AP-42 Section 11.6
Reference 65
Report Sect. 4
Reference 78

EVALUATION OF WASTE COMBUSTION IN A DRY-PROCESS CEMENT KILN AT LONE STAR INDUSTRIES, OGLESBY, ILLINOIS

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Contract No. 68-02-3149
Work Assignment No. 11-1

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CINCINNATI, OHIO 45268

December 1984

OVER 10 TPY, HAPs

FULL TEST REPORT

NOTICE

This document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Hazardous Waste Engineering Research Laboratory (HWERL) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This report describes a demonstration program on hazardous waste incineration in a dry process Portland Cement Kiln. It will be used to support technically defensible regulations in the evaluation of the future effort to develop the technology. The regulatory agencies as well as cement plants contemplating the use of waste fuels will find the results presented in this report helpful. Further information on this subject may be obtained by contacting the Thermal Destruction Branch, Alternative Technologies Division (HWERL).

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ABSTRACT

The incineration of chlorinated and other liquid organic wastes was investigated in a 6-day test program at Lone Star Industries in Oglesby, Illinois. The test program included monitoring for principal organic hazardous constituents (POHCs) in the waste and emissions, products of incomplete combustion, particulate matter, SO_2, NO_x, HCl, and total hydrocarbons. The fate and distribution of chlorine and metals were also determined.

The test results for POHCs showed that the cement kiln was generally capable of achieving a destruction efficiency of 99.99 percent or greater. Most of the additional chlorine was removed with the waste dust, and an increase in HCl emissions was observed as the chlorine entering the kiln increased. Waste combustion appeared to change the distribution of lead such that a higher percentage of the lead was removed with the waste dust. Particulate matter comparisons were inconclusive because of a malfunctioning electrostatic precipitator. NO_x emissions increased slightly; however, emissions of SO_2 and total hydrocarbons were not significantly different during the waste burn. Polychlorinated dibenzodioxins and dibenzofurans were not detected in the stack emissions during any of the tests.

This report was submitted in fulfillment of Contract No. 68-02-3149 (Work Assignment 11-1) under the sponsorship of the U.S. Environmental Protection Agency. This report covers a period from November 1983 to December 1984 and work was completed as of December 1984.

CONTENTS

CONTENTS (continued)

FIGURES

TABLES (continued)

ACKNOWLEDGMENTS

The authors gratefully acknowledge the assistance provided by corporate and plant personnel of Lone Star Industries at Oglesby. Their assistance in arranging and conducting the test was invaluable to its completion. The guidance, support, and experience supplied by Robert Mournighan, U.S. Environmental Protection Agency, is also appreciated. The hard work provided by the Engineering Science field sampling crew in the cold weather is also gratefully acknowledged.

1.0 INTRODUCTION

1.1 PROGRAM BACKGROUND AND OBJECTIVES

Preliminary feasibility studies and tests have indicated that some industrial facilities with high-temperature combustion processes may provide a cost-effective alternative to the disposal of hazardous wastes in incinerators. These industrial processes have the potential for recovering the heating value of the waste, removing chlorides, and providing a destruction and removal efficiency (DRE) equivalent to hazardous waste incinerators. However, insufficient data are available to establish standards for waste/facility combinations, waste feed rates, air pollution control requirements, or facility operating conditions to assure environmental protection equivalent to that provided by regulations for dedicated land-based incinerators.

Several industrial processes can provide temperatures and residence times similar to those required for hazardous waste incinerators. Examples include cement, lime, and aggregate kilns, industrial boilers, and blast furnaces. Cement and lime (calcining) kilns are of particular interest because of their potential for reducing the environmental impact of disposal in a cost-effective manner. The promising characteristics of cement kilns include:

- Existing high-temperature combustion process at 1,350° to 1,650° C (2,500° to 3,000° F) with a gas residence time on the order of seconds.
- Large number of plants scattered throughout the country, which could potentially handle large quantities of combustible hazardous waste liquids.
- Large-scale equipment in place, including process control and pollution control; relatively small capital investment required.
- Instantaneous temperature excursions unlikely because of the huge thermal inertia.
- The alkaline environment in a cement kiln absorbs HCl from chlorinated waste combustion.

- Kilns are operated underdraft (slight vacuum); therefore, there would be little outward leakage of fumes, mostly inward leakage of air.
- Ash may be incorporated into the product.
- Energy savings from substitution of waste fuel for oil, coal, or gas.

Several calcining kilns are either currently cofiring wastes as supplemental fuel or have expressed an interest in obtaining the necessary permits to do so. The cement industry has an economic incentive to use the wastes as a low-cost fuel because 65 percent of the direct cost of cement production is energy cost, and waste solvents have been used to supply 40 percent or more of the kiln's energy requirements. Therefore, the initial focus of the project was to determine which plants had permits for either burning the waste routinely or permits for conducting a trial burn, and were willing to cooperate with our research program.

A comprehensive test program was developed to obtain the data that were required to evaluate the environmental impact of hazardous waste destruction in cement kilns. The test program was designed to:

- Calculate DREs of principal organic hazardous constituents (POHCs).
- Compare baseline operation (no waste fuel burned) to the operation with waste fuel.
- Determine if products of incomplete combustion (PICs) are formed and, if so, identify them.
- Determine the fate and distribution of metals.
- Measure the effect of fuel-burning on HCl emissions, and determine the fate and distribution of chlorine through a material balance.
- Examine the effects of waste fuel burning and process conditions on other pollutants (e.g., particulate matter, NO_x, SO_2, total hydrocarbons).
- Relate the kiln's operating parameters and process conditions to emissions and continuous monitoring results.

The specific sampling and analysis methods that were used to accomplish these objectives are discussed in detail in later sections of this report.

1.2 PLANT SELECTION AND SAMPLING OBJECTIVES

Lone Star Industries (LSI) had expressed an interest in obtaining the necessary permits to cofire wastes as supplemental fuel in their cement kiln at Oglesby, Illinois. Through arrangements with EPA Region 5, LSI arranged for a trial burn to collect preliminary data on the possible effects of waste fuel combustion. LSI agreed to spike the waste fuel with Freon 113 (1,1,2-trichloro-1,2,2-trifluoroethane) to provide additional research information on the DRE of a compound that is difficult to destroy by combustion. The Oglesby plant also provided the opportunity to test a representative dry-process cement kiln.

A pretest meeting was held with LSI representatives to discuss the scope of the test. A survey was made on November 16 and arrangements were made to start testing in early December. Delays were experienced as temporary storage facilities were prepared and arrangements were made to purchase an adequate quantity of waste fuel. Two days of baseline testing were conducted on December 13 and 14, 1983. Problems were experienced with the waste fuel handling system; consequently, testing during waste fuel combustion was delayed until December 17 and 18. Because of the bitter cold weather, the test objectives were changed to collect data at 25-, 35-, and 45-percent replacement rates. The runs for 25- and 35- percent replacement rates were conducted on December 17, and the 45-percent rate was used the next day.

The test program included (1) the sampling and analysis of stack gas for principal organic hazardous constituents (POHCs), products of incomplete combustion (PICs), particulate matter, hydrogen chloride (HCl), sulfur dioxide (SO_2), nitrogen oxides (NO_x), carbon monoxide (CO), carbon dioxide (CO_2), total hydrocarbons (THC), oxygen (O_2), and metals; (2) the sampling of process streams such as kiln feed, coal/coke, waste fuel, cement clinker, and ESP dust for analyses of a variety of components; and (3) obtaining detailed process data and observations for the sampling period.

1.3 PROJECT ORGANIZATION AND RESPONSIBILITY

This project was funded by EPA's Incineration Research Branch of the Industrial Environmental Research Laboratory in Cincinnati, Ohio, under Contract No. 68-02-3149, Work Assignment No. 11-1, to the Research Triangle

Institute (RTI). The work effort was divided between RTI and Engineering-Science (ES) through a subcontract. RTI was responsible for managing the project, quality assurance, preparation of organic sampling modules, and laboratory analyses. ES was responsible for organizing and conducting the comprehensive field testing which included operating the Modified Method 5 train, volatile organic sampling train (VOST), six continuous gas analyzers, collecting samples of process streams, and collecting process data. This test report was written jointly by RTI and ES.

2.0 CONCLUSIONS

1. Burning waste fuel in this kiln did not result in increased emissions of the POHCs contained in the waste fuel. DREs of 99.99 percent or greater were obtained for all POHCs except methylene chloride for all test days. Methylene chloride DREs of 99.99 percent were obtained for the 37-percent replacement rate.

2. No conclusions can be drawn with respect to the effects of burning waste fuel on particulate matter emissions because the ESP malfunctioned during the test.

3. The usage of waste fuel resulted in increased emissions of lead and cadmium. The increases in cadmium and lead emissions were greater than the increase attributable only to the increased particulate emissions from the malfunctioning ESP. Waste fuel combustion appeared to shift the distribution of cadmium and lead such that a higher percentage of both were removed with the waste dust and stack gas.

4. HCl emissions, chlorine in the waste dust, and chlorine in the recycled dust increase as the total chlorine from the waste fuel increases.

5. Waste fuel combustion increased the lead concentration in the clinker, waste dust, and recycled dust. A slight increase in the cadmium concentration of the waste dust was also noted.

6. Waste fuel combustion did not significantly affect emission rates of SO_2, CO, or total hydrocarbons. A small increase in NO_x emissions was observed.

7. Dibenzodioxins and dibenzofurans were not found in the stack gas at a detection limit <1 ppb (by weight).

3.0 DESCRIPTION OF PROCESS AND WASTE FUEL SYSTEM

Lone Star Industries (LSI) Inc., operates a dry-process cement kiln in Oglesby, Illinois. The kiln was constructed in 1972 and has a clinker production capacity of 1,320 Mg (1,450 tons) per day. A process schematic is given in Figure 3-1.

3.1 PROCESS DESCRIPTION

The Oglesby plant facilities include:

- Raw material handling (quarry, raw grind mill, feed silo)
- Coal and coke facilities (storage, coal mill, feed system).
- A burner system for coal/coke and another for coal/coke/waste fuel.
- A rotary kiln to convert the dry feed into cement clinker.
- Clinker cooling, storage, and a finish mill.
- Temporary storage, pumping, and piping for the waste fuel.
- A kiln emissions-handling system which includes cyclones, a water quench, an electrostatic precipitator (ESP), waste dust handling, an induced draft fan, and a stack.

The plant uses the dry process for cement production in which a ground mixture of limestone, clay, and silica is pneumatically conveyed to the kiln as the raw material feed. The kiln is a horizontal cylinder 4.6 m (15 ft) in diameter at the inlet, 158 m (520 ft) in length, and inclined 3° from horizontal. The kiln is lined with refractory brick and rotates at 1.5 revolutions per minute. The solid's residence time in the kiln is about 1.8 hours (164 revolutions). The kiln is normally fired with a pulverized coal/coke mixture at the downslope end. The raw materials are fed at the upslope end and travel down through the various drying and reaction zones of the kiln.

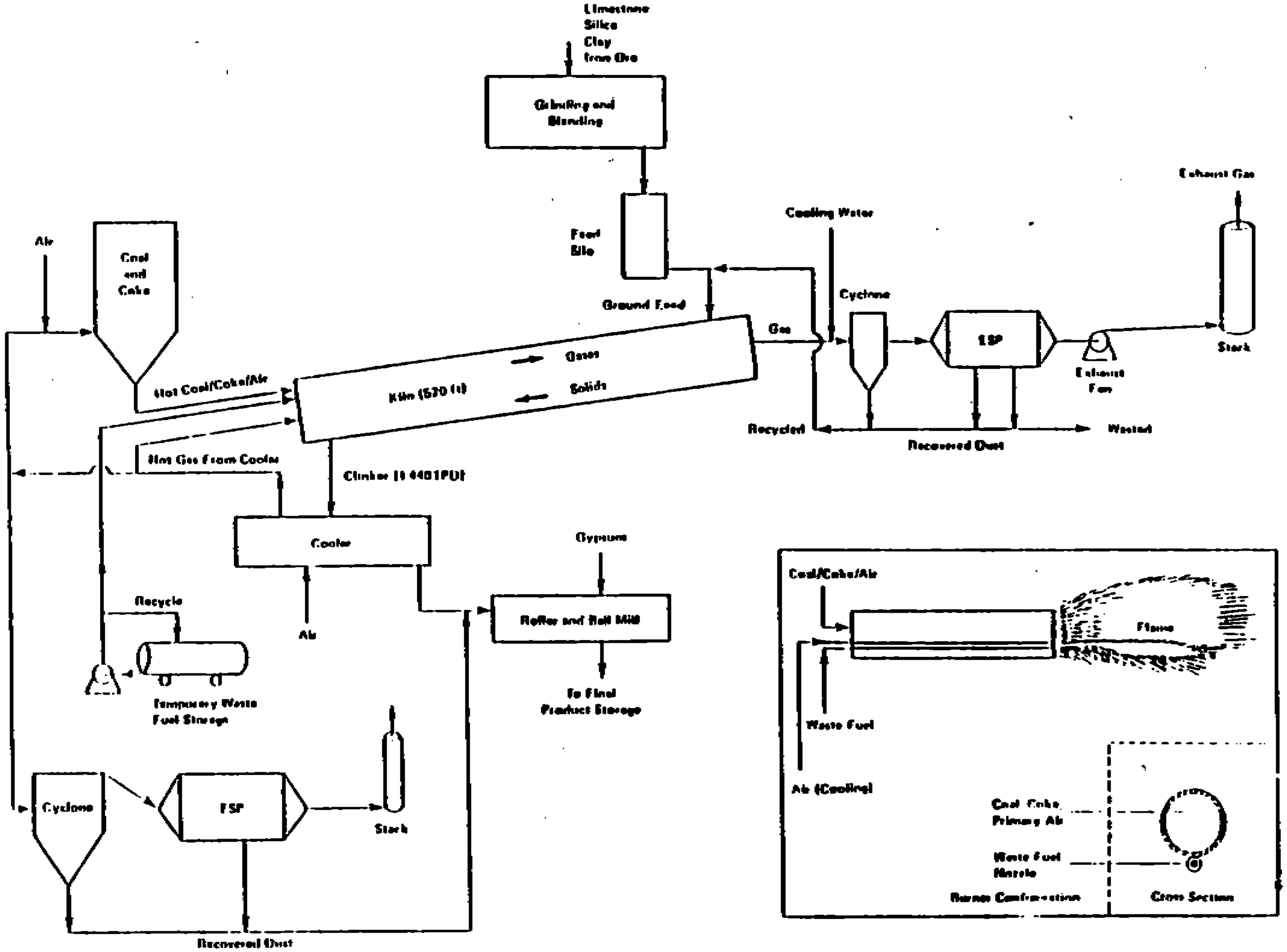

Figure 3-1. Lone Star coal/coke-fired dry process cement kiln at Oglesby, Illinois (1972).

The first 9 to 14 m (30 to 45 ft) of the kiln at the upslope end contain chains to aid in heat transfer, mixing, and drying of the feed. Drying and preheating are accomplished in the first 76 m (250 ft). The next kiln section is the calcining zone (about 24 m in length) where CO_2 is dissociated from calcium carbonate. The last kiln section is the clinkering zone which is about 30 m (100 ft) in length. At this point, the clinker product is formed at temperatures of 1,370°-1,430°C (2,500°-2,600° F).

The clinker is discharged from the kiln into the clinker cooler which uses ambient air to cool the product. Approximately 65 percent of the cooling air is directed back into the kiln as preheated combustion air, and the balance of the cooling air is discharged through a cyclone and electrostatic precipitator. The kiln production rate is typically 60 tons of clinker per hour, and the energy usage is about 3.8 million Btu per ton of clinker.

The combustion and calcination gases travel upslope through the kiln and are exhausted at the feed end. Fresh water is sprayed into the exhaust gases to cool the gases below 370° C (700° F) to protect the ESP. The cooled gases pass through a cyclone and ESP before discharge through a stack. The ESP has two chambers and five fields, only four of which are energized. Approximately 205 Mg (225 tons) per day of dust are collected. About 182 Mg (200 tons) of the dust are recycled to the kiln with the feed mixture and about 23 Mg (25 tons) per day are wasted.

3.2 WASTE FUEL SYSTEM

The waste fuel handling system at Oglesby was designed as a temporary storage facility with three railcars for primary storage and a tank truck as the main feed vessel to the kiln. Tank truck shipments of the waste solvent were arranged by Systech, Inc., and were unloaded into one of the three railcars. Recirculation pumps and jet mixers provided agitation and mixing in the railcars. The tank cars were vented through a drum of activated charcoal, and the entire area around the cars was diked for spill control. From the railcar, the waste fuel was transferred to a tank truck located near the kiln. A recirculation pump and jet mixer kept the waste fuel well-mixed. The area around the tanker was also diked, and the tanker was vented through a charcoal drum.

The waste fuel was pumped from the tank truck into the kiln through a newly designed burner pipe. The coal/coke burner pipe diameter was reduced to accommodate a reduced coal/coke feed rate. As shown in Figure 3-1, a waste fuel line was installed under the main coal/coke burner with a nozzle to provide pressure atomization of the liquid. Low-pressure air was injected around the waste fuel line in a concentric pipe to provide protective cooling.

The waste fuel was a gray liquid composed primarily of hydrocarbon solvents, a wide range of other minor organic compounds, and some resins and solids typical of paint wastes. The designated POHCs were methylene chloride, toluene, methyl ethyl ketone, 1,1,1-trichloroethane, and Freon 113, which was spiked into the waste fuel.

3.3 SAMPLING LOCATIONS

Two locations were used for stack gas emission sampling. The VOST, MM5, and HCl samples were taken through the ports in the stack as shown in Figure 3-2. The figure also shows the location of the sample port for the continuous analyzer probe. The MM5 ports were in the 8.5-ft diameter stack 55 ft up from the base, 28 ft (3.3 diameters) from the nearest upstream disturbance (the breeching), and 19.5 ft (2-3 diameters) from the stack discharge. The EPA Method 2 upstream disturbance criterion required 24 traverse points--one on each of two perpendicular diameters for the Method 5 sampling and velocity determinations. VOST samples were taken from a single point through the port not being used for the MM5 sampling. The HCl samples were taken from a port between the MM5 and VOST ports.

The continuous monitor port was installed in the breeching primarily to avoid the congestion and activity of the MM5/VOST/HCl location. The CEM port, which was downstream of the fan and at a slight positive pressure, was selected to allow sampling the same exhaust gas as that sampled in the stack. This was confirmed through spot comparisons with LSI's CO_2 and O_2 analyzers with probes at the ESP inlet and with Orsat analyses of grab samples from the stack location.

All process samples were collected by LSI personnel using their standard sampling equipment and procedures. Prior to sampling, the locations, methods, and schedule were agreed to among ES, RTI, and LSI personnel. The samples taken during all test runs were solid fuel (coal/coke), kiln feed, recycle

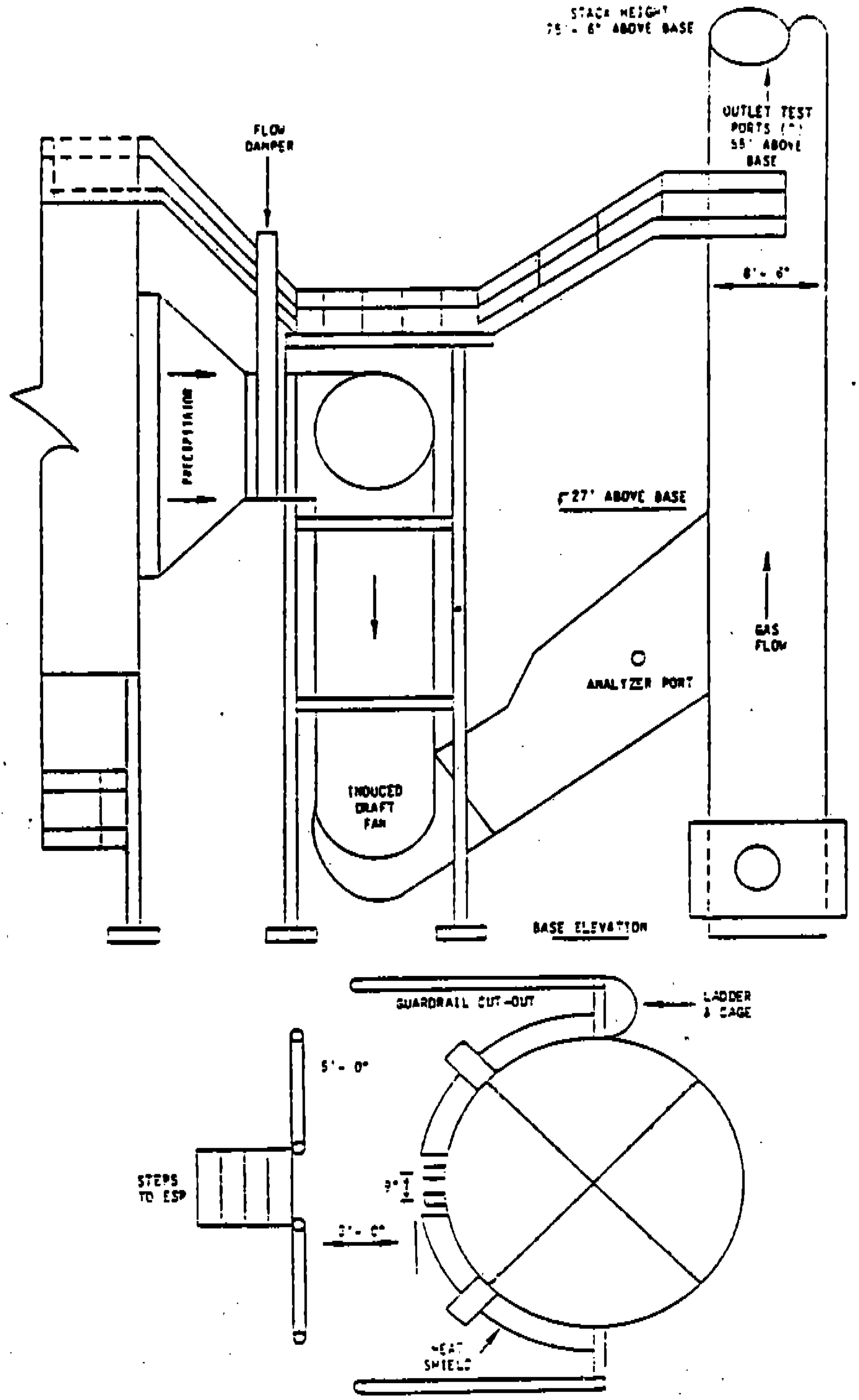

Figure 3-2. Sampling points.

dust, waste dust, clinker, and quench water. Waste fuel samples were taken during the trial burn. Samples of all of the process streams, except quench water, were collected at 2-hour intervals by LSI personnel and composited for the test period by ES personnel.

The coal/coke samples were taken with a cyclone sampler from the duct between the pulverizer and burner pipe, which provides an "as-fired" sample. Clinker samples were obtained with a scoop from the drag conveyor that moves product from the clinker cooler breaker to interim storage. Raw feed is pneumatically conveyed to a feed bin at the cool end of the kiln. The feed sample was taken with an automatic sampler that LSI had installed in the feed line. Dust samples were taken with a scoop from the screw conveyor discharge from the ESP. Waste fuel samples were taken from a drain line on the fuel supply line at the tank truck, which served as the main feed vessel for each run.

4.0 TEST DESCRIPTION

The primary goal of the sampling effort was to determine the destruction and removal efficiency of the hazardous constituents in the waste fuel. However, these data are of limited use for environmental assessment if nothing is known about the destruction process, combustion byproducts, trace metals emissions, effects on various pollutants, and the process variables that affect the type and rate of emissions. Therefore, a comprehensive sampling program was designed to evaluate all significant pollutants leaving through the stack and to track the source and fate of specific elements entering the kiln. Table 4-1 summarizes the revised sampling and analytical activities for this project.

4.1 TEST SCHEDULE

Initially, the test program was planned to consist of 2 days of baseline testing (coal/coke only) and 5 days of testing while cofiring hazardous waste. Each day of sampling was to be identical and consist of one MM5 run, six VOST runs, two HCl runs, and operation of the continuous analyzers and collection of process samples. Figure 4-1 graphically portrays the actual testing.

The start of the test was delayed because waste fuel storage facilities and arrangements for waste fuel took longer than anticipated. After the baseline testing, LSI experienced problems with the waste fuel handling and delivery system. When the waste burn was started, an arctic cold front moved in and temperatures dropped to -20° F. The delays and cold weather prevented the completion of the test as originally planned. The cold weather created extreme problems for the sampling crew and the sampling equipment.

EPA, LSI, ES, and RTI personnel met, and a revised test plan was implemented. The initial plan was to collect data for 5 days with 25-, 30-, 35-, 40-, and 45-percent replacement rates. The revised plan was to conduct testing at 25-, 35-, and 45-percent replacement rates.

TABLE 4-1. SUMMARY OF SAMPLING AND ANALYTICAL PROGRAM FOR LSI's OGLESBY PLANT (December 13-18, 1983)

Parameter	Sampling Method	Analytical Method	Number & Duration of Sample Collection Periods	Total Number of Samples
Stack Gas				
POHCs	VOST	GC/MS, Thermal Desorption	24 @ 40 minutes each	60
Particulate Matter	EPA MM5	EPA M5	5 @ 4-6 hours each	6
Metals	EPA MM5	AAS, ICAP	5 @ 4-6 hours each	6
PICs	EPA MM5	GC/MS, Solvent Extraction	5 @ 4-6 hours each	6
HCl	Impinger Absorption	Ion chromatography (IC)	9 @ 20 minutes each	10
CO_2	Continuous Monitor	Nondispersive IR	4 days @ 4-7 hours/day	NA
NO	Continuous Monitor	Chemiluminescence	4 days @ 4-7 hours/day	NA
SO_2^x	Continuous Monitor	Nondispersive IR	4 days @ 4-7 hours/day	NA
CO	Continuous Monitor	Nondispersive IR	4 days @ 4-7 hours/day	NA
Total Hydrocarbons	Continuous Monitor	Flame Ionization	4 days @ 4-7 hours/day	NA
O_2	Continuous Monitor	Electrochemical Fuel Cell	4 days @ 4-7 hours/day	NA
Waste Fuel	Grab		1 sample/run for 5 runs composited from grab samples taken during waste fuel test every 2 hours during stack gas sampling + 1 split	4
Principal Organics		GC/MS		
Metals		AAS, ICAP		
Chlorine, Sulfur		ASTM D-808, D-129/IC		
Btu Heating Value		ASTM D240-76		
Ash Content		ASTM D482-80		
ESP Waste Dust	Grab		1 sample/run composited from grab samples taken every 2 hours + 1 split	6
Metals		AAS, ICAP		
Chlorine		ASTM D-808/IC		
Clinker	Grab		1 sample/run as composited from grab samples taken every 2 hours + 1 split	6
Metals		AAS, ICAP		
Chlorine		ASTM D-808/IC		

TABLE 4-1 (continued)

Parameter	Sampling Method	Analytical Method	Sample Collection Periods	Total Number of Samples
Kiln Feed Metals Chlorine	Grab	AAS, ICAP ASTM, D-808/IC	1 sample/run as composited from grab samples taken every 2 hours + 1 split	6
Primary Fuel (coal/coke) Metals Chlorine, Sulfur Btu Heating Value	Grab	AAS, ICAP ASTM D-808, C-25 ASTM D240-76 or	1 sample/run as composited from grab samples taken every 2 hours + 1 split	6
Quench Water POHCs	Grab	GC/MS	2 for 3 runs during waste fuel burn	6

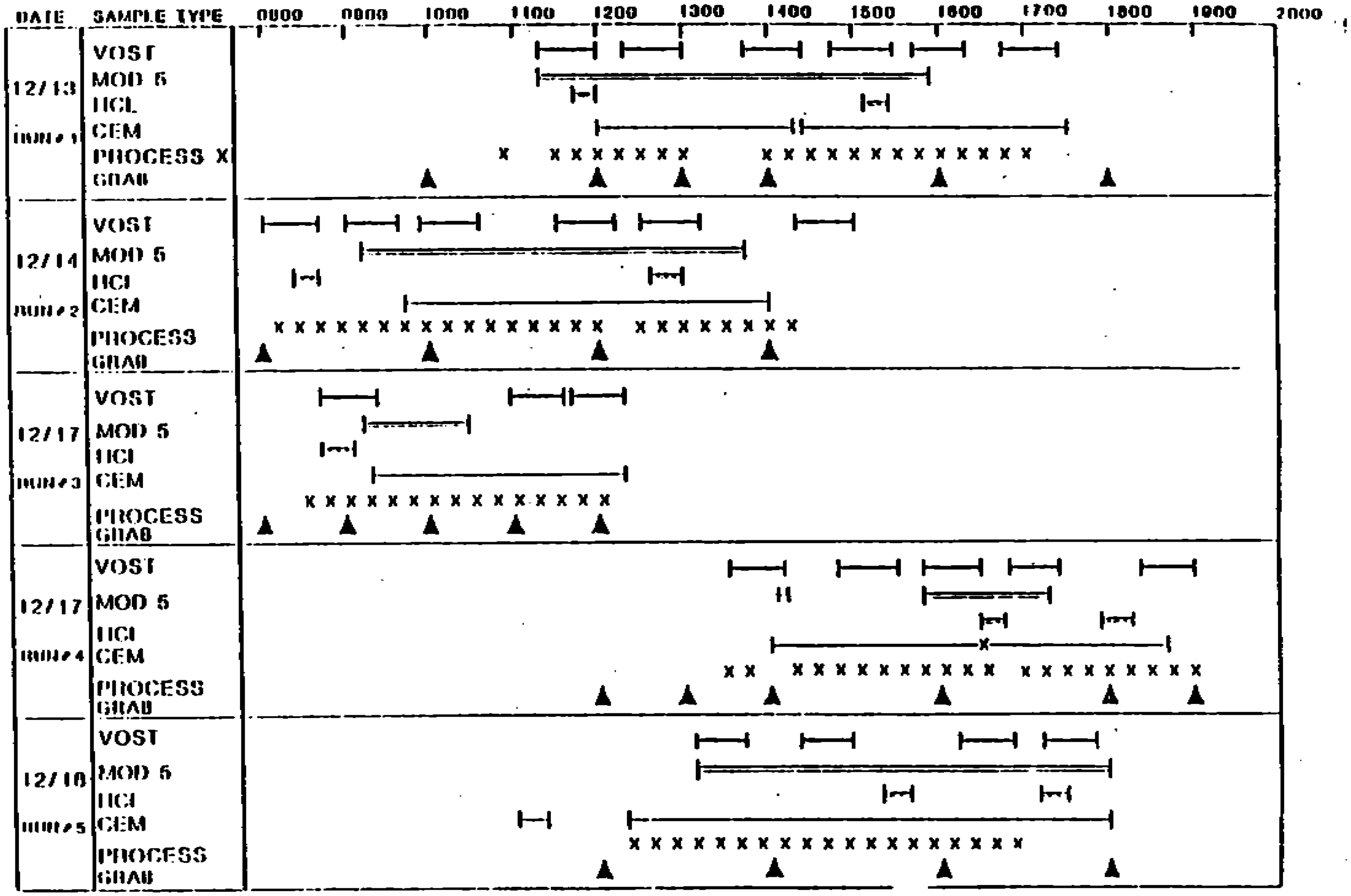

Figure 4-1. Lone Star test log.

Figure 4-1 shows the number and duration of each of the sampling runs. The graph shows that 3, 5, and 4 VOST samples were collected for the 25-, 35-, and 45-percent replacement rates (Runs 3, 4, and 5), respectively. Modified Method 5 sampling for particulate matter was curtailed for two of the three waste fuel tests. Run 4 was a single-point isokinetic sample, Run 3 was stopped after a partial traverse due to excessive particulate loading, and Run 5 was a complete run.

4.2 PROCESS SCHEDULE

The process schedule was to conduct 2 days of baseline testing and a revised plan to conduct three runs at different waste fuel replacement rates. Freon 113 was added as a POHC at about 1 percent to track the DRE of a compound difficult to destroy by combustion. Table 4-2 summarizes the general conditions and test runs actually conducted.

TABLE 4-2. TEST CONDITIONS

Run	Date	Type	Percent Coal[a]	Percent Waste Fuel[a]
1	12/13/83	Baseline	100	0
2	12/14/83	Baseline	100	0
3	12/17/83	Waste burn	75	25
4	12/17/83	Waste burn	63	37
5	12/18/83	Waste burn	58	42

[a] Percent based on Btu heating content.

5.0 SAMPLING PROCEDURES

The Quality Assurance Project Plan (QAPP) for this project discussed the general approach to sampling and analysis for the pollutants to be measured. It described equipment, operating procedures, and quality control practices for sampling and analysis. This section describes how these procedures were applied at the Oglesby plant.

In summary, the VOST was used to sample emissions for POHC analysis. The MM5 was used to collect the particulate and PIC samples. A midget impinger train was used to collect HCl samples. Continuous gas analyzers were used to measure O_2, CO_2, CO, SO_2, THC, and NO_x. Process samples were taken and composited over an 8-hour period.

Analytical procedures and measurement principles are described in Section 6.

5.1 VOST

Volatile organic constituents (normal boiling points less than 100° C) are adsorbed on Tenax and Tenax/charcoal cartridges. Figure 5.1 depicts the VOST sampling train and its various components.

The general draft procedure "Protocol for Collection of Volatile POHCs Using a Volatile Organic Sampling Train (VOST)," Larry Johnson, U.S. Environmental Protection Agency (August 1983), was followed for sample collection.

<u>Procedure Highlights</u>

- Leak checks were performed by evacuation of the system to at least 10" Hg vacuum less than operating pressure and maintaining this vacuum for 1 minute with 0.1 inch Hg, or less, loss. Ambient air was drawn through charcoal when releasing the vacuum of the system.
- Sampling rate - 0.5 liters per minute for 40 minutes per sample (pair of tubes).

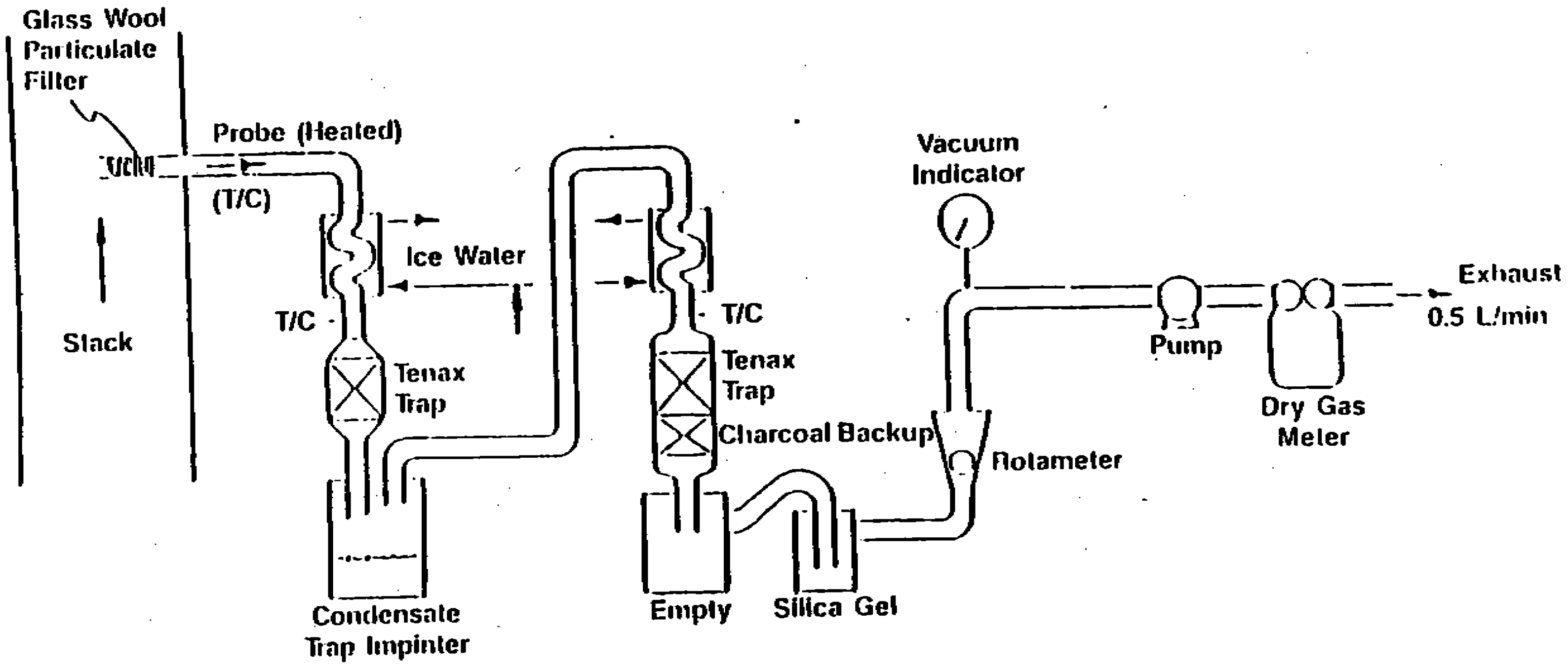

Figure 5-1. VOST schematic.

- The probe temperature was maintained at or above 130° C.
- Tubes/test - 6 pairs (except limited test days).
- Total sampling time - 6 x 40 min = 240 minutes per test.
- Single-point sampling.
- Tenax temperature - <20°C controlled by ice water flow to the condensers.
- Cleaning - chromerge, water, methanol before field test.

Sampling Train

Components of the VOST train are listed below with specifications for each:

Sampling Module

- Probe - 4' stainless steel sheath with a 1/4" O.D. quartz liner with a filter of precleaned quartz wool in the end of the probe. The probe was heated at or above 130° C.
- Teflon/glass stopcock - a 3-way stopcock capable of maintaining a leak-free system, purging the probe, purging the sampling train, or sampling the stack gas.
- First condenser - water-cooled coil condenser with leak-free fittings to the stopcock and Tenax trap.
- Tenax trap - glass trap containing 1.6 grams (g) of Tenax.
- Flask - a 250-mL or 125-mL flask fitted with leak-free connectors to the bottom of the Tenax trap and to 1/4" O.D. tube to connect to the second condenser with leak-free fittings.
- Second condenser - a straight tube-type of water-cooled condenser installed in a manner which allowed any additional condensate to drain to a second flask with leak-free fittings.
- Tenax/charcoal trap - glass trap containing approximately 1 g each of Tenax and charcoal.
- Flask - a 125-mL flask as above to connect to the silica gel trap.
- Silica gel trap - silica gel impinger to remove any remaining moisture.
- Umbilical line - a leak-free sample line to connect the sampling module to the control module and an electrical cable harness which includes: power lines for probe and water pump; thermo-couple lines

for temperature readings at probe, stack, entrance to the first sorbent trap; and ambient air.

Control Module

- Vacuum gauge - 0-29" Hg; used to assess leak rates and the vacuum during the testing period.
- Main valve - a needle-type valve capable of controlling flows in 0-3000 mL/min range.
- Fine adjust valve - a needle-type valve capable of regulating the pumping capacity of the pump.
- Pump - a small leak-free Teflon diaphragm pump capable of delivering 20" Hg vacuum at a flow of 1 L/min.
- Dry gas meter - Singer 1 liter per revolution, capable of measuring accurately (± 2%) volumes of gas at a low (0.25-3.0 L/min) flow rate.
- Rotameter - a dual ball rotameter with 0-1000 mL/min range with the upper ball and a 0-3000 mL/min range with the lower ball.
- Thermocouple readout - a digital panel meter readout to indicate temperatures of: stack, probe exit, entrance to trap 1, dry gas meter, ambient air.
- Voltage regulators - capable of controlling heat in the probe from 4° to 180° C.
- Pressure gauge - to measure the pressure at the dry gas meter, 0 to 3" H_2O.

Pretest Operations

Before transport to the field, all portions of the train which contact the sample gas were subjected to vigorous cleaning. Components were first immersed in a mixture of chromous chloride and sulfuric acid (chromerge). The immersion was followed by a thorough tapwater rinse, and then with organic-free chromatographic-grade distilled water. The final cleaning was a rinse with chromatographic-grade methanol. The components were sealed with aluminum foil previously rinsed with high-grade methylene chloride.

At the beginning of each test day, a set of empty sorbent tubes was installed, and the entire system, including probe, leak-checked. The vacuum was released by admitting ambient air through charcoal, first to the probe, then to the remainder of the system. The ice bath was prepared and ice water circulated through the condensers. On some days, the ice bath was prepared by melting the block of ice in the water reservoir.

The probe was inserted in the stack and a pair (one Tenax and one Tenax/charcoal) of sorbent tubes installed. The train was again leak-checked (excluding probe) in the same manner.

Sample Collection

Sample gas was drawn from the stack through a probe maintained at 130° C at 1/2 L/min. Total sampling time was 40 minutes per pair of tubes, with six pair of tubes constituting a test day. The sample rate was calculated to result in approximately 20 liters at standard conditions for one pair of tubes. The sample volume has been established by EPA-sponsored experiments, as the maximum (with a 100-percent safety margin) that can be passed through a tube before the sorbed POHCs begin to elute or be stripped from the resin.

During sampling, appropriate data were recorded every 10 minutes and adjustments to sampling variables made to maintain desired conditions such as sampling rate, probe temperatures, condenser outlet temperature, etc.

Post-Test Procedure

At the end of each sampling period, the stopcock was closed, the pump turned off, and final readings made. The train was again leak-checked with the probe in the stack. The sorbent tubes were removed and a fresh pair installed.

This process was repeated until all pairs of sample tubes had been collected. As previously mentioned, the desired number was six pairs per condition; however, this was not achieved for each run because of schedule delays and cold weather.

Once each day, a pair of sorbent tubes was taken to the sampling site, opened, and exposed to ambient air for the length of the time needed to install them in the train, capped, and returned to their containers. These "shadow" or field blanks were taken to account for potential contamination from the ambient air at the sampling location, as well as general sample handling and transport procedures.

After sample collection and sorbent tube removal, the tubes were capped with their own stainless steel caps and placed into their own screw-cap glass culture tubes for onsite storage and shipment to the laboratory. The capping and double-sealing are done to minimize sample cross contamination and external contamination. In addition to the field blanks, a pair of tubes (trip blanks) was taken to the field but never opened, and two pairs of tubes from the same lot remained in the analytical laboratory (lab blanks).

5.2 MODIFIED METHOD 5

This sampling train is used to collect products of incomplete combustion (PICs) as well as to estimate the particulate matter emission rate by EPA Method 5 (40 CFR Part 60, Appendix A).

Extracts, rinses, and related materials from the probe/train system for each sampling period were chemically analyzed to determine the presence of polychlorinated biphenyl (PCB) compounds and dioxins as well as weighed to determine particulate matter. A total of nine runs were conducted.

Sampling Train

The gas stream sampled by the probe is directed to a modified EPA Method 5 train, depicted in Figure 5.2. This system consists of the following components in series: nozzle, probe, heated particle filter, one sorbent module, a bank of impingers, and a meter box. A detailed discussion of the physical construction of the unmodified Method 5 train and its assembly is given by Martin; maintenance is given by Rom (APTD-0581, APTD-0576).

A glass fiber (particle) filter is enclosed in a glass housing and supported by a stainless steel mesh. This section of the train is contained in an electrically heated box that is manually regulated to maintain a sample gas temperature of about 120° C. The filter was tared before use.

A typical sorbent module/condenser is also depicted in Figure 5.2. There are separate sections for cooling the incoming gas stream and for trapping organic gas constituents. Cooling is accomplished by routing the gas through a coil of glass tubing surrounded by water circulated from an ice and water bath. Organic constituents of the gas are removed by 20/40 mesh XAD-2 resin contained in an all-glass trap. High collection efficiencies (90-100 percent)

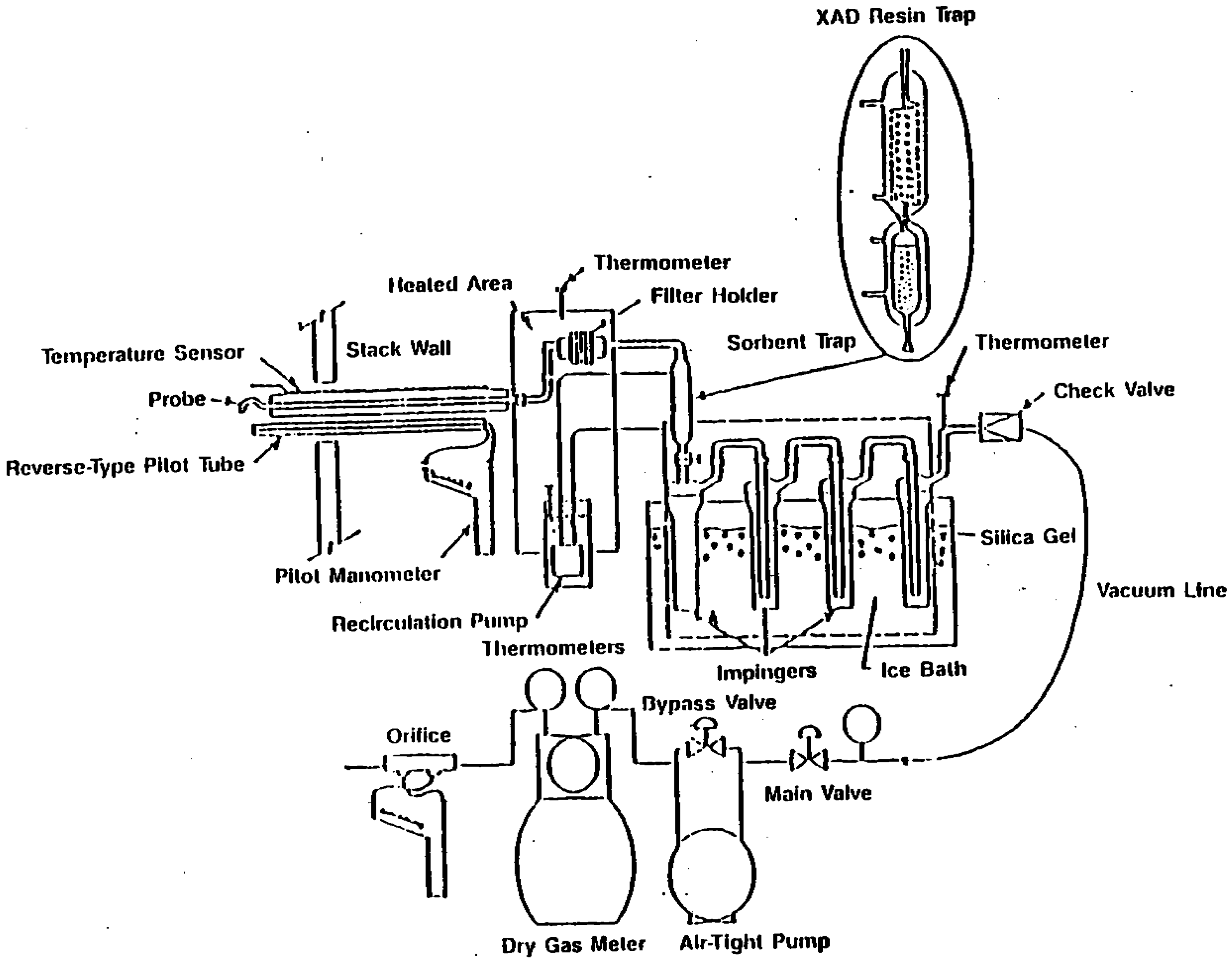

Figure 5-2. Modified Method 5 schematic.

are typical for vapor phase organic species with boiling points greater than 100° C.

The temperature of the gas at the outlet of the sorbent was measured and maintained between the limits of 0° and 20° C. Cooling of the gas condenses part of the sample gas moisture which may entrain and/or dissolve certain organic species. To insure that this material was collected, the sorbent module was positioned vertically such that the condensate percolated through the resin bed and into the bank of impingers.

The impinger bank consisted of four impingers connected in series. The first impinger is initially empty and collects the condensate from the preceding sorbent module. The Greenberg-Smith nozzle was replaced by a very short stem such that the sampled gas did not bubble through the collected condensate.

The second and third impingers were included to remove acid species from the gas, and each contained 100 mL chromatographic-grade distilled water. The fourth impinger was filled with silica gel to absorb moisture remaining in the gas, thereby assuring accurate gas flow measurements and preventing damage to the pumping system.

A standard Method 5 meter box containing a variety of gas handling and metering devices followed the impinger bank.

All components of the sampling train were joined either by stainless steel Swagelok® fittings or by ground glass ball-and-socket joints capable of leak-free seals under sampling conditions. Stopcock grease was not used at any point in the system. All components in contact with sample gas were cleaned as described for the VOST.

Prior to each run, the individual components of the sampling train were assembled, and the probe/sampling train was leak-tested. First, the heating and cooling systems were allowed to reach equilibrium. Then, the nozzle was plugged and the system was evacuated to 200 mm Hg (15"). If the leakage exceeded the lesser of 4 percent of the average sampling rate or 0.02 cfm, the leak was corrected.

Sampling Procedure

The isokinetic MM5 sampling rate was determined by nozzle size and selected to achieve between 100 and 200 cubic feet of sampled gas. At the end of most tests, a MM5 sample of about 150 ft^3 had been collected over 4-1/2 to 6 hours.

Operation of the sampling train followed EPA Method 5. The stack diameter and the distances to nearest upstream and downstream flow disturbances were measured (3.3 and 2.3 equivalent diameters, respectively). Generally, samples were collected from 24 points in the duct through two ports. Traverse points were located as specified in Method 1 and gas velocity and flow rate determined as stated in EPA Method 2 during the MM5 sampling. Multipoint isokinetic sampling was performed as described in Method 5. After the pretest leak check, the probe was inserted into the stack, the pump started, and the sample rate adjusted to maintain isokinetic conditions at the nozzle.

Post-Test Operations

At the conclusion of the test, the train was leak-checked and allowed to cool. The probe/nozzle unit was removed and capped, and the filter holder inlet capped. All components were taken to the cleanup area for sample recovery. The basic procedures of EPA Method 5 were followed, modified as necessary for recovery of samples for organic analysis. The probe, nozzle, and filter holder were each rinsed three times with acetone and then three times with methylene chloride. All liquid samples were transferred to glass bottles with Teflon-lined caps which had been cleaned as described for the VOST glassware. The XAD module was removed from the train as a unit and sealed with grease-free glass balls and sockets. The preweighed impingers were removed and weighed to determine the mass of condensed water collected. The percolated condensate from the first impinger was transferred to a sample bottle along with rinses from the condenser. The contents of the second and third impingers were transferred to another sample bottle, to which were added acetone and methylene chloride rinses of all three impingers and connecting glassware. All bottles were tightly capped, sealed with Teflon-lined caps, and the liquid level marked on the bottles.

For this test, one XAD module was exposed as a field blank and one was used as a trip blank. The field blank was installed into the entire sample train, leak-checked, heated to 120°C for 4 hours, and then recovered along with the other sample train fractions.

5.3 HCl AS CHLORIDE

The sampling train that was used to obtain gas samples for chloride analysis is essentially the EPA Method 6 midget impinger train, as shown in Figure 5.3. Each of the first two impingers were charged with 15 mL of distilled deionized water as absorbing solution. A glass wool plug for particle filtration was placed in the stack end of a heated glass probe and stack gas extracted at a rate of 2 L/min for 20 minutes.

At the beginning and end of each run, the train was leak-checked at 10" Hg. After sample collection, the train was taken to a sample recovery area for cleanup. The contents of the impingers were transferred to a 250-mL polyethylene bottle along with triplicate water washes of the impingers and connecting glassware.

5.4 CONTINUOUS ANALYZERS

The stack gas was analyzed for CO, CO_2, NO_x, O_2, SO_2, and total hydrocarbons (THC) with continuous emission monitors. Gas samples for the CEM's were extracted through a single sample probe in the duct just upstream from the VOST port. The probe was equipped with an instack particle filter followed by a three-way valve out of the stack. The valve was used to direct either the stack gas or zero/span gases through the sample line including the conditioning system. Following the valve were an ice water/air-cooled condenser/moisture trap and a Perma Pure moisture removal system. The Perma Pure system is a nonreactive semipermeable membrane shell and tube moisture removal device placed in a heated compartment. All CEM sample and span gas lines were Teflon or stainless steel. A flow diagram of the CEM/sampling system is shown in Figure 5.4. The analyzers were calibrated twice daily (before and after manual sampling) and operated over the duration of the run.

The review of previous test data comparing stack gas concentrations of CO_2 and O_2 with Lone Star's kiln discharge CO_2 and O_2 monitoring data showed 15- to 20-percent ambient air inleakage through the multiclone, ESP, and connecting ductwork. At the beginning of the test program, a spot check of the CEM port versus data collected by LSI at the kiln discharge showed the same amount of inleakage. Inleakage and stratification were not investigated further. The CEM data at this location provided an adequate process monitor

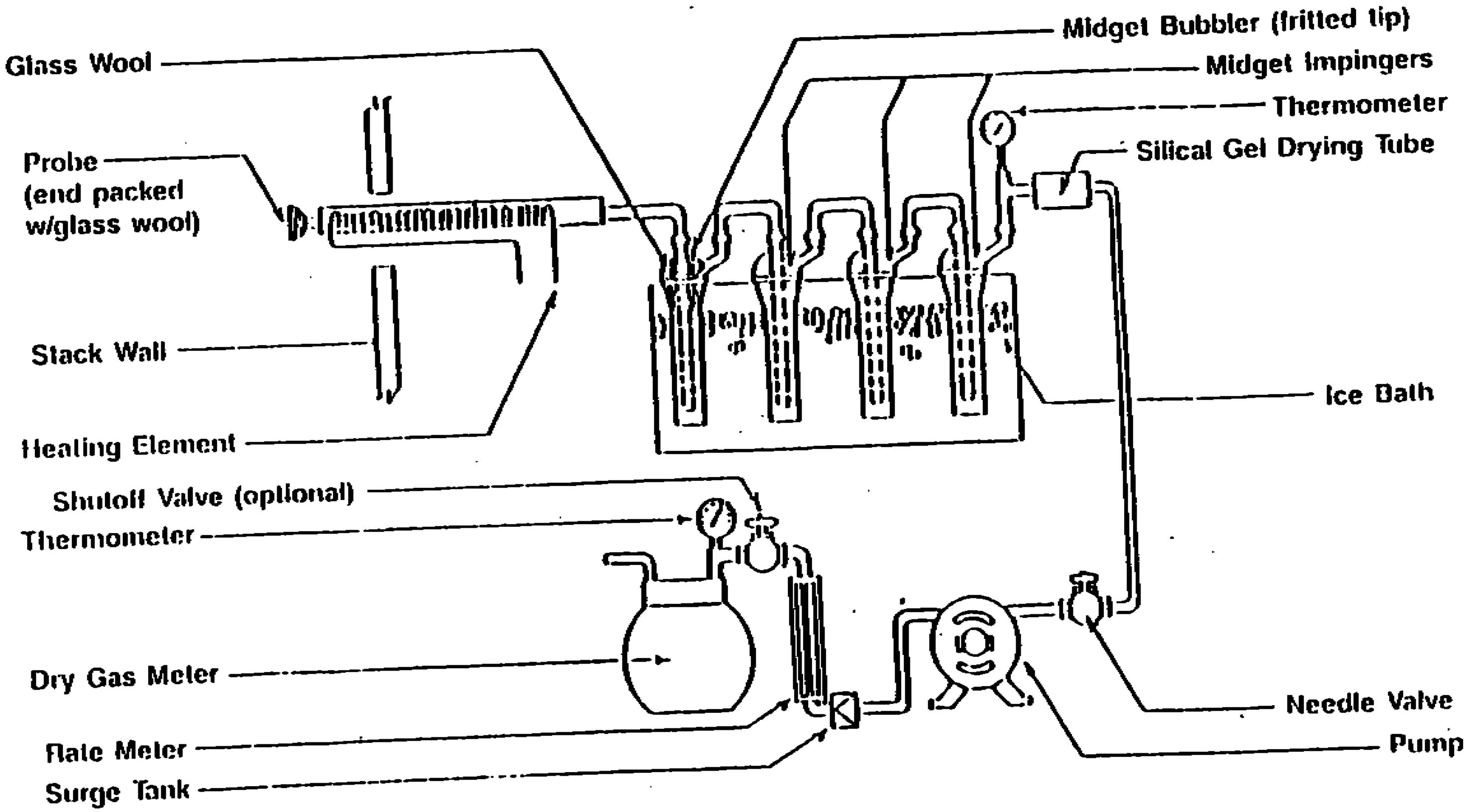

Figure 5-3. HCl sampling train.

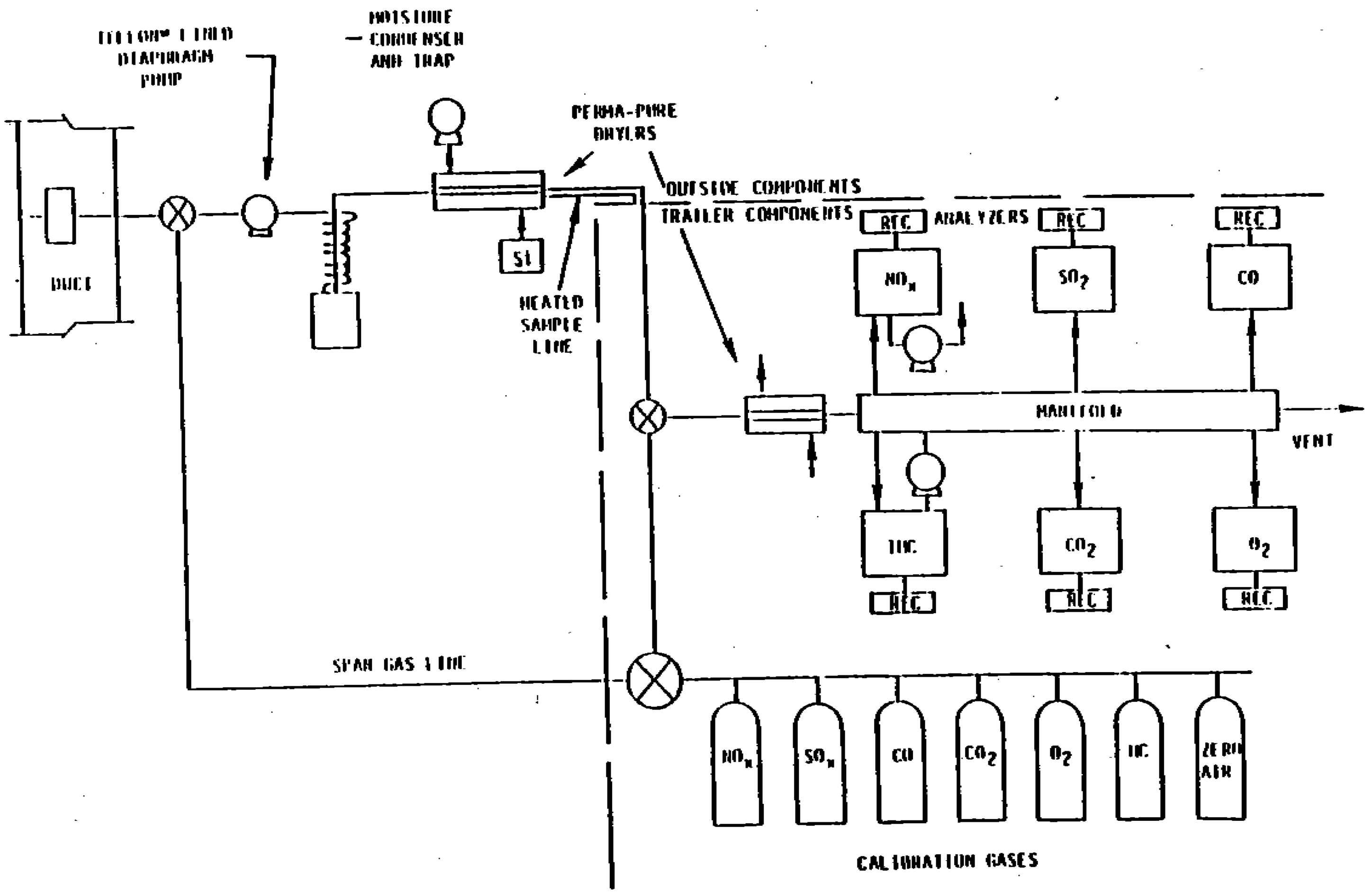

FIGURE 5.4 CONTINUOUS MONITOR SAMPLE SYSTEM

and would allow calculation of the gas concentrations in the undiluted kiln discharge, if desired.

5.5 PROCESS SAMPLES

Lone Star personnel collected samples of various process streams every 2 hours which were composited by ES personnel into a single sample for each run condition. During baseline testing, daily composites were made for kiln raw feed, clinker, coal/coke, waste ESP dust, and recycled dust, and grab samples of quench water were taken. During waste fuel testing, composite samples of the waste fuel were also taken. Kiln feed samples were taken from LSI's automatic sampler. Coal/coke samples were taken with a cyclone sampler at a location between the pulverizer and burner. Clinker samples were taken from the drag chain moving product to storage and/or finish mill, after the clinker cooler and breaker. ESP dust samples were taken from the screw conveyor that removed the dust from the ESP. Grab samples of quench water were taken on the waste fuel test days from a drain on the pump discharge. Waste fuel samples were taken from the supply tank outlet by LSI personnel. Both the water samples and waste fuel samples were collected in headspace-free vials used for volatile organic analysis.

6.0 ANALYTICAL PROCEDURES

6.1 POHCs FROM VOST

Upon receipt by the laboratory, the VOST cartridge was spiked with an internal standard (bromochloromethane) and thermally desorbed at 180° to 200° C with organic-free nitrogen in a thermal desorption unit. From the desorption unit, the gas was bubbled through 5 mL of organic-free water and trapped on an analytical adsorbent trap.

After the 10-minute desorption, the analytical adsorbent trap was rapidly heated to 180° C with the carrier gas flow reversed so that the effluent flow from the analytical trap was directed into the GC/MS. The volatile POHCs were separated by temperature-programmed gas chromatography and detected by low-resolution mass spectrometry. The concentrations of volatile POHCs were calculated using the internal standard technique. Details of the purge and trap GC/MS analysis are described in EPA Method 624. The volatile POHCs of interest in this test were methylene chloride, Freon 113, 2-butanone, toluene, and 1,1,1-trichloroethane.

The two tubes collected from the first test of each run condition were analyzed individually to determine if breakthrough had occurred. Subsequent tubes were analyzed in pairs and provided sufficient quantities of POHCs for analytical detection.

Calibration standards were prepared at three concentration levels for each POHC of interest to bracket the expected sample concentrations. The calibration standards were prepared by spiking a blank Tenax or Tenax/charcoal trap with a methanolic solution of the calibration standard (including the internal standard) using the flash evaporation technique. The trap was analyzed according to the purge and trap chromatographic procedures described in Section 11 of EPA Method 624. A calibration standard was analyzed for both Tenax and Tenax/charcoal cartridges.

After analysis of the calibration standards, the area response of the characteristic ions of each analyte was tabulated against the concentration of each and the internal standard. A response factor (RF) was calculated for each compound by:

$$RF = A_s C_{is} / A_{is} C_s$$

where:

A_s = Area of the characteristic ion for the analyte to be measured.
A_{is} = Area of the characteristic ion for the internal standard.
C_{is} = Amount (ng) of the internal standard.
C_s = Amount (ng) of the volatile POHC in calibration standard.

The working calibration curve or RF was verified on each working day by the measurement of one or more of the calibration standards. If the response for the POHCs varied by more than 3 standard deviations from the previously established response, new calibration standards were prepared and analyzed.

After the sample cartridges were analyzed, the amount of a specific analyte in the cartridge was calculated by:

$$\text{Amount of POHC} = A_s C_{is} / A_{is} RF$$

where:

A_s = Area of the characteristic ion for the analyte to be measured.
A_{is} = Area of the characteristic ion of the internal standard.
C_{is} = Amount (ng) of internal standard.

Results were tabulated in ng/cartridge for single cartridges and ng/cartridge pair for tubes analyzed in pairs.

6.2 MODIFIED METHOD 5 (MM5) PROCEDURES

The particulate matter catch was determined from the filter catch and probe rinse. The filters were desiccated for at least 24 hours to a constant weight, and the results were reported to the nearest 0.1 mg. The probe rinse in acetone was evaporated to dryness in a steam bath. The dried residue was desiccated to a constant weight, and results were reported to the nearest 0.1 mg.

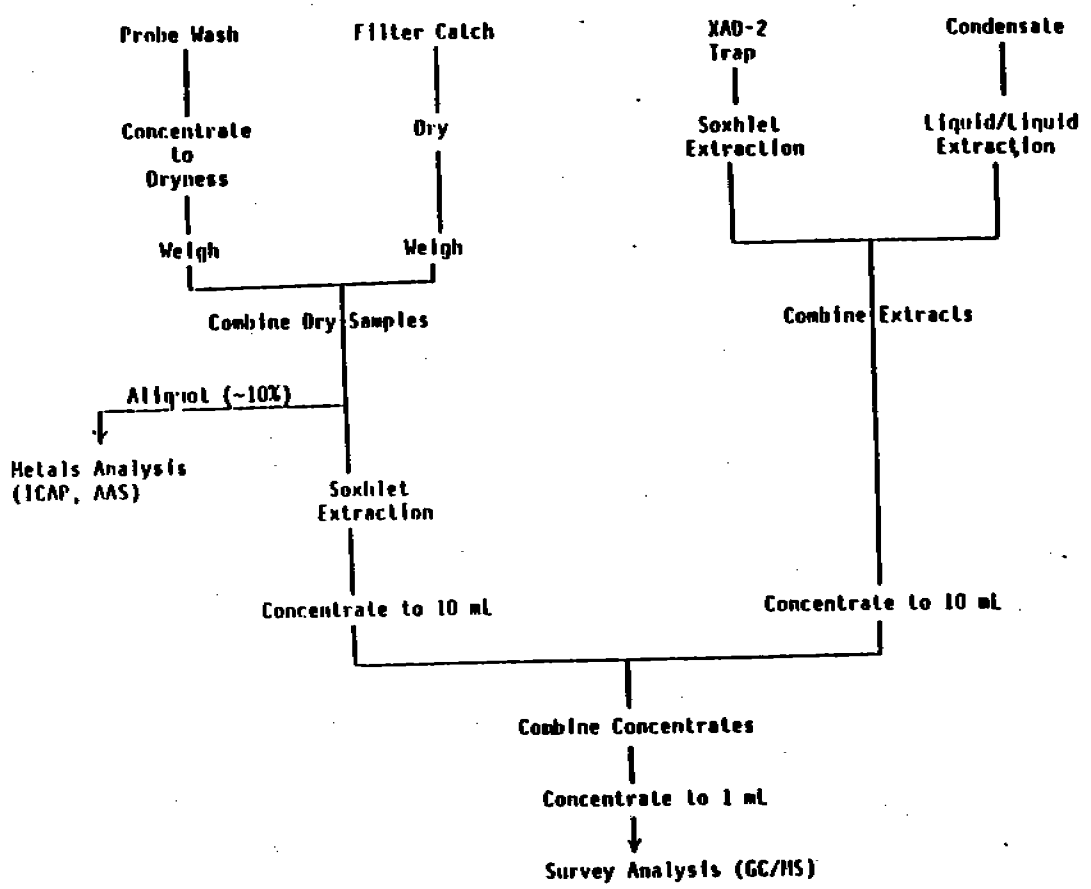

Figure 6-1. Analysis scheme for modified Method 5 samples.

The organic analysis scheme for the components of the MM5 is given in Figure 6-1. A 10-percent aliquot of the particulate matter was retained for metals analysis. The balance of the probe and filter catch was extracted with methylene chloride and concentrated to 10 mL. The XAD-2 sorbent was also extracted with methylene chloride in a Soxhlet extractor for 24 hours. Serial extractions were performed on the condensate with the condensate first being made acidic (pH 2) and then basic (pH 12). The extracts from the XAD-2 and condensate were then combined and concentrated to 10 mL. The concentrates from the two portions of the train were combined and concentrated to 1 mL and spiked with an internal standard (2-fluorobiphenyl) for a survey analysis by gas chromatograph/mass spectrometry (GC/MS). From the survey analysis, the major compounds of interest were identified. Quantitation standards for the compounds were prepared to determine their response with respect to the internal standard's response. The compounds in the extracts were then semiquantified based on the relative response factors for the quantitation standards. The term "semiquantitation" is used because certain compounds were grouped and only one response factor was used for that group (e.g., C_3-benzenes). Characteristic ions for the isomers of dibenzodioxins and dibenzofurans were monitored to determine the presence or absence of these compounds. These compounds were not found in any of the MM5 extracts at a detection limit of 1 to 5 ng per injection.

6.3 CONTINUOUS ANALYZERS

The stack gas was analyzed for six gases (SO_2, NO_x, CO_2, CO, O_2, and THC) by pumping the sample gas as previously described into a manifold located in a trailer near the sampling location. A brief description of the analytical methods used is followed by a list of the analyzers and operational parameters.

Nondispersive infrared absorption spectroscopy was used for SO_2, CO, and CO_2. Each of these gases absorbs infrared radiation of a characteristic wavelength, and the absorption is proportional to the concentration of the pollutant. Oxides of nitrogen were measured by chemiluminescence where the characteristic light emitted by the gas phase reaction of NO with ozone and resulting decay of excited NO_2 is measured. Total hydrocarbons were measured using a flame ionization detector burning sample gas in hydrogen flame and measuring the electron flow resulting from the ionization from oxidizing C to CO_2 in the flame.

Each analyzer was given a multipoint calibration prior to the test using zero gas and three span gases to establish instrument linearity (or calibration curve in the case of CO_2). Subsequently, instrument zero and span values were established with a single gas with periodic checks of other concentrations to verify calibration. The span gas was selected to be representative of concentrations observed in the stack. The following list identified the specific analyzers and calibration gases that were used for this test.

CO
Analyzer Model: Horiba PIR-2000
Measurement Principle: nondispersive infrared
Analysis Range: 0-1000, 3000, 5000 ppm
Calibration Gases: CO in N_2 - 250, 500, 900 ppm

CO_2
Analyzer Model: Infrared Industries 702
Measurement Principle: nondispersive infrared
Analysis Range: 0-10, 30%
Calibration Gases: CO_2 in N_2 - 4, 20, 30%

O_2
Analyzer Model: MSA 803P
Measurement Principle: Zirconium oxide fuel cell
Analysis Range: 0-10%, 20%
Calibration Gases: O_2 in N_2 - 1.7, 12.6, 20.8%

SO_2
Analyzer Model: Horiba, AIA-23
Measurement Principle: nondispersive infrared
Analysis Range: 0-500, 1000, 1500, 3000 ppm
Calibration Gases: SO_2 in N_2 - 98, 460, 899, 1411 ppm

NO_x
Analyzer Model: TECO Model 44
Measurement Principle: chemiluminescence
Analysis Range: 0-2, 5, 10, 20, 50, 100, 250, 500, 1,000, 2,000, 5,000, 10,000 ppm
Calibration Gases: NO_x in N_2 - 125, 450, 900 ppm

Total Hydrocarbons
Analyzer Model: MSA THC Analyzer
Measurement Principle: flame ionization
Analysis Range: 0-1, 5,10, 50, 100, 500, 1,000, 5,000 ppm
Calibration Gases: CH_4 in air - 15, 50, 90 ppm

6.4 ANALYSIS OF PROCESS SAMPLES FOR ELEMENTS

The kiln feed, coal/coke, clinker, waste and recycle dust, waste fuel, and particulate catch were analyzed for metals using atomic absorption (AA) and inductively coupled argon plasma (ICAP) techniques. The major elements of interest are the additional metals that may be introduced by the waste fuel (e.g., As, Cd, Dr, Cu, Hg, Ni, Pb, Se, Zn). The digestion procedure used for arsenic, selenium, and mercury in all sample matrices except coal is found in "Appendix D - Aqua Regia Digestion Procedure" of EPA's <u>Procedures Manual: Level 1 Environmental Assessment</u> (EPA-600/7-78-201). Approximately 1 gram of sample was put into a distillation flask of a reflux apparatus. Sixty milliliters of constant boiling aqua regia solution (4:1 HNO_3:HCl) were added to the flask and the mixture refluxed overnight. The solution was then filtered through a Whatman filter (No. 41), collected in a 100-mL volumetric flask, and brought up to volume with deionized water. For analysis of As, Se, and Hg in coal, the oxygen bomb procedure in Appendix C ("Parr Bomb Combustion Procedure") of the previously cited reference was used. Approximately 0.5 g of sample was put into the sample cup and 10 mL of 10 percent HNO_3 were added to the quartz liner of the bomb. The bomb was then assembled and pressurized to 24 atmospheres with oxygen. The bomb was ignited and allowed to cool, and the pressure was released. The bomb contents were then transferred to a 50-mL volumetric flask and brought up to volume with deionized water.

An acid digestion bomb method was used as the digestion procedure for analysis of all other metals in all of the sample matrices. A sample was first ashed in a muffle furnace overnight. A total of 100 mg of the ash was then placed in the decomposition vessel, 1 mL of aqua regia (1:3 HNO_3:HCl) was added to the ash, followed by 3 mL of hydrofluoric acid. The bomb was closed and heated in a muffle furnace at 140° to 150° C for 1 hour. After cooling, the solution was transferred to a Teflon beaker, and 2.8 g of boric acid were added. The solution was transferred to a 50-mL volumetric flask and brought up to volume with deionized water.

Elemental measurements were performed by atomic absorption and inductively-coupled plasma emission techniques. Atomic absorption methods included flame (FAA), graphite furnace (GFAA), and cold vapor (CVAA) atomization. Aluminum, magnesium, lead, and cadmium were analyzed by FAA. Aluminum required a nitrous oxide/acetylene flame instead of the more common air/acetylene flame used for the other elements determined by FAA. Arsenic and selenium were analyzed by GFAA, and mercury was determined by CVAA. All other elements were analyzed by the ICAP procedure essentially as described in Method 200.7.

Corrections for background levels were used when necessary. Within each sample type, the method of standard addition was used to check for other possible matrix effects. The EPA analytical methods that were used are listed below:

Element	Technique	EPA Method
Al	AA	202.1
As	AA	206.2
Cd	AA	213.1
Pb	AA	239.1
Mg	AA	242.1
Hg	AA	245.1
Se	AA	270.2
All Others	ICAP	200.7

The procedure that was proposed in the quality assurance plan was to use AA to determine arsenic, selenium, and mercury and to use ICAP for to determine other elements. However, the AA was also used to measure aluminum, cadmium, lead, and magnesium, because of spectral interference problems with the ICAP.

6.5 CHLORINE AND SULFUR ANALYSIS

The kiln feed, coal/coke, clinker, waste and recycle dust, and waste fuel were analyzed for chlorine content. In addition, the coal/coke and waste fuel were analyzed for sulfur content. For both analyses, the samples were oxidized by combustion in a Parr bomb containing oxygen under pressure. The chlorine and sulfur compounds that are liberated are absorbed in a sodium carbonate solution and are determined as chloride and sulfate by ion chromatography.

A total of 10 mL of Na_2CO_3 solution (50 g/L) was placed in the bomb, and approximately 0.4 g of sample was added. Approximately 10 drops of paraffin oil were also added for the coal, clinker, dust, and slurry samples; waste fuel samples were bombed as received. The bomb was then assembled and pressurized to 24 atmospheres with oxygen. The bomb was immersed in a cold water bath, ignited, cooled for 10 minutes, and depressurized. Deionized water was used to rinse the interior of the bomb, sample cup, terminals, and inner surface of the bomb cover into a 100-mL volumetric flask, which was then diluted to 100 mL total volume.

The solutions were analyzed by injection into the ion chromatograph. Standards covering the range of concentrations found in the samples were analyzed on the ion chromatograph, and a calibration curve was generated from a linear regression analysis. When sulfate was found to be in excess of 100 ppm, a dilution was made and the sample was reanalyzed.

The HCl samples from stack gas sampling were originally analyzed by the specific ion electrode. However, unacceptable results were obtained on audit standards, and most samples had chloride concentrations below the detection limit of 5 mg/L. Using ion chromatography, acceptable results were obtained on audit samples from two laboratories and EPA. In addition, detectable concentration values were obtained for nearly all samples. Therefore, ion chromatography was used to determine the chloride content in the impingers from HCl stack sampling. Analysis of the water blank by IC yielded </mg/L compared to <5 mg/L reported by the specific ion electrode analysis.

6.6 ANALYSIS OF WASTE FUEL AND WATER FOR ORGANIC COMPOUNDS

The analysis of organic components in the waste fuel was conducted on a Finnigan gas chromatograph/mass spectrometer/computer system with a 30-m fused silica DB-5 capillary column operated in the split injection mode. After loading the internal standards, the samples were injected and each identified component was quantified relative to a standard of known concentration of that compound injected into the GC/MS.

The POHCs for this test were methylene chloride, Freon 113 (1,1,2-trichloro-1,2,2-trifluoroethane), methyl ethyl ketone (2-butanone), 1,1,1-trichloroethane, and toluene. These POHCs were quantified relative to the bromochloromethane internal standard. In addition to the POHCs, other compounds that were identified in the survey analysis were quantified for each waste fuel sample after determining the relative response of a standard solution of these compounds to the 2-fluorobiphenyl internal standard. Characteristic ions were monitored for other specific compounds to determine if they were present at detectable levels. These compounds included polychlorinated biphenyls (PCBs) with one to ten chlorine atoms, chlorophenols with one to five chlorine atoms, and polychlorinated dibenzodioxins and dibenzofurans with four to six chlorine atoms. None of these compounds were found at a detection limit of about 1 ng/µL injected.

Samples of the water that was used to quench the hot exhaust gases from the kiln were collected and analyzed for POHCs. The purge and trap procedure in EPA's Method 624 was followed, and bromochloromethane was used as the internal standard for quantitation of the POHCs.

6.7 FUEL QUALITY

Samples of coal and waste fuel were submitted to a commercial fuel-testing laboratory for ash, Btu, moisture, and waste fuel density determinations. The ASTM analytical methods ash and Btu are listed in Table 4-1.

7.0 QA/QC RESULTS

Quality Assurance/Quality Control goals for precision, accuracy, and percent completeness were set prior to conducting the sampling and analysis at LSI's cement kiln in Oglesby, Illinois. The approved quality assurance plan for this project was entitled "Quality Assurance Plan for Sampling and Analysis of Emissions From Hazardous Waste Incineration in Calcining Kilns" (June 10, 1983).

A summary of the number of samples planned and those actually collected is given in Table 7-1. The table reflects the revised goals after schedule delays with plant operations and cold weather shortened the sampling effort.

A summary of the goals for precision and accuracy is given in Table 7-2. Results of the QA/QC program are presented in the following sections. Relative percent difference is defined as the difference between two sample values divided by their mean times 100. Percent bias is the difference between the known and measured value divided by the known value times 100.

A systems audit of sampling activities was conducted during the testing from a check list prepared by the QA officer. The QA officer wrote a detailed report of these audit results and described the sampling procedures as conducted. A comparison of the procedures as proposed in the test plan with the procedures actually used was made. No significant differences were noted.

7.1 QA/QC FOR METALS

For those metals determined by atomic absorption, a calibration curve was constructed using three aqueous standards bracketing the concentrations found in the sample digest. To assess the drift in instrument response, two of these calibration standards were rerun after every 5 to 10 samples. The responses were stable to within 5 percent.

The results of analyses of split samples for metals analysis are given in Table 7-3. Acceptable precisions were achieved for most elements in all process samples except for waste fuel in which Al, Cr, Fe, Mg, Ni, and Ti

TABLE 7-1. Percent Completeness

Parameter	Number of Samples		Percent Completeness		
	Goal	Actual (Collected)	Goal	Collected	Analyzed
VOST tubes	60	48[a]	95	80	80[b]
Particulate matter	6	6	100	100	100
PICs	6	6	100	100	100
HCl	6	6	100	100	100
Continuous monitors	5	5	100	100	100
POHCs, waste fuel	3	3	100	100	100
Metals	33	33	100	100	100
Chlorine	28	28	100	100	100
Sulfur	8	8	100	100	100
Btu	8	8	100	100	100
Ash	8	8	100	100	100

[a] The number of VOST runs was reduced because of weather problems and rescheduling of the waste fuel burn.

[b] All VOST tubes collected were analyzed. However, the results from 13 of 24 runs (26/48 samples) were validated and 11/24 runs were rejected because of equipment failure and contamination problems.

TABLE 7-2. Goals for Precision and Accuracy

Parameter	Precision (RPD)	Accuracy (percent bias)
POHCs, VOST	NA	±20
Particulate matter	NA	± 5 dry gas meter; ± 0.2 balance
PICs	25	±20
HCl	10	±10
Continuous monitors	2	± 5
POHCs, waste fuel	10[a]	±20[a]
Metals	20[a]	±20[a]
Chlorine	10	±10
Sulfur	10	±10
Btu, ash	10	±10

[a] Revised based on audit results from previous cement kiln test.

TABLE 7-3. RESULTS OF SPLIT SAMPLE ANALYSES FOR METALS

	Relative Percent Difference				
Element	Clinker	Kiln Feed	Waste dust	Recycled dust[a]	Waste fuel
Al	6	14	8	4,2	58
As	43	56	26	35,12	11
Ba	1	4	1	3.2	-
Ca	0.4	2	4	2,1	0[b]
Cd	34	5	1	5,0.6	3
Cr	14	4	0	3,14	23
Cu	0[b]	0[b]	1	8,0[b]	-
Fe	5	6	1	6,0.9	30
Hg	5	6	4	33,77	10
Mg	3	0[b]	4	1,3	57
Mn	3	6	0.2	6,3	0[b]
Ni	3	0[b]	0[b]	0,0	41
P	2	3	0	5,7	-
Pb	120	3	1	29,0.2	14
Se	13	17	0.6	79,2	0[b]
Sn	0[b]	0[b]	0[b]	0[b],0[b]	-
Ti	37	1	5	4,4	47
V	18	3	2	7,0	0[b]
Zn	2	0	8	4,5	3

[a] Replicate analyses were performed on two recycled dust samples.

[b] Both analyses were below the detection limit.

precisions were unacceptable. Arsenic precisions were unacceptable for all other process samples. Precisions for Cd, Pb, and Ti were also unacceptable for clinker and Hg, Pb, and Se precisions were unacceptable for recycled dust.

Five NBS standard reference materials (SRM) were supplied to the analytical laboratory as performance evaluation samples. These SRMs were chosen to simulate the process sample matrices:

	SRM	Process sample
1645	River Sediment	Kiln Feed
1632a	Bituminous Coal	Coal/Coke
1634a	Fuel Oil	Waste Fuel
634	Portland cement	Clinker
1633a	Fly ash	Waste dust, MM5 particulate catch

Low levels for metals in the fuel oil precluded its use as an effective evaluation sample for the waste fuel. Results for these SRMs are presented in Tables 7-4, 7-5, and 7-6.

TABLE 7-4. RESULTS OF NBS 634 CEMENT STANDARD, NBS 1633a FLY ASH STANDARD, AND NBS 1634a WATER STANDARD ANALYSES (µg/g unless otherwise noted)

Element	Expected value	Measured values	Accuracy (percent bias)
Al (%)[a]	2.75	2.95, 2.75, 2.93, 3.11	7
As (mg/L)[b]	76	76	0
Cd[c]	1.0	0.78	-22
Cd (mg/L)[b]	10	10.5	5
Cr[a]	0.055	0.054, 0.055, 0.057, 0.065	5
Fe (%)[a]	1.99	1.63, 1.99, 1.69, 1.85	-10
Mg (%)[a]	1.99	1.68, 1.99, 1.70, 1.75	-11
Mn[a]	0.195	0.154, 0.195, 0.159, 0.173	-13
Pb (µg/L)[b]	27	24	-11
Se (µg/L)[b]	11	10.2	-7
Ti[a]	0.170	0.098, 0.17, 0.10, 0.11	-30
Zn[a]	0.016	0.020, 0.016, 0.019, 0.019	16

[a] Cement standard.

[b] Water standard.

[c] Fly ash standard

The results in Table 7-4 are for standards that were analyzed at the same time that the field samples were analyzed. The results in Tables 7-5 and 7-6 are for standards that were analyzed prior to the analysis of field samples.

TABLE 7-5. Metals Results for NBS 1633a (Fly Ash)

Metal	Expected value (µg/g)	Measured value[a] (µg/g)	Accuracy (% bias)	RSD
Al	14%	12.6%	-10	-
As	145 ± 15	145	0	-
Ba	0.15%	0.097	-35	16
Co	46	39	-15	-
Cr	196 ± 6	213	9	16
Cu	118 ± 3	116	-2	14
Hg	0.16 ± 0.01	0.195	22	-
Mg	4,550 ± 100	4,457	-2	-
Mn	190	141	-26	19
Ni	127 ± 4	150	18	6
Pb	72.4 ± 0.4	84.8	17	-
Se	10.3 ± 0.6	9.1	-12	-
Ti	0.8%	0.79%	-1	15
V	300	298	-0.7	8
Zn	220 ± 10	258	17	17

[a] Measured values are averages.

[b] RSD = relative standard deviation reported when three or more analyses were made.

TABLE 7-6. Metals Results for NBS 1632a (Coal) and NBS 1645 (River Sediment)

Metal	Expected value (µg/g)	Measured value (µg/g)	Accuracy (percent bias)
(1632a)			
Al	3.07%	2.89%	-6
As	9.3 ± 1	7.8	-16
Ba	130	106	-18
Cr	34.4 ± 1.5	37	8
Ca	2,300	2,270	-1
Cu	16.5 ± 1	18	9
Hg	0.13 ± 0.03	0.135	4
Mg	1,300	1,040	-20
Mn	28 ± 2	26	-7
Ni	19.4 ± 1	29	49
Pb	12.4 ± 0.6	16.2	31
Se	2.6 ± 0.7	3.1	19
Ti	0.175%	0.145%	-17
V	44 ± 3	51	16
Zn	28 ± 2	33.5	20
(1645)			
Cr	2.96%	2.58%	-13
Cu	109	88.6	-19
Mn	785	661	-16
Ni	45.8	39.9	-13
V	23.5	107	456
Zn	1,720	1,609	-6

7.2 QA/QC RESULTS FOR CHLORINE, SULFUR, AND BTU

The results of the split samples analyses for chlorine and sulfur are given in Table 7-7. Accuracy results are shown in Table 7-8. Both show acceptable results for precision and accuracy. Btu results for accuracy are given in Table 7-9. Accuracy results for chlorine determination by ion chromatography on aqueous standards are summarized in Table 7-10 and show very low percent bias over a range of 1 to 1,000 mg/L. HCl emission measurements were obtained from ion chromatography analysis of the impinger solution. The chloride specific ion electrode analysis conducted initially gave unacceptable results for audit standards, and many concentrations were below its detection limit of 5 mg/L.

TABLE 7-7. REPLICATE ANALYSES OF SPLIT SAMPLES FOR CHLORINE AND SULFUR

Sample	Analysis	Replicate results	Relative percent difference
Waste fuel	chlorine (%)	1.60, 1.67	4
	sulfur (ppm)	455, 490	7
Kiln feed	chlorine (ppm)	425, 425	0
Recycled dust 1	chlorine (%)	1.88, 1.89	0.5
Recycled dust 2	chlorine (%)	1.30, 1.29	0.8
Waste dust	chlorine (%)	8.06, 8.09	0.4

TABLE 7-8. ACCURACY RESULTS FOR CHLORINE AND SULFUR

Analysis	Expected value (percent)	Measured value (percent)	Accuracy (percent bias)
Sulfur	2.85[a]	2.81	-1
Sulfur	3.50[b]	3.26	-7
Chlorine	0.25[b]	0.27	8

[a] Fuel oil standard (NBS SRM 1634a)

[b] Coal standard (LECO coal standard)

TABLE 7-9. BTU RESULTS FOR ACCURACY

Sample	Expected value (Btu/lb)	Measured value (Btu/lb)	Accuracy (% bias)
Fuel standard (LECO)	19,779	19,835	0.3
Coal standard (LECO)	12,755	12,814	0.5

TABLE 7-10. ACCURACY RESULTS FOR CHLORINE BY ION CHROMATOGRPAHY

Standard	Expected value (mg/L)	Measured value (mg/L)	Percent bias
RTI Audit Sample	1,000	1,000	0
E-S Field Spike 1	50	50	0
E-S Field Spike 2	50	50	0
E-S Standard A	50	50	0
E-S Standard B	50	50	0
EPA Acid rain <u>QA samples</u>:			
2142	10.33	10.13	-2
3905	4.17	4.48	7
1239	1.01	0.99	-2
3905	4.17	4.21	-1

7.3 QA/QC FOR CONTINUOUS ANALYZERS

The QC activities for the continuous analyzers are largely those described in the QAPP-multipoint calibrations to establish linearity, pre- and post-test zero and span calibrations, mid-run span checks, flowing calibration gases through the sampling system to verify the absence of line losses, and the duct traverse to quantify the extent of stratification in the gases, if any.

Certain data collection goals were established in the QAPP, and the above actions were taken to attain these goals. The monitor performance criteria were span gas error (from linearity) less than 5 percent and zero value less than 2 percent of span value; these criteria were met for all data collected. Other QC actions that were taken include pressurizing the sample line for as much of its length as possible (to prevent inward leakage) and the use of Teflon®, glass, or stainless steel for components contacting sample gas. The QA objectives that were identified in the plan were met.

Limits of instrument drift were not specifically established in the QAP, but the criteria that were applied were zero and span drift <2 percent. The system drift did not exceed 2 percent of full scale for any of the tests, so the initial calibrations were used; multipoint checks were used periodically for verification of system response.

7.4 QA/QC FOR MM5 EXTRACTS AND WASTE FUEL ANALYSES

Tables 7-11 and 7-12 present the precision and accuracy results for splits and spikes for compounds found in the MM5 extracts. Table 7-13 presents the results for a waste fuel sample that was split and analyzed at the same time that the waste fuel samples for Runs 3 and 4 were analyzed.

The waste fuel sample for Run 5 was inadvertently left in storage and was not analyzed as quickly as the other two samples were. After lengthy storage, very low concentrations of the POHC compounds were found. In addition, attempts to recover spikes of POHCs in this waste fuel sample were unacceptable. Consequently, efforts to analyze this sample were aborted because of the loss of volatile compounds and because of spiking/analytical difficulties.

7.5 VOST QA AUDIT

An audit of Engineering Science's VOST sampling and RTI's analysis was conducted before the test trip on December 5, 1983. An NBS gas cylinder containing known quantities of five compounds was used to prepare two types of samples: (1) samples collected from the cylinder through the entire sampling train, and (2) cartridges loaded directly from the cylinder. The results of the audit are given in Table 7-14. For directly loaded cartridges, the accuracy results show that the percent bias from the NBS value ranged from -22 to 26 percent. For samples collected through the entire train, the percent bias ranged from -29 to 24 percent. (Previously published guidance for VOST accuracy suggests that an accuracy of better than ±50 percent should be expected.) The audit goal was to collect three samples from the VOST and three samples directly from the cylinder. Data for one sample from the VOST were lost when

TABLE 7-11. RESULTS OF SPLIT ANALYSIS OF MM5 EXTRACTS FOR RUN 1

Compound	Results (ng/μL)	Precision (RPD)
Styrene	2,2	0
Ethyl benzene	<1,1	-
C_3-benzenes	4,5	22
C_4-benzenes	10,9	11
C_6-benzenes	1,1	0
Biphenyl	7,7	0
Benzaldehyde	38,37	3
Naphthalenes	36,35	3
Methyl naphthalenes	5,6	18

TABLE 7-12. RESULTS OF SPIKED MM5 EXTRACTS FOR ACCURACY

Compound	Quantity spiked (ng/μL)	Quantity measured (ng/μL)	Accuracy (percent bias)
Ethylbenzene	434	542	25
Xylene	440	391	-11
Chloroform	372	560	51
Benzene	440	567	29
Trichloroethylene	365	430	18
Perchloroethylene	405	16	-96
C_3-benzene	430	324	-25
C_4-benzene	430	260	-40
C_6-benzene	430	291	-32
Biphenyl	547	364	-33
Diethylthalate	307	422	37
Benzaldehyde	520	465	-11
Naphthalene	349	390	12
Methylnaphthalene	515	563	9

TABLE 7-13. RELATIVE PERCENT DIFFERENCE FOR WASTE FUEL SPLITS (LAB)

Compound	Measure value (g/L)	Relative percent difference
Methylene chloride	14.13, 11.95	17
Freon 113	0.135, 0.131	3
2-Butanone	10.11, 7.00	36
Toluene	15.22, 10.68	35
1,1,1-Trichloroethane	0.634, 0.593	7

the GC/MS computer malfunctioned, and one sample from the direct loading was found to be broken when received in the laboratory.

7.6 QA/QC FOR VOST ANALYSES

The complete results of the VOST analyses are given in Table 7-15. The samples listed consecutively through Run 4-2 were all analyzed on or before December 29, 1983-- within 11 days from the end of the test. Because of a GC/MS computer failure, the remaining samples were not analyzed until February 3, 1984. Severe analytical difficulties were experienced with the second set of samples.

Internal standard response and surrogate recoveries are presented in Table 7-16. The internal standard response for the first set of samples analyzed was very consistent with only one run exceeding 50-percent RPD and three runs exceeding 22-percent RPD. The initially reported surrogate recoveries (in parentheses) were high but very consistent, i.e., a relatively constant area response. An investigation revealed that the surrogate quantitation originated from an inaccurate response factor based on comparison with other VOST analyses and with response factors generated at this same time for water analyses. Using corrected response factors, the surrogate recoveries shown in Table 7-16 were calculated from the measured area counts of the internal standard and surrogates. The response factors for the target POHCs were also examined. No correction was needed because there was an agreement between these response factors and those generated for the same POHCs for: (1) previous VOST analyses, (2) waste fuel analyses using direct injection of a standard solution, and (3) water samples.

TABLE 7-14. QA Audit Results for VOST Sampling and Analysis

Audit gases	NBS value (ppb)	Measured value, entire train (ppb)	Percent Bias	Measured value, cartridge only (ppb)	Percent Bias
Carbon tetrachloride	21	15, 21	-29, 0	20, 19	-5, -10
Chloroform	23	18, 19	-22, -17	19, 18	-17, -22
Perchloroethylene	29	29, 36	0, 24	36, 33	24, 14
Vinyl Chloride	31	32, 24	3, -23	39, 32	26, 3
Benzene	18	19, 19	6, 6	17, 19	-6, 6

TABLE 7-15. VOST RESULTS (ng/pair cartridges)

Run	Freon 113	Toluene	MEK	1,1,1-TCE	Methylene chloride
1-1	37	2,640	138	<8	185
1-2	Line plugged - no data				
1-3[a]	65	1,562	<50	<8	285
1-4[a]	17	883	<50	<8	575
1-5	465	398	<50	<8	2,308
1-6	71	842	<50	<8	479
Field Blank 1	32	10	<50	<8	162
2-1	617	1,058	100	21	1,644
2-2	No internal standard found				
2-3	67	894	78	13	2,167
2-4	423	1,071	106	43	3,589
2-5	90	740	93	<8	238
2-6	<10	68	86	<8	9,249
Field Blank 2	15	35	<50	<8	527
3-1	74	1,155	151	<8	1,780
3-2	59	435	58	<8	626
3-3	<10	308	61	<8	250
4-1	<10	440	<50	<8	183
4-2	66	528	82	<8	147
4-3	No internal standard found				607
4-4[a]	194	215	434	73	10,379
4-5[a]	333	4,296	12,400	115	
Field Blank 4[a]	1,924	5,397	<50	1,074	12,208
5-1[a]	6,750	6,716	3,685	3,270	16,903
5-2[a]	10,280	8,867	4,151	5,133	14,048
5-3[a]	5,100	5,862	5,792	6,341	6,958
5-4[a]	8,100	9,302	5,741	8,580	13,387
Field Blank 5[a]	8,734	18,990	3,124	5,826	13,515
Lab Blank 1[a]	5,920	6,814	1,795	2,501	9,169
Lab Blank 2[a]	9,564	11,652	4,170	3,966	8,940

[a] Internal standard outside of control range. Data invalidated because the low internal standard response yields an overestimate for quantity of POHC compounds.

TABLE 7-16. INTERNAL STANDARD RESPONSE AND SURROGATE RECOVERIES

Date	Run[a]	Standard response	Relative percent difference[b]	Corrected surrogate recoveries (%)[c] d_4-dichloroethane	Corrected surrogate recoveries (%)[c] d_6-benzene
12/19	1-1 TX	74,900	22	52 (131)	71 (125)
	1-1 TC	47,600	22	54 (136)	57 (101)
	1-4	14,500	76	44 (198)	309 (1,300)
12/20	FB-1	48,800	14	67 (299)	85 (369)
	1-5	43,900	3	66 (294)	119 (505)
	1-6	35,500	17	53 (234)	127 (540)
12/29	2-1 TX	76,800	13	77 (336)	123 (528)
	2-1 TC	61,200	10	76 (332)	60 (368)
	3-1 TC	44,100	35	74 (328)	94 (399)
	2-6	83,000	22	78 (337)	131 (557)
	2-5	67,700	0.5	72 (314)	134 (569)
	2-3	79,700	17	67 (289)	132 (562)
	3-1 TX	49,100	28	74 (187)	134 (235)
	2-4	60,600	11	67 (169)	129 (227)
	FB-2	67,500	0.7	90 (227)	117 (206)
	4-2	72,700	7	73 (185)	139 (244)
	3-3	79,000	16	75 (189)	132 (233)
	4-1 TX	65,600	3.5	79 (200)	149 (262)
	3-2	77,100	13	73 (183)	136 (239)
1/3	4-1 TC	13,800		75 (190)	104 (183)
2/3	5-1 TX	93,400	105	11 (47)	19 (81)
	4-4	31,100	32	25 (11)	35 (152)
	5-1 TC	2,560	94	61 (380)	179 (770)
	LB-1	16,500	64	77 (336)	37 (402)
	5-4	89,800	97	0.8 (5)	24 (103)
	LB-2	19,200	58	92 (404)	81 (347)
	5-3	184,000	305	0 (0)	19 (82)
	4-5	3,170	93	62 (269)	224 (965)
	FB-5	10,900	76	10 (65)	102 (440)
	FB-4	427	99	182 -	- -
	5-2	49,100	8	1 (5)	27 (120)

---

[a] TX = Tenax, TC = Tenax/charcoal, FB = field blank, LB = lab blank

[b] RPD from average daily response

[c] Corrected response factors used. Values in parentheses were generated by GC/MS computer with inaccurate response factors for surrogates. See text.

The criteria that are used to assess the quality of the data are the precision of the internal standard response and the accuracy of the surrogate recoveries. Two conditions must be satisfied: (1) The surrogate recoveries for both surrogates must be in the range of 50-150 percent, and (2) the deviation from the daily average internal standard response (ISR) must not exceed 50 percent. For the first set of data, the ISR limit is effectively 35 percent because there are no runs with differences between 35 and 50 percent.

Using the criteria described above, it is obvious that none of the data generated on February 3 can be validated. The swings in ISR and poor surrogate recoveries indicate that the reported values may be off by as much as two orders of magnitude. The lab blank results indicate that contamination was a problem and that these results would overstate actual stack gas concentrations.

An investigation was conducted to try to determine the causes of the unacceptable results for analyses performed on February 3, 1984. The starting point was two lab blanks analyzed on that day which showed high levels of the target compounds and a low internal standard response (ISR). The GC/MS output showed significant area counts for the POHCs; therefore, although the low ISR would overstate actual quantities, significant quantities of the POHCs were present and detected. The GC/MS output was closely examined and showed no other significant hydrocarbons (or aromatics) from the lab blanks; consequently, the source of contamination must have been a relatively pure source of the POHCs. If the contamination had occurred from waste fuel samples, from dirty vapors during transport or laboratory storage, or from other VOST cartridges, then other hydrocarbons would have been expected. The only pure source of the POHC compounds that we found were calibration standards used for preparing response factor cartridges, water standards, and waste fuel standards. After a review of the spiking procedure, the QA Officer felt that accidental spiking of all of the samples with calibration standards was unlikely. In addition, the proportion of POHC compounds found on the lab blanks was different from the proportion in the calibration standards.

VOST cartridges are spiked in the laboratory by flash evaporation from a methanol solution. All samples, field blanks, lab blanks, and response factor cartridges are spiked with a constant quantity of the internal standard solution and a constant quantity of the solution containing the two surrogates. The response factor cartridges are also spiked with varying levels of the POHC standard solution for calibration purposes. The internal standard and surrogate solutions were checked and found to be free of the POHC compounds.

The QA Officer also examined the GC results that were generated when checking the cleaned cartridges before shipment to the field. The results showed no contamination; therefore, the initial preparation and cleanup of VOST tubes before the test was not the source of contamination.

The spiking procedure was repeated in an attempt to duplicate potential causes of contamination. For example, if a response factor cartridge were loaded with the calibration standard and cold spots existed in the flash evaporation unit, then traces of the POHCs may be left behind in the unit. Blank cartridges loaded with internal standard solutions following the loading of response factor cartridges showed no traces of POHCs from the calibration standard. The flash evaporation technique appeared to be adequate for spiking cartridges without contamination.

Another source of a relatively pure mixture of the POHC compounds was the calibration standard used for the liquid injection analysis of waste fuel samples. Because different plumbing is used for this GC/MS analysis, contamination of the VOST plumbing with this standard appears unlikely.

The low internal standard response for February 3 indicates that either the internal standard was not spiked accurately or that loss of the internal standard occurred from leakage. Previous consistent results, the constant spiking procedure, and consistently low results indicate that spiking probably was not the problem. Several other factors indicate that leakage, either during storage or during desorption (from the GC/MS plumbing), was the likely cause.

A close examination of the VOST cartridges revealed that cartridges from 6 of the 10 runs that were analyzed on February 3 had chipped stems or hairline cracks in the stem. In addition, the cartridges for Runs 2-2 and 4-3, which showed no internal standard, had chips or hairline cracks. It is not known whether the cracks occurred in the field, during transport, during spiking, or during insertion into the GC/MS plumbing. Discussions with analytical personnel indicated that some were cracked when received, and fractures may have been created or worsened during analysis. Analytical personnel also noted that after heating for desorption, some VOST fittings had loosened and were only finger tight. This was likely caused by the different coefficients of expansion of the seal materials. Leakage can explain the low

ISR response; however, it does not completely explain the apparent contamination problem.

The history of the samples and other factors were examined to try to determine how those samples were different and what may have caused the problems. These VOST cartridges were collected in the coldest weather of the test (-20° F) and probably warmed to freezing (32° F) during storage. The samples were stored for 6-7 weeks because of the GC/MS computer failure and repair difficulties. During storage, the samples probably experienced some thermal cycling as ice packs thawed out and were replaced. The lab blanks experienced the same storage conditions as the field samples. These factors increased the opportunity for contamination and provided less than ideal conditions for maintaining sample integrity.

A difference between these VOST cartridges and the QA audit samples is that the QA samples were generated from a clean, dry gas stream. The field samples were collected from a wet and very acidic gas stream; consequently, the Tenax from field sampling contained a significant amount of water and HCl (and possibly hydrofluoric acid from the Freon 113). Water can decrease an adsorbent's adsorptive capacity, and the effect of an acidic medium is unknown. Discolored samples have been observed and may be related to the acidity. Under these conditions, is the methanolic solution of standards always adsorbed by the Tenax?

Could incomplete volatilization or condensation of water in the GC/MS plumbing trap POHCs and release them in a subsequent run? For example, water may condense in the line between the desorption chamber and purge water trap. The condensation of this acidic water could cause cross contamination between runs and has been observed to cause serious corrosion problems if it contacts any metal fittings. Occasional plugging of lines was also observed. If the plugging was caused by particles of Tenax, then another mechanism for cross contamination exists. Similar problems may be created if the plugging resulted from stack particulate matter which was excessively high during the waste fuel burn.

At this point, we cannot state conclusively the absolute cause of the problems with the February 3 data. It is apparent that leakage was contributory, and corrective actions can be taken to prevent or minimize leakage. The long storage time, cracked tubes, potential loss of volatiles and standards, and increased opportunity for contamination during storage probably contributed to the analytical problems. From this experience, several recommendations can be made that may help laboratories performing VOST analyses in the future:

1. Before each day of analysis, run a laboratory blank and check for contamination, ISR, and surrogate recoveries before any field samples are run. Continue to run lab blanks periodically throughout the day, and immediately stop analysis of samples and troubleshoot whenever problems are observed. This is particularly important for VOST samples, which are expensive to collect and provide only one opportunity for analysis (i.e., the sample is destroyed by analysis).

2. Throughout the day, monitor the ISR and surrogate recoveries from the field sample. Investigate and take corrective actions on a sample-by-sample basis.

3. Analyze VOST tubes immediately upon receipt, if possible. Storage time should not exceed 2 weeks.

4. Be convinced that all tubes are tightly sealed at all stages of sampling and analysis.

5. Include VOST tubes loaded with the target compounds from audit gas cylinders for shipment to the field and as unknowns during GC/MS analysis.

8.0 RESULTS

8.1 ANALYTICAL RESULTS FOR WASTE FUEL

The major components in the waste fuel were identified and the quantity estimated for each sample of waste fuel. The GC/MS results for Run 3 and 4 are summarized in Table 8-1. Major compounds other than the POHCs that were found in the waste fuel include styrene, ethylbenzene, xylene, trichloroethylene, tetrachloroethylene, benzaldehyde, C_3 benzenes, and C_4 benzenes. The waste fuel was also checked for polychlorinated biphenyls (PCBs) with one to ten chlorine atoms, chlorophenols with one to five chlorine atoms, and polychlorinated dibenzodioxins and dibenzofurans with four to six chlorine atoms by monitoring at least two characteristic ions for each compound. None of these compounds was detected at an estimated detection limit of about 1 ng/µL in the waste fuel (1 mg/L). The results for Run 5 are discussed in Section 7.

8.2 POHC EMISSION RATES AND DRE

Several approaches are possible to evaluate POHC emissions and DRE. Two sets of results are presented here, one with blank corrections and one without blank corrections. No corrections for the measured baseline emissions were applied for the DRE calculation (POHC emission rates). The basic evaluation is the most conservative (restrictive) that can be made and is based on the following assumptions:

- All POHCs that are measured in the stack gas result from waste fuel combustion. This further assumes 100% DRE of any POHCs present in or formed from the coal, that the kiln feed does not contribute any POHCs to the flue gas, and that no POHCs are volatilized from the quench water.
- All of the POHCs that are measured on the sample tubes result from stack gas, not from residual blank values or contamination.

TABLE 8-1. RESULTS OF GC/MS ANALYSIS OF WASTE FUEL (g/L)

COMPOUND	Run Number 3	Run Number 4
Methylene chloride	3.70	3.77
Freon 113	8.26	6.28
2-Butanone	8.89	21.0
1,1,1-Trichloroethane	9.58	13.9
Toluene	21.6	40.8
Styrene	10.0	15.0
Ethylbenzene	7.41	15.4
O-xylene	9.07	20.9
Chloroform	0.021	0.020
Benzene	0.206	0.193
Trichloroethylene	16.2	23.4
Tetrachloroethylene	10.4	13.5
Benzaldehyde	14.2	23.2
C_{11} aliphatics	0.335	1.13
C_3 benzenes	0.399	1.22
C_4 benzenes	0.308	1.36
C_6 benzenes	0.001	0.010
Biphenyl	0.0009	0.007
Diethylphthalate	0.003	0.020
Naphthalene	0.066	0.231
Methyl Naphthalenes	0.012	0.081

- The POHCs present in the ambient air do not contribute to the measured stack gas concentrations even though there is ambient air inleakage (15-20%) into the ESP system.

A second set of calculations is presented where the second assumption is not made, i.e., a blank/contamination correction has been applied to the analytical result. These calculations were performed to evaluate the impact of blank values on the calculated DREs.

The calculation procedure is much the same as that described in Sections 8.4 and 8.5 for HCl and particulate matter emissions, except for the DREs. A metered sample volume was corrected to standard conditions and the mass of POHC on each pair of tubes divided by this volume to give a concentration in ng/standard liter. The concentration (equivalent to $\mu g/M^3$) was multiplied by the daily average stack flow rate as measured for the MM5 to yield a POHC emission rate (W_{out}) for each run in µg/sec. The POHC input rate (W_{in}) was determined by calculating the product of the daily average fuel flow rate and analyzed POHC concentration to yield a POHC input rate. The DRE is simply $(W_{in} - W_{out}) \div W_{in} \times 100\%$.

The blank value correction procedure is not so straightforward. An average of the daily field (exposure) blank was calculated. If the field blank value is significantly different from the sample value (factor of two or greater), then the blank correction was applied. No correction is made when the field blank value is not significantly different from the sample value. No blank corrections were required for 1,1,1-trichloroethane or methyl ethyl ketone. Blank corrections were applied for the other three POHCs; however, the blank correction for toluene was generally less than 5 percent of the sample value.

The VOST results that met the QA criteria described in Section 7 are given in Table 8-2. Analytical problems were experienced for several VOST runs and meaningful data could not be extracted. (The complete listing of VOST results and discussion of data validation are covered in Section 7.)

8.2.1 POHC Emission Rates

Table 8-3 contains the concentrations of POHCs (uncorrected for blanks) in the stack gas, which were calculated from the metered sample volume and mass of POHC given in Table 8-2. The corresponding POHC emission rates are

TABLE 8-2. VOST RESULTS (ng/pair cartridges)

Run number	Volume sampled (L)	Freon 113	Toluene	MEK	1,1,1-TCE	CH_2Cl_2
1-1	20.4	37	2,640	138	<8	185
1-5	18.9	465	398	<50	<8	2,308
1-6	18.9	71	842	<50	<8	479
2-1	19.3	617	1,058	100	21	1,644
2-3	18.9	67	894	78	13	2,167
2-4	19.1	423	1,071	106	43	3,589
2-5	18.8	90	740	93	<8	238
2-6	19.3	<10	68	86	<8	9,249
3-1	20.4	74	1,155	151	<8	1,780
3-2	19.7	59	435	58	<8	626
3-3	20.7	<10	308	61	<8	250
4-1	20.2	<10	440	<50	<8	183
4-2	20.6	66	528	82	<8	147
Field blank 1		32	10	<50	<8	162
Field blank 2		15	35	<50	<8	527

MEK = methyl ethyl ketone
1,1,1-TCE = 1,1,1-trichloroethane
CH_2Cl_2 = methylene chloride

TABLE 8-3. POHC CONCENTRATIONS (ng/L)[a]

Run number	Freon 113	Toluene	MEK	1,1,1-TCE	CH_2Cl_2
1-1	1.81	129	6.76	<0.39	9.07
1-5	24.6	21.1	<2.65	<0.42	122
1-6	3.76	44.6	<2.65	<0.42	25.3
2-1	32.0	54.8	5.18	1.09	85.2
2-3	3.54	47.3	4.13	0.688	115
2-4	22.1	56.1	5.55	2.25	188
2-5	4.79	39.4	4.95	<0.43	12.7
2-6	<0.52	3.52	4.46	<0.41	479
3-1	3.63	56.6	7.40	<0.39	87.3
3-2	2.99	22.1	2.94	<0.41	31.8
3-3	<0.48	14.9	2.95	<0.39	12.1
4-1	<0.50	21.8	<2.48	<0.40	9.06
4-2	3.20	25.6	3.98	<0.39	7.14

[a] Concentration in the stack gas, uncorrected for blanks.

given in Table 8-4 (uncorrected) and Table 8-5 (blank-corrected). The average POHC emission rates for the waste burn are all less than or equal to the baseline emission rates. Freon 113 was detected in the baseline samples, but there is no reason to believe that it could be present in the stack gas during the baseline test. Sporadic, low-level contamination is the likely source of the Freon 113; however, this is difficult to confirm because the field blanks associated with these runs had relatively low levels (15 and 32 ng per pair of cartridges). Consequently, the blank-corrected emission rates for Freon 113 in Table 8-5 are still higher for the baseline than during the waste fuel burn.

The conclusion from the emission rate data is that no increase in POHC emission rates was measured when the waste fuel was burned in the kiln. If the source of Freon 113 and methylene chloride in the baseline testing is sporadic contamination, then actual POHC emission rates are likely to be lower than those reported.

8.2.2 DREs

The mass flow rates of the POHCs into the kiln were calculated from the concentrations in Table 8-1, the specific gravity of the waste fuel (0.96), and the mass flow rate of waste fuel. The POHCs into the kiln (W_{in}) are given in Table 8-6. DREs were calculated as previously described from W_{in} (Table 8-6) and W_{out} (Tables 8-4 and 8-5).

The DRE results are given in Table 8-7. The DREs for Freon 113 and 1,1,1-trichloroethane average 99.999 percent or greater. These two compounds are the POHCs most unique to the waste fuel. The DREs for toluene and methyl ethyl ketone averaged 99.995 and 99.998 percent, respectively. The DREs for methylene chloride, the most troublesome POHC with respect to contamination, averaged 99.96 percent (uncorrected) and 99.97 percent (blank-corrected). Note that blank corrections had no significant effect on the other reported DREs. (Also remember that no blank correction is applied if the sample value and blank value are not significantly different.)

The consistently highest DREs were observed for Run 4 which had the higher rate of waste fuel usage (37 vs. 25 percent replacement of coal/coke). The DREs for all five POHCs, including methylene chloride, were 99.99 percent or greater for both of the runs at 37-percent replacement.

TABLE 6-4. POHC EMISSION RATES - UNCORRECTED FOR BLANKS
($\mu g/s$)

Run number	Freon 113	Toluene	MEK	1,1,1-TCE	CH_2Cl_2
1-1	68.4	4,730	248	<14	333
1-5	903	774	<97	<15	4,480
1-6	138	1,640	<97	<15	929
2-1	1,180	2,020	191	40.1	3,140
2-3	130	1,740	152	25.3	4,230
2-4	813	2,064	204	82.8	6,920
2-5	176	1,450	182	<15.8	467
2-6	<19	130	164	<15.1	17,600
3-1	126	1,960	257	<13.5	3,030
3-2	104	767	102	<14.2	1,100
3-3	<16.7	517	102	<13.5	420
4-1	<17.3	754	<85.8	<13.5	313
4-2	111	886	138	<13.5	247
Baseline	428	1,820	167	<27.8	4,760
Waste burn	75	977	137	<13.6	1,020

TABLE 8-5. POHC EMISSION RATES - CORRECTED FOR BLANKS
(ug/s)

Run number	Freon 113	Toluene	MEK	1,1,1-TCE	CH_2Cl_2
1-1	23.4	4,700	248	<14	333[a]
1-5	855	727	<97	<15	3,820
1-6	91.4	1,590	<97	<15	260
2-1	1,130	1,970	191	40.1	2,480
2-3	83.9	1,700	152	25.3	3,550
2-4	769	2,020	204	82.8	6,260
2-5	129	1,400	182	<15.8	467[a]
2-6	<19[a]	85.7	164	<15.1	17,000
3-1	85.0	1,930	257	<13.5	2,440
3-2	61.8	725	102	<14.2	496
3-3	<16.7[a]	479	102	<13.5	420[a]
4-1	<17.3[a]	713	<85.8	<13.5	313[a]
4-2	70.6	848	<138	<13.5	247[a]
Baseline	388	1,770	167	<28	4,270
Waste burn	50	939	137	<13.6	783

[a] Blank value indistinguishable from sample value. No blank correction applied as suggesed in VOST protocol.

TABLE 8-6. W_{in} FOR POHCs

POHC	Run 3[a] Percent	Run 3[a] W_{in} (g/s)	Run 4[b] Percent	Run 4[b] W_{in} (g/s)
Methylene chloride	0.385	2.51	0.393	3.58
Freon 113	0.860	5.59	0.654	5.96
Methyl ethyl ketone	0.926	6.02	2.19	19.93
1,1,1-trichloroethane	0.998	6.49	1.45	13.19
Toluene	2.25	14.63	4.25	38.72

[a] Based on a waste fuel rate of 650 g/s.

[b] Based on a waste fuel rate of 911 g/s.

TABLE 8-7. DRE RESULTS[a]

Run number	Freon 113	Toluene	MEK[b]	1,1,1-TCE[b]	Methylene chloride
3-1	99.998 (NC)	99.986 (99.987)	99.996 (NC)	>99.999 (NC)	99.88 (99.90)
3-2	99.999 (99.999)	99.995 (NC)	99.998 (NC)	>99.999 (NC)	99.96 (99.98)
3-3	>99.999 (NC)[b]	99.996 99.997	99.998 (NC)	99.999 (NC)	99.98 (NC)[b]
4-1	>99.999 (NC)[b]	99.998 (NC)	>99.999 (NC)	>99.999 (NC)	99.99 (NC)[b]
4-2	99.998 (99.999)	99.998 (NC)	99.999 (NC)	>99.999 (NC)	99.99 (NC)[b]
Average	99.999 (NC)	99.995 (NC)	99.998 (NC)	>99.999 (NC)	99.96 (99.97)

MEK = methyl ethyl ketone
1,1,1-TCE = 1,1,1-trichloroethane
NC = no change

[a] Uncorrected for blanks. Values for blank corrections are in parentheses.

[b] Blank value was indistinguishable from sample value. No blank correction applied as suggested in VOST protocol.

8.3 PRODUCTS OF INCOMPLETE COMBUSTION

Estimates of organic emissions were obtained by the Modified Method 5 sampling which is designed to capture compounds with boiling points greater than 100° C. The MM5 results are given in Table 8-8 as the total weight detected in the final concentrate and are converted in Table 8-9 to an estimated mass emission rate. Blank corrections were not necessary because the field blank showed no significant levels of these organics. Low levels of phthalates were found but not reported because the blank contained slightly higher levels than the samples.

The MM5 extracts were also screened by GC/MS for the isomers of dibenzodioxins and dibenzofurans by monitoring the characteristic ions. None of these compounds were detected at a detection limit of about 1 ng per µL injected. The final concentrate volume was 1 mL which implies that the total quantity of the dibenzodioxins and dibenzofurans that were collected in each MM5 run could be no more than 1 µg. Based on the lowest and highest volumes samples (0.83 and 4.55 m^3), the concentration of dibenzodioxins and dibenzofurans was less than 0.2 to 1.2 $\mu g/m^3$. For a molecular weight of 29.7 g/g-mol for the stack gas, the concentration yields less than 0.15 to 0.91 ppb by weight (1.5 to 9.1×10^{-10} g/g) for these compounds in the stack gas.

The emission rates of styrene, ethylbenzene and xylenes show no increases when the waste was burned during Runs 3 through 5. The emission rates of the C_3- and C_4-benzenes appeared to increase during Run 4. The waste fuel analysis in Table 8-1 indicated that the waste fuel for Run 4 contained about three times the quantity of these compounds found in Run 3. The trend is reversed for the C_6-benzenes, which was found in very low concentrations in the waste fuel for both Runs 3 and 4.

The emission rates for the other organic compounds during the waste burn show increases over the baseline. The average emission rates for the baseline and waste burn were: biphenyl (43 vs. 87 µg/s), benzaldehyde (180 vs. 230 µg/s), naphthalenes (170 vs. 530 µg/s), and methyl naphthalenes (31 vs. 85 µg/s).

TABLE 8-8. TOTAL WEIGHT OF COMPOUNDS IN MM5 EXTRACT (mg)[a]

Compound	Run Number 1	2	3	4	5
Styrene	0.002	ND	ND	ND	ND
Ethylbenzene	0.001	ND	ND	ND	ND
Xylene	ND	ND	ND	ND	ND
C_3-benzenes	0.004	ND	ND	0.008	0.001
C_4-benzenes	0.010	ND	0.002	0.011	0.003
C_6-benzenes	0.001	ND	0.011	0.001	0.009
Biphenyl	0.007	0.003	0.002	0.003	0.007
Benzaldehyde	0.038	0.004	0.004	0.010	0.017
Naphthalenes	0.036	0.005	0.015	0.023	0.022
Methylnaphthalenes	0.005	0.002	0.002	0.004	0.004

[a] Nominal detection limit of 1 μg (1 ng/μL injected from 1 mL final concentrate).

TABLE 8-9. EMISSION RATES OF COMPOUNDS IN MM5 EXTRACTS (μg/s)

Compound	Run Number 1	2	3	4	5
Styrene	16.1	<11	<42	<30	<12
Ethylbenzene	8.1	<11	<42	<30	<12
Xylene	<8	<11	<42	<30	<12
C_3-benzenes	32	<11	<42	243	12
C_4-benzenes	81	<11	84	334	37
C_6-benzenes	8.1	<11	460	30	111
Biphenyl	56	33	84	91	86
Benzaldehyde	307	44	167	304	209
Naphthalenes	290	55	627	698	271
Methylnaphthalenes	40	22	84	121	49

TABLE B-10. STACK PARAMETERS

Run number	Temperature °C (°F)	Moisture %	CO_2 %	O_2 %	Molecular weight g/g-mol	Velocity m/s (ft/s)	Volumetric flow rate	
							Actual m^3/min (acfm)	Standard DN m^3/min (dscfm)
1	264 (506)	15.0	21.5	7.5	29.7	15.4 (50.5)	4,864 (171,800)	2,202 (77,770)
2	263 (505)	15.0	21.5	7.5	29.7	15.6 (51.3)	4,945 (174,600)	2,207 (77,930)
3	283 (542)	14.3	21.8	7.1	29.8	14.6 (48)	4,626 (163,400)	2,082 (73,540)
4	274 (525)	14.3	21.5	7.5	29.8	14.3 (47)	4,534 (160,100)	2,077 (73,350)
5	287 (532)	14.9	21.4	7.6	29.7	15.8 (51.8)	4,992 (176,300)	2,260 (79,820)

8.4 PARTICULATE MATTER

Tables 8-10 and 8-11 summarize the results of the velocity, temperature, and MM5 sampling measurements for particulate matter. During the waste burn, sampling conditions were very difficult because of extremely cold weather (approaching -20° F), and because of a very high loading of particulate matter when the electrostatic precipitator malfunctioned. Run 3 was an abbreviated run because of plugging problems, and Run 4 represents an abbreviated run from a single-point isokinetic sample. Runs 1, 2, and 5 were complete MM5 runs as originally planned. The average emission rates show a large increase from the baseline to the waste burn test conditions (53 to 240 kg/h). However, serious maintenance problems developed with the electrostatic precipitator (ESP) and could not be corrected during the test period. Faced with bitter cold weather, the test crew continued the testing even though it was apparent that particulate matter results only provided data for a malfunctioning ESP. Although the measurements show an increase in particulate matter during the waste burn, the increase cannot be conclusively attributed to the burning of the waste. Resampling under both test conditions with a properly operating ESP would be required to determine the effect of waste fuel combustion on particulate matter emissions.

8.5 HCl EMISSIONS

HCl sampling was conducted twice during each MM5 run to estimate HCl emissions based on the chloride content of the impinger catch. The HCl results are given in Table 8-12. The average emission rate increased from an average of 1.3 kg/h for the baseline to 11.5 kg/h for the waste burn. Table 8-12 shows that the HCl emission rate increased as the chloride entering with the fuel increased. The emission rate for Run 5 appears disproportionately high compared to Runs 3 and 4. During Runs 3 and 4, HCl emissions were about 3 to 8 percent of the chloride rate into the kiln. During Run 5, the HCl rate was about 37 percent of the chloride rate into the kiln. A more detailed discussion of the source and fate of chloride is given in the material balance results in Section 8.8.

TABLE 8-11. PARTICULATE MATTER EMISSIONS

Run number	Sample Volume DN m^3	Sample time (min)	Percent isokinetic	Total mass (mg)	mg/DN M^3	kg/h (lb/h)
1	4.55	240	94.7	1,017.4	233	30.8 (67.9)
2	3.32	240	100.9	1,733.5	563	74.6 (164)
3	0.83	80	86.9	2,330.7	2,790	348 (768)
4	1.14	90	104.5	1,315.1	1,160	145 (320)
5	3.06	240	98.0	5,155.6	1,680	227 (502)
Baseline average						52.7 (115)
Waste burn average						240 (530)

TABLE 8-12. STACK EMISSIONS OF HCl

Run number	HCl emissions (kg/h)		Chlorine in fuel (kg/h)
	Range	Average	
1	0.62 - 2.59	1.61	10.2
2	1.02 - 1.09	1.06	10.6
3	2.20	2.20	59.8
4	1.36 - 9.55	5.46	70.7
5	25.0 - 28.4	26.7	72.4
Baseline average		1.3	10.4
Waste burn average		11.5	67.6

8.6 METALS EMISSIONS

The evaluation of the emission rates of various metallic elements was made by analyzing the solid residue from the MM5 train as described in Section 6. The particulate catch was analyzed to determine the fraction of the mass for a given element. A field blank filter was also analyzed and an average contribution for each element subtracted to calculate the net metal emission rate using a ratio of metal mass to total particle mass times emission rate of particulate matter.

The total estimated weight of metals in each MM5 sample is given in Table 8-13 along with the field blank value used to correct for the filter, field handling, and lab handling contribution to the estimated metals content. These weights are converted to an estimated mass emission rate in Table 8-14 based on the total particulate catch and the particulate matter emission rates. Table 8-15 presents a comparison of the emission rates during the baseline (Runs 1 and 2) and during the waste burn (Runs 3 through 5). All of the elements show an increase except for titanium (88 percent decrease) and selenium (about the same for both conditions).

The significance of this increase must be tempered by the fact that the ESP malfunctioned during the waste burn and total particulate matter emissions increased dramatically. An increase in metals emissions is expected because of the ESP malfunction. The increase in total particulate matter was about 360 percent. If the percent change in Table 8-15 is adjused to a constant particulate matter emission rate, then it appears that the increase in lead and cadmium emission rates could be attributed to the burning of waste fuel. The increases in emission rates for the other elements cannot be conclusively attributed to the waste fuel because the percent increase is roughly equal to or less than the increase in total particulate emissions.

8.7 CONTINUOUS MONITOR DATA

The continuous monitors were used to measure the emission concentrations of selected pollutants (NO_x, SO_2, total hydrocarbons, and CO) and CO_2 and O_2 to determine whether waste fuel combustion changed these emissions and, if so, how much. The continuous monitoring results are summarized in Table 8-16.

TABLE 8-13. TOTAL MASS OF METALS IN MM5 PARTICULATE CATCH
(corrected for field blank, unless otherwise noted)

Element	Baseline Run 1	Baseline Run 2	Run 3	Run 4	Run 5	Field blank
Al (mg)	6.2	11.6	2.3	BBV	25.3	15.8
As	9.8	9.3	18	5.7	37.2	ND
Ca (mg)	144	203	143	32.4	407	55.6
Cd	26.5	36.0	182	33.9	250	ND
Cr	ND	163	ND	ND	ND	ND
Fe (mg)	10.9	13.6	10.0	2.7	27.3	0.7
Hg	2.7	3.8	7.3	3.0	20.8	ND
Mg (mg)	BBV	0.9	BBV	BBV	5.6	6.0
Mn	530	697	613	313	1,690	ND
Ni	ND	ND	ND	ND	ND	ND
Pb	88	136	7,490	3,890	2,306	16
Se	88	131	37	15.8	74.3	ND
Ti	82	409	BBV	7	64	160
V	ND	ND	38	ND	77	ND
Zn	58	91	29	15	149	48

BBV = below blank value
ND = not detected

TABLE 8-14. ESTIMATED STACK EMISSION RATES FOR METALS (mg/s)

Element	Run 1	Run 2	Run 3	Run 4	Run 5
Al	52	138	95	BBV	309
As	0.082	0.11	0.75	0.17	0.45
Ca	1,210	2,410	5,930	992	4,980
Cd	0.22	0.43	7.5	1.0	3.1
Cr	ND	1.9	ND	ND	ND
Fe	92	162	415	83	334
Hg	0.023	0.045	0.30	0.092	0.25
Mg	BBV	11	BBV	BBV	68
Mn	4.5	8.3	25.4	9.6	20.7
Ni	ND	ND	ND	ND	ND
Pb	0.74	1.62	311	119	28.2
Se	0.74	1.56	1.53	0.48	0.91
Ti	0.69	4.86	BBV	0.21	0.78
V	ND	ND	1.58	ND	0.94
Zn	0.49	1.08	1.20	0.46	1.82

BBV = below blank value
ND = not detected

TABLE 8-15. COMPARISON OF METALS EMISSION RATES (mg/s)

Element	Baseline average	Wasteburn average	Percent change
Al - Aluminum	95	135	+42
As - Arsenic	0.096	0.46	+379
Ca - Calcium	1,810	3,970	+119
Cd - Cadmium	0.33	3.87	+1,070
Cr - Chrome	<0.95	ND	-
Fe - Iron	127	277	+118
Hg - mercury	0.034	0.214	+529
Mg - Magnesium	<6	<23	-
Mn - Manganese	6.4	18.6	+191
Ni - Nickel	ND	ND	-
Pb - Lead	1.15	153	+13,200
Se - Selenium	1.15	0.97	-16
Ti - Titanium	2.78	<0.33	-88
V - Valladium	ND	<0.84	-
Zn - Zinc	0.79	1.16	+47

ND = not detected

TABLE E-16. SUMMARY OF CONTINUOUS EMISSION MONITORING RESULTS

	Run 1	Run 2	Run 3	Run 4	Run 5
Average NO_x (ppm)	570	670	840	771	831
Range	520-630	540-810	680-1080	400-1610	430-1020
Average SO_2 (ppm)	1.5	11.9	38	13	5
Range	0-12.5	8.5-16.9	25-53	6-39	5
Average THC (ppm)	2.5	2.4	9.2	4.8	1
Range	2.4-3.6	2.4	2.4-70	2.4-29	0-4
Average CO (ppm)	40	35	43	49	24
Range	40	35	40-45	40-90	20-25
Average CO_2 (%)	23.8	23.4	24.6	20.4	22.3
Range	23.1-24.3	23.1-23.8	24.0-25.9	17.3-23.6	21.2-23.4
Average O_2 (%)	6.5	6.6	6.7	7.3	7.5
Range	6.3-6.9	6.3-6.9	6.4-7.1	6.5-8.4	7.1-7.8
NO_x[a] (kg/h)	155	182	215	197	232
SO_2 (kg/h)	0.57	4.50	13.6	4.63	1.94
THC[b] (kg/h)	0.24	0.23	0.82	0.43	0.10

AVG. 736 ppm

AVG. 196 Kg/Hr
or
432 Lb/HR

with 60 TPH clinker production (p. 9),
Lbs of NO_x / Ton of clk = 7.2

[a] As NO_2

[b] As methane

The average NO_x concentration was above 570 ppm for all runs. A baseline average concentration of 610 ppm increased to an average of 814 ppm during the waste burn. SO_2 concentrations were 6.7 ppm during the baseline and 19 ppm during the waste burn. Total hydrocarbons (THC) increased from about 2.5 ppm to 5 ppm; however, the THC concentration for the highest waste fuel rate (Run 5) was lower than the two baseline runs. The average concentrations for the other gases changed very little (CO at 38 and 39 ppm, CO_2 at 23.6 and 22.4 percent, and O_2 at 6.6 and 7.2 percent).

The 15-minute averages for each run are presented in Tables 8-17 through 8-20. These results show very steady readings for most of the monitored gases within each run. The swings in NO_x concentrations were greatest during the waste burn and ranged from 400 to 1610 ppm. SO_2 concentrations showed the greatest changes with time within a run; however, SO_2 concentrations were relatively low throughout the test and ranged from 0-53 ppm. Note that the monitoring results for Run 5 on December 18 at the highest waste fuel rate were the most constant of any test. The combustion conditions were relatively consistent during this run as the NO_x stayed consistently high, SO_2 was constant at 5 ppm, and THC were very low at 0-2 ppm.

Secondary Air Temperature

Steady periodic oscillations of roughly 100 ppm were observed for the NO_x concentration throughout the test. The frequency of the NO_x oscillation matched exactly the oscillations observed in the undergrate pressure. NO_x peaks were observed when the undergrate pressure was low and NO_x dropped as the undergrate pressure increased.

The CEM results were compared to process observations for each run to determine if any obvious relationships existed. For the most part, both the process conditions and CEM results were steady throughout each run. In addition, the reported concentrations for SO_2, THC, and CO were consistently low and provided little insight into cause and effect relationships.

During Run 1, SO_2 increased from 2.5 ppm to 12 ppm and back to 0 ppm over the period between 1230 and 1330. Over the same time, NO_x went from 570 to 610 ppm, a small change. The only significant change was in the average undergrate pressure:

TABLE 8-17. CEM RESULTS FOR RUN 1
(December 13, 1983)

Hour	Minutes	NO_x (ppm)	SO_2 (ppm)	THC (ppm)	CO (ppm)	CO_2 (%)	O_2 (%)
12	:00-14	550.0	2.5		40.0	23.6	6.5
	:15-29	560.0	2.5	2.4	40.0	23.9	6.7
	:30-44	580.0	2.5	2.4	40.0	24.3	6.3
	:45-59	600.0	12.5	2.4	40.0	24.0	6.3
13	:00-14	610.0	10.0	2.4	40.0	24.2	6.3
	:15-29	620.0		2.4	40.0		6.5
	:30-44	630.0	0.0	2.4	40.0	23.4	6.3
	:45-59	620.0	0.0	2.4	40.0	24.0	6.3
14	:00-14		0.0	2.4	40.0	24.3	6.3
	:15-29						
	:30-44	570.0	0.0	2.4	40.0	24.3	6.5
	:45-59	560.0	0.0	2.4	40.0	24.3	6.3
15	:00-14	560.0	0.0	2.4	40.0	24.3	6.5
	:15-29	580.0	0.0	2.4	40.0	24.0	6.7
	:30-44	580.0	0.0	2.4	40.0	23.8	6.5
	:45-59						
16	:00-14	560.0	0.0	2.4	40.0	23.7	6.5
	:15-29	540.0	0.0	3.6	40.0	23.4	6.9
	:30-44	530.0	0.0	3.6	40.0	23.4	6.9
	:45-59	530.0	0.0		40.0	23.5	6.9
17	:00-14	520.0	0.0	2.4	40.0	23.4	6.9
	:15-29	530.0	0.0	2.4	40.0	23.1	6.9
	:30-44						
	:45-59						
Total Hours of data		4.7	4.7	4.5	5.0	4.7	5.0
Average Daily Concentration		570.0	1.5	2.5	40.0	23.8	6.5
Daily maximum		630.0	12.5	3.6	40.0	24.3	6.9
Daily minimum		520.0	0.0	2.4	40.0	23.1	6.3

TABLE 8-18. CEM RESULTS FOR RUN 2
(December 14, 1983)

Hour	Minutes	NO_x (ppm)	SO_2 (ppm)	THC (ppm)	CO (ppm)	CO_2 (%)	O_2 (%)
9	:00-14						
	:15-29						
	:30-44						
	:45-59						
	:45-59	790.0	8.5	2.4	35.0	23.6	6.5
10	:00-14	810.0	8.5	2.4	35.0	23.6	6.5
	:15-29	790.0		2.4	35.0		6.3
	:30-44	800.0	8.5	2.4	35.0	23.8	6.5
	:45-39	740.0	14.1	2.4	35.0	23.8	6.5
11	:00-14	700.0	11.3	2.4	35.0	23.2	6.7
	:15-29	710.0	11.3	2.4	35.0	23.1	6.9
	:30-44	720.0	11.3	2.4	35.0	23.6	6.7
	:45-59	720.0	16.9	2.4	35.0	23.8	6.7
12	:00-14	650.0	11.3	2.4	35.0	23.4	6.6
	:15-29	640.0	14.1	2.4	35.0	23.1	6.5
	:30-44	630.0	16.9	2.4	35.0	23.1	6.7
	:45-59	620.0	11.3	2.4	35.0	23.3	6.7
13	:00-14	590.0	14.0	2.4	35.0	23.4	6.7
	:15-29	570.0	8.5	2.4	35.0	23.8	6.9
	:30-44	550.0	11.3	2.4	35.0	23.8	6.8
	:45-59	540.0	11.3	2.4	35.0	23.4	6.8
14	:00-14	540.0	14.1	2.4	35.0	23.1	6.9
	:15-29						
	:30-44						
	:45-59						
Total Hours of Data		4.5	4.2	4.5	4.5	4.2	4.5
Average Daily Concentration		627.7	11.9	2.4	35.0	23.4	6.6
Daily maximum		810.0	16.9	2.4	35.0	23.8	6.9
Daily minimum		540.0	8.5	2.4	35.0	23.1	6.3

TABLE 8-19. CEM RESULTS FOR RUNS 3 AND 4 (December 17, 1983)

Hour	Minutes	NO_x (ppm)	SO_2 (ppm)	THC (ppm)	CO (ppm)	CO_2 (%)	O_2 (%)
9	:00-14						
	:15-29	970		70.0			
	:30-44	1080			40		7.1
	:45-59	1080		2.4	40		7.0
10	:00-14	940		2.4	40	24.8	6.6
	:15-29	720	53	16.0	45	24.8	6.5
	:30-44	680	37	2.4	45	24.0	6.6
	:45-59	720	49	2.4	45	24.5	6.4
11	:00-14	760	43	2.4	45	24.3	6.6
	:15-29	850	25	2.4	45	24.2	6.6
	:30-44	880	43	2.4	45	24.5	6.7
	:45-59	780	25	2.4	40	25.9	6.9
12	:00-14	730		2.4	45		6.8
	:15-29	710	30	2.4	45	24.2	6.4
	:30-44						
	:45-59	550	28	2.4	45	24.5	6.1
13	:00-14	720	92	7.0	45	17.6	7.1
	:15-29		9	29.0	40	16.7	8.0
	:30-44	+++++					
	:45-59	1610	12	5.0	40	23.6	7.6
14	:00-14		39	29.0	45	23.0	7.1
	:15-29	1200	11		40	17.3	8.0
	:30-44						
	:45-59		31	3.0	50	19.1	8.4
15	:00-14	580	6	3.6	65	19.0	8.1
	:15-29	460		5.0	85		7.5
	:30-44	400		10.0	90		7.5
	:45-59	460		3.6			
16	:00-14	520		2.4			
	:15-29	590	6	2.4	40	17.6	7.8
	:30-44	670		2.4	40	17.9	7.8
	:45-59	790		2.4	40		7.7
17	:00-14			2.4	40		6.5
	:15-29	760	6	2.4	40		6.5
	:30-44						
	:45-59	910	6	2.4	40	21.5	7.2
18	:00-14	920	12	2.4	45	21.8	6.5
	:15-29	930	15	2.4	45	21.5	7.2
	:30-44		6	2.4	45	21.5	6.5
	:45-59		9		45	20.6	6.5

(32)

(23)
593

792 ppm

26 ppm

7.1%

TABLE 8-20. CEM RESULTS FOR RUN 5 (December 18, 1983)

Hour	Minutes	NO_x (ppm)	SO_2 (ppm)	THC (ppm)	CO (ppm)	CO_2 (%)	O_2 (%)
11	:00-14	1000					
	:15-29						
	:30-44						
	:45-59						
12	:00-14	880	5	1	20	21.5	7.5
	:15-29	880	5	2	20	22.1	7.6
	:30-44	880	5	2	20	23.1	7.1
	:45-59	980	5	1	35	22.5	7.4
13	:00-14	1020	5	2	25	23.4	7.5
	:15-29	880	5	1	25	23.1	7.5
	:30-44	840	5	1	25	23.4	7.4
	:45-59	820	5	4	20	22.1	7.6
14:	:00-14						
	:15-29	800		2	25		
	:30-44	680	5	0	25	23.1	7.5
	:45-59						
15	:00-14	750		0	20		7.6
	:15-29	600		0	25		7.1
	:30-44	430		0	25		
	:45-59	660	5	0	25	21.2	7.6
16	:00-14	690	5	0	25	22.1	7.6
	:15-29	820	5	0	25	21.5	7.6
	:30-44		5		25	21.5	7.6
	:45-59	940	5	0	25	22.5	7.6
17	:00-14	880	5	2	25	22.1	7.4
	:15-29	900	5	1	25		7.5
	:30-44	960	5	2	25		7.8
	:45-59	1000	5	2	25		
18	:00-14						
Total Hours of Data		5.5	4.5	5.25	5.75	3.7	4.7
Average Daily Concentration		831	5	1	24	22.3	7.5
Daily maximum		1020	5	4	25	23.4	7.8
Daily minimum		430	5	0	20	21.2	7.1

Time	Undergrate pressure (in H_2O)	Time	NO_x (ppm)	SO_2 (ppm)
1215	11.4	1215-1230	560	2.5
1235	10.9	1230-1300	600	12.5
1255	11.3	1300-1330	610	10
1330	11.3	1330-1345	630	0

During Run 4, the excess air rate was increased twice and then decreased, and the coal rate decreased between 1445 and 1505. During the same period, NO_x dropped from 1200 to 580 ppm, SO_2 dropped from 31 to 6 ppm, and the kiln exit O_2 increased from 3.0 to 5.0 percent at 1500 and decreased to 3.4 percent at 1515.

During Run 5 at 1500 to 1545, the NO_x dropped from 750 to 430 ppm. The corresponding process observations were a decrease in primary air temperature (415° to 230° F), an increase in primary air flow, an increase in coal feed rate (6 to 6.7 tons/hr), and an increase in kiln exit oxygen (2.2 to 3.7 percent).

8.8 MATERIAL BALANCE

Samples of the various process streams were taken to attempt a kiln material balance for metals and chlorine. The major inlet streams are the kiln feed, coal/coke, and waste fuel; the major outlet streams include the clinker, waste dust, and exhaust gas. The purpose of the material balance is to identify the sources of the elements and their fate and distribution in the various streams leaving the kiln. For example, the combustion of chlorinated hydrocarbons significantly increases the kiln's chlorine loading. A chlorine material balance indicates how the additional chlorine is distributed among the clinker, waste dust, and stack emissions. Similar information is needed for metals that may be introduced with the supplemental fuel.

Two basic measurements are required for a material balance: (1) the mass flow rate of each process stream, and (2) the concentration of the element of interest in the process stream. At this plant, the clinker and waste dust are not routinely weighed. Raw materials are received and the final cement product is shipped in bulk quantities, and both may be stored or stockpiled in varying amounts. Accurate estimates of raw material usage and clinker production are obtained from long-term historical inventories. Accurate short-term measurements of these bulk materials are difficult to obtain. The coal and kiln feed rates were measured by weigh feeders, and an average rate was determined from totalizer readings for each test period. The clinker rate and dust rate were estimated from historical data based on the kiln feed rate. The waste fuel was metered to the kiln and an average rate was determined from the totalizer readings and the length of the test. A summary of the process stream flow rates for each run is given in Table 8-21.

TABLE 8-21. PROCESS FLOW RATES

Run number	Kiln Feed (Mg/h)	Coal (Mg/h)	Waste Fuel (Mg/h)	Clinker (Mg/h)	Waste Dust (Mg/h)
1	85.2	9.29	-	51.6	0.69
2	91.2	9.62	-	55.3	0.74
3	88.3	7.34	2.34	53.5	0.71
4	92.4	6.14	3.28	56.0	0.75
5	91.2	5.65	4.00	55.3	0.74

The process flow rates and analytical results for specific elements are used to estimate the quantities in and out of the kiln. Percent closure, which has been estimated as quantity-out/quantity-in x 100, provides a measure of the success at determining the fate of specific elements. However, percent closure is significantly affected by potential errors in both the estimates of mass rates and concentration measurements. For example, mass rates can easily vary ±10 percent; on a short-term (e.g., hourly) basis, the variation may be greater than 10 percent, particularly for those process streams for which direct measurements are not available. Similar errors are possible in the concentration measurements. To examine the effects of these errors on percent closure, consider the case in which the inlet rates and concentrations are overestimated by 10 percent, and the outlet rates and concentrations are underestimated by 10 percent. The percent closure for this case would be 67 percent (0.81 ÷ 1.21 x 100). For a greater extreme of ±20 percent, the percent closure could be as low as 44 percent. This analysis indicates that poor closure results may occur during any single test day because long-term flow rate and concentration data are needed to reduce random variations. However, when the material balance results are examined over a period of several test days, reasonable inferences can be made on the source, fate, and distribution of the specific elements.

8.8.1 Chlorine Material Balance

The results of the chlorine analysis of the process streams are given in Table 8-22. The chlorine content of both the waste dust and recycled dust increased as the total chlorine into the kiln increased during Runs 3, 4, and 5. The waste dust averaged 3.5 percent chloride during the baseline and increased to an average of 6.6 percent during the waste burn. The recycled dust's chlorine concentration increased from 0.73 percent to 1.5 percent.

The results of the chlorine material balance are given in Table 8-23. During the baseline tests, the coal appeared to be the major contributor of chlorine; however, note that the kiln feed may have provided an equal quantity if chlorine were present in the feed at or near the detection limit. (A detection limit value of <125 ppm was reported for the feed.) During the baseline, the chlorine appeared to be removed with the waste dust, with about 5 percent of the measurable chlorine leaving with the stack gas. During the waste fuel burn, the waste fuel contributed 84-91 percent of the measurable chlorine entering the kiln. Most of the additional chlorine was removed with the waste dust. During Runs 3 and 4, 90-95 percent of the measurable chlorine was removed with the dust; however, only 56 to 70 percent was removed with the dust during Run 5 and the balance was removed with the clinker and the stack gas.

Over the period of the entire test, total chlorine into the kiln averaged 45 to 56 kg/h and total chlorine out averaged 46 to 56 kg/h. During the three waste burn runs, total chlorine in averaged 68 to 79 kg/h and total chlorine out averaged 60 to 71 kg/h.

8.8.2 Metals Material Balance

The kiln feed, coal/coke, waste fuel, clinker, waste dust, and recycled dust were analyzed for 19 metals. The analytical results for samples composited for each run are given in Tables 8-24 through 8-29. The kiln feed and coal/coke analyses showed no significant variations in metals for the dif-

TABLE 8-22. RESULTS OF CHLORINE ANALYSIS OF PROCESS SAMPLES

Process Sample	Run 1	Run 2	Run 3	Run 4	Run 5
Kiln feed (ppm)	<125	<125	<125	<125	<125
Coal (%)	0.11	0.11	0.13	0.12	0.12
Waste fuel (%)	-	-	2.15	1.93	1.64
Clinker (ppm)	<125	<125	<125	<125	<380
Waste dust (%)	3.67	3.32	5.73	6.06	8.06
Recycled dust (%)	0.80	0.66	1.29	1.39	1.88

TABLE 8-23. CHLORINE MATERIAL BALANCE (kg/h)

Process stream	Run 1	Run 2	Run 3	Run 4	Run 5
Kiln feed	<10.7	<11.4	<11.0	<11.6	<11.4
Coal	10.2	10.6	9.5	7.4	6.8
Waste fuel	-	-	50.3	63.3	65.6
Clinker	<6.5	<6.9	<6.7	<7.0	<21
Waste dust	25.3	24.6	40.7	45.5	59.6
Stack gas	1.6	1.0	2.1	5.3	25.9
Total in	10.2-20.9	10.6-22.0	59.8-70.8	70.7-82.3	72.4-83.3
Total out	26.9-33.4	25.6-32.5	42.8-49.5	50.8-57.8	85.5-106.5

TABLE 8-24. RESULTS OF KILN FEED ANALYSES FOR METALS
(μg/g unless otherwise noted)

Element	Sample number/Run number					Detection limit
	54/1	55/2	113/3	117/4	130/5	
Al (%)	1.63	0.81	0.73	0.72	1.90	0.1
As	13.5	13.8	14.3	14.7	13.4	0.05
Ba	91	50	33	36	94	5
Ca (%)	31.4	31.5	32.1	31.7	31.8	0.25
Cd	0.69	0.69	0.68	0.69	0.60	0.1
Cr	25	<20	<20	<20	24	20
Cu	<20	<20	<20	<20	<20	20
Fe (%)	1.01	0.49	0.42	0.39	1.00	.0005
Hg	1.30	1.55	1.54	1.66	1.74	0.1
Mg (%)	0.82	0.82	0.81	0.79	0.79	.0005
Mn	877	410	378	364	886	1
Ni	<20	<20	<20	<20	<20	20
P	1,030	500	400	460	1,100	200
Pb	36.1	35.2	42.6	45.0	43.0	0.5
Se	<0.1	<0.1	<0.1	<0.1	<0.12	0.1
Sn	<50	<50	<50	<50	<50	50
Ti	160	77	73	65	157	0.05
V	31	<20	<20	<20	32	20
Zn	17	<10	<10	<10	20	10

TABLE 8-25. RESULTS OF COAL/COKE ANALYSES FOR METALS
(μg/g unless otherwise noted)

Element	Sample number/Run number					Detection limit
	50/1	51/2	111/3	116/4	131/5	
Al (%)	0.14	0.26	0.14	0.10	0.15	0.10
As	5.24	5.14	5.34	5.05	4.87	0.05
Ba	8	18	8	5	9	5
Ca (%)	0.14	0.32	0.13	0.08	0.15	0.25
Cd	0.64	0.46	0.58	0.94	0.52	0.1
Cr	<20	67	59	172	181	20
Cu	13	24	16	37	13	10
Fe (%)	0.11	0.16	0.12	0.12	0.14	0.0005
Hg	0.80	0.88	0.67	0.74	0.75	0.1
Mg	111	208	116	84	118	5
Mn	12	29	13	13	16	1
Ni	421	145	621	354	895	20
P	<200	<200	<200	<200	<200	200
Pb	13.1	15.2	13.7	15.5	14.3	0.5
Se	2.15	1.56	1.75	2.81	2.01	0.05
Sn	<50	<50	<50	<50	<50	50
Ti	72	114	68	57	74	0.05
V	43	100	47	35	51	20
Zn	25	31	21	25	26	10

TABLE 8-26. RESULTS OF CLINKER ANALYSES FOR METALS
(μg/g unless otherwise noted)

	Sample number/Run number					
Element	52/1	53/2	110/3	115/4	134/5	Detection limit
Al (%)	1.14	2.94	2.77	2.75	3.07	0.1
As	24.7	29.9	26.3	21.0	28.3	0.05
Ba	59	172	208	231	230	5
Ca (%)	46.0	48.2	49.3	50.1	49.1	0.25
Cd	0.91	0.99	0.34	0.27	0.50	0.1
Cr	32	77	95	120	115	20
Cu	<20	<20	<20	<20	22	20
Fe (%)	0.64	1.61	1.39	1.50	1.69	.0005
Hg	2.07	2.08	1.90	2.02	1.93	0.1
Mg (%)	1.16	1.27	1.17	1.19	1.25	.0005
Mn	524	1,291	1,200	1,314	1,370	1
Ni	27	41	35	34	36	20
P	640	1,390	1,480	1,525	1,590	200
Pb	5.47	5.85	16.7	45	42.7	0.5
Se	0.79	1.11	0.86	0.75	1.29	0.05
Sn	<50	<50	<50	<50	<50	50
Ti	511	806	783	860	1,540	0.05
V	31	70	55	56	67	20
Zn	10	47	56	54	69	10

TABLE 8-27. RESULTS OF WASTE DUST ANALYSES FOR METALS (μg/g unless otherwise noted)

	Sample number/Run number					
Element	56/1	59/2	114/3	119/4	133/5	Detection limit
Al (%)	2.58	2.59	0.84	1.96	2.03	0.1
As	17.6	18.0	13.8	12.4	12.6	0.05
Ba	123	133	38	107	119	5
Ca (%)	24.3	24.4	18.7	17.6	18.7	0.25
Cd	18.9	16.3	30.6	35.9	28.5	0.1
Cr	28	35	<20	25	28	20
Cu	22	<20	<20	63	83	20
Fe (%)	1.14	1.19	0.38	0.86	0.95	.0005
Hg	1.08	0.95	1.06	1.18	1.50	0.1
Mg (%)	0.68	0.70	0.52	0.48	0.53	.0005
Mn	658	651	236	551	553	1
Ni	27	25	<20	<20	<20	20
P	1,060	1,050	420	880	990	200
Pb	124	108	1,809	2,772	3,356	0.5
Se	4.71	5.96	5.41	5.93	3.42	0.05
Sn	<50	<50	<50	<50	<50	50
Ti	456	484	161	345	447	0.05
V	64	68	17	44	42	20
Zn	36	34	10	46	51	10

TABLE 8-28. RESULTS OF WASTE FUEL ANALYSES FOR METALS (μg/g)

	Sample number/Run number			
Element	103/1	105/4	136/5	Detection limit
Al	101	163	233	30
As	0.14	0.61	0.74	0.05
Ca	<600	<600	<600	600
Cd	4.45	3.82	3.50	0.5
Cr	197	247	67	20
Fe	548	626	260	5
Hg	0.22	0.13	0.20	0.1
Mg	30	65	70	0.5
Mn	<10	<10	<10	10
Ni	1,430	959	63	20
Pb	603	1,341	1,690	0.5
Se	<0.1	<0.1	<0.1	0.1
Ti	<10	18	24	10
V	<10	<10	<10	10
Zn	85	156	149	10

TABLE 8-29. RESULTS OF RECYCLED DUST ANALYSES FOR METALS
(μg/g unless otherwise noted)

	Sample number/Run number					
Element	56/1	57/2	112/3	118/4	132/5	Detection limit
Al (%)	2.18	2.37	2.15	2.10	2.19	0.1
As	13.6	14.5	12.9	13.9	14.1	0.05
Ba	114	116	120	124	116	5
Ca (%)	30.9	31.6	29.1	30.2	29.4	0.25
Cd	13.7	16.1	15.9	17.0	11.7	0.1
Cr	29	38	36	43	39	20
Cu	<20	<20	<20	<20	26	20
Fe	1.16	1.18	1.08	1.11	1.16	.0005
Hg	0.31	1.30	1.62	0.94	1.23	0.1
Mg (%)	0.85	0.87	0.78	0.79	0.76	.0005
Mn	861	867	831	880	859	1
Ni	24	24	23	22	21	20
P	1,050	1,070	1,080	1,130	1,170	200
Pb	70.9	78.7	559	369	508	0.5
Se	3.33	4.36	4.28	2.39	2.33	0.1
Sn	<50	<50	<50	<50	<50	50
Ti	411	431	435	449	430	0.05
V	58	59	47	46	45	20
Zn	29	40	57	65	45	10

ferent runs. The clinker analyses are also consistent except for lead content. During the baseline, the clinker averaged 5.7 µg/g lead. The lead concentration increased to an average of 35 µg/g during the waste burn. Increases in both lead and cadmium were noted for the waste dust. Lead and cadmium concentrations of 116 and 18 µg/g, respectively for the baseline increased to 2,650 and 32 µg/g, respectively, for the waste burn. The recycled dust also showed an increase in lead concentration (75 to 480 µg/g); however, the concentration of cadmium was similar in the recycled dust for both test conditions. Lead, nickel, iron, aluminum, zinc, and chromium were the metals found in the highest concentrations in the waste fuel. Cadmium ranged from 3.5 to 4.5 µg/g, and mercury ranged from 0.1 to 0.2 µg/g.

The results of the metals material balance for each run are presented in Tables 8-30 through 8-34. The major source of Al, Ba, Ca, Mg, Mn, and P entering the kiln is the kiln feed. The vast majority of these elements are removed with the clinker product.

During the baseline tests, the coal/coke contributed about 3-4 percent of the arsenic, 8 percent of the cadmium, 2 percent of the iron, 6 percent of the mercury, 4 percent of the lead, 6 percent of the titanium, and about 15 percent of the zinc that entered the kiln. The kiln feed supplied the balance of these elements. During the waste burn, the waste fuel contributed about 17 percent of the cadmium (6 percent from the coal and 77 percent from the kiln feed), 0.3 percent of the mercury (2.9 percent from the coal/coke and 96.8 percent from the kiln feed), and an average of 47 percent of the lead (1 percent from the coal/coke and 52 percent from the kiln feed). The waste fuel made no other significant contribution of metals.

Chromium, copper, nickel, and zinc were contributed by the coal/coke and waste fuel in similar quantities. However, the source of these metals is inconclusive because a significant quantity could come from the kiln feed for concentrations near the detection limit. The coal appeared to be the major source of selenium.

The vast majority of the arsenic, chromium, copper, iron, mercury, nickel. titanium, vanadium, and zinc leaving the kiln stayed with the clinker. The balance of these elements (<5 percent) was removed with the waste dust. No significant change in distribution or fate was observed for these metals when the waste fuel was burned.

TABLE S-30. METALS MATERIAL BALANCE FOR RUN 1 (kg/h)

Element	Kiln feed	Coal	Clinker	Waste dust	Stack	Percent closure
Al	1,390	13	588	17.8	0.2	43
As	1.15	0.05	1.27	0.01	NS	107
Ba	7.75	0.07	3.04	0.08	-	45
Ca	26,800	13	23,700	167	4.4	89
Cd	0.06	0.006	0.05	0.01	8×10^{-4}	92
Cr	2.13	<0.2	1.65	0.02	ND	78
Cu	<1.7	0.12	<1.0	0.02	-	NA
Fe	861	10.2	330	7.9	0.3	39
Hg	0.11	0.007	0.11	7×10^{-4}	8×10^{-5}	95
Mg	699	1.0	599	4.7	NS	86
Mn	74.7	0.11	27.0	0.5	0.02	37
Ni	<1.7	3.91	1.39	0.02	ND	NA
P	67.8	<1.9	33.0	0.73	-	38
Pb	3.08	0.12	0.28	0.09	0.003	12
Se	$<9 \times 10^{-3}$	20×10^{-3}	41×10^{-3}	3×10^{-3}	3×10^{-3}	NA
Sn	<4.3	<0.5	<2.6	<0.03	NS	NA
Ti	13.6	0.67	26.4	0.31	NS	187
V	2.64	0.40	1.60	0.04	ND	54
Zn	1.45	0.23	0.52	0.02	NS	32

NA = not applicable - detection level values in a process stream may significantly affect material balance.
ND = not detected in stack gas.
NS = not significant, i.e., the mass emission rate in the stack gas is too low to affect material balance.

TABLE 8-32. METALS MATERIAL BALANCE FOR RUN 3 (kg/h)
(25-percent waste fuel replacement)

Element	Kiln feed	Coal	Waste fuel	Clinker	Waste dust	Stack	Percent closure
Al	645	10.3	0.24	1,480	6.0	0.3	227
As	1.26	0.04	3×10^{-4}	1.41	0.01	NS	108
Ba	2.91	0.06	-	11.1	0.03	-	374
Ca	28,300	10	<1.4	26,400	133	21	94
Cd	0.06	0.004	0.01	0.02	0.02	0.027	71
Cr	<1.8	0.43	0.46	5.08	<0.01	ND	NA
Cu	<1.8	0.12	-	<1.1	<0.01	-	NA
Fe	371	8.8	1.3	744	2.7	1.5	197
Hg	0.14	0.005	0.0005	0.10	8×10^{-4}	1.1×10^{-3}	70
Mg	715	0.9	0.07	626	3.7	-	88
Mn	33.4	0.1	<0.02	64.2	0.17	0.09	192
Ni	<1.8	4.56	3.35	1.9	<0.01	ND	NA
P	35.3	<1.5	-	79.2	0.30	-	224
Pb	3.76	0.1	1.41	0.89	1.28	1.12	63
Se	$<9 \times 10^{-3}$	13×10^{-3}	$<0.2 \times 10^{-3}$	46×10^{-3}	4×20^{-3}	5.5×10^{-3}	NA
Sn	<4.4	<0.4	-	<2.7	<0.04	-	NA
Ti	6.45	0.50	<0.02	41.9	0.11	-	604
V	<1.8	0.34	<0.02	2.94	0.01	NS	NA
Zn	<0.88	0.15	0.20	3.00	0.007	0.004	NA

NA = not applicable - detection level values in a process stream may significantly affect material balance.
ND = not detected in stack gas.
NS = not significant, i.e., the mass emission rate in the stack gas is too low to affect material balance.

TABLE 8-31. METALS MATERIAL BALANCE FOR RUN 2 (kg/h)

Element	Kiln feed	Coal	Clinker	Waste dust	Stack	Percent closure
Al	739	25	1,630	19.2	0.5	216
As	1.26	0.05	1.65	0.01	NS	127
Ba	8.30	0.17	9.51	0.10	-	113
Ca	28,600	31	26,700	181	8.7	94
Cd	0.06	0.004	0.05	0.01	0.0015	97
Cr	<1.8	0.64	4.26	0.03	0.007	NA
Cu	<1.8	0.23	<1.1	<0.01	-	NA
Fe	447	15.4	890	8.81	0.6	195
Hg	0.14	0.008	0.12	7 x 10^{-4}	2 x 10^{-4}	82
Mg	748	2.00	702	5.2	NS	94
Mn	37.4	0.28	71.4	0.48	0.03	191
Ni	<1.8	1.39	2.27	0.02	ND	NA
P	45.6	<1.9	76.9	0.78	-	170
Pb	3.21	0.15	0.32	0.08	0.006	12
Se	<9 x 10^{-3}	15 x 10^{-3}	61 x 10^{-3}	4 x 10^{-3}	5.6 x 10^{-3}	NA
Sn	<4.6	<0.5	<2.8	<0.04	-	NA
Ti	14.6	1.10	44.6	0.36	0.017	287
V	2.83	0.96	3.87	0.05	ND	103
Zn	1.55	0.30	2.60	0.03	NS	142

NA = not applicable - detection level values in a process stream may significantly affect material balance.
ND = not detected in stack gas.
NS = not significant, i.e., the mass emission rate in the stack gas is too low to affect material balance.

TABLE 8-33. METALS MATERIAL BALANCE FOR RUN 4 (Kg/hr)
(37-percent waste fuel replacement)

Element	Kiln feed	Coal	Waste fuel	Clinker	Waste dust	Stack	Percent closure
Al	665	6.1	0.53	1,540	120	-	247
As	1.36	0.03	0.002	1.18	0.08	NS	91
Ba	3.33	0.03	-	12.9	0.66	-	405
Ca	29,300	5	<2	28,100	1,100	3.6	100
Cd	0.06	0.006	0.013	0.02	0.22	0.004	54
Cr	<1.8	1.06	0.81	6.72	0.15	ND	NA
Cu	<1.8	0.23	-	<1.1	0.39	-	NA
Fe	360	7.4	2.1	840	53	0.3	243
Hg	0.15	0.005	4×10^{-4}	0.11	0.007	3.3×10^{-4}	75
Mg	730	0.5	0.21	666	29	-	95
Mn	33.6	0.1	<0.03	73.6	3.4	0.03	228
Ni	4.8	2.2	3.1	1.9	0.12	ND	NA
P	42.5	<1.2	-	85.4	5.4	-	214
Pb	4.16	0.10	4.40	2.52	17.0	0.43	230
Se	$<9 \times 10^{-3}$	17×10^{-3}	$<0.3 \times 10^{-3}$	42×10^{-3}	36×10^{-3}	1.7×10^{-3}	NA
Sn	<4.6	<0.3	-	<2.8	<0.3	-	NA
Ti	6.01	0.35	0.06	48.2	2.12	NS	728
V	<1.8	0.21	<0.03	3.14	0.27	ND	NA
Zn	<0.9	0.15	0.51	3.02	0.28	NS	NA

NA = not applicable - detection level values in a process stream may significantly affect material balance.

ND = not detected in stack gas.

NS = not significant, i.e., the mass emission rate in the stack gas is too low to affect material balance.

TABLE 8-34. METALS MATERIAL BALANCE FOR RUN 5 (kg/h) (42-percent waste fuel replacement)

Element	Kiln feed	Coal	Waste fuel	Clinker	Waste dust	Stack	Percent closure
Al	1,730	8.5	0.93	1,700	15.0	1.1	99
As	1.22	0.03	0.003	1.56	0.01	NS	126
Ba	8.57	0.05	-	12.7	0.09	-	148
Ca	29,000	8.5	<2.4	27,200	138	17.9	94
Cd	0.05	0.003	0.014	0.03	0.02	0.011	91
Cr	2.19	1.02	0.27	6.36	0.02	ND	183
Cu	<1.8	0.07	-	1.2	0.06	-	NA
Fe	912	7.9	2.5	935	7.0	1.2	102
Hg	0.16	0.004	8×10^{-4}	0.11	0.001	9×10^{-4}	68
Mg	720	0.7	0.3	691	3.9	0.2	96
Mn	80.8	0.09	<0.04	75.8	0.4	0.07	94
Ni	<1.8	5.1	0.25	2.0	<0.01	ND	NA
P	101	<1.1	-	87.9	0.73	-	88
Pb	3.92	0.08	6.76	2.36	2.48	0.10	46
Se	11×10^{-3}	11×10^{-3}	4×10^{-4}	71×10^{-3}	3×10^{-3}	3.3×10^{-3}	344
Sn	<4.6	<0.3	-	<2.8	<0.04	-	NA
Ti	14.3	0.42	0.1	85.2	0.33	NS	578
V	2.92	0.29	<0.04	3.71	0.03	NS	117
Zn	1.82	0.15	0.60	3.82	0.04	NS	150

NA = not applicable - detection level values in a process stream may significantly affect material balance.

ND = not detected in stack gas.

NS - not significant, i.e., the mass emission rate in the stack gas is too low to affect material balance.

The distribution of cadmium, mercury, lead, and selenium appeared to change when the waste fuel was burned:

		Distribution (Percent)		
Element	Condition	Clinker	Dust	Stack Gas
Cadmium	Baseline	78	20	2
Cadmium	Waste burn	29	51	20
Mercury	Baseline	99.3	0.6	0.1
Mercury	Waste burn	96.7	2.6	0.7
Lead	Baseline	77	22	1
Lead	Waste burn	29	58	13

When waste fuel was burned, a higher percentage of the cadmium, mercury, and lead were removed with the waste dust and stack gas while a smaller percentage remained with the clinker.

8.9 FUEL ANALYSES FOR SULFUR, BTU, AND ASH

The coal/coke and waste fuel used to fire the kiln were analyzed for sulfur, Btu, and ash to examine fuel quality and the potential effects on emissions. The results of the coal/coke analyses are given in Table 8-35 and show that the coal/coke was uniform in quality throughout the test. The waste fuel results are given in Table 8-36 and also show uniform quality with a heating value that is roughly the same as the coal/coke fuel.

Table 8-37 shows that the rate of sulfur and ash entering the kiln decreased when the waste fuel was burned. SO_2 emissions are also presented and show no obvious relationship between sulfur loading in the kiln and SO_2 emissions. Table 8-38 is a summary of the kiln's energy usage. The calculated coal/coke replacement rates (adjusted for the loss of 8-percent moisture in coal) were 25, 37, and 42 percent, respectively, for Runs 3, 4, and 5.

8.10 WATER ANALYSES

Samples of the river water used to quench the hot exhaust gases from the kiln were taken for analysis of POHCs. Any POHCs present in the quench water

TABLE 8-35. RESULTS OF COAL/COKE ANALYSES

Run number	Moisture (%)	Ash (%)	Sulfur (%)	Btu/lb
1	2.6	11.3	2.79	12,680
2	2.1	11.1	2.62	12,850
3	2.2	11.1	2.88	12,750
4	2.2	11.6	2.56	12,720
5	2.1	11.1	2.90	12,750

TABLE 8-36. RESULTS OF WASTE FUEL ANALYSES FOR BTU, ASH, SULFUR, AND DENSITY

Run number	Btu/lb	Ash (%)	Sulfur (ppm)	Density (lb/gal)
3	12,470	3.94	661	7.96
4	12,310	4.27	733	8.05
5	12,170	4.81	473	8.04

TABLE 8-37. SULFUR AND ASH RATES FROM THE FUEL (kg/h)

Run number	Ash	Sulfur	SO_2 Emissions
1	1,050	259	0.6
2	1,070	252	4.5
3	910	213	13.6
4	850	160	4.6
5	820	166	1.9

TABLE 8-38. SUMMARY OF KILN's ENERGY USAGE

Run number	Million Btu/h			Percent replacement
	Coal/Coke	Waste fuel	Total	
1	239	-	239	0
2	252	-	252	0
3	191	64	255	25
4	160	95	255	37
5	145	107	252	42

(avg 250)

would be volatilized and emitted through the stack. The only POHC detected in the water samples was methylene chloride which was reported present at 400 to 540 ng/mL. The average rate of water usage was 34 to 47 gal/min (2.1 to 3.0 L/s). If methylene chloride were actually present and completely volatilized, the emission rate of methylene chloride would have been 840 to 1,600 µg/s. This is roughly the same order of magnitude as the methylene chloride emission rates measured during the baseline test, which ranged from 333 to 17,600 µg/s and averaged 4,760 µg/s. The methylene chloride results from the water must be qualified by the fact that methylene chloride was used in the field and in the laboratory. Because only trace quantities were found, methylene chloride contamination of the water sample is a possibility. No corrections for a contribution from the water were made for the methylene chloride emission rates or DREs.