

**Shell Oil Products U.S., Inc.
Shell Martinez Refinery
Martinez, California
CAD 009 164 021**



**Trial Burn Plan for
CO Boiler Units 1, 2 and 3**

Revision 2



**ENSR Corporation
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GLOSSARY OF TERMS AND ACRONYMNS

Ag	silver
Al	aluminum
Amp	ampere
As	arsenic
ASTM	American Society for Testing and Materials
AWFCO	automatic waste feed cut-off
BAAQMD	Bay Area Air Quality Management District
Ba	barium
Be	beryllium
BFB	bromofluorobenzene
Btu	British thermal unit
CCU	Catalytic Cracking Unit
Cd	cadmium
CEMS	continuous emission monitoring system
Cl ₂	chlorine (gas)
Co	cobalt
CO	carbon monoxide
CO ₂	carbon dioxide
COD	coefficient of determination
Cr	chromium
Cu	copper
CVAAS	cold vapor atomic absorption spectroscopy
DI	deionized (water)
DNF	dissolved nitrogen float
DNPH	dinitrophenylhydrazine
DOT	Department of Transportation
DRE	destruction and removal efficiency
DTSC	Department of Toxic Substances Control
dscf	dry standard cubic feet
dscfm	dry standard cubic feet per minute
dscm	dry standard cubic meter
EPA	Environmental Protection Agency (U.S.)
ESP	electrostatic precipitator
FID	flame ionization detector
FXG	Flexigas®
g/s	grams per second
GC/MS	gas chromatography/mass spectrometry
gpm	gallons per minute
gph	gallons per hour
gr	grain (7,000 grains = 1 pound)

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H ₂ O ₂	hydrogen peroxide
HCl	hydrogen chloride (gas) or hydrochloric acid
Hg	mercury
HNO ₃	nitric acid
HPLC	high performance liquid chromatography
Hr	hour
HRA	hourly rolling average
HRGC/HRMS	high resolution gas chromatography / high resolution mass spectrometry
HWC	hazardous waste combustor
ICAP	inductively coupled argon plasma
ICP-MS	inductively coupled plasma mass spectrometry
ICV	initial calibration verification
kVA	kilovolts amperes
lb	pound
LCS	laboratory control sample
LPG	liquid propane gas
LSC	laboratory services coordinator
MDL	method detection limit
mg/kg	milligrams per kilogram
Mn	manganese
MS	matrix spike
NDIR	non-dispersive infrared
Ni	nickel
NO _x	nitrogen oxides
O ₂	oxygen
PAHs	polycyclic aromatic hydrocarbons
Pb	lead
PCDDs	polychlorinated dibenzo-p-dioxins
PCDFs	polychlorinated dibenzofurans
PICs	products of incomplete combustion
P&ID	process and instrumentation diagram
PM	particulate matter
POHC	principal organic hazardous constituent
ppmv	parts per million on a volume basis
psig	pounds per square inch, gauge
QAO	quality assurance officer
QAPP	quality assurance project plan
QA/QC	quality assurance/quality control
RCRA	Resource Conservation and Recovery Act
RFG	refinery fuel gas
RPD	relative percent difference
RRF	relative response factor

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RSD	relative standard deviation
Sb	antimony
scfm	standard cubic feet per minute
Se	selenium
SMR	Shell Martinez Refinery
S/N	signal-to-noise ratio
SO ₂	sulfur oxides
SOP	standard operating procedure
SPCCs	system performance check compounds
STL	Severn Trent Laboratories
SVOCs	semi-volatile organic compounds
TBP	Trial Burn Plan
TICs	tentatively identified compounds
Tl	thallium
V	vanadium
VOA	volatile organic analysis
VOCs	volatile organic compounds
VOST	volatile organic sampling train
w.c.	water column
Zn	zinc

1.0 INTRODUCTION

1.1 Project Background

Shell Oil Products US (Shell) operates an oil refining and manufacturing complex located in Martinez, California (U.S. EPA ID# CAD 009 164 021). The Shell Martinez Refinery (SMR) currently operates three carbon monoxide boilers (CO Boilers), storage tank 12038, and a bio-treatment unit that manage hazardous waste under a Part B Permit.

This Trial Burn Plan (TBP) and integral Quality Assurance Project Plan (QAPP) describe how SMR intends to conduct a Trial Burn on one of the three identical CO Boilers at the Martinez, California facility. The Trial Burn will be conducted as part of the RCRA permitting process. This TBP specifies how testing will be conducted to demonstrate that the regulated units comply with applicable emission standards and to establish operating limits that will be used in an operating permit. In addition, this plan describes testing that will be conducted to generate information for use in health risk assessments, in accordance with recent U.S. EPA policy and guidance. It is also noted that the testing described herein will evaluate all emission parameters to be regulated in the future under the Phase II Final rules for hazardous waste combustors (HWC). The standards affecting Shell are delineated in 40 CFR 63.1217, promulgated on October 12, 2005. These rules are effective on December 12, 2005 and have a compliance date of October 14, 2008.

SMR proposes to conduct the Trial Burn under three boiler operating conditions to fully meet permit requirements and to establish new operating limits. Test Condition 1 is designed for system operation at minimum (~30-kVA) ESP power input. Test Condition 2 is designed for all risk-based testing while the unit is under normal operating conditions. Test Condition 3 is designed for system operation at a low firebox temperature, maximum firebox pressure, and maximum waste feed rate. Additional details on these test conditions are provided in Section 4.0.

As specified in Section V.F.2 of the Hazardous Waste Facility Permit issued by the California EPA, Department of Toxic Substances Control (DTSC) on December 30, 1995, and last modified on August 21, 2003, SMR plans to conduct Trial Burn testing on one of the CO Boilers and use data-in-lieu-of testing to establish limits on the other two units.

This TBP is being submitted to the DTSC and the Bay Area Air Quality Management District (BAAQMD) as part of a RCRA Part B Permit Application.

1.2 Facility Description and Location

This section provides an overview of the TBP, including a general description of the facility, Trial Burn program objectives, and overall document organization. SMR operates an oil refining and chemical manufacturing complex located in Martinez, California. General facility information is provided below:

Shell Martinez Refinery

Owner: Shell Oil Products US, doing business as Equilon Enterprises LLC

Facility: Shell Martinez Refinery
PO Box 711
3485 Pacheco Blvd.
Martinez, California 94553

US EPA ID No: CAD 009 164 021

Facility Contact: Mr. Steven Overman
Phone Number: (925) 313-3281
e-mail: steven.overman@shell.com

SMR currently manufactures LPG, gasoline, intermediate fuels (jet and diesel), industrial fuels, asphalt, petroleum coke, sulfur, and catalysts.

1.3 Trial Burn Objectives

This TBP and integral QAPP describe how SMR intends to conduct a Trial Burn on CO Boiler No. 1. The Trial Burn will be conducted as part of the RCRA permitting process. Trial burn plans are generally developed to describe how testing will be conducted to demonstrate that the regulated units comply with applicable emission standards and to establish operating limits that will be used in an operating permit. Recent U.S. EPA policy and guidance has also stipulated that trial burn plans be developed and trial burns be conducted to generate information for use in a site-specific health risk assessment. This document addresses all of these areas. The major objectives of the Trial Burn are listed below and explained in detail in Section 2.0.

1. Conduct a Trial Burn as required by Section V.F.2 of the facility's permit.
2. Demonstrate that the CO Boilers comply with the applicable emission standards and operating limits (performance standards) outlined in Section V.C.3 of the facility's permit.
3. Revise certain operating limits as presently outlined in Section V.C.3 of the facility's permit.
4. Generate required emission data that can be used to update the health risk assessment.

Additional details regarding the specific design of test conditions, parameters measured, and emission data collected are provided later in this document.

1.4 Document Organization

This TBP is organized in a logical manner to facilitate Agency review.

- Section 1.0 Introduces the project.
- Section 2.0 Provides a technical description of the combustion units along with their auxiliary and pollution control systems.
- Section 3.0 Describes the nature and characteristics of the hazardous and non-hazardous waste streams fed to the regulated units.
- Section 4.0 Provides an overview of the Trial Burn test protocol and planned operating conditions.
- Section 5.0 Represents the QAPP for this project and describes all sampling and analytical protocols to be followed during the program as well as all related QA/QC.

Additional detailed information is provided in the appendices. Also, Table 1-1 provides a cross-reference between the contents of this document and the required elements of a trial burn plan as outlined in Title 22 of the California Code of Regulations (22 CCR), Division 4.5, Chapter 20, Article 6, Section 66270.62(b)(2).

This TBP and associated QAPP are being submitted as part of a RCRA Part B permit application. The permitting process will also include the completion of a health risk assessment. Work plans for these assessments are being provided under separate cover.

Table 1-1 Trial Burn Plan Contents as Required Under 22 CCR 66270.62(b)(2)

Topic	Regulatory Citation (22 CCR)	Section No. in this Document
Waste Analysis Data	66270.62(b)(2)(A)	Section 3.0
Detailed Engineering Description of Incinerator	66270.62(b)(2)(B)	Section 2.0
Detailed Description of Sampling and Monitoring Procedures	66270.62(b)(2)(C)	Sections 2.5 and 5.0
Detailed Test Schedule	66270.62(b)(2)(D)	Section 4.5 and Table 4-5
Detailed Test Protocol	66270.62(b)(2)(E)	Section 4.0
Description of and Planned Operating Conditions for Emission Control Equipment	66270.62(b)(2)(F)	Section 4.4 and Table 4-4
Procedures for Rapidly Stopping Hazardous Waste Feed and Controlling Emissions During Equipment Malfunction	66270.62(b)(2)(G)	Sections 2.3 and 2.8
Other Required Information	66270.62(b)(2)(H)	N/A

2.0 ENGINEERING DESCRIPTION OF CO BOILERS

This section provides a technical, engineering description of the CO Boilers as well as all associated equipment and ancillary systems. A general description of the boiler feed streams normally processed is also provided.

2.1 Combustion Unit

The three CO Boilers operated by SMR are of identical design. They are designated as sources S1507, S1509, and S1512 with the BAAQMD. Each boiler is a forced draft boiler and is operated continuously. Alcorn Combustion Manufacturing Company built the three boilers on the basis of a single design, without a model number.

The firebox (the combustion chamber space between the burners and the boiler heat exchanger tubes) of each boiler has inside dimensions of 29.6 feet length, 19.16 feet width, and 12.9 feet height. The firebox is L shaped and its volume is less than the product of these dimensions. The inside volume of the firebox is approximately 5,300 cubic feet (ft³). The minimum residence time of gases in the firebox is 0.5 seconds at 1,800 degrees Fahrenheit (°F), which is calculated from the firebox volume and the maximum flow rate of combustion gases. The maximum heat duty of each unit is 207 million British thermal units per hour (10⁶ Btu/hr) and the pressure is normally about 5 inches of water (pressure).

Each firebox has four fuel burners with two being used for burning waste material (Burners No. 1 and 4). Refinery fuel gas is burned in all four burners as a support fuel. Each burner has a central gun and gas pilot. Each burner has a central gun that uses steam to atomize the waste liquid (combined DNF solids and biosolids) with a waste turndown ratio of 3:1.

During normal operation, each boiler is operated in the temperature range of 1,700 to 1,800°F and the maximum stack gas flow is 154,400 standard cubic feet per minute (scfm). Stack gas oxygen levels are typically 2 to 4 percent (dry volume basis) while stack gas CO levels are normally less than 100 parts per million on a dry volume basis (ppmv).

The boilers are each rated to generate 150,000 pounds per hour (lb/hr) of steam (maximum of 170,000 lb/hr for one hour) at 650 pounds per square inch, gauge (psig) pressure, and 750°F. The steam goes to the plant-wide steam distribution system.

2.2 Boiler Feed Streams

The CO Boilers burn three gaseous fuels and one waste feed stream classified as a hazardous waste. These materials are referred to as Catalytic Cracking Unit regenerator off gas; Flexigas®; refinery fuel gas; and a waste feed stream which is a mixture of waste biosolids and dissolved nitrogen flotation (DNF) solids from the Effluent Treating Plant. Additional details on these feed materials are provided in Section 3.0.

2.3 Automatic Waste Feed Cutoff System

Each boiler is equipped with an automatic waste feed cutoff (AWFCO) system to prevent waste from being injected into the firebox when the boiler is running outside of permitted operating conditions. When a shutoff trip is activated, the waste feed shutoff valve closes quickly (there is approximately a 3-second delay) to stop the waste flow. Fuel, off gas, and air continue flowing into the firebox, and the boiler continues operating in a normal fashion. When operating conditions in the boiler have returned to within the permit limits, waste feed is again introduced into the firebox by resetting the solenoid that opens the shutoff valve and adjusting the flow controller to the desired flow.

The AWFCO system is tested monthly for correct operation of the waste shutoff valve. Waste feed flow to the firebox is shut off when conditions in a boiler exceed the permitted conditions. The waste flow shutoff valve remains closed until the boiler system has returned to permitted conditions. Because of the automatic waste feed shutoff, waste feed is not combusted at conditions that are not in compliance with the permit. In the event of operation beyond the permit conditions, the DTSC is notified according to the terms of the facility permit.

2.4 Air Pollution Control Equipment

Each of the 3 CO Boilers utilizes an electrostatic precipitator (ESP) to control particulate matter emissions, and a urea injection system and over-fired air system to control NO_x emissions.

2.4.1 Electrostatic Precipitator

The flue gas from each boiler is cooled in the boiler heat exchange section prior to entering an ESP at approximately 600°F. The ESP has two parallel chambers with four fields in each chamber. The ESP is of the plate and wire type design and is designed for a maximum flue gas flow rate of 174,000 scfm at a stack gas exit temperature of 550° to 600°F. The ESP normally operates with a power setting of between about 80 and 150 kVA. However, previous Trial Burns have shown that the ESP is capable of complying with particulate matter limits at a power level as low as about 20 kVA.

Perforated distribution plates at the inlet spread the gas uniformly across the ESP. The plates and wires maintain a field voltage between 200 to 220 volts and current between 0.5 to 1.0 amp/field to capture particulate matter. The particulates captured on the plates are later dislodged from the hoppers with a combination of an air horn vibration system, air cannons, and mechanical vibrators.

The ash (catalyst fines and fly ash solids) is removed from each hopper through a rotary star valve into an enclosed screw conveyor, which moves the solids to the main dust hopper. The main dust hopper has a vent that allows equalization of hopper pressure with ambient pressure. The vent is covered with a bag filter. As solids are removed, a net flow of gas of about 2 cubic feet per hour moves with the solids and eventually out through the vent. Solids are emptied from the hopper into sling bags, which are transported off site for disposal.

2.4.2 Urea Injection System

Each boiler is equipped with a urea injection system for low NO_x control, consisting of a 54,000-gallon storage tank, a transfer pump, filters, a system to dilute urea with condensate from the steam system, atomizing injectors, and an individual control system for each boiler.

A 50 percent urea solution is periodically delivered to the storage tank by truck. With the condensate dilution system, the solution is diluted to 40 percent urea as the tank is filled. This prevents crystallization from occurring. The tank is equipped with a tank level indicator, mixer, and a high level alarm and beacon. Any spills in the truck unloading area are collected in a sump and released to the process sewer after testing.

The transfer pump has a low flow alarm and minimum flow control system that recycles urea solution back to the storage tank. The concentrated urea solution discharges from the pump and flows through two parallel filters that can be manually or automatically back-flushed.

The urea solution is further diluted with condensate prior to being injected into the boiler. The concentrated urea stream and the condensate stream are merged immediately downstream of their control stations and mixed via an in line mixer. The resulting diluted urea solution is then piped to each boiler's four injectors.

The injectors are mounted on the north wall of each CO Boiler firebox downstream of the firebox and just underneath the boiler convection section. Nozzles in the tips of the injectors, which extend 1 to 4 inches into the boiler, direct the atomized spray down into the main flow of stack gas. The injectors have two air supplies, one for atomizing the urea solution and the other for cooling the injector assemblies. There is a flow alarm on the atomizer air to each injector and a low pressure alarm on the air supply.

2.5 Process Instrumentation

Instrumentation for each boiler is shown on the process flow diagram, **Figure 2-1**. Process monitors and instrumentation are listed in **Table 2-1** and include temperature, pressure, and flow monitors and control devices. The stack gas CO concentration, firebox temperature, and flue gas oxygen concentration are continuously monitored.

2.6 Sampling Locations

The CO boiler stack has a diameter of 8 feet and is equipped with a sampling platform to allow sampling of emissions from the sampling ports. Stack dimensions and sample port locations are depicted subsequently in Section 5.0. The sampling platform is permanently installed and completely encircles the stack at the sampling and monitoring level. The platform is 54 feet above the base of the stack. The width of the sampling platform is about 3.5 feet.

2.7 Facility Inspections

The boiler operator inspects the boiler at least daily for fugitive emissions, leaks, spills, and signs of wear or tampering. Any leak or spill is cleaned up, and any emission point or worn equipment is corrected as soon as possible. Incidents and abnormal inspection results are noted in the operating log.

The boiler operator and utilities board operator attend to the boiler operation on a full time basis. They continuously check the operating data and make any necessary adjustments in control set points. Boiler operating data is collected and retained by the process control computer or strip charts.

2.8 Emergency Shutdown

In the event that an emergency shutdown of the boiler is initiated, the AWFCO system is activated and flow of waste feed is stopped immediately. Fuel and air are also shut off. Regenerator off gas will continue moving through the boiler and exhaust gas control system until the operator diverts the gas to the other two boilers.

The boiler is not equipped with a bypass (dump) stack. However, under extreme circumstances, regenerator off gas may be diverted upstream of the boiler to a bypass stack. Any leak or spill of waste feed and any effects on personnel or surroundings is reported to the appropriate Agencies, as required. Any leak or spill is promptly cleaned up.

Table 2-1 Process Monitoring Instrumentation – CO Boiler No. 1

Process Parameter	Measurement Location	Instrument Tag ID #	Units	Measurement Basis (a)	
				Instant.	HRA
Regenerator Off-Gas Flow Rate	Feed Line to Boiler	9F1370	10 ⁶ scfd	X	
FXG Flow Rate	FXG Line to Boiler	9F2461	10 ⁶ scfd	X	
RFG Flow Rate (2-inch)	RFG Line to Boiler	9F123	10 ⁶ scfd	X	
RFG Flow Rate (6-inch)	RFG Line to Boiler	9F564	10 ⁶ scfd	X	
Waste Feed Rate	Feed Line to Boiler	9FI2669	gpm	X	
Waste Feed Rate	Feed Line to Boiler	F2669AVG	gpm		X
Waste Feed Differential Pressure	Waste Feed Injection Nozzle	9PI1555 / 9PI1556	psi	X	
Firebox Temperature (East and West)	Firebox	9TC3176	°F	X	
Firebox Pressure	Firebox	9PI1724	in. w.c.		X
Urea Flow Rate	Upstream of inline Mixer	9F2574	gph	X	
Power to ESP	ESP	9EI2670	KVA	X	
Stack Gas Flow Rate (Annubar)	Stack	9FI1595	in. w.c.	X	
Stack Gas Opacity	Stack	9A2529	%	X	
Stack Gas SO ₂	Stack	9A2530	ppmv	X	
Stack Gas NO _x	Stack	9A2561	ppmv	X	
Stack Gas O ₂	Stack	9A2610	% v	X	
Stack Gas CO	Stack	9AI2640A	ppmv		X

(a) Instant = Instantaneous
HRA = Hourly Rolling Average

3.0 DESCRIPTION OF CO BOILER FEED STREAMS

3.1 General Overview

The CO Boilers burn three gaseous fuels and one waste feed stream classified as a hazardous waste. These materials are referred to as Catalytic Cracking Unit (CCU) regenerator off gas; Flexigas® (FXG) produced at the Flexicoker®; refinery fuel gas (RFG); and a waste feed stream which is a mixture of waste biosolids and dissolved nitrogen flotation (DNF) solids from the Effluent Treating Plant.

3.2 Catalytic Cracking Unit Regenerator Off Gas

CCU off gas, a fuel containing CO, is burned continuously in the CO Boilers and represents the primary fuel for the CO boilers. Combustion of the regenerator off gas does not produce enough heat to support its own combustion and, therefore, additional fuels must be burned to keep the regenerator off gas above the minimum temperature required for sufficient combustion. Representative data for this feed stream is provided in **Table 3-1**.

3.3 Flexigas®

FXG, another fuel containing CO, is burned in the boilers as a fuel as required to meet steam demand. FXG is introduced through nozzles into the boiler. Combustion air is controlled by varying the blower speed to maintain a constant excess oxygen concentration in the flue gas. The typical composition of FXG is provided in **Table 3-2**.

3.4 Refinery Fuel Gas

RFG, a common refinery fuel similar to natural gas, is a mixture of natural gas and hydrocarbon gas which is produced in the refinery and is burned continuously in the CO Boilers as a support fuel. RFG is burned directly in the burners with combustion air being controlled by varying the blower speed to maintain a constant excess oxygen concentration in the flue gas. Analytical data for RFG are summarized in **Table 3-3**.

3.5 Waste Feed Stream

A waste feed stream, also burned directly in the burners, is primarily a mixture of waste DNF solids and biosolids from the Effluent Treatment Plant. The DNF solids are a listed RCRA waste and have been assigned a Federal RCRA waste code of K048 and a California waste code of CWC 222. The biosolids is a non-hazardous waste. A representative summary for the waste feed analytical results is listed in **Table 3-4**. A more detailed compilation of waste feed analyses conducted over the past 10 years is presented in **Appendix A**.

Table 3-1 Representative Composition Data for Regenerator Off-Gas

Component	Units	Average	Range
Carbon Monoxide	% vol. (dry)	6.2	3.5 – 9.0
Carbon Dioxide	% vol. (dry)	13.6	12.0 – 15.5
Oxygen	% vol. (dry)	0.04	0.04
Nitrogen	% vol. (dry)	80.2	75.5 – 84.5

Note: Water content typically about 20%.

Table 3-2 Representative Composition Data for Flexigas®

Component	Units	Average	Minimum	Maximum
Carbon Monoxide	% vol. (dry)	21.1	19.1	23.9
Carbon Dioxide	% vol. (dry)	8.2	5.2	9.5
Hydrogen	% vol. (dry)	16.7	12.0	20.5
Nitrogen	% vol. (dry)	52.1	46.3	57.7
Methane	% vol. (dry)	1.4	0.6	1.8
Ethane	% vol. (dry)	0.0	0.0	0.1
Oxygen / Argon	% vol. (dry)	0.5	0.3	0.9
Component Total	% vol. (dry)	100.0		
Net Heating Value	Btu/scf	126.8	113.7	143.6

Data for January 2004 – March 2005

Note: Water content typically about 3%.

Table 3-3 Representative Composition Data for Refinery Fuel Gas

Component	Units	Average	Minimum	Maximum
Carbon Monoxide	% vol. (dry)	0.59	0.0	1.31
Carbon Dioxide	% vol. (dry)	0.19	0.0	0.41
Hydrogen	% vol. (dry)	27.28	16.44	44.30
Nitrogen	% vol. (dry)	6.25	1.34	11.0
Methane	% vol. (dry)	41.96	21.03	59.96
Ethane	% vol. (dry)	8.34	3.77	10.84
Ethylene	% vol. (dry)	4.45	0.40	6.11
Propane	% vol. (dry)	3.82	1.15	12.90
Propylene	% vol. (dry)	2.04	0.22	16.47
Isobutane	% vol. (dry)	1.77	0.35	4.04
n-Butane	% vol. (dry)	1.92	0.18	7.91
Butene-1	% vol. (dry)	0.10	0.00	0.24
Isobutylene	% vol. (dry)	0.12	0.00	0.28
t-Butene-2	% vol. (dry)	0.10	0.00	0.20
Isopentane	% vol. (dry)	0.53	0.19	1.87
n-Pentane	% vol. (dry)	0.09	0.04	0.42
cis-2-butene	% vol. (dry)	0.05	0.00	0.14
2-Methyl-1-butene	% vol. (dry)	0.03	0.00	0.15
2-Methyl-2-butene	% vol. (dry)	0.05	0.00	0.19
trans-2-pentene	% vol. (dry)	0.03	0.00	0.08
cis-2-Pentene	% vol. (dry)	0.00	0.00	0.10
Oxygen / Argon	% vol. (dry)	0.07	0.00	0.78
Component Total	% vol. (dry)	99.79		
Net Heating Value	Btu/scf	944	790	1,194

Note: Water content typically less than 1%.

Table 3-4 Typical Waste Feed Characteristics

Parameter	Units	Average	Minimum	Maximum
Physical Properties --				
High Heating Value	Btu/lb	408	< 100	1,240
Chlorine	%	0.09	0.042	0.45
Ash	%	0.69	0.26	1.38
Water Content	% wt.	95.7	90.0	98.7
Ultimate Analysis --				
Carbon	%	1.82	0.31	3.61
Oxygen	%	82.6	58.9	86.9
Nitrogen	%	0.18	0.03	0.34
Hydrogen	%	10.8	9.67	11.45
Phosphorus	ppm	266	40	560
Organics --				
Benzene	mg/kg	1.9	ND	6.5
Chlorobenzene	mg/kg	ND	ND	ND
Toluene	mg/kg	13	ND	77
Metals --				
Arsenic (As)	mg/kg	0.45	ND	0.52
Barium (Ba)	mg/kg	24.6	1.56	110
Cadmium (Cd)	mg/kg	ND	ND	ND
Chromium (Cr)	mg/kg	2.61	ND	8.64
Lead (Pb)	mg/kg	2.56	ND	3.33
Mercury (Hg)	mg/kg	0.78	0.07	3.7
Selenium (Se)	mg/kg	8.1	ND	14.8
Silver (Ag)	mg/kg	6.4	0.59	39

4.0 TRIAL BURN PROTOCOL OVERVIEW

This section provides an overview of Trial Burn design, including testing requirements, unit to be tested, test conditions and operating scenarios, selection criteria for a principal organic hazardous constituent (POHC), number of runs, and test parameters. The section also describes how SMR proposes to modify some of the current permit limits from the results of the Trial Burn. The manner in which the facility intends to operate the boilers after the Trial Burn is conducted but before the revised permit is issued is also discussed.

4.1 Permit-Required Testing and Trial Burn Strategy

The Trial Burn is designed to meet the objectives that were previously described in Section 1.0 of this TBP. The test objectives represent a combination of factors based on current permit requirements and the facility's desire to establish several new operating limits.

4.1.1 Permit-Required Testing

The Trial Burn will be conducted to demonstrate that the CO Boilers meet the following performance standards outlined in Section V.C.3.a. of the facility permit:

- Destruction and removal efficiency (DRE) of 99.99 percent for each POHC.
- Emissions of hydrogen chloride (HCl) and chlorine (Cl₂) no greater than 18.3 and 1.05 grams per second (g/s), respectively.
- Emissions of particulate matter (PM) no greater than 0.08 grains per dry standard cubic foot (gr/dscf) corrected to 7 percent oxygen.
- Ratio of 2,3,7,8-TCDD equivalents (for all three boilers) to the risk-specific dose for 2,3,7,8-TCDD shall not exceed 1.0.
- Mass emission rates of toxic metals shall not exceed the limits outlined in the table below:

Metal	Emission Rate, g/s	Metal	Emission Rate, g/s
Arsenic	6.77 E-05	Thallium	7.60 E-02
Barium	6.00 E-01	Antimony	7.60 E-02
Chromium	6.00 E-04	Lead	7.40 E-02
Beryllium	6.77 E-05	Mercury	5.60 E-02
Cadmium	4.60 E-04	Silver	5.10 E-01

The Trial Burn will also need to demonstrate compliance with the operating conditions delineated in Section V.C.3.b. of the facility's permit. It is noted, however, that SMR will seek to modify several of these limits during the Trial Burn. A summary of current and expected permitted operating conditions is provided in **Table 4-1**. As noted in **Table 4-1**, the facility is seeking to modify the following current permit limits:

- For individual CO Boilers, SMR would like to increase the waste feed rate (DNF solids and biosolids) on an hourly rolling average basis from 10.0 gpm to approximately 12.0 gpm. However, SMR would like to add a total waste feed rate limit of 30.0 gpm (HRA) for the 3 CO Boilers combined. The 30.0 gpm limit will ensure that total waste firing allowed by the permit does not increase.
- SMR would like to eliminate the annual limit of 36,500 ton/yr of biosolids, a non-hazardous waste. Elimination of this limit will allow SMR to increase annual biosolids firing only if the annual DNF solids, a RCRA hazardous waste, are fired at below the permitted throughput of 28,000 ton/yr.
- For individual CO Boilers, SMR would like to eliminate the waste feed rate limit of 12.3 gpm on an instantaneous basis. SMR believes that limits on the hourly rolling average waste feed rate are sufficient to ensure continuous compliance with emission limitations.
- Currently each CO Boiler has a stack gas CO concentration limit of 100 ppm (uncorrected for stack gas oxygen content). SMR requests that this limit be retained but be corrected to 7% O₂ so as to be consistent with DTSC and other regulations, particularly the hazardous waste combustor MACT rule. Such a correction prevents compliance with the CO limit through dilution of the exhaust gas stream with extra combustion air.
- SMR would like to increase the permitted firebox pressure at each CO Boiler from 6.6 to approximately 7.5 inches of water column on an hourly rolling average basis. This change will provide SMR with increased operating flexibility and prevent unnecessary waste feed cutoffs.
- SMR requests that the new permit limit for minimum firebox temperature (to be established during Condition 1) be based on an hourly rolling average rather than instantaneous measurement basis. SMR would monitor temperature on an HRA basis during the trial burn to establish this new limit.
- SMR expects to retain the current limit on maximum stack gas flow rate of 154,400 scfm. This limit will not be demonstrated during the Trial Burn due to the difficulty in establishing such a conflicting parameter.
- Additionally, two other permit limits would need to be modified since SMR no longer burns fuel oil or waste sulfinol reclaimer bottoms.

4.1.2 Health Risk Assessment Testing

In accordance with Section V.E. of the facility permit, SMR is required to update the status of prior health risk assessment evaluations by performing testing for additional parameters deemed important by current U.S. EPA health risk assessment guidance. Therefore, this Trial Burn will also incorporate emission measurements for the following pollutants while operating under normal boiler conditions:

- Ammonia, PM, HCl and Cl₂.
- Metals required by permit including antimony, arsenic, barium, beryllium, cadmium, chromium (total), lead, mercury, silver and thallium.
- Additional metals specifically for the health risk assessment including aluminum, hexavalent chromium, cobalt, copper, manganese, nickel, selenium, vanadium, and zinc.
- Polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDDs/PCDFs).
- Polycyclic aromatic hydrocarbons (PAHs).
- Target volatile organic compounds (VOCs) and TICs (see list of target compounds in Appendix E).
- Target semi-volatile organic compounds (SVOCs) and TICs (see list of target compounds in Appendix E).
- Carbonyl compounds (aldehydes).

Further details regarding the risk assessment are outlined in the "Protocol for the CO Boiler Health Risk Assessment (ENSR Document No. 05975-140-800) being submitted under separate cover.

4.2 CO Boiler to Be Tested

As discussed previously, SMR plans to conduct Trial Burn testing on one unit and use data-in-lieu-of testing to establish limits on the other two identically designed boilers. Whereas the facility permit implies in, Section V.F.2., that CO Boiler No. 2 is the unit designated to be tested, based on the previous Trial Burn schedules, the next scheduled unit should be CO Boiler No. 1. Therefore, at this time, SMR plans to test CO Boiler No. 1. The last Trial Burn of CO Boiler No. 1 was conducted in 1989. A Trial Burn was conducted more recently at CO Boilers No. 2 and 3 in 1991 and 1993, respectively.

Should CO Boiler No. 1 experience any significant operating problems immediately prior to the Trial Burn, SMR will conduct the Trial Burn on one of the other boilers and will notify DTSC and EPA Region 9 if there is a change in the unit planned for testing.

4.3 POHC Selection and Spiking Strategy

This section provides information regarding both selection of the appropriate POHC for the Trial Burn and a POHC spiking strategy for the Trial Burn.

4.3.1 Evaluation of Candidate POHCs

Chemical compounds that have been used in the past as Trial Burn POHCs at SMR include:

- Benzene (potentially a trace contaminant in the primary treated wastewater)
- Toluene (potential contaminant in the DNF solids waste stream)

An ideal POHC for RCRA Trial Burn program would be a compound that is native to the waste stream, easily sampled and analyzed and considered difficult to incinerate. POHC incinerability is based on thermal stability, a method developed at the University of Dayton Research Institute. The current POHC incinerability list is taken from the "Technical Implementation Document for EPA's Boiler and Industrial Furnace Regulations", EPA-530-R-92-011, March 1992. This guidance is based on gas-phase thermal stability under oxygen-starved conditions. Compounds are ranked on the basis of the temperature required for 99 percent destruction at a residence time of two seconds. Thus, compounds ranked high on the list (Class 1) are considered the most difficult to incinerate. Current thinking on the use of this list says that the ability to successfully destroy a given compound implies the ability to destroy all other compounds in the same class as well as those below. EPA's use of the thermal stability list to date has focused mainly on the class a compound falls into and not on the absolute ranking within the class.

Benzene is a Class 1 compound and thus considered one of the most difficult compounds to incinerate. Toluene is a Class 2 compound and is therefore considered less difficult to incinerate than benzene. However, benzene is not considered a good candidate because it can be emitted as a product of incomplete combustion (PIC) and therefore may adversely affect DRE calculations. In addition, benzene poses numerous difficulties with respect to toxicity, safe handling, potential environmental impacts, worker safety, cost, and availability. Even though Class 1 compounds are not typically present in the waste stream handled at SMR, it is preferred that the Trial Burn be conducted using a Class 1 compound because at times, trace quantities of a few Class 1 compounds have been detected.

Considering all of these factors, SMR is proposing to use only one compound - monochlorobenzene (MCB or chlorobenzene) as the Trial Burn POHC. MCB is also a Class 1 compound (and thus considered equally difficult to incinerate as benzene) but is not encumbered with the additional toxicity, environmental, and safety-related concerns. Additionally, MCB will not be formed as a PIC. On this basis, MCB represents the best choice for a POHC for this Trial Burn as it can readily be sampled and analyzed by EPA Method 0030 (VOST). An overall summary of the POHC evaluation criteria considered is provided in **Table 4-2**.

Section V.C.2.b.(1) of the permit states that the Permittee shall not incinerate hazardous constituents that have a thermal stability ranking higher than benzene. Since both benzene and MCB are considered to be in the class of compounds that is the most difficult to incinerate (Class 1), this permit condition is not necessary because there are no compounds with a stability class greater than benzene or MCB. Assuming that compliance with the DRE limit is demonstrated using MCB as the Trial Burn POHC, SMR requests that the permit condition currently listed in Section V.C.2.b.(1) of the permit be removed from the reissued permit.

4.3.2 POHC Spiking Strategy

Since MCB would not be present in the waste stream at a high enough concentration to enable detection at the 99.99 percent DRE level, it will need to be spiked (injected) into the waste feed material. Therefore, to demonstrate adequate DRE on this difficult to destroy compound, it will be spiked at a predetermined rate that is sufficient to allow calculation of at least 99.99 percent DRE yet not so high as to exceed the upper calibration range of the GC/MS instrumentation used for VOST analysis. **Table 4-3** provides general calculations on the appropriate feed quantity, based on assumptions regarding achievable DRE, stack gas flow rate and VOST sample volume. This information will be used to ensure that the POHC is fed at the minimum desired rate. On the basis of these calculations, the expected target trial burn spiking rate for MCB will be about 50-75 pounds per hour (lb/hr).

A general schematic diagram of the type of spiking system to be used is provided in **Figure 4-1**. Spiking operations would be subcontracted to a third-party contractor specializing in this type of activity.

4.4 Test Conditions

Section 1.0 described the overall test objectives for achieving program goals. For this program, multiple test conditions must be conducted to demonstrate compliance with the emission standards, to provide data to re-validate or revise operating permit limits and to collect appropriate data for updating the health risk assessment. As a result, SMR proposes to conduct Trial Burn test runs under three separate operating conditions. **Table 4-4** summarizes the Trial Burn operating conditions that will be evaluated to meet these regulatory requirements.

4.4.1 Test Condition 1

Test Condition 1 is designed to evaluate ESP efficiency for particulate removal at minimum power input (approximately 30 kVA). Therefore testing for PM only will be conducted during Condition 1. This test condition will also be used to provide the BAAQMD with information regarding PM emissions and ESP power input.

4.4.2 Test Condition 2

Test Condition 2 will represent normal boiler operation and therefore all health risk-related testing will be performed during this condition. Condition 2 will entail testing for the following emission parameters:

- Method 0050 (Ammonia, PM, HCl and Cl₂)
- Method 29 (Metals)
- Method 0061 (Hexavalent Chromium)
- Method 0023A (PCDDs/PCDFs and PAHs)
- Method 0010 (Semi-Volatile Organics)
- Method 0030 (Volatile Organics)
- Method 0011 (Aldehydes)
- Method 25A (Total Hydrocarbons)

4.4.3 Test Condition 3

Test Condition 3 is designed for boiler operation at a minimum firebox (combustion chamber) temperature and high firebox pressure. Under this minimum temperature condition, DRE testing would be performed and emission measurements for total hydrocarbons (THC) would be conducted. Condition 3 would be used to establish new permit limits for minimum firebox temperature, maximum firebox pressure, and minimum waste feed atomization pressure. It is also expected that the waste feed rate would be maximized during this test in order to achieve the desired low firebox temperature.

It should be noted that Shell has not proposed a maximum firebox temperature condition since this is consistent with current EPA thinking as embodied by the hazardous waste combustor (HWC) MACT rule (40 CFR 63.1219, April 20, 2004). EPA now recognizes that typical combustion chamber temperatures encountered in hazardous waste burning incinerators and boilers are more than sufficient to volatilize all metals and thus no longer imposes a maximum combustion chamber (firebox) temperature limit to address metals control.

4.5 Test Logistics and Schedule

The test matrix described in **Table 4-4** was developed to satisfy Trial Burn objectives. The test matrix will provide the data needed to demonstrate compliance and establish permit conditions. In development of the test matrix, SMR also considered:

- The physical constraints of the sampling location and how this will impact the test schedule
- Appropriate operating conditions necessary to generate emissions data for use in updating the facility risk assessment

Each of these factors is discussed below.

4.5.1 Concurrent Sampling

CO Boiler No. 1 is equipped with a stack sampling arrangement consisting of four ports at one elevation, with each port oriented at a 90-degree separation from the others. Although this arrangement will allow for all sampling to be completed concurrently during Conditions 1 and 3, this will not be possible during Condition 2. The “normal” operating test condition will include all risk-related testing which incorporates six isokinetic methods, one continuous single point method and one semi-continuous single point method. Testing for all these parameters cannot be done concurrently and thus one day will be required for each run of Condition 2. An overall Trial Burn schedule as well as an example daily schedule is presented in **Table 4-5**.

4.5.2 Health Risk Assessment Sampling

Because the emission data used as input to a health risk assessment is evaluated over a period of 30 years or more, using very conservative models, it is most appropriate that the input data represent typical or normal facility operation. Therefore, Condition 2 will encompass testing for all health risk assessment parameters while the CO Boiler is operating within normal ranges for all parameters.

4.6 Process Interruptions

The system will be lined out on Trial Burn feed materials for one hour prior to test initiation. This will serve to establish all hourly rolling averages (HRAs) at or near their desired set points when sampling begins. If there is a waste feed interruption (i.e., AWFCO), the following guidelines will be followed:

- Sampling will be stopped as quickly as possible after the interruption.
- If the interruption is less than five minutes, there will be no line out period, and testing will recommence as soon as possible.
- If the interruption is between five and 30 minutes, there will be a 15-minute line out period, and then sampling will recommence.
- If the interruption is between 20 and 60 minutes, there will be a 30-minute line out period and then sampling will recommence.
- If the interruption exceeds 60 minutes, there will be a one-hour line out period before testing is resumed.

4.7 Post-Trial Burn Operation

Upon completion of the Trial Burn, the facility will return to normal operations as defined within the current hazardous waste facility permit until such time as a new or modified permit is received.

Figure 4-1 General Schematic for POHC Spiking

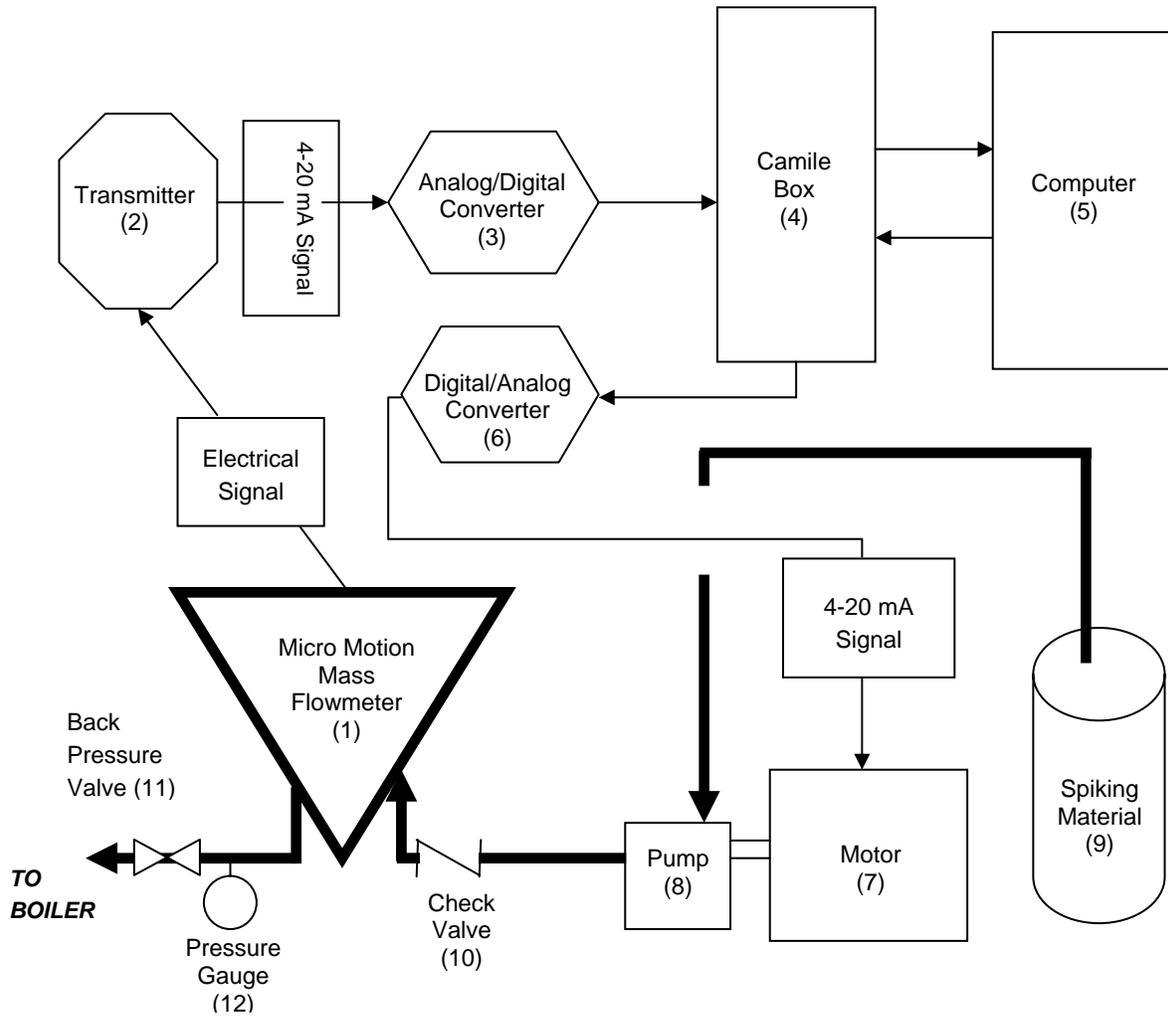


Table 4-1 Current and Expected Permit Operating Limits

Parameter	Units	Measurement Basis (a)	Current Part B Limit	Expected Part B Limit
Maximum Waste Feed Rate to each CO Boiler (DNF Solids + Biosolids)	gpm	HRA	10.0	~ 12.0
Maximum Waste Feed Rate to each CO Boiler (DNF Solids + Biosolids)	gpm	Instant.	12.3	No limit
Maximum Total DNF Solids (RCRA waste) to all 3 CO Boilers	ton/yr	HRA	28,000	28,000
Maximum Total Biosolids (non-hazardous) to all 3 CO Boilers	ton/yr	HRA	36,500	No Limit
Maximum Total Waste Feed Rate to all 3 CO Boilers (DNF Solids + Biosolids)	gpm	HRA	No limit	30.0
Maximum Total Sulfinol Reclaimer Bottoms to all 3 CO Boilers	ton/yr	HRA	18.0	0
Minimum Waste Feed Atomization Pressure (b)	psig	Instant.	37.6	~ 38.0
Minimum Fuel Oil Differential Atomization Pressure	psig	Instant.	39.1	None (No Fuel Oil)
Minimum Firebox Temperature	°F	Instant.	1,603	No Limit
Minimum Firebox Temperature	°F	HRA	No Limit	1,600 -1,625
Maximum Firebox Pressure	in. w.c.	HRA	6.6	~ 7.5
Minimum ESP Power	kVA	Instant.	20	20
Maximum Stack Gas Flow Rate [Measured as in. w.c. and calculated as scfm]	scfm	Instant.	154,400	154,400
Maximum Stack Gas CO	ppmv	HRA	100	100 @ 7% O ₂

(a) HRA = Hourly Rolling Average; Instant = Instantaneous

(b) Waste Feed Atomization Pressure is defined as the differential atomization fluid pressure between atomizing fluid and waste feed.

Table 4-2 POHC Evaluation Criteria

Evaluation Factors	POHC Candidate Compound		
	Benzene	Toluene	Chlorobenzene
Incinerability (Thermal Stability)	Class 1	Class 2	Class 1
Native to Waste?	Trace	Yes	No
Stack Gas Sampling Method	Method 0030 (VOST)	Method 0030 (VOST)	Method 0030 (VOST)
Toxicity (HMIS Rating*)	2	2	2
TWA (NIOSH), ppm	0.10	100	10
Flammability (HMIS Rating*)	3	3	3
Reactivity (HMIS Rating*)	0	0	0
Special Handling Requirements	Freezes at about 42°F	No Problems	No Problems
Availability	Most difficult to obtain	Easiest to obtain	Only one domestic source
Other Considerations	Known carcinogen; "Zero" emissions in CA		
Approximate Cost	Up to \$8.00/lb	~ \$1.00/lb	~ \$1.00/lb
Physical Properties --			
Molecular Weight, g/g-mole	78.11	92.14	112.56
Boiling Point, °C	80	110.6	132
Vapor Pressure, mmHg	74.6	N/A	11.8
Vapor Density, g/L	2.77	N/A	3.86
Flash Point, °F	12	40	81

* HMIS = Hazardous Material Information System (0 = best; 4 = worst)

Table 4-3 POHC DRE Calculations

POHC or Analytical Parameter	Feed Rate (lb/hr)	Assumed DRE	Stack Emissions (g/hr)	Total Collected (ng)
Volatile POHC - min.	25.0	99.99%	1.134	105
Volatile POHC - max.	225	99.99%	10.206	941
Volatile POHC - min.	175	99.999%	0.794	73
Volatile POHC - max.	2,200	99.999%	9.979	920
GC/MS Method Dynamic Range	Stack Gas Assumptions			
25 - 1,000 ng	Method 0030 (VOST):	Value	Units	
	Sample Volume	20	dsL	
		0.71	dscf	
	Stack Gas Flow Rate	127,700	dscfm	

Table 4-4 Planned Trial Burn Test Conditions (a)

Operating Parameter and (Measurement Basis / Tag #)	Units	Condition 1	Condition 2	Condition 3
Waste Feed Rate (DNF Solids + Biosolids) (HRA / F2669AVG)	gpm	< 10	< 10	~ 12.0
Waste Feed Rate (DNF Solids+ Biosolids) (Instantaneous / 9FI2669)	gpm	< 12.3	< 12.3	> 12.3
Waste Feed Atomization Pressure (b) (Instantaneous / 9PI1555/1556)	psig	> 70	> 70	~ 38
Firebox Temperature (HRA / New Tag)	°F	> 1,700	> 1,700	~ 1,600
Firebox Pressure (HRA / 9PI1724)	in. w.c.	< 6.6	< 6.6	~ 7.5
ESP Power (Instantaneous / 9EI2670)	kVA	~ 30	> 80	> 80
Stack Gas Flow Rate (Instantaneous / 9FI1595)	scfm (c)	< 154,400	< 154,400	< 154,400
Stack Gas Oxygen (One-Minute Average / New Tag)	% by volume	3.0 - 4.0	3.0 – 4.0	> 4.0
Stack Gas CO (HRA / A2640AVG)	ppmv	< 100 @ 7% O ₂	< 100 @ 7% O ₂	< 100 @ 7% O ₂
Emission Parameters to be Measured During Each Test Condition	Units	Condition 1	Condition 2	Condition 3
Particulate Matter		Yes	Yes	No
Hydrogen Chloride and Chlorine		No	Yes	No
Metals		No	Yes	No
Carbonyls (Aldehydes)		No	Yes	No
PCDDs/PCDFs and PAHs		No	Yes	No
Target Volatile and Semi-Volatile Organics		No	Yes	No
Carbon Monoxide and Total Hydrocarbons		Yes	Yes	Yes
POHC DRE		No	No	Yes

(a) Planned operating conditions are targets only and may vary by $\pm 20\%$ during the trial burn.

(b) Waste Feed Atomization Pressure is defined as the differential atomization fluid pressure between atomizing fluid and waste feed.

(c) Measured as inches water column (in. w.c.) and calculated as scfm

Table 4-5 Detailed Trial Burn Test Schedule

General Overview of Planned Schedule

Activity	Schedule
Arrival on site, site safety training and equipment set-up	Day 1
Preliminary measurements followed by Condition 1, Runs 1-3 (C1-R1, C1-R2 & C1-R3) for particulate matter	Day 2
Condition 2, Run 1 (C2-R1) for all risk parameters	Day 3
Condition 2, Run 2 (C2-R2) for all risk parameters	Day 4
Condition 2, Run 3 (C2-R3) for all risk parameters	Day 5
Condition 3, Runs 1-3 (C3-R1, C3-R2 and C3-R3) for POHC DRE	Day 6
Ship samples. Pack equipment and depart site.	Day 7

Example of Detailed Daily Schedule – Day 3 Above

Test Activity	Time
CO Boiler No. 1 lined out on Trial Burn waste; CEMS daily calibrations conducted	06:00
All operating conditions and associated hourly rolling averages at or near their target values	07:00
Begin C2-R1 for Method 0011 (Aldehydes), Method 0050 (Ammonia, PM, HCl and Cl ₂), Method 29 (Metals) and Method 0061 (Cr ⁺⁶)	08:00
Complete C2-R1 for above parameters	11:15
Begin C2-R1 for Method 0023A (PCDDs/PCDFs/PAHs), Method 0030 (VOCs), Method 0010 (SVOCs) and Method 25A (THC)	12:15
Complete C2-R1 for above risk parameters	16:00
Complete sample train recoveries and sample train setup / preparations for C2-R2	16:00 to 18:00

5.0 QUALITY ASSURANCE PROJECT PLAN

This section of the Trial Burn Plan (TBP) provides a Quality Assurance Project Plan (QAPP) for the sampling and analytical work associated with the proposed Trial Burn to be conducted at Shell Oil Products US, Martinez Refinery (SMR). The proposed Trial Burn is described in Sections 1.0 through 4.0 of this TBP. The QAPP included in this section, presents the Quality Assurance and Quality Control (QA/QC) goals, objectives, and procedures for the SMR Trial Burn program. The QA/QC procedures and criteria for this program will comply with the requirements of this document and its updates. The analytical work conducted will incorporate the QA/QC requirements of the approved methods. This QAPP has been prepared using available guidance provided in the following EPA documents:

- "EPA Requirements for Quality Assurance Project Plans", EPA QA/R-5, November 1999.
- "Component 2 – How to Review a Quality Assurance Project Plan (including Attachment A – Generic Trial Burn QAPP)", Hazardous Waste Combustion Unit Permitting Manual, U.S. EPA Region 6, January 1998.
- "Handbook – Quality Assurance/Quality Control (QA/QC) Procedures for Hazardous Waste Incineration" (EPA/625/6-89/023 January 1990).

5.1 Trial Burn Description

The proposed Trial Burn will consist of a comprehensive sampling and analysis program designed to demonstrate compliance with the facility's current permit requirements, establish several new permit limits and conduct extensive testing for updating a previous health risk assessment. Testing will be performed under three distinct process operating conditions, entailing triplicate sampling runs for each condition. The reader is referred to other sections of this document for further details on program scope, test objectives and target parameters for emission measurements and process monitoring. The remainder of this section outlines the detailed measures that will be followed to ensure collection of valid data. A brief overview of the measurements to be made during each test condition is provided in **Table 5-1**. A more detailed summary of the sampling and analytical program is provided later in Section 5.6.

5.2 Project Organization

ENSR International (ENSR) will be responsible for all emission measurements on this Trial Burn. The ENSR Project Manager, Mr. Mike Dudasko, will provide overall direction of the program and will report to the SMR's Project Manager, Mr. Steven Overman.

5.2.1 SMR Project Manager

Mr. Steven Overman is a Senior Staff Engineer in the Environmental Affairs Department for the SMR and will serve as the SMR's project manager for the Trial Burn program. He will be responsible for coordinating the plant effort during the Trial Burn (including collection of waste feed samples) and for managing all of SMR's contractors involved with the project. He will be the principal point of contact during Trial Burn implementation.

5.2.2 ENSR Project Manager

Mr. Dudasko will be responsible for project design and implementation, communicating with the client, scheduling all activities, reviewing all project data and preparing all reports. He will be assisted in the oversight of Quality Assurance activities by the program Quality Assurance Officer (QAO) and each Analytical Laboratory Services Coordinator (LSC). Each contract laboratory will have one individual designated as the person responsible for project activities.

5.2.3 ENSR QA Officer

Mr. Douglas Roeck of ENSR will serve as the project QAO and will be responsible for review and approval of the Quality Assurance Project Plan presented in this section, as well as any subsequent revisions. He will monitor implementation of field and laboratory activities, scheduling performance and/or system audits as warranted. The QAO will report to the Project Manager on any conditions noted which may adversely affect data quality.

Mr. Roeck will provide independent oversight for data verification and data quality assessment activities. He will prepare a section for the Final Report summarizing QA/QC activities and provide an overall evaluation of data quality.

5.2.4 Laboratory Services Coordinators

Each analytical laboratory will designate a coordinator, who will be the principal point of contact for the ENSR Project Manager. The LSC will review QA requirements with all laboratory staff to ensure that all required measures are taken to meet data quality objectives. They will monitor the shipment and receipt of samples, track analytical progress and review data as reported from the laboratories for completeness. Ms. Martha Maier will serve as the LSC for Alta Analytical Laboratories in El Dorado Hills, California. Mr. Rich LaFond will serve as the LSC for STL in Knoxville, Tennessee. Ms. Surinder Sidhu will serve as the LSC for STL in Pleasanton, California.

Each LSC will be responsible for validation of all data generated by the laboratory for this program and will provide all necessary documentation for inclusion in the final report.

5.3 QA/QC Program Objectives

5.3.1 Precision, Accuracy and Completeness

The collection of data to fully characterize the boiler waste feed material and stack gas emissions requires that sampling and analysis procedures be conducted with properly operated and calibrated equipment by trained personnel. QA objectives specific to each analytical methodology performed by the subcontractor laboratories are presented later in Section 5.9. The overall program has been designed with consideration of sampling parameters and analytical limits to ensure that the achieved method detection limits (MDLs) for emissions will be more than adequate for regulatory limit decisions. Critical MDL determinations are addressed subsequently in Section 5.5.3.

Precision is defined as a measurement of mutual agreement among individual measurements made under prescribed similar conditions. Precision is expressed in terms of relative percent difference (RPD) between duplicate determinations and in terms of relative standard deviation (RSD) when 3 or more determinations are made. Overall precision for analysis of the waste feed streams will be assessed through the analysis of one set of duplicate samples for each designated parameter.

Accuracy is the degree of agreement of a measurement with an accepted reference or true value. Analytical accuracy will be measured through the recoveries of surrogate spikes, matrix spikes, analysis of standard reference materials, or audit sample analysis. Surrogates are compounds added to samples submitted for organic analyses prior to extraction and analysis; their recoveries are measured to assess sample-specific analytical efficiency and accuracy. Matrix spike samples for the waste feed will be prepared by spiking known amounts of target analytes into a portion of the sample. Matrix spike samples for the stack organic analyses will be prepared by spiking known amounts of target analytes into the sampling media and then carrying the spiked sample through the entire preparation and analysis sequence. Recoveries are monitored to assess laboratory and method accuracy. Laboratory control samples (LCS) will also be used to distinguish between method performance and matrix effects on accuracy. LCS and MS spiking solutions will be independent from calibration standards.

Completeness is a measure of the amount of valid data obtained compared to the amount that was expected under normal conditions. The overall program objective is to obtain valid data for three (3) runs for each test condition. For all data considered critical to the investigation, a completeness objective of 100 percent has been established. As a result, critical priority data from each set of three (3) runs should achieve the precision and accuracy goals established herein. This completeness criterion applies to all permit parameters in emissions samples as well as any feed/process stream samples. Individual samples for which the critical data points do not achieve accuracy and/or precision data quality objectives may require reanalysis. Results for samples where matrix interferences preclude meeting objectives for the recoveries of surrogates or spikes will be evaluated for potential bias to calculated emission results. In summary, the completeness goals are stated at 100 percent, since three valid runs are necessary to assess operation at any one condition.

5.3.2 Representativeness and Comparability

It is recognized that the usefulness of the data is also contingent upon meeting the criteria for representativeness and comparability. Wherever possible, reference methods and standard sampling procedures will be used. The QA objective is that all measurements be representative of the matrix and operation being evaluated. The detailed requirements for sampling given in the various EPA Reference Methods will be followed to ensure representative sampling of flue gases. The frequent grab sampling of incinerator feed and process streams during each test run will provide representative samples of these matrices.

The corresponding QA objective is that all data resulting from sampling and analysis be comparable with other representative measurements made by the field sampling team, on this or a similar process operating under similar conditions. The use of published sampling and analytical methods and standard reporting units will aid in ensuring the comparability of the data.

5.3.3 Method Detection Limit Determinations

MDLs for the various analytes to be measured in this program will be determined following well-established laboratory procedures in accordance with standard EPA protocols. These are described below for those parameters deemed most crucial to the program. Projected emission rates at the MDL for various parameters considered important to the health risk assessment are provided in **Appendix B**.

5.3.3.1 VOST - Methods 5041A/8260B

The method detection limit is determined in accordance to SW-846 standard practices via the analysis of low level replicate spike analysis. MDLs for organic methods are performed at the subcontract laboratory on an annual basis and match the matrix to the analysis (i.e. spiking VOST tubes for Method 5041A/8260B MDL determinations). The MDL is the student's t-value multiplied by the standard deviation of the replicate data where t is approximately equal to 3 for 7-8 replicates. In the subcontract laboratory's organic MDL studies, 7-10 samples are usually spiked and analyzed. MDLs performed in this manner should be considered as estimates only since repeating the process will provide slightly differing values for each analyte. In addition, it is worth noting that these MDLs assume clean sample matrices. Sample detection limits may be higher based on sample related interferences.

5.3.3.2 PCDDs/PCDFs - Methods 0023A/8290

In accordance with EPA Method 23 (40 CFR Part 60 Appendix A Method 23), SW-846 Methods 0023A and 8290, sample specific MDLs are calculated using the following formula:

$$\text{MDL} = [2.5 \times H_n \times Q_{IS}] / [H_{IS} \times W \times \text{RRF}]$$

Where: 2.5 = the minimum signal to noise ratio

H_n = Height of the native (noise height, peak to peak)

Q_{IS} = the quantity, in pg, of internal standard added to the sample

H_{IS} = the peak height of the internal standard

W = the weight or volume of the sample

RRF = relative response factor from initial calibration

5.3.3.3 Metals - Method 6010B

Reporting limits for all metals are determined based on the results of the latest MDL studies performed for each metal. The reporting limit for non-detectable metals is a chosen whole number above the MDL, usually in the range of 1.5-2 times the MDL value.

5.4 Sampling and Monitoring Procedures

This section describes the procedures that will be followed during the field sampling program. Throughout the overall program, all sampling will be performed using sampling protocols described herein and approved by EPA. Regulatory agency approval will be obtained for any deviations from or changes to the approved Trial Burn Plan which may be warranted prior to program implementation as a result of changes in personnel or facility circumstances. If situations occur during the trial burn testing which necessitate deviations from the plan, the agency will be notified and on-site approval requested. Any deviations from the specified protocols will be fully documented in the final Trial Burn Report.

5.4.1 Field Program Description

A detailed description of the compliance strategy and test conditions was provided previously in Sections 1.0 and 4.0. In general, however, the test program is presently configured to collect samples during three runs for each of three process operating conditions. **Table 5-2** provides a detailed listing of the sampling and analytical parameters and methods planned for this program.

5.4.2 Pre-sampling Activities

Pre-sampling activities include equipment calibration, sample media preparation, cleaning of sample train glassware, preparation of computer-generated sample labels, and other miscellaneous tasks. Each of these activities are described or referenced in the following subsections. Other pre-sampling activities include such details as team meetings, equipment packing and shipment, equipment setup, and finalization of all details leading up to the coordinated initiation of the sampling program.

5.4.2.1 Equipment Calibration

A most important aspect of pre-sampling preparations is the inspection and calibration of all equipment planned to be used for the field effort. Equipment is inspected for proper operation and durability prior to calibration. Calibration of equipment is conducted in accordance with the procedures outlined in the EPA document entitled "Quality Assurance Handbook for Air Pollution Measurement Systems; Volume III—Stationary Source Specific Methods" (EPA/600/R-94/038c, September 1994). Equipment calibration is performed in accordance with EPA guidelines and/or manufacturer's recommendations. Documentation of all calibration records will be kept in the project file during the field program and will be available for inspection by test observers. Examples of field equipment used and typical calibration requirements for each are as follows:

- **Probe nozzles** (QA Handbook Section 3.4.2, pg. 19) - make three measurements of the nozzle ID (to the nearest 0.001 in.) using different diameters with a micrometer. Difference between the high and low values should not exceed 0.004 in. Post-test check - inspect for damage.
- **Pitot tubes** (QA Handbook Section 3.1.2, pg. 1-13) - measured for appropriate spacing and dimensions or calibrate in a wind tunnel. Rejection criteria given on the calibration sheet. Post-test check - inspect for damage.
- **Thermocouples** (QA Handbook Section 3.4.2, pg. 15-18) - verify against a mercury-in-glass thermometer at two or more points including the anticipated measurement range. Acceptance limits - impinger $\pm 2^{\circ}\text{F}$; DGM $\pm 5.4^{\circ}\text{F}$; stack ± 1.5 percent of stack temperature.
- **Dry gas meters** (QA Handbook Section 3.4.2, pg. 1-12) - calibrate against a wet test meter. Acceptance criteria - pretest $Y_i = Y \pm 0.02$; post test $Y = \pm 0.05 Y_i$.
- **Field barometer** (QA Handbook Section 3.4.2, pg. 18-19) - compare against a mercury-in-glass barometer or use Airport Station BP and correct for elevation. Acceptance criteria - ± 0.02 in. Hg; post-test check - same.

5.4.2.2 Glassware Preparation

Sample train glassware and sample containers require specialized pre-cleaning to avoid contamination of the sample from the collection container or devices. Cleaning/storage procedures for sample train glassware are summarized below. Note that all bottle caps are fitted with Teflon liners which are cleaned in the same manner as the bottles themselves. Sample containers used for waste feed streams are purchased pre-cleaned and sealed to specified EPA protocols.

- **EPA Method 0023A/0010** glassware and containers (PCDDs/PCDFs and other semi-volatile organics) - wash with soap and water, rinse three times with deionized (DI) water, bake at 400°C for 2-hours, rinse three times with pesticide grade methylene chloride, rinse three times with pesticide grade toluene and air dry. Open ends will be sealed prior to shipment to the field with clean aluminum foil.
- **EPA Method 29/0060/0061** glassware and containers (metals) – wash with soap and water, rinse with hot tap water, and rinse three times with reagent water. The glassware is next soaked in a 10 percent nitric acid solution for a minimum of 4 hours, rinsed three times with reagent water, rinsed a final time with acetone and air-dried. All glassware openings where contamination can occur will be covered until the sampling train is assembled prior to sampling.
- **EPA Method 0050** glassware and components (ammonia, particulate matter and HCl/Cl₂) - wash with soap and water, rinse three times with DI water and air dry. Open ends will be sealed prior to shipment to the field with paraffin.
- **EPA Method 0030** glassware and containers (volatile organics) - wash with detergent (Alconox) and hot water, rinse three times with HPLC grade water and oven dry at 110°C for 2 hours. Open ends will be sealed prior to shipment to the field with clean aluminum foil.

5.4.2.3 Sample Media Preparation

All reagents will be checked in accordance with ENSR's existing QC Program to minimize the probability of using contaminated solvents. This includes the use of the proper grade reagents/solvents as specified in the test method, selection of reagents from the same lot and the collection and analysis of the appropriate blanks. Sampling media will be procured and prepared in accordance with the appropriate test methods as described below:

- **Tenax and Tenax/charcoal sorbent traps** will be conditioned in accordance with protocols outlined in Methods 0030 and/or 5041A.
- **XAD resin** is purchased new and packed in specially designed sorbent traps. All glass cleaning and sorbent packing procedures will follow the protocols specified in EPA Methods 0023A and/or 0010.
- **Teflon and Glass filters** used in the Method 0050 sampling train are purchased from Pallflex Products Co. with designated technical specifications and efficiency ratings.
- **Quartz filters** used in the Method 29/Method 0060 sampling train are purchased from Pallflex Products Co. who pre-screen filters for metals content.

5.4.2.4 Other Pre-sampling Activities

Sample team meetings will be held to designate responsibilities to each team member. Assignments will be based on individual experience and relative importance of the assigned task. Other pre-sampling activities in the office will include generation of sample checklists, printing of computer-generated sample labels, and proper packing of all equipment. Equipment will then be transported by freight or truck to the sampling location. Site setup is the final pre-sampling activity. This task will involve moving the equipment to the vicinity of the sample collection area. A separate office trailer or other suitable on-site facility will be used to serve as a sample train setup and recovery area and sample custody area.

Normally, preliminary tests are conducted at the stack location to verify the absence or presence of cyclonic flow conditions and to determine flue gas moisture, temperature and velocity. These measurements facilitate determination of nozzle size selection and sample train operation rates for the isokinetic sampling trains. Prior testing at the Shell facility indicates that cyclonic flow conditions do exist and therefore appropriate methods will be used to account for this.

5.4.3 Sampling Locations

5.4.3.1 Waste Feed Stream

The waste feed material will be sampled prior to being fed to the boiler in accordance with acceptable protocols. Waste feed sampling will occur upstream of any POHC spiking location. Taps in the feed lines will be used to access feed streams. Samples will be collected using methodologies described later in Section 5.6.4.

5.4.3.2 Stack Sampling Locations

Gaseous emissions samples will be collected from test ports that meet the minimum criteria specified in EPA Method 1. One test port level (4 sampling ports) is available to accommodate testing of all emissions test parameters. **Figure 5-1** provides a schematic of the CO Boiler No. 1 stack showing the location of the sampling ports and the upstream/downstream distances from flow disturbances. This schematic drawing also provides information related to the traverse point locations applicable to the isokinetic sampling trains as well as key stack parameters needed to select the appropriate size sampling nozzle.

5.4.4 Waste Feed Stream Sampling Procedures

The waste feed material fed during the test will be collected from taps in the feed line, located upstream of the POHC spiking location. The waste feed stream will be sampled at the beginning, middle and end of each run and analyzed for the parameters listed in **Table 5-2**. Facility personnel will collect these samples under ENSR's direction using pre-cleaned sample bottles suitable for the type of sample being collected and the intended analysis.

ENSR will provide all sample containers and assume custody of the samples at the end of each day. Prior to initiating Trial Burn testing activities, ENSR will hold a training session with facility staff responsible for sample collection to review grab sampling techniques, size of sample aliquots, compositing procedures and sample bottles to be used. Agency staff who will be providing Trial Burn oversight are invited to attend this training session. The following tables summarize the regimen to be followed for collection of waste fuel samples.

Waste Sample Collection During Conditions 1 and 3

Analytical Parameter	Bottle Size	Grab Amount	Bottles per run
Metals	500-mL	150-mL	1
Volatile Organics	40-mL VOA	40-mL	3
Semi-Volatile Organics	500-mL	150-mL	1
Physical Parameters	500-mL	150-mL	1

Waste Sample Collection During Condition 2

Analytical Parameter	Bottle Size	Grab Amount	Bottles per run
Metals	950-mL	150-mL	1
Volatile Organics	40-mL VOA	40-mL	3
Semi-Volatile Organics	950-mL	150-mL	1
Physical Parameters	950-mL	150-mL	1

The feed stream will be characterized for metals, ash content, water content, heat content, and total chlorides.

5.4.5 Stack Sampling Methodologies

Gases discharged from the exhaust stack will be sampled for the following parameters:

- Flue gas velocity, flow rate, temperature, moisture content and fixed gas (O₂ and CO₂) composition.
- RCRA Permit Metals – antimony, arsenic, barium, beryllium, cadmium, chromium (total), lead, mercury, silver, and thallium.
- Other Metals for the Health Risk Assessment – aluminum, copper, hexavalent chromium, cobalt, manganese, nickel, selenium, vanadium, and zinc.

- Ammonia, Particulate matter, HCl and Cl₂.
- Target Volatile Organics.
- PCDDs/PCDFs and PAHs.
- Carbonyl compounds (aldehydes).
- Target Semi-Volatile Organics.
- Total Hydrocarbons (THC).
- CO corrected to 7 percent O₂.

The following sections provide summaries of the sampling methodologies to be followed. In addition, example Trial Burn field data sheets to be used during the program are provided in **Appendix C**. Summaries of relevant information pertaining to setup and recovery of each isokinetic sampling train are provided in **Appendix D**.

5.4.5.1 Gas Stream Velocity, Moisture and Fixed Gases

Gas stream flow rate, moisture, and fixed gas concentration will be determined concurrent with each of the isokinetic sampling trains (e.g., Methods 0050, 29, 0061, 0010, 0011 and 0023A). Gas stream velocity will be determined using a pitot tube and water manometer in accordance with EPA Method 2. Gas stream temperature will also be determined at each of the Method 2 traverse points using a Type “K” thermocouple and pyrometer. Gas stream moisture will be determined as specified in EPA Method 4 concurrent with the isokinetic sampling methods. In this procedure the impinger contents are measured or weighed before and after each test run and used in conjunction with the metered gas volume to determine the gas stream moisture content. Fixed gases (O₂ and CO₂) for gas stream molecular weight determination and constituent oxygen correction will be determined in accordance with EPA Method 3A (continuous monitor) during each test run.

5.4.5.2 Metals

EPA Method 29 will be utilized for the collection of the target Permit and Health Risk Assessment metals mentioned earlier. Specific sampling details for the Method 0060 sampling train are as follows:

- Target sampling rate – 0.75 cfm
- Sample run time – 2-hr
- Estimated sample volume – 2.5 dscm (90 dsf)
- Number of sampling points per stack traverse – 12
- Total number of sampling points – 24
- Number of field reagent blanks collected – 1

5.4.5.3 Hexavalent Chromium

EPA Method 0061 will be followed, but because of the high stack temperature, will require modification, as outlined below. This sampling train will be utilized for the collection of chromium in the hexavalent state and therefore specific procedures and components are necessary to ensure that collected material is not reduced to the trivalent state. These steps include continuous recirculation of the sampling reagent through the sample liner and nozzle, use of glass, quartz or Teflon components, a post-test nitrogen purge of the sampling train and filtration of the collected impinger solution through a 0.45 μm acetate filter (or equivalent).

Specific additional sampling details for the Method 0061 sampling train are as follows:

- Target sampling rate - 0.75 cfm
- Sample run time - 2-hr
- Number of sampling points per stack traverse — 12
- Total number of sampling points – 24
- Number of field reagent blanks collected – 1

Specific modifications that will be required for this sampling train include the use of a one-piece quartz nozzle/probe assembly and a quartz or Teflon aspirator tube located inside the probe liner for KOH recirculation. This modification is required due to the expected gas stream temperature being greater than 300°F.

5.4.5.4 Ammonia, Particulate Matter (PM), HCl and Cl₂

Sampling for ammonia, PM, HCl and Cl₂ will be performed in accordance with EPA Method 0050, as written. Specific sampling details for the Method 0050 sampling train are as follows:

- Target sampling rate – 0.75 cfm
- Sample run time – 2-hr
- Estimated sample volume – 2.5 dscm (90 dscf)
- Number of sampling points per stack traverse – 12
- Total number of sampling points – 24
- Number of field reagent blanks collected – 1

5.4.5.5 Target Volatile Organics

EPA Method 0030 will be used to determine stack gas concentrations of the volatile POHC as well as volatile PICs and TICs. Data collected from VOST samples will be used to calculate the DRE for the volatile POHC, chlorobenzene.

The VOST method utilizes Tenax and Tenax/Charcoal cartridges to adsorb target volatile organic compounds; each cartridge is preceded by a condensing module. Specific sampling details for the Method 0030 train are as follows:

- Sampling rate – 1.0 Lpm
- VOST pair run time – 20-minutes
- VOST sample volume per tube pair – 20 L
- VOST tube pairs collected per run – 4 (a, b, c and d)
- VOST tube pairs designated for analysis – 3 (a, b and d)
- Minimum probe temperature – 135 °C
- Number of field blank pairs collected – 1 per each day of sampling
- Number of trip blank pairs collected – 1 per sample shipment

The recovery activities for the VOST method will include:

- Sealing the sorbent cartridges with threaded caps and Swagelok fittings and placing them in their original glass culture tubes with glass wool to absorb shock.
- Transferring the collected condensate into a 40 mL VOA vial, noting the volume collected by marking the VOA vial with a black indelible marker and diluting to volume with HPLC water to decrease headspace and the possibility of revolatilization of the compounds.
- Further reducing reactivity by storing all samples at 4°C.

5.4.5.6 PCDDs/PCDFs and PAHs

A combined Method 0023A/0010 sampling train will be used to sample for all target parameters. PCDDs/PCDFs will be collected following the procedures outlined in EPA Method 0023A. Target PAHs will be collected following the procedures outlined in Method 0010. Specific sampling details for the Method 0023A/0010 sampling train are as follows:

- Target sampling rate – 0.75 cfm
- Sample run time – 3-hr
- Minimum sample volume required – 3.0 dscm (105.6 dscf)
- Sample train rinse solvents: acetone, methylene chloride and toluene
- Number of sampling points per stack traverse – 12
- Total number of sampling points – 24
- Number of field reagent blanks collected – 1

5.4.5.7 Target Semi-Volatile Organics

A Method 0010 sampling train will be used to sample for semi-volatile organic PICs and TICs. Specific sampling details for the Method 0010 sampling train are as follows:

- Target sampling rate – 0.75 cfm
- Sample run time – 3-hr
- Minimum sample volume required – 3.0 dscm (105.6 dscf)
- Sample train rinse solvents: methanol / methylene chloride (1:1 v/v)
- Number of sampling points per stack traverse – 12
- Total number of sampling points – 24
- Number of field reagent blanks collected – 1

5.4.5.8 Carbonyl Compounds (Aldehydes)

A Method 0011 sampling train will be used to sample for target carbonyl compounds. Specific sampling details for the Method 0011 sampling train are as follows:

- Target sampling rate - 0.75 cfm
- Sample run time – 2-hr
- Estimated sample volume – 2.5 dscm (90 dscf)
- Number of sampling points per stack traverse – 12
- Total number of sampling points – 24
- Number of field reagent blanks collected – 1

This method uses 2,4-Dinitrophenylhydrazine (DNPH) reagent as the collection medium in the sample train impingers. The DNPH reagent must be prepared in the laboratory within 5 days of use in the field. When a container of the DNPH is opened in the field, it must be used within 48 hrs. Every effort must be made to avoid acetone contamination of the sample train glassware or the DNPH.

5.4.5.9 Continuous Emissions Monitoring

Plant-owned CEMS, installed in the boiler's stack, will be used during the Trial Burn to monitor the concentrations of O₂ and CO in the stack gas for reporting of CO concentrations corrected to 7% oxygen. In addition, the testing firm will provide a CEMS for continuous measurement of CO₂ and O₂ (for the purpose of determination of stack gas molecular weight) and total hydrocarbons (THC). The contractor-supplied CEMS will be operated in accordance with the procedures outlined in EPA Methods 3A (CO₂ and O₂) and 25A (THC).

5.5 Sample Handling, Traceability and Holding Times

Sample integrity will be maintained throughout all phases of the sampling and analysis program. Samples will be held within sight of the samplers or sample custodian, or will be kept in sealed or secured containers at all times. Sealed coolers and DOT shipping boxes will be used to ship samples to each designated laboratory via Priority 1 overnight FedEx service.

Preprinted sample identification labels are used by ENSR to ensure that all required information is fully documented. When sample batches are shipped to the specified laboratory, a sample packing list (see **Figure 5-2**) accompanies the shipment. This form is based on established laboratory format and will be used to document sample transfer in the field and from sampling personnel to the laboratory.

All samples will be given a unique sample code that will serve to identify the sample location, condition number, sample procedure, run number and sample fraction. Although the exact sample code has not yet been finalized, the coding system will follow the basic format cited below.

Example Sample Code: COB1-M29-FHR-C2-R3

where:

- COB1 – Location Identification (e.g., CO Boiler No. 1)
- M29 – Sampling Method (e.g., EPA Method 29)
- FHR – Sample Fraction (e.g., front-half rinse)
- C2 – Test Condition Number (e.g., Condition 2)
- R3 – Run Number (e.g., Run No. 3)

The ENSR Field Team Leader will coordinate the packing and shipment of all samples. Worksheets specifically designed for this program will be generated prior to the field effort. These sheets will assist the Field Team Leader in assuring that all samples have been collected, accounted for, and shipped under sample traceability documentation to the appropriate laboratory. Requirements pertaining to sample preservation and recommended holding times are noted in **Table 5-3**.

All materials such as field and laboratory notebooks and logbooks, field and laboratory data records, correspondence, reports, sample tags, traceability records and instrument printouts will be clearly labeled with the project number and become a permanent part of the project file. Project samples will be disposed of in an appropriate manner 60 days after acceptance and approval of a final report. All project-related documentation at both ENSR and the subcontractor laboratories will be kept on file for 2 years following submittal of the final report.

5.6 Analytical Methods and Calibration Procedures

This section delineates the analytical protocols that will be followed to analyze samples during this test program. The methods cited will be followed as written unless specific modifications are made in the standard operating procedures (SOPs) by the laboratory. Samples of waste feed and stack gas will be collected and analyzed for the parameters previously discussed using the appropriate laboratory protocols detailed in this section and as outlined previously in **Table 5-2**. All referenced EPA methods will be from SW-846, 3rd edition, unless noted otherwise.

5.6.1 Analysis of Waste Feed Material

5.6.1.1 Chemical and Physical Properties

Analyses to determine the chemical and physical properties of the waste feed material will be performed using appropriate ASTM or EPA analytical methods as outlined in the table below.

Total chlorine (preparation)	ASTM E 776 or EPA M 5050
Total chlorine (analysis)	EPA M 300.0 or EPA M 9056
Ash content	ASTM D 482
Moisture (Karl-Fischer)	ASTM D 1744
Heat content	ASTM D 240

Quality assurance requirements for the determinations of chemical and physical properties of the waste feed materials are summarized in **Table 5-4**.

5.6.1.2 Metals in Waste Feed Material

Target metals for this program were mentioned earlier in Section 4.1.1. Analyses for metals other than mercury will be performed using inductively coupled plasma - mass spectroscopy (ICP-MS) as described in EPA Method 6020. Mercury analysis will be performed using EPA Method 7471A. EPA Method 3050B will be followed for analytical preparation. Quality assurance requirements for the analyses of metals in waste feed samples are summarized in **Table 5-5**.

5.6.1.3 Organics in Waste Feed Material

The waste feed will be analyzed for volatile and semi-volatile organic constituents following EPA Methods 3585/8260B (VOCs) and 3580A/8270C (SVOCs). Quality assurance requirements for the analyses of organics in waste feed are summarized in **Table 5-6**.

5.6.2 Analysis of Stack Gas Samples

5.6.2.1 Metals in Stack Gas Samples

Analysis - Each sampling train will be prepared for analysis in accordance with EPA Method 29 and employing the option of combining fractions 1A and 2A as delineated in Section 7.5.4 of the method.

From each sampling train, seven individual samples are generated for analysis. The first two samples, labeled Fractions 1A and 1B consists of the digested sample from the front half of the train, consisting of the particulate filter and the front-half nitric acid probe rinse. Fraction 1A is for ICP analysis and Fraction 1B is for mercury analysis. Fractions 2A and 2B consist of digestates from the moisture knock out and HNO₃/H₂O₂ impingers 1, 2, and 3. Fraction 2A is for ICP analysis and Fraction 2B is for mercury analysis. Fractions 3A, 3B, and 3C consist of the impinger contents and rinses from the empty and permanganate impingers 4, 5, and 6. These fractions will be analyzed for mercury. A combined front-half and back-half analysis will be performed for all metals except mercury.

Analyses for metals other than mercury will be performed using Inductively Coupled Plasma - Mass Spectroscopy (ICP-MS) as described in EPA Method 6020. Mercury analysis will be performed using cold vapor atomic absorption spectroscopy (CVAAS) as specified in EPA Method 7470A. All quality control procedures, including the interference check standard, will be followed as described in the respective method. QA/QC requirements for the analysis of metals in stack gas samples are summarized in **Table 5-7**.

Calibration – Instrument calibration will be performed daily in accordance with the procedures described in the analytical methods cited and the manufacturer's instructions. The calibration is verified daily by analysis of an instrument check standard prepared from an EPA quality control concentrate or other independent standard.

5.6.2.2 Hexavalent Chromium in Stack Gas Samples

Analysis - Each sampling train will be prepared and analyzed according to EPA Method 7199. Upon completion of sampling, the probe assembly is disconnected and the train assembly is purged with nitrogen. The first impinger is recovered and the pH of its contents checked with wide-range pH paper. Impingers 1, 2, and 3 are drained into a pre-cleaned graduated cylinder and the volume recorded. The impinger solution will be combined with the DI water rinses of the glass nozzle, aspirator, sample and recirculation lines, impingers, and connecting tubing and filtered through a 0.45-micron acetate filter. The volume of this filtrate and rinses are recorded and sent to the laboratory for analysis. The sample is analyzed for hexavalent chromium by ion chromatography coupled with a post-column reactor (IC/PCR). QA requirements associated with this method are summarized in **Table 5-8**.

5.6.2.3 Aldehydes in Stack Gas Samples

Analysis - Each sampling train will be prepared and analyzed according to EPA Method 8315A. This method entails high performance liquid chromatography (HPLC) with ultraviolet/visible detection. Procedure 1 of Method 8315A is followed for stack gas samples collected by Method 0011. HPLC operating conditions are summarized in Section 7.5.1 of Method 8315A. Target analytes for the program will include acetaldehyde, crotonaldehyde, formaldehyde and propionaldehyde. QA requirements associated with this method are summarized in **Table 5-9**.

Calibration – Specific calibration procedures are denoted in Section 7.6 of Method 8315A.

5.6.2.4 Particulate Matter in Stack Gas Samples

Gravimetric analyses will be performed on samples collected from the Method 0050 Particulate/HCl/Cl₂ train. Weights will be obtained on the front-half acetone rinse and particulate filter using a Mettler H35 analytical balance. Balance accuracy is checked by using Class "S" standard weights before and after tare weighings and sample determinations.

5.6.2.5 Ammonia and Total Chlorides (HCl/Cl₂) in Stack Gas Samples

Impinger samples from the Method 0050 sampling train will be analyzed by ion chromatography in accordance with EPA Method 9057 for determination of total chlorides. A portion of the 0.1N sulfuric acid impinger catch will also be analyzed for ammonia by EPA Method 350.1, automated colorimetric analysis. QA/QC procedures for stack gas analyses for chloride are presented in **Table 5-10**.

5.6.2.6 Target Volatile Organics in Stack Gas Samples

Stack gas samples will be analyzed for volatile organics using EPA Method 5041A (VOST tubes) and EPA Method 8260B (condensate). Target analytes will include the full method scan plus the top 10 non-target compounds, which will be denoted as tentatively identified compounds (TICs). A list of target compounds is provided in **Appendix E**.

Analysis — The samples collected from each VOST run will consist of a Tenax cartridge, a Tenax/charcoal backup cartridge, and a flue gas condensate. Cartridges will be desorbed and analyzed for volatile organics using the thermal desorption GC/MS procedures specified in Method 5041A of SW 846. Condensate samples will be analyzed using Method 8260B. Test program spiking and sampling parameters have been predefined to preclude the possibility for breakthrough of the volatile POHC from the Tenax tube to the backup Tenax/charcoal tube in the VOST train. Breakthrough volumes for the POHC are ≥ 8 L/g of Tenax at 100°F (38°C); since the front tubes contain 1.5 g of Tenax and the temperature will be held at 20°C, no breakthrough should occur with the sample volumes limited to 20 L. Nevertheless, to provide definitive information on whether breakthrough has occurred, the first pair of traps from each run will be desorbed individually; if breakthrough has not occurred, remaining traps from the run will be codesorbed. All audit and blank samples will be analyzed via codesorption.

All QA/QC requirements of EPA Method 5041A for instrument calibration and performance will be met prior to sample analyses, including:

- System performance checks using the five system performance check compounds (SPCCs) will be conducted initially and after every 12 hours of analysis. The minimum response factors for the volatile SPCCS will be 0.100 (0.300 for chlorobenzene).
- Daily calibration of the system, including evaluation of the internal standard responses and retention times in the check calibration standard. Performance criteria specified in the method will be used to determine whether the system has malfunctioned. If samples are analyzed under conditions of malfunction, an evaluation of the impact of that malfunction on data quality will be performed, with the results of the investigation presented in the final report.

Thermal desorption will be conducted using an automated desorption unit which is designed to accommodate sorbent cartridges in series. The desorption gas is plumbed to direct flow through each pair of traps, then through a purge vessel to trap desorbed water and, finally, onto the head of a smaller sorbent column (Tenax/silica gel/OV-1) which is located in a Tekmar LSC-2 purge and trap device. The volatile components adsorbed onto the secondary trap are then thermally desorbed onto the GC by heating the trap to 180°C as detailed in Method 5041A. Prior to analysis, the volatile surrogate compounds and internal standards listed in the method will be flash vaporized onto each Tenax cartridge set. Additionally, isotopically-labeled MCB (chlorobenzene d₅) will be spiked as an internal standard.

The analytical performance check for the designated POHC will be completed prior to the program in accordance with SW-846 Method 0030, Section 7.1 by the laboratory conducting the analyses. The amount spiked for this analysis will be at or near the anticipated "critical level" for the POHC for this project (250 ng) per component and will be recognized as having passed the check if the recovery is within 50 to 150 percent of the expected values.

Calibration for Method 5041A - The GC/MS will be tuned to BFB at the beginning of each 12-hour analysis sequence, applying the acceptance criteria for key ion abundance listed in the method.

Upon compliance with all system criteria, the GC/MS will be initially calibrated at a minimum of three to five calibration levels by analyzing sets of adsorbent tubes spiked with the volatile POHCs, internal standard, and surrogates.

Calibration standards for the POHC must cover the range of concern for DRE demonstration. Calibration standards will be prepared at five different concentration levels for each analyte of interest. Compounds of interest, surrogate compounds, and internal standards are spiked into the purge water for generation of a multi-point calibration curve. When samples are analyzed, surrogate compounds are spiked onto the sampling tubes using flash vaporization techniques, but internal standards are spiked into the purge water. Response factors for each compound are determined and used for the calculation of analytical results.

QA/QC requirements for VOST analyses are provided in **Table 5-11**.

5.6.2.7 Stack Gas - Analysis for PCDDs/PCDFs and PAHs

Stack flue gas samples collected using the Method 0023A/0010 sampling train will be analyzed for polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDDs/PCDFs) and polycyclic aromatic hydrocarbons (PAHs). Each M0010/M0023A train will be prepared and split appropriately for the designated analyses. A combined front half and back half analysis will be performed for each analyte category.

Briefly, the XAD and filter will be spiked with internal standards for PCDDs/PCDFs and PAHs and then sequentially extracted with methylene chloride and toluene. The methylene chloride and acetone rinses will be combined and added to the methylene chloride Soxhlet extract. This combined sample will be concentrated and split. The portion allocated for PAH analyses will be combined with the acid/base neutral extracts of the impinger contents. The portion allocated for PCDD/PCDF analysis will be combined with an appropriate fraction of the toluene extract.

Method 23 analyses (which include high resolution GC/MS as per EPA Method 8290) incorporate five isotopically labeled PCDD and PCDF field surrogates and nine labeled PCDD/PCDF internal standards. The field surrogates are spiked into the XAD resin prior to field sampling; their recoveries are monitored to assess overall method accuracy and precision. The internal standards are added to the combined XAD/filter/rinse concentrate sample at a level of 2,000 pg/sample prior to Soxhlet extraction. These internal standards are used for direct quantification of all surrogate and native PCDD/PCDF species. The addition of these standards prior to the extraction and cleanup procedures permits internal correction for any losses of target analytes that might occur during the preparation steps.

Method 8290 details instrument tune, GC column performance, and instrument calibration requirements for the analysis of stack gas samples by high-resolution gas chromatography/high-resolution mass spectrometry. Instrument calibration will be performed for all 15 2,3,7,8-substituted PCDD and PCDF isomers; data will be reported for each of these target analytes and for the total dioxins and total furans at each level of chlorination from Cl₄ through Cl₈.

Additional analyses for target PAHs will be conducted in accordance with California Air Resources Board Method 429. This method employs isotopically labeled internal standards and HRGC/HRMS analysis for target PAHs. The use of the method is intended to supplant similar data provided by Method 8270C data for target PAHs, because the method provides lower detection limits for use in the health risk assessment.

QA/QC requirements for these analyses are summarized in **Tables 5-12 and 5-13**.

5.6.2.8 Semi-Volatile Organics in Stack Gas Samples

Stack flue gas samples collected using the Method 0010 sampling train for semi-volatile organic PICs will be analyzed as specified in EPA Method 8270C. Target SVOCs (see list of target compounds provided in **Appendix E**) will include all analytes listed in Method 8270C (except PAHs, Aroclors, and organochlorine pesticides) where Methods 3540/3541 are listed as the appropriate preparation technique. Method 3542, which is the preferred preparation method, will be used for these analyses. In addition to the analysis for target compounds, data will be searched against the EPA/NIH library of mass spectral data using the instrument automated software routine for tentative identification of up to approximately 15 additional compounds. Up to 10 peaks with areas of 10 percent or more of the nearest internal standard will be searched. Estimated quantification of these compounds will be based upon the area of the compound compared to that of the nearest internal standard, using a relative response factor of 1 unless the TIC is structurally similar to a closely-eluting target compound for which a response factor is already established.

All components of the Method 0010 sampling train will be submitted to the laboratory for extraction and analysis as specified in EPA Method 3542. Analysis for semi-volatile organics will be performed by low resolution mass spectrometry following the analytical protocol of SW-846, Method 8270C. Surrogates will be added prior to extraction to monitor analytical accuracy. Method 8270C surrogates to be used are: 2-Fluorobiphenyl, 2-Fluorophenol, Phenol-d₅, Terphenyl-d₁₄, 2,4,6-Tribromophenol and Nitrobenzene-d₅. Method 8270C internal standards to be used are: 1,4-Dichlorobenzene-d₄, Naphthalene-d₈, Acenaphthene-d₁₀, Phenanthrene-d₁₀, Chrysene-d₁₂ and Perylene-d₁₂.

QA/QC requirements for these analyses are summarized in **Table 5-14**.

5.7 Internal QA Program

Quality control checks will be performed to ensure the collection of representative samples and the generation of valid analytical results for these samples. These checks will be performed by project participants throughout the program under the direction of the Project Manager and the QA Officer.

5.7.1 Data Collection and Sampling QC Procedures

QC checks for the process data collection and sampling aspects of this program will include, but not be limited to, the following:

1. Use of standardized data sheets, checklists, and field notebooks to ensure completeness, traceability, and comparability of the process information and samples collected.
2. Field checking of standardized forms by the Field Team Leader and a second person to ensure accuracy and completeness.

3. Strict adherence to the sample traceability procedures.
4. Submission of field biased blanks.
5. Leak checks of sample trains before and after sample collection and during the test, when appropriate.

5.7.1.1 Sampling Equipment QC Checks and Frequency

Calibration of the field sampling equipment is performed in accordance with procedures recommended by the manufacturer. Copies of the calibration sheets will be available on site during the field sampling program for inspection, will be kept in the project file and will be submitted in the final report. Calibrations will be performed as described in the EPA publication "Quality Assurance Handbook for Air Pollution Measurement Systems, Volume III, Stationary Source Specific Methods;" Section 4.2.1 presents acceptance limits.

Leak checks of the sample trains will be conducted in accordance with the protocol called out for each method. Leak checks will be conducted prior to and at the end of sample collection and during the test run, when appropriate.

5.7.1.2 Sample Collection QC Checks

Field-biased blanks of reagents and collection media (deionized water, filters, impinger solutions, etc.) will be placed in appropriately cleaned and sized sample containers in the field and handled in the same way as actual field samples, to provide a QC check on sample handling.

For this program, sample collection QC checks and frequency for samples to be analyzed in the laboratory are listed below:

- One field blank VOST train (i.e., one set of blank traps exposed to conditions analogous to actual samples) for each day of sampling and one trip blank for each sample shipment.
- Three pairs of VOST tubes collected from any EPA audit cylinder provided
- One set of field blank reagents from the Method 29 sampling train
- One set of field blank reagents from the Method 0061 sampling train
- One set of field blank reagents from the Method 0050 sampling train
- One set of field blank reagents from the Method 0023A/0010 sampling train
- One set of field blank reagents from the Method 0010 sampling train
- One set of field blank reagents from the Method 0011 sampling train

5.7.2 Analytical QC Procedures for Samples to be Analyzed in the Laboratory

The Quality Control program for laboratory analysis makes use of a number of different types of QC samples to document the validity of the generated data. The following types of QC samples will be used during the program.

5.7.2.1 Quality Control Samples and Blanks

Method Blanks

Method blanks contain all the reagents used in the preparation and analysis of samples and are processed through the entire analytical scheme to assess spurious contamination arising from reagents, glassware, and other materials used in the analysis.

Calibration Check Samples

One of the working calibration standards which are periodically used to check that the original calibration is still valid.

Laboratory Control Samples (LCS) or Blank Spikes

These samples are generated from spikes prepared independently from the calibration concentrates. The LCS are used to establish that an instrument or procedure is in control. An LCS is normally carried through the entire sample preparation and analysis procedure also.

Surrogate Spikes

Samples requiring analysis by GC/MS are routinely surrogate-spiked with a series of deuterated analogues of the components of interest. It is anticipated that these compounds would assess the behavior of actual components in individual program samples during the entire preparative and analysis scheme.

The percent recovery for each surrogate will be calculated in accordance with method-specific procedures. Any values which fall outside the target QC limits described in the applicable analytical method will be flagged. Some of these recovery values may be outside the QC limit owing to matrix interferences. The following guidelines will be used:

1. All recovery data are evaluated to determine if the QC limits are appropriate and if a problem may exist even though the limits are being achieved (e.g., one compound that is consistently barely within the lower limit).
2. Any recovery data which are outside the established limits are investigated. This evaluation will include an independent check of the calculation.
3. Corrective action will be performed if any of the following are observed:

- All recovery values in any one analysis are outside the established limits, where one analysis is considered to be one sample analyzed by one method,
- Over 10 percent of the values for a given sample delivery group are outside limits, or
- One compound is outside the limits in over 10 percent of the samples.

An analysis batch is defined as a group of ten or fewer samples carried through the entire preparation and analysis procedure in one batch.

Reagents used in the laboratory are normally of analytical reagent grade or higher purity; each lot of acid or solvent used is checked for acceptability prior to laboratory use. All reagents are labeled with the date received and date opened. The quality of the laboratory deionized water is routinely checked. All glassware used in the sampling and analysis procedures will be pre-cleaned according to the method requirements. Standard laboratory practices for laboratory cleanliness, personnel training, and other general procedures are used. The results of these quality control procedures will be included in the final report.

5.7.2.2 Quality Control of Sorbents

Sorbents used for the organic sampling trains are provided by the laboratory after QC verification has been performed following recommended procedures in each applicable method. Additional details on sample media preparation were provided previously in Section 5.6.2.3.

5.8 Data Reduction, Verification and Data Reporting

Specific QC measures will be used to ensure the generation of reliable data from sampling and analysis activities. Proper collection and organization of accurate information followed by clear and concise reporting of the data is a primary goal in all such projects.

5.8.1 Field Data Reduction

Appendix C presents the standardized forms that will be used to record field sampling data. The Field Team Leader and at least one other field crewmember will review the data collected from each train in its entirety in the field. Errors or discrepancies will be noted and dealt with accordingly. The Field Team Leader has the authority to institute correction actions in the field. The QA officer will also be notified for resolution if the situation warrants. At a minimum, the QA officer is apprised of all deviations from standard protocol. Field data reduction (checking of valid isokinetic sampling rate and other sampling parameters) is done with a laptop computer using standardized Excel spreadsheets. **Appendix D** provides recovery schematics and a description of solutions and reagents to be used in each impinger train required for the overall program. All sample recovery sheets will be checked for completeness.

5.8.2 Laboratory Analysis Data Reduction

Analytical results will be reduced to appropriate units by the laboratory using the equations given in the applicable analytical method. Unless otherwise specified, results from the analysis of waste feed and process samples for specific target constituents will be reported in units of mg/kg or % wt. Other parameters will be reported in standard units such as g/cc, Btu/lb, etc.

The laboratory typically reports results from the analysis of stack flue gas samples as total mass detected for the sample submitted. For those sample fractions where liquid impinger condensate is analyzed, the laboratory will measure the total liquid volume submitted and multiply by the measured concentrations of target analytes in these samples. The laboratories will generally report data as follows:

- Volatile organics (VOST) – total µg collected
- Particulate matter - total mg collected in each fraction (front-half rinse and filter)
- All metals except mercury – total µg of each metal in the combined front-half and back-half sample train fractions
- Hexavalent chromium – total µg collected
- Mercury –total µg in each sample train fraction (front-half and back-half)
- HCl /Cl₂ - total µg as either HCl or Cl₂
- Ammonia – total µg collected
- PCDDs/PCDFs - total pg collected
- PAHs - total ng collected
- SVOCs - total µg collected
- Aldehydes - total µg or mg collected gr/dscf

Each LSC will be responsible for reviewing all results and calculations and verifying the completeness of the data set. The laboratory reports submitted by each laboratory will include the following deliverables:

- Transmittal letter listing all samples and analyses and a case narrative identifying any difficulties associated with the analyses and any anomalous QA/QC results
- Copies of Chain of Custody Forms
- Sample Report forms with sample field and laboratory identifier, dates of sample preparation and analysis, analytical results and detection limits
- Method Blank results
- Matrix spike and matrix spike duplicate results (as applicable)
- Replicate sample analyses (as applicable)
- Laboratory Control Sample results

Reports for organics in stack samples will include the following additional information:

- Surrogate recoveries
- Summary of initial calibrations
- Continuing calibration summaries
- Instrument tunes

5.8.3 Data Verification

Data verification is the process of reviewing data and accepting, qualifying or rejecting it on the basis of method-specific criteria. The independent project QAO will use validation methods and criteria appropriate to the type of data and the purpose of the measurement. Records of all data will be maintained, even that judged to be an "outlying" or spurious value.

Field sampling data will be validated by the Field Team Leader based on a judgment of the representativeness of the sample, maintenance and cleanliness of sampling equipment and the adherence to an approved, written sample collection procedure.

Analytical data will be validated by the subcontractor laboratory QC or supervisory personnel using criteria outlined in their laboratory-specific QA Plan and/or written SOPs. Results from field and laboratory method blanks, replicate samples and internal QC samples will be used to further validate analytical results. Analytical results on field blanks and replicate field samples are valuable for validation of sample collection also. QC personnel will review all subcontractor laboratory raw analytical data to verify calculated results presented.

The following criteria will be used to evaluate the field sampling data:

- Use of approved test procedures
- Proper operation of the process being tested
- Use of properly operating and calibrated equipment
- Leak checks conducted before and after tests
- Use of reagents that have conformed to QC specified criteria
- Use of NBS traceable CEM calibration gases (as applicable)
- Proper chain-of-custody maintained
- All sample trains --check to ensure proper sample gas volume collected

The criteria listed below will be used to evaluate the analytical data:

- Use of approved analytical procedures
- Use of properly operating and calibrated instrumentation
- Precision and accuracy achieved should be comparable to that achieved in previous analytical programs and consistent with objectives stated in this document.

5.8.4 Final Data Reporting

Stack gas concentrations for each applicable parameter will be calculated from laboratory results and field sampling data. The total weight of the analyte detected will be divided by the volume of gas sampled to provide emission concentrations. Typically, all emission concentrations are further corrected to 7 percent oxygen for comparison to published standards.

For this program, two types of samples are allowed to be blank-corrected in accordance with method-specific procedures. First, gravimetric analyses for PM follow the procedures outlined in EPA Reference Method 5. Section 3.2 of Method 5 allows acetone residue blank correction up to a maximum of 0.001 percent of the weight of the acetone (0.01mg/g). Second, blank correction for reagent contamination for all metals analyzed is allowed as per Sections 8.3 and 8.5 of Method 29.

A complete Trial Burn Report outlining the goals, methods and results for the program will be prepared and any deviations from this test plan will be documented. The Final Report will include a section on evaluation and discussion of QA/QC results. Results will be compared to expected limits for accuracy, precision, and/or completeness as targeted in this protocol. The final test report will also include the results of any internal audits conducted on the program as well as:

- All field data sheets showing sampling method, dates, run times, personnel, equipment; sample preservation, identification and compositing records.
- Field equipment calibration data.
- Analytical lab reports and relevant supporting documentation.

5.9 Routine Maintenance Procedures and Schedules

The field sampling team follows an orderly program of positive actions to prevent the failure of equipment or instruments during use. This preventive maintenance and careful calibration helps to ensure accurate measurements and minimal field delays.

All equipment that is scheduled for field use is calibrated as outlined previously in Section 5.6.2.1. Prior to each field use for a specific project, the equipment is cleaned and checked to ensure it is in good working order. An adequate supply of spare parts and sample train glassware is brought to each site to minimize downtime and field sampling delays. Any equipment that does experience problems is appropriately tagged in the field to ensure that it is repaired upon return to the office.

5.10 QA/QC Assessment Procedures

The QA activities implemented in this program will provide a basis for assessing the accuracy and precision of the analytical measurements. Section 5.8 of this QAPP discusses the QA activity that will generate the accuracy and precision data for each sample type. A generalized form of the equations that will be used to calculate accuracy, precision and completeness follows.

5.10.1 Accuracy

Percent accuracy will be determined using the following equation:

$$\% \text{ Recovery} = \frac{(X - S)}{T} \times 100$$

where:

X = experimentally determined concentration of the spiked sample

T = true concentration of the spike

S = sample concentration before spiking

5.10.2 Precision

Precision will be determined using the following equation:

$$\text{Relative Percent Difference (RPD)} = \left[\frac{(D_1 - D_2)}{\left\{ \frac{D_1 + D_2}{2} \right\}} \right] \times 100$$

where:

D_1 and D_2 = results of duplicate measurements or standard deviation relative to the average value expressed as relative standard deviation:

Relative standard deviation will be expressed as follows:

$$\text{Relative Standard Deviation (\% RSD)} = \left\{ \frac{\sigma_{(n-1)}}{\bar{x} (x_1 \dots x_n)} \right\} \times 100$$

where:

$\sigma_{(n-1)}$ = standard deviation of the sample data

n = number of replicates

$\bar{x}_{(x_1 \dots x_n)}$ = arithmetic mean of the sample data

5.10.3 Completeness

Data completeness is a measure of the extent to which the database resulting from a measurement effort fulfills objectives for the amount of data required. For this program, completeness will be defined as the percentage of valid data for the total valid tests. Completeness is assessed using the following equation:

$$\text{Completeness (\%)} = \left[\frac{D_r}{D_c} \right] \times 100$$

where:

D_r = number of samples for which valid results are reported

D_c = number of valid samples that are collected and reach the laboratory for analysis

The completeness objective will help to evaluate the accuracy and precision of the analytical measurements.

5.11 External QA Program

The External Quality Assurance Program includes both performance and system audits as independent checks on the quality of data obtained from sampling, analysis, and data gathering activities. Every effort is made to have the audit assess the measurement process in normal operation. Either type of audit may show the need for corrective action.

5.11.1 Performance Audits

The sampling, analysis, and data handling segments of a project are checked in performance audits. A different operator/analyst prepares and conducts these audit operations to ensure the independence of the quantitative results.

EPA Quality Control concentrates or other standards will be used to assess the analytical work. Results will be reviewed by the subcontractor laboratory and QC personnel. Any additional audit samples presented by the regulatory agencies will be analyzed along with program samples, by the appropriate lab and at the same time as all other samples. It will, however, be the responsibility of the regulatory agency to obtain these samples, and present them to the facility project manager in a form that is amenable and appropriate to the analytical methods being utilized. Should the regulatory agencies be interested in conducting a VOST audit, please note the following:

- The VOST audit cylinder needs to be provided by EPA through their subcontractor and brought or shipped to the test location;
- The audit cylinder needs to be accompanied by an audit cylinder kit containing the necessary instructions and hardware/glassware for connecting the cylinder to the VOST sampling equipment;

- The target concentration for the POHC (MCB) should be in the appropriate range for subsequent GC/MS analysis: 1-23 ppb (3-100 $\mu\text{g}/\text{m}^3$) for a pre-specified 10-L sample volume or 0.3-11 ppb (1.3-52 $\mu\text{g}/\text{m}^3$) for a pre-specified 20-L sample volume; and
- The audit cylinder will be sampled only after the field program has been completed so as not to “contaminate” the pre-cleaned glassware with MCB.

If the regulatory agency advises facility program manager that audit results fall outside of acceptable ranges, the analytical data will be further reviewed for error in conjunction with the agency. If a simple, correctable error is found (e.g., an arithmetic error), correction will be made and results resubmitted. If no error is found, an investigation into other causes of the failure (e.g., lack of sample integrity) will be conducted and results evaluated in terms of the impact on sample data integrity.

5.11.2 Corrective Action

The acceptance limits for the sampling and analyses to be conducted in this program will be those stated in the method or defined by the project manager. The corrective actions are likely to be immediate in nature and most often will be implemented by the analyst or Project Manager; the corrective action will usually involve recalculation, reanalysis, or repeating a sample run. Ongoing corrective action policy is described here.

5.11.2.1 Immediate Corrective Action

Specific QC procedures and checklists are designed to help analysts detect the need for corrective action. Often the person's experience will be more valuable in alerting the operator to suspicious data or malfunctioning equipment.

If a corrective action can be taken at this point, as part of normal operating procedures, the collection of poor quality data can be avoided. Instrument and equipment malfunctions are amenable to this type of action and QC procedures include troubleshooting guides and corrective action suggestions. The actions taken should be noted in field or laboratory notebooks but no other formal documentation is required, unless further corrective action is necessary. These on-the-spot corrective actions are an everyday part of the QA/QC system.

Corrective action during the field sampling portion of a program is most often a result of equipment failure or an operator oversight and may require repeating a run. When equipment is discovered to be defective (i.e., pre- and post-sampling leak check) it is repaired or replaced and a correction factor is established as per the EPA method. If a correction factor is unacceptable the run is repeated. Operator oversight is best avoided by having field crew members audit each other's work before and after a test. Every effort is made by the field team leader to ensure that all QC procedures are followed. Economically, it is preferred to repeat a run during a particular field trip rather than return at a later date.

Corrective action for analytical work would include re-calibration of instruments, reanalysis of known QC samples and, if necessary, of actual field samples.

If the problem is not solved in this way, more formalized long-term corrective action may be necessary.

5.11.2.2 Long-Term Corrective Action

The need for this action may be identified by standard QC procedures, control charts, performance or system audits. Any quality problem which cannot be solved by immediate corrective action falls into the long-term category. The condition is reported to a person responsible for correcting it who is part of the closed-loop action and follow-up plan.

The essential steps in the closed-loop corrective action system are:

- Identify and define the problem.
- Assign responsibility for investigating the problem.
- Investigate and determine the cause of the problem.
- Determine a corrective action to eliminate the problem.
- Assign and accept responsibility for implementing the corrective action.
- Establish effectiveness of the corrective action and initiate implementation.
- Verify that the corrective action has eliminated the problem.

Documentation of the problem is important to the system. A Corrective Action Request Form is filled out by the person finding the quality problem. This form identifies the problem, possible causes and the person responsible for action on the problem. The responsible person may be an analyst, field team leader, department QC coordinator or the QA Director. If no person is identified as responsible for action, the QA Director investigates the situation and determines who is responsible in each case.

The Corrective Action Request Form includes a description of the corrective action planned and the date it was taken, and space for follow-up. The QA Director checks to be sure that initial action has been taken and appears effective and, at an appropriate later date, checks again to see if the problem has been fully solved. The QA Director receives a copy of all Corrective Action Forms and then enters them in the Corrective Action Log. This permanent record aids the QA Director in follow-up and makes any quality problems visible to management; the log may also prove valuable in listing a similar problem and its solution.

5.11.3 Quality Assurance Reports to Management

5.11.3.1 Internal Reports

The LSC will prepare a case narrative on QC activities associated with this project for the Quality Assurance Director. This report will detail the results of quality control procedures, problems encountered and any corrective action, which may have been required.

Any Corrective Action Forms are submitted to the QAO for initial approval of the corrective action planned and a copy is provided to the Program Manager. All system audit reports are provided to the Program Manager and the QAO.

5.11.3.2 Reports to Client

The final report will include a section summarizing QA/QC activities during the program. The Project Manager, Laboratory Services Coordinators, and the QAO will participate in preparing this section. This section will provide summary QA/QC results for method blanks, surrogate spikes and laboratory control spike recoveries. This section will evaluate overall data quality in terms of accuracy, precision and completeness. Any discrepancies or difficulties noted in program work, protocol deviations or documentation gaps will be identified and discussed.

Table 5-1 General Sampling and Analytical Program Overview – Stack Gas

Parameter	Sampling Method	Analytical Methods	Test Condition(s)
POHC DRE	EPA Method 0030 (VOST)	EPA Methods 5041A/8260B	3
Target Volatile Organics	EPA Method 0030 (VOST)	EPA Methods 5041A/8260B	2
Particulate Matter	EPA Method 0050	EPA Method 5 (Gravimetric)	1 & 2
HCl/Cl ₂	EPA Method 0050	EPA Method 9057 (Ion Chromatography)	2
Ammonia	EPA Method 0050	EPA Method 350.1 (Colorimetric)	2
Mercury	EPA Method 29	EPA Method 7471 (CVAAS)	2
Metals	EPA Method 29	EPA Method 6020 (ICP-MS)	2
Hexavalent Chromium	EPA Method 0061	EPA Method 7199 (IC-PCR)	2
Carbonyls (Aldehydes)	EPA Method 0011	EPA Method 8315A	2
PCDDs/PCDFs and PAHs	EPA Methods 0023A and 0010	EPA Method 8290 and CARB Method 429	2
Target Semi-Volatile Organics	EPA Method 0010	EPA Method 8270C	2
Total Hydrocarbons	EPA Method 25A	EPA Method 25A (GC/FID)	1, 2 & 3
Carbon Monoxide	EPA Method 10	EPA Method 10 (NDIR)	1, 2 & 3
Flow, Fixed Gases and Moisture	EPA Methods 2, 3A and 4	EPA Methods 2, 3A and 4	1, 2 & 3

Table 5-2 Overall Summary of Trial Burn Sampling and Analysis Program

Sample Matrix and Sampling Method	Analytical Parameters	Analytical Method	Lab (a)	Total Samples Analyzed				
				Total Runs	Reagent Blanks	Audit	Lab QC	Total
Waste Feed								
(Grab/Comp)	Heat Content	ASTM D 240	STL-P	9	0	0	1	10
	Ash Content	ASTM D 482	STL-P	9	0	0	1	10
	Water Content	ASTM D 1744	STL-P	9	0	0	1	10
	Total Chlorine	ASTM E 776 / EPA M 9056	STL-P	9	0	0	2	11
	VOCs	EPA M 8260B	STL-P	9	0	0	2	11
	SVOCs	EPA M 8270C	STL-P	9	0	0	2	11
	Metals (b)	EPA M 6020 / 7471A	STL-P	9	0	0	2	11
Stack Flue Gas								
EPA M 0050	PM	EPA M 5	ENSR	6	1	0	1	8
	Ammonia	EPA Method 350.1	STL	3	1	0	1	5
	HCl and Cl ₂	EPA M 9057	STL	3	1	2	1	7
EPA M 0023A /	PCDDs/PCDFs	EPA M 0023A / M 8290	ALTA	3	1	1	1	6
EPA M 0010	PAHs	CARB M 429	ALTA	3	1	0	1	5
EPA M 0010	SVOCs	EPA M 8270C	STL	3	1	0	1	5
EPA M 0011	Carbonyls	EPA M 8315A	ENTH	3	1	1	1	6
EPA M 29	Metals (b)	EPA M 6020 / 7470A	STL	3	1	1	1	6
EPA M 0061	Cr ⁺⁶	EPA M 7199	STL	3	1	1	1	6
EPA M 0030 (VOST)								
VOST Tube Pairs	POHC / PICs (c)	EPA M 5041A / 8260B	STL	18	6	3	4	31
VOST Tube Prep		EPA M 5041A	STL	45				45
VOST Condensate	POHC / PICs (c)	EPA M 8260B	STL	6	1	0	1	8
EPA M 3A	O ₂ and CO ₂	EPA M 3A (CEM)	ENSR	9	0	0	0	9
EPA M 25A	THC	EPA M 25A (CEM)	ENSR	9	0	0	0	9
Facility CEM	O ₂ & CO	Facility CEM QA Plan	Shell	9	0	0	0	9
<p>(a) ALTA = Alta Analytical Laboratories - El Dorado Hills, CA ENSR -- Field or ENSR Air Toxics Laboratory - Harvard, MA ENTH = Enthalpy Analytical, Inc. - Durham, NC STL = Severn Trent Laboratories - Knoxville, TN and West Sacramento, CA STL-P = Severn Trent Laboratories, Pleasanton, CA</p> <p>(b) Metals include : Sb, As, Ba, Be, Cd, Cr, Pb, Hg, Ag and TI (RCRA) + Al, Cu, Co, Mn, Ni, Se, V and Zn (Risk Assessment)</p> <p>(d) Volatile POHC is Chlorobenzene. Full method scan also to be performed during Condition 2.</p>								

Table 5-3 Sample Preservation and Holding Time Requirements

Stack Gas Samples ^(a)

Parameter	Matrix	Preservation	Holding Time
Volatile Organics (Method 0030)	Aqueous	Cool, 4°C	14 days
	Tenax and Tenax/Charcoal	Cool, <10°C	14 days
PCDDs/PCDFs/PAHs and Semi-Volatile Organics (Method 0023A/0010)	XAD Resin	Cool, 4°C	30 days (to extraction)
			45 days (extraction to analysis)
Carbonyls (Method 0011)	DNPH Reagent	Cool, 4°C	extracted and analyzed within 30 days
Chloride / Chlorine and Ammonia (Method 0050)	Aqueous	N/A	30 days
Metals (Methods 29 and 0061) (except Hg)	Aqueous	Cool, 4°C	6 months
	Solid / Filter	Cool, 4°C	6 months
Mercury (Method 29)	Aqueous	Cool, 4°C	28 days
	Solid/Filter	Cool, 4°C	28 days
(a) Holding times will be calculated from the day of sample collection.			

Waste Feed Samples

Parameter	Matrix	Preservation	Holding Time
Metals	Organic Liquid	Cool	6 months
Metals – Mercury	Organic Liquid	Cool	28 days
Semi-Volatile Organics	Organic Liquid	Cool	14 days (to extraction) 40 days (extraction to analysis)
Volatile Organics	Organic Liquid	Cool	14 days
Total Chlorides	Organic Liquid	Cool	30 days

Table 5-4 Summary of QA/QC Procedures for Chemical/Physical Properties in Waste Feed

Quality Parameter	Method Determination	Frequency	Target Criteria
Calibration	Initial analysis standards	Prior to sample analysis	Instrument dependant
	Continuing calibration standards	Before and after sample analysis; once every 20 samples	90%-110% of expected value
Interference check	Interference check sample	Before and after sample analysis	90%-110% of true value
Accuracy - calibration	Analysis of calibration check standard	After every calibration	90%-110% of expected value
Accuracy - spikes (chlorine)	Spike sample in accordance with laboratory SOP	Once every 20 samples	90% to 110% of spiked value
Precision	Duplicate preparation and analysis of at least one run's samples	Once every 20 samples	Range < 30% if sample result above lowest standard
Blank	Method blank carried through all sample preparation and analysis steps	Once every 20 samples	Below detection limit

Table 5-5 Summary of QA/QC Procedures for Metals in Waste Feed Samples

Quality Parameter	Method Determination	Frequency	Target Criteria
Calibration	Initial analysis of standards at different concentration levels	At least once before sample analysis	Instrument-dependent. Linear corr. coefficient of std. Data ≥ 0.995
	Continuing mid-range calibration standard	Before and after sample analysis	80% to 120% of expected value for CVAA. 90% to 110% of expected value for ICAP
Interference check	Interference check sample	Before and after ICAP analysis	80% to 120% of expected value
Accuracy – calibration	Analysis of calibration check standard	After every initial calibration	90% to 110% of expected value
Accuracy – spikes (pre-digestion)	Aliquot of one sample from a run spiked with analytes in accordance with laboratory SOP	One per sample matrix	70% to 130% recovery
Precision	Duplicate preparation and analysis of one sample from each matrix	One per sample matrix	Range < 35% if sample result above lowest standard
Blank	Method blank carried through all sample preparation and analysis steps	Once per sample batch	Below detection limit
CVAA = cold vapor atomic absorption ICAP = inductively coupled argon plasma			

Table 5-6 Summary of QA/QC Procedures for Organics in Waste Feed Samples

Quality Parameter	Method Determination	Frequency	Target Criteria
Blanks – verify no lab contamination and system control	Lab blanks	Daily, before analysis of samples and in-between high-level samples	Less than lowest standard
Initial calibration of GC/MS	5 standards bracketing expected level	Prior to sample analysis	Variability of average RRF less than or equal to 20% RSD
Calibration check standard	Mid-level standard different from initial calibration standards	After each standard preparation and initial calibration	Within continuing calibration criteria
Continuing calibration	Mid-level standard	Before and after sample analysis (every 10 samples for GC)	RRF within $\pm 15\%$ of initial calibration (GC) and RRF within $\pm 20\%$ of initial calibration (GC/MS)
Consistency in chromatography	Monitor internal standard retention time and area	Every sample, standard and blank	Retention time within ± 30 sec of last calibration check; area within -50% to $+ 100\%$ from last daily calibration check
Accuracy – spikes	One sample from each matrix spiked prior to preparation	One per sample matrix	50% to 130% recovery
Blanks	Method blank carried through all sample preparation steps	Once per sample batch	< 5% of sample levels
LCS	Spiked method blank	Once per sample batch	70% to 130% recovery
RSD = Relative Standard Deviation RRF = Relative Response Factor			

Table 5-7 QA Requirements for Metals in Stack Gas by ICP or ICP-MS

Quality Parameter	Method Determination	Frequency	Target Criteria
Calibration	Initial analysis of standards	Daily	Analysis of calibration check standard within 10% of true value
	Continuing mid-range calibration standard	At least once before and after sample analysis	90-110%
	Continuing calibration blank	With continuing calibration standard	Subject to interpretation
Accuracy - ICV	Analysis of calibration check standard	After every initial calibration	90% to 110% of true value
Accuracy - filters	Analysis of NIST standard reference filters or EPA audit filters, if provided	Once per test	70% to 130% of reference value
Accuracy	Post-digestion spikes	Once per test	70% to 130% recovery
Precision	Post-digestion spikes	Once per test	RPD < or = 35%
Blanks	Field Reagent Blanks and Method Blanks	One each per test	Evaluated on case by case basis
RPD = Relative Percent Difference ICAP = Inductively Coupled Argon Plasma ICP-MS = Inductively Coupled Plasma – Mass Spectrometry ICV = Initial Calibration Verification			

Table 5-8 Summary of QA/QC Procedures for Cr⁺⁶ in Stack Gas Samples

Quality Parameter	Method Determination	Frequency	Target Criteria
Calibration	Initial analysis of standards at multiple levels	At least once before and after sample analysis	Method-dependent. Linear correlation coefficient of standard data: >0.995
	Continuing mid-range calibration standard	Every 10 sample analyses	
Accuracy-calibration	Analysis of calibration check	After every initial calibration	90% to 110% of true value
Accuracy-spikes	Analysis of a blank sampling train spiked in accordance with laboratory SOP	Once per test	70% to 130% recovery
	Analysis of a laboratory spike at two to three times the detection limit	Once per test	70% to 130% recovery
Precision	Duplicate analysis of samples	All samples from test	< 25% RPD
Blanks	Field reagent blanks and Method blanks	One each per test	Evaluated on a case-by-case basis
RPD = relative percent difference			

Table 5-9 Summary of QA/QC Procedures for Aldehydes in Stack Gas Samples

Quality Parameter	Method Determination	Frequency	Target Criteria
Calibration – Linear	Initial 5-point calibration	Every 10 sample analyses	RSD \leq 20%
Calibration – Non-Linear	Initial 5-point calibration	Every 10 sample analyses	COD \geq 0.99
Accuracy-calibration	Analysis of calibration check	After every initial calibration	85% to 115% of true value
Accuracy	Analysis of Lab Control Samples (LCS) and Matrix Spikes	Once per sample batch	70% to 130% recovery
Precision	Duplicate analysis of samples	Once per sample batch	< 25% RPD
Blanks	Field reagent blanks and Method blanks	One each per test	Evaluated on a case-by-case basis
RSD = Relative Standard Deviation COD = Coefficient of Determination RPD = relative percent difference			

Table 5-10 QA Requirements for Chlorides in Stack Gas

Quality Parameter	Method Determination	Frequency	Target Criteria
Calibration (Qualitative)	Average retention time	Every calibration curve	Within retention time window of standards
Calibration (quantitative)	Initial calibration with a minimum of four standards	At least once before sample analysis	Linear correlation coefficient > 0.995
	Continuing calibration	Every 10 samples and at end of day	90% - 110% of theoretical concentration
Accuracy (calibration)	Laboratory control sample	After every initial calibration and before sample analysis	90% - 110% of true value
Accuracy (spikes)	Matrix spikes	Once per test	70% - 130% recovery
Precision	Duplicate analyses	All samples	RPD < or = 35%
Field Reagent Blanks	Collection of method-specified volumes of each reagent	Once per test	Less than 5% of sample levels
Blank	One method blank carried through sample preparation and analysis	Once per test	Less than 5% of sample levels
RPD = Relative Percent Difference			

Table 5-11 QA Objectives for VOST Analyses

Quality Parameter	Method Determination	Frequency	Target Criteria
Blanks – sample integrity and field contamination	Field blanks, 1 pair of traps	One pair per sampling day	Less than lowest standard
Blanks – verify no contamination from storage and/or shipment	Trip blanks, 1 pair of traps	One pair per shipment to lab	Less than lowest standard
Blanks – verify no lab contamination and system control	Lab blanks, 1 pair of traps	Daily, before analysis of samples and in-between high-level samples	Less than lowest standard, except common lab contaminants allowed at up to 5x reporting limit as per laboratory SOP
Initial calibration - GCMS	3-5 standards bracketing DRE level	Prior to sample analysis	Variability of average RRF \leq 20% RSD
Continuing calibration	Midlevel standard	Prior to sample analysis, then every 12 hr, or after sample set	RRF within \pm 25% of initial calibration (RRF)
Consistency in chromatography	Monitor internal standard; retention time and area	Every sample, standard and blank	Retention time within \pm 30 sec of last calibration check; area within 65% to 135% from last daily calibration check
Precision and accuracy	Replicate analysis of 3 traps spiked at the expected level of 99.99% DRE	Demonstrated prior to sample analysis	50% - 150% recovery
Continuing accuracy check	Surrogate spikes	Every sample	50% to 150% recovery
Verification of VOST system accuracy	Analysis of samples from EPA audit cylinder, if provided	Once per test	Within 50% - 150% of certified concentration
VOST condensate: precision and accuracy	Surrogate spikes	All condensate samples	50% to 150% recovery
Breakthrough determination	Separate analysis of front and back traps	At least first pair from each run Unnecessary for blanks	Quantity on TX/C must be $<$ 30% of amount on TX trap - does not apply when $<$ 75 ng on TX/C trap
RSD = Relative Standard Deviation RRF = Relative Response Factor			

Table 5-12 QA Objectives for PCDD/PCDF Analysis of Stack Gas Samples

Quality Parameter	Method Determination	Frequency	Target Criteria
Calibration	Five-level calibration curve; continuing calibration standard	At least once; continuing calibration check at beginning of each 12-hr shift	<u>Initial:</u> <=20% RSD for unlabeled standards <=30% RSD for internal standards S/N ratio >=2.5; Isotope ratios within control limits <u>Continuing:</u> <=20% of ICAL for 17 unlabelled stds <=30% of ICAL for internal standards S/N ratio >=2.5; Isotope ratios within control limits
Accuracy-calibration	Analysis of calibration check	After every initial calibration	80% - 120% of theoretical value
Accuracy-surrogates	Spiked into samples prior to sampling	Every sample	70% - 130% recovery
Accuracy-internal standards	Spiked into samples prior to extraction and analysis	Every sample	40%-135% recovery for all homologs
Accuracy – audit samples	Prepared and analyzed along with program samples, if provided	Presented by the regulatory agency	Determined by regulatory agency
Blanks	Method blank for each component	One per batch of samples	ND or <5% of field concentration
	Field reagent blanks	Once per test	Evaluated on a case-by-case basis
Mass Spectrometer Performance	Section 8.2.2 of Method 8290	At beginning of each 12-hr period	Static resolving power of 10,000 (10% valley definition)
Qualitative Identification	Retention Time and GC Column Performance	Every sample	Compliance with Section 8.2.1 of Method 8290
S/N = Signal to Noise Ratio RSD = Relative Standard Deviation			

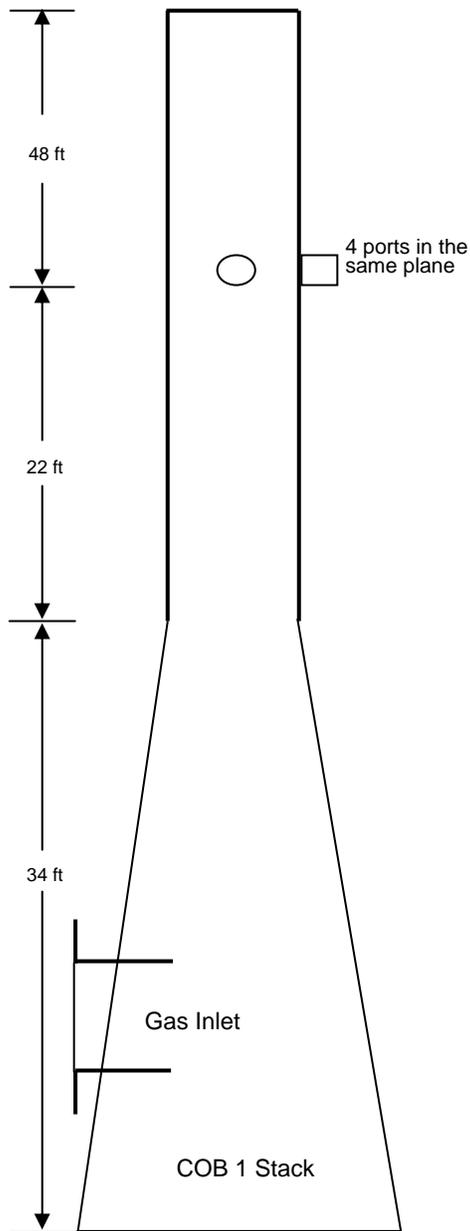
Table 5-13 QA Objectives for PAH Analysis of Stack Gas Samples

Quality Parameter	Method Determination	Frequency	Target Criteria
Calibration	Five-level calibration curve	Once before samples analyzed	<u>Initial:</u> <=30% RSD for unlabeled standards <=30% RSD for internal standards S/N ratio >=10
	Continuing calibration	Beginning and end of every 12-hour analysis shift	<u>Continuing:</u> <=30% RPD of ICAL for unlabeled stds <=30% RPD of ICAL for internal stds S/N ratio >=10 Internal standard retention times ± 30 sec of initial calibration mean All confirmation ions present
Accuracy-surrogates	Spiked into media before sampling	All samples	50% - 150% recovery
Accuracy-internal standards	Spiked into samples prior to extraction and analysis	Every sample	50% - 150% recovery
Accuracy-spikes	Laboratory control samples prepared by spiking XAD with independently prepared solution of analytes	Duplicate preparation and analysis for each set of 15 or less samples	S/N >10 for all analytes 50% - 150% recovery < 50% RPD
Mass Spectrometer Performance	Section 7.3.3 of CARB Method 429	At beginning and end of each 12-hour period	Static resolving power of 8,000 (10% valley definition)
Method Blank	Blank XAD extracted and analyzed with samples	Once for each set of 15 or fewer samples	Less than PQL or 5% of analyte concentration in field samples
RSD = Relative Standard Deviation; RRF = relative response factor RPD = Relative Percent Difference; PQL = practical quantitation limit			

Table 5-14 QA Objectives for SVOC Analysis of Stack Gas Samples

Quality Parameter	Method Determination	Frequency	Target Criteria
Calibration	Five-level calibration curve; continuing calibration standard	At least once; at the beginning of day; continuing calibration once every 12 hours and at end of day	<30% RSD of average RRF; within 30% of average RRF from calibration
Accuracy (calibration)	Analysis of calibration check	After every initial calibration	70% - 130% of theoretical value
Accuracy (surrogates)	Isotopically-labeled compound spiked into samples prior to sampling and/or analysis	Every SVOC sample	Nitrobenzene d5 - 35-122% 2-Fluorobiphenyl - 34-115% Terphenyl d14 - 28-132% Phenol d5 - 15-124% 2-Fluorophenol - 19-100% 2,4,6-Tribromophenol - 33-130%
Accuracy (spike)	Representative SVOCs spiked onto blank XAD trap	Once per Trial Burn	Phenol - 26-90% 2-Chlorophenol - 25-102% N-Nitrosodipropylamine 41-126% 4-Cl-3-methylphenol 26-103% Acenaphthene 31-137% 4-Nitrophenol 11-114% 2,4-Dinitrotoluene 28-89% Pyrene 35-142%
Precision (surrogates)	Same as for accuracy - surrogates pool results for each SVOC component	Every SVOC sample	<40% RPD of surrogate recovery. If more than 3 determinations - RSD <35%
Blanks	Method blank for each SVOC	Once per batch of samples	Blank value <2 x DL. If greater, DL is changed to 1.5x blank level
	Field reagent blank	Once per test	Evaluated on a case-by-case basis
RSD = Relative Standard Deviation RRF = Relative Response Factor RPD = Relative Percent Difference			

Figure 5-1 Stack Sampling Traverse Point Locations



KEY STACK PARAMETERS		
Parameter	Units	Value
Temp.	°F	600
Moisture	% v/v	15.0
O ₂	% v/v	5.0
CO ₂	% v/v	12.0
Flow Rate	dscfm	127,700
Vel. Press.	in. w.c.	1.12
Static P.	in. w.c.	-1.2

TRAVERSE POINT DATA		
Pt. No.	% of Diam.	Dist. Incl. Port (in.)
1	2.1%	6.0
2	6.7%	10.4
3	11.8%	15.3
4	17.7%	21.0
5	25.0%	28.0
6	35.6%	38.2
7	64.4%	65.8
8	75.0%	76.0
9	82.3%	83.0
10	88.2%	88.7
11	93.3%	93.6
12	97.9%	98.0

Stack ID = **96** inches
 Port + Wall = **4.0** inches

APPENDIX A
DETAILED WASTE ANALYTICAL DATA

APPENDIX B
PROJECTED MDL EMISSION RATES

APPENDIX C
TRIAL BURN FIELD DATA SHEETS

APPENDIX D

ISOKINETIC SAMPLING TRAIN SETUP AND RECOVERY SCHEMATICS

APPENDIX E

TARGET ORGANICS AND INORGANICS FOR THE TRIAL BURN

Shell Martinez- Trial Burn Plan

Disclaimer- The attachments are not posted at this time due to their large file size. These are available through the DTSC project manager.