Gas Fired Boiler—Test Report Refinery Site A

Characterization of Fine Particulate Emission Factors and Speciation Profiles from Stationary Petroleum Industry Combustion Sources

Regulatory and Scientific Affairs

PUBLICATION NUMBER 4703 JULY 2001

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> American Petroleum Institute

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<u>API STAFF CONTACT</u> Karin Ritter, Regulatory and Scientific Affairs

MEMBERS OF THE PM SOURCE CHARACTERIZATION WORKGROUP

Lee Gilmer, Equilon Enterprises LLC, Stationary Source Emissions Research Committee, Chairperson Karl Loos, Equilon Enterprises LLC Jeff Siegell, ExxonMobil Research and Engineering

GE ENERGY AND ENVIRONMENTAL RESEARCH CORPORATION

<u>PROJECT TEAM MEMBERS</u> Glenn England, Project Manager Stephanie Wien, Project Engineer Bob Zimperman, Field Team Leader Barbara Zielinska, Desert Research Institute Jake McDonald, Desert Research Institute

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EXECUTIVE SUMMARY

In 1997, the United States Environmental Protection Agency (EPA) promulgated new ambient air standards for particulate matter smaller than 2.5 micrometers in diameter (PM2.5). Source emissions data are needed to assess the contribution of petroleum industry combustion sources to ambient PM2.5 concentrations for receptor modeling and PM2.5 standard attainment strategy development. There are few existing data on emissions and characteristics of fine aerosols from petroleum industry combustion sources, and the limited information that is available is incomplete and outdated. The American Petroleum Institute (API) developed a test protocol to address this data gap, specifically to:

- Develop emission factors and speciation profiles for emissions of primary fine particulate matter (i.e., particulate present in the stack flue gas including condensible aerosols), especially organic aerosols from gas-fired combustion devices; and
- Identify and characterize secondary particulate (i.e., particulate formed via reaction of stack emissions in the atmosphere) precursor emissions.

This report presents results of a pilot project to evaluate the test protocol on 550,000 pounds per hour steam (approximately 650×10^6 British thermal units per hour) boiler firing refinery process gas. The tangentially fired boiler has a waterwall furnace with two rows of burners in each corner of the furnace. The unit has no controls for NO_x emissions. The boiler operated at approximately 57 percent of capacity, and flue gas temperature at the stack was approximately 345 degrees Fahrenheit during the tests.

The particulate measurements at the stack were made using both a dilution tunnel research test method and traditional methods for regulatory enforcement of particulate regulations. The dilution tunnel method is attractive because the sample collection media and analysis methods are identical to those used for ambient air sampling. Thus, the results are directly comparable with ambient air data. Also, the dilution tunnel method is believed to provide representative results for condensible aerosols. Regulatory methods are attractive because they are readily accepted by regulatory agencies and have been used extensively on a wide variety of source

types; existing regulatory methods for condensible aerosols may be subject to significant bias, however, and sampling/analytical options are limited.

Emission factors for all species measured are extremely low, which is expected for gas-fired sources. Emission factors for primary particulate, including: total particulate, PM10 (particles smaller than nominally 10 micrometers), and PM2.5; elements; ionic species; and organic and elemental carbon are presented in Table E-1. Since the boiler was firing refinery process gas with a heating value different from natural gas, emission factors are expressed in pounds of pollutant per million British thermal units of gas fired (lb/MMBtu). All tests were performed in triplicate. As a measure of the bias, precision, and variability of the results, the uncertainty and 95 percent confidence upper bound also are presented.

Emission factors for semivolatile organic species are presented in Table E-2. The sum of semivolatile organic species is approximately three percent of the organic carbon. Emission factors for secondary particulate precursors (NO_x , SO_2 , and volatile organic species with carbon number of 7 or greater) are presented in Table E-3.

The preceding tables include only those substances that were detected in at least one of the three test runs. Substances of interest that were not present above the minimum detection limit for these tests are listed in Table E-4.

A single ambient air sample was collected at the site. In some cases, the emission factors reported in Tables E-1 to E-3 resulted from in-stack concentrations that were near ambient air concentrations. Those species concentrations that are within a factor of 10 of the ambient air concentration are indicated on the table by an asterisk (*).

The primary particulate results presented in Table E-1 also may be expressed as a PM2.5 speciation profile, which is the mass fraction of each species contributing to the total PM2.5 mass. The speciation profile is presented in Figure E-1.

The main findings of these tests are:

- Particulate mass emissions from the boiler were extremely low, consistent with levels expected for gaseous fuel combustion.
- Two methods for determining the average emission factor for primary PM2.5 mass gave results which differed in magnitude by a factor of 27: 0.000358 lb/MMBtu using the dilution tunnel; and 0.00974 lb/MMBtu using conventional in-stack methods for filterable and condensible particulate.
- Sampling and analytical artifacts principally caused by gaseous SO₂ in the stack gas were shown to produce a relatively large positive bias in condensible particulate as measured by conventional in-stack methods. Most of the difference between the dilution tunnel and conventional method results can be explained by these measurement artifacts. The results using conventional EPA methods are nominally consistent with published EPA emission factors for external combustion of natural gas (U. S. EPA, 1998). Therefore, the published EPA emission factors derived from tests using similar measurement methods also may be positively biased.
- Chemical species accounting for 74 percent of the measured PM2.5 mass were quantified.
- Organic and elemental carbon comprise 68 percent of the measured primary PM2.5 mass.
- Sulfates, iron, copper, chloride, and smaller amounts of other elements account for another 6 percent of the measured PM2.5 mass.
- Less than 26 percent of the measured PM2.5 mass is unspeciated.
- Most elements are not present at levels significantly above the background levels in the ambient air or the minimum detection limits of the test methods.
- Most organic species are not detected at levels significantly above background levels in the ambient air or field blanks. All detected organics are present at extremely low levels consistent with gaseous fuel combustion.
- Emissions of secondary particle precursors are low and consistent with levels expected for gaseous fuel combustion.

	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~			
Substance		Emission	Uncertainty	95% Confidence
Particulate	Condensible Particulate (inorganic)	9.07E-3	107	1.58E-2
	Condensible Particulate (organic)	6.36E-4	290	1.89E-3
	Total Condensible Particulate	9.16E-3	118	1.66E-2
	Total Filterable PM (in-stack method)	1.66E-4	332	5.40E-4
	Filterable PM10 (in-stack method)	1.58E-4	n/a	n/a
	Filterable PM2.5 (in-stack method)	2.64E-5	n/a	n/a
	PM2.5 (dilution tunnel)	5.58E-4	80	8.69E-4
Elements	Aluminum*	2.65E-7	54	3.68E-7
	Arsenic	2.11E-7	79	3.27E-7
	Calcium*	4.46E-7	147	8.93E-7
	Chlorine	7.12E-7	n/a	n/a
	Cobalt (1)	1.13E-8	450	3.66E-8
	Chromium*	1.61E-8	n/a	n/a
	Copper*	1.55E-6	112	2.74E-6
	Iron*	1.93E-6	79	2.99E-6
	Potassium*	1.87E-7	116	3.36E-7
	Magnesium* B	1.38E-7	292	4.11E-7
	Nickel	2.25E-7	86	3.59E-7
	Lead*	5.82E-8	746	2.74E-7
	Silicon*	1.27E-6	64	1.84E-6
	Sodium	2.13E-6	162	4.48E-6
	Sulfur*	8.94E-6	76	1.37E-5
	Titanium*	4.75E-8	n/a	n/a
	Uranium (1)	1.45E-8	n/a	n/a
	Vanadium	3.90E-7	97	6.51E-7
	Zinc*	1.59E-7	87	2.55E-7
Ions	Sulfate*	1.43E-5	68	2.11E-5
	Nitrate	ND	n/a	n/a
	Chloride (1)	8.46E-7	n/a	n/a
	Ammonium*	1.60E-6	95	2.64E-6
Carbon	Organic Carbon (dilution tunnel)	1.55E-4	55	2.16E-4
	Elemental Carbon (dilution tunnel)	9.41E-5	114	1.68E-4
	Total Carbon (dilution tunnel)	2.49E-4	59	3.54E-4
	Organic Carbon (in-stack)	1.05E-4	70	1.57E-4
	Elemental Carbon (in-stack)	2.03E-4	121	3.72E-4
	Total Carbon (in-stack)	3.08E-4	55	4.32E-4

Table E-1. Summary of Primary Particulate Emission Factors for Gas-Fired Refinery Boiler.

* <10x ambient

(1) <10x detection limit, ambient=ND

B <10x blank

n/a - not applicable; only one run within detectable limits

		Emission		95% Confidence
		Factor	Uncertainty	Upper Bound
	Substance	(lb/MMBtu)	(%)	(lb/MMBtu)
Semivolatile	Phenanthrene	1.03E-06	94	1.71E-06
Organic	Perinaphthenone	3.78E-07	134	7.29E-07
Compounds	Fluoranthene	2.83E-07	136	5.49E-07
(Dilution	Biphenyl	2.49E-07	372	8.78E-07
Tunnel/	Pyrene	1.99E-07	126	3.72E-07
PUF/XAD)	Cholestane B	1.91E-07	75	2.94E-07
,	Coronene*	1.80E-07	62	2.64E-07
	Fluorene*	1.11E-07	76	1.72E-07
	Naphthalene*	1.04E-07	544	3.88E-07
	Anthracene	7.83E-08	112	1.39E-07
	Acenaphthylene	6.04E-08	283	1.77E-07
	Acenaphthenequinone B	5.48E-08	136	1.06E-07
	B-methylphenanthrene	5.10E-08	113	9.14E-08
	2-methylnaphthalene*	4.44E-08	159	9.31E-08
	1.4+1.5+2.3-dimethylnaphthalene*	4.41E-08	n/a	n/a
	3-methylbiphenyl*	4.41E-08	125	8.24E-08
	1.3+1.6+1.7-dimethylnaphthalene*	4.06E-08	140	8.00E-08
	Anthraquinone* B	4.00E-08	64	5.90E-08
	9-methylanthracene	3.66E-08	n/a	n/a
	2-methylphenanthrene*	3.55E-08	150	7.22E-08
	A-methylphenanthrene*	3 34E-08	145	6 70E-08
	Benzanthrone* B	3 22E-08	56	4 59E-08
	2-phenylnaphthalene	3 13E-08	126	5.86E-08
	Xanthone B	3 10E-08	n/a	n/a
	9-fluorenone	2.82E-08	n/a	n/a
	Benzo(b+i+k)fluoranthene*	2.78E-08	58	4 00E-08
	1-methylnaphthalene*	2.77E-08	169	5.99E-08
	Benz(a)anthracene*	2.51E-08	137	4.88E-08
	Benzo(b)chrysene*	2.39E-08	56	3.40E-08
	1-methylpyrene+C-methylpyrene/fluorene	2.36E-08	188	4.63E-08
	Benz(a)anthracene-7.12* B	2.17E-08	65	3.20E-08
	4H-cvclopenta(def)phenanthrene B	2.07E-08	97	3.49E-08
	2.6+2.7-dimethylnaphthalene*	1.99E-08	122	3.69E-08
	7-methylbenzo(a)pyrene (1)	1.94E-08	75	2.98E-08
	Chrysene* B	1.84E-08	71	2.79E-08
	F-trimethylnaphthalene*	1.84E-08	264	4.28E-08
	C-dimethylphenanthrene*	1.82E-08	315	5.72E-08
	Dibenzofuran*	1.80E-08	66	2.68E-08
	B-dimethylphenanthrene	1.76E-08	238	3.88E-08
	1.2-dimethylnaphthalene*	1.68E-08	n/a	n/a
	1+2-ethylnaphthalene*	1.65E-08	214	3.44E-08
	C-methylphenanthrene*	1.57E-08	79	2.45E-08
	Acenaphthene*	1.55E-08	63	2.27E-08
	E-trimethylnaphthalene*	1.54E-08	297	4.64E-08
	1-phenylnaphthalene (1)	1.17E-08	126	2.20E-08
	Anthrone* B	1.17E-08	69	1.76E-08
	D-dimethylphenanthrene	1.17E-08	76	1.81E-08
	E-dimethylphenanthrene*	1 14E-08	445	3 67E-08

Table E-2. Summary of Semivolatile Organic Species Emission Factors for Gas-Fired Refinery Boiler.

Substance	Emission Factor (lb/MMBtu)	Uncertainty	95% Confidence Upper Bound (lb/MMBtu)
B methylfluorana	1 12E 08	(70)	(10/1010100)
$2.3.5 \pm 1$ trimethylnaphthalane*	1.13E-08	11/a 76	175E 08
2, 5, 5 + 1-timethyliaphthalene*	1.13E-08	76	1.75E-08
C-unneurymaphiliaiene	1.10E-08	144	1.70E-08
1 4 abricanaquinana* D	1.10E-00	144	2.19E-00
1,4-cm ysenequillone B	1.08E-08	100	2.46E-08
D trimethylpenhthelene*	9.30E-09	99	1.01E-08
D-unneuryinapinnalene	9.30E-09	92	1.3/E-08
2-methylolphenyl (1) B	9.4/E-09	n/a	n/a 1 45E 09
A-trimetnyinaphtnaiene*	9.05E-09	84	1.45E-08
Benzo(gni)perylene* B	8.8/E-09	/8	1.38E-08
1-methylfluorene	8.87E-09	79	1.39E-08
Benzo(a)pyrene* B	8.75E-09	68	1.31E-08
1-ethyl-2-methylnaphthalene*	7.99E-09	127	1.51E-08
3,6-dimethylphenanthrene*	7.80E-09	258	2.16E-08
Dibenz(ah+ac)anthracene* B	7.33E-09	79	1.15E-08
A-dimethylphenanthrene*	7.04E-09	662	3.02E-08
4-methylbiphenyl* B	6.60E-09	141	1.30E-08
B-methylpyrene/methylfluorene	6.57E-09	230	1.69E-08
A-methylfluorene	6.38E-09	n/a	n/a
Indeno[123-cd]pyrene* B	6.15E-09	70	9.31E-09
4-methylpyrene*	6.09E-09	202	1.45E-08
2,4,5-trimethylnaphthalene*	5.13E-09	140	1.01E-08
1,7-dimethylphenanthrene*	4.70E-09	105	8.16E-09
9,10-dihydrobenzo(a)pyrene* B	4.56E-09	94	7.59E-09
Benzo(e)pyrene B	4.22E-09	116	7.64E-09
D-methylpyrene/methylfluorene	4.19E-09	143	8.34E-09
1,2,8-trimethylnaphthalene*	3.83E-09	123	7.12E-09
9-anthraldehyde (1) B	3.69E-09	400	1.11E-08
5+6-methylchrysene (1)	3.51E-09	133	6.75E-09
Benzonaphthothiophene	3.19E-09	100	5.43E-09
Perylene B	3.01E-09	117	5.47E-09
A-methylpyrene B	2.11E-09	175	4.65E-09
E-methylpyrene/methylfluorene*	1.25E-09	246	3.35E-09
Sum of All SVOCs	4.06E-06		

Table E-2 (continued). Summary of Semivolatile Organic Species Emission Factors for Gas-Fired Refinery Boiler.

Substance		Emission	Uncertainty	95%
		Factor	(%)	Confidence
		(lb/MMBtu)		Upper Bound
				(lb/MMBtu)
Semi-	Naphthalene	4.09E-08	131	7.80E-08
Volatile				
Organic	2-methylnaphthalene	1.29E-08	773	6.24E-08
Compounds	1-methylnaphthalene	8.54E-09	594	3.38E-08
(in-stack	Acenaphthene	7.01E-09	713	3.19E-08
filter)	Perinaphthenone	6.75E-09	691	3.00E-08
	Biphenyl	5.77E-09	n/a	n/a
	Dibenzofuran	3.42E-09	520	1.23E-08
	Benzo(a)pyrene	3.24E-09	465	1.07E-08
	Benz(a)anthracene	2.91E-09	n/a	n/a
	2-methylphenanthrene	1.87E-09	249	4.21E-09
	Benzo(b)chrysene	9.28E-10	567	3.55E-09
	1-methylphenanthrene	8.02E-10	177	1.53E-09
	1,4-chrysenequinone	5.29E-10	n/a	n/a
	Anthone	5.25E-10	n/a	n/a
	Sum of All SVOCs	9.61E-08		

Table E-2 (continued). Summary of Semivolatile Organic Species Emission Factors for Gas-Fired Refinery Boiler.

* <10x ambient

(1) <10x detection limit, ambient = ND

B <10x blank

n/a not applicable; only one run within detectable limits

	Substance	Emission Factor (lb/MMBtu)	Uncertainty (%)	95% Confidence Upper Bound (lb/MMBtu)
Gases	NO _X	1.02E-01	42	1.39E-01
	$SO_2$	9.39E-03	42	1.28E-02
Volatile	1,2,4-trimethylbenzene*	7.23E-07	77	1.13E-06
Organic	2-methyloctane*	3.70E-07	210	9.03E-07
Compounds	Acetophenone	5.21E-05	76	8.09E-05
(Carbon	Benzaldehyde	5.85E-05	106	1.02E-04
number >7)	Benzonitrile	5.54E-06	56	7.90E-06
	Biphenyl	5.76E-07	273	1.65E-06
	Butylated hydroxytoluene*	8.98E-06	188	2.06E-05
	Decane* B	2.26E-07	112	4.03E-07
	Dodecane*	3.05E-07	72	4.65E-07
	Eicosane	3.23E-07	158	6.74E-07
	Ethylbenzene*	2.45E-07	92	4.04E-07
	Heptadecane*	6.72E-07	68	1.01E-06
	Hexadecane*	4.72E-07	171	1.03E-06
	m&p-xylene*	1.07E-06	94	1.78E-06
	Nonadecane	3.74E-07	127	7.06E-07
	Nonane	3.63E-07	121	6.70E-07
	o-xylene*	5.06E-07	95	8.49E-07
	Octadecane	5.71E-07	58	8.21E-07
	p-isopropyltoluene*	3.45E-08	n/a	n/a
	Pentadecane*	4.83E-07	323	1.54E-06
	Phenol	2.40E-05	79	3.75E-05
	Styrene*	2.53E-06	60	3.66E-06
	Tetradecane*	6.11E-07	171	1.33E-06
	Tridecane*	5.41E-07	76	8.38E-07
	Undecane*	4.53E-07	80	7.15E-07

Table E-3. Summary of Secondary Particulate Precursor Emission Factors for Gas-Fired Refinery Boiler.

* <10x detection limit, ambient = ND

(1) <10x blank

B <10x detection limit, blank = ND

n/a - not applicable; only one run within detectable limits

Antimony	Barium
Bromine	Cadmium
Gallium	Gold
Indium	Lanthanum
Manganese	Mercury
Molybdenum	Palladium
Phosphorous	Rubidium
Selenium	Silver
Strontium	Tin
Thallium	Yttrium
Zirconium	Nitrate
1-methylphenanthrene	1-methylpyrene
1,4,5-trimethylnaphthalene	1,8-dimethylnaphthalene
2-ethyl-1-methylnaphthalene	7-methylbenz(a)anthracene
Bibenzene	J-trimethylnaphthalene
1-hexadecene	1-methylindan
1-nonene	1-undecene
1,2,3-trimethylbenzene	1,3,5-trimethylbenzene
2-methylindan	3-methyloctane
7-Hexadecene	Cyclohexanone
Dimethyloctane	Dodecene
Indan	Indene
m-ethyltoluene	m-isopropyltoluene
Nonanal	o-ethyltoluene
o-isopropyltoluene	p-ethyltoluene
Propylbenzene	

Table E-4. Substances of Interest Not Detected in Stack Emissions from Gas-Fired Boiler.



Figure E-1. Speciation Profile for Primary Particulate Emissions from Gas-Fired Boiler (Refinery Site A).

ES-10

# Section 1 PROJECT DESCRIPTION

#### PROJECT OVERVIEW

In 1997, the United States Environmental Protection Agency (EPA) promulgated new ambient air standards for particulate matter, including for the first time particles with aerodynamic diameter smaller than 2.5 micrometers (PM2.5). There are few existing data regarding emissions and characteristics of fine aerosols from petroleum industry combustion sources, and such information that is available is fairly old. Traditional stationary source air emission sampling methods tend to underestimate or overestimate the contribution of the source to ambient aerosols because they do not properly account for primary aerosol formation that occurs after the gases leave the stack. This issue was extensively reviewed by API in a recent report (England et al., 1997), which concluded that dilution sampling techniques are more appropriate for obtaining a representative sample from combustion systems. These techniques have been widely used in research studies (Hildemann et al., 1994; McDonald et al., 1998), and use clean ambient air to dilute the stack gas sample and provide 80-90 seconds residence time for aerosol formation prior to sample collection for determination of mass and chemical speciation.

As a result of the API review, a test protocol was developed based on the dilution sampling system described in this report, which was then used to collect particulate emissions data from petroleum industry combustion sources, along with emissions data obtained from conventional sampling methods. This test program is designed to provide reliable source emissions data for use in assessing the contribution of petroleum industry combustion sources to ambient PM2.5 concentrations. The goals of this test program were to:

- Develop emission factors and speciation profiles for emissions of fine particulate matter, especially organic aerosols;
- Identify and characterize PM2.5 precursor compound emissions.

This test report describes the results of tests performed on a gas-fired boiler at Refinery Site A on July 14-20, 1998.

# PROJECT OBJECTIVES

The specific objectives of this test were to:

# Primary objectives

- Compare PM2.5 mass measured using an in-stack filter and an iced impinger train (EPA Method 201A/202), and mass measured using a dilution tunnel;
- Develop emission factors and speciation profiles for organic aerosols and PM2.5 mass;
- Characterize sulfate, nitrate, ammonium, elemental carbon (EC) and organic carbon (OC) in particulate matter collected on filter media after stack gas dilution;
- Characterize key secondary particle precursors in stack gas samples: volatile organic compounds (VOC) with carbon number of 7 and above; sulfur dioxide (SO₂); and oxides of nitrogen (NO_X);
- Document the relevant process design characteristics and operating conditions during the test.

# Secondary Objective

• Characterize ions (sulfate, nitrate and ammonium), OC, and EC in particulate collected on filter media in stack gas sampling trains.

# TEST OVERVIEW

The scope of testing is summarized in Table 1-1. The emissions testing included collection and analysis of both in-stack and diluted stack gas samples. All emission samples were collected from the stack of the unit. An ambient air sample also was collected. The samples were analyzed for the compounds listed in Table 1-2. Boiler process data and fuel gas samples were collected during the tests to document operating conditions.

# Source Level (In-stack) Samples

In-stack sampling and analysis for filterable (total, PM10 and PM2.5) and condensible particulate matter (CPM), NO_x, oxygen (O₂), carbon dioxide (CO₂), carbon monoxide (CO) and SO₂ was performed using traditional EPA methods. In-stack cyclones and filters were used for filterable particulate matter. Sample analysis was expanded to include OC, EC and organic species on the in-stack quartz filters.

	Number of Samples at each Sampling Location				
Sampling Location	Fuel Gas Header	Stack	Ambient Air		
EPA Method 201A/202 Train		3			
EPA Method 17 Train		3			
Dilution tunnel		3	1		
Teflon [®] filter					
TIGF/PUF/XAD-4					
Quartz filter					
Tenax					
Fuel sample	6				
$NO_x$ , $SO_2$ , $CO$ , $O_2$ , $CO_2$		continuous			
Process monitoring		continuous			

Table 1-1. Overview of Sampling Scope,

TIGF=Teflon[®]-impregnated glass fiber filter PUF=polyurethane foam XAD-4 = Amberlite[®] sorbent resin

# **Dilution Stack Gas Samples**

Dilution sampling was used to characterize PM2.5 including aerosols formed in the near-field plume. The dilution sampler extracted a sample stream from the stack into a mixing chamber, where it was diluted approximately 6:1 with purified ambient air. Because PM2.5 behaves aerodynamically like a gas at typical stack conditions, the samples were extracted nonisokinetically. A slipstream of the mixed and diluted sample was extracted where it resided for approximately 80 seconds to allow time for low-concentration aerosols, especially organics, to condense and grow. The diluted and aged sample then passed through cyclone separators sized to remove particles larger than 2.5 microns, after which samples were collected on various media: high-purity quartz, Teflon[®] membrane filter (TMF), and Teflon[®]-impregnated glass fiber (TIGF) filters; a polyurethane foam (PUF)/Amberlite[®] sorbent resin (XAD-4)/PUF cartridge to collect gas phase semivolatile organic compounds; and a Tenax cartridge to VOCs. Three samples were collected on three sequential test days.

	In-Stack			Dilution Tunnel					
		Quartz			Quartz	TIGF/			
Parameters	Cyclones	Filter	Impingers	Gases	Filter	XAD-4	TMF	Tenax	Gases
Total PM mass	Х	Х							
PM10 ^{mass}	Х	Х							
PM2.5 mass	Х	Х					Х		
Condensible									
particulate mass			Х						
Sulfate			Х		Х				
Chloride			Х		Х				
Ammonium			Х		Х				
Nitrate			Х		Х				
Elements			Х				Х		
Organic carbon		Х			Х				
Elemental carbon		Х			Х				
Semivolatile									
organic									
compounds		Х				Х			
Volatile organic									
compounds*								Х	
NO _x				Х					
$SO_2$				Х					
СО				Х					
$O_2$				Х					
$CO_2$				Х					
Moisture or									
relative humidity			Х						Х
Velocity				Х	[				
Temperature				Х					Х

 Table 1-2
 Summary of Analytical Targets

 $TMF = Teflon^{\mathbb{R}}$  membrane filter

 $TIGF = Teflon^{\mathbb{R}}$ 

*Carbon number of 7 or greater

An ambient air sample was collected to establish background concentrations of measured substances. The same sampling and analysis procedures used for the dilution tunnel were applied for collecting ambient air samples.

#### Process Samples

A sample of the fuel gas burned in the boiler was collected on each day of testing and analyzed for specific gravity, heating value, and hydrocarbon speciation. Samples of liquid hydrocarbon from the fuel gas knockout drum were planned; however, there was no liquid accumulation during the tests.

# **KEY PERSONNEL**

Energy and Environmental Research Corporation, a General Electric company, (GE-EER) had

primary responsibility for the test program. Key personnel involved in the tests were:

- Glenn England (GE-EER) Program Manager (949) 859-8851
- Stephanie Wien (GE-EER) Project Engineer (949) 552-1803
- Bob Zimperman (GE-EER) Field Team Leader (949) 552-1803
- Barbara Zielinska (Desert Research Institute) Dilution Sampling and Laboratory Analysis (775) 674-7066
- Karl Loos (Equilon Enterprises LLC) API Work Group Chairman (281) 544-7264
- Karin Ritter (API) API Project Officer (202) 682-8472

#### Section 2

# PROCESS DESCRIPTION

The tests were performed on a gas-fired boiler at Refinery Site A. The boiler has a capacity of 550,000 pounds of steam per hour, corresponding to a firing rate of approximately 650 million British thermal units per hour (MMBtu/hr). The furnace is corner-fired (tangential) with two elevations of conventional gas burners at each corner. It is a forced draft unit with a regenerative air preheater. The boiler is fired with refinery process gas. The unit is not equipped with air pollution controls for  $NO_X$ ,  $SO_2$  or particulate. The boiler appeared to be in good working condition during the test. Boiler load normally varies depending upon refinery steam demand and availability of steam from other sources. Operating conditions during the test are given in Section 4. Process operating parameters monitored during testing include: fuel gas flow rate, specific gravity, heating value and hydrogen sulfide (H₂S) content; steam flow rate and temperature; and excess oxygen at the boiler outlet.

#### SAMPLING LOCATIONS

Figure 2-1 provides an overview of the boiler process and the sampling and monitoring locations. Flue gas samples were collected from the stack. The single stack is equipped with a 180° sampling platform located 52 feet above the ground, which is accessible via a ladder. The sampling platform is 40 inches wide with an additional 6-inch gap between the sampling platform and the stack. There are two 4-inch diameter sampling ports on the stack which are at 90° to one another and are located 35 inches up from the platform. The ports are flanged with 4-inch nipples. The stack diameter at this elevation is 105 inches. The sample ports are located 264 inches (2.5 diameters) downstream of flow disturbances. The stack does not have a pulley, lights or power outlets, but there is a 480 volt power supply approximately 50 feet from the base of the stack. The stack temperature is normally approximately 340°F, and typically ranges from 320°F to 400°F. All sampling was performed at a single point in the center of the stack to facilitate co-location of the dilution tunnel and EPA Method 201A/202 probes.

Fuel gas samples were collected once per day from the fuel drum that distributes refinery fuel gas to boilers and heaters in the refinery. Samples of any liquid collecting in the fuel gas

2-1

knockout drum were planned; however, none was found during these tests. Ambient air samples were collected at near ground level close to the combustion air fan inlet.



Figure 2-1. Boiler Process Overview and Sampling/Monitoring Locations.

#### Section 3

# **TEST PROCEDURES**

An overview of the sampling and analysis procedures is given in Table 3-1. Figure 3-1 shows the testing chronology for the dilution tunnel and in-stack methods. The time of day for the start and finish of each measurement run is shown on the figure. For example, Method 201A/202 Run 1 began at 16:24 hours and finished at 22:24 hours on Wednesday, July 15. Dilution tunnel testing and in-stack testing were performed on different days due to limited space on the stack platform. All samples were collected at approximately the same point in the center of the stack.

#### STACK GAS FLOW RATE, MOISTURE CONTENT AND MOLECULAR WEIGHT

An S-type Pitot tube (EPA Method 2) was used to determine the stack gas velocity and volumetric flow rate. Stack gas molecular weight was calculated in accordance with EPA Method 3. Moisture content of the sample was determined based on weight gain of the impingers used in the Method 201A/202 train according to EPA Method 4. A full velocity traverse of the stack was performed before and after most of the tests to determine total stack gas flow rate. In those few cases where velocity was not directly measured, stack gas flow rate was calculated using fuel flow rate and dry F factors according to EPA Method 19.

#### O₂, CO₂, CO, NO_x AND SO₂

Major gases and pollutant concentrations in the stack sample were measured using a continuous emission monitoring system (CEMS), illustrated schematically in Figure 3-2. Table 3-2 lists the CEMS specifications. The sample was collected from a single traverse point in the stack after verifying that the gas concentration profile deviated by less than 10 percent of the mean concentration. Sample gas was passed through a primary in-stack sintered metal filter, a heated stainless steel probe, a heated Teflon[®] transfer line, a primary moisture removal system (heat exchanger impingers in an ice bath), a heated secondary filter, a diapgragm pump, and a heated back-pressure regulatory to a thermoelectric water condenser. The condenser's heat exchangers are specially designed impingers that separate the condensate from the gas sample with a minimum of contgact area to avoid loss of the water soluble gas fraction. The condensate was removed with a peristaltic pump through the bottom of the heat exchanger. All contact

Sampling	Measurements	Sampling	Sample	Reference
Location		Approach	Analyses	
Stack	Total PM,	In-Stack series	Mass organic	U.S. EPA Method
<b>S</b> 1	PM10, PM2.5	cyclones and filter	species	201A (modified)
	and			
	composition			
	PM	In-stack filter	Organic carbon,	U.S. EPA Method
	composition		elemental carbon	17 (modified)
	Condensible	Impingers	Mass (organic and	U.S. EPA Method
	PM and		inorganic), sulfate,	202 (modified)
	composition		chloride, nitrate,	
			ammonium	
		<u>a</u>	elements	
	Gaseous	Continuous	$SO_2$ and $NO_X$ ( $O_2$ ,	U.S. EPA Methods
	PM2.5		$CO_2$ , $CO$ also	3A/6C/7E/10
	precursors		measured)	
Stack (Dilution	PM2.5 and	Filters	Mass, organic	U.S. EPA, 1999a
l'unnel)	chemical		carbon, elemental	Hildemann et al.,
81	composition		carbon, organic	1989
			species, sulfate,	
			nitrate, chloride,	
	VOC	Т		7.1.1.1.1.100
	VUC	I enax	Speciated VOC	Zielinska et al., 1996
	SVOC	PUF/XAD-4/PUF	Speciated SVOC	U.S. EPA Method TO13
Ambient Air	PM2.5 and	Filters	Mass, organic	U.S. EPA, 1999a
(Forced Draft	chemical		carbon, elemental	, ,
Fan Inlet)	composition		carbon, organic	
S2	-		species, sulfate,	
			nitrate, chloride,	
			ammonium	
	VOC	Tenax	Speciated VOC	Zielinska et al., 1996
	SVOC	PUF/XAD-4/PUF	Speciated SVOC	U.S. EPA Method
				TO13
Fuel gas feed	Fuel gas	Integrated grab	Hydrocarbon	ASTM D3588; U.S.
to heater	composition	sample (bag or	speciation and	EPA Method 19
(S3)		canister)	heating value	
Fuel gas	Liquid	Composite grab	Ultimate analysis	ASTM D3176; U.S.
knockout drum	hydrocarbons	sample	(C, H, N, S, O,	EPA Method 19 (or
(S4)			ash), hydrocarbon	equivalent)
			speciation	

Table 3-1. Summary of Test Procedures

		Boiler Stack					
	Time	Velocity	Method 201/202	CEMS	Dilution Tunnel	Fuel Gas Samples	
		5					
7/1//1008	0.00						
Тие	10.00						
Tue	11.00						
	12.00						
	13.00						
	14.00						
	15:00						
	16:00						
	17:00						
	18:00	Preliminary	Moisture				
	19:00	18:52	18:42				
	20:00	19:53	19:27				
7/15/1998	9:00		l l				
Wed	10:00					* Grab	
	11:00			Stratification			
	12:00			12:11			
	13:00	Pre-test		13:18			
	14:00	14:27					
	15:00	14:56					
	16:00		R1 / 16:24	R1 / 16:24			
	17:00						
	18:00						
	19:00			18:58			
	20:00			20:05			
	21:00			21:34	-		
	22:00		22:24				
7/16/1998	9:00				4		
Thurs	10:00		R2 / 10:10	R2 / 10:22		* Grab	
	11:00						
	12:00			10.54			
	13:00			12:56			
	14:00			13:51			
	15:00		16.10	15:22	-		
	16:00		16:10	•			
	17:00						
	18:00						
	19:00						
	20:00						
	21:00						

Figure 3-1. Chronology for Gas-Fired Boiler (Refinery Site A).

		Boiler Stack					
	Time	Velocity	Method 201A/202	CEMS	Dilution Tunnel	Fuel Gas Samples	
7/17/1998	8:00		R3 / 8:15		Ambient / 8:30		
Fri	9:00			R3 / 9:14			
	10:00					* Grab	
	11:00			11:12			
	12:00			11:47			
	13:00						
	14:00		14:15	14:16			
	15:00						
	16:00				16:30		
	17:00						
7/18/1998	9:00						
Sat	10:00					* Grab	
	11:00						
	12:00			1 DT / 12:45	1 DT / 12:45		
	13:00						
	14:00						
	15:00			15:22*			
	16:00			16:27			
	17:00			10.40	10.40		
	18:00			18:48	18:48		
7/10/1000	19:00						
//19/1998	8:00						
Sun	9:00					* Croh	
	10.00			2 DT / 11-25	2 DT / 11-25	Glab	
	12:00			2 D1 / 11.55	2 D1 / 11.55		
	12.00						
	14.00			14.33*			
	15.00			14.54			
	16:00			1			
	17:00			17:30	17:30		
	18:00						
	19:00						
7/20/1998	8:00			3 DT / 8:45	3 DT / 8:45		
Mon	9:00						
	10:00					* Grab	
	11:00			11:22*			
	12:00			11:45			
	13:00						
	14:00	Post-test		14:45	14:45		
	15:00	15:56					
	16:00	16:14	-				
	17:00						

DT - Dilution tunnel testing run

*Run interrupted for calibration check

Figure 3-1 (continued). Chronology for Gas-Fired Boiler (Refinery Site A).



# Figure 3-2. CEMS Schematic.

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		Oxides of Carbon Carbon		Sulfur	
Instrument/	Oxygen	nitrogen	monoxide	dioxide	dioxide
Specification	(O ₂ )	(NO _x )	(CO)	(CO ₂ )	$(SO_2)$
Instrument manufacturer	Taylor-Servomex	Thermo- Electron	Thermo- Electron	ACS	Bovar/Western Research
Model Number	Model 1400	Model 10AR with molybdenum NO ₂ converter	Model 48H	Model 3300	Model 720 AT2
Detection principal	Paramagnetism	Chemi- luminescence	Gas filter correlation infrared absorption	Non-dispersive infrared absorption (NDIR)	Ultraviolet absorption (UV)
Units measured	%	ppmv	ppmv	%	ppmv
Detection limit	0.10%	1 ppm	0.5 ppm	0.10%	1 ppm
Ranges	0-25	0-100	0-100	0-20	0-100

Table 3-2. Description of CEMS Instrumentation used for Gas-Fired Boiler Test (Refinery Site A).

components were constructed of inert materials such as glass, stainless steel and tetrafluoroethylene (TFE). All components preceding the condenser (probe, sample line, sample bypass regulator, pump) were heated to  $248^{\circ}$  F to prevent condensation. The sample was conducted from the chiller outlet through the TFE line to a tertiary filter preceding the sample manifold. Samples were analyzed for O₂ and CO₂ using instrumental methods according to EPA Method 3A. Oxygen was measured using a paramagnetic analyzer, and CO₂ was measured using a non-dispersive infrared (NDIR) analyzer. Samples were analyzed for NO_x using a low-pressure chemiluminescent analyzer with a molybdenum nitrogen dioxide (NO₂)-to-nitric oxide (NO) converter according to EPA Method 7E. Sulfur dioxide was determined in the sample using a non-dispersive ultraviolet analyzer according to EPA Method 6C. Carbon monoxide was determined using a NDIR analyzer following EPA Method 10.

## **IN-STACK METHOD TESTS**

Total particulate, PM10 and PM2.5 filterable at stack temperature were determined using instack methods. CPM, defined as the material collected in chilled impingers, also was measured for the in-stack samples.

# In-Stack Total Filterable PM, PM10 and PM2.5

Two in-stack cyclones followed by an in-stack filter (Figure 3-3) were used to measure total particulate and particulate matter with nominal aerodynamic diameters less than or equal to 10  $\mu$ m (PM10) and 2.5  $\mu$ m (PM2.5). EPA Method 201A, modified to accommodate the second cyclone, was used following the constant-rate sampling procedure. Sampling time was six hours for each of the three runs. The sample recovery field procedure is summarized in Figure 3-4. Sampling was performed as published except for the following modifications and clarifications:

- A PM10 cyclone and a PM2.5 cyclone (Andersen Model Case-PM10 and Case-PM2.5) were attached in series to the filter inlet. Sample recovery procedures were modified accordingly;
- The sample was collected from a single traverse point near the center of the stack to preserve the integrity of the dilution tunnel method comparison. It was assumed that any particulate present was small enough to mix aerodynamically in the same manner as a gas; therefore, the magnitude of the particle concentration profile was assumed to be no greater than the gas concentration profile. Quartz filters were used. The filters were preconditioned in the same manner as those used in the dilution tunnel, as described below.

The particulate mass collected in the two cyclones and on the filter was determined gravimetrically (Figure 3-5). The Gelman filters (No. RPJ047) were weighed before and after testing on a microbalance with a sensitivity of 1 microgram. Pre- and post-test weighing was performed after drying the filters in a dessicator for a minimum of 72 hours; repeat weighings were then performed at a minimum of 6-hour intervals until constant weight was achieved. Probe and cyclone acetone rinses were recovered in glass sample jars for storage and shipment, then transferred to tared beakers for evaporation, finally to tared watch glasses for final evaporation and weighing. Acetone and filter blanks also were collected and analyzed. See Section 4 for discussion of data treatment.

Subsequent to these tests, EPA published preliminary method PRE-4, entitled "Test Protocol PCA PM10/PM2.5 Emission Factor and Chemical Characterization Testing" (U.S. EPA, 1999b). This protocol, developed by the Portland Cement Association (PCA), is intended for use by Portland cement plants to measure PM10 and PM2.5 emission factors applicable to a variety


Series cyclone and filter assembly

Figure 3-3. PM2.5/PM10 Train Configuration for Method 201A/202.



Figure 3-4. Method 201A (Modified) Sample Recovery Procedure.



Figure 3-5. Method 201A (Modified) Sample Analysis Procedure.

of particulate sources. Method PRE-4 describes substantially the same sampling equipment and sample collection procedures used in these tests. The analytical procedures differ slightly in the scope of chemical analysis performed.

Total particulate samples also were collected using EPA Method 17 (Figure 3-6). A 47-mm flat filter assembly loaded with quartz filters was used. Quartz filters are preconditioned in the same manner as those used in the dilution tunnel. These samples were used only for determination of in-stack OC, EC and speciated semivolatile organic compounds (SVOC). The analytical procedures were the same as those described below for dilution tunnel samples. These samples were collected at different times than the Method 201A/202 samples because of limited access at the sampling location (see Figure 3-1).



Figure 3-6. Sampling Train Configuration for EPA Method 17.

# Condensible Particulate Matter Mass and Chemical Analysis

CPM was determined using EPA Method 202. After the in-stack filter, the sample passed through a heated Teflon[®] line to a series of impingers placed in an ice bath used for the Method 201A train. The contents of the impingers were recovered with distilled deionized (DI) water and dichloromethane (Figure 3-7). The samples were analyzed in the laboratory according to the method, including optional analyses for sulfate and chloride (Figure 3-8). The method was performed as published except for the following modifications and clarifications:

- The impinger train consisted of 4 impingers. The first two impingers contained DI water, the third was empty, and the fourth contained silica gel. For Runs 1 and 3, the first and third impingers were modified Greenburg-Smith (G-S) type and the second was a standard G-S type. For Run 2 the first impinger was a modified G-S type and the second and third impingers were standard G-S type;
- A quartz filter was placed between the second and third impingers to improve capture efficiency and capture any aerosols that may have passed through the first two impingers, as described in the method as an optional procedure;
- The Method 202 impinger trains were not purged with nitrogen after the test because the post-test pH of the impinger solutions was greater than 4.5;
- Total sampling time was six hours for all runs;
- An aliquot of the impingers was analyzed for sulfate ion (SO₄⁻) by ion chromatography, as described in the method as an optional procedure;
- The first inorganic fraction drying step was finished at ambient temperature in a dessicator, as described in the method as an optional procedure;
- Ammonium hydroxide was added to the inorganic fraction during analysis to stabilize sulfate and chloride compounds, as described in the method;
- The inorganic fraction final residue was analyzed for chloride ion (Cl⁻) by ion chromatography, as described in the method as an optional procedure.
- Several months after the initial sample analysis, archived inorganic fraction residue samples (the unused portion of the dissolved residue that was initially analyzed for chloride) were analyzed for additional ions and elements by ion chromatography, colorimetry, and inductively coupled plasma mass spectrometry. This was performed to obtain more complete speciation of the inorganic CPM. Because of the age of these samples, some degradation may have occurred and the results should be considered qualitative.



Figure 3-7. Method 202 Sample Recovery Procedure.

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Figure 3-8. Method 202 Sample Modified Analysis Procedure.

#### DILUTION TUNNEL TESTS

PM2.5 mass and chemical speciation in the stack gas was determined using a dilution tunnel (Figure 3-9). A stainless steel probe with a buttonhook nozzle was used to withdraw the stack gas sample at a rate of approximately 30 liters per minute. The sample was transported through a heated copper line into the dilution tunnel. The sample was mixed in the tunnel with purified ambient air under turbulent flow conditions to cool and dilute the sample to near-ambient conditions. The ambient air used for dilution was purified using a high efficiency particulate air (HEPA) filter to remove particulate matter and an activated carbon bed to remove gaseous organic compounds. After passing through a tunnel length equal to 10 tunnel diameters, approximately 60 percent of the diluted sample was withdrawn into a large chamber, where the sample aged for approximately 80 seconds to allow low-concentration aerosols (especially organic aerosols) to fully form. The aged sample was withdrawn through two cyclone separators (each operating at a flow rate of approximately 110 liters per minute) to remove particles larger than 2.5 µm and delivered to the sample collection media (TMF, quartz filter, Tenax cartridge, and TIGF/PUF/XAD-4/PUF cartridge). The sample flow rate through the probe was monitored using a venturi flow meter and thermocouple. The venturi velocity head was measured continuously during the test with a Magnehelic[®] gauge. An S-type Pitot tube with electronic pressure transducer and thermocouple were used to monitor the velocity in the stack. The thermocouples and pressure transducers were connected to a laptop computer data acquisition system. The dilution airflow and back-pressure were adjusted to maintain the target dilution ratio and sample flow rates. Total sampling time for each test run was six hours.

A dilution ratio of approximately 40:1 was originally planned, consistent with the prior work of Hildemann et al. (1989). Hildemann selected this ratio both to cool the sample and to ensure complete mixing between the sample and dilution air prior to the residence time chamber takeoff. For these tests, flow rates were set in the field to achieve a dilution ratio of approximately 10:1 to improve minimum detection limits since very low concentrations of the target substances were anticipated. During a post-test calibration of the venturi it was discovered that the actual dilution ratio during testing was approximately 6:1. Hildemann's results suggest that mixing between the sample and the dilution air begins to degrade at a dilution ratio of approximately 10:1. Therefore, the sample drawn into the residence time chamber may have been incompletely mixed



Figure 3-9. Dilution Tunnel Sampling System.

3-16

with the dilution air. Based on profiles reported by Hildemann, this may produce a slight (estimated 10-20 percent) positive bias in the reported emission factors but should not affect chemical speciation profiles significantly.

A single ambient air sample was collected using the dilution tunnel. The dilution tunnel setup was modified by removing the sample probe and attaching a special inlet adapter in place of the HEPA and charcoal filters. The ambient air sample was drawn into the tunnel without dilution through the special inlet adapter. The sampling period was increased to eight hours to improve minimum detection limits. The same sampling media were used as described below and in Figure 3-8.

#### PM2.5 Mass

Samples for PM2.5 mass measurements were collected on a 47-mm diameter Gelman #RPJ047 polymethylpentane ringed, 2.0  $\mu$ m pore size, TMF placed in an aluminum filter holder. The filter packs were equipped with quick release connectors to ensure that no handling of the filters was required in the field. The flow rate through the filter was set prior to sample collection and checked after sample collection by placing a calibrated rotameter on the inlet side of the copper sampling line and setting the position of the needle valve to achieve the desired flow rate. Weighing was performed on a Cahn 31 electro-microbalance with  $\pm 1$  microgram sensitivity.

#### **Elements**

Energy dispersive x-ray fluorescence (ED-XRF) analysis was performed on the TMFs for the following 40 elements: aluminum (Al), silver (Ag), arsenic (As), gold (Au), barium (Ba), bromine (Br), calcium (Ca), cadmium (Cd), chlorine (Cl), cobalt (Co), chromium (Cr), copper (Cu), iron (Fe), gallium (Ga), mercury (Hg), indium (In), potassium (K), lanthanum (La), magnesium (Mg), manganese (Mn), molybdenum (Mo), sodium (Na), nickel (Ni), phosphorus (P), lead (Pb), palladium (Pd), rubidium (Rb), sulfur (S), antimony (Sb), selenium (Se), silicon (Si), tin (Sn), strontium (Sr), titanium (Ti), thallium (Tl), uranium (U), vanadium (V), yttrium (Y), zinc (Zn), and zirconium (Zr). Magnesium and Na results are considered semi-quantitative because of analytical technique limitations.

A Kevex Corporation Model 700/8000 ED-XRF analyzer with a side-window, liquid-cooled, 60 keV, 3.3 milliamp rhodium anode x-ray tube and secondary fluorescers was used. The silicon detector had an active area of 30 mm², with a system resolution better than 165 eV. The analysis was controlled, spectra were acquired, and elemental concentrations were calculated by software on a microcomputer which was interfaced to the analyzer. Five separate XRF analyses were conducted on each sample to optimize the detection limits for the specified elements. The filters were removed from their petri slides and placed with their deposit sides downward into polycarbonate filter cassettes. A polycarbonate retainer ring kept the filter flat against the bottom of the cassette. The cassettes were loaded into a carousel in the x-ray chamber. The sample chamber was evacuated to  $10^{-3}$  Torr. A computer program controlled the positioning of the samples and the excitation conditions. Complete analysis of 16 samples under five excitation conditions required approximately 6 hours.

# Sulfate, Nitrate, Chloride and Ammonium

Samples for determining water-soluble Cl⁻, nitrate (NO₃⁻), SO₄⁼ and ammonium (NH₄⁺) were collected on quartz fiber filters. The flow rate through the filter holder was set prior to sample collection and checked after sample collection by placing a calibrated rotameter on the outlet of the holder and setting the position of the needle valve to achieve the desired flow rate.

Each quartz fiber filter was cut in half, and one filter half was placed in a polystyrene extraction vial with 15 ml of DI water. The remaining half was used for determination of OC and EC as described below. The extraction vials were capped and sonicated for 60 minutes, shaken for 60 minutes, then aged overnight to assure complete extraction of the deposited material. After extraction, these solutions were stored under refrigeration prior to analysis. The unanalyzed filter half was archived in the original petri slide. Chloride ion,  $NO_3^-$ , and  $SO_4^-$  were measured with a Dionex 2020i ion chromatograph (IC). Approximately 2 ml of the filter extract was injected into the ion chromatograph.

A Technicon TRAACS 800 Automated Colorimetric System (AC) was used to measure  $NH_4^+$  concentrations by the indolphenol method. Each sample was mixed with reagents and subjected to appropriate reaction periods before submission to the colorimeter. Beer's Law relates the

liquid's absorbency to the amount of the ion in the sample. A photomultiplier tube measured this absorbency through an interference filter which is specific to  $NH_4^+$ . Two ml of extract in a sample vial were placed in a computer-controlled autosampler. Technicon software operating on a microcomputer controlled the sample throughput, calculated concentrations, and recorded data.

#### Organic and Elemental Carbon

Quartz fiber filters were used to collect samples for determination of OC and EC mass (see above). The filters were heated in air for at least three hours at approximately 900°C prior to use. Pre-acceptance testing was performed on each lot of filters. Filters with levels exceeding 1.5 micrograms per square centimeter ( $\mu$ g/cm²) of OC and 0.5  $\mu$ g/cm² of EC were refired or rejected. Pre-fired filters were sealed and stored in a freezer prior to preparation for field sampling.

The thermal/optical reflectance (TOR) method was used to determine OC and EC on the quartz filters. The TOR method is based on the principle that different types of carbon-containing particles are converted to gases under different temperature and oxidation conditions. The TOR carbon analyzer consists of a thermal system and an optical system. Reflected light is continuously monitored throughout the analysis cycle. The negative change in reflectance is proportional to the degree of pyrolytic conversion of carbon that takes place during OC analysis. After oxygen is introduced, the reflectance increases rapidly as the light-absorbing carbon burns off the filter. The carbon measured after the reflectance attains the value it had at the beginning of the analysis cycle is defined as EC.

#### Volatile Organic Compounds

Glass cartridges filled with Tenax-TA (a polymer of 2,6-diphenyl-p-phenylene oxide) solid adsorbent were used to collect VOC samples. Two Tenax cartridges in parallel were used simultaneously for each test run due to the low concentrations expected in the sample. Each cartridge contained approximately 0.2 grams of Tenax resin. A sample rate of approximately 0.1 liters per minute through each Tenax tube was used. The flow rate through the Tenax cartridges was set prior to sample collection and checked after sample collection by placing a rotameter on

the outlet of each Tenax tube and setting the position of the needle valve to achieve the desired flow rate.

The Tenax samples were analyzed by the thermal desorption-cryogenic preconcentration method, followed by high resolution gas chromatographic separation and flame ionization detection (FID) of individual hydrocarbons for peak quantification, and/or combined mass spectrometric/Fourier transform infrared detection (MSD/FTIR), for peak identification. The resultant peaks were quantified and recorded by the chromatographic data systems.

# Semivolatile Organic Compounds

SVOCs were determined in two different samples: dilution tunnel filter/absorbent cartridges and in-stack filters. The dilution tunnel samples were collected using a filter followed by an adsorbent cartridge. The media used for collecting SVOCs were as follows:

- Pallflex (Putnam, CT) T60A20 102-mm TIGF filters;
- PUF sheets, purchased from E.R. Carpenter Company, Inc. (Richmond, VA) and cut into 2-inch diameter plugs;
- XAD-4 resin (20-60 mesh) purchased from Aldrich Chemical Company, Inc.

The sample was transferred from the aging chamber through a 1/2-inch copper manifold leading to a momentum diffuser chamber. The diffuser chamber is followed by the cartridge holder and is connected to a vacuum pump through a needle valve. The flow through the sampler was set prior to sample collection by placing a calibrated rotameter on the inlet side of the copper sampling line and setting the position of the needle valve to achieve the desired flow rate.

The samples were isotopically spiked, extracted in dichloromethane, and concentrated prior to analysis. Sample extracts were analyzed by the electron impact (EI) gas chromatography/mass spectrometric (GC/MS) technique, using a Hewlett-Packard 5890 GC equipped with a model 7673A Automatic Sampler and interfaced to a model 5970B Mass Selective Detector (MSD). To assist in the unique identification of individual compounds, selected samples were analyzed by combined gas chromatography/Fourier transform infrared/mass spectrometry (GC/IRD/MSD)

technique, i.e., using the Fourier transform infrared detector to aid mass spectrometric identification. Quantification of polyaromatic hydrocarbon (PAH), and other compounds of interest, was obtained by multiple ion detection (MID).

# Section 4

### TEST RESULTS

All stack emission results are presented in units of milligrams per dry standard cubic meter (mg/dscm) and pounds per hour (lb/hr). Concentrations are corrected to a standard temperature of 68°F and a standard pressure of 29.92 inches of mercury unless otherwise indicated. See the conversion factors presented at the beginning of this report to convert results to SI units. Compounds that were not detected in any of the three runs generally are not listed on the tables. Where shown, undetected data are flagged "ND", treated as zeroes in sums, and excluded from averaged results. The approximate minimum in-stack detection limits achieved for all measured substances are given in Table 4-1.

# PROCESS OPERATING CONDITIONS

Boiler operating conditions during testing are summarized in Table 4-2. The boiler operated at 53 to 59 percent of full steam capacity during the tests. Superheated steam was delivered at approximately 640 pounds per square inch gauge (psig) and 740°F. Excess  $O_2$  measured at the boiler outlet (upstream of the air heater) was 3.6-5.2 percent.

The average fuel higher heating value (HHV) during each test was calculated from fuel gas grab sample analysis results (Table 4-3) and normalized over the entire run using the specific gravity of the grab sample and the average specific gravity measured by continuous specific gravity monitor. The average heat input to the boiler during the test is the product of average fuel gas flow rate and the average fuel HHV. The average heat input was used to convert in-stack emission rates (lb/hr) to emission factors (lb/MMBtu), which are presented in Section 5. The concentration of  $H_2S$  in the fuel gas in parts per million by volume (ppmv) was calculated from continuous  $H_2S$  monitor data using the specific gravity of the fuel and the  $H_2S$  concentration in grains per 100 standard cubic feet (gr/100scf).

# PRELIMINARY TEST RESULTS

Preliminary tests were conducted to establish a single point in the stack for sample collection. The O₂ concentration profile was measured prior to testing by traversing the CEMS probe across

4-1

	In-stack methods	mg/dscm	3.4E-06	1.1E-06	1.4E-03	3.8E-05	5.6E-07	3.7E-05	6.2E-06	5.6E-07	1.9E-05	1.5E-04	1.1E-06	1.6E-05	3.4E-06	4.5E-06	1.7E-05	3.4E-06	3.5E-05	5.6E-07	8.4E-06	5.6E-07	5.6E-07	1.1E-06	6.8E-05	5.3E-07	3.4E-06	4.5E-06	5.4E-04	5.6E-04	1.1E-06	4.5E-06	2.2E-06	3.4E-05	2.2E-06	1	1.3E+00
	Dilution	mg/dscm	3.2E-07	1.1E-07	1.3E-04	3.6E-06	5.3E-08	3.5E-06	5.8E-07	5.3E-08	1.8E-06	1.4E-05	1.1E-07	1.5E-06	3.2E-07	4.2E-07	1.6E-06	3.2E-07	3.3E-06	5.3E-08	8.0E-07	5.3E-08	5.3E-08	1.1E-07	6.4E-06	5.0E-08	3.2E-07	4.3E-07	5.1E-05	5.2E-05	1.1E-07	4.2E-07	2.1E-07	3.2E-06	2.1E-07	3.0E-02	:
(A).		Substance	Benzo(ghi)pervlene	Benzonaphthothiophene	Bibenzene	Biphenvl	B-MePy/MeFl	B-methyl fluorene	B-methvlphenanthrene	B-trimethylnaphthalene	<b>C-dimethylphenanthrene</b>	Cholestane	Chrysene	C-methylphenanthrene	Coronene	<b>C-trimethylnaphthalene</b>	D-dimethylphenanthrene	Dibenz(ah+ac)anthracene	Dibenzofuran	D-MePy/MeFl	E-dimethvlphenanthrene	E-MePy/MeFl	E-trimethylnaphthalene	Fluoranthene	Fluorene	F-trimethylnaphthalene	Indeno[123-cd]pyrene	J-trimethylnaphthalene	Naphthalene	Perinaphthenone	Perylene	Phenanthrene	Pyrene	Retene	Xanthone	Volatile Organic Compounds	NU, CU
etinery	In-stack methods	mg/dscm	3.5E-05	1.1E-06	5.6E-07	2.6E-05	1.3E-04	0.0E+00	1.1E-05	1.1E-06	0.0E+00	3.4E-06	3.9E-06	1.7E-06	1.5E-05	7.5E-05	2.6E-05	1.5E-05	3.4E-06	5.8E-05	2.6E-05	5.9E-05	2.7E-05	5.6E-07	0.0E+00	3.0E-05	5.6E-07	1.1E-06	1.9E-05	3.4E-06	2.1E-05	5.1E-06	3.4E-06	1.1E-06	5.6E-07	6.2E-06	3.4E-06
ests (Ko	Dilution	mg/dscm	3.3E-06	1.1E-07	5.3E-08	2.5E-06	1.2E-05	0.0E+0.0	1.0E-06	1.1E-07	0.0E+0.0	3.3E-07	3.7E-07	1.6E-07	1.4E-06	7.1E-06	2.4E-06	1.4E-06	3.2E-07	5.5E-06	2.5E-06	5.6E-06	2.5E-06	5.3E-08	0.0E+00	2.9E-06	5.3E-08	1.0E-07	1.8E-06	3.2E-07	2.0E-06	4.8E-07	3.2E-07	1.1E-07	5.3E-08	5.8E-07	3.3E-07
for Uas-Fired Boiler 16		Substance	2-methvlnaphthalene	2-methylphenanthrene	2-phenylnaphthalene	3,6-dimethylphenanthrene	3-methylbiphenyl	4H-cyclopenta(def)phenanthrene	4-methylbiphenyl	4-methylpyrene	5+6-methylchrysene	7-methylbenz(a)anthracene	7-methylbenzo(a)pyrene	9,10-dihydrobenzo(a)pyrene	9-anthraldehyde	9-fluorenone	9-methylanthracene	Acenaphthene	Acenaphthenequinone	Acenaphthylene	A-dimethylphenanthrene	A-methylfluorene	A-methylphenanthrene	A-methvlpvrene	Anthracene	Anthraquinone	Anthrone	A-trimethylnaphthalene	<b>B-dimethylphenanthrene</b>	Benz(a)anthracene	Benz(a)anthracene-7,12	Benzanthrone	Benzo(a)pyrene	Benzo(b)chrysene	Benzo(b+j+k)fluoranthene	Benzo(c)phenanthrene	Benzo(e)pyrene
nieved	In-stack methods	mg/dscm	1	ł	ł	ł	ł	ł	ł	ł	ł	ł	ł	ł	5.8E-02	1.3E-02	3.4E-06	3.9E-05	1.3E-04	5.3E-05	5.7E-05	2.8E-06	1.9E-05	3.9E-05	7.2E-05	1.1E-06	9.0E-06	3.7E-05	2.1E-05	1.2E-05	4.5E-06	2.8E-06	1.7E-06	4.5E-06	6.0E-05	9.3E-05	8.9E-05
Its Acl	Dilution	mg/dscm	6.9E-06	1.8E-05	1.6E-05	1.4E-05	1.6E-05	8.1E-06	6.9E-06	1.1E-05	7.3E-04	7.3E-04	7.3E-04	7.3E-04	5.5E-03	1.3E-03	3.2E-07	3.7E-06	1.2E-05	5.0E-06	5.4E-06	2.7E-07	1.8E-06	3.7E-06	6.8E-06	1.1E-07	8.5E-07	3.5E-06	2.0E-06	1.2E-06	4.2E-07	2.7E-07	1.6E-07	4.2E-07	5.7E-06	8.8E-06	8.4E-06
e In-Stack Detection Lim		Substance	Sr	Ti	TI	U	Λ	Y	Zn	Zr	S04=	NO3-	NH4+	CI-	00	EC	1,2,8-trimethylnaphthalene	1.2-dimethylnaphthalene	1,3+1,6+1,7-dimethylnaphthalene	1,4,5-trimethylnaphthalene	1,4+1,5+2,3-dimethylnaphthalene	1,4-chrysenequinone	1,7-dimethylphenanthrene	1.8-dimethylnaphthalene	1+2-ethylnaphthalene	1-ethyl-2-methylnaphthalene	1-MeFl+C-MePv/Fl	1-methylfluorene	1-methylnaphthalene	1-methylphenanthrene	1-methylpyrene	1-phenylnaphthalene	2.3.5+I-trimethylnaphthalene	2,4,5-trimethylnaphthalene	2,6+2,7-dimethylnaphthalene	2-ethyl-1-methylnaphthalene	2-methylbiphenyl
<b>XIMA</b>	In-stack methods	mg/dscm	2.6E-04	2.6E-04	2.6E-04	ł	ł	ł	1	ł	ł	1	ł	ł	1	ł	ł	ł	ł	1	ł	1	1	I	ł	1	1	ł	ł	1	1	ł	ł	1	ł	1	;
Appro	Dilution	mg/dscm	1	I	4.8E-04	7.5E-05	6.2E-05	1.0E-05	1.9E-05	3.2E-04	6.2E-06	2.8E-05	7.5E-05	6.2E-05	5.5E-06	1.2E-05	6.9E-06	9.4E-06	1.2E-05	1.6E-05	8.1E-05	3.8E-05	3.9E-04	0.0E+00	1.0E-05	1.7E-05	0.0E+00	5.5E-06	3.5E-05	1.9E-05	6.9E-05	6.2E-06	3.1E-05	1.1E-04	7.5E-06	3.9E-05	1.1E-04
able 4-1.		Substance	fotal PM mass	PM10 mass	PM2.5 mass	Ag	AI	As	Au	Ba	Br	Ca	Cd	G	Co	Cr	Cu	Fe	Ga	Нд	In	K	La	Mg	Mn	Mo	Na	N	Р	Pb	Pd	Rb	S	Sb	Se	S	Sn

1 and 1 2. 1100033 Dam 101 043 1 1104 DOILDI	VILLAL D DILLA	· • )·						
DATE	Units	14-Jul-98	15-Jul-98	16-Jul-98	17-Jul-98	18-Jul-98	19-Jul-98	20-Jul-98
Steam Flow	Mlb/hr	262	315	315	310	303	310	325
Main Steam Pressure	psig	637	642	643	641	639	642	646
Main Steam Temperature	ч°	732	742	741	735	732	736	746
Fuel Flow Rate	MMscfd	7.43	8.03	7.94	7.46	7.04	7.34	8.12
Excess $O_2$ (boiler outlet, wet basis)	$\Lambda^{0}_{0}$	5.17	3.89	3.78	4.79	4.76	4.37	3.59
Boiler Outlet Flue Gas Temperature (Before Air Heater)	ч°	638	647	645	650	644	646	653
Fuel Gas Specific Gravity	I	0.702	0.710	0.712	0.756	0.778	0.763	0.731
$ m H_2S$ in Blended Fuel Gas Header	gr/100scf	1.94	2.00	3.21	2.89	2.01	4.04	2.58
H ₂ S ⁽¹⁾	bpm	30.8	31.8	51.1	46.0	32.0	64.2	41.1
Fuel Gas Net Heating Value (at header)	Btu/scf	1043	1055	1055	1107	1127	1103	1064
Fuel Heat Input	MMBtu/hr	364	397	394	392	380	389	413
	57 F							

Process Data for Gas-Fired Boiler (Refinery Site A) Table 4-2 ⁽¹⁾calculated from plant process monitors using specific gravity and gr/100scf.

4-3

MIb/hr = thousand pounds per hour psig = pounds per square inch (gauge) °F = degrees Farenheit MMscfd = million standard cubic feet per day gr/100scf = grains per hundred standard cubic feet Btu/scf = British thermal units per standard cubic foot MMBtu/hr = million British thermal units per hour

ppm = parts per million

Date	Units	7/15/1998	7/16/1998	7/17/1998	7/18/1998	7/19/1998	7/20/1998
Specific Gravity		0.75	0.77	0.82	0.84	0.79	0.86
Net Heating Value	Btu/cu. ft.	1167	1182	1258	1287	1106	1306
Gross Heating	Btu/cu. ft.	1281	1297	1378	1409	1231	1429
Value							
Hydrogen	Mol %	33.0	31.5	25.1	25.0	24.5	21.9
Oxygen	Mol %	ND	0.1	ND	ND	1.0	ND
Nitrogen	Mol %	1.9	2.2	2.0	2.2	8.0	2.1
Carbon Dioxide	Mol %	0.2	0.2	0.3	0.2	0.4	0.3
Carbon Monoxide	Mol %	0.4	0.4	0.4	0.4	0.3	0.4
Methane	Mol %	22.8	24.2	27.5	25.7	27.2	29.7
Ethylene	Mol %	3.9	3.9	4.0	4.0	3.8	3.6
Ethane	Mol %	22.0	21.1	22.9	23.6	21.0	19.7
Propylene	Mol %	1.1	1.0	1.3	1.5	0.9	3.9
Propane	Mol %	5.9	5.7	6.7	6.7	5.3	9.5
Isobutane	Mol %	2.0	2.1	2.0	2.4	1.7	1.9
Normal Butane (C4)	Mol %	4.2	4.6	4.9	5.1	3.9	4.3
1- Butene	Mol %	0.1	0.1	0.0	0.1	ND	0.1
Iso Butylene	Mol %	0.1	0.1	0.1	0.1	ND	0.1
Cis-2-Butene	Mol %	0.1	0.1	0.1	0.1	ND	0.1
Trans-2-Butene	Mol %	0.1	0.1	0.1	0.1	ND	0.1
Isopentane	Mol %	1.2	1.2	1.2	1.4	1.0	1.1
Normal Petane (C5)	Mol %	0.3	0.3	0.3	0.4	ND	0.3
C6 and Heavier	Mol %	1.0	1.1	1.1	1.1	0.9	1.0

Table 4-3. Fuel Gas Analyses for Gas-Fired Boiler (Refinery Site A).

ND - not detected

the stack, while measuring  $O_2$  simultaneously with a second system at a single point in the stack. The data from the second system were used to correct the spatial traverse results for temporal variations. The deviation from the average concentration was determined to be less than ten percent (Table 4-4). Under the conditions of these tests, fine particles are expected to mix like a gas. Therefore, it is assumed that the magnitude of any fine particle concentration profile that may have existed was similar to the  $O_2$  concentration profile. A velocity profile was developed by traversing the stack with the Pitot probe. Several points near the central region of the stack also were traversed, corresponding to the location of the co-located sampling probes. The resulting velocity profile was used to correct the velocities measured at the center during sampling to the overall stack average velocity.

# STACK GAS CONDITIONS AND FLOW RATE

A summary of the stack gas conditions during testing is presented in Table 4-5. Average stack gas temperature during the tests was 341-364°F. The O₂ concentration at the stack was 6.5-8.2

Date:	15-Jul-98					
Port	Traverse Point	Distance from the stack wall (inches)	Sampling Time (hh:mm)	O ₂ (%)*	Reference O ₂ (%)**	Normalized O ₂ (%)***
2	8	124	13:08	7.25	7.03	7.25
	7	115	13:12	7.17	7.05	7.15
	6	104	13:16	7.02	7.00	7.05
	5	87	13:20	7.33	7.03	7.33
	4	41.5	13:24	7.37	7.04	7.36
	3	24.9	13:28	7.41	7.05	7.39
	2	13.5	13:32	7.29	7.01	7.31
	1	4.1	13:36	7.33	7.03	7.33
1	8	124	13:45	6.72	7.02	6.73
	7	115	13:49	6.68	6.99	6.72
	6	104	13:53	6.73	7.02	6.74
	5	87	13:57	6.73	7.02	6.74
	4	41.5	14:01	6.90	6.97	6.96
	3	24.9	14:05	7.28	6.90	7.42
	2	13.5	14:09	7.37	7.03	7.37
	1	4.1	14:13	7.26	7.01	7.28
Ref point	: Port 2 Point 2		Maximum	7.41	7.05	7.42
			Minimum	6.68	6.90	6.72
			Average	7.12	7.01	7.13
			Stratifica	tion		9.8%

Table 4-4. Stratification Data for Gas-Fired Boiler (Refinery Site A).

Facility: Refinery Site A

Unit: Gas-Fired Boiler

15 1.1 00 **D** /

Stratification = 100*(maximum-minimum)/average

* this probe was traversed

** this probe remained stationary

***traverse O2 normalized for variations in O2 measured by stationary probe

percent (dry basis) during the tests, higher than at the boiler outlet, which corresponds to approximately 25 percent air leakage in the air heater. This is slightly high but within the normal range for regenerative air heaters, especially considering the low load operating conditions. The CO₂ and moisture concentrations are roughly consistent with the carbon and hydrogen contents of the fuel gas. The moisture content of the flue gas on July 20 was not measured; it was

estimated by averaging the moisture content measured on July 15-17. Stack gas flow rate during dilution tunnel testing on July 20 was calculated using this estimated value. The stack gas flow rates on July 18 and 19 were not measured directly. They were calculated by combustion calculations derived from the fuel gas analysis, CEMS and process data using the dry F factor procedure given in EPA Method 19. The F factor was adjusted slightly based on measured flow rates on July 14-17.

	Units	Day 1	Day 2	Day 3	Day 4	Day 5	Day 6	Day 7
Date		14-Jul-98	15-Jul-98	16-Jul-98	17-Jul-98	18-Jul-98	19-Jul-98	20-Jul-98
Stack Temperature	°F	344	344	347	350	343	364	341
$O^2$ (dry)	%v		7.27	7.08	8.00	8.16	7.22	6.53
$\rm CO^2  (dry)$	%v		8.32	8.39	7.92	7.91	8.44	8.81
Moisture	%v	16.20 ⁽¹⁾	16.80	16.40	15.40			16.20 ⁽¹ )
Velocity	ft/sec	36.8	34.9	33.3	33.4			38.0
	m/sec	11.2	10.7	10.1	10.2			11.6
Flow Rate	acfm	216,500	194,300	195,000	194,800			224,200
	dscfm	116,000	104,700	104,800	106,100	111,800 ⁽²⁾	97,300 ⁽²⁾	121,000
	dscmm	328,6	2,960	2,970	3,000	3,200 ⁽²⁾	2,760 ⁽²⁾	3,430

Table 4-5. Stack Gas Summary for Gas-Fired Boiler (Refinery Site A).

⁽¹⁾ Moisture on 7/14 and 7/20 estimated based on average moisture on 7/15, 7/16, 7/17.

 $^{(2)}$ Flow rates estimated using F factor, O₂, fuel gas flow rate, and correction factor derived from direct flow measurements on other days.

ft/sec = feet per second

m/sec = meters per second

acfm = actual cubic feet per minute

dscfm = dry standard cubic feet per minute

dscmm = dry standard cubic meters per minute

### CO, NO_X AND SO₂ EMISSIONS

Nitrogen Oxide and SO₂ are precursors of secondary particulate matter. Average NO_X and SO₂ concentrations (corrected to 3 percent O₂, dry basis) were 73-79 ppmv and 3-6 ppmv, respectively (Table 4-6). The data are corrected for analyzer drift and bias. The NO_X concentration is at the lower end of the typical range for gas-fired boilers. This is fairly typical for tangentially fired furnace designs, which tend to produce lower NO_X emissions compared to wall-fired and most other designs. The SO₂ concentration is nominally consistent with the measured H₂S concentration in the fuel gas, assuming total conversion to SO₂. Carbon monoxide is an indicator of boiler combustion performance. Carbon monoxide typically fluctuated relatively rapidly about an average of approximately 30 ppmv during the tests,

	Date	7/15/1998	7/16/1998	7/17/1998	7/18/1998	7/19/1998	7/20/1998
	Run No	In-Stack	In-Stack	In-Stack	Dilution	Dilution	Dilution
		Run 1	Run 2	Run 3	Run 1	Run 2	Run 3
	Time Period	16:24-	10:22-	09:14-	12:45-	11:35-	08:45-14-
		21:34	15:22	14:15	18:48	17:30	45
	$O_2$ (%)	7.27	7.08	8.00	8.16	7.22	6.53
CO	ppm (dry, as	29	28	10	17	19	34
	measured)						
	ppm (dry, 3% O ₂ )	38	37	13	23	25	42
	lb/hr	13	13	4.4	8.2	7.9	18
NO _X	ppm (dry, as	26	58	57	52	57	61
	measured)						
	ppm (dry, 3% O ₂ )	34	76	79	73	74	76
	lb/hr	20	44	43	42	40	53
$SO_2$	ppm (dry, as	4.1	3.8	4.1	2.2	4.1	3.2
	measured)						
	ppm (dry, 3% O ₂ )	5.4	4.9	5.6	3.1	5.4	3.9
	lb/hr	4.4	4.0	4.4	2.4	4.0	3.7

Table 4-6. CEMS Data for Gas-Fired Boiler (Refinery Site A).

indicating slight combustion inefficiency in the boiler. The fireball in the boiler furnace appeared somewhat lazy with a few areas that were bright orange in color (indicating the presence of soot particles), providing visual confirmation of imperfect combustion conditions. This is probably an artifact of low load operation and is not considered unusual for the operating conditions.

# IN-STACK AND IMPINGER METHOD RESULTS

#### Particulate Mass

Filterable particulate matter (FPM) results as measured by Method 201A are presented in Table 4-7. Total FPM, which includes all particulate collected in the in-stack nozzle/cyclone assembly and on the in-stack filter, ranged from 0.027 to 0.42 mg/dscm. Because of a relatively large catch in the first cyclone rinse, FPM in Run 1 was several times greater than the other two runs. FPM < 10 micrometers, which includes the portion of total FPM collected downstream of the PM10 cyclone, was 0.027 mg/dscm in Run 2 and below detection limits in Runs 1 and 3. FPM < 2.5 micrometers, which includes the portion of FPM collected downstream of the PM2.5 cyclone, was the same as FPM < 10 micrometers. All the filters had a light coating of visible soot deposits, which is consistent with the observations noted above for the CO results and boiler

4-7

furnace observations. The net weight gains in the cyclone rinses and on the filters were extremely low, in the range of 0-0.5 milligrams (mg). The detection limit of the analytical balance used to weigh the samples was 1 microgram (0.001 mg). Final results are corrected for acetone field recovery blank results.

	Units		Value	Value	Value	Average	RSD
Run Number	-	Ι	In-stack Run 1	In-stack Run 2	In-stack Run 3		
Date	-		15-Jul-98	16-Jul-98	17-Jul-98		
Total FPM	mg/dscm		0.42	0.053	0.027	0.17	132%
	lb/hr		0.17	0.021	0.011	0.066	132%
FPM<10 µm	mg/dscm	(1)	ND	0.027	(1) ND	0.027	n/a
	lb/hr	(1)	ND	0.010	(1) ND	0.010	n/a
FPM<2.5 μm	mg/dscm	(1)	ND	0.027	(1) ND	0.027	n/a
	lb/hr	(1)	ND	0.010	(1) ND	0.010	n/a

Table 4-7. Filterable Particulate Matter (Method 201A) for Gas-Fired Boiler (Refinery Sites A).

(1) The acetone blank correction causes these results to fall below zero, they are reported here as "ND" The average does not include zero values.

n/a = not applicable; only one run within detectable limits

RSD = relative standard deviation

ND = not detected

FPM = filterable particulate matter

In some cases, the acetone field recovery blank weight exceeded the sample weight resulting in net weights less than zero. The net filter weights (including the field blank) all were a few micrograms less than zero, probably due to the loss of miniscule pieces of the filters during sample recovery. Because of this, the reported particulate result for each run is attributed entirely to the acetone rinses. The total net weight gain in field blank train was very similar to the sample results. Although an analytical resolution of 1 microgram was achieved for the samples, the results suggest that the particulate mass loading at the stack in these tests may be near or below the practical limits of the overall method.

Table 4-8 presents results for CPM as measured using Method 202. CPM concentration was approximately 200 times greater than FPM for runs 2 and 3; it was only 23 times higher for Run 1. Eighty-nine to ninety-nine percent of the CPM was found in the inorganic fraction, with two of the three runs exceeding 96 percent. The inorganic CPM (and hence the total CPM) results are reasonably consistent from run to run, with a standard deviation of 38 percent of the average

result. Run 2 organic CPM was several times greater than the other two runs. Since operating conditions were similar for all three runs and no unusual events occurred during Run 2, this variation can most likely be attributed to measurement procedures and the extremely small net weight gains.

Parameter	Units	Value				
Run Number	-	Run 1	Run 2	Run 3	Average	RSD
Date	-	15-Jul-	16-Jul-	17-Jul-		
		98	98	98		
Inorganic CPM	mg	38.9	44.6	19.6	34.4	38%
	mg/dscm	10.3	11.8	5.2	9.1	38%
	lb/hr	4.03	4.64	2.1	3.6	37%
Organic CPM	mg	0.80	5.60	0.80	2.4	115
						%
	mg/dscm	0.212	1.49	0.215	0.639	115
						%
	lb/hr	0.08	0.58	0.09	0.251	115
						%
Dichloromethane Recovery	mg	1.11				
Blank						
Water Recovery Blank	mg	1.3				
Sulfate in Impingers (as SO4=)	mg/dscm	1.56	1.83	1.08	1.49	25%
	lb/hr	0.612	0.717	0.429	0.586	25%
Chloride (as NH4Cl)	mg/dscm	0.540	0.541	0.314	0.46	28%
	lb/hr	0.211	0.212	0.125	0.183	28%
Total CPM	mg/dscm	10.0	12.8	4.9	9.2	43%
(corrected for blanks, NH4+ and H2O)	lb/hr	3.90	5.00	1.95	3.618	43%

Table 4-8. Condensible Particulate for Gas-Fired Boiler (Refinery Site A).

RSD - relative standard deviation

CPM = condensible particulate matter

 $SO_4 = =$  sulfate ion

 $NH_4Cl = ammonium chloride$ 

 $NH_4$ + = ammonium ion

 $H_2O = water$ 

Total CPM results have been corrected for dichloromethane and water recovery blank results. The data also are corrected for ammonium ion retained and combined water released in the acid base titration. These data handling procedures follow Method 202. For two of the runs, the dichloromethane blank weight exceeded the organic CPM weight. Therefore, separate results for inorganic and organic CPM shown in Table 4-8 are not blank corrected.

The  $SO_4^{=}$  content of the raw impinger contents and the Cl⁻ content of the inorganic residue were determined following Method 202. Sulfate mass, expressed as sulfate ion, accounts for approximately 60 percent of the total CPM. Although  $SO_4^{=}$  was measured in an aliquot of the raw impinger contents prior to the organic extraction, it is assumed that any  $SO_4^{=}$  present partitions to the inorganic fraction. Chloride mass in the inorganic residue, expressed as ammonium chloride, accounts for approximately 20 percent of the total CPM. To confirm these somewhat surprising results, the inorganic residue was re-analyzed for a broader range of elements and ions several months after the original analysis. On average, the second analysis showed  $SO_4^{=}$ , Cl⁻ and NH₄⁺ account for 6.0 mg/dscm, or 77 percent, of the total CPM (Table 4-9). Sodium, K, and Ca account for an average of 0.76 mg/dscm, or 8 percent, of the total average CPM. The remaining 16 elements and ions that were detected account for an average of 0.3 mg/dscm, or 3 percent, of the average CPM.

		0		mg/o	dscm				
	]	Run No. 1	Ru	ın No. 2	Rı	ın No. 3		Average	RSD (%)
Al	<	0.013		0.013		0.020	$\langle$	0.016	25
Ba		0.0072		0.013		0.010		0.010	30
Be		ND		D		ND		ND	n/a
Cd	<	0.0015	<	0.0015	<	0.0015	<	0.0015	0.6
Ca	<	0.088	<	0.089	<	0.089	<	0.089	0.6
Cr	<	0.0017	<	0.0017	<	0.0018	<	0.0017	0.6
Co		ND		ND		ND		ND	n/a
Cu		0.0048		0.0043		0.0072		0.0054	28
Fe		0.033		0.0067		0.014		0.018	78
Pb	<	0.0094	<	0.0094	<	0.0095	<	0.0094	0.6
Mg	<	0.023	<	0.023	<	0.023	<	0.023	0.6
Mn	<	0.0027	<	0.0027	<	0.0027	<	0.0027	0.6
Мо		ND		ND		ND		ND	n/a
Ni		ND		ND		ND		ND	n/a
Р	<	0.027	<	0.027	<	0.027	<	0.027	0.6
Κ	<	0.44	<	0.44	<	0.45	<	0.44	0.6
Ag		ND		ND		ND		ND	n/a
Na		0.29		0.21		0.16		0.22	30
Sn		0.00067		0.00067		0.00068		0.00067	0.6
T1	<	0.027	<	0.027	<	0.027	<	0.027	0.6
V	<	0.0023	<	0.0023	<	0.0023	<	0.0023	0.6
Zn	<	0.032		0.016		0.10		0.050	92
Ammonium		2.41		1.9		1.31		1.9	30
Bromide		ND		ND		ND		ND	n/a
Chloride		0.20		0.19		0.11		0.17	28
Fluoride	<	0.020	<			0.085	<	0.042	90
Nitrate		0.076				0.065		0.067	12
Nitrite		ND		ND		ND		ND	n/a
Phosphate		ND		ND		ND		ND	n/a
Sulfate		7.0		4.6		0.33		4.0	85
Total		10.7		7.6		2.8		7.1	56

Table 4-9. Method 202 Inorganic Residue Analysis.

< = concentration was below the reporting limit of the method

n/a = not applicable; only one or fewer runs within detectable limits

ND = not detected

RSD = relative standard deviation

Except for Run 3, which appears to be anomalous, the second analysis shows  $SO_4^=$  to be the dominant compound in the inorganic residue. This is in qualitative agreement with the first analysis although the relative fraction of  $SO_4^=$  appears to be somewhat higher in the second analysis.  $NH_4^+$  also comprises a relatively large fraction, which is expected since ammonium hydroxide (NaOH) is added to the sample during analysis to stabilize  $SO_4^=$ . The second analysis shows Cl⁻ present at a little more than half of the concentration determined in the first analysis.

It is possible that the samples degraded somewhat during the several months of storage between the first and second analyses, which may partially explain the differences in absolute results. Neglecting the differences in absolute values and NaOH which is added to the sample during analysis, the second set of analytical results confirm that the majority of CPM is comprised of  $SO_4^=$  and Cl⁻ with much smaller amounts of other ions and elements. It is believed the majority of  $SO_4^=$ , and perhaps Cl⁻, found in the impinger contents is an artifact resulting from gaseous  $SO_2$ and hydrogen chloride (HCl) in the stack gas. This is discussed further in Section 7.

#### OC, EC and SVOCs

OC, EC and SVOCs were determined on in-stack filters. To preserve the integrity of the Method 201A filters for gravimetric analysis, a separate EPA Method 17 sampling train was used to collect samples for these analyses. Total carbon is the sum of OC and EC. OC was approximately 0.1 mg/dscm in all three samples, while EC ranged from approximately 0.1 to 0.3 mg/dscm (Table 4-10). It is interesting to note that these values are greater than the FPM results reported above. Caution should be used when comparing results of completely different analytical methods, but given the visible soot deposits on the filters and the difficulty of obtaining accurate filter weight gains from the Method 201A results. In any case, it is apparent that OC and EC could account for essentially all of the FPM emissions measured in these tests.

A few SVOCs were detected on the in-stack filters at very low levels (Table 4-11). Naphthalene was the most abundant substance detected on the in-stack filters, with an average concentration of 0.00004 mg/dscm. The sum of the detected SVOCs is only 1/1000 of one percent of the OC reported above. This apparent gap in speciation of the OC may be a consequence of how OC is defined and measured, unextractable organic matter on the filter, and/or other analytical challenges.

	Units			Value		
Run Number	-	Run No. 1	Run No. 2	Run No. 3	Average	RSD
Date	-	15-Jul-98	16-Jul-98	17-Jul-98		
Organic	mg/dscm	0.13	0.10	0.089	0.11	19%
Carbon	lb/hr	0.050	0.039	0.035	0.042	18%
Elemental	mg/dscm	0.10	0.23	0.27	0.20	44%
Carbon	lb/hr	0.040	0.092	0.11	0.08	44%
Total	mg/dscm	0.23	0.33	0.36	0.31	22%
Carbon	lb/hr	0.090	0.13	0.14	0.12	23%

Table 4-10. In-Stack Organic and Elemental Carbon Results for Gas-Fired Boiler

ND - not detected

n/a - not applicable; only one run within detectable limits

RSD - relative standard deviation

Figure 4-11. In-Stack SVOC Results for Gas-Fired Boiler (Refinery Site A).

	mg/dscm				
Run Number	Run No.1	Run No. 2	Run No. 3		RSD
Date	15-Jul-98	16-Jul-98	17-Jul-98	Average	(%)
Naphthalene	6.4E-5	3.3E-5	2.7E-5	4.1E-5	48
2-methylnaphthalene	2.1E-5	5.3E-6	ND	1.3E-5	84
1-methylnaphthalene	1.3E-5	4.8E-6	ND	8.6E-6	63
Acenaphthene	1.1E-5	ND	3.2E-6	7.1E-6	77
Perinaphthenone	1.0E-5	ND	3.2E-6	6.8E-6	74
Biphenyl	5.9E-6	ND	ND	5.9E-6	n/a
Dibenzofuran	4.8E-6	2.1E-6	ND	3.5E-6	54
Benzo(a)pyrene	ND	2.1E-6	4.3E-6	3.2E-6	48
Benz(a)anthracene	ND	2.9E-6	ND	2.9E-6	n/a
2-methylphenanthrene	2.1E-6	ND	1.6E-6	1.9E-6	19
Benzo(b)chrysene	1.3E-6	ND	5.4E-7	9.3E-7	60
1-methylphenanthrene	8.0E-7	ND	8.1E-7	8.0E-7	0.7
1,4-chrysenequinone	ND	5.3E-7	ND	5.3E-7	n/a
Anthrone	5.3E-7	ND	ND	5.3E-7	n/a
Total	1.3E-04	5.1E-05	4.0E-05	7.5E-05	0.7

ND - not detected

n/a - not applicable; only one run within detectable limits

RSD - relative standard deviation

# DILUTION TUNNEL RESULTS

# Particulate Mass

PM2.5 mass measurements using the dilution tunnel should include both solid particles and any aerosols that condense under simulated stack plume conditions. The dilution tunnel determines only the PM2.5 fraction of particulate emissions. PM2.5 concentration in the stack gas ranged from approximately 0.25 to 0.40 mg/dscm with an average of 0.34 mg/dscm (Table 4-12). Precision of the data over the three runs is good, with a relative standard deviation (RSD) of 25 percent. The blank results were insignificant when compared to the sample results. PM2.5 concentration measured in the ambient air (Table 4-13) was only 6 percent of the level measured in the boiler stack gas.

	Units				Average	RSD
Run Number	-	Run No. 1	Run No. 2	Run No. 3		
Date	-	18-Jul-98	19-Jul-98	20-Jul-98		
PM2.5	mg/dscm	0.245	0.404	0.389	0.346	25%
	lb/hr	0.103	0.147	0.177	0.142	26%

Table 4-12. Stack Gas PM 2.5 Results for Gas-Fired Boiler (Refinery Site A).

Table 4-13. Ambient Air PM2.5 Results	for Gas-Fired Boiler (	(Refinery Site A).
---------------------------------------	------------------------	--------------------

	Units	
Run Number	-	Run No. 1
Date	-	17-Jul-98
PM2.5	mg/dscm	0.020
	lb/hr	n/a

n/a- not applicable

RSD - relative standard deviation

The concentration of PM2.5 using the dilution tunnel is a factor of 12 higher than FPM <2.5 micrometers measured using Method 201A and a factor of 26 lower than CPM measured using Method 202. CPM is normally included in regulatory definitions of PM2.5. The dilution tunnel and EPA method results clearly indicate that condensible aerosols do contribute to PM2.5 emissions, but that the results are strongly method-dependent. Because the dilution tunnel replicates conditions experienced by the stack emissions as they mix with the atmosphere more accurately than Method 202, and because of the suspected artifacts associated with Method 202, it is believed the dilution tunnel results are more representative of the true primary PM2.5 emissions.

# Sulfate, Chloride, Nitrate and Ammonium

Quartz filters were analyzed for  $SO_4^{=}$ ,  $C\Gamma$ ,  $NO_3^{-}$ , and  $NH_4^{+}$  ion. Of these,  $SO_4^{=}$  had the highest concentration at 0.014 mg/dscm, followed by  $NH_4^{+}$  at 0.0015 mg/dscm (Table 4-14). Chlorine was detected in only one run at levels near the lower method detection limit. Nitrate ion was not detected in any of the three runs. Concentrations of ions in the field blanks were insignificant. Quartz filters used in ambient air sampling have the potential for a positive  $SO_4^{=}$  bias. However, at the low  $SO_2$  concentrations present in the samples, the artifact is probably not significant for these tests. The  $SO_4^{=}$  concentrations from the dilution tunnel are approximately 1/100 to 1/500 of the concentrations reported above for Method 202 (1.1-7.0 mg/dscm). Chloride ion results also are several hundred times lower. This difference supports the possibility of a potential artifact in Method 202.

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	Units				Average	RSD	
Run Number	-	Run No. 1	Run No. 2	Run No. 3			Ambient
Date	-	18-Jul-98	19-Jul-98	20-Jul-98			17-Jul-98
Sulfate	mg/dscm	1.6E-2	1.1E <b>-</b> 2	1.4E-2	1.4E-2	18%	4.4E-3
	lb/hr	6.5E-3	4.0E-3	6.4E-3	5.6E-3	26%	n/a
Nitrate	mg/dscm	ND	ND	ND	ND	n/a	7.6E-4
	lb/hr	ND	ND	ND	ND	n/a	n/a
Chloride	mg/dscm	7.7E-4	ND	ND	7.7E-4	n/a	ND
	lb/hr	3.2E-4	ND	ND	3.2E-4	n/a	n/a
Ammonium	mg/dscm	1.0E-3	1.6E-3	2.0E-3	1.5E-3	32%	1.5E-3
	lb/hr	4.3E-4	5.8E-4	9.0E-4	6.4E-4	38%	n/a

Table 4-14. Dilution Tunnel Sulfate, Nitrate, Chloride and Ammonium Results for Gas-Fired Boiler (Refinery Site A).

ND - not detected

n/a- not applicable; only one run within detectable limits RSD - relative standard deviation

# OC, EC and Organic Species

Organic Carbon and EC were measured on the quartz filters from the dilution tunnel. Organic carbon concentration is 0.14 to 0.16 mg/dscm and EC concentration is 0.06 to 0.13 mg/dscm (Table 4-15). Organic carbon accounts for approximately two-thirds of the total carbon mass. Compared to the in-stack filter OC/EC results, OC concentration is similar and EC is lower on the dilution tunnel filters. On average, the total carbon on the in-stack filters is approximately 30 percent higher.

	Units	Value					
Run Number	-	Run No. 1	Run No. 2	Run No. 3	Average	RSD	Ambient
Date	-	18-Jul-98	19-Jul-98	20-Jul-98			17-Jul-98
Organic	mg/dscm	0.16	0.15	0.14	0.15	7%	ND
Carbon	lb/hr	0.065	0.055	0.062	0.061	9%	n/a
Elemental	mg/dscm	0.073	0.063	0.130	0.089	41%	ND
Carbon	lb/hr	0.030	0.023	0.059	0.038	51%	n/a
Total	mg/dscm	0.23	0.21	0.27	0.237	12%	ND
Carbon	lb/hr	0.10	0.08	0.12	0.098	22%	n/a

Table 4-15. Dilution Tunnel Organic and Elemental Carbon Results for Gas-Fired Boiler (Refinery Site A).

ND - not detected

n/a - not applicable; only one run within detectable limits

RSD - relative standard deviation

SVOCs were determined on the combined TIGF/PUF/XAD-4/PUF cartridge used with the dilution tunnel. This method determines both particulate and vapor phase SVOCs together. All SVOCs detected were present at extremely low levels (Table 4-16). Naphthalene concentration is approximately twice the concentration found on the in-stack filters. Phenanthrene, which was not detected on the in-stack filters, is the most abundant SVOC in the dilution tunnel samples with an average concentration of 0.00098 mg/dscm. In general, the average stack gas concentrations are within a factor of ten of the ambient air concentration, which suggests the levels in the stack may be indistinguishable from the background levels. The average stack gas concentrations of 1+2-ethylnaphthalene, 1,2-dimethylnaphthalene, 1,3+1,6+1,7- dimethylnaphthalene, 2,4,5-trimethylnaphthalene, 2,6+2,7-dimethylnaphthalene, 2,3,5+I-trimethylnaphthalene, a-trimethylnaphthalene, b-trimethylnaphthalene, dibenzofuran, e-trimethylnaphthalene, f-trimethylnaphthalene and naphthalene are less than the detected ambient air concentration. 1-methylphenanthrene and j-trimethylnaphthalene were both detected in the ambient air sample but not in any of the stack gas samples.

		0101 040			- <u>-</u>	
Parameter		mg/c	lscm		%	mg/dscm
Run Number	Run No. 1	Run No. 2	Run No. 3	Average	RSD	Ambient
Date	18-Jul-98	19-Jul-98	20-Jul-98			17-Jul-98
Phenanthrene	1.3E-3	8.7E-4	7.5E-4	9.8E-4	31	4.9E-5
Perinaphthenone	5.6E-4	2.3E-4	2.8E-4	3.6E-4	49	ND
Fluoranthene	4.2E-4	2.1E-4	1.7E-4	2.7E-4	50	8.6E-6
Biphenyl	6.2E-4	5.0E-5	1.6E-5	2.3E-4	148	1.6E-5
Pyrene	2.9E-4	1.5E-4	1.3E-4	1.9E-4	46	5.7E-6
Cholestane	2.0E-4	2.1E-4	1.4E-4	1.8E-4	21	ND
Coronene	1.6E-4	1.6E-4	2.0E-4	1.7E-4	12	3.0E-5
Fluorene	1.3E-4	9.5E-5	9.0E-5	1.1E-4	21	2.0E-5
Naphthalene	1.3E-4	ND	5.6E-5	9.5E-5	57	1.7E-4
Anthracene	1.1E-4	6.6E-5	5.0E-5	7.4E-5	39	4.1E-6
Acenaphthylene	1.3E-4	3.4E-5	8.0E-6	5.7E-5	112	ND
Acenaphthenequinone	8.2E-5	4.1E-5	3.3E-5	5.2E-5	50	1.6E-6
B-methylphenanthrene	6.1E-5	6.0E-5	2.7E-5	4.9E-5	40	ND
3-methylbiphenyl	6.2E-5	2.6E-5	3.6E-5	4.1E-5	45	1.9E-5
2-methylnaphthalene	5.2E-5	1.3E-5	5.8E-5	4.1E-5	60	2.6E-4
1,4+1,5+2,3-	4.0E-5	ND	ND	4.0E-5	n/a	4.1E-5
9-methylanthracene	ND	3.9E-5	ND	3.9E-5	n/a	ND
Anthraquinone	3.3E-5	3.8E-5	4.4E-5	3.8E-5	14	4.8E-6
1,3+1,6+1,7-	5.5E-5	1.6E-5	4.2E-5	3.8E-5	52	1.8E-4
2-methylphenanthrene	5.4E-5	3.1E-5	1.6E-5	3.4E-5	56	1.7E-5
A-methylphenanthrene	5.1E-5	2.2E-5	2.2E-5	3.1E-5	54	1.1E-5
Benzanthrone	3.1E-5	3.2E-5	2.9E-5	3.1E-5	5	7.1E-6
2-phenylnaphthalene	4.5E-5	2.4E-5	2.0E-5	3.0E-5	46	5.2E-7
Xanthone	2.8E-5	ND	ND	2.8E-5	n/a	ND
Benzo(b+j+k)fluoranthene	2.8E-5	2.4E-5	2.8E-5	2.7E-5	8	3.8E-6
9-fluorenone	2.6E-5	ND	ND	2.6E-5	n/a	ND
1-methylnaphthalene	3.5E-5	6.6E-6	3.5E-5	2.6E-5	64	1.8E-4
Benz(a)anthracene	3.5E-5	1.1E-5	2.4E-5	2.3E-5	50	3.3E-6
Benzo(b)chrysene	2.4E-5	2.3E-5	2.2E-5	2.3E-5	5	3.9E-6
1-MeFl+C-MePy/Fl	2.3E-5	ND	2.0E-5	2.1E-5	7	ND
Benz(a)anthracene-7,12	2.4E-5	1.9E-5	1.9E-5	2.1E-5	14	4.2E-6
4H-cyclopenta(def)phenanthrene	2.7E-5	1.9E-5	1.4E-5	2.0E-5	32	6.5E-7
2,6+2,7-dimethylnaphthalene	2.5E-5	9.3E-6	2.2E-5	1.9E-5	44	8.2E-5
7-methylbenzo(a)pyrene	1.8E-5	1.5E-5	2.2E-5	1.8E-5	21	3.1E-6
F-trimethylnaphthalene	ND	2.1E-5	1.5E-5	1.8E-5	22	1.9E-5
Chrysene	2.1E-5	1.8E-5	1.4E-5	1.8E-5	18	4.5E-6
B-dimethylphenanthrene	ND	2.0E-5	1.5E-5	1.8E-5	18	ND
Dibenzofuran	1.9E-5	1.4E-5	1.7E-5	1.7E-5	15	1.9E-5
C-dimethylphenanthrene	4.1E-5	4.6E-6	4.8E-6	1.7E-5	125	6.3E-6

Table 4-16. Dilution Tunnel SVOC Results for Gas-Fired Boiler (Refinery Site A).

Table 4-10 (colic). Dilucion Tunner	SVUC RC	suns for Oa	is-rincu Du			ι <i>Π</i> ].
Parameter		mg/c	lscm.		%	mg/dscm
	Run No. 1	Run No. 2	Run No. 3	Average	RSD	Ambient
Date	18-Jul-98	19-Jul-98	20-Jul-98			17-Jul-98
1.2-dimethvlnaphthalene	1.5E-5	ND	ND	1.5E-5	n/a	1.6E-5
1+2-ethylnaphthalene	1.6E-5	ND	1.4E-5	1.5E-5	13	4.5E-5
Acenaphthene	1.4E-5	1.7E-5	1.4E-5	1.5E-5	12	1.2E-5
C-methylphenanthrene	1.8E-5	1.1E-5	1.5E-5	1.5E-5	23	6.8E-6
E-trimethylnaphthalene	3.3E-5	5.2E-6	4.0E-6	1.4E-5	117	2.0E-5
Anthrone	1.3E-5	9.1E-6	1.1E-5	1.1E-5	17	1.1E-6
D-dimethylphenanthrene	1.4E-5	1.0E-5	9.4E-6	1.1E-5	21	ND
1-phenylnaphthalene	1.7E-5	8.4E-6	8.0E-6	1.1E-5	46	ND
2,3,5+I-trimethylnaphthalene	1.3E-5	9.5E-6	9.4E-6	1.1E-5	21	2.5E-5
C-trimethylnaphthalene	1.3E-5	8.7E-6	9.7E-6	1.0E-5	21	1.8E-5
E-dimethylphenanthrene	1.4E-5	ND	7.0E-6	1.0E-5	46	2.0E-6
Retene	1.7E-5	6.9E-6	7.3E-6	1.0E-5	54	ND
B-methylfluorene	1.0E-5	ND	ND	1.0E-5	n/a	ND
1.4-chrysenequinone	1.9E-5	6.6E-6	5.3E-6	1.0E-5	72	2.2E-6
B-trimethylnaphthalene	1.2E-5	7.3E-6	7.7E-6	9.0E-6	30	2.3E-5
Benzo(c)phenanthrene	1.2E-5	6.1E-6	8.6E-6	8.9E-6	33	1.9E-6
2-methylbiphenyl	ND	ND	8.6E-6	8.6E-6	n/a	ND
A-trimethylnaphthalene	1 1E-5	7 9E-6	6 9E-6	8.6E-6	26	2 2E-5
1-methylfluorene	8 2E-6	1 1E-5	6 9E-6	8 6E-6	$\frac{1}{23}$	3 6E-6
Benzo(ghi)nervlene	6.8E-6	1 1E-5	8 5E-6	8.6E-6	$\frac{1}{22}$	1 2E-6
Benzo(a)pyrene	8.8E-6	6 8E-6	9.3E-6	8 3E-6	16	1.2E °
1-ethyl-2-methylnaphthalene	1 1E-5	6.9E-6	4 5E-6	7.6E-6	46	5 1E-6
3 6-dimethylphenanthrene	1 6E-5	3 5E-6	2.6E-6	7 3E-6	102	3 5E-6
Dibenz(ah+ac)anthracene	5 6E-6	8 8E-6	6 9E-6	7 1E-6	23	1 2E-6
A-dimethylphenanthrene	1 0E-5	3 3E-6	ND	6 6E-6	71	3 4E-6
4-methylbinhenyl	2 7E-6	7 1E-6	9 3E-6	6.0 <u>E</u> 0	52	6 0E-6
B-MePv/MeFl	1 2E-5	5.4E-6	1 1E-6	6.2E-6	90	6 3E-7
Indeno[123-cd]nyrene	4 8E-6	6 9E-6	6 1E-6	5.2E 0	18	1 1E-6
A-methylfluorene	5.8E-6	ND	ND	5.8E-6	n/a	ND
4-methylpyrene	1 1F-5	4 4E-6	2 1E-6	5.8E-6	78	1 7E-6
2 4 5-trimethylnanhthalene	7 7E-6	3.8E-6	3 0E-6	4 8F-6	52	7 1E-6
1 7-dimethylphenanthrene	5 1E-6	5.8E-6	2 7E-6	4 6E-6	36	2 6E-6
9 10-dihydrobenzo(a)pyrene	4 0F-6	3.0E 0	5 7E-6	4 3E-6	31	1 1E-6
Benzo(e)nyrene	2 4E-6	3.9E-6	5.7E-6	4.5E-6	41	3.8F-7
D-MePy/MeFl	6 3E-6	3.6E-6	2 1E-6	4.0E-6	53	1.5E-7
1 2 8-trimethylnanhthalene	4 5E-6	1 7E-6	2.1E 0 4 5E-6	3.6E-6	$\Delta \Delta$	8.4F-7
9-anthraldehyde	2 4E-6	ND	4.3E-6	3.0E-0	40	ND
5+6-methylchrysene	2.4L=0 2.7E=6	$2.0E_{-6}$	5.1E-6	3.4E-0	10	1 0E-6
Benzonanbthothionhene	4.7E-6	2.0L-0 2.7E-6	2.1L-0	3.0E-6	3/	$6.7E_{-7}$
Pervlene	1.2L=0	2.7E-6	$4.1E_{-6}$	2.0E-0	12	5.7E-7
$\Delta_{-methylnyrene}$	$2.7E_{-6}$	2.7L-0 3.0E-6	4.12-0	2.7L-0 2.1E-6	67	1.5E-7
F-MePy/MeF1	$\frac{2.7 \text{ L}}{4.8 \text{ F}}$	2.01-0 $2.7E_6$	$6.4F_7$	1.12-0	97	$8 4 F_7$
1_methylphenanthrene	ND	2.7L-0 ND	ND	ND	n/a	5.4E-7
Ltrimethylnanhthalene	ND	ND	ND	ND	n/a	3.6E-6
Total	5 3E 02	2 7E 02	2 6E 02	3 5E 02	$\int d$	$1/E^2$
110101	J.JE-03	2./E-U3	2.0E-03	J.JE-03	U.4	1.4E-J

Table 4-16 (cont) Dilution Tunnel SVOC Results for Gas-Fired Boiler (Refinery Site A)

ND - not detected

MeFl - methylfluorene; MePy - methylpyrene n/a - not applicable; only one run within detectable limits

RSD - relative standard deviation

Most of the average SVOC stack gas concentrations are at least a factor of ten greater than their respective field blank concentrations. The field blank concentrations of 2-methylbiphenyl, 4-methylbiphenyl, 9,10-dihydrobenzo(a)pyrene, 9-anthraldehyde, a-methylpyrene, anthrone, cholestane and dibenz(ah+ac)anthracene are greater than their average stack gas concentrations, which indicates the stack gas results for these SVOCs are unreliable (see Section 6 for further details).

Tenax sorbent was used for determining VOCs. The analysis focused on VOCs with a carbon number greater than 7 since these are believed to be the most significant precursors for secondary organic aerosols. Benzaldehyde was the most abundant VOC detected during sampling, with an average concentration of 0.057 mg/dscm (Table 4-17). Acetophenone was the second most abundant on average (0.057 mg/dscm). In general, the average VOC concentration in the stack gas was within a factor of ten of the ambient air concentration. 1,2,4-trimethylbenzene, decane, dodecane, m- & p-xylenes, o-xylene, p-isopropyltoluene, pentadecane and undecane all have average stack gas concentrations that are lower than their respective ambient air concentration. The average stack gas concentrations of styrene and decane are within a factor of ten of their concentrations in the field blank sample (see Section 6), which may indicate unreliable stack gas results for these VOCs.

#### **Elements**

Element concentrations were determined by XRF analysis of the TMFs used in the dilution tunnel. On average, S is the most abundant element and Na the second most abundant (Table 4-18). The S results are in fair agreement with the dilution tunnel  $SO_4^{=}$  results presented earlier, within a factor of two on a mole-for-mole basis. Sodium results are considered semi-quantitative because of analytical limitations. Chlorine, Ni, V, Cu, and to a lesser degree S and Cr, are significantly enriched in the stack gas samples compared to the ambient air. Anitomy, Ba, Cd, Ga, Au, In, La, Mn, Hg, Mo, Pd, P, Se, Ag, Tl, Sn and Y concentrations are below detection limits in all three sample runs (not listed in the table). In addition, Br, Rb, Sr, and Zr were detected in the ambient sample but not in the sample runs. The concentration of most compounds in the stack gas is within a factor of ten of their respective ambient air concentration. Aluminum and Ca concentrations are higher than in the ambient air than in the stack gas.

4-19

Parameter		mg/c	lscm	- ( -	%	mg/dscm
Run Number	Run No.1	Run No.2	Run No.3	Average	RSD	Ambient
Date	18-Jul-98	19-Jul-98	20-Jul-98	e		17-Jul-98
Benzaldehvde	5.2E-2	8.0E-2	3.9E-2	5.7E-2	36%	5.5E-3
Acetophenone	3.9E-2	6.0E-2	5.3E-2	5.0E-2	21%	3.8E-3
Phenol	1.9E-2	2.9E-2	2.1E-2	2.3E-2	23%	2.3E-3
Butylated Hydroxytoluene	1.5E-2	6.4E-3	3.6E-3	8.5E-3	72%	1.2E-2
Benzonitrile	5.2E-3	5.6E-3	5.2E-3	5.3E-3	4%	2.6E-4
Styrene	2.7E-3	2.3E-3	2.3E-3	2.4E-3	9%	2.2E-3
m-& p-xylenes	1.3E-3	6.8E-4	1.0E-3	1.0E-3	30%	3.7E-3
1,2,4-trimethylbenzene	7.9E-4	5.1E-4	7.4E-4	6.8E-4	22%	1.7E-3
Heptadecane	6.7E-4	5.2E-4	7.2E-4	6.4E-4	16%	2.1E-4
Tetradecane	4.2E-4	3.0E-4	9.9E-4	5.7E-4	65%	2.6E-4
Octadecane	5.0E-4	5.6E-4	5.8E-4	5.5E-4	7%	1.2E-4
Biphenyl	1.2E-3	1.2E-4	2.9E-4	5.3E-4	108%	8.0E-5
Tridecane	4.0E-4	5.7E-4	6.0E-4	5.2E-4	21%	2.7E-4
o-xylene	6.3E-4	3.4E-4	4.6E-4	4.8E-4	31%	1.4E-3
Pentadecane	1.6E-4	7.0E-5	1.1E-3	4.4E-4	128%	5.6E-4
Hexadecane	5.6E-4	1.1E-4	6.4E-4	4.4E-4	65%	2.2E-4
Undecane	5.5E-4	3.6E-4	3.8E-4	4.3E-4	24%	4.8E-4
Nonadecane	2.3E-4	5.6E-4	3.1E-4	3.7E-4	46%	ND
2-methyloctane	7.5E-5	3.3E-4	6.5E-4	3.5E-4	82%	2.4E-4
Nonane	3.1E-4	2.1E-4	5.0E-4	3.4E-4	43%	7.6E-4
Eicosane	2.1E-4	5.4E-4	2.1E-4	3.2E-4	59%	ND
Dodecane	2.6E-4	2.6E-4	3.5E-4	2.9E-4	19%	4.2E-4
Ethylbenzene	2.6E-4	1.5E-4	2.8E-4	2.3E-4	30%	1.2E-3
Decane	2.3E-4	1.2E-4	2.9E-4	2.1E-4	39%	5.7E-4
p-isopropyltoluene	3.1E-5	ND	ND	3.1E-5	n/a	1.2E-4
1,3,5-trimethylbenzene	ND	ND	ND	ND	n/a	5.2E-4
l-methylindan	ND	ND	ND	ND	n/a	3.9E-4
l-methylnaphthalene	ND	ND	ND	ND	n/a	3.4E-4
l-nonene	ND	ND	ND	ND	n/a	4.8E-5
2-methylindan	ND	ND	ND	ND	n/a	2.6E-4
2-methylnaphthalene	ND	ND	ND	ND	n/a	5.5E-4
Cyclohexanone	ND	ND	ND	ND	n/a	4.6E-5
Dodecene	ND	ND	ND	ND	n/a	1.1E-4
Indan	ND	ND	ND	ND	n/a	2.2E-4
m-ethyltoluene	ND	ND	ND	ND	n/a	1.10E-3
Nonanal	ND	ND	ND	ND	n/a	1.4E-3
o-ethyltoluene	ND	ND	ND	ND	n/a	4.1E-4
p-ethyltoluene	ND		ND	ND	n/a	4.5E-4
Propylbenzene	ND	ND	ND	ND	n/a	3.5E-4

 Table 4-17
 Dilution Tunnel VOC Results for Gas-Fired Boiler (Refinery Site A)

ND - not detected

MeFl - methylfluorene; MePy - methylpyrene n/a - not applicable; only one run within detectable limits

RSD - relative standard deviation

Parameter		mg/	dscm		%	mg/dscm
Run Number	Run No. 1	Run No. 2	Run No. 3	Average	RSD	Ambient
Date	18-Jul-98	19-Jul-98	20-Jul-98	-		17-Jul-98
Aluminum	2.5E-4	2.7E-4	2.4E-4	2.5E-4	7%	3.6E-4
Arsenic	1.5E-4	2.3E-4	2.3E-4	2.0E-4	24%	ND
Bromine	ND	ND	ND	ND	n/a	2.3E-6
Calcium	3.4E-4	2.3E-4	6.8E-4	4.2E-4	55%	6.8E-4
Chlorine	6.5E-4	ND	ND	6.5E-4	n/a	1.0E-5
Cobalt	ND	7.3E-6	1.4E-5	1.1E <b>-</b> 5	46%	ND
Chromium	1.5E-5	ND	ND	1.5E-5	n/a	2.3E-6
Copper	1.1E <b>-3</b>	2.2E-3	1.2E-3	1.5E-3	40%	1.5E-4
Iron	1.4E-3	1.8E-3	2.3E-3	1.8E-3	24%	4.9E-4
Potassium	1.1E <b>-</b> 4	1.8E-4	2.6E-4	1.8E-4	42%	1.7E-4
Magnesium	1.0E-4	3.2E-4	9.2E-7	1.4E-4	116%	6.9E-5
Manganese	ND	ND	ND	ND	n/a	1.3E-5
Nickel	1.6E-4	2.1E-4	2.8E-4	2.1E-4	28%	7.4E-6
Lead	2.3E-5	ND	8.3E-5	5.3E-5	81%	1.3E-5
Rubidium	ND	ND	ND	ND	n/a	8.4E-7
Silicon	1.0E-3	1.2E-3	1.4E-3	1.2E-3	15%	1.1E-3
Sodium	3.4E-3	1.5E-3	1.1E-3	2.0E-3	62%	ND
Strontium	ND	ND	ND	ND	n/a	3.6E-6
Sulfur	6.87E-3	8.06E-3	1.1E <b>-2</b>	8.5E-3	23%	1.2E-3
Titanium	ND	ND	4.3E-5	4.3E-5	n/a	3.6E-5
Uranium	ND	1.5E-5	ND	1.5E-5	n/a	ND
Vanadium	2.5E-4	3.6E-4	5.0E-4	3.7E-4	33%	1.9E-5
Zinc	1.2E-4	1.3E-4	2.0E-4	1.5E-4	28%	6.6E-5
Zirconium	ND	ND	ND	ND	n/a	2.8E-6

Table 4-18. Dilution Tunnel Elemental Results for Gas-Fired Boiler (Refinery Site A).

ND - not detected

n/a - not applicable; only one run within detectable limits

RSD - relative standard deviation

Indium and P were present at detectable levels in the blank, but not in the field samples.

Magnesium in the field blank was within a factor of ten of the average stack gas concentration.

All other compounds detected in the field blank were present at insignificant levels (see Section 6 for further details).

#### Section 5

# EMISSION FACTORS AND SPECIATION PROFILES

Emission factors were determined by dividing the emission rate, in lb/hr, by the measured heat input, in MMBtu/hr, to give pounds per million British thermal unit (lb/MMBtu). Heat input is the product of the measured fuel flow rate and the average fuel heating value (based on fuel grab sample analysis and continuous fuel specific gravity monitoring). Average emission factors were determined by averaging detected data. Undetected data were excluded.

#### UNCERTAINTY

An uncertainty analysis was performed to determine the 95 percent confidence interval and to estimate the upper limit of the measured emission factor and the mass speciation results (ASME, 1990). In the tables that follow, the reported results, the total uncertainty, and a 95 percent confidence upper bound are given for each of the substances of interest. The total uncertainty represents the 95 percent confidence interval, based on a two-tailed Student "t" distribution. The 95 percent confidence upper bound estimate is based on the single-tailed Student "t" distribution at the 95 percent confidence level.

#### EMISSION FACTORS FOR PRIMARY EMISSIONS

Table 5-1 presents emission factors for primary emissions, including filterable and condensable particulate mass, and elements and ions as measured on the dilution tunnel filters. FPM includes all particulate captured in the in-stack cyclones, probe and filter. Inorganic and organic CPM have not been individually blank corrected, however the total CPM has been corrected in accordance with Method 202 guidelines. The average emission factor for total PM2.5 (including CPM) measured using in-stack methods is 27 times higher than the emission factor for PM2.5 by the dilution tunnel. As discussed previously in Section 4, this is believed to be due to sampling and analytical artifacts associated with the method for CPM. Therefore, the emission factor derived from the dilution tunnel results is considered the most reliable.
Substance		Emission	Uncertainty	95% Confidence
		Factor	(%)	Upper Bound
		(lb/MMBtu)		(lb/MMBtu)
Particulate	CPM (inorganic)	9.07E-3	107	1.58E-2
Mass				
	CPM (organic)	6.36E-4	290	1.89E-3
	Total CPM	9.71E-3	118	1.66E-2
	Total Filterable PM (in-stack method)	1.66E-4	332	5.40E-4
	Filterable PM10 (in-stack method)	1.58E-4	n/a	n/a
	Filterable PM2.5 (in-stack method)	2.64E-5	n/a	n/a
	PM2.5 (Dilution Tunnel)	3.58E-4	80	5.58E-4
Elements	Aluminum	2.65E-7	54	3.68E-7
	Arsenic	2.11E-7	79	3.27E-7
	Calcium	4.46E-7	147	8.93E-7
	Chlorine	7.12E-7	n/a	n/a
	Cobalt	1.13E-8	450	3.66E-8
	Chromium	1.61E-8	n/a	n/a
	Copper	1.55E-6	112	2.74E-6
	Iron	1.93E-6	79	2.99E-6
	Potassium	1.87E-7	116	3.36E-7
	Magnesium	1.38E-7	292	4.11E-7
	Nickel	2.25E-7	86	3.59E-7
	Lead	5.82E-8	746	2.74E-7
	Silicon	1.27E-6	64	1.84E-6
	Sodium	2.13E-6	162	4.48E-6
	Sulfur	8.94E-6	76	1.37E-5
	Titanium	4.75E-8	n/a	n/a
	Uranium	1.45E-8	n/a	n/a
	Vanadium	3.90E-07	97	6.51E-07
	Zinc	1.59E-07	87	2.55E-07
Ions	Sulfate (by DT)	1.43E-5	68	2.11E-5
	Nitrates (by DT)	ND	n/a	n/a
	Chloride (by DT)	8.46E-7	n/a	n/a
	Ammonium (by DT)	1.60E-6	95	2.64E-6
n/a-	not applicable; only one run within dete	ctable limits	-	•

Table 5-1. Primary Emissions – Particulate Mass and Elements.

ND - not detected

Table 5-2 presents emission factors for OC, EC, total carbon, and SVOCs. SVOC emission factors are very low, with phenanthrene having the highest emission factor  $(1.0x10^{-6} \text{ lb/MMBtu})$  for the dilution tunnel samples and naphthalene having the highest value  $(4.1x10^{-6} \text{ lb/MMBtu})$ 

5-2

for the in-stack filter samples. Since the dilution tunnel samples are expected to collect SVOCs which condense in the plume, these results are considered more representative for receptor modeling purposes.

	Average	Uncertainty	95% Confidence
Compound	(lb/MMBtu)	(%)	Upper Bound
			(lb/MMBtu)
Method 201A/202			
Organic Carbon	1.1E-4	70.2	1.57E-4
Elemental Carbon	2.0E-4	121	3.72E-4
Total Carbon	3.1E-4	55.5	4.32E-4
Dilution Tunnel			
Organic Carbon	1.5E-4	54.8	2.16E-4
Elemental Carbon	9.4E-5	114	1.68E-4
Total Carbon	2.5E-4	59.2	3.54E-4
Semi-Volatile Organic Compounds (as measured by	the dilution tunne	1)	
1+2-ethylnaphthalene	1.65E-8	214	3.44E-8
1,2,8-trimethylnaphthalene	3.83E-9	123	7.12E-9
1,2-dimethylnaphthalene	1.68E-8	n/a	n/a
1,3+1,6+1,7-dimethylnaphthalene	4.06E-8	140	8.00E-8
1,4+1,5+2,3-dimethylnaphthalene	4.41E-8	n/a	n/a
1,4-chrysenequinone	1.08E-8	188	2.48E-8
1,7-dimethylphenanthrene	4.70E-9	105	8.16E-9
1-ethyl-2-methylnaphthalene	7.99E-9	127	1.51E-8
1-methylfluorene+C-methylpyrene/methylfluorene	2.36E-8	188	4.63E-8
1-methylfluorene	8.87E-9	78.7	1.39E-8
1-methylnaphthalene	2.77E-8	168.5	5.99E-8
1-phenylnaphthalene	1.17E-8	126	2.20E-8
2,3,5+I-trimethylnaphthalene	1.13E-8	75.7	1.75E-8
2,4,5-trimethylnaphthalene	5.13E-9	140	1.01E-8
2,6+2,7-dimethylnaphthalene	1.99E-8	122	3.69E-8
2-methylbiphenyl	9.47E-9	n/a	n/a
2-methylnaphthalene	4.44E-8	159	9.31E-8
2-methylphenanthrene	3.55E-8	150	7.22E-8
2-phenylnaphthalene	3.13E-8	126	5.86E-8
3,6-dimethylphenanthrene	7.80E-9	258	2.16E-8
3-methylbiphenyl	4.41E-8	125	8.24E-8
4-methylbiphenyl	6.60E-9	141	1.30E-8
4-methylpyrene	6.09E-9	202	1.45E-8
4H-cyclopenta(def)phen	2.07E-8	97	3.49E-8
5+6-methylchrysene	3.51E-9	133	6.75E-9
7-methylbenzo(a)pyrene	1.94E-8	75.0	2.98E-8
9,10-dihydrobenzo(a)pyrene	4.56E-9	94	7.59E-9
9-anthraldehyde	3.69E-9	400	1.11E-8
9-fluorenone	2.82E-8	n/a	n/a
9-methylanthracene	3.66E-8	n/a	n/a
A-dimethylphenanthrene	7.04E-9	662	3.02E-8
A-methylfluorene	6.38E-9	n/a	n/a
A-methylphenanthrene	3.34E-8	145	6.70E-8
A-methylpyrene	2.11E-9	175	4.65E-9
A-trimethylnaphthalene	9.05E-9	84.1	1.45E-8
Acenaphthene	1.55E-8	62.6	2.27E-8
Acenaphthenequinone	5.48E-8	136	1.06E-7
Acenaphthylene	6.04E-8	283	1.77E-7
Anthrone	1.17E-8	68.9	1.76E-8

Table 5-2. Primary Emissions - Carbon and Semi-Volatile Organic Compounds.

· · · · · ·	Average	Uncertainty	95% Confidence
Compound	(lb/MMBtu)	(%)	Upper Bound
-	· · · · · ·		(lb/MMBtu)
Anthracene	7.83E-8	112	1.39E-7
Anthraquinone	4.00E-8	64.4	5.90E-8
B-dimethylphenanthrene	1.76E-8	238.1	3.88E-8
B-methylpyrene/methylfluorene	6.57E-9	230	1.69E-8
B-methylfluorene	1.13E-8	n/a	n/a
B-methylphenanthrene	5.10E-8	113	9.14E-8
B-trimethylnaphthalene	9.50E-9	91.9	1.57E-8
Benzo(a)pyrene	8.75E-9	67.7	1.31E-8
Benz(a)anthracene	2.51E-8	137	4.88E-8
Benz(a)anthracene-7,12	2.17E-8	64.6	3.20E-8
Benzanthrone	3.22E-8	56.1	4.59E-8
Benzo(b)chrysene	2.39E-8	56.0	3.40E-8
Benzo(b+j+k)fluoranthene	2.78E-8	58.1	4.00E-8
benzo(c)phenanthrene	9.50E-9	99.1	1.61E-8
Benzo(ghi)perylene	8.87E-9	77.7	1.38E-8
Benzonaphthothiophene	3.19E-9	100	5.43E-9
Benzo(e)pyrene	4.22E-9	116	7.64E-9
Biphenyl	2.49E-7	372	8.78E-7
C-dimethylphenanthrene	1.82E-8	315	5.72E-8
C-methylphenanthrene	1.57E-8	78.7	2.45E-8
C-trimethylnaphthalene	1.10E-8	75.6	1.70E-8
Cholestane	1.91E-7	75.3	2.94E-7
Chrysene	1.84E-8	70.9	2.79E-8
Coronene	1.80E-7	62.5	2.64E-7
D-dimethylphenanthrene	1.17E-8	76.4	1.81E-8
D-methylpyrene/methylfluorene	4.19E-9	143.1	8.34E-9
Dibenz(ah+ac)anthracene	7.33E-9	78.5	1.15E-8
Dibenzofuran	1.80E-8	66.3	2.68E-8
E-dimethylphenanthrene	1.14E-8	445	3.67E-8
E-methylpyrene/methylfluorene	1.25E-9	246	3.35E-9
E-trimethylnaphthalene	1.54E-8	297	4.64E-8
F-trimethylnaphthalene	1.84E-8	264.2	4.28E-8
Fluoranthene	2.83E-7	136	5.49E-7
Fluorene	1.11E-7	76.4	1.72E-7
Indeno[123-cd]pyrene	6.15E-9	70	9.31E-9
Naphthalene	1.04E-7	544	3.88E-7
Perinaphthenone	3.78E-7	134	7.29E-7
Perylene	3.01E-9	117	5.47E-9
Phenanthrene	1.03E-6	93.8	1.71E-6
Pyrene	1.99E-7	126	3.72E-7
Retene	1.10E-8	144	2.19E-8
Xanthone	3.10E-8	n/a	n/a

Table 5-2 (continued). Primary Emissions – Carbon and Semi-volatile Organic Compounds.

	Average	Uncertainty	95% Confidence
Compound	(lb/MMBtu)	(%)	Upper Bound
			(lb/MMBtu)
Semi-Volatile Organic Compounds (as mea	sured on the in-	stack filter)	
1,4-chrysenequinone	5.29E-10	n/a	n/a
1-methylnaphthalene	8.54E-9	594	3.38E-8
1-methylphenanthrene	8.02E-10	177	1.53E-9
2-methylnaphthalene	1.29E-8	773	6.24E-8
2-methylphenanthrene	1.87E-9	249	4.21E-9
Acenaphthene	7.01E-9	713	3.19E-8
Anthrone	5.25E-10	n/a	n/a
Benzo(a)pyrene	3.24E-9	465	1.07E-8
Benz(a)anthracene	2.91E-9	n/a	n/a
Benzo(b)chrysene	9.28E-10	567	3.55E-9
Biphenyl	5.77E-9	n/a	n/a
Dibenzofuran	3.42E-9	520	1.23E-8
Naphthalene	4.09E-8	131	7.80E-8
Perinaphthenone	6.75E-9	691	3.00E-8

Table 5-2 (continued). Primary Emissions - Carbon and Semi-volatile Organic Compounds.

n/a- not applicable; only one run was within detectable limits.

Table 5-3 presents the emission factors for VOCs with a carbon number greater than 7. All VOCs are present at extremely low levels, with benzaldehyde being the most abundant  $(5.6 \times 10^{-5} \text{ lb/MMBtu})$ .

Emission factors for SO₂ and NO_x are presented in Table 5-4.

# PM2.5 SPECIATION PROFILES

# Dilution Tunnel

Table 5-5 shows the speciation profile for PM2.5 as measured by the dilution tunnel. This table includes all results from the ED-XRF analysis of the dilution tunnel TMFs, the ion analysis of the dilution tunnel quartz filters and the OC/EC analysis of the dilution tunnel quartz filters. The mass fractions presented are the ratio of the emission factor of the emitted compound over the emission factor of the sum of the species. The sum of the species excludes results for Na and Mg (these are considered semi-quantitative), Cl⁻ (because total Cl by ED-XRF is included), total carbon (because EC and OC are included), and S (because  $SO_4^-$  by IC is included).

	Average	Uncertainty	95% Confidence
	(lb/MMBtu)	(%)	Upper Bound
		77	
1,2,4-trimetnyibenzene	7.23E-7	210	1.1E-0
2-methyloctane	3./0E-/	210	9.0E-7
Acetophenone	5.21E-5	76	8.1E-5
Benzaldehyde	5.85E-5	106	1.0E-4
Benzonitrile	5.54E-6	56	7.9E-6
Biphenyl	5.76E-7	273	1.6E-6
Butylated hydroxytoluene	8.98E-6	188	2.1E-5
Decane	2.26E-7	112	4.0E-7
Dodecane	3.05E-7	72	4.6E-7
Eicosane	3.23E-7	158	6.7E-7
Ethylbenzene	2.45E-7	92	4.0E-7
Heptadecane	6.72E-7	68	1.0E-6
Hexadecane	4.72E-7	171	1.0E-6
m & p-xylenes	1.07E-6	94	1.8E-6
Nonadecane	3.74E-7	127	7.1E-7
Nonane	3.63E-7	121	6.7E-7
o-xylene	5.06E-7	95	8.5E-7
Octadecane	5.71E-7	58	8.2E-7
p-isopropyltoluene	3.45E-8	n/a	n/a
Pentadecane	4.83E-7	323	1.5E-6
Phenol	2.40E-5	79	3.8E-5
Styrene	2.53E-6	60	3.7E-6
Tetradecane	6.11E-7	171	1.3E-6
Tridecane	5.41E-7	76	8.4E-7
Undecane	4.53E-7	80	7.1E-7
Total	1.61E-4		

Table 5-3. Emission Factors for Secondary Organic Aerosol Precursors (VOC).

n/a - not able to calculate standard deviation because there is only one run ND - not detected

Table 5-4	<b>Emission Factors</b>	for Second	lary Organic	Aerosol Precurso	$rs - NO_{u}$ and	SO ₂
1 auto 3-4.	Limssion i actors		ary Organic		15 100x and	$\mathbf{SO}_{2}$

Parameter	Average	Uncertainty	95% Confidence
	(lb/MMBtu)	(%)	Upper Bound
CEMS Values			
NO _x	1.02E-1	41.62	1.39E-1
$SO_2$	9.39E-3	41.62	1.28E-2

	Average	Uncertainty	95% Confidence
Compound	Mass Fraction (1)	(%)	Upper Bound
	(%)		(%)
Aluminum	9.8E-2	194	2.3E-1
Arsenic	7.7E-2	203	1.8E-1
Calcium	1.6E-1	237	4.3E-1
Chlorine	2.6E-1	n/a	n/a
Cobalt	4.1E-3	810	2.1E-2
Chromium	5.9E-3	n/a	n/a
Copper	5.7E-1	218	1.4E+0
Iron	7.1E-1	203	1.7E+0
Potassium	6.9E-2	220	1.7E-1
Magnesium*	5.1E-2	347	1.7E-1
Nickel	8.3E-2	205	2.0E-1
Lead	2.1E-2	1005	1.3E-1
Silicon	4.7E-1	197	1.1E+0
Sodium*	7.8E-1	247	2.1E+0
Sulfur*	3.3E+0	202	7.8E+0
Titanium	1.7E-2	n/a	n/a
Uranium	5.3E-3	n/a	n/a
Vanadium	1.4E-1	210	3.5E-1
Zinc	5.8E-2	206	1.4E-1
Organic Carbon	56.8	194	1.3E+2
Elemental Carbon	34.6	219	8.6E+1
Total Carbon*	91.4	196	2.1E+2
Sulfate	5.25	198	1.2E+1
Nitrate	ND	n/a	n/a
Chloride*	0.31	n/a	n/a
Ammonium	0.59	209	1.4E+0
Total	100		

Table 5-5. Speciation Profile for Dilution Tunnel Primary Emissions for Gas-Fired Boiler (Refinery Site A).

ND - all three runs were non-detect

n/a- not applicable; only one run within detectable limits.

1-Mass fraction is emission factor of species divided by emission factor of sum of species.

Speciated mass was greater than total PM2.5 mass measured on the dilution tunnel filter.

*These compounds are not included in the sum of species.

The average emission factor for the PM2.5 mass  $(3.6 \times 10^{-4} \text{ lb/MMBtu}, \text{ measured})$ 

gravimetrically) is approximately 30 percent greater than the average emission factor for the sum

of species (2.7 x 10⁻⁴ lb/MMBtu). This difference is most likely due to the bias associated with the different analytical methods used to determine the speciation of the mass versus the gravimetric analysis used to measure total PM2.5 mass. In addition, the dilution sampler used two different types of filters: TMFs were used for the elemental analysis and particulate mass, while quartz filters were used for OC/EC analysis and ionic analysis. It is possible that variations in particle deposition occurred between the different filters, resulting in a bias. Inhomogeneous deposition on the filter could also cause a bias because the OC/EC analysis and ion analysis each take only part of the filter for analysis, and the total mass on the filter is normalized assuming that this mass is evenly distributed over the collection area.

Figure 5-1 shows the data presented in Table 5-5 divided into elements (results of the ED-XRF analysis and carbon from TOR), ions and OC/EC (subset of total carbon). The majority of the mass is OC (57 percent) and EC (35 percent). Compounds with all runs below detectable levels are not included in the figure. Chloride ion, S, Na and Mg were all measured at detectable levels, but are not included in the sum of species to avoid double counting (Cl⁻ and Cl, S and SO₄⁼) and because Na and Mg data are semi-quantitative. Therefore, these compounds are not included as mass fractions in the figure.

### Method 201A/202

Table 5-6 shows the speciation profile of the PM2.5 mass as measured by Method 201A/202. Mass fraction is the ratio of the measured quantity to the total PM2.5 mass (FPM plus CPM). In this table, blank corrected total CPM data are presented, and have been subdivided to show the amount accounted for by  $SO_4^=$  and  $CI^-$ .

The data from Table 5-6 are shown in Figure 5-2. As can be seen from the figure, nearly all of the PM2.5 mass comes from inorganic CPM mass (greater than 99 percent).

### SPECIATION PROFILES FOR ORGANIC AEROSOLS

#### **Dilution Tunnel Organic Speciation**

Table 5-7 shows the organic aerosol speciation profile, expressed as a mass fraction. This mass fraction is determined by dividing the average emission factor of the emitted quantity by the average emission factor for OC.

5-8



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	Average		95% Confidence
Compound	Mass Fraction	Uncertainty	Upper Bound
	(%)	(%)	(%)
Filterable PM2.5	0.29	215	4.5
Total CPM	99.9	221	250
-Sulfate (as SO ₄ ⁼ )*	16	203	39
-Chloride (as NH ₄ Cl)*	3.3	206	8
Organic Carbon**	1.1	200	2.7
Elemental Carbon**	2.2	223	5.5
Total Carbon**	3.3	195	7.7

Table 5-6. Speciation Profile for PM2.5 for Gas-Fired Boiler (Refinery Site A) (Method 201A/202.

*Sulfate and Chloride are a subset of the total CPM.

**Organic, elemental and total carbon are a subset of the filterable particulate.

The data from Table 5-7 are shown in Figure 5-3. As can be seen on the figure, the most abundant fraction of the speciated organic aerosol is phenanthrene (0.7 percent), followed by perinaphthenone (0.2 percent).

# Method 201A/202 Organic Speciation

Table 5-8 shows the organic aerosol speciation for the Method 201A/202 data.

Figure 5-4 shows the data from Table 5-8. The most abundant of the speciated organics aerosol measured on the in-stack filter is napththalene (0.04 percent), followed by 2-methylnaphthalene (0.01 percent).



Compound	Average Mass	Uncertainty	95% Confidence
1	Fraction (1) (%)	(%)	Upper Bound (%)
1+2-ethylnanhthalene	0.01	707	0.05
1 2 8-trimethylnaphthalene	0.002	224	0.05
1.2.0 unifetilyinaphthalene	0.002	$\frac{22}{n/a}$	n/a
1 3+1 6+1 7-dimethylnaphthalene	0.01	233	0.07
1.4+1.5+2.3-dimethylnaphthalene	0.03	233 n/a	n/a
1 4-chrysenequinone	0.007	265	0.02
1.7-dimethylphenanthrene	0.003	203	0.007
1-ethyl-2-methylnanhthalene	0.005	226	0.007
1-MeFl+C-MePv/Fl	0.005	699	0.07
1-methylfluorene	0.006	202	0.01
1-methylnaphthalene	0.02	251	0.01
1-nhenylnaphthalene	0.02	225	0.02
235+I-trimethylnaphthalene	0.007	201	0.017
2 4 5-trimethylnanhthalene	0.00	233	0.01
2 6+2 7-dimethylnaphthalene	0.00	233	0.01
2-methylbinhenyl	0.015	n/a	n/a
2-methylnaphthalene	0.03	245	0.08
2-methylphenanthrene	0.02	239	0.06
2-phenylnaphthalene	0 020	225	0.05
3 6-dimethylphenanthrene	0.01	319	0.02
3-methylbiphenyl	0.028	225	0.07
4-methylbiphenyl	0.004	234	0.01
4-methylpyrene	0.00	275	0.01
4H-cvclopenta(def)phenanthrene	0.013	210	0.033
5+6-methylchrysene	0.00	229	0.01
7-methylbenzo(a)pyrene	0.013	201	0.030
9,10-dihydrobenzo(a)pyrene	0.003	209	0.007
9-anthraldehyde	0.00	783	0.01
9-fluorenone	0.02	n/a	n/a
9-methylanthracene	0.024	n/a	n/a
A-dimethylphenanthrene	0.005	944	0.03
A-methylfluorene	0.00	n/a	n/a
A-methylphenanthrene	0.022	236	0.06
A-methylpyrene	0.00	256	0.00
A-trimethylnaphthalene	0.01	205	0.01
Acenaphthene	0.01	197	0.02
Acenaphthenequinone	0.0354	231	0.09
Acenaphthylene	0.04	339	0.13
Anthrone	0.01	199	0.02
Anthracene	0.051	217	0.126
Anthraquinone	0.026	197	0.06
B-dimethylphenanthrene	0.011	715	0.052
B-MePy/MeFl	0.004	296	0.01
B-methylfluorene	0.01	n/a	n/a

Table 5-7. Organic Aerosol Speciation Profile.

Compound	Average Mass	Uncertainty	95% Confidence
-	Fraction (1) (%)	(%)	Upper Bound (%)
B-methylphenanthrene	0.033	218	0.08
B-trimethylnaphthalene	0.006	208	0.01
Benzo(a)pyene	0.01	198	0.01
Benz(a)anthracene	0.02	231	0.04
Benz(a)anthracene-7,12	0.01	197	0.03
Benzanthrone	0.02	195	0.05
Benzo(b)chrysene	0.02	195	0.04
Benzo(b+j+k)fluoranthene	0.018	195	0.04
Benzo(c)phenanthrene	0.006	211	0.02
Benzo(ghi)perylene	0.006	202	0.014
Benzonaphthothiophene	0.002	212	0.005
Benzo(e)pyrene	0.00	220	0.01
Biphenyl	0.16	416	0.62
C-dimethylphenanthrene	0.012	366	0.04
C-methylphenanthrene	0.010	202	0.02
C-trimethylnaphthalene	0.01	201	0.02
Cholestane	0.12	201	0.29
Chrysene	0.01	199	0.03
Coronene	0.117	197	0.27
D-dimethylphenanthrene	0.008	201	0.018
D-MePy/MeFl	0.003	235	0.007
Dibenz(ah+ac)anthracene	0.00	202	0.01
Dibenzofuran	0.012	198	0.03
E-dimethylphenanthrene	0.0074	808	0.037
E-MePy/MeFl	0.001	309	0.00
E-trimethylnaphthalene	0.01	350	0.03
F-trimethylnaphthalene	0.01	724	0.05
Fluoranthene	0.18	231	0.47
Fluorene	0.072	201	0.171
Indeno[123-cd]pyrene	0.0040	199	0.01
Naphthalene	0.07	866	0.36
Perinaphthenone	0.244	229	0.628
Perylene	0.00	220	0.0
Phenanthrene	0.67	209	1.62
Pyrene	0.129	225	0.33
Retene	0.01	236	0.02
Xanthone	0.02	n/a	n/a

Table 5-7 (continued). Organic Aerosol Speciation Profile.

n/a - not applicable, only one run was within detectable limits.





Compound	Average	Uncertainty	95%
	Mass	(%)	Confidence
	Fraction (1)		Upper
	(%)		Bound (%)
1,4-chrysenequinone	0.0005	n/a	n/a
1-methylnaphthalene	0.0081	898	0.0444
1-methylphenanthrene	0.0008	697	0.0034
2-methylnaphthalene	0.0122	1025	0.0747
2-methylphenanthrene	0.0018	718	0.0081
Acenaphthene	0.0067	981	0.0392
Anthrone	0.0005	n/a	n/a
Benzo(a)pyrene	0.0031	818	0.0156
Benz(a)anthracene	0.0028	NA	NA
Benzo(b)chrysene	0.0009	881	0.0048
Biphenyl	0.0055	n/a	n/a
Dibenzofuran	0.0033	851	0.0170
Naphthalene	0.0389	228	0.0995
Perinaphthenone	0.0064	965	0.0372

Table 5-8. Organic Aerosol Speciation Profile (Method 201A/202).

n/a - not applicable; only one run was within detectable limits.



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# Section 6 QUALITY ASSURANCE

### SAMPLE STORAGE AND SHIPPING

All samples were stored on-site in an ice chest prior to shipment to Desert Research Institute (DRI) for analysis. Samples were shipped and stored in a manner to prevent breakage. Upon receipt of samples at DRI, those requiring refrigeration were stored at 4°C.

### DILUTION TUNNEL FLOWS

Flows through the various sampling components of the dilution tunnel were determined by averaging the flow measured before testing commenced and after sampling was completed. Results from the pre- and post-test flow checks are presented in Table 6-1. All post-test flows were within 20 percent of their respective pre-test flow values.

# GRAVIMETRIC ANALYSIS

Prior to testing, unused filters were stored for at least one month in a controlled environment, followed by one week of equilibration in the weighing environment, to achieve stable filter tare weights. New and used filters were equilibrated at  $20 \pm 5^{\circ}$ C and a relative humidity of  $30 \pm 5^{\circ}$  percent for a minimum of 24 hours prior to weighing. Weighing was performed on a Cahn 31 electro-microbalance with  $\pm 1$  microgram sensitivity. The electrical charge on each filter was neutralized by exposure to a polonium source for 30 seconds prior to the filter being placed on the balance pan. The balance was calibrated with a 20 mg Class M weight and the tare was set prior to weighing each batch of filters. After every 10 filters were weighed, the calibration and tare were rechecked. If the results of these performance tests deviated by more than  $\pm 5 \mu g$ , the balance was recalibrated. If the difference exceeded  $\pm 15 \mu g$ , the balance was recalibrated and the previous 10 samples were reweighed. One hundred percent of initial weights and at least 30 percent of exposed weights were checked by an independent technician, and samples were reweighed if these check-weights did not agree with the original weights within  $\pm 0.015$  mg. Preand post-weights, check weights and reweights (if required) were recorded on data sheets as well as being directly entered into a database via an RS232 connection.

bite Hj.					
Run	Pre-test (scfh)	Post-test (scfh)	Average	% Difference	
Quartz Filter Flow (scfh)					
1	85.00	88.00	86.50	-4%	
2	85.00	70.00	77.50	18%	
3	85.00	74.00	79.50	13%	
	Tefle	on [®] Filter Flow (s	cfh)		
1	85.00	88.00	86.50	-4%	
2	85.00	70.00	77.50	18%	
3	85.00	74.00	79.50	13%	
	M	ake Up Flow (scfl	n)		
1	250.00	256.00	253.00	-2%	
2	248.00	218.00	233.00	12%	
3	244.00	222.00	233.00	9%	
		PUF/XAD (scfh)			
1	250.00	246.00	248.00	2%	
2	248.00	244.00	246.00	2%	
3	244.00	238.00	241.00	2%	
Tenax Tube A (scfh)					
1	0.10	0.10	0.10	0%	
2	0.10	0.09	0.09	12%	
3	0.10	0.08	0.09	20%	
	T	enax Tube B (scfh	l)		
1	0.10	0.10	0.10	-2%	
2	0.10	0.09	0.09	13%	
3	0.10	0.09	0.10	6%	

Table 6-1. Pre-and Post-Test Dilution Tunnel Flow Checks for the Gas-Fired Boiler (Refinery Site A).

Table 6-2 presents the results of the dichloromethane, water and acetone rinse blanks. These blank values were used to correct the EPA Method 201A/202 particulate data. In some cases, the measured organic mass was less than the mass measured in the dichloromethane reagent blank. Acetone blank correction of the Method 201A data resulted in negative weights for Runs 1 and 3. They are reported as undetected and excluded from summations and averages, where applicable.

Results of the filter blank weights are also presented in Table 6-2. All Method 201A in-stack filter weights were negative and treated as a zero in sums. These results indicate that the particulate levels are below the practical quantitation limits of the method.

Blank Result	Mass (mg)
Water Recovery Blank	1.3
Dichloromethane Recovery Blank	1.1
Acetone Recovery Blank	0.4

Table 6-2. Method 201A/202 Blank Results.

Filter Blanks	mg/dscm
In-stack Filter	not valid
Dilution Tunnel	5.4E-4

The acetone rinse blank results are presented in Table 6-3. A detection limit was calculated by multiplying the standard deviation of the results of the field-blank acetone rinses and the acetone recovery blank by three. The resulting detection limit of approximately 2 milligrams further indicates that the filterable particulate levels at the boiler are below detection limits. Therefore, the filterable particulate data from Methods 201A are presented here for qualitative purposes.

Table 6-3. Results from Field Blank Acetone Rinses.

	Mass (mg)
PM10 Catch, Acetone Wash	0.5
PM2.5 Catch, Acetone Wash	1.5
2.5-front half Acetone Wash	0.3
Recovery Blank	0.4
Detection Limit (3*standard deviation	n) 2

# ELEMENTAL (XRF) ANALYSIS

Three types of XRF standards were used for calibration, performance testing and auditing: 1) vacuum-deposited thin-film elements and compounds (supplied by Micromatter, Deer Harbor, WA); 2) polymer films; and 3) NIST thin-glass films. The vacuum deposit standards cover the largest number of elements and were used as calibration standards. The polymer film and NIST standards were used as quality control standards. Standards from the National Institute of Standards and Technology (NIST) are the definitive standard reference material, but are only available for the species Al, Ca, Co, Cu, Mn, and Si (SRM 1832) and Fe, Pb, K, Si, Ti, and Zn (SRM 1833). A separate Micromatter thin-film standard was used to calibrate the system for each element.

A quality control standard and a replicate from a previous batch were analyzed with each set of 14 samples. When a quality control value differed from specifications by more than  $\pm 5$  percent, or when a replicate concentration differed from the original value (when values exceed 10 times the detection limits) by more than  $\pm 10$  percent, the samples were reanalyzed. If further tests of standards showed that the system calibration had changed by more than  $\pm 2$  percent, the instrument was recalibrated as described above. All XRF results were directly entered into the DRI databases.

Results from the field blank are presented in Table 6-4. Indium and phosphorous were present at detectable levels in the blank, but not in the field samples. Magnesium in the field blank was within an order of magnitude of the average sample concentration. All other compounds detected in the field blank were present at insignificant levels compared to levels contained in the stack samples.

Element	mg/dscm
Aluminum	2.1E-5
Indium	1.6E-5
Magnesium	4.6E-5
Phosphorus	7.0E-6
Silicon	8.8E-6
Sulfur	5.7E-6

Table 6-4. Field Blank for Elements.

# ORGANIC AND ELEMENTAL CARBON ANALYSIS

The TOR system was calibrated by analyzing samples of known amounts of methane, carbon dioxide, and potassium hydrogen phthalate (KHP). The FID response was compared to a reference level of methane injected at the end of each sample analysis. Performance tests of the instrument calibration were conducted at the beginning and end of each day's operation. Intervening samples were reanalyzed when calibration changes of more than  $\pm 10$  percent were found.

Known amounts of American Chemical Society (ACS) certified reagent grade crystal sucrose and KHP were committed to TOR as a verification of the organic carbon fractions. Fifteen

different standards were used for each calibration. Widely accepted primary standards for elemental and/or organic carbon are still lacking. Results of the TOR analysis of each filter were entered into the DRI database.

Results of the field blank are presented in Table 6-5. Blank levels were much lower than sample levels for both the dilution tunnel filters and the Method 201A filters.

	OC	EC
In-stack Sample Run 1	1.3E-1	1.0E-1
In-stack Sample Run 1 (Replicate)	1.3E-1	9.8E-2
In-stack Field Blank	4.1E-3	ND
Dilution Tunnel Field Blank	5.5E-3	7.7E-6

Table 6-5. Organic and Elemental Carbon Blanks and Replicate Sample (mg/dscm).

# SULFATE, NITRATE, CHLORIDE, AND AMMONIUM ANALYSIS

The primary standard solutions containing NaCl, NaNO₃ and (Na)₂SO₄ were prepared with reagent grade salts which were dried in an oven at 105 °C for one hour and then brought to room temperature in a desiccator. These anhydrous salts were weighed to the nearest 0.10 mg on a routinely calibrated analytical balance under controlled temperature (approximately 20 °C) and relative humidity (±30 percent) conditions. These salts were diluted in precise volumes of DI water. Calibration standards were prepared at least once each month by diluting the primary standard solution to concentrations covering the range of concentrations expected in the filter extracts and stored in a refrigerator. The calibration concentrations prepared were at 0.1, 0.2, 0.5, 1.0, and 2.0 µg/ml for each of the analysis species. Calibration curves were performed weekly. Chemical compounds were identified by matching the retention time of each peak in the unknown sample with the retention times of peaks in the chromatograms of the standards. A DI water blank was analyzed after every 20 samples and a calibration standard was analyzed after every 10 samples. These quality control checks verified the baseline and calibration, respectively. Environmental Research Associates (ERA, Arvada, CO) standards were used daily as an independent quality assurance (QA) check. These standards (ERA Wastewater Nutrient and ERA Mineral WW) were traceable to NIST simulated rainwater standards. If the values obtained for these standards did not coincide within a pre-specified uncertainty level (typically

three standard deviations of the baseline level or  $\pm 5$  percent), the samples between that standard and the previous calibration standards were reanalyzed.

After analysis, the printout for each sample in the batch was reviewed for the following: 1) proper operational settings; 2) correct peak shapes and integration windows; 3) peak overlaps; 4) correct background subtraction; and 5) quality control sample comparisons. When values for replicates differed by more than  $\pm 10$  percent, or values for standards differed by more than  $\pm 5$  percent, samples before and after these quality control checks were designated for reanalysis in a subsequent batch. Individual samples with unusual peak shapes, background subtractions, or deviations from standard operating parameters were also designated for reanalysis.

Five standard concentrations of ammonium standards were prepared from ACS reagent-grade  $(NH_4)_2SO_4$  following the same procedure as that for IC standards. Each set of samples consisted of 2 distilled water blanks to establish a baseline, 5 calibration standards and a blank, then sets of 10 samples followed by analysis of one of the standards and a replicate from a previous batch. The computer control allowed additional analysis of any filter extract to be repeated without the necessity of loading the extract into more than one vial.

Results from the field blank are presented in Table 6-6. Nitrates were not present at detectable levels in the field blank. Concentrations in the field blanks are insignificant compared to levels in the stack samples.

Table 6-6.	Ion Blank Results.
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Ion	mg/dscm
Chloride	6.0E-5
Nitrate	ND
Sulfate	3.2E-5
Ammonium	3.4E-5

ND- not detected

# SVOC ANALYSIS

Prior to sampling, the XAD-4 resin was Soxhlet extracted with methanol, followed by dichloromethane, each for 24 hours. The cleaned resin was dried in a vacuum oven heated to

40°C and stored in sealed glass containers in a clean freezer. The PUF plugs were Soxhlet extracted with acetone, followed by 10 percent diethyl ether in hexane. The TIGF filters were cleaned by sonification in dichloromethane for 30 minutes followed by another 30-minute sonification in methanol. Then they were dried, placed in aluminum foil, and labeled. Each batch of precleaned XAD-4 resin and approximately 10 percent of the precleaned TIGF filters and PUF plugs were checked for purity by solvent extraction and GC/MS analysis of the extracts. The PUF plugs and XAD-4 resins were assembled into glass cartridges (10 g of XAD between two PUF plugs), wrapped in hexane-rinsed aluminum foil and stored in a clean freezer prior to shipment to the field.

Prior to extraction, the following deuterated internal standards were added to each filter-sorbent pair:

naphthalene-d8	9.76	ng/µl	
acenaphthene-d8	10.95	ng/µl	(for acenapththene and acenaphthylene)
biphenyl-d10	7.56	ng/µl	
phenanthrene-d10	4.61	ng/µl	
anthracene-d10	3.5	ng/µl	
pyrene-d10	5.28	ng/µl	(for fluoranthene and pyrene)
chrysene-d12	3.54	ng/µl	(for benz[a]anthracene and chrysene)
benzo[e]pyrene-d12	4.20	ng/µl	
benzo[a]pyrene-d12	4.68	ng/µl	
benzo[k]fluoranthene-d12	2.0	ng/µl	
benzo[g,h,i]perylene-d12	1.0	ng/µl	(for indeno[1,2,3-cd]pyrene,
			dibenzo[ah+ac]anthracne,
			benzo[ghi]perylene and coronene)

Calibration curves for the GC/MS/MID quantification were made for the molecular ion peaks of the PAH and all other compounds of interest using the corresponding deuterated species (or the deuterated species most closely matched in volatility and retention characteristics) as internal standards. NIST Standard Reference Material (SRM) 1647 (certified PAH), with the addition of deuterated internal standards and compounds not present in the SRM, was used to make calibration solutions. Three concentration levels for each analyte were employed, and each calibration solution was injected twice. After the three-level calibration was completed, a standard solution was injected to perform calibration checks. If deviation from the true value

exceeded 20 percent, the system was recalibrated. The mass selective detector (MSD) was tuned daily for mass sensitivity using perfluorotributylamine.

In addition, one level calibration solution was run daily. If the difference between true and measured concentrations exceeded 20 percent, the system was recalibrated.

Table 6-7 presents the field blank results for the dilution tunnel SVOCs. Only compounds present at detectable levels are included. Most of the average SVOC sample concentrations are at least an order of magnitude greater than their respective field blank concentrations. The field blank concentrations of 2-methylbiphenyl, 4-methylbiphenyl, 9,10-dihydrobenzo(a)pyrene, 9-anthraldehyde, a-methylpyrene, anthrone, cholestane and dibenz(ah+ac)anthracene are all greater than their average sample concentrations. Bibenzene is present at detectable levels in the blank but not present in the stack samples.

In addition, replicate analyses of a dilution tunnel sample were performed to determine reproducibility of results (Table 6-8).

### VOC ANALYSIS

Calibration curves were performed weekly. Volatile organic compounds were identified by matching the response factors of each unknown sample with the response factors of the standards. Tenax cartridges spiked with a mixture of paraffinic (in the C₉-C₂₀ range) and aromatic (C₄, C₅, and C₆ benzenes) hydrocarbons were periodically analyzed by GC/FID to verify quantitative recovery from the cartridges. Three to five different concentrations of the HC standard and one zero standard were injected, and the response factors obtained. If the percent difference of the response factor from the mean was more than 5 percent, the response factors were corrected before proceeding with the analysis.

Table 6-8 shows the results of the Tenax field blank. Only compounds with concentrations above the detection limit are shown. The average sample concentrations of styrene and decane are within an order of magnitude of their concentrations in the field blank sample. 1,2,3-trimethylbenzene was present at detectable levels in the field blank but not in the stack or

Compound	mg/dscm
1.4-chrysenequinone	2.46E-5
1-MeFl+C-MePy/Fl	1.00E-6
1-methylnaphthalene	2.43E-6
1-phenylnaphthalene	7.00E-7
2.3.5+I-trimethylnaphthalene	4.75E-7
2-methylbiphenyl	1.46E-5
2-phenylnaphthalene	2.25E-7
4-methylbiphenyl	7.68E-6
4H-cvclopenta(def)phenanthrene	7.50E-6
9,10-dihydrobenzo(a)pyrene	3.63E-5
9-anthraldehyde	2.95E-5
A-methylpyrene	2.25E-6
Acenaphthenequinone	2.00E-5
Anthracene	9.50E-7
Anthraquinone	1.46E-5
Anthrone	2.30E-4
B-trimethylnaphthalene	2.00E-7
Benz(a)anthracene	1.58E-6
Benz(a)anthracene-7,12	6.40E-6
Benzanthrone	6.78E-6
Benzo(a)pyrene	9.25E-7
Benzo(b)chrysene	1.63E-6
Benzo(b+i+k)fluoranthene	4.25E-7
Benzo(e)pyrene	2.18E-6
Benzo(ghi)pervlene	6.68E-6
Bibenzene	2.45E-4
C-trimethylnaphthalene	5.50E-7
Cholestane	2.26E-5
Chrysene	4.18E-6
Dibenz(ah+ac)anthracene	1.69E-5
Fluoranthene	3.00E-7
Indeno[123-cd]pyrene	4.60E-6
Pervlene	2.20E-6
Phenanthrene	1.80E-6
Pyrene	2.25E-6
Xanthone	7.18E-6

Table 6-7. SVOC PUF/XAD Field Blank Results.

ambient samples. All other compounds present at detectable levels in the field blank are at least one order of magnitude lower than those present in the stack samples.

	Sample	Replicate
Compound	(mg/dscm)	(mg/dscm)
1+2-ethylnaphthalene	ND	ND
1,2,8-trimethylnaphthalene	1.2E-6	1.0E-6
1,2-dimethylnaphthalene	ND	ND
1,3+1,6+1,7-dimethylnaphthalene	ND	ND
1,4+1,5+2,3-dimethylnaphthalene	ND	ND
1,4,5-trimethylnaphthalene	2.1E-5	2.3E-5
1,4-chrysenequinone	2.4E-4	2.5E-4
1,7-dimethylphenanthrene	ND	ND
1,8-dimethylnaphthalene	ND	ND
1-ethyl-2-methylnaphthalene	5.0E-6	6.0E-6
1-MeFl+C-MePy/Fl	ND	ND
1-methylfluorene	3.7E-6	ND
1-methylphenanthrene	3.2E-6	2.7E-6
1-methylpyrene	ND	ND
1-phenylnaphthalene	1.3E-5	1.2E-5
2,3,5+I-trimethylnaphthalene	1.4E-5	1.4E-5
2,6+2,7-dimethylnaphthalene	7.0E-6	1.2E-5
2-ethyl-1-methylnaphthalene	2.8E-5	2.6E-5
2-methylbiphenyl	1.7E-4	1.6E-4
2-methylphenanthrene	1.5E-5	1.5E-5
2-phenylnaphthalene	1.1E-5	1.2E-5
3,6-dimethylphenanthrene	ND	ND
3-methylbiphenyl	1.1E-4	1.1E <b>-</b> 4
4-methylbiphenyl	8.4E-5	9.4E-5
4-methylpyrene	5.0E-7	3.2E-6
4H-cyclopenta(def)phenanthrene	8.0E-5	7.7E-5
7-methylbenz(a)anthracene	ND	ND
7-methylbenzo(a)pyrene	5.5E-6	2.8E-5
9,10-dihydrobenzo(a)pyrene	3.6E-4	3.6E-4
9-anthraldehyde	3.0E-4	2.9E-4
9-fluorenone	2.8E-5	1.1E <b>-</b> 4
9-methylanthracene	3.5E-6	ND
A-dimethylphenanthrene	ND	ND
A-methylfluorene	2.8E-5	2.7E-5
A-methylphenanthrene	1.1E-5	1.5E-5
A-methylpyrene	2.3E-5	2.1E-5
A-trimethylnaphthalene	5.2E-6	5.7E-6
Acenaphthylene	ND	ND
Anthrone	2.3E-3	2.3E-3
B-dimethylphenanthrene	1.6E-5	1.7E-5
B-MePy/MeFl	1.5E-6	2.5E-7

Table 6-8. SVOC PUF/XAD Replicate Analysis Results.

	Sample	Replicate
Compound	(mg/dscm)	(mg/dscm)
B-methylfluorene	ND	ND
B-methylphenanthrene	1.0E-5	1.3E-5
Benz(a)anthracene	2.4E-5	4.3E-5
Benz(a)anthracene-7,12	7.9E-5	8.4E-5
Benzanthrone	7.9E-5	1.0E-4
Benzo(a)pyrene	1.2E-5	3.1E-5
Benzo(b)chrysene	2.6E-5	5.5E-5
Benzo(b+j+k)fluoranthene	2.6E-5	5.6E-5
Benzo(c)phenanthrene	4.2E-6	6.5E-6
Benzo(e)pyrene	2.4E-5	3.6E-5
Biphenyl	2.5E-5	2.4E-5
C-dimethylphenanthrene	ND	ND
C-methylphenanthrene	6.5E-6	1.1E-5
C-trimethylnaphthalene	1.2E-5	1.3E-5
Chrysene	7.0E-5	7.1E-5
Coronene	1.3E-4	3.0E-4
D-dimethylphenanthrene	1.6E-5	1.5E-5
Dibenz(ah+ac)anthracene	1.7E-4	1.8E-4
Dibenzofuran	7.2E-6	6.5E-6
E-dimethylphenanthrene	ND	ND
E-trimethylnaphthalene	4.0E-6	3.5E-6
F-trimethylnaphthalene	7.0E-6	8.2E-6
Fluoranthene	1.0E-4	9.7E-5
Fluorene	7.1E-5	6.7E-5
Indeno[123-cd]pyrene	4.9E-5	5.5E-5
J-trimethylnaphthalene	1.0E-6	ND
Naphthalene	8.7E-4	7.7E-4
Perinaphthenone	7.3E-5	1.4E-4
Perylene	2.3E-5	2.8E-5
Phenanthrene	5.6E-4	5.3E-4
Pyrene	9.7E-5	9.4E-5
Retene	7.5E-6	6.5E-6
Xanthone	4.8E-5	5.7E-5

Table 6-8 (continued). SVOC PUF/XAD Replicate Analysis Results.

MeFl- Methylfluorene MePy- Methylpyrene ND- not detected

# CEMS ANALYSIS

The response of the CO analyzer to  $CO_2$  was determined prior to testing to allow correction of results for any resulting bias, if necessary. The instruments generally were calibrated, at a minimum, at the beginning, middle, and end of the test day, with more frequent calibration and zero drift checks if necessary. Test results were corrected for any drift in excess of the method specifications (generally  $\pm 3$  percent).

# Section 7 DISCUSSION AND FINDINGS

### PM2.5 MASS MEASUREMENTS

PM2.5 mass measured using in-stack methods (including CPM as measured by Method 201A/202) was approximately 27 times greater than the PM2.5 mass measured by the dilution tunnel. The PM2.5 mass measured by the dilution tunnel is 17 times greater in the stack than in the ambient air. The dilution tunnel is designed to capture filterable matter plus any aerosols that condense under simulated stack plume conditions. The dilution tunnel cools the stack sample to the ambient temperature, which in these tests was typically between 70-88°F. The in-stack methods are designed to collect particles that are filterable at the stack temperature plus those which condense in a series of impingers placed in an ice bath. The gas temperature leaving the impingers is typically between 55-65°F; thus, both systems cool the sample to similar final temperatures. The in-stack methods cool the sample rapidly without dilution by quenching the gas sample in water maintained near freezing, while the dilution tunnel cools the sample more slowly by mixing it with ambient temperature air. Since aerosol condensation mechanisms depend on temperature, concentration, residence time and other factors, it is not entirely surprising that the results of the two methods differ. However the magnitude of the difference in these tests is greater than can easily be explained by mechanistic differences alone.

Greater than 99 percent of the mass from in-stack methods was contained in the condensible particulate fraction, approximately 96 percent of which was inorganic (i.e., not extractable in dichloromethane). While sulfate was found to be a significant component of the inorganic fraction, most of the inorganic condensibles were unspeciated following the analytical procedure prescribed by Method 202. Based on a more extensive analysis of the inorganic fraction residue conducted several months after the initial results were obtained, most of the inorganic CPM mass is sulfate and ammonium (Figure 7-1). The ammonium is most likely present due to addition of ammonium hydroxide to the inorganic fraction during analysis to stabilize sulfate for gravimetric analysis. The large fraction of sulfate, however, was not expected given the very low concentration of SO₂ in the stack gas. Sulfur dioxide levels in the flue gas averaged approximately 3.6 ppm over the six days of testing at the boiler. Compared to this value, the

sulfate levels measured by the dilution tunnel accounted for approximately 0.2 percent of the  $SO_2$  in the flue gas, while the levels measured by Method 202 accounted for approximately 16 percent.

Artifacts from  $SO_2$  absorption in the impingers of the Method 202 train leading to a positive bias in the results have been previously documented for  $SO_2$  concentrations on the order of 2000 ppm



Figure 7-1. Speciation of Inorganic Impinger Fraction (Refinery Boiler Site A).

(Filadelfia and McDannel, 1996). Sulfur dioxide and  $O_2$  dissolve in the impinger solution (water), and some of the SO₂ slowly oxidizes to SO₃⁻ which is absorbed as SO₄⁼. To minimize this bias, Method 202 recommends a purge of the impingers with nitrogen (or, as a lesser preference, air) immediately following sample collection to remove dissolved SO₂ prior to sample storage. Method 202 optionally allows the post-test purge to be omitted if the pH of the impingers is above 4.5. The pH of the impingers met this criteria in these tests, therefore the purge was not performed. Filadelfia and McDannel demonstrated the post-test purge does not entirely eliminate SO₂ bias under the conditions of their study. No literature was found to evaluate if this artifact would be significant at sub-10 ppm SO₂ concentrations.

A laboratory scale study was undertaken to evaluate potential bias at low SO₂ concentrations and with long (6-hour) test runs (see Appendix A for complete details). Simulated combustion products (O₂, CO₂, NO, N₂, and SO₂) were passed through Method 202 impinger trains. No condensible substances were added. Tests were performed with and without a post-test nitrogen purge and for 1-hour and 6-hour sampling runs at 0, 1, and 10 ppm SO₂. The results with no purging showed that there was significant sulfate present in the samples in proportion to the SO₂ concentration in the gas for both 1-hour and for 6-hour runs (Figure 7-2). The post-test purge did significantly reduce the sulfate concentration but did not entirely eliminate the bias. The purge was considerably less efficient for the 6-hour runs compared to the 1-hour runs, indicating that significant SO₂ oxidation occurs within this time frame. The figure also compares the sulfate results from the field tests to the lab results. Although there is significant scatter, the amount of sulfate detected in the field samples is reasonably consistent with the amount expected from the lab tests. This clearly shows that the sulfate, and hence most of the condensible particulate, collected in the Method 202 stack samples results from gaseous SO₂ in the stack sample and not from condensible sulfate species.

The particulate emission factors obtained from the Method 201A/202 trains agree qualitatively with results reported by EPA in its AP-42 emission factor database for natural gas combustion in external combustion devices. The EPA results were obtained using the same methods, therefore a similar bias may be present in those data. Nevertheless, the semi-quantitative agreement of the results from these tests to EPA's using the same methods provides additional confidence in the integrity of tests.

The above results show that traditional source testing methods (i.e., EPA Method 202) may significantly overestimate particulate mass emissions and the contribution of sulfates to primary emissions. All of the Method 201A filter weights were negative due to the loss of small filter pieces during sample recovery. These low weights indicate that the particulate masses collected were at or below the practical limits of the method as practiced in these tests. Dilution tunnel



Figure 7-2. Results of Laboratory Tests Showing Effect of SO₂ and Purge on Method 202 Sulfate Bias.

methods provide conditions which more closely simulate true atmospheric condensation conditions than do impinger condensation methods. For these reasons, the dilution tunnel results are considered more indicative of the actual particulate mass emissions from the boiler than EPA Methods 201A/202. Future tests will include a more extensive and accurate analysis of the condensible fraction to determine the reasons for the differences between methods.

### CHEMICAL SPECIATION OF PRIMARY PM2.5 EMISSIONS

The results obtained using the dilution tunnel are believed to provide the best representation of chemical species present in the stack gas. Ions, carbon and other elements were detected in both stack and ambient air samples. Aluminum and calcium concentrations were slightly higher in the ambient air sample than in the stack sample (Figure 7-3); therefore, it is questionable that these compounds originated from the boiler combustion process. Bromine, manganese, rubidium, strontium, zirconium and nitrate were detected in the ambient air but not in the stack samples (N.B., the detection limits for in-stack samples are a factor of approximately 6 higher than those for ambient air samples because of stack sample dilution). The average concentrations of several other compounds, including sulfates and ammonium, were within a factor of ten of their respective concentrations in the ambient air. Thus, many of those compounds detected in the stack samples cannot be distinguished reliably from the background ambient level. Those compounds that were present at concentrations significantly above the ambient level are OC, EC, sodium, copper, chlorine, vanadium, nickel, and arsenic. Cobalt, chromium, and uranium also appeared elevated in the stack sample above the ambient level; however, these and other compounds were present at levels too near (i.e., within a factor of ten) the minimum method detection limits (Figure 7-4) to be considered reliable.

By subtracting ambient from in-stack concentrations and ignoring compounds measured near the detection limits, those compounds considered good markers of boiler emissions should be revealed. The resulting emissions profile (Figure 7-5) shows the most significant compounds are OC, EC, sulfates/sulfur, sodium, iron, copper and chloride/chlorine. Sodium results, however, should be ignored because they are not accurately quantified by the analytical method. Organic Carbon and EC account for 68 percent of the measured PM2.5 mass. Chlorine was detected in only one of the three test runs, so the uncertainty in the emission level is unknown but could be very large.

1.E+00

Boiler Ambient 1.E-01 1.E-02 Concentration (mg/dscm) 1.E-03 1.E-04 7-6 1.E-05 1.E-06 1.E-07 Мg Ŵ Na Вb 5 5 5 5 3 PP s is si n > R As ā e E ¥ ïŻ PM2.5 mass

Figure 7-3. In-Stack and Ambient Species Concentrations (Dilution Tunnel).

-£0N

NH4+ CC-

S04=

۳Z

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Figure 7-4. Comparison of Species Concentrations to Detection Limits (Dilution Tunnel).

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Figure 7-5. Mean Species Concentrations and Standard Deviation (Dilution Tunnel)

Arsenic, nickel, vanadium and ammonium are present at levels high enough to be potential secondary markers, although the scatter in the ammonium data (as indicated by the standard deviation represented by a dot on Figure 7-5) indicates considerable uncertainty in its emission level. The absence of a dot (standard deviation) in Figure 7-5 indicates the compound was detected in only one run. Other compounds were present at lower levels but the low concentrations and high or unknown standard deviations associated with most of these data tend to suggest they may not be reliable markers.

The sum of the species represented in Figure 7-5 account for 74 percent of the total PM2.5 mass generated by the boiler. Part of the difference can be explained by the fact that most of the elements will be present in the oxide form; the weight of oxygen is not included in the sum of the elemental species. The overall agreement is good, and is probably within the total uncertainty of the measurements.

Another potentially useful marker for source emissions is the organic emissions profile. All of the SVOCs detected were present at extremely low concentrations. Approximately two-thirds of the SVOCs were detected at concentrations less than 10 times the level detected in the ambient air, and approximately one-third of the compounds were detected at less than 10 times the field blank levels. Thus, the SVOCs contributed by the boiler are largely undistinguishable from the background levels. SVOCs also were measured on the in-stack filters, but very few compounds were present at detectable levels compared to the dilution tunnel samples. The purpose of analyzing the in-stack filters for SVOC species was to estimate the particulate-bound SVOCs, while using the dilution tunnel to collect total particulate, condensed, and gaseous SVOCs. The sum of SVOCs collected on the in-stack filters (arguably, particulate-bound SVOC) is 2 percent of the total SVOCs measured in the dilution tunnel samples. The sum of detected SVOCs accounts for only about 3 percent of OC, indicating the possible presence of unspeciated organics. This large difference can be explained at least in part by the difference in analytical methods (the TOR method defines OC somewhat arbitrarily) and the presence of organic species that are not quantifiable by the methods used in this project. This gap in the speciation of OC has been observed to varying degrees in most other studies of similar scope (e.g., Hildemann et al., 1994). Only a handful of SVOCs are present at more than 10 times the ambient air or blank

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concentration (but still at extremely low concentrations): 2-phenylnaphthalene, acenaphthenequinone, pyrene, fluoranthene, 4h-cyclopenta(def)phenanthrene, dmethylpyrene/methylfluorene, phenanthrene, anthracene, biphenyl, and benzo(e)pyrene. These compounds are characteristic of fuel pyrolysis products that escape complete combustion.

#### SECONDARY PM2.5 PRECURSOR EMISSIONS

Secondary precursor emissions considered in this project were NO_X, SO₂, ammonia/ammonium, and VOCs. Nitrogen Oxide emissions arise from three mechanistic sources: "thermal NO" from high temperature dissociation of molecular nitrogen; "fuel NO" from the oxidation of fixed nitrogen species present in the fuel; and "prompt NO" from reaction of molecular nitrogen with oxygen radicals in the early part of the flame. In gas combustion, thermal NO and prompt NO are the prinicpal sources of Nitrogen Oxide emissions since the fuel is usually free of significant fixed nitrogen species. Nitrogen Oxide concentration is 73-79 ppm (dry, corrected to 3 percent oxygen) which is in the range expected for gas combustion in this boiler design and operating conditions. Sulfur dioxide concentration averaged 3-4 ppm during these tests. This is nominally consistent with the measured H₂S content of the refinery fuel gas. No measurements for gaseous ammonia were made, since ammonia was not expected in the flue gas. Ammonium measurements from the dilution tunnel showed ammonium present at very low and variable levels.

VOCs with a carbon number greater than 7 are believed to be precursors for secondary organic aerosols (Turpin and Huntzinger, 1991). Of the VOCs with a carbon number greater than 7 detected in the stack samples, the majority were present at concentrations less than a factor of ten above the ambient air concentration. All VOC concentrations were extremely low. Benzaldehyde and acetophenone were the first and second highest average concentrations measured, respectively. The other VOCs present were characteristic of partially combusted fuel fragments and pyrolysis products which escape complete combustion.

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# Appendix A

### GLOSSARY

, 2	· ,• ,				
μg/cm ²	micrograms per square centimeter				
AC	automated colorimetry system				
actm	actual cubic feet per minute				
ACS	American Chemical Society				
Ag	silver				
Al	aluminum				
API	American Petroleum Institute				
As	arsenic				
ASME	American Society of Mechanical Engineers				
Ba	barium				
Br	bromine				
Btu/scf	British thermal units per standard cubic foot				
Ca	calcium				
Cd	cadmium				
CEMS	continuous emissions monitoring system				
C _x	compound containing 'x' carbon atoms				
Cl	chloride ion				
Cl	chlorine				
Co	cobalt				
СО	carbon monoxide				
$CO_2$	carbon dioxide				
CPM	condensible particulate matter				
Cr	chromium				
Cu	copper				
DI	distilled deionized				
DRI	Desert Research Institute				
dscfm	dry standard cubic feet per minute				
dscmm	dry standard cubic meters per minute				
ED-XRF	energy dispersive x-ray fluorescence				
EER	GE Energy and Environmental Research Corporation				
EC	elemental carbon				
EI	electron impact				
EPA	Environmental Protection Agency				
ERA	Environmental Research Associates				
°F	degrees Fahrenheit				
Fe	iron				
FID	flame ionization detection				
FPM	filterable particulate matter				
FTIR	Fourier transform infrared detection				
ft/sec	feet per second				
Ga	gallium				
GC	gas chromatography				
	gas emomatography				

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### GLOSSARY (continued)

GC/IRD/MSD	gas chromatography/infrared detector/mass selective detector
GC/MS	gas chromatography/mass spectrometry
GE	General Electric
GE EER	General Electric Energy and Environmental Research Corporation
gr/100dscf	grains per hundred standard cubic feet
G-S	Greenburg-Smith
Hg	mercury
$H_2S$	hydrogen sulfide
HCl	hydrochloric acid
HEPA	high efficiency particulate air
HHV	higher heating value
IC	ion chromatography
In	indium
Κ	potassium
KHP	potassium hydrogen phthalate
La	lanthanum
lb/hr	pounds per hour
lb/MMBtu	pounds of pollutant per million British thermal units of gas fired
m/sec	meters per second
Mg	magnesium
mg	milligram
mg/dscm	milligrams per dry standard cubic meter
MID	multiple ion detection
Mlb/hr	thousand pounds per hour
MMBtu/hr	million British thermal units per hour
Mn	manganese
Мо	molybdenum
MSD	mass spectrometric detector
MSD/FTIR	mass selective detector/Fourier transform infrared detection
Na	sodium
Na ₂ CO ₃	sodium carbonate
NaCl	sodium chloride
NaHCO ₃	sodium bicarbonate
NaNO ₃	sodium nitrate
NaOH	sodium hydroxide
$(Na)_2SO_4$	sodium sulfate
NDIR	non-dispersive infrared
$\mathrm{NH_4}^+$	ammonium ion
$(NH_4)_2SO_4$	ammonium sulfate
Ni	nickel
NIST	National Institute of Standards and Technology
NO	nitric oxide
NO ₂	nitrogen dioxide

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## GLOSSARY (continued)

NO ₃ ⁻	nitrate ion
NO _x	oxides of nitrogen
$O_2$	molecular oxygen
OC	organic carbon
Р	phosphorus
РАН	polycyclic aromatic hydrocarbon
Pb	lead
PCA	Portland Cement Association
Pd	palladium
PM	particulate matter
PM10	particulate with aerodynamic diameter less than 10 micrometers
PM2.5	particulate with aerodynamic diameter less than 2.5 micrometers
ppmv	parts per million (volume)
psig	pounds per square inch (gauge)
PUF	polyurethane foam
QA	quality assurance
Rb	rubidium
RSD	relative standard deviation
S	sulfur
Sb	antimony
Si	silicon
Sn	tin
$SO_2$	sulfur dioxide
$SO_4^{=}$	sulfate ion
Sr	strontium
SRM	standard reference material
SVOC	semivolatile organic compound
TFE	tetrafluoroethylene
Ti	titanium
TIGF	Teflon [®] -impregnated glass fiber
T1	thallium
TMF	Teflon [®] -membrane filter
TOR	thermal/optical reflectance
U	uranium
V	vanadium
VOC	volatile organic compound
XRF	x-ray fluorescence
XAD-4	Amberlite [®] sorbent resin (trademark)
Y	yttrium
Zn	zinc
Zr	zirconium

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# Appendix B

## SI CONVERSION FACTORS

	<u>English (US) units</u>	×	<u>Factor</u>	=	<u>SI units</u>
Area:	$1 \text{ ft}^2$	×	9.29 x 10 ⁻²	=	$m^2$
	$1 \text{ in}^2$	×	6.45	=	cm ²
Flow Rate:	1 gal/min	×	6.31 x 10 ⁻⁵	=	m ³ /s
	1 gal/min	×	6.31 x 10 ⁻²	=	L/s
Length:	1 ft	×	0.3048	=	m
C	1 in	×	2.54	=	cm
	1 yd	×	0.9144	=	m
Mass:	1 lb	×	$4.54 \ge 10^2$	=	g
	1 lb	×	0.454	=	kg
	1 gr	×	0.0648	=	g
Volume:	$1 \text{ ft}^3$	×	28.3	=	L
	$1 \text{ ft}^3$	×	0.0283	=	$m^3$
	1 gal	×	3.785	=	L
	1 gal	×	3.785 x 10 ⁻³	=	m ³
Temperature:	°F-32	×	0.556	=	°C
1	°R	×	0.556	=	Κ
Energy:	Btu	×	1055.1	=	Joules
Power:	Btu/hr	×	0.29307	=	Watts

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