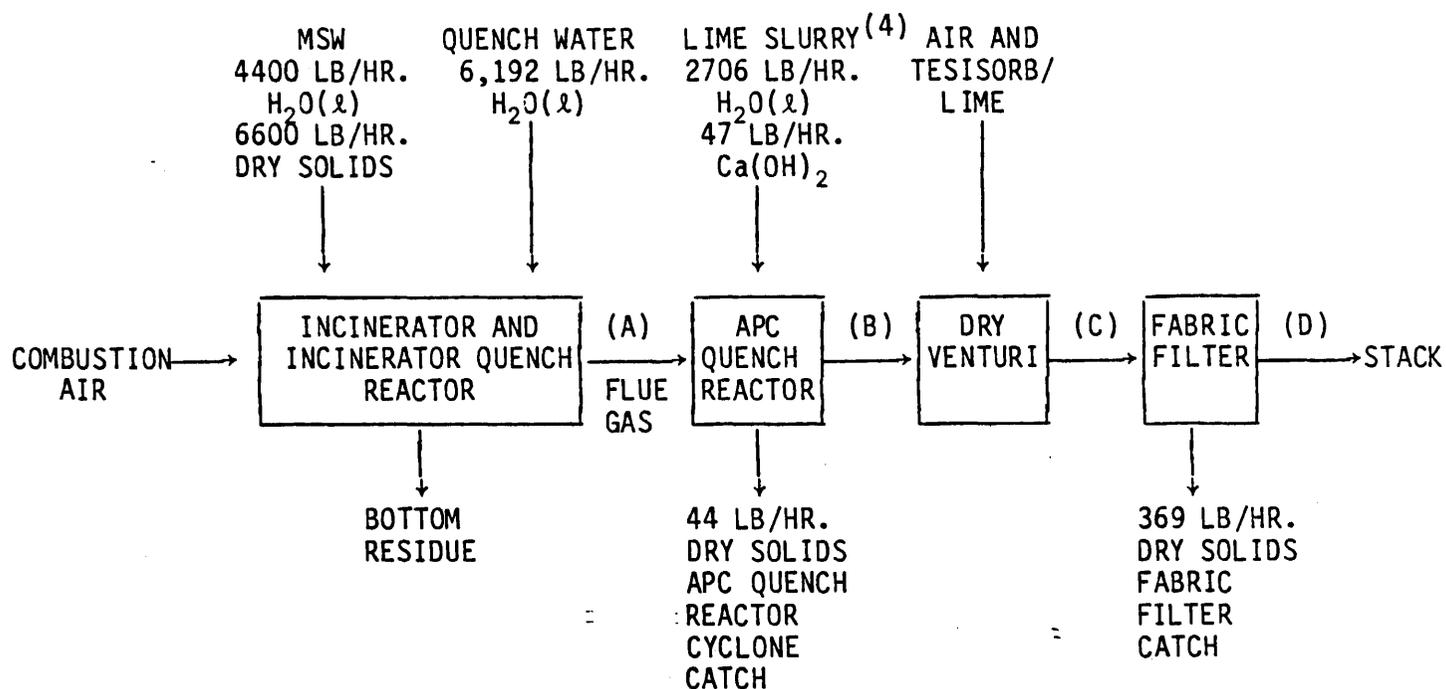
(1) Rounded off for mass balance.

(2) Temperature at preheater outlet.

(3) Calculated for mass balance as particulate at point B plus dry lime plus Tesisorb.

FIGURE 2.3-6

Mass Balance - Sampling Run 2-2



COMPONENT	STREAM	COMB. AIR	A	B	DRY LIME & TESISORB	C	D
N ₂ , mol/hr.		1,571	1,571	1,597	482	2,079	
O ₂ , mol/hr.		418	241	248	128	376	
CO ₂ , mol/hr.		-	166	166		166	
H ₂ O(g), mol/hr.		41	761	911	13	924	
SDCFM(1)		12,600	13,000	13,000		17,000	
SCFM(1)		12,800	17,000	18,000		22,000	
ACFM(1)		12,800	38,000	34,000		39,000	37,000
H ₂ O(l), lb/hr.							
Lime, lb/hr.					86		
Tesisorb, lb/hr.					106		
Temperature, °F		320-644(2)	680	500		440	390
Particulate, lb/hr (Front Half)			167	177		369(3)	1.3
HCl, lb/hr.			13	<1		<1	<1

(1) Rounded off for mass balance.

(2) Temperature at preheater outlet.

(3) Calculated for mass balance as particulate at point B plus Tesisorb. Measured value of 2.082 gr/SDCF corresponds to 301 lb/hr.

(4) Also adds 26 mol/hr. N₂ and 7 mol/hr. O₂.



3 AIR EMISSIONS TESTING METHODOLOGY

3.1 Purpose

As described previously, the facility utilizes two identical TESI APC systems (quench reactor, dry venturi, and fabric filter) to treat the flue gas from two Martin incinerators burning MSW. The air emission testing of the facility was conducted to obtain an evaluation of the performance of the TESI air pollution control equipment and to quantify certain non-criteria pollutant emissions. The facility was chosen for testing because this type of air pollution control equipment represents Best Available Control Technology (BACT) as is required for the West County Agency of Contra Costa County (WCA) waste-to-energy project. The Japanese installation was the first full-scale TESI system of this type available for testing.

As outlined in the Introduction, the PCDD/PCDF testing at the facility was conducted in conjunction with a large monitoring program that assessed the performance of the TESI APC for control of:

- sulphur dioxide (SO₂);
- hydrogen chloride (HCl);
- hydrogen fluoride (HF);
- particulate matter (PM); and,
- trace heavy metals.

The sampling protocol and results of these tests are contained in Cooper Engineers, Inc's report (Cooper, 1985). This chapter addresses the specific locations and methods used for sampling PCDD/PCDF and provides details on the analytical procedures utilized.

3.2 Sampling Locations

The sampling points were selected on the basis of project requirements and the site configuration.

In order to:

- determine the types and locations of existing sampling ports, and the locations in the existing ducting where new sampling ports could be installed; and,
- initiate discussions to assist in procuring sampling equipment and supplies, including scaffolding, in Japan;

a pretest trip to the site occurred in April 1983.

The sampling locations used for the testing are shown in Figure 2-1, a cross-section of the plant.

Testing was carried out at:

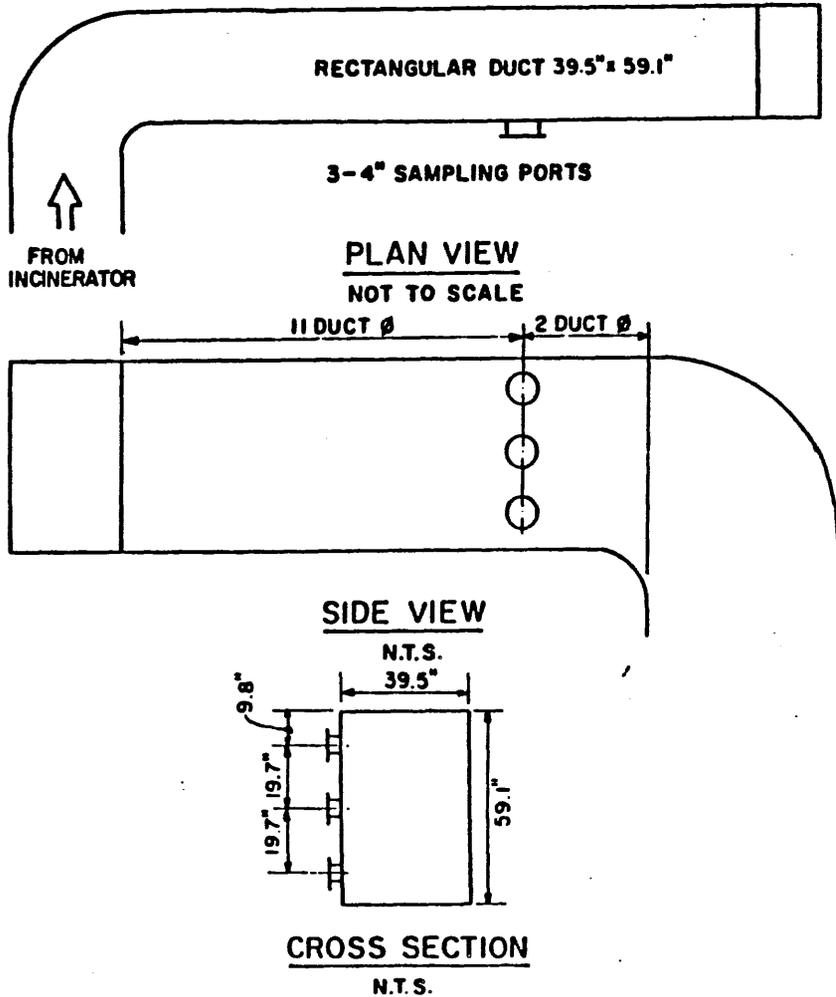
- A. Incinerator Outlet/APC Quench Reactor Inlet;
- B. APC Quench Reactor Outlet/Dry Venturi Inlet;
- C. Dry Venturi Outlet/Fabric Filter Inlet; and,
- D. Fabric Filter Outlet.

Details of the ducting and sampling port arrangements for each of these locations are shown in Figures 3.2-1 and 3.2-2. All sample ports were installed by plant staff prior to the testing team's arrival on site.

Fly ash samples were collected from the ash conveyors below the APC quench reactor and fabric filter. A combined APC quench reactor and fabric filter fly ash sample was also obtained from the ash conveyor before the fly ash pug mill.

FIGURE 3.2-1

**SAMPLE POINT A
APC QUENCH REACTOR INLET**



**SAMPLE POINT B
APC QUENCH REACTOR OUTLET/DRY VENTURI INLET**

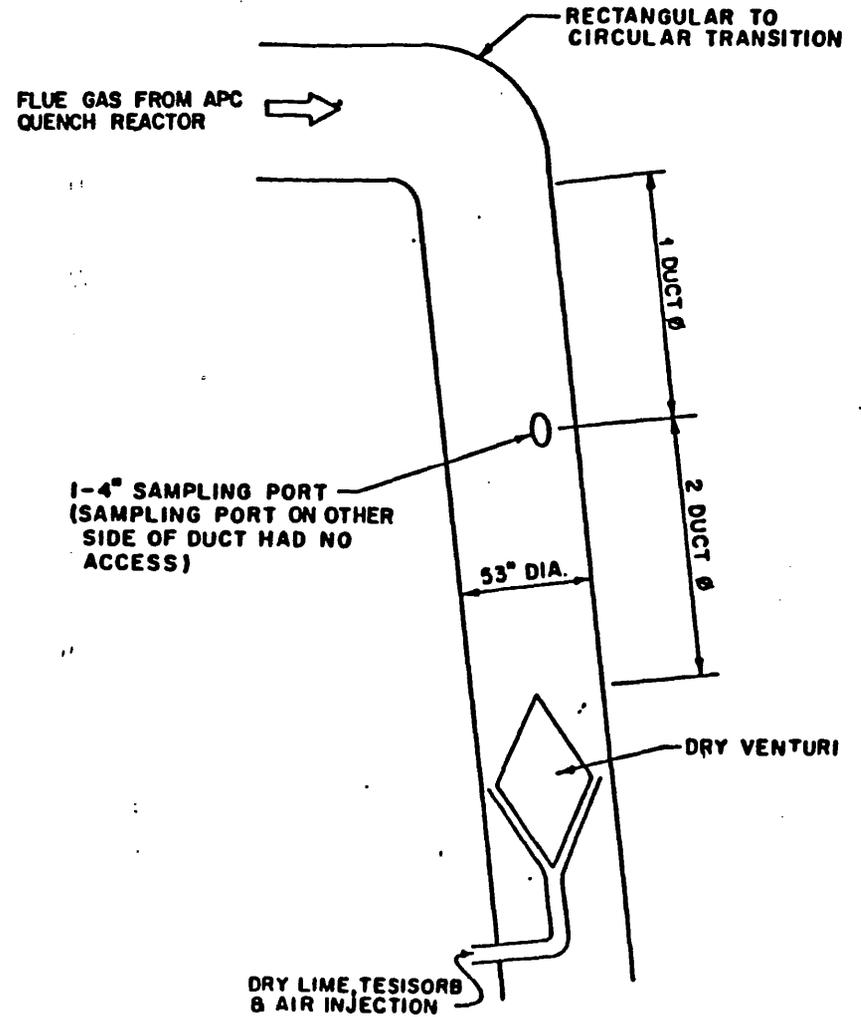
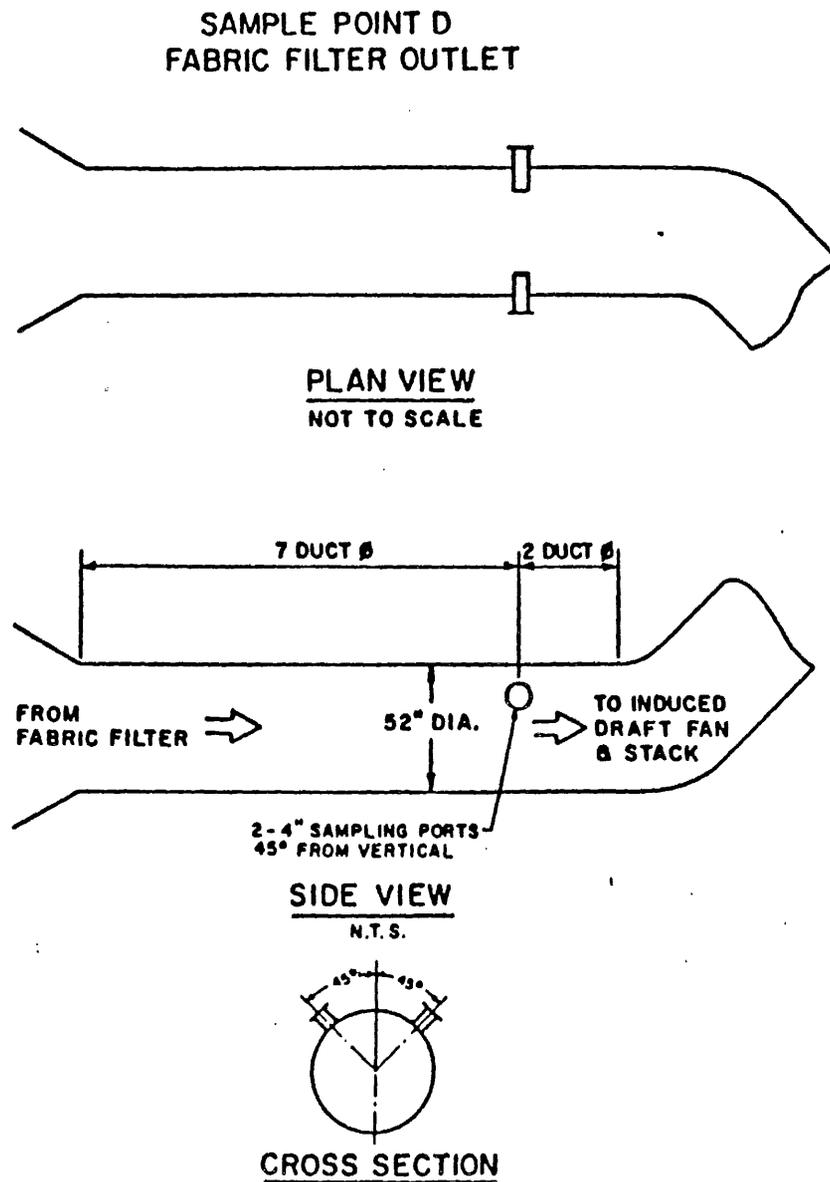
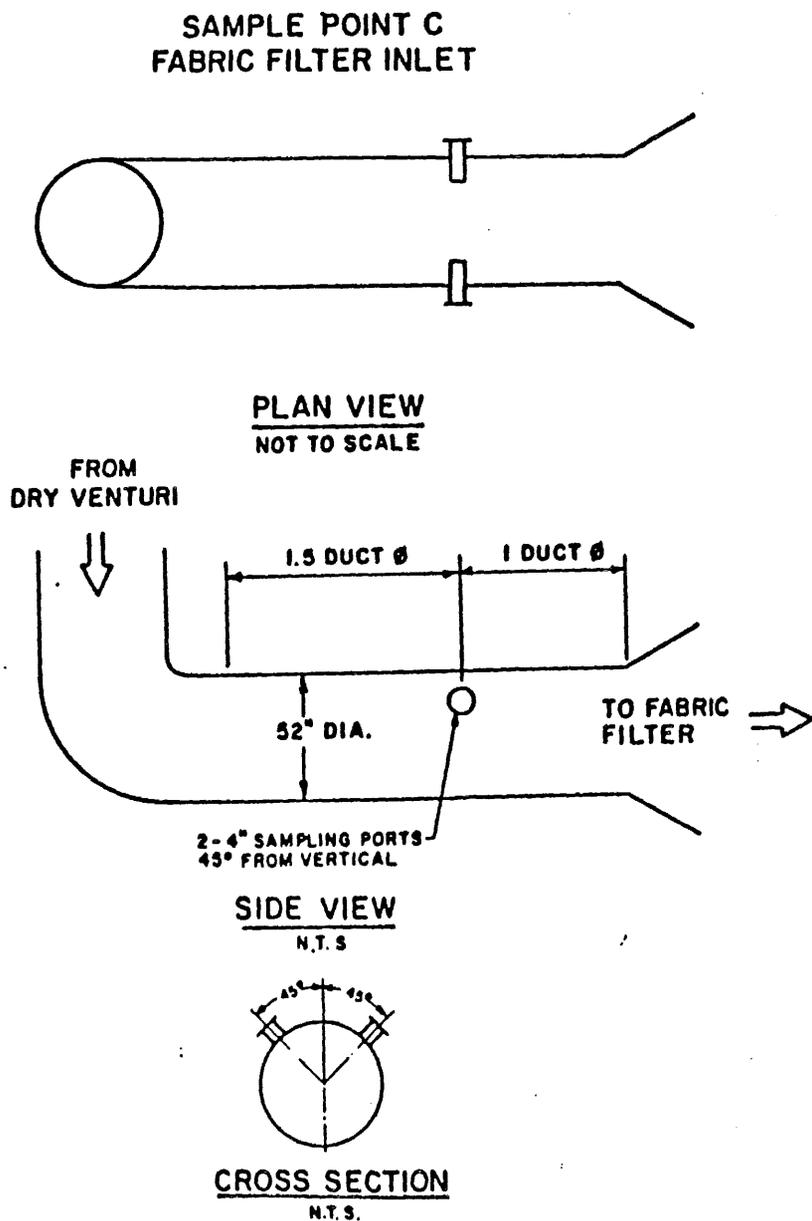


FIGURE 3.2-2



3.3 Final Testing Schedule

The final schedule for the PCDD/PCDF testing is described in Table 3.3-1 along with all other testing completed. All the air emissions testing was performed at night, 8:00 p.m. to 8:00 a.m., as required by the plant operators. This tended to complicate the test program in that the test personnel had to adapt to the new work hours, as well as jet lag, and procurement of testing supplies, e.g. ice, was most difficult at 0300 hours in Japan.

3.4 Sampling Methods

3.4.1 Standard PCDD/PCDF Procedures

Considerable discussion of potential PCDD/PCDF sampling methods led to modifications to the EPA Method 5 train. The modifications were based upon existing experience at the time of the test protocol development. The modifications consisted of adding a pair of XAD-2 resin sorbent traps in series after the third impinger in the standard EPA Method 5 train. Details of the sampling train (Figure 3.4-1) and procedure are summarized in the following paragraphs.

SAMPLING APPARATUS

A standard EPA Method 5 train was modified for sampling at points B, C and D.

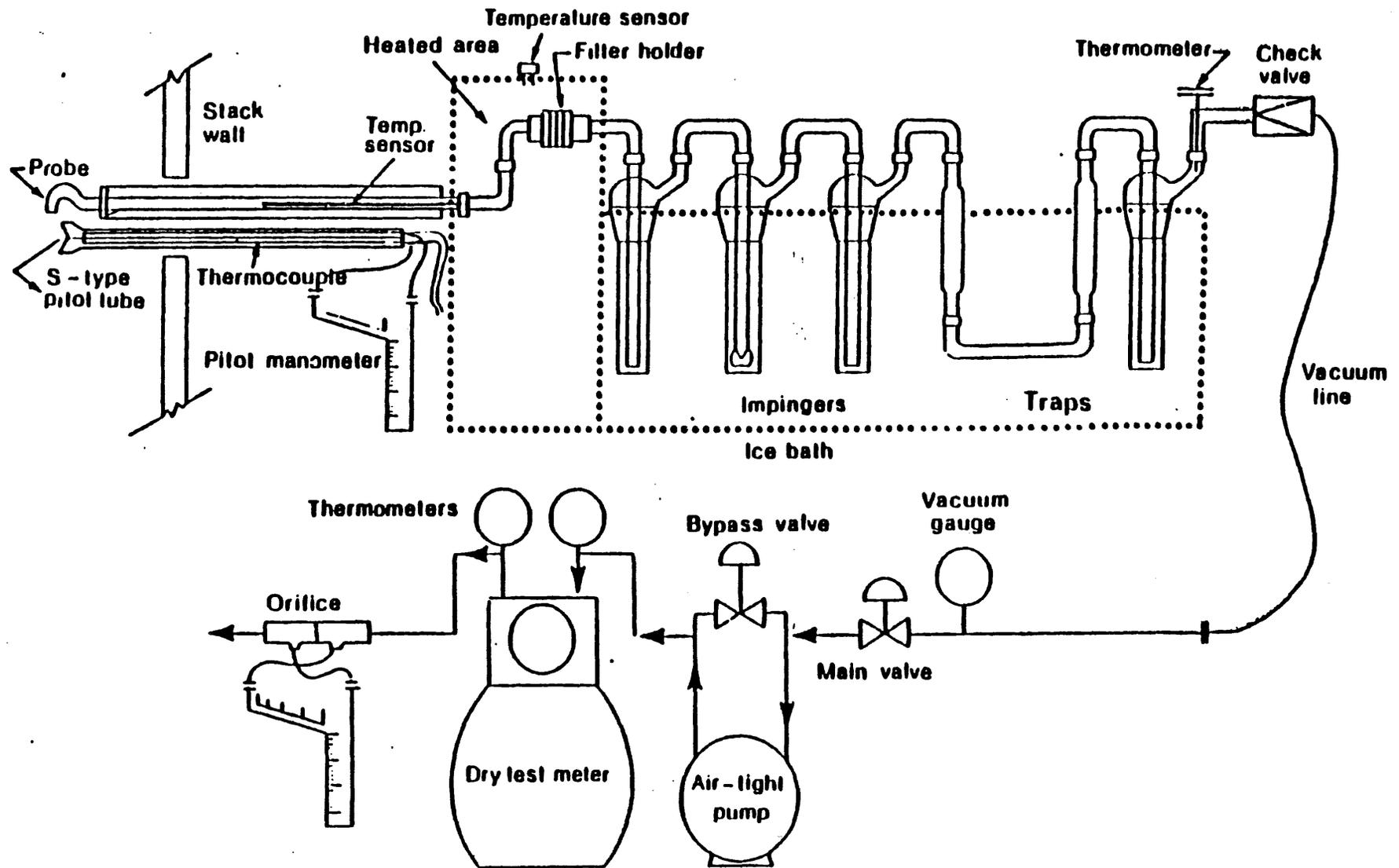
The apparatus consisted of a nozzle, heater wrapped probe and heated filter holder. A series of three large Greenburg-Smith impinger-absorbers were connected in tandem following the filter and these were immersed in an ice bath. Impingers #1 and #2 each contained 100 ml of distilled water; impinger #3 was empty. Between the third impinger and the indicating silica gel, a pair of resin-packed cartridges, in series, were used to absorb any PCDD/PCDF that may not have been absorbed in the

Daily Testing Schedule for APC Quench Reactor (QR), Dry Venturi (DV) and Fabric Filter (FF)
(with Methods)

SAMPLING LOCATIONS								
DATE	POINT A APC QR INLET		POINT B APC QR OUTLET/DV INLET		POINT C DV OUTLET/FF INLET		POINT D FF OUTLET	
10/13/83	SO ₂	U.S. EPA Method 6 (3 runs)			PM SO ₂	U.S. EPA Methods 5 & 8 with condens- ibles (3 runs)	PM SO ₂	U.S. EPA Method 5 & 8 with condens- ibles (3 runs)
10/14/83	PM HCl HF PCDDs PCDFs	U.S. EPA Modified Method 17 with condensibles (2 runs)	PM HCl HF PCDDs PCDFs	U.S. EPA Modified Method 5 with condensibles (2 runs)	PM HCl PCDDs PCDFs	U.S. EPA Modified Method 5 with condensibles (2 runs)	PM HCl HF PCDDs PCDFs	U.S. EPA Modified Method 5 with condensibles (2 runs)
10/15/83			Particle Sizing, HCl, HF, Heavy Metals, & PCDDs PCDFs	Multiclone & Andersen (3 runs each) Multiclone	Particle Sizing, HCl, HF, Heavy Metals, & PCDDs PCDFs	Multiclone & Anderson (3 runs each) Multiclone	Particle Sizing, HCl, HF, Heavy Metals, & PCDDs PCDFs	Multiclone & Andersen (1 continuous run each) Multiclone
10/16/83	Hg PM con- densibles only HCl, HF (1 run)	U.S. EPA Method 101 (2 runs) In-duct Glass Plug with Acid Gas Train					Hg PM HCl, HF	U.S. EPA Method 101 (2 runs) U.S. EPA Method 17 with con- densibles (1 run)

FIGURE 3.4-1

Schematic Diagram Of Organic Sampling Train



impingers. The resin-packed cartridges were supplied by the Brehm Laboratories of Wright-State University. The absorption train was followed by a gas drying tube containing indicating silica gel, a diaphragm pump, dry test meter and a calibrated restriction orifice fitted with a magnehelic differential pressure gauge.

In-duct filtration, as per EPA Method 17, was utilized at sampling point A. The in-stack filter was housed in a quartz housing. The gas absorption train for this system was also modified by the addition of series resin cartridges between the 3rd impinger and the silica gel trap.

Sampling and recovery procedures were similar for both EPA Methods 5 and 17.

PRESAMPLING PROCEDURE

Before sampling all glassware (nozzle, probe, filter holder, and impingers) was rinsed with acetone and toluene then sealed with aluminum foil (which had also been cleaned with acetone and toluene).

SAMPLING PROCEDURE

A computer program was used to select suitable sampling points, and nozzle size and orifice constant for the sampling train at a specification. After assembly the probe heaters were brought to temperature and the apparatus was leak tested. Successful leak checks were followed by insertion of the probe and nozzle to the first sampling point. The pump was immediately started and adjusted to obtain the isokinetic sample rate.

Duct conditions were monitored throughout the sampling period with a type "S" pitot tube and a thermocouple positioned simultaneously at the

traverse point. Conditions at the sampling apparatus and the metering device were regularly monitored and recorded on the data sheet. Isokinetic sampling rates, in terms of orifice differential pressure, are calculated by computer for each set of duct and sampling apparatus conditions. Data was relayed between the computer and site by radio.

On completion of sampling at all traverse points, the apparatus was removed, leak-checked, sealed from possible contamination and transported to the laboratory for sample recovery.

SAMPLE RECOVERY PROCEDURES

After the weight of the impingers was determined for percent moisture calculations, all impinger contents were placed in glass bottles (pre-cleaned with acetone and toluene). Impingers and connecting glassware were then rinsed three times with toluene and the rinsings were placed in another glass bottle. Samples were recovered from the probe and nozzle with three rinsings of distilled water, acetone and toluene. Contents from each type of rinsing were placed in separate, labelled, glass bottles. The resin-packed cartridges were sealed with glass stoppers, placed in their original storage containers and shipped to Wright State University for analysis. Filters were placed in petri-dishes or sample bottles for shipment to the laboratory.

3.4.2 Aerodynamic Particle Size Distribution

Interest in both particle size distribution and PCDD/PCDF concentrations in the various fractions led to the use of an SRI Three-Stage Series cyclone sampler.

PCDD/PCDF analysis was to be performed on only five samples from the multiclone system (2 each from points B and C) and 1 from point D.

SAMPLING APPARTUS

According to the Part 1 Appendix of Cooper (1985), the sampler consists of a series of three stainless steel cyclones and flat glass filter back-up, however, only cyclone I and IV are denoted in any of the sample recovery data. This sample designation suggests that the five stage SRI type sampler was used and cyclones II, III and V were bypassed for the testing. Data was reduced using the standard five cyclone equations. As sample is drawn through the sampler at a constant rate, particles are fractioned according to their aerodynamic properties and the critical dimensions of the cyclones.

The sampler was connected in series to:

- a sample probe,
- a Greenburg-Smith impinger (filled with 100 ml distilled water),
- an empty impinger (empty liquid trap),
- a silica gel drying tube,
- a vacuum pump,
- a dry test meter, and
- a calibrated restriction orifice.

SAMPLING PROCEDURE

A traverse point of average duct velocity was chosen for sampling. A nozzle, for which the isokinetic sampling rate could be maintained, was selected and attached to the sampler. The sampler was connected to the sampling probe, inserted into the duct and allowed to reach duct temperature (30 minutes). The nozzle was then positioned directly into the duct gas stream and the pump started immediately. The isokinetic sampling rate was maintained over the period of the test by monitoring the orifice meter differential pressure. At the end of the test period, the sampler was withdrawn from the duct, sealed from possible contamination and transported to the laboratory for recovery.

SAMPLE RECOVERY PROCEDURE

The contents of each section of the sampler was removed with a camel hair brush and if necessary with small amounts of acetone. Each fraction was transferred to a tared glass jar, dessicated and weighed. In the case of runs 3B1 and 3B2 as well as 3C1, 3C2, and 3D1 the jars were then sealed for shipment to the Wright State laboratory for PCDD/PCDF analysis. The particle size (50% effective cut off diameter), percent of total weight and accumulative percent weight for each fraction was computed and recorded.

3.4.3 Ash Sampling

As noted in Section 3.2 fly ash samples were collected from the ash conveyors below the APC quench reactor and fabric filter. A combined APC quench reactor/fabric filter fly ash sample was obtained from the ash conveyor before the fly ash pug mill. These samples were placed in separate pre-cleaned and labelled glass jars for transportation to the analytical laboratories

3.4.4 Gas Sampling

Carbon Monoxide, Carbon Dioxide and Oxygen

An integrated gas sample was withdrawn from the particulate sampling trains for Orsat analysis of CO, CO₂ and O₂.

Sulphur Dioxide, Sulphur Trioxide

SO₂/SO₃ at Point A was measured using US EPA Method 6; at Points C and D these pollutants were measured using US EPA Method 8. SO₂/SO₃ data is presented in Cooper (1985).

Nitrogen Oxides

Emissions data for this parameter were obtained from the plant on-line continuous monitor. The sampling port, at the fabric filter outlet, was connected to a Fuji Electric dual cell infrared SO_2/NO_x monitor (Type ZRL AD241-6D24). This particular monitor is not approved by US EPA for use as a continuous emissions monitor as it is not a chemiluminescence monitor. The data are thus provided only as reference material.

Acid Gases, Hydrogen Chloride and Hydrogen Fluoride

During PCDD/PCDF testing these gases were collected in the particulate sampling train impingers. The analysis procedures for these are detailed in the next section. Again this information is reproduced in this report for reference purposes.

3.5 Analytical Procedures

The Brehm Laboratory at Wright State University has a formalized sample receipt procedure which checks the sample and generates the necessary documentation of identifying information and observed quality. This procedure is presented in Appendix A, along with the detailed analytical method. This section provides an overview of important PCDD/PCDF analysis procedures. It also details HCl/HF analysis procedures as these are considered important for interpretation of test results.

3.5.1 Sample Designations

Both modified EPA Method 5 and Method 17 sampling trains were used to sample the incinerator emissions at four different locations (designated A, B, C and D, respectively) and these trains ultimately yielded several different types of samples for analyses. The types of samples which were provided to the Brehm Laboratory are listed below. The number of each

type of sample received is indicated in parentheses following the sample type.

1. Particulate filters (9);
 2. Acetone rinse of probe and nozzle (also contains particulates) (9);
 3. Toluene rinse of probe and nozzle (9);
 4. Impinger liquids (14);
 5. Acetone rinse of impingers (9);
 6. Toluene rinse of impingers (9);
 7. XAD-2 resin traps (18);
 8. Multi-clone particulate fractions and filters (15);
 9. Ash samples (3);
 10. Acetone prewash of sampling train (1);
 11. Toluene prewash of sampling train (1);
- Total Samples Provided for Analyses 97

Some of these samples were analyzed for polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs), others were analyzed for the selected metals as reported in Cooper, 1985. Portions of some samples were analyzed for fluorides and chlorides. In addition, the weights of total particulates collected in each sampling test, and the weights of the residues resulting from concentration of a portion of the impinger liquids to dryness were determined.

3.5.2 Measurement of Volumes of Liquids Received

The glass vessels containing the liquid samples, obtained using the sample recovery procedures outlined previously, were marked by the field team to indicate the original level of liquids in the bottles. Upon receipt of the samples at the Brehm Laboratory, it was visually evident that loss of liquids had occurred in some samples. Since it could not be determined whether these losses were due to evaporation of solvents or to leakage from the bottles, no correction of the analytical data for these losses was possible. However, the volume of each liquid sample received

was determined using a graduated cylinder and, after removing the actual sample, the volume of liquid required to fill the sample bottle to the original fill line was also determined.

3.5.3 Determination of Particulate Weights

Particulate matter collected from the flue gases were present in three types of the train samples, that is, the particulate filters of the MM-5 and M-17 trains, the Multi-Clone sized particulate fractions from those tests in which the Multi-Clone sampler was used, and the acetone rinses of the sampling probe and nozzle sections of the train.

The particulate filters were received either in sample bottles or in Petri dishes. Upon receipt at the Brehm Laboratory, the sample vessels were opened and each open vessel, (with the filter and particulate inside), was placed in a closed desiccator containing a moisture sorbing material (Drierite). After standing for 12-16 hours, each sample vessel containing the filter and particulate matter was removed and weighed. The drying and weighing procedures were then repeated until the weight of each sample vessel (and contents) was constant, within 5%, on two successive weighings. The filter and particulates from each bottle were then removed to another sample bottle and the original vessel was rinsed with a small volume of toluene and dried. The original vessel was then weighed. The tare weight of each original particulate filter, obtained by Chemecology prior to use in the sampling train, and provided to the Brehm Laboratory, was then added to the weight of the sample vessel. This weight was subtracted from the combined weight of the original sample vessel, the filter and the particles to obtain the weight of particulate matter only.

The weights of particulate matter in the acetone probe and nozzle rinses of the MM-5 and M-17 sampling trains were determined by concentrating each rinse solution to dryness in a previously tared sample vessel,

(using a stream of dry nitrogen while heating the sample vessel to 55°C in a water bath) and weighing the bottle and residual particulate matter, then subtracting the vessel weight to obtain the weight of particulate only. The weight of this particulate matter was then added to the weight of particulate matter collected on the filter for the corresponding sampling train to arrive at the total particulate weights for each of the MM-5 and M-17 sampling train tests.

Each of the sized fractions collected with the Multi-Clone sampler were weighed.

3.5.4 Determination of Condensable Residues in Impinger Liquids

An aliquot of each of the combined impinger solutions from each sampling train was transferred to a separate tared sample vessel and the liquid was evaporated by passing a gentle stream of dry nitrogen over the liquid while heating the sample bottle in a bath. When the solution had been concentrated to dryness, the sample vessel and residue were again weighed and the weight of the bottle was subtracted to obtain the weight of the residue.

3.5.5 Determination of Chloride and Fluoride Concentration in Impinger Liquids

An aliquot, one-half of the combined impinger liquids from each sampling train, was extracted, as described in Section 3.5.6, to remove organic constituents. The residual aqueous fraction was then analyzed for chloride and fluoride content. These analyses were accomplished by Howard Laboratories, Dayton, Ohio, a laboratory certified by the Ohio EPA, working under subcontract to the Brehm Laboratory of Wright State University. The procedures utilized for the fluoride analyses were as described in the U.S. EPA Methods for Chemical Analysis of Water and Waste, March, 1979, Section 240.1 and 340.2. Fluoride concentration was measured with an Orion Model-901 Millivolt/pH Meter, fitted with a

Model 9409 Fluoride electrode and a Model 9401 Reference electrode. Procedures used for chloride analyses were as described in the U.S. EPA Methods for Chemical Analyses of Water and Wastes, March, 1979, Section 325.3. This procedure is effectively a titrimetric method.

The samples provided to Howard Laboratories by the Brehm Laboratory were identified only by code numbers. In addition to the impinger liquid samples, the Brehm Laboratory prepared and submitted, for chloride and fluoride analyses, a blank (distilled water) sample and a spiked water sample containing 261 $\mu\text{g}/\text{mL}$ of chloride and 1.90 $\mu\text{g}/\text{L}$ of fluoride. These samples were submitted in blind fashion, identified only by code numbers and were indistinguishable from the impinger liquids by Howard Laboratories analysts. The latter samples were, of course, intended to provide a Quality Assurance performance check on Howard Laboratories analyses.

3.5.6 Determination of Chlorinated Dibenzo-p-dioxins and Dibenzofurans in Samples from MM-5 and M-17 Sampling Trains and from Multi-Clone Samplers

1. Combining of Train Samples for CDDs/CDFs Analyses

Some of the individual samples from each sampling train were combined to create either three or four samples from each train before analysis to determine the content of polychlorinated dibenzo-p-dioxins (CDDs) and dibenzofurans (CDFs).

In the case of the MM-5 train the particulate filter and the toluene probe and nozzle rinse from each train were combined to create one sample. This was accomplished by using the toluene rinse liquid as the extracting liquid for the Soxhlet apparatus in which the particulate filter was extracted. The Soxhlet extraction procedure is described in greater detail in Appendix A.

The particulate residue from the acetone probe and nozzle rinse from the MM-5 train was analyzed separately, and again was Soxhlet extracted.

The third sample from the MM-5 train was obtained by combining the impinger liquids with the acetone and toluene impinger rinses. This was achieved by first combining the toluene and acetone rinses and concentrating these to near dryness using a stream of dry nitrogen while heating the sample vessel in a 55°C water bath. The residue was reconstituted by adding 40 mL of hexane. One-half of this solution was then added to one-half of the combined impinger liquids, and the mixture was agitated in order to extract the organic components from the aqueous impinger liquid into the hexane phase. The hexane phase was analyzed for chlorides and fluorides, as described previously.

The fourth sample analyzed for PCDDs/PCDFs from each MM-5 train was one-half of the sorbent in the first XAD-2 resin trap. For all of the MM-5 tests, only the front (or first) XAD-2 trap was analyzed. Again analyses entailed Soxhlet extraction of the resins.

Combining of samples from the M-17 trains for PCDDs/PCDFs analyses was accomplished somewhat differently than for the MM-5 train samples. The M-17 particulate filter (and particulates thereon) was Soxhlet extracted and analyzed as a separate sample for PCDDs/PCDFs. The acetone and toluene probe and nozzle rinses and the acetone and toluene impinger rinses were combined with the impinger liquids (in a manner similar to that described above for the corresponding MM-5 train samples) to yield a second sample for PCDDs/PCDFs analyses. Finally, the XAD-2 trap was analyzed. In one M-17 test (2A1) only one-half of the resin in the front XAD-2 trap was analyzed, whereas in the second M-17 test, one-half of the resin in both the front and back XAD-2 traps were analyzed.

While the impinger liquids from the separate impingers on most of the trains were combined prior to PCDDs/PCDFs analyses, in one case (test 2D2), the impinger contents in separate impingers were separately analyzed.

2. Other Samples

Three different fly ash samples from these tests were also analyzed separately, as were acetone and toluene samples from prewashing of a sample train prior to use in the testing.

3. Analytical Procedures on Prepared Samples

Organic analyses involved several steps:

- extraction of the recovered sample,
- clean-up of the extract, and
- analysis by multiple ion detection gas chromatography - mass spectrometry (GC/MS-MID).

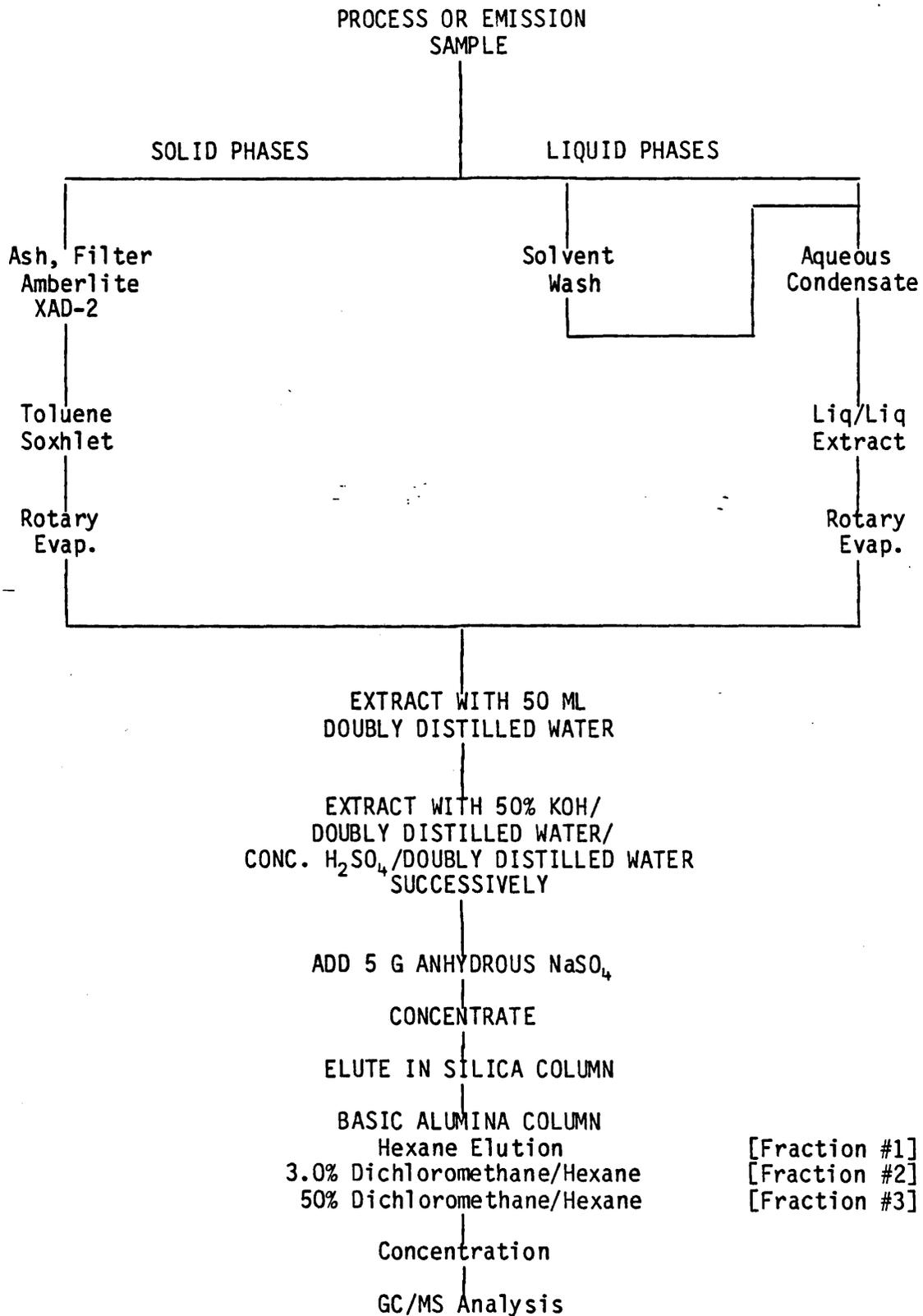
PCDD/PCDF analysis procedures tend to follow the ASME analytical draft protocol, although this project predates that document's creation. Details of the laboratory procedures are provided in Appendix A. The appendix also contains the latest ASME protocol.

The generalized procedures for PCDD/PCDF analysis as performed by the Brehm Laboratory is outlined in Figure 3.5-1. The procedure is described below.

All solid samples for PCDD/PCDF analyses, train, ash or resin samples were soxhlet extracted with toluene for a period of 16 to 24 hours. Water and impinger contents were extracted with hexane in separatory funnels. Each sample was internally-spiked with a surrogate standard mixture of isotopically-labelled isomers prior to extraction.

For PCDD/PCDF analysis concentrated raw extracts were washed with doubly distilled water, 50% KOH, water, concentrated H_2SO_4 and water before

FIGURE 3.5-1
Flowchart of PCDD/PCDF Extraction and Clean-Up Procedures



being passed through a series of two columns which removed, by reaction and selective adsorption, the bulk of the organic matrix co-extracted with PCDD/PCDF.

Processed sample extracts were concentrated to small, known volumes, and split into two samples, one for PCDD and one for PCDF analysis.

Qualitative and quantitative analysis of all samples were performed by GC/MS-MID. For each congener group, two characteristic ions were selectively monitored. Identification was achieved when target ions were detected in the correct abundance ratio within established retention time windows. Quantitation, including internal spike recovery determination, was based upon the use of an external calibration standard mixture.

3.6 Data Handling Procedures

As mentioned previously much of the data collected during the testing program contained in Cooper (1985). Data obtained on PCDD/PCDF concentrations at various points in the system were processed at the same time and issued for peer review. As part of the review of the Cooper work, the data collected by the field team was reprocessed from the field data sheets contained in Part 1 of the Appendix of Cooper (1985). Initial evaluation of the data presented in the Draft reports by Cooper indicated transcription and arithmetic errors to be present. Rather than simply change the numbers it was decided that it would be prudent to re-do all calculations from field data sheets to final form. Doing this by computer provided limited opportunity for compilation errors while speeding up the process. This results in some changes from the original values published in a 1984 version of the report which was circulated mainly for peer review. Rather than enumerate these changes we have double checked all values and consider the ones contained in Chapter 5 to be correct. Appendix material will allow readers to check this for themselves. The methods used for this processing and the assumptions used are outlined in the following sections.

3.6.1 Isokinetic Sampling Data

All isokinetic data were entered into a BASIC computer programme which calculated test isokinetic ratios and emission rate data. All data provided on the printouts, (Appendix B), were reviewed prior to their use and validated from sources such as field notes and the laboratory report (Appendix A), which provided particulate weight data.

Several observations were made during the examination of the isokinetic data:

- leak checks were not performed consistently before and after moving the probe from port to port;
- large leak volumes were apparent on one test (2C1), and on this test a ball joint broke at the last sample point;
- an acetone blank, particulate on evaporation value, of 1 mg was consistently subtracted from the total particulate catch in the Cooper data;
- some inconsistencies between calculated and reported values for the isokinetic results were found; this was particularly noticeable with the % moisture data.

The significance of these issues is addressed in the QA/QC chapter (Chapter 4).

All recalculations were undertaken at 68°F and 29.92 in. Hg standard reference conditions as defined in the ASME MM-5 protocol. Data is presented at normal conditions (0°C and 29.92 in Hg) to allow comparison to other data.

3.6.2 Process Data

Plant process data were read from the instrumentation in the control room. The values were logged on an hourly basis and the results were tabulated. No attempt has been made to verify these data, the information has been transcribed from the various Cooper references.

3.6.3 Analytical Data

Analytical results from the laboratory for all train samples were received as total weights of the particular compound of interest. The raw results are presented in Appendix B as part of the Wright State data. Preliminary examination of this data and the Cooper data showed both transcription and calculation errors, particularly with the PCDD/PCDF data. This prompted the use of a spreadsheet program to recalculate the various parameters. The raw analytical data was entered into the spreadsheet, combined with data from the isokinetic program and the resulting concentration data calculated.

Various calculations are performed by the laboratory on all analytical data and the reader is advised to consider these points when reviewing the data.

1. All PCDD/PCDF data is reported in recovery corrected form. Recovery of the labelled PCDD internal spike is represented by the gradient of sample and calibration responses for:

- $^{13}\text{C}_{12}$ - 2,3,7,8 TCDD
- $^{37}\text{Cl}_4$ - 1,2,3,4,6,7,8 Hepta CDD
- $^{13}\text{C}_{12}$ - OCDD

Recovery factors are reported with the laboratory data in Appendix B. Conversations with the laboratory indicate that it is not possible to determine the uncorrected values.

2. While method blank corrections were performed on all data, blank corrections for:

- reagents,
- sample train proofing, and
- blank sample trains,

were not undertaken.



4 QUALITY ASSURANCE ISSUES

In reviewing the Cooper (1985) work the authors were asked not only to review and check all data and analytical procedures, but also to compare the methods used to contemporary standards. The chapter that follows discusses the differences between this study and the protocols published by various agencies. The chapter addresses each aspect of the program in the order it was presented in Chapter 3.

4.1 Sampling Location

Most existing test protocols specify both acceptable sampling locations, and the number of sampling points required. Examples include:

- EPA Method 1, (Sample and Velocity Traverses for Stationary Sources); or,
 - Ontario Source Testing Code (Version #2)
- a) The preferred location is in a straight vertical section with 10 equivalent diameters between upstream and downstream disturbances; sample at eight equivalent diameters from the upstream disturbance. For this situation the codes specify the number of required sampling points based upon duct diameter.
- b) If the preferred situation cannot be satisfied EPA Method 1 determines the number of sampling points based upon the following:

Distance from last disturbance to sampling point (Equiv. Dia.)	3-5	5-6	6-7	7-8
Required Number of Sample Points	24	20	16	12

- c) Ontario further specifies that: if upon measuring the stack gas velocity the ratio of velocities at any two points is greater than 2:1 the total number of sampling points must be doubled.

For the sampling locations at the test facility the ideal situation was not always available. Chapter 3 illustrates the sampling locations and details; a comparison of the locations and code requirements follows.

Sampling Point A is located satisfactorily, 11 diameters downstream of the preceding disturbance and 2 diameters upstream of the following disturbance.

Sampling Point B is only one duct diameter after a rectangular to circular transition and 2 duct diameters upstream of the dry venturi, (the dry lime, Tesisorb injection location). This sample location does not satisfy the EPA Method 1 requirements but the sampling team required data from this region of the system. To further complicate the siting access was only available on one side. A total of 24 sampling points were used on the one traverse of the 4'-5" diameter duct. The minimum number of traverse sample points suggested by EPA Method 1 would be at least 24 but the method does not cover the situation of such tight upstream spacing. Justifiably, the sampling team chose to get as far upstream from the dry venturi as possible.

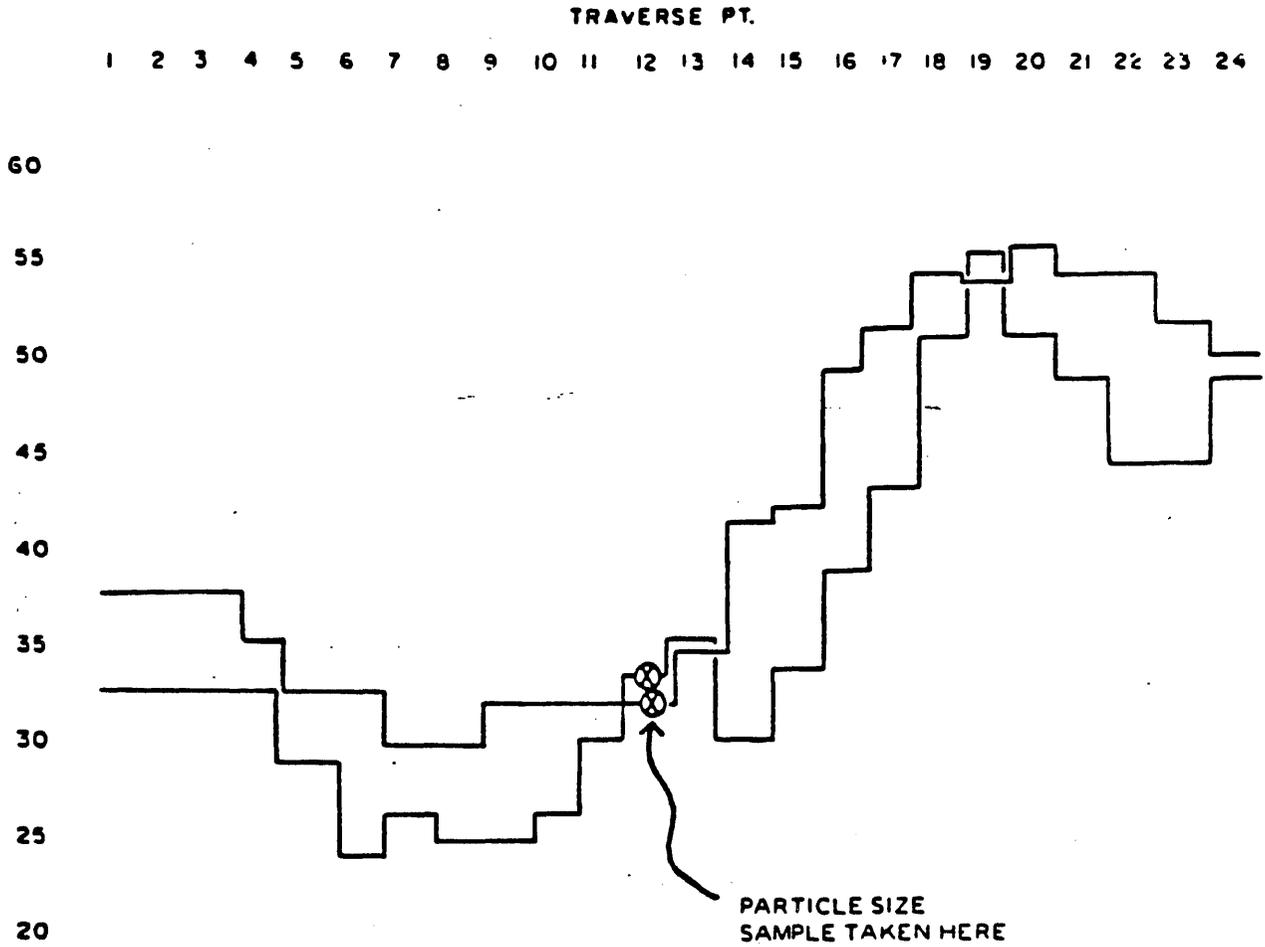
Velocity traverse data at Point B is shown in Figure 4.1-1. These present the results of the tests run on day 2 and show:

- average velocity 2B1 - 40.7 ft./sec.
2B2 - 35.9 ft./sec.

- maximum velocity 2B1 location 19 - 57 fps
2B2 location 20 - 56 fps

FIGURE 4-1.1

VELOCITY PROFILE DRY VENTURI INLET (POINT B)



- minimum velocity 2B1 locations 7,8,9 - 30 fps
2B2 location 6 - 24 fps

The pattern shows a trend to higher velocities towards the outside of the elbow preceding the sampling location as would be expected. On the basis of the 2B1 run the additional velocity ratio criterion of Ontario would be satisfied. The second run, however, shows greater variability and the criterion was not satisfied.

In reviewing the report, H.G. Rigo commented that the higher velocities at sampling points 1-5 suggest that a vortex situation may be superimposed on the turbulent plug flow situation (Rigo, 1984). He cautions, as does Cooper (1985), that the data must be reviewed carefully given this velocity pattern.

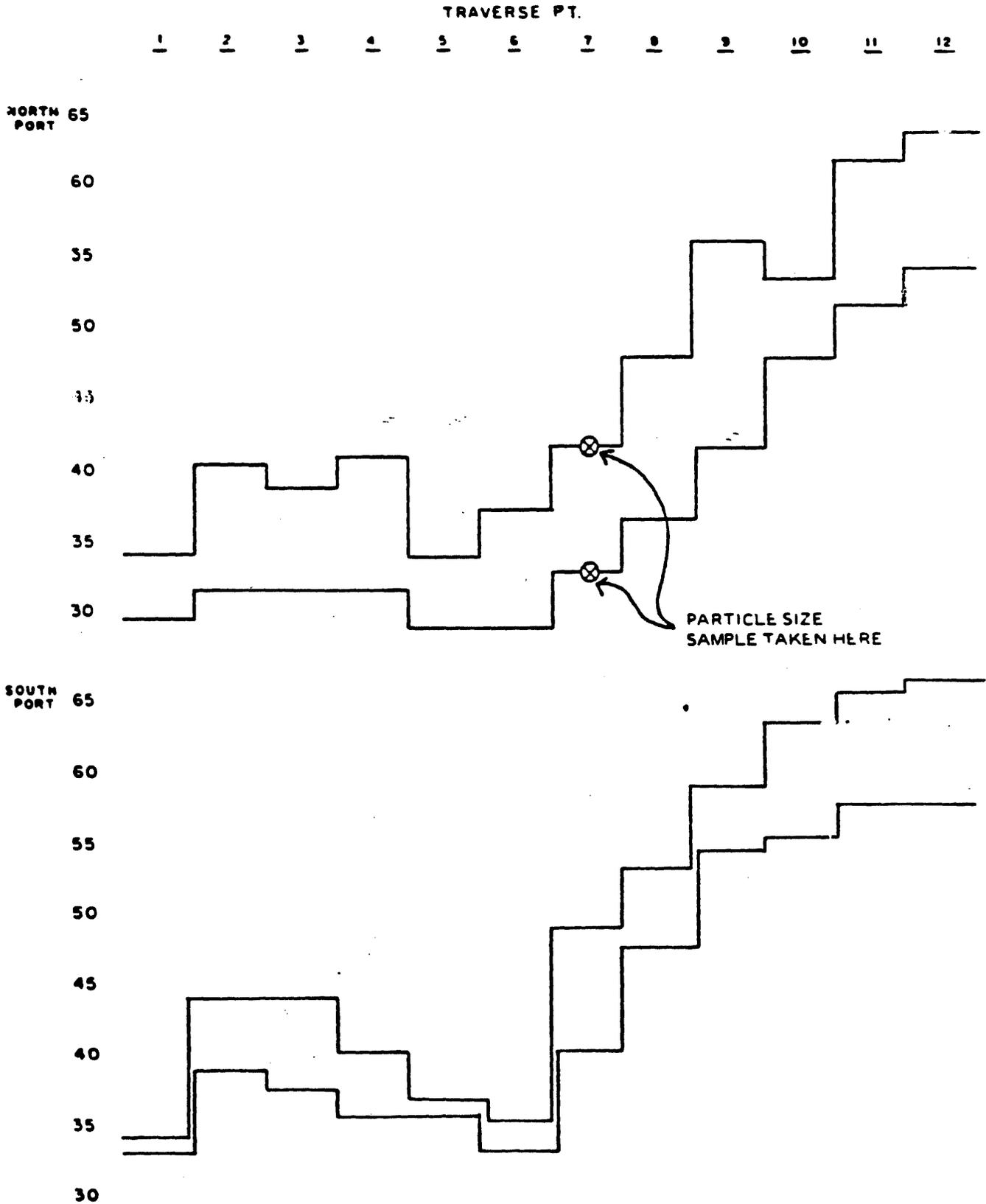
The velocity profile could also contribute to difficulties in obtaining accurate particle size distribution data. This is addressed in the Cooper (1985) report.

Sampling Point C is 1.5 diameter downstream and 1 diameter upstream of disturbances. This location does not satisfy EPA Method 1. Twelve sample points on each of two traverses were used for the tests of this 4'-4" diameter duct, which complies with the maximum number of sample points recommended by Method 1.

Measured velocity data, as shown in Figure 4.1-2, suggests the ratio of minimum to maximum velocity will satisfy the 2:1 criteria of the MOE. The velocity pattern is similar to that for Point B and the same limitations would be evident.

Sampling Point D is 7 diameters downstream and 2 upstream of disturbances suggesting a relatively normal situation for testing. With 24 sampling

FIGURE 4.1-2

VELOCITY PROFILE
FABRIC FILTER INLET (POINT C)

points in the 4'-4" diameter duct the EPA Method 1 criteria of 16 points is satisfied. The velocity data, available in Appendix B shows the minimum to maximum ratio of velocities to be 0.9:1.0 and 0.7:1.0 thereby satisfying to MOE requirement.

In summary, recognizing the site-imposed limitations, the sample locations were the best that could be obtained under the circumstances. It would have been preferable to have more sample points at sites B and C, however the error induced in the measurements of PCDD/PCDF and velocity at these points is considered to be acceptable when compared to the precision of organic analysis. More limited is data obtained with the particle sizing trains, this is discussed in Chapter 6.

4.2 Sampling Methodology

4.2.1 Train Configuration

The basic PCDD/PCDF measurement procedure involved the use of an EPA Method 5 particulate monitoring train with "sorber" cartridges to capture contaminants that passed through the impingers. The system was similar to that described in the Ontario Ministry of the Environment methodology, "Stack Sampling for Trace Organic Contaminants (Version 5 - SWARU) developed by the Source Measurement Unit of the Ministry (Figure 3.4-1). The major difference between the MOE method and the one used for this study was the use of XAD-2 sorber resin as opposed to florosil. XAD-2 is the sorber of choice for both the ASME protocol and Operator's Manual for MM5 train (Little, 1985). Both these latter publications provide a number of fundamental changes in the train configuration and reflect more recent thinking on test protocols.

New train configurations call for the use of a water cooled condenser immediately after the filter holder. This condenser is followed by a

water-cooled sorbent cartridge trap and a condensate collector before the impingers.

Both train configurations have been used to collect PCDD/PCDF contaminants in flue gases. Hagenmaier (1985) compares results from the use of several systems on the same source and states that there is no substantial difference in performance of the various systems. Several observations can be made particularly with respect to the authors' experiences during the NITEP P.E.I. testing study (Concord, 1985):

- Integral condenser/sorbent cartridges were used on some trains during the PEI test work. These were returned to the laboratory for sample recovery and clean-up. This ensured that the most highly contaminated sample containers were treated under controlled laboratory conditions.
- Sample recovery procedures for the split condenser/sorbent cartridge involved field clean-up of the condenser with laboratory recovery of the sorbent resin. Under these circumstances recovery crew personnel observed it was more difficult to clean the condenser since no internal scrubbing was possible.
- Cleaning of impingers, such as those used in this study is also not an easy task, especially if done in the field and "on-the-fly" between consecutive tests. One hypothesis advanced for higher Hepta (Hp) and Octa (O) CDF compounds on some boiler inlet samples at PEI was the previous use of the impingers for sampling either in the conventional configuration and/or also in the MOE configuration. These higher levels were noticeable on the glassware proof data suggesting that cleaning of these compounds is difficult.

In summary it may be easier to adequately clean the condenser/resin trap combination than three impingers. The impingers in the ASME MM5 protocol

act as back-up to the sorbent cartridge and see little, if any, PCDD/PCDF compounds.

Several other cautions are clearly stated in the ASME and EPA MM5 protocols:

- all parts in contact with the gas stream being sampled must be glass, Teflon or another inert material, with the exception of the nozzle which can be nickel-plated;
- the sorbent cartridge should be covered with aluminum foil to protect it from sunlight and it should be maintained at temperatures below 70°F (21°C). At no time should the resin be subjected to temperatures above 122°F (50°C).
- Teflon is the only acceptable material for sealing surfaces in the system; under no circumstances should rubber, silicone grease or asbestos rope be used to effect sealing since these materials contain contaminants.

Descriptions of the test apparatus made available for this review do not explicitly state that all these procedures were followed. If they were not followed, the data are of limited use for direct comparison to other studies, however this should not limit the analysis of and comparison to data taken at various points in the system. While slightly higher gas inlet temperatures are found at the sample points preceding D the configuration and operation of the train would not have differed that much from sampling point to sampling point. The relative errors would thus be anticipated to be similar.

It is important to note that the ASME protocol (1984 Draft) warns that the method they describe is so designed that only the total amount of each chlorinated organic compound in the stack emissions can be determined. They go on to state:

"To date, no studies have been performed to demonstrate that the particulate and/or gaseous chlorinated organic compounds collected in separate parts of the sampling train accurately describes the actual partition of each in the stack emission".

This statement suggests that it is premature to comment on the composition of the stack effluent based upon the location of the material in the train samples (extremely fine material could escape capture on the filter or in the impingers, but would be trapped in a deep bed resin cartridge).

4.2.2 Sampling Procedure

Three major issues should be addressed in this section:

- glassware cleaning before testing;
- length of sampling; and,
- leak check procedures.

Glassware Cleaning

The procedures provided suggest that all glassware, including sample containers were pre-cleaned by rinsing with acetone and toluene. Samples of pre-washes from the D train were provided to the analytical laboratory. The results of these analyses show:

- no detectable PCDD in the acetone prewash with the exception of HpCDD and OCDD;
- no detectable PCDD in the toluene prewash with the exception of OCDD; and,

- no detectable PCDF in either the acetone or toluene prewash with the exception of HpCDF and OCDF.

These data would suggest that OCDD and OCDF contaminants were present in the impingers before testing, or in the reagents used for recovery. Under either circumstance the magnitude of the contamination will be compared to the results of the sampling presented in the next chapter.

More rigorous pre-cleaning procedures should be followed in future test programs, and rinses of clean glassware should be subjected to proofing analysis.

Length of Sampling

Most sampling runs during this program were short compared to the accepted durations quoted by ASME and Little (1985). Sample time is directly related to the total amount of sample collected and longer sampling times generally improve the level of sensitivity for the analytical method. Each sampling run on day two was between 60 and 90 minutes in duration (see Appendix B). Due to the apparent level of PCDD/PCDF materials in the stack samples the total contaminant weights for each homologue are generally above the laboratory detection limit, with the notable exception being the HpCDF, OCDF and OCDD levels. More samples from sampling point D exhibit levels below the detection limit than for any other location. This would be anticipated given the level of control offered by the APC system.

While the short sample times limit the accuracy of emission level calculations it is still possible to determine maximum anticipated levels for the test periods. These are simply those levels that arise from using the detection level as the absolute value for the catch. The short sampling durations were generally the same for all locations allowing a time series comparison of the results.

Given the upsets in the furnace operation, as noted in Chapter 2, it is fortuitous that sampling durations were so short. This allows the data to be compared more closely to the actual operating conditions, and provides some insights into both the variability of emissions and PCDD/-PCDF concentrations and factors that can influence emission measurements. On the other hand, as will be discussed in Chapter 6, the short sampling duration and the variability of fabric filter removal efficiencies, particularly after cleaning cycles, contribute in no small part to the difficulties of interpreting the data from this study.

In future tests attempts should be made to sample for four hours under relatively steady state operating conditions.

Leak Check Procedures

It is presumed that leak checks on the assembled trains were performed at least at the start and finish of each run. The trains were not always leak checked before and after changing sample ports. This understanding of leak check procedures was derived from a review of the protocol supplied and a check of the meter readings at traverse changes.

As noted in Chapter 3, a substantial leak occurred on run 2C1 at the midpoint and a broken ball joint was found at the end of the run. No notes on adjustments nor final leak check flows are available from this run's data sheets. Procedures are supplied to adjust the meter volume if this situation occurs and the run cannot be repeated (ASME, 1984). The substitution for V_m is:

$$V_{m_{adj}} = \left[V_m - \sum_{i=1}^n \theta_i (L_i - L_a) - \theta_p (L_p - L_a) \right]$$

where V_m = meter volume from dry gas meter (dscf)

L_a = maximum allowable leakage rate (0.02 ft.³/min.) or 4% of average sampling rate whichever is smaller

- L_p = leakage rate observed at end of period (ft.³/min.)
 L_i = leakage rate observed at start of period (ft.³/min.)
 θ_i = sampling time between successive leak checks (min.)
 θ_p = sampling time between last leak check and end of test

Substitute only for those leakages (L_i and L_p) which exceed L_a .

Without all the 2C1 data, it is impossible to apply this correction factor to the run with any degree of accuracy.

The noted absence of leak checks at the port changes would have seriously compromised the other run data had leakages been found to be excessive at the end of the test.

Future testing should follow the recommended protocol, if for no other reason than, to minimize the potential for lost data. Leak checks should be performed:

- before the probe is inserted into the first port;
- after the probe is removed from the first port;
- after the probe is moved to the second port;
- after the probe is removed from the second port;
- at the end of the testing run; and,
- should equipment changes be necessary during the run, before and after the equipment is changed.

4.2.3 Sample Recovery

The procedure for sample recovery used for organic sampling programs is generally the same as that defined for EPA Method 5. All samples are retained for analyses, the equipment is thoroughly cleaned and the cleaning fluid is saved for analyses. Differences in the MM5 method involve the solvents used for recovery, the order of their use, the use of cleaned and proofed sample containers, and the procedures used for

determination of particulate weights in the various sample fractions. Most of these issues have already been addressed in this report and sampling handling is discussed with respect to the analytical program, so the only issue outstanding is the solvents to be used and the exact order of their use.

The data presented in the previous chapter indicates that the various sample train components were rinsed with acetone and then toluene. This serves as a starting point for comparison to ASME and Little (1985).

ASME suggests acetone rinsing (3 times) followed by 3 rinses with hexane for sample recovery. This procedure is used on all components but the 2nd, 3rd and 4th impingers. The second and third impingers receive triple rinses with de-ionized distilled water. The silica gel impinger is ignored.

Little (1985) suggests that all train components before the filter be cleaned with a methanol/methylene chloride (50:50) solvent solution. They also note that distilled water can be used. After the filter and through to the condensate trap methylene chloride is the preferred solvent.

Concord (1985) utilized a third alternative during the NITEP PEI work. Acetone and hexane rinses prescribed by ASME were followed by a methylene chloride rinse to improve the recovery of samples and ensure clean glassware. After each clean-up the train components were grouped:

- to the front half of the filter holder,
- the back half of the filter holder and the condenser; and,
- the knock-out trap and impinger #1,

rinsed three times, and the final rinse was saved as a proof sample.

The level of complexity for sample recovery is somewhat dependant upon project requirements, and, in reality, the project budget. With respect to the procedures used for this project they were judged adequate at the time and cannot be criticized three years later. Some difficulties with cross-contamination of samples may exist, as it is our understanding that, while a dedicated train was used for each site, the samples from that train were recovered and the train was immediately returned to service. No proof samples were collected nor does the protocol clearly spell out the "between sample" cleaning procedure. These limitations are not considered particularly critical.

One point noted by an analytical reviewer concerned sample shipment procedures. No indication is given that the samples recovered from the testing were refrigerated until they arrived at the laboratory. Indeed, the laboratory staff note on one memo that it took UPS eight days to forward the samples from California to Ohio, and it is unlikely that the samples were kept cool. This could explain some of the sample loss problems encountered with liquid samples.

4.3 Laboratory Procedures

In this section of the report the issues of sample handling, and analytical procedures are addressed. An initial review of analytical procedures was completed internally before two independent outside reviews were requested. The results of these external reviews are appended (Appendix C). These comments and those from the internal review are condensed in this chapter.

Following the internal review, a QA/QC Laboratory Audit was conducted by contractor personnel at the Brehm Laboratory.

4.3.1 Laboratory Systems Audit

A laboratory system audit was performed at Brehm Laboratories, Wright State University, Dayton, Ohio in late April 1986. The objective of this system audit was to:

- review the sample handling and processing procedures to ensure that any loss or breakage was noted upon receipt at the laboratory;
- examine transference of sample designation for transcription errors; and,
- ensure that the analytical data presented in the Brehm Laboratory report was accurate and complete.

This was accomplished by obtaining and reviewing information on the sample processing systems, laboratory notebooks (preparation and analysis) and chain of custody documentation (i.e sample log-in sheets, sample tracking forms and laboratory sample log book). A complete cross reference of all samples in all the various Brehm Laboratory documentation was also performed.

Sample Processing

Brehm Laboratory have established detailed sample handling and tracking procedures which are consistent with those recommended by the US EPA's National Enforcement Investigations Centre. These procedures are briefly described in this section. Brehm Laboratory has a designated Sample Custodian who is responsible for preparing and maintaining relevant sample custody and tracking documentation for all samples received by the Laboratory for analysis. This custodian and his assistants receive, unpack and inspect all samples and complete three separate documents, namely a sample log-in sheet, the laboratory sample log book and a memorandum for the central contract file.

The sample log-in sheet lists the samples received for analysis using the sample designation provided by the originator on the sample vessels. A corresponding Brehm Laboratory sample number is then assigned to each sample and recorded on the Sample log-in sheet. Other relevant information such as the sample condition, size, characteristics, etc., are also recorded on this form.

The sample custodian then lists all samples in the Brehm Laboratory Log Book and prepares a detailed sample receipt memorandum which is placed in the centralized contract file. These documents contain the same information as the sample log-in sheet.

As the samples are analyzed they are accompanied by a detailed Sample Tracking form which:

- identifies the sample by the assigned Brehm Laboratory sample number;
- identifies the analysts (signatures) who performed the sample preparation (extraction) and analysis; and,
- specifies the sample type, weight, internal standard spike levels, and the dates of sample preparation and analysis.

Details regarding the processing and analysis for each sample are documented in a Sample Preparation Laboratory Notebook and in a GC/MS Analysis Laboratory Notebook. Each book is numbered and the notebook number and page number are also recorded on the Sample Tracking form.

With this system in place it was possible to completely cross-reference all samples in all the Brehm Laboratory documentation.

Brehm Laboratory provided the auditor with the originals of all laboratory documentation relating to the analysis of this project's samples.

An examination of these documents was performed and each sample was subjected to review from the point of receipt at the laboratory through to the reporting of GC/MS analytical data. The findings of the audit are summarized below:

- The chain of custody procedures were well documented, clear and of appropriate detail.
- The sample log-in procedures are detailed, thorough and identified problems and potential sources of problems.
- No discrepancies, errors or omissions were observed and the reported data in the Brehm Analytical Report are accurate and complete.
- Sample losses were well documented and the original sample volume was approximated by filling the sample bottle to the original fill line.

In summary, although some doubt has existed as to the accuracy of the sample descriptions accompanying the published results, no evidence of such errors was uncovered during the audit.

4.3.2 Analytical Methodology

As outlined in the previous chapter and detailed in Appendix A, the analytical procedures involved extraction, clean-up and GC/MS identification/quantitation. Generally, all reviewers considered the work to be done in a highly professional manner although there were some minor concerns. As was pointed out by one reviewer, the work follows the protocol since adopted by ASME, and Dr. T.O. Tiernan was one of the experts who drafted the ASME protocol.

Specific plaudits were noted:

- good level of documentation;
- the extraction ion current profiles (EICP's) yield readily interpreted PCDD chromatograms with similar patterns for both filter and impinger samples;
- the EICP's for PCDF were obscured somewhat by the PCDE (polychlorinated diphenyl ether) ion;
- retention times for TCDD were readily reproducible as witnessed by February 2 and April 10, 1984 EICP's (even this potential problem was covered by the spiking protocol);
- recoveries were excellent; and,
- standards were well documented although, it would be helpful to have purity data for these.

Several general comments were made concerning discrepancies or improvements that may be beneficial for future studies.

A general concern about sample splitting as noted by all reviewers. In discussions with laboratory personnel it was determined that half of each resin sample was retained for subsequent use should the laboratory have lost a sample. In no case did this actually occur and, in retrospect, it may have been more appropriate to take the chance and analyze the whole resin sample thereby eliminating any doubts about sample splitting and increasing the sensitivity of the method by having higher extract concentrations. It is presumed that care was taken to ensure that a representative sample was taken from the resin but this does not address any problems associated with a heterogeneous distribution of contaminants on the resin. The second cartridge served primarily as a back-up. The

concern about splitting impinger samples is noteworthy since no guarantee of homogeneity for such splitting is possible. It is not possible to determine the effect this might have on the final results. This, however, is one of the compromises that must occur with any sampling program.

Examination of the EICP's by one outside reviewer prompted the conclusion that, while the protocol was not completely clear on the definition procedure for retention windows, there did not appear to have been any missed peak in the analysis of the CDD and CDF congeners.

The identification criteria for PCDD/PCDF suggests that only elution in the retention window and correct ion ratio $\pm 30\%$ were used. The correct ion ratio normally accepted today is $\pm 15-20\%$ and this was used for NITEP PEI (Concord, 1985).

The reviewers also noted that:

- The LRMS analysis included monitoring of the $(M-COC1)^+$ ion and this is usually an identification criterion. The monitoring of the M^+ ion for the chlorinated diphenyl ethers with 2 chlorines more than the PCDF being monitored is also very useful and its absence must be a criterion for PCDF presence. One final identification criterion which is usually employed is the signal to noise ratio of 3:1 - 5:1 for the M^+ and $(M+2)^+$ ions. On the basis of the report it is not clear if these last 3 criteria were used.
- The fragment ion, M-COC1 of PCDD/PCDF was listed in Table A for monitoring. In TIC plots, different ions were used, e.g. in Figures 444, 446 and 448, the monitored ions are M-COC1-2 (M/e 257), M-COC1 (M/e 291) and M-COC1+2 (M/e 329) respectively. Evidently these ions had higher responses than M-COC1 in different congeners and were selected. For the purpose of consistency, Table A should be modified to list the individually monitored ions.

- The reviewer's surveyed limited EICP's but one notes that it was not clear how the area measurements for the peaks were obtained. Laboratory audit procedures reviewed this issue and found that procedures were in a state of flux at the time of the analytical work. The laboratory was moving from a partially to fully automated system. Checks of data showed the results to be consistent for either approach.
- Laboratory clean-up and analysis procedures differ and these differences were readily apparent in one set of review comments:
 - the reviewers' laboratory uses an acid clean-up on solid samples;
 - the laboratory does not use the water wash step 3a and 3b in Appendix A;
 - accelerating voltage of 4 Kv seemed high in their experience, and they suggested that it could lead to interferences.
- The reviewers questioned the concentration and sample splitting procedure for separate analysis of PCDD/PCDF in light of 2A2-17 filter data which provides both PCDD and PCDF data on the same data plot. They also suggest that the wording of the section concerning spiking (pg. 12 and 13 Sec. 6.6 Appendix A) requires a change in line 4 pg. 13 to replace "internal" with "native" to bring the modifiers into line. The procedure is agreed to, the wording is misleading.

Finally, several anomalies were uncovered. These relate chiefly to data presented for the ratio of 332 ion (C_{13} -TCDD) and the 328 ion (C_{17} -TCDD) and the reported recovery. In most cases a good agreement exists however for:

- 2A2 impinger, the $13C_{12}$ -TCDD recovery was reported as 93% yet the EICP's show a ratio of $332/328 = 33\%$;
- 2D2 sample shows 95% recovery of $13C_{12}$ -TCDD but a $332/328$ ratio of 26%;
- EICP's for sample 2D1 shows analysis at two different times and 72 and 14% ratios with a reported 73% recovery rate; and,
- $37Cl_4$ -HpCDD and $37Cl_4$ -TCDD responses show similar discrepancies for 2D2 - 1st impinger and 2A2 impinger samples while the others checked appear to provide internal consistency.

A subsequent discussion with the senior analyst in the laboratory revealed that different injection volumes were utilized for these samples and the detailed procedure had not been documented in the report. The reviewers comments serve to highlight missing information in the report.

On the whole the external reviewers thought the EICPs were very good chromatograms with good resolution and peak shape. Example chromatograms are contained in Appendix B.

4.3.3 Internal Laboratory Quality Control

The ultimate objective of the internal QA/QC procedures applied to the laboratory portion of a study is to ensure that the data produced by individual analysis method are complete, of highest possible quality and reported with information on accuracy and precision of analysis.

For any environmental measurement the usefulness of the measurement data depends upon the extent to which the quality of the data is known. It is therefore important to establish an internal quality control program and document the precision and accuracy of the data. While not specifically undertaken for this project, the data produced by the laboratory does

provide some means of checking quality. The principles of QC checks are presented before presenting the results for this study.

Quality Control Checks

Quality control samples are analyzed in the same way as field samples and interspersed with the field samples for analysis. The results of analyzing the QC samples are used to document the validity of the data and to control the quality of the data within pre-determined tolerance limits. QC samples include blank samples, analytical replicates and spiked samples.

Blank Samples

These are analyzed to assess possible contamination from the field and/or laboratory, so that corrective measures may be taken, if necessary. Blank samples include field blanks, method blanks and reagent blanks.

FIELD BLANKS - are exposed to field and sampling conditions and analyzed to assess possible contamination from the field.

METHOD BLANKS - are prepared in the laboratory and are analyzed to assess possible laboratory contamination (one for each lot of samples analyzed).

REAGENT AND SOLVENT BLANKS - are prepared in the laboratory and analyzed to determine the background levels of contamination in the reagents or solvents used in an analysis.

Analytical Replicate

Replicate analyses of specific samples are performed to determine the analytical precision or to check on the validity of anomalous samples.

Spiked Samples

All samples should be spiked with one or more selected surrogate compounds prior to extraction and analysis. The data on surrogate concentration are used to calculate the recovery of surrogate compounds as one measure of the accuracy of the sample preparation and analysis procedures.

Precision

Precision is defined as a measure of mutual agreement among individual measurements of the same property. Precision may be expressed in terms of the following parameters:

- **Analysis of Standards:** One of the QA objectives should be that the correlation coefficient for each calibration curve (including all data points for standards analyzed subsequent to the most recent recalibration of the instrument) be greater than some specified value (e.g. 0.9, 0.99).
- **Analysis of Replicate Samples:** Another QA objective should be that the results of laboratory replicate samples be within specified limits when at least three replicates are analyzed. A final QA objective should be that the relative standard deviation for analysis of surrogate compounds (internal standards) in replicate samples be within specified limits. At least 10 percent of all analysis performed should be triplicate QC checks.

The estimate of precision for a series of replicate measurements is expressed as relative standard deviation (RSD):

$$\text{RSD (\%)} = \frac{\text{SD}}{C} \times 100$$

$$\text{where SD} = \text{standard deviation} = \sqrt{\frac{\sum_{i=1}^n (C_i - \bar{C})^2}{n-1}}$$

\bar{C} = mean concentration for the sample set.

The standard deviations calculated should be compared with the goals identified.

Accuracy

Accuracy is defined as the degree of agreement of a measurement, or average of measurements, with an accepted reference or true value (US EPA, 1984). Generally, the accuracy is determined using reference materials of the highest known purity for calibrations and spiking. Accuracy may be expressed in terms of the following parameters:

- **Reference Materials:** All reference materials used as calibration standards or surrogate compounds should be of the highest documented purity;
- **Instrument Performance:** Each instrument must be checked each day samples are analyzed to demonstrate performance. One of the QA objectives should be that the absolute instrument response (e.g. area counts/ng injected for standards or surrogate compounds in a GC/MS analysis) be within a stated percentage of comparable measurements made subsequent to the most recent calibration of the instrument.
- **Recovery of Surrogates:** Surrogate compounds are usually stable isotopically labelled standards which are added at the beginning of the sample preparation/analysis scheme and quantified at the same

time as the native analyte. Recovery data should be reported with the sample data.

The recovery of a surrogate compound is defined as:

$$\text{RECOVERY (\%)} = \frac{C_s \times V_s \text{ (or } W_s) \times 100}{Q_s}$$

where C_s = measured concentration of surrogate compound in sample,
 $V_s(W_s)$ = total volume (or weight) of sample to which the surrogate was added,
 Q_s = quantity of surrogate added to the sample.

The mean and standard deviation of the recovery data should be compiled on a cumulative basis for each surrogate compound in each type of sample matrix.

4.3.4 Review of Present Data

The internal laboratory QA/QC procedures performed during the analysis of the field samples included:

- the analysis of field blanks (blank train - 2E1, acetone prewash-2D and toluene prewash-2D);
- the analysis of method blanks with each batch of samples processed;
- the addition of three isotopically-labelled internal standards to each sample prior to processing ($^{13}\text{C}_{12}$ -2,3,7,8-TCDD; $^{37}\text{Cl}_4$ -1,2,3,4,6,7,8-HpCDD; $^{13}\text{C}_{12}$ -OCDD); and
- the construction of calibration curves.

Unfortunately, due to cost, no duplicate or replicate organic analyses were performed.

The field blank data are shown in Table 4.3-1. For the most part, the quantities of PCDDs and PCDFs found in the blanks are less than the detection limits. Measurable quantities are observed for HpCDD and HpCDF and OCDDs and OCDFs. These quantities are negligible compared to the total PCDD and PCDF levels measured in the field samples.

The recovery data of the isotopically labelled internal standards can be used to determine the accuracy of the sample preparation and analysis procedures. Numerical QA objectives for accuracy of analysis procedures have been developed (Harris, 1984) based on previous experience in applying comparable procedures to a variety of complex sample matrices. The objectives for internal standards set by Harris are:

	<u>Mean</u>	<u>Standard Deviation</u>
Aqueous Liquids	>70%	<30%
Organic Liquids (Stack gas samples)	>50%	<40%

To evaluate the analytical results from this project the mean and standard deviation of the recovery data for each internal standard in each of the sample matrices was determined and compared to the numerical QA objective described above. The recovery data for each of the internal standards is presented in Tables 4.3-2 to 4.3-4 and indicates that the analytical methodology applied, and the results obtained, are acceptable.

TABLE 4.3-1

**PCDD and PCDF Sample Blanks
(ng per Sample) Uncorrected for Recovery**

Run	Matrix	PCDDs					PCDFs				
		TCDD	PeCDD	HxCDD	PcCDD	OCDD	TCDF	PeCDF	HxCDF	HpCDF	OCDF
2D	Acetone Prewash	<.05	<.07	<.16	.40	1.4	<.05	<.07	<.07	.40	.40
2D	Toluene Prewash	<.05	<.05	<.08	<.13	.50	<.05	<.05	<.09	.40	.40
2E1	Particulate Filter, Toluene Probe & Nozzle Rinse Combined	<.35	<.15	<.66	.44	1.3	<.26	<.22	<.40	1.3	1.5
2E1	Acetone Probe and Nozzle Rinse	<.05	<.10	<.25	1.4	3.0	<.05	<.10	<.20	1.2	.80
2E1	XAD Trap Front	<.10	<.15	<.20	<.30	.50	<.10	<.15	<.15	<.40	<.50
2E1	Impinger Water Acetone & Toluene Impinger Rinses Combined	<.20	<.50	<.80	<.50	<1.5	<.20	<.50	<.80	<.70	<1.5

TABLE 4.3-2

**Internal Standard
% Surrogate Recovery**

SURROGATE: 2,3,7,8 TCDD

MATRIX	TRAIN	n	max	min	mean	Std. Dev.	% RSD
Particulate Filter, toluene probe and nozzle rinse combined	Method 5	7	85	57	76	10	3
Acetone probe and nozzle rinse	Method 5	7	100	76	89	8	9
XAD	Method 5	7	88	68	79	7	9
Impinger Solutions (2) Acetone and toluene impinger rinses combined	Method 5	7 6	95 95	15 67	71 80	26 10	37 12
Filter	Method 17	2	75	74	74.5		
Impinger solutions acetone & toluene. Probe & nozzle rinses, acetone and toluene impinger rinses combined	Method 17	2	93	82	87.5		
XAD Traps	Method 17	3	86	74	81		
Filter	Multi-cyclone	4	95	71	85	10	12
Mc IV	Multi-cyclone Stage 4	4	91	77	82	6	7
Mc I	Multi-cyclone Stage 1	4	81	38	60	23	38

TABLE 4.3-3

**Internal Standard
% Surrogate Recovery**

SURROGATE: 2,3,4,6,7,8 HpCDD

MATRIX	TRAIN	n	max	min	mean	Std. Dev.	% RSD
Particulate Filter, toluene probe and nozzle rinse combined	Method 5	7	100	49	75	17	23
Acetone probe and nozzle rinse	Method 5	7	100	78	94	9	9
XAD	Method 5	7	100	62	82	15	18
Impinger Solutions (2) Acetone and toluene impinger rinses combined	Method 5	7 6	100 100	11 55	71 81	32 19	45 23
Filter	Method 17	2	78	68	73		
Impinger solutions acetone & toluene. Probe & nozzle rinse, acetone and toluene Impinger rinses combined	Method 17	2	100	71	85.5		
XAD Traps	Method 17	3	90	40	66		
Filter	Multi-cyclone	4	100	91	96	5	5
Mc IV	Multi-cyclone Stage 4	4	100	81	92	9	10
Mc I	Multi-cyclone Stage 1	4	80	46	63	15	24

TABLE 4.3-4

**Internal Standard
% Recovery**

SURROGATE: 1,3 OCDD

MATRIX	TRAIN	n	max	min	mean	Std. Dev.	% RSD
Particulate Filter, toluene probe and nozzle rinse combined	Method 5	7	100	40	76	23	30
Acetone probe and nozzle rinse	Method 5	7	100	72	94	11	12
XAD	Method 5	7	100	36	81	24	30
Impinger Solutions (2) Acetone and toluene impinger rinses combined	Method 5	7	95	13	70	29	41
		6	95	60	79		
Filter	Method 17	2	75	68	71.5		
Impinger solutions acetone & toluene. Probe & nozzle rinse, acetone and toluene impinger rinses combined	Method 17	2	99	80	89.5		
XAD Traps	Method 17	3	100	42	67		
Filter	Multi-cyclone	4	100	80	95	10	10
Mc IV	Multi-cyclone Stage 4	4	100	81	93	9	10
Mc I	Multi-cyclone Stage 1	4	77	56	63	10	17

The laboratory report notes that since the internal standards are added prior to the sample preparation/analysis procedures and quantified at the same time as the native analytes, they do reflect the losses of PCDDs and PCDFs incurred during the course of sample handling and analysis. The internal standards may not correct for the effects of the sample matrix (i.e. the internal standard added may not penetrate the sample and become sorbed in the same fashion as the PCDD and PCDF incorporated in the particulates resulting from combustion). In addition the procedures assume that the chemical/physical properties of the labelled isomers are parallel to and represent several isomers in the same class or other classes. The external reviewers concur, however, that this approach currently represents the best methods for assessing the efficiency of the overall analytical procedure.

4.4 Summary of QC/QC Issues

While better placement of sampling locations at B and C would be desirable the facility's layout would not allow this and the results are the best that could be obtained. The particulate matter and PCDD/PCDF concentrations measured at all points are not considered to be seriously compromised by the sample locations.

Sample train configuration was considered acceptable and comparable to other methods although the system has some limitations for clean-up of the sample train components.

The length of sampling chosen was too short to adequately represent the system's operating characteristics but the short duration revealed some interesting characteristics of PCDD/PCDF emissions from combustion processes that suffer upsets.

The leak check procedures followed by the sample team were poorly documented and lead directly to discounting the results of the 2C1 sampling run.

Sample recovery procedures have been changed since the time of the project and it is recommended that the new procedures be adopted for future work. Difficulties in this area only reduce the total emission factor for all sample locations but the degree of this reduction cannot be quantified. This is not a serious impediment to using this data.

All laboratory procedures were found to be above reproach, with the possible exception of sample splitting which is realized to be a necessary expediency, and the work was considered to be excellent by all who reviewed it. No evidence was found to indicate any problems with sample labelling nor the transportation of data. The results of the laboratory analysis are the best that could be expected. In future tests QA/QC procedures including more analyses should be undertaken, and the results compared to predetermined standards. Sample handling and shipping procedures should be tightened up for future studies.

5.0 PRESENTATION OF TESTING RESULTS

Plant operating data for the test periods on Oct. 14 and 15, 1983 is presented in Chapter 2. This chapter summarizes the results obtained from:

- the particulate and trace organic (PCDD/PCDF) sampling on Oct. 14, 1983; and
- the particle sizing runs on Oct. 15, 1983 during which samples for PCDD/PCDF analyses were collected.

As outlined in the previous chapter, the data have been completely recalculated from the raw information contained in the Part 1 Appendix of Cooper (1985).

The recalculated field data sheets for the 8 particulate sampling runs and the 7 particle sizing runs are contained in Appendix B. The results of the laboratory analyses along with sample chromatograms are provided in Appendix B.

The data presented in this section is expressed in a standardized form of mass per NM^3 @ 12% CO_2 . This is a dry gas flow rate at 32°F (0°C) and 29.92 inches Hg pressure. Cooper (1985) notes that even though excess lime is present in the flue gas train, this should not significantly influence the CO_2 levels. A comparison of flow rate data for standard dry cubic feet per minute (SDCFM) @ 12% CO_2 and SDCFM @ 7% O_2 shows good agreement further reducing any concern over errors arising from the 12% CO_2 correction procedure (Cooper, 1985).

Another convention is used in presenting the PCDD/PCDF data. The homologue classes, a group of isomers with the same degree of chlorination, are referred to by acronyms:

No. of Chlorine Atoms	Acronym	Example
4	T	1,4,7,8-TCDD
5	Pe	PeCDD
6	Hx	HxCDD
7	Hp	HpCDD
8	O	OCDD
1 through 8	P	PCDDs/PCDFs

as per NRCC (1981).

5.1 Stack Data

As part of the testing procedure, data on stack velocities, temperatures and gas concentrations were collected. This information is summarized in Table 5.1-1. for the particulate and PCDD/PCDF sampling runs. Similar data from the particle sizing runs is not available since this procedure does not include a traverse of the stack.

5.2 Particulate Matter Sampling Data

Particulate matter catch data is summarized in Table 5.2-1. The data is split into three categories with the filter and washings commonly referred to as the front half catch and the impingers as the back half catch.

Several comments are required to thoroughly explain the limitations of this information:

- original data in the Part 1 Appendix of Cooper (1985) shows that an acetone blank value of 1.0 mg was subtracted from all particulate

TABLE 5.1-1

Stack Conditions During Particulate Testing

PARAMETER	SAMPLE LOCATION AND TEST								
	A		B		C		D		
	1	2	1	2	1	2	1	2	
Time									
Start	2300	0350	2301	0357	2258	0402	2301	0353	
Stop	0040	0455	0013	0509	0041	0526	0031	0518	
Total Duration	60	60	72	72	67	70	72	72	
Average Velocity (fpm)	2575	2245	2445	2155	2975	2790	2940	2525	
Average Temperature (°F)	646	632	482	478	439	439	410	395	
Stack Pressure ("Hg)	29.88	29.88	29.69	29.69	29.69	29.69	29.25	29.25	
<u>Gas Data</u>									
Oxygen % (Dry)	11.0	12.22	11.7	12.4	14.0 ⁽¹⁾	14.1	14.0 ⁽¹⁾	14.6	
Carbon Dioxide % (Dry)	9.0	8.44	8.5	8.0	6.4 ⁽¹⁾	6.3	6.4 ⁽¹⁾	6.0	
Moisture %	34.7	27.88	37.1	30.7	NA (leak)	28.6	31.7	27.3	
<u>Volumetric Flow</u>									
ACFM	41754	36390	37445	33023	43871	41098	43340	37215	
Nm ³ /hr	20558	20049	20773	20225	29909	27030	27788	25816	
Nm ³ /hr @ 12% CO ₂	15418	14034	14714	13483	15951	14190	14820	12906	

Notes: (1) Estimated from CEM Data

TABLE 5.2-1

Particulate Catch Data Summary

Sample Location	Test Number	Sample Volume (Nm ³)	Catch (grams)			
			Filter	Washing	Impinger ³	Total
A	1	0.7952	2.41	NA ²	0.239	2.649
	2	0.6720	2.54	NA	0.426	2.966
B	1	0.7631	0.811	1.609	0.011	2.431
	2	0.7489	0.660	2.311	0.035	3.006
C	1	0.3 ¹	0.467	1.079	0.0274	1.5734
	2	0.8982	1.534	3.00	0.135	4.669
D	1	0.9650	0.005	0.009	0.0174	0.0314
	2	0.8012	0.008	0.011	0.205	0.224

- Notes:
1. A leak occurred during this run and the meter data was corrected for this leak.
 2. Not applicable since filter was in the stack.
 3. Does not include acetone blank correction.

catch data. This correction was not used for the data in Table 5.2-1. The 1 mg of residue from Train E1 represents not only the blank for residue in the reagent (acetone) but also material collected in the blank train. EPA Method 5 suggests that only distilled in glass acetone is appropriate and a residue greater than 0.001% should cause rejection of the reagent. Actual residue measured in 50 ml, assuming a density of 0.7857 g/ml, was 0.0005% or 0.2 mg for 39.3 g. This would suggest that the reagent was satisfactory. To supply a correction of this nature however assumes that 250 ml of acetone were utilized for each train clean-up. Data in the Brehm Laboratory report suggests that less than 250 ml were used for most clean-ups, and appropriate compensation data were thus not available.

- the use of filters in-stack at sample point A precludes the availability of probe washing samples for this location.
- on run 2C1 (C1 in Tables 5.1-1 and 5.1-2) a leak was reported near the end of the run. EPA Method 5 and the ASME protocol both suggest that such an occurrence should prompt a meter volume correction. Such a correction is defined by:

$$V_{\text{mcorr}} = [V_m - \sum_{i=1}^n (L_i - L_a) \theta_i - (L_p - L_a) \theta_p]$$

where V_m = meter reading volume

L_i = initial leakage rate (ft³/min.)

L_a = allowable leakage rate (0.02 ft³/min.)

θ_i = sample time between 2 successive component changes (minutes)

θ_p = sample time between final change and end of test (minutes)

L_p = post test leakage rate (ft³/min.)

if a component is changed in the train or without the summation term
if no components are changed.

Unfortunately the final leak check data for run 2C1 does not provide an indication of the leakage rate with the broken fitting; the reported post-test leakage rate is 1/4 of the allowable value.

Also noted on the data sheet is a significant change in meter volume at the mid-test port change; 36 minutes were consumed for the port change and nearly 2 cubic feet of gas passed through the meter. It would appear that the system had a leakage rate in excess of the allowable after the first traverse and the fittings were tightened until the leak stopped. This likely led to the subsequent ball-joint failure. Again no leakage rate data was provided.

Correction of the meter volume cannot be accomplished by using the formula given above since:

- the leakage rate after the first traverse is missing, and
- the leakage rate after the second traverse appears to be incorrect.

Cooper (1985) has provided a correction for the data by assuming that the particulate concentrations at C were similar for all runs. This suggests that the leakage rate was at least 0.37 SDCFM for the whole test run. The sample volume has been corrected by this value (24.8 DSCF) to retain the data for presentation only.

Particle sizing catch data are summarized in Table 5.2-2. The filter catch data for the baghouse outlet (D) location has been estimated as explained in the table. The particle sizing data do not include the back-half catch from the sampling train and any comparisons to the particulate monitoring data should be on the basis of front half catches (filter and washings) only.

TABLE 5.2-2

Particulate Size Data for Runs with PCDD/PCDF Analyses

Sample Location	Test Number	Sample Volume (Nm ³)	Catch (grams)			
			Filter	Cyclone IV	Cyclone I	Total
B	2	0.191	0.106	0.038	0.600	0.744
	3	0.128	0.088	0.041	0.423	0.522
C	2	0.200	0.200	0.189	0.245	0.634
	3	0.128	0.117	0.218	0.468	0.803
D	1	2.144	0.003 ¹	0.003	0.002	0.008

Notes: 1. Filter was partially burned and a portion was lost. An estimated value of 0.003 g was derived from the cascade impactor data in Cooper (1985).

5.3 Gaseous Sampling Results

Since the acid gases present in the stack can provide an indication of process operation and may be helpful in reviewing the trace organic data, HCl Table 5.3-1(a and b) and HF Table 5.3-2(a and b) data from the Cooper (1985) report are reproduced in this report. Also reproduced (Table 5.3-3) for reference purposes, is the NO_x data, but, as mentioned previously, these data were not collected with an EPA approved monitor.

5.4 PCDD/PCDF Analytical Data

5.4.1 Particulate Train Samples

As discussed in the methods section, various samples were returned to the laboratory for analyses of PCDD/PCDF concentrations. The results of these analyses are reported in Appendix B but are also summarized in the Table 5.4-1. These values represent the total quantity of PCDDs and PCDFs analysed in the train samples recovered in the field. No correction for blank train data is included in these values, however the blank train data (sample E1) are provided for comparison.

All totals were derived by summing the individual quantities for each train sample. In the case where sample quantities are reported as less than the detection limit, this limit was used for the summation process. If all train components yielded values less than the detection limit the total is shown with a less than symbol (<).

In all cases the totals arise from the analysis of only the front of the two XAD-2 cartridges, except for the 2A2 run where both cartridges were analysed. Data from this run shows approximately 5 percent of the total PCDD and PCDF recovered from this train was present on the second cartridge. Nearly 20% of the total of these components was found on the

TABLE 5.3-1(a and b)

HCl Data Summary

Date and Location	Time	Run No.	Test Method	Gas Composition (dry)		Concentration of Gaseous HCl, ppm _v	
				% CO ₂	% O ₂	Uncorrected	@ 12% CO ₂
Point A							
10/14	2300-0040	2A1	17	9.0	11.0	244	325
10/14	0350-0455	2A2	17	8.4	12.2	182	260
Point B							
10/14	2301-0013	2B1	5	8.5	11.7	10.0	14.1
10/14	0357-0509	2B2	5	8.0	12.4	4.2	6.3
10/15	0036-0106	3B1	Multiclone	8.9	11.1	1.41	19.0
10/15	0352-0437	3B2	Multiclone	8.2	12.0	16.2	23.7
10/15	0725-0755	3B3	Multiclone	6.8	13.2	66.5	117
Point C							
10/14	2258-0041	2C1	5	6.4	14.0 ⁽¹⁾	9.3 ⁽²⁾	17.5 ⁽²⁾
10/14	0402-0526	2C2	5	6.3	14.1	9.9	18.9
10/15	0036-0106	3C1	Multiclone	7.0	13.0	15.1	25.9
10/15	0352-0437	3C2	Multiclone	6.6	13.4	11.5	20.9
10/15	0722-0752	3C3	Multiclone	6.6	13.4	17.8	32.4
Point D							
10/14	2301-0031	2D1	5	6.4	14.0 ⁽¹⁾	3.3	6.2
10/14	0353-0518	2D2	5	6.0	14.6	7.1	14.2
10/15	2058-0458	3D1-M	Multiclone	6.7	13.4	4.23	7.6
10/15	2120-0520	3D1-A	Andersen	6.7	13.4	4.05	7.3
Removal Efficiency							
			Percent		Averages		
Point A to D		Averaged Data		97.0	Point A	213	293
Point A to D		Runs 2A1 - 2D1		98.1	Point B	22.2	36.0
		Runs 2A2 - 2D2		94.6	Point C	13.1	26.4
		Runs 4A3 - 4D3		99.1	Point D	4.7	8.8

1. Composition estimated from CEM Data.
2. Leak - corrected values, not included in averages.

Note: Points B and C concentrations may be affected by excess lime in the sampling trains (see text)

TABLE 5.3-1(a and b)

HF Data Summary

Date and Location	Time	Run No.	Test Method	Gas Composition (dry)		Concentration of Gaseous HCl, ppmv		
				% CO ₂	% O ₂	Uncorrected	@ 12% CO ₂	
<u>Point A</u>								
10/14	2300-0040	2A1	17	9.0	11.0	1.3	1.51	
10/14	0350-0455	2A2	17	8.4	12.2	0.44	0.63	
<u>Point B</u>								
10/14	2301-0013	2B1	5	8.5	11.7	0.05	0.07	
10/14	0357-0509	2B2	5	8.0	12.4	0.02	0.03	
10/15	0036-0106	3B1	Multiclone	8.9	11.1	0.33	0.44	
10/15	0352-0437	3B2	Multiclone	8.2	12.0	0.06	0.09	
10/15	0725-0755	3B3	Multiclone	6.8	13.2	0.25	0.44	
<u>Point C</u>								
10/14	2258-0041	2C1	5	6.4	14.0 ⁽¹⁾	0.07 ⁽²⁾	0.15 ⁽²⁾	
10/14	0402-0526	2C2	5	6.3	14.1	0.03	0.06	
10/15	0036-0106	3C1	Multiclone	7.0	13.0	0.42	0.72	
10/15	0352-0437	3C2	Multiclone	6.6	13.4	0.32	0.58	
10/15	0722-0752	3C3	Multiclone	6.6	13.4	0.22	0.40	
<u>Point D</u>								
10/14	2301-0031	2D1	5	6.4	14.0 ⁽¹⁾	0.42	0.79	
10/14	0353-0518	2D2	5	6.0	14.6	0.49	0.98	
10/15	2058-0458	3D1-M	Multiclone	6.7	13.4	0.36	0.64	
10/15	2120-0520	3D1-A	Andersen	6.7	13.4	0.22	0.39	
<u>Removal Efficiency</u>				<u>Percent</u>		<u>Averages</u>		
Point A to D		Averaged Data		34.6		Point A	0.78	1.07
						Point B	0.14	0.21
						Point C	0.25	0.44
						Point D	0.37	0.70

1. Composition estimated from CEM Data.

2. Leak - corrected values, not included in averages.

Note 1: Points B and C concentrations may be affected by excess lime in the sampling trains (see Cooper, 1985).

Note 2: Limit of precision for HF analyses is estimated at ± 0.5 ppmv with the sampling procedures used.

TABLE 5.3-2

NO_x
From the Facility's Continuous Emission Monitor After Point D

<u>Date and Time</u>		<u>@ 12% O₂</u>	<u>@ 7% O₂</u>	<u>@ 3% O₂</u>	<u>12% CO₂ (1)</u>
10/14	1900	110	172	221	153
	2000	95	148	191	133
	2100	90	141	181	126
	2200	150	234	302	209
	2300	110	172	221	153
	2400	160	250	322	223
	0100	175	273	352	244
	0200	110	172	221	153
	0300	120	187	241	167
	0400	70	109	141	98
	0500	140	219	282	195
	0600	85	133	171	119
	0700				
	Daily Average		118	184	237
10/15	1900	80	125	161	112
	2000	165	258	332	230
	2100	115	180	231	160
	2200	140	219	282	195
	2300	140	219	282	195
	2400	90	141	181	126
	0100	45	70	91	63
	0200	140	219	282	195
	0300	130	203	261	181
	0400	140	219	282	195
	0500	120	187	241	167
	0600	110	172	221	153
	0700	150	234	302	209
0800	150	234	302	209	
Daily Average		122.5	191	246	171

(1) Assume 8.6 % CO₂ with 12% O₂

TABLE 5.4-1

Total PCDD/PCDF Quantities in Train Samples (ng)

Run/ Component	Homologue						
	T	Pe	Hx	Hp	O	P	
2A1	CDD	43.6	43.6	26.0	7.1	2.8	123.1
	CDF	190.1	69.7	16.7	4.9	2.1	283.5
2A2	CDD	93.5	44.7	29.2	13.3	4.0	184.7
	CDF	1427	399	59.6	12.8	2.6	1901
2B1	CDD	59.2	54.4	34.2	9.0	4.5	161.3
	CDF	181.3	102.9	16.0	6.3	<2.2	308.7
2B2	CDD	136.2	81.3	32.6	14.7	5.4	270.2
	CDF	1589	637.6	82.5	9.9	3.8	2322.8
2C1*	CDD	26.0	21.0	15.5	3.9	6.9	73.3
	CDF	89.5	34.1	6.1	4.5	5.0	139.2
2C2	CDD	95.7	64.8	21.2	6.4	4.2	192.3
	CDF	1050.0	461.0	39.1	5.7	3.6	1459.4
2D1	CDD	403.2	223.9	104.5	10.9	9.6	752.1
	CDF	194.3	89.4	15.5	3.2	<2.2	304.6
2D2	CDD	290.1	325.2	323.2	79.3	35.7	1053.5
	CDF	1235.7	439.1	57.9	14.0	5.1	1751.8
2E1	CDD	<0.7	<0.9	<1.91	2.44	6.3	12.25
	CDF	<0.61	<0.97	<1.55	3.6	4.3	11.03

* Included even though train had a major leak.

front cartridge of this train. Other front cartridges contained between 1.0 and 8.8 percent of the total PCDD and 1.0 and 12.6 percent of the total PCDF. This data would suggest that:

- breakthrough on most of the trains was unlikely to be a major contributor to low readings for PCDD/PCDF; and,
- the system is relatively successful at trapping PCDD/PCDF components in the exhaust gas stream.

One other aspect of the sample data is the apparent distribution in the various train components. The MM5 train results show that between less than 1% and 25% of the total trace organic catch was found in the filter and probe section. In all but the D sample location this proportion is a significantly smaller portion of the total PCDD/PCDF values than the dust loading of these components is of the total dust loading. This could suggest that a high proportion of PCDD/PCDF materials are present in the gaseous state until removed in the fabric filter. This assumption is tenuous as:

- a) the train and the allocation of a specific sample location in the train to a specific phase in the stack is not verified as of yet; and,
- b) some stripping may occur as the material sits in the sampling filter at the elevated temperatures used for sampling.

5.4.2 Particle Size Fraction

Table 5.4-2 presents the results of PCDD/PCDF analysis of size fractions captured in the cyclone sampler used at locations B, C and D. These numbers are obtained by converting the ppb analysis values in Appendix B to nanograms on the basis of the weight of particulate in the various sampler fractions as outlined in Table 5.2-2.

TABLE 5.4-2

PCDD/PCDF Distribution Data for Particle Size Runs (ng)

Run/ Component	Homologue						
	T	Pe	Hx	Hp	O	P	
3B2 CDD	FILTER	<0.1	<0.08	<0.21	0.23	<0.21	0.83
	CIV	0.17	<0.08	<0.27	0.13	<0.15	0.80
	CI	0.90	0.36	<0.21	<0.30	<0.24	2.01
	TOTAL	1.17	0.52	<0.68	0.66	<0.60	3.64
3B2 CDF	FILTER	<0.1	<0.21	<0.16	<0.1	<0.21	<0.78
	CIV	0.22	<0.10	<0.08	<0.08	<0.15	0.62
	CI	<1.5	<0.42	0.09	<0.24	<0.30	4.8
	TOTAL	0.92	<1.81	<1.32	<0.78	<1.56	6.39
3B3 CDD	FILTER	<0.09	<0.09	<0.13	<0.10	<0.22	<0.63
	CIV	<0.21	<0.29	<1.03	<0.21	<0.29	<2.03
	CI	18.6	10.2	4.7	0.42	<0.42	34.34
	TOTAL	18.9	10.58	5.86	0.73	<0.93	37.0
3B3 CDF	FILTER	<0.09	<0.22	<0.13	<0.09	<0.18	<0.71
	CIV	<0.21	<0.41	<0.41	<0.21	<0.25	<1.49
	CI	<0.21	<0.21	<0.34	<0.21	<0.42	<1.39
	TOTAL	<0.51	<0.84	<0.88	<0.51	<0.85	<3.59
3C2 PCDD	FILTER	<0.06	<0.10	<0.20	0.10	0.10	0.56
	CIV	<0.13	<0.08	<0.19	<0.08	<0.19	<0.67
	CI	0.37	0.25	0.25	<0.12	0.25	1.24
	TOTAL	0.56	0.43	0.64	0.30	0.54	2.47
PCDF	FILTER	<0.10	<0.14	<0.10	<0.10	<0.20	<0.64
	CIV	<0.09	<0.19	<0.09	<0.09	<0.19	<0.65
	CI	<0.12	<0.20	<0.15	<0.12	<0.22	<0.81
	TOTAL	<0.31	<0.53	<0.34	<0.31	<0.61	<2.1
3C3 PCDD	FILTER	<0.08	<0.18	<0.29	<0.29	<0.47	<1.31
	CIV	<0.07	0.44	0.22	<0.11	<0.11	0.95
	CI	7.5	3.5	3.0	<0.47	<0.70	15.17
	TOTAL	7.65	4.12	3.51	<0.87	<1.28	17.43
PCDF	FILTER	<0.12	<0.18	<0.29	<0.35	<0.47	<1.41
	CIV	<0.07	<0.15	<0.11	<0.07	<0.11	<0.51
	CI	<0.47	<0.70	<0.70	<0.94	<0.70	<3.51
	TOTAL	<0.66	<1.03	<1.10	<1.36	<1.28	<5.43
3D1	CDD	<0.05	<0.06	<0.15	<0.15	<0.35	<0.76
	CDF	<0.05	<0.05	<0.15	<0.12	<0.20	<0.57

5.4.3 Process Samples

Three samples of process wastes were analysed for PCDD/PCDF. These were:

- fabric filter flyash from Oct. 14;
- dry scrubber flyash from Oct 14; and,
- a combined fabric filter/dry scrubber flyash sample.

Results reported in ppb are presented in Appendix B and for comparison purposes these results are repeated in Table 5.4-3.

5.5 Derived Results

The data presented in the previous sections can be utilized to derive potential emission rate data and to examine the changes in distribution and concentration of PCDDs/PCDFs that occur throughout the system. A summary of this data follows. The emission data has been corrected to 12% CO₂ and all concentration information is expressed in g/Nm³.

Particulate emission data is provided in Table 5.5-1.

PCDD/PCDF concentration data for the particulate train samples is summarized by homologue in Table 5.5-2.

The concentration data determined from particle sizing runs and the size distribution of the particulate matter at the three test locations are provided in Table 5.5-3. Homologue distribution data for these tests is provided in Table 5.5-4.

TABLE 5.4-3

PCDD/PCDF Concentrations in Process Waste Samples (ng/g or ppb)

Sample/ Component	Homologue					
	T	Pe	Hx	Hp	O	P
Combined Quench Reactor and Fabric Filter						
CDD	28	29	27	1.6	<0.70	86.3
CDF	5.4	3.8	1.3	0.4	0.4	11.3
Quench Reactor						
CDD	0.40	<0.15	<0.20	<0.20	<0.50	<1.45
CDF	<0.10	<0.10	<0.10	<0.15	<0.50	<0.95
Fabric Filter						
CDD	20	9.5	9.0	1.5	<0.70	40.7
CDF	7.5	1.9	0.60	0.20	<0.50	10.7

TABLE 5.5-1
Particulate Concentration Data

Sample/ Location	Test Number	CO ₂ %	Concentration (g/Nm ³)			Normalized Concentration (g/Nm ³ @12 % CO ₂)	
			Front	Back	Total	Total	Front Half
A	1	9.0	3.03	0.30	3.33	4.44(19) ¹	4.04(17)
	2	8.4	3.78	0.63	4.41	6.30(25)	5.40(21)
B	1	8.5	3.17	0.01	3.18	4.50(18)	4.49(18)
	2	8.0	3.97	0.05	4.02	6.02(23)	5.95(22)
C	1		not available due to leak in train				
	2	6.3	5.05	0.15	5.20	9.90(39)	9.61(38)
D	1	6.4	0.015	0.018	0.033	0.06(0.2)	0.03(0.1)
	2	6.0	0.02	0.26	0.28	0.56(2)	0.04(0.1)

Notes: 1. Values in parenthesis represent g/s emission values.

TABLE 5.5-2

PCDD/PCDF Concentration Data (ng/Nm³ @ 12 % CO₂)

Run	%CO ₂	Component	Homologue					
			T	Pe	Hx	Hp	O	P
2A1	9.0	CDD	73	73	44	12	5	207
		CDF	319	117	28	8	3	475
2A2	8.4	CDD	199	95	62	28	8	392
		CDF	3034	848	127	27	5	4041
2B1	8.5	CDD	110	101	63	17	8	299
		CDF	335	190	30	12	<4	571
2B2	8.0	CDD	273	163	65	29	11	541
		CDF	3183	1277	165	20	8	4653
2C2	6.3	CDD	203	137	45	14	9	408
		CDF	2227	766	83	12	8	3096
2D1	6.4(1)	CDD	783	435	203	21	19	1461
		CDF	378	174	30	6	<4	592
2D2	6.0	CDD	724	812	807	198	89	2630
		CDF	3085	1096	144	35	13	4373

(1) estimated from CEM data.

TABLE 5.5-3

Size Ranges and Concentration Data Particle Size Sampling

Run	CO ₂ %	Size (μm)	Proportion %	Concentration Data (@ 12 % CO ₂)		
				Particulate (g/Nm ³)	PCDD (ng/Nm ³)	PCDF (ng/Nm ³)
3B2	8.2	<1.5	81	4.6	6	<6
		2.87	5	0.3	6	5
		12.93	14	0.8	<15	<37
		TOTAL	100	5.7	28	49
3B3	6.8	<1.3	77	5.9	9	<10
		2.64	7	0.5	28	<21
		12.33	16	1.2	473	<19
		TOTAL	100	7.6	510	<49
3C2	6.6	<1.1	39	2.3	5	<6
		2.20	30	1.7	6	<6
		11.03	31	1.8	11	<7
		TOTAL	100	5.8	22	<19
3C3	6.6	<1.3	58	6.6	<19	<20
		2.60	27	3.1	<13	<7
		12.13	15	1.7	215	<50
		TOTAL	100	11.4	250	<77
3D1	6.7	<1.15	27	0.0017	NA	NA
		2.30	40	0.0025	NA	NA
		11.25	33	0.0021	NA	NA
		TOTAL	100	0.0063	<0.63	<0.48

TABLE 5.5-4

**Homologue Distribution Total Catch Particle Sizing
(ng/Nm³ @ 12 % CO₂)**

Run	Component	T	Pe	Homologue		O	P
				Hx	Hp		
3B2	CDD	9.0	4.0	<5.0	5.0	<5.0	28
	CDF	7.0	<14.0	<10.0	<6.0	<12.0	49
3B3	CDD	260	145	81	10	<13	510
	CDF	<7	<12	<12	<7	<12	<49
3C2	CDD	5	4	6	3	6	22
	CDF	<3	<5	<3	<3	<5	<19
3C3	CDD	110	59	50	<12	<18	250
	CDF	<9	<15	<16	<20	<18	<78
3D1	CDD (pg/Nm ³)	<50	<60	<150	<150	<350	<760
	CDF (pg/Nm ³)	<50	<50	<150	<120	<200	<570