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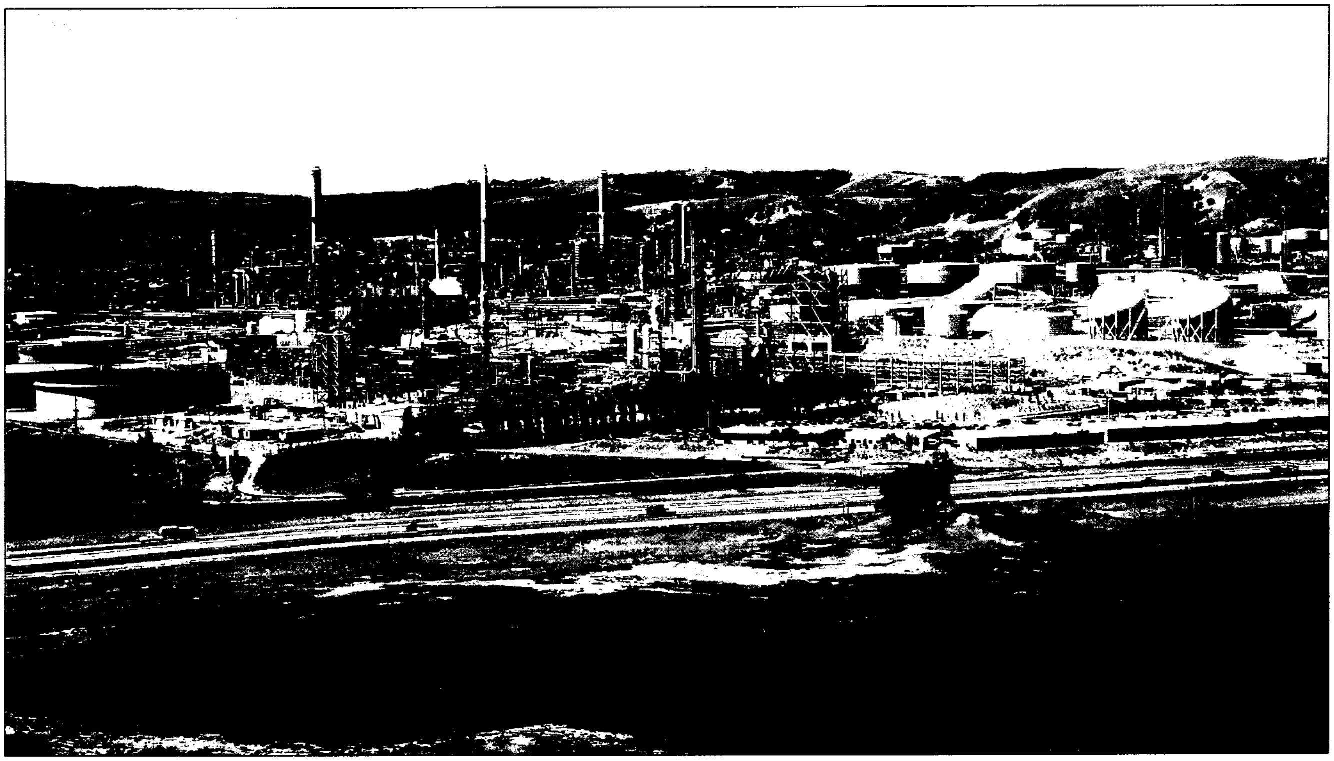
Prepared for:
Shell Oil Products US
Shell Martinez Refinery
3485 Pacheco Boulevard
Martinez, CA 94553



Trial Burn Report for CO Boiler No. 2 Condition 3 Retest

Final Report

ENSR Corporation
March 2007
Document No.: 05975-140-640A

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Reviewed By: Michael Dudasko

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LIST OF ACRONYMS / DEFINITIONS

Acronym	Definition
acfm	Actual cubic feet per minute
aL	Actual liters
ASTM	American Society for Testing and Materials
BAAQMD	Bay Area Air Quality Management District
CARB	California Air Resources Board
CEMS	Continuous Emissions Monitoring System
CFR	Code of Federal Regulations
CO	Carbon Monoxide
CO_2	Carbon Dioxide
COB-2	CO Boiler No. 2
COC	Chain of Custody
DAS	Data Acquisition System
DI	Deionized (water)
DOT	Department of Transportation (U.S.)
DRE	Destruction and Removal Efficiency
dscfm	Dry standard cubic feet per minute
dsL	Dry standard liters
DTSC	Department of Toxic Substances Control (California)
EPA	Environmental Protection Agency (U.S.)
ESP	Electrostatic Precipitator
gpm	Gallons per Minute
GC / MS	Gas Chromatography / Mass Spectrometry
gr/dscf	Grains per dry standard cubic foot
HL	Herguth Laboratories
HRA	Hourly Rolling Average
INST	Instantaneous
in. w.c.	Inches Water Column
lb/hr	Pounds per hour
LCS / LCSD	Laboratory Control Sample / Laboratory Control Sample Duplicate
Lpm	Liters per Minute
MACT	Maximum Achievable Control Technology
MCB	Monochlorobenzene
MDL	Method Detection Limit
ND	Not detected or non-detect
NELAC	National Environmental Laboratory Accreditation Conference
NO_x	Oxides of Nitrogen
OMA	One Minute Average

Acronym	Definition
O_2	Oxygen
PCDDs/PCDFs	Polychlorinated dibenzo-p-dioxins/polychlorinated dibenzofurans
POHC	Principal Organic Hazardous Constituent
ppm	parts per million
QA/QC	Quality Assurance/Quality Control
RCRA	Resource Conservation and Recovery Act
RL	Reporting Limit
RPD	Relative Percent Difference
SMR	Shell Martinez Refinery
SOP	Standard Operating Procedure
TBP	Trial Burn Plan
TEQ	Toxic Equivalency
THC	Total Hydrocarbons
TX / TX-C	Tenax / Tenax-Charcoal
VOST	Volatile Organic Sampling Train

1.0 Condition 3 Retest Emissions Summary

Shell Oil Products US (Shell) operates the Shell Martinez Refinery (SMR) located in Martinez, California. SMR conducted RCRA Trial Burn testing on one of its carbon monoxide (CO) boilers during the weeks of June 5 and June 12, 2006. Trial burn testing was performed on CO Boiler No. 2 (COB-2) in response to a request from the California Department of Toxic Substances Control (DTSC). The test was conducted in accordance with an approved Trial Burn Plan (TBP) and under full oversight of the DTSC. In addition, the Bay Area Air Quality Management District (BAAQMD) was apprised of the tests.

The June 2006 trial burn consisted of three test conditions and started on June 6. The first test condition addressed settings on the electrostatic precipitator and Test Condition 2 collected stack samples for chemical analysis to provide input to a Health Risk Assessment. Test Condition 3, the destruction and removal efficiency (DRE) test, was performed on June 13, 2006. The summary of the trial burn is contained in the Trial Burn Report for CO Boiler No. 2 (ENSR, September 2006). The DRE test conducted on June 13, 2006 did not meet trial burn objectives as the performance standard of 99.99% DRE was met for only one of three runs. All other test parameters for the June trial burn complied with both current permit limits and future MACT standards. The causes for not achieving the DRE standard were carefully scrutinized and after detailed investigation, a retest was scheduled and successfully executed. The Condition 3 retest was successfully performed during the week of December 11-15, 2006, also under the oversight of DTSC. Two operating conditions (designated as Conditions 3A and 3B) were evaluated during the December retest. Planned operations for the DRE retest were outlined in the "Trial Burn DRE Retest Plan for CO Boiler No. 2 – Revision 1" submitted to DTSC in November 2006.

This report documents all data and information associated with the successful DRE retest and serves as an addendum to the original trial burn report which was issued in September 2006. A summary of DRE results is provided in **Table 1-1**. Both test conditions fully complied with the DRE requirement of 99.99%. In addition, **Table 1-2** depicts trial burn results compared to the future MACT standards for this source category that were promulgated by the United States Environmental Protection Agency (US EPA) on October 12, 2005.

Table 1-1 Condition 3 Retest Results for DRE Performance

Emission Parameter and Sampling Method	Units	Condition 3A Average	Condition 3B Average	Current Permit Limit
POHC DRE (Method 0030) --				
Monochlorobenzene	%	99.9967	99.9995	> 99.99
Facility CEMS --				
Carbon Monoxide	ppm	18.7	17.1	100

Note: Monochlorobenzene (MCB) was used as the principal organic hazardous constituent (POHC) during the Condition 3 retest, as done during the original June 2006 trial burn.

Table 1-2 Trial Burn Emissions Compared to Future MACT Standards

Emission Parameter	Units	Test Averages June 2006	Test Averages December 2006	Future MACT Limit [a]
Destruction and Removal Efficiency				
Total Hydrocarbons @ 7% O_2	ppm	< 1.0	< 1.0	10
Monochlorobenzene	%	99.9638	99.9981	> 99.99
PCDDs/PCDFs				
Toxic Equivalents (TEQs)	ng/m³	1.3E-05	NT	0.40
Particulate Matter and Halides --				
Particulate Matter	gr/dscf	0.0046	NT	0.035
Hydrogen Chloride & Chlorine	ppm	0.83	NT	31
Metals --				
Mercury	µg/m³	2.92	NT	19
Cadmium, Lead & Selenium	µg/m³	40.3	NT	150
Arsenic, Beryllium, Chromium, Antimony, Cobalt, Manganese & Nickel	µg/m³	4.59	NT	370
Facility CEMS --				
Carbon Monoxide @ 7% O_2	ppm	13.4	17.9	100

[a] Final MACT standards for liquid fuel-fired boilers were published in the Federal Register on October 12, 2005. See 70 FR 59402, Section 63.1217.

Note: All emission data are corrected to 7% oxygen.

NT = Not Tested

2.0 Introduction

2.1 Project Background and Schedule

Shell operates three CO boilers that burn RCRA-listed hazardous waste at its refinery in Martinez, California. These boilers are identified as COB-1, COB-2 and COB-3. Shell responded to DTSC requests requiring the submission of an updated RCRA Part B Application, including a TBP. The Trial Burn test was conducted in accordance with the approved TBP, Revision 2, dated November 2005 and subsequent page revisions in January 2006. The Condition 3 retest was also conducted in accordance with the approved TBP and the DRE Retest Plan submitted in November 2006.

The Condition 3 retest was performed during the week of December 11-15, 2006. Two distinct operating conditions (triplicate runs per condition) were evaluated:

- Condition 3A was completed on December 13 and represented operating conditions similar to the Condition 3 test performed on June 13, 2006; and
- Condition 3B was completed on December 14 and represented slightly more conservative operating parameters than Condition 3A.

Tables 2-1 and 2-2 depict individual and overall run times associated with the volatile organic sampling train (VOST). Individual run times are those for each unique set of VOST tubes while the "overall" run period is defined as the duration from the start of the first VOST tube set to the end of the last (fourth) VOST tube set. These overall run periods were used to generate the minimum, maximum and average values for the process data collected by Shell and to also provide an overall run average for the spiked organic constituent (monochlorobenzene or MCB).

2.2 Investigation of Causes for the June 2006 DRE Failure

During the weeks and months following the June 2006 trial burn, ENSR and Shell reviewed the reasons for not achieving 99.99% DRE in all three runs of Test Condition 3. The required DRE had previously been successfully demonstrated in 1993. ENSR and Shell first worked with the analytical laboratory and the stack test subcontractor (the Avogadro Group) to verify the accuracy of the preliminary findings.

After verification that the reported results were indeed correct, ENSR and Shell reviewed operating conditions, waste feed analyses and other process data and also reviewed records of the 1993 test. A series of engineering tests were also undertaken to better understand the mechanics of boiler operation and the effects of several key parameters upon boiler performance and destruction capabilities of organic hazardous constituents using monochlorobenzene (MCB) as the indicator compound. (MCB was also used as the principle organic hazardous constituent (POHC) in the June 2006 DRE tests). The engineering evaluations included spiking of MCB into the waste feed to COB 2 and measuring the effects by using a field gas chromatograph / mass spectrometer (GC/MS) operated by Field Portable Analytical Inc. of Orangevale, California. Through the use of semi-continuous online GC/MS, a total of 24 preliminary engineering tests were conducted over the October 31 – November 2 time period and also during the two days (December 11-12) prior to the formal Condition 3 retest. The use of online GC/MS provided instantaneous emission data and a direct understanding of the variables that had the biggest effect on DRE performance. The conditions of the June 2006 DRE Test were also replicated. In addition, a range of values associated with the following principal boiler operating variables were investigated over the course of the engineering tests:

- waste feed rate;
- atomization pressure;
- firebox temperature; and
- MCB injection location and feed rate.

The results of the engineering tests demonstrated achievement of the 99.99% DRE over a broad range of conditions for the primary variables. Following a review of the data, potential causes for DRE failure in June 2006 were believed to be the following:

1. The POHC injection point selected for the June trial burn was downstream of a control valve to allow the shortest path to the CO boiler waste feed burners. However, this may have inadvertently resulted in a situation where the MCB was not properly mixed with the feed by the time it was sent to the burners in the CO boiler. It has also been theorized that this prior injection location could have resulted in an uneven distribution of MCB going to each of the two burner guns. The MCB injection location used for the December DRE retest was upstream of the control valve to promote good mixing.

2. The waste fed to the boiler during Condition 3 averaged 99.6% water versus the lower values of 96.6% observed during Condition 1 and 96.5% observed during Condition 2. It was subsequently determined that some temporary equipment placed in service in the Effluent Treatment Plant during the Condition 3 test program may have caused the higher observed water content of the waste. This was not known at the time of the DRE test.

The December retest achieved DREs of 99.9967% and 99.9995% and therefore demonstrated full compliance, even one with a higher feed rate than the 1993 test. This indicates that the June 2006 test was anomalous and the CO Boiler can reliably achieve the minimum required 99.99% DRE.

2.3 Report Organization

This report is organized in a manner that should facilitate review of all results and supporting documentation. Section 1.0 summarized emission results for key parameters and Section 2.0 provides a brief narrative concerning the project background, schedule and scope. Section 3.0 provides detailed information on process operating conditions and facility monitoring data and summarizes expectations regarding future regulatory-imposed permit limitations based on test results. Section 4.0 presents an overall summary of the sampling methodologies employed while Section 5.0 presents detailed results for the retest program. Finally, Section 6.0 outlines applicable QA/QC measures implemented during both the field and analytical portions of the program to ensure valid data. Appendices provide all pertinent supporting documentation including:

- Facility process monitoring data (**Appendix A**);
- The report on field sampling activities prepared by The Avogadro Group, LLC (**Appendix B**);
- The POHC spiking report prepared by Triad Chemicals, LLC. (**Appendix C**);
- Field sampling data sheets and related documentation provided by ENSR (**Appendix D**); and
- Analytical data reports provided by each subcontractor laboratory (**Appendix E**).

Table 2-1 Individual VOST Sample Train Run Times

Run #	Date	VOST - Condition 3A	
		Start	Stop
1A	13-Dec-06	09:55	10:15
1B	13-Dec-06	10:28	10:48
1C	13-Dec-06	11:01	11:21
1D	13-Dec-06	11:29	11:49
2A	13-Dec-06	12:29	12:49
2B	13-Dec-06	13:00	13:20
2C	13-Dec-06	13:33	13:53
2D	13-Dec-06	14:11	14:31
3A	13-Dec-06	14:52	15:12
3B	13-Dec-06	15:20	15:40
3C	13-Dec-06	15:49	16:09
3D	13-Dec-06	16:17	16:37
Run #	Date	VOST - Condition 3B	
		Start	Stop
1A	14-Dec-06	09:00	09:20
1B	14-Dec-06	09:27	09:47
1C	14-Dec-06	09:55	10:15
1D	14-Dec-06	10:24	10:44
2A	14-Dec-06	11:00	11:20
2B	14-Dec-06	11:30	11:50
2C	14-Dec-06	11:57	12:17
2D	14-Dec-06	12:25	12:45
3A	14-Dec-06	13:07	13:27
3B	14-Dec-06	13:40	14:00
3C	14-Dec-06	14:18	14:38
3D	14-Dec-06	14:54	15:14

Table 2-2 Overall Condition 3 Retest Run Times

Run #	Date	Overall	
		Start	Stop
C3A-R1	13-Dec-06	09:55	11:49
C3A-R2	13-Dec-06	12:29	14:31
C3A-R3	13-Dec-06	14:52	16:37

Test Condition 3B

Run #	Date	Overall	
		Start	Stop
C3B-R1	14-Dec-06	09:00	10:44
C3B-R2	14-Dec-06	11:00	12:45
C3B-R3	14-Dec-06	13:07	15:14

3.0 Process Operating Conditions and Compliance Strategy

3.1 Overview of Test Conditions

The two operating conditions evaluated during the DRE retest program consisted of two low temperature test modes (Conditions 3A and 3B). The specific objectives for each of these conditions were:

Low Temperature Mode A (Test Condition 3A) --

Test Condition 3A was designed for boiler operation at a minimum firebox (combustion chamber) temperature, maximum feed rates, minimum waste feed atomization pressure and high firebox pressure. Under this minimum temperature condition, DRE testing would be performed and emission measurements for total hydrocarbons (THC) would also be conducted. Condition 3A 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 to achieve the desired low firebox temperature. Condition 3A was expected to be similar to Condition 3 of the June 2006 trial burn tests.

Low Temperature Mode B (Test Condition 3B) --

Test Condition 3B was designed for a more conservative approach than Test Condition 3A to establish new permit limits for minimum firebox temperature, maximum firebox pressure, maximum waste feed rates, and minimum waste feed atomization pressure. Successful results from Condition 3B would be used to establish CO Boiler permit condition limits should Condition 3A not demonstrate 99.99% DRE over all three runs.

3.2 Facility Monitoring Data

Throughout the DRE retest program, detailed process information was collected continuously by the facility's process control computers and data acquisition system (DAS). **Tables 3-1 and 3-2** provide summaries of process data including minimum, maximum and average values for key process variables recorded during both test conditions. Specific parameters reported in Tables 3-1 and 3-2 including the time basis for the measurement are outlined below. Supporting documentation including all one-minute averages (OMAs) throughout each trial burn run period is provided in **Appendix A**. In general, target operating conditions specified in the DRE retest plan were achieved.

Parameter	Tag ID #	Units	Measurement Basis (a)		
			Instant.	OMA	HRA
Waste Feed Rate	F2672AVG	gpm			X
Waste Feed Atomization Pressure	9PDI1565 9PDI1566	psig	X		
Firebox Temperature	T3182AVG	°F			X
Firebox Pressure	P1725AVG	in. w.c.			X
ESP Power	9EI2673	KVA	X		
Stack Gas Flowrate	9FI1596	in. w.c.	X		
Stack Gas Flowrate (calculated)		scfm	X		
CO Concentration at 7% Oxygen	A2642AVG	ppm			X
Oxygen Concentration	9AI2611	%		X	

3.3 Data-in-lieu-of Testing

For this program, Shell conducted trial burn testing on one unit (COB-2) and is using data-in-lieu-of to establish limits on the other two identically designed units (COB-1 and COB-3).

3.4 Anticipated Permit Conditions

On the basis of the original trial burn testing completed on COB-2 in June 2006 and the successful retesting performed in December 2006, Shell would expect permit limits to be established as delineated in **Table 3-3**.

Table 3-1 Process Operating Data Summary – DRE Retest Condition 3A

		C3A-R1			C3A-R2		
	Date	13-Dec-06			13-Dec-06		
	Start	09:55			12:29		
	Stop	11:49			14:31		
Operating Parameters (a)	**Units**	Min.	Max.	Avg.	Min.	Max.	Avg.
Process Parameters --							
Waste Feed Rate (HRA)	gpm	12.00	12.00	12.00	12.00	12.10	12.10
Waste Feed Atom. Press. (INST)	psig	50.0	50.3	50.1	50.0	50.4	50.2
Firebox Temperature (HRA)	°F	1,603	1,625	1,614	1,600	1,622	1,613
Firebox Pressure (HRA)	in. w.c.	5.46	5.93	5.76	5.46	6.05	5.74
ESP Power (INST)	kVa	111.6	167.7	153.1	128.4	167.5	154.6
Stack Gas Flowrate (INST)	in. w.c.	1.40	1.69	1.56	1.38	1.67	1.54
Stack Gas Flowrate (calculated)	wet scfm	103,830	113,970	109,330	103,760	114,520	108,470
CEM Parameters --							
CO Conc. @ 7% O_2 (HRA)	ppm	19.8	20.8	20.2	17.7	19.7	19.0
O_2 Concentration (OMA)	%	2.94	3.27	3.08	2.81	3.46	3.11

		C3A-R3			RCRA Trial Burn December 13, 2006 Condition 3A Averages		
	Date	13-Dec-06					
	Start	14:52					
	Stop	16:37					
Operating Parameters (a)	**Units**	Min.	Max.	Avg.	**MIN**	**MAX**	**AVG**
Process Parameters --							
Waste Feed Rate (HRA)	gpm	12.00	12.20	12.10	**12.00**	**12.10**	**12.07**
Waste Feed Atom. Press. (INST)	psig	50.1	50.4	50.2	**50.0**	**50.4**	**50.2**
Firebox Temperature (HRA)	°F	1,593	1,627	1,613	**1,599**	**1,625**	**1,613**
Firebox Pressure (HRA)	in. w.c.	5.46	6.08	5.78	**5.46**	**6.02**	**5.76**
ESP Power (INST)	kVa	135.0	166.2	157.0	**125.0**	**167.1**	**154.9**
Stack Gas Flowrate (INST)	in. w.c.	1.38	1.68	1.54	**1.39**	**1.68**	**1.55**
Stack Gas Flowrate (calculated)	wet scfm	103,160	114,040	108,500	**103,583**	**114,177**	**108,767**
CEM Parameters --							
CO Conc. @ 7% O_2 (HRA)	ppm	16.7	17.7	17.0	**18.1**	**19.4**	**18.7**
O_2 Concentration (OMA)	%	2.94	3.48	3.24	**2.90**	**3.40**	**3.14**

(a) HRA = Hourly Rolling Average INST = Instantaneous OMA = one-minute average

Table 3-2 Process Operating Data Summary – DRE Retest Condition 3B

Operating Parameters (a)		C3B-R1			C3B-R2		
	Date	14-Dec-06			14-Dec-06		
	Start	09:00			11:00		
	Stop	10:44			12:45		
	Units	Min.	Max.	Avg.	Min.	Max.	Avg.
Process Parameters --							
Waste Feed Rate (HRA)	gpm	9.99	10.16	10.08	9.99	10.01	10.00
Waste Feed Atom. Press. (INST)	psig	60.0	60.8	60.3	60.0	60.7	60.3
Firebox Temperature (HRA)	°F	1,627	1,652	1,639	1,629	1,651	1,640
Firebox Pressure (HRA)	in. w.c.	5.71	6.04	5.87	5.71	6.09	5.91
ESP Power (INST)	kVa	105.8	159.7	143.1	129.7	166.0	152.8
Stack Gas Flowrate (INST)	in. w.c.	1.47	1.75	1.63	1.47	1.77	1.65
Stack Gas Flowrate (calculated)	scfm	105,540	116,420	111,530	106,480	118,030	112,340
CEM Parameters --							
CO Conc. @ 7% O_2 (HRA)	ppm	13.4	15.8	14.8	16.4	19.4	18.4
O_2 Concentration (OMA)	%	3.29	3.61	3.48	3.36	3.72	3.54
		C3B-R3			**RCRA Trial Burn December 14, 2006 Condition 3B Averages**		
	Date	14-Dec-06					
	Start	13:07					
	Stop	15:14					
Operating Parameters (a)	**Units**	Min.	Max.	Avg.	**MIN**	**MAX**	**AVG**
Process Parameters --							
Waste Feed Rate (HRA)	gpm	9.99	10.01	10.00	**9.99**	**10.06**	**10.03**
Waste Feed Atom. Press. (INST)	psig	59.4	60.7	60.3	**59.8**	**60.7**	**60.3**
Firebox Temperature (HRA)	°F	1,627	1,655	1,640	**1,628**	**1,653**	**1,640**
Firebox Pressure (HRA)	in. w.c.	5.71	6.21	5.96	**5.71**	**6.11**	**5.91**
ESP Power (INST)	kVa	120.2	165.4	148.8	**118.6**	**163.7**	**148.2**
Stack Gas Flowrate (INST)	in. w.c.	1.51	1.84	1.66	**1.48**	**1.79**	**1.65**
Stack Gas Flowrate (calculated)	scfm	106,520	117,340	112,560	**106,180**	**117,263**	**112,143**
CEM Parameters --							
CO Conc. @ 7% O_2 (HRA)	ppm	14.0	22.4	18.2	**14.6**	**19.2**	**17.1**
O_2 Concentration (OMA)	%	3.32	3.90	3.62	**3.32**	**3.74**	**3.55**

(a) HRA = Hourly Rolling Average INST = Instantaneous OMA = one-minute average

Table 3-3 Anticipated Permit Conditions

Process Parameter	Units	Meas. Basis **(a)**	Value From? **(b)**	Expected Limit
Maximum Waste Feed Rate to each CO Boiler (DNF Solids + Biosolids + MCB spike)	gpm	HRA	C3A	12.24
Maximum Total DNF Solids (RCRA Waste) to all 3 CO Boilers	ton/yr	HRA	Current Limit	28,000
Maximum Total Waste Feed Rate to all 3 CO Boilers (DNF Solids + Biosolids)	gpm	HRA	C3A	36.71
Minimum Waste Feed Atomization Pressure **(c)**	psig	INST	C3A	50.0
Minimum Firebox Temperature	°F	HRA	C3A	1,599
Maximum Firebox Pressure	in. w.c.	HRA	C3B	6.1
Minimum ESP Power	kVa	INST	C1	31.2
Maximum Stack Gas Flowrate .	scfm	INST	Prior Trial Burn	154,400
CO Conc. @ 7% O_2	ppm	HRA	Regulation	100

(a) HRA = Hourly Rolling Average INST = Instantaneous OMA = one-minute average

(b) C1 = Test Condition 1 (June 6, 2006); C3A = Test Condition 3A (December 13, 2006);
C3B = Test Condition 3B (December 14, 2006)

(c) Defined as the differential fluid pressure between atomizing fluid and waste feed.

Note 1: The waste feed rate includes the contribution from the MCB added (0.14 gpm)

4.0 Sampling and Analytical Program Overview

This section provides a brief overview of the methods and procedures followed for the field test program. A complete and more detailed summary of the sampling and analytical methodologies employed can be found in Sections 5.4 and 5.6 of the approved TBP.

The DRE retest program was conducted in December 2006 and was implemented by a diverse team of experienced project managers and technical specialists from SMR, ENSR and subcontractors. Key project participants and associated responsibilities were as follows:

- Steven Overman – Shell Senior Staff Engineer and overall RCRA permit renewal and trial burn coordinator
- Charles Herich – Shell Operations Support Engineer for Utilities and CO Boilers, coordinator of operational targets and process data collection
- Fred Ferrante and Juan Echeverria – Shell Shift Team Leaders and coordinator of CO Boiler operations, waste feed sampling and POHC spiking
- Joe Hornsby – Shell Operations Specialist for Utilities and CO Boiler operations
- Tony Cofield – Shell Operations Maintenance Coordinator, coordinator of CO Boiler maintenance and the installation of temporary facilities for the trial burn
- Ray Fong – Shell Operations Support Engineer for the Effluent Treatment Plant (ETP) and coordinator of ETP operational targets
- John Aimar – Shell Operations Specialist for the EFT, wharf and asphalt plant and coordinator of ETP and T12038 operations
- Eben Demong – Shell Control Systems Engineer and coordinator of process control systems and data collection
- Mike Dudasko – ENSR program manger
- Doug Roeck – ENSR field test coordinator and task manager for TBP development and final data reporting
- Shawn Nelezen – Field sampling test team leader for the Avogadro Group, LLC
- Dan Schenk – Field Portable Analytical coordinator for continuous on-line GC/MS analysis during preliminary engineering test programs
- Marty Friedman – POHC spiking team leader for Triad Chemicals, LLC

4.1 Waste Feed Stream

Throughout the test program, samples of the liquid waste feed stream were collected periodically and composited over the course of each run. Samples were collected in 500-mL sample bottles and a field data sheet was completed denoting the times that these samples were taken. The waste feed samples collected were submitted to Herguth Laboratories (HL) in Vallejo, CA for physical parameters (ash, total chlorides, density, moisture and heat content). The following analytical methods were used: HL Methods 0808-1.6 / 1151 (total chlorides), ASTM D 4052 (density), ASTM D 240 (heat content) and thermal gravimetric analysis (TGA) for ash and moisture determination.

4.2 Spiking Material

The MCB material provided by Triad was not sampled during the program as it was a pure grade product. The supplier of the MCB provided a certificate of analysis which documented the product purity to be 99.9944%. The feed rates reported by Triad accounted for this product purity. The target feed rate for the MCB was 75.0 lb/hr during Condition 3A and 150 lb/hr during Condition 3B. These spiking rates were achieved with excellent accuracy throughout each test. The full report submitted by Triad can be found in Appendix C.

4.3 Stack Gas

The following sections provide brief overviews of the sampling methodologies employed for all target parameters. Except where noted otherwise, all methods are from SW-846, 3rd edition, final (promulgated) Update III. All samples were collected from the single stack sampling platform available on COB-2. All stack sampling was performed by Avogadro and their full field test report can be found in **Appendix B**.

4.3.1 Carbon Dioxide, Carbon Monoxide, Oxygen and Total Hydrocarbons

During all sampling runs, Avogadro continuously collected and analyzed samples of stack gas for oxygen (O_2), carbon dioxide (CO_2) and total hydrocarbons (THC). The O_2 and CO_2 data were used in the calculation of stack gas molecular weight. EPA Reference Method 3A (40 CFR Part 60, Appendix A) was used for the analytical procedure (continuous emission monitor). EPA Reference Method 25A was used for the THC determination. In addition, SMR continuously measured data for CO corrected to 7% oxygen during all runs with the facility's permanently installed CEMS.

4.3.2 Stack Gas Velocity and Moisture Content

Because calculation of POHC DRE requires a value for stack gas flowrate and because no other isokinetic sampling trains were being used during the Condition 3 retest, separate flow measurements were performed. Volumetric flowrates were made using EPA Reference Methods 1 and 2F. Stack gas moisture determination was made using EPA Method 4.

Method 2F is applicable for the determination of yaw angle, pitch angle, axial velocity and the volumetric flow rate of a gas stream in a stack or duct using a three-dimensional (3–D) probe. This method determines the yaw angle directly by rotating the probe to null the pressure across a pair of symmetrically placed ports on the probe head. The pitch angle is calculated using probe-specific calibration curves. From these values and a determination of the stack gas density, the average axial velocity of the stack gas is calculated. The average gas volumetric flow rate in the stack or duct is then determined from the average axial velocity.

Method 4 involves the collection of a gas sample at a constant rate from the source; moisture is removed from the sample stream and then determined either volumetrically or gravimetrically.

4.3.3 POHC DRE

EPA Method 0030 was followed as written without modification during both Conditions 3A and 3B to determine stack gas concentrations of MCB. The VOST methodology was used to determine emission levels of MCB for assessment of POHC DRE. During each run, four (4) pairs of VOST tubes were collected, each at a sampling rate of 1.0 liter per minute (Lpm) over a 20-minute period, resulting in a sample volume of approximately 20 liters per pair. Three of the four pairs from each run (a, b and d) were designated for analysis. All VOST tubes from each test run were analyzed individually to provide an assessment of compound breakthrough. A single condensate sample representative of each four-run set was also collected, but because the amount of collected water was so small (< 5 mL over each 4 tube set), these samples were not submitted for analysis. Samples were submitted to Air Toxics Ltd. (Folsom, CA) for analysis by EPA Method 5041A (VOST tubes). VOST blanks collected included field blanks and trip blanks.

5.0 DRE Retest Trial Burn Results

This section presents all sampling and analytical results for the trial burn associated with the DRE retest conducted on COB-2. All data presented are judged to be completely acceptable based on a thorough data review and comparison with documented QA protocols. All pertinent QA/QC data and related discussions are presented subsequently in Section 6.0. The field sampling report prepared by The Avogadro Group, LLC is provided in **Appendix B**. Additional field data sheets and other related field documentation coordinated by ENSR are found in **Appendix D**. Analytical data reports provided by each of the subcontractor laboratories for all field sample analyses are located in **Appendix E**.

5.1 Waste Feed Stream

For the DRE retest program, the waste feed material fed to the combustor during each test condition was analyzed for physical parameters only. Results are presented in **Table 5-1**. The samples were allowed to settle and separate into its natural phases. The Condition 3A samples settled into 2 phases and the Condition 3B samples settled into 3 phases. The density of all phases was close to that of water. The water content of the waste material ranged from about 74 – 83% and the ash content ranged from about 9 – 19%.

5.2 Spiking Material

The spiking of MCB during the Condition 3 DRE retest was accomplished without incident and at rates at or near the target levels of 75.0 lb/hr (Condition 3A) and 150 lb/hr (Condition 3B). The full report prepared by Triad Chemicals, LLC is presented in **Appendix C.**

5.3 Stack Gas Measurements

5.3.1 Oxygen, Carbon Dioxide and Total Hydrocarbons

Continuous measurement of fixed gases (O_2 and CO_2) and THC was performed throughout each test run. Results are summarized below:

Run No.	O_2	CO_2	THC
C3A-R1	3.0%	14.8%	< 2 ppm
C3A-R2	3.0%	14.7%	< 2 ppm
C3A-R3	3.1%	14.6%	< 2 ppm
C3B-R1	3.4%	14.1%	< 2 ppm
C3B-R2	3.5%	13.9%	< 2 ppm
C3B-R3	3.5%	13.9%	< 2 ppm

5.3.2 Stack Gas Flowrate

Measurements for stack gas flowrate and moisture content were performed concurrently with all VOST runs to allow calculation of the MCB emission rate. EPA Methods 2F (velocity) and 4 (moisture) were used in this determination. A summary of results is presented in **Table 5-2**.

5.3.3 POHC DRE

The VOST methodology was used during the Condition 3 retest to determine the emission rate for MCB to allow calculation of the DRE for this compound. A summary of sampling parameters for all VOST runs is shown in **Table 5-3 and 5-4**. Emission results and DRE calculations for both conditions evaluated are shown in **Tables 5-5 and 5-6**.

Excellent results were obtained for both test conditions. During Condition 3A, the overall average DRE was 99.9967%. During Condition 3B, the overall average DRE was 99.9995%.

Table 5-1 Waste Stream Analytical Results for Physical Parameters

Analytical Parameters	Units	Test Condition 3A			
		C3A-R1	C3A-R2	C3A-R3	Avg.
Total Chlorides	mg/kg	278	195	201	**225**
Ash Content	%	12.8	9.2	18.5	**13.5**
Heat Content	Btu/lb	167	190	161	**173**
Water Content	%	78.9	82.6	73.5	**78.3**
Density	g/cc	0.9889	0.9843	0.9898	**0.9877**
Analytical Parameters	**Units**	**Test Condition 3B**			
		C3B-R1	**C3B-R2**	**C3B-R3**	**Avg.**
Total Chlorides	mg/kg	272	279	278	**276**
Ash Content	%	11.0	10.1	13.2	**11.4**
Heat Content	Btu/lb	358	401	190	**316**
Water Content	%	79.5	79.8	73.5	**77.6**
Density	g/cc	0.9295	ND	ND	**0.9295**

ND = Not Determinable

Table 5-2 Stack Properties and Flowrate Measurements

Run #	Stack Temp. °F	% Moisture	Stack Flowrate dscfm	Stack Flowrate wet scfm
C3A-R1	667	16.7	108,356	130,079
C3A-R2	669	17.3	106,114	128,312
C3A-R3	668	17.0	112,588	135,649
C3B-R1	668	16.9	112,096	134,893
C3B-R2	663	18.6	109,627	134,677
C3B-R3	664	16.9	109,191	131,398
AVG:	**667**	**17.2**	**109,662**	**132,501**

Table 5-3 VOST Sampling Parameters (Condition 3A)

Date	Bar. Press. in Hg	Run ID No.	Sampling Times		Sample Volume aL	Meter Temp. °C	Sample Volume dsL
			Start	Stop			
13-Dec-06	29.81	1A	09:55	10:15	19.980	29.5	19.072
13-Dec-06	29.81	1B	10:28	10:48	21.270	31.2	20.192
13-Dec-06	29.81	1C	11:01	11:21	20.180	36.0	18.861
13-Dec-06	29.81	1D	11:29	11:49	19.940	37.5	18.545
13-Dec-06	29.84	2A	12:29	12:49	19.930	32.5	18.858
13-Dec-06	29.83	2B	13:00	13:20	19.500	31.7	18.495
13-Dec-06	29.81	2C	13:33	13:53	19.860	33.6	18.704
13-Dec-06	29.81	2D	14:11	14:31	20.210	30.6	19.226
13-Dec-06	29.81	3A	14:52	15:12	20.580	31.1	19.542
13-Dec-06	29.81	3B	15:20	15:40	20.120	34.0	18.928
13-Dec-06	29.81	3C	15:49	16:09	20.040	31.3	19.020
13-Dec-06	29.83	3D	16:17	16:37	19.650	31.7	18.637

Table 5-4 VOST Sampling Parameters (Condition 3B)

Date	Bar. Press. in Hg	Run ID No.	Sampling Times Start	Sampling Times Stop	Sample Volume aL	Meter Temp. °C	Sample Volume dsL
14-Dec-06	29.78	1A	09:00	09:20	19.770	21.9	19.337
14-Dec-06	29.78	1B	09:27	09:42	19.530	22.2	19.084
14-Dec-06	29.78	1C	09:55	10:15	19.570	22.5	19.105
14-Dec-06	29.78	1D	10:24	10:44	20.090	25.3	19.430
14-Dec-06	29.78	2A	11:00	11:20	19.890	25.8	19.201
14-Dec-06	29.78	2B	11:30	11:50	19.510	24.7	18.904
14-Dec-06	29.78	2C	11:57	12:17	19.740	24.2	19.163
14-Dec-06	29.78	2D	12:25	12:45	19.860	24.7	19.243
14-Dec-06	29.78	3A	13:07	13:27	20.380	26.9	19.601
14-Dec-06	29.78	3B	13:40	14:00	22.210	33.1	20.930
14-Dec-06	29.78	3C	14:18	14:38	19.930	34.9	18.671
14-Dec-06	29.78	3D	14:54	15:14	20.150	30.3	19.167

Table 5-5 DRE Calculations for Monochlorobenzene (Condition 3A)

POHC Feed Parameters				Stack Gas Parameters					
Run No.	Run Date Start Time Stop Time	(a) POHC Purity (% wt)	POHC Spike Rate (lb/hr)	VOST Run No.	Volume Sampled (dsL)	POHC Quantity Detected (µg)	(b) Stack Gas Flowrate (dscfm)	POHC Emission Rate (lb/hr)	Calculated DRE
C3A-R1	13-Dec-06			1-A	19.072				
	09:55			1-B	20.192				
	11:49			1-C	HOLD				
				1-D	18.545				
Overall C3A-R1:		**99.9944%**	**75.05**		**57.809**	**0.260**	**108,356**	**1.83E-03**	**99.9976%**
C3A-R2	13-Dec-06			2-A	18.858				
	12:29			2-B	18.495				
	14:31			2-C	HOLD				
				2-D	19.226				
Overall C3A-R2:		**99.9944%**	**74.96**		**56.578**	**0.480**	**106,114**	**3.37E-03**	**99.9955%**
C3A-R3	13-Dec-06			3-A	NA				
	14:52			3-B	18.928				
	16:37			3-C	19.020				
				3-D	18.637				
Overall C3A-R3:		**99.9944%**	**75.18**		**56.585**	**0.292**	**112,588**	**2.18E-03**	**99.9971%**
			AVG DRE, RUNS C3A-R1 -- C3A-R3 :						**99.9967%**

(a) POHC purity is provided for information only; the spike rate provided by Triad already accounts for POHC purity.

(b) The stack gas flowrate used for the VOST runs is taken from the Method 2F / 4 trains run concurrently by Avogadro.

Table 5-6 DRE Calculations for Monochlorobenzene (Condition 3B)

POHC Feed Parameters				Stack Gas Parameters						
Run No.	Run Date Start Time Stop Time	(a) POHC Purity (% wt)	POHC Spike Rate (lb/hr)	VOST Run No.	Volume Sampled (dsL)	POHC Quantity Detected (µg)	(b) Stack Gas Flowrate (dscfm)	POHC Emission Rate (lb/hr)	Calculated DRE
C3B-R1	14-Dec-06 09:00 10:44			1-A	19.337				
				1-B	19.084				
				1-C	HOLD				
				1-D	19.430				
Overall C3B-R1:		**99.9944%**	**149.96**		**57.851**	**0.112**	**112,096**	**8.13E-04**	**99.9995%**
C3B-R2	14-Dec-06 11:00 12:45			2-A	19.201				
				2-B	18.904				
				2-C	HOLD				
				2-D	19.243				
Overall C3B-R2:		**99.9944%**	**149.90**		**57.349**	**0.106**	**109,627**	**7.59E-04**	**99.9995%**
C3B-R3	14-Dec-06 13:07 15:14			3-A	19.601				
				3-B	20.930				
				3-C	HOLD				
				3-D	19.167				
Overall C3B-R3:		**99.9944%**	**150.08**		**59.698**	**0.120**	**109,191**	**8.22E-04**	**99.9995%**
			AVG DRE, RUNS C3B-R1 -- C3B-R3 :						**99.9995%**

(a) POHC purity is provided for information only; the spike rate provided by Triad already accounts for POHC purity.

(b) The stack gas flowrate used for the VOST runs is taken from the Method 2F / 4 trains run concurrently by Avogadro.

6.0 Quality Assurance / Quality Control (QA/QC)

This DRE retest program incorporated a variety of QA/QC measures to ensure the validity of the final results for documentation of the performance of SMR's CO boiler unit. These measures were based upon routine field and laboratory practices as well as specific requirements delineated in the approved Trial Burn Plan, DRE Retest Plan and the applicable sampling and analytical protocols.

This section presents the results of all QA/QC measures evaluated during both the field sampling program and during all phases of sample analysis. Data generated for the program are judged to be completely valid since overall accuracy and precision goals consistent with general program objectives were achieved. Analytical QA/QC data are presented to support all sample results used for determining compliance with performance criteria and/or emission standards.

6.1 Sample Collection QA/QC

6.1.1 Waste Feed Stream

Samples of the waste feed material were collected at the beginning, middle and end of each run as specified in Section 5.4.4 of the original TBP and Section 5.1 of the DRE Retest Plan. Field data sheets were completed by the sampler (SMR personnel) and are included in **Appendix D**. No problems were encountered during any periods of waste sample collection.

6.1.2 Stack Gas

All samples were collected at the stack sampling platform on COB-2 as planned. For this program, which included VOST sampling only, two (2) field blanks (one per day of testing) and one trip blank were submitted for analysis along with program samples.

Sampling QA/QC measures for this program included the calibration of all applicable sampling equipment according to EPA procedures identified in 40 CFR 60, Methods 1-5, as well as manufacturer's specifications. Details of specific calibrations are summarized in Appendix B of Avogadro's report contained in **Appendix B** of this trial burn report.

Chain-of-custody (COC) procedures for all stack samples was initiated and maintained as follows:

- Samples were collected, sealed and labeled with preprinted sample labels. Each Method 4 isokinetic sampling train was setup and recovered in the Avogadro mobile trailer set up in close proximity to the tested unit.
- Preprinted sample lists were used to check that all samples were collected and each container was checked upon completion of recovery and labeling.
- All samples were packed in bubble wrap or other absorbent material and placed in either sample coolers or appropriate DOT shipping packages (dangerous goods items). All samples were subsequently driven by ENSR or Avogadro to the designated laboratory.

6.2 Laboratory Analysis QA/QC

This section provides a detailed presentation of QA/QC results from sample analysis as reported by each analytical laboratory. Key QC data related to matrix spikes, surrogate spikes, duplicate analyses, laboratory control samples (blank spikes), method blanks and/or field blank results are presented in tabular format. Other QC procedures followed such as calibration checks and additional method-specific protocols are described in the case narratives and analytical data packages provided in **Appendix E**. Also, unless noted otherwise, all holding times and method-specific QC criteria were met and reported results met all applicable NELAC requirements.

6.2.1 Waste Feed Stream – Physical Parameter Analyses

Evaluation of the validity of the physical parameter analyses was based on the following QA objectives:

- Results of analysis of laboratory control samples (LCS) for density and total chlorides.
- Verification of temperature control on the thermal gravimetric analysis (TGA) instrument used for moisture determination.
- Analysis of a benzoic acid spike used in the bomb calorimeter for determination of heat content.

Results summarized in **Table 6-1** indicate that all target criteria were met. Therefore, program quality control objectives were met and completeness was determined to be 100% for all waste feed physical parameter (total chlorides, ash, moisture, density and heat content) analyses.

Table 6-1 Overall QC Summary for Waste Feed Stream Physical Parameter Analyses

QC Parameter	Target Criteria	Program Results
Lab Control Samples (LCS) for Density	DI water = 1.0000 g/cc	Result = 0.9991 g/cc
LCS for total chlorides	Acceptable range of 9 – 11 ppm	Result = 10.36 ppm
Verification of TGA Temperature Control	Curie point for alumel in the range of 154.2°C ± 10.8°C	Result = 149.87°C
Analysis of Benzoic Acid Spike	11,200 – 11,546 Btu/lb	Result = 11,383 Btu/lb

6.2.2 Stack Gas Analyses

6.2.2.1 Monochlorobenzene (Conditions 3A and 3B)

Evaluation of the validity of the data resultant from the analysis of the VOST samples for MCB was based on the following indicators:

- Recoveries of 4 surrogate compounds (dibromofluoromethane, 1,2-dichloroethane-d4, toluene-d8 and 4-bromofluorobenzene) added to the VOST samples prior to analysis.
- Replicate analysis of traps spiked with standards (LCS samples).
- Separate analysis of the front and back VOST tubes for each program sampling run to determine whether compound breakthrough had occurred.
- Results of analyses of field, trip and lab blank samples.

Due to the fact that so little condensate was collected (~ 1 mL) over the course of each run, a decision was made to not have these samples analyzed.

All surrogate recoveries were within the 70-130% recovery range and MCB was not detected in any of the lab, field or trip blank samples. LCS recoveries were all excellent and ranged from 104-122% recovery. No MCB was detected in any of the back-half cartridges and thus breakthrough was not an issue. Based on the overall results summarized in **Table 6-2**, completeness was therefore determined to be 100% for all VOST analyses.

Table 6-2 Overall QC Summary for Volatile Organics in Stack Gas Samples

QC Parameter	Target Criteria	Program Results
Field Blanks, Trip Blank and Method Blank	Below detection limit	No compounds detected above RL
Lab Control Samples	50%-150% recovery	All samples within control limits and good precision demonstrated (< 15% RPD).
Breakthrough Determination	TX/C trap should contain < 75 ng or < 30% of amount on TX trap.	No breakthrough observed for MCB
Accuracy-Surrogate Recoveries	70%-130% recovery	All surrogate recoveries within limits