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Gas Fired Heater—Test Report Site B

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

Regulatory and Scientific Affairs

PUBLICATION NUMBER 4704 AUGUST 2001

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PREPARED UNDER CONTRACT BY: GE ENERGY AND ENVIRONMENTAL RESEARCH CORPORATION 18 MASON IRVINE, CA 92618



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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aerosols from petroleum industry combustion sources, and the limited information that is available is incomplete and outdated.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 a 114 million British thermal unit (MMBtu) per hour gas-fired refinery process heater. The process heater has a refractory-lined rectangular box furnace with a single row of burners on two opposing sides of the furnace with a tubular process fluid heat exchanger located at the top of the furnace. The unit has no controls for NO_x emissions. The flue gas temperature at the stack was approximately 680°F 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 were 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 process heater 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% confidence upper bound also are presented.

Emission factors for semi-volatile organic species are presented in Table E-2. The sum of semi-volatile organic species is approximately 3% 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 in-stack 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.

ES-2

The main findings of these tests are:

- Particulate mass emissions from the process heater 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 89:0.000054 lb/MMBtu using the dilution tunnel; and 0.0048 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 100% of the measured PM2.5 mass were quantified.
- Organic and elemental carbon comprise 49% of the measured primary PM2.5 mass.
- Sulfate, ammonium, chloride and nitrate together account for approximately 32% of the measured PM2.5 mass; sulfate alone accounts for approximately 22%.
- Cobalt, calcium, silicon, copper, zinc, iron, aluminum and lanthanum account for approximately 17% of the measured PM2.5 mass. Smaller amounts of ten other detected elements comprise the remaining 2%.
- 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		Flag	Emission	Uncertainty	95 %
			Factor	(%)	Confidence
			(lb/MMBtu)		Upper
					Bound
					(lb/MMBtu)
Particulate	Condensible Particulate (inorganic)		4.8E-3	201	1.1E-2
Mass	Condensible Particulate (organic)		2.4E-4	161	4.9E-4
	Total condensible particulate		4.6E-3	209	1.1E-2
	Total Filterable PM (in-stack method)	B	1.0E-3	51	1.4E-3
	Filterable PM10 (in-stack method)	B	6.4E-4	82	1.0E-3
	Filterable PM2.5 (in-stack method)	В	2.2E-4	62	3.1E-4
	PM2.5 (in-stack method)	(2)	4.8E-3	_	_
	PM2.5 (Dilution Tunnel)	*	5.4E-5	309	1.7E-4
Elements	Aluminum	*	8.7E-7	218	2.2E-6
	Barium	*	5.6E-7	205	1.1E-6
	Bromine	*	1.1E-8	n/a	n/a
	Calcium	*	1.9E-6	297	5.6E-6
	Chlorine		1.9E-6	1075	1.2E-5
	Chromium	(1)	2.6E-8	n/a	n/a
	Cobalt		3.8E-6	421	1.5E-5
	Copper		1.3E-6	110	2.3E-6
	Iron	*	1.1E-6	284	3.1E-6
	Lanthanum	(1)	7.1E-7	n/a	n/a
	Magnesium	*	8.1E-8	340	2.2E-7
	Manganese	*	5.9E-8	n/a	n/a
	Nickel	*	5.9E-8	153	1.2E-7
	Phosphorous		9.8E-8	168	1.8E-7
	Potassium	*	2.7E-7	221	6.8E-7
	Silicon	*	1.4E-6	270	4.1E-6
	Sodium	*, B	1.0E-7	n/a	n/a
	Strontium		2.8E-8	n/a	n/a
	Sulfur	*	3.3E-6	278	9.6E-6
	Zinc		1.1E-6	199	2.6E-6
Ions	Chloride	(1)	2.7E-6	530	9.8E-6
	Nitrate	*	1.1E-6	n/a	n/a
	Sulfate	*	1.5E-5	992	8.9E-5
	Ammonium	*	3.3E-6	696	1.5E-5
Carbon	Organic Carbon (dilution tunnel)	*, B	2.8E-5	89	4.5E-5
	Elemental Carbon (dilution tunnel)	*	1.9E-5	n/a	n/a
	Total Carbon (dilution tunnel)	*	3.4E-5	145	6.8E-5

Table E-1. Summary of Primary Particulate Emission Factors for Gas-Fired Process Heater.

* <10x ambient

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

(2) Sum of total condensible PM and filterable PM2.5

B <10x blank

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

			Emission		95 % Confidence
	Substance		Factor (lb/MMBtu)	Uncertainty (%)	Upper Bound (lb/MMBtu)
Dilution	Dilution Coronene		1 6E-7	189	3 6E-7
Tunnel	2-methylbinhenyl	* B	8 3E-8	n/a	n/a
	3-methylbinhenyl	* B	5.7E-8	n/a	n/a
	Phononthrono	, D *	5.7E 8	65	7 6E-8
	9 fluoronono	(1) (2)	1 OE 8	05 n/a	7.0L-0
	2 mathulnanhthalana	(1), (2) * D	4.96-0	11/a	11/a n/a
	C mothylphononthrono	, р	4.312-8	n/a	n/a
		р	4.3E-0 2.0E.9	11/a	
	Elementer	Б	3.9E-0	255	0.0E-0 1.1E-7
	Fluoranthene	(1) (2)	3.8E-8	219	1.1E-7
	A-methylfiluorene	(1), (2)	3.0E-8	/5	5.5E-8
	1-methyinaphthalene	*, B	2.6E-8	n/a	n/a
	I-methylfluorene	(1), (2)	2.2E-8	n/a	n/a
	B-methylphenanthrene		2.1E-8	233	5.6E-8
	1,3+1,6+1,7-dimethylnaphthalene	*	2.1E-8	n/a	n/a
	Benzo(b+j+k)fluoranthene	*, В	1.5E-8	205	3.6E-8
	C-dimethylphenanthrene	(1), (2)	1.5E-8	n/a	n/a
	2-methylphenanthrene	*	1.4E-8	170	3.1E-8
	4-methylbiphenyl	*, B	1.4E-8	872	7.6E-8
	B-dimethylphenanthrene	*	1.4E-8	361	3.8E-8
	Pyrene	*, B	1.3E-8	76	2.0E-8
	2,6+2,7-dimethylnaphthalene	*	1.1E-8	n/a	n/a
	Benz(a)anthracene-7,12	(1), B	1.1E-8	937	6.1E-8
	9-methylanthracene	(1), (2)	1.0E-8	756	5.0E-8
	Benzo(b)chrysene	*, B	1.0E-8	183	2.3E-8
	2,3,5+I-trimethylnaphthalene	*	9.8E-9	130	1.9E-8
	1.2.8-trimethylnaphthalene		8.2E-9	n/a	n/a
	C-trimethylnaphthalene	*	8.1E-9	121	1.5E-8
	Benzanthrone	*. B	7.6E-9	168	1.6E-8
	Anthrone	*. B	7.3E-9	99	1.2E-8
	A-dimethylphenanthrene	(1), (2)	6.9E-9	n/a	n/a
	A-trimethylnaphthalene	*	6.8E-9	118	1.2E-8
	Dibenz(ah+ac)anthracene	* B	6.8E-9	213	1.4E-8
	B-trimethylnanhthalene	*	6 3E-9	82	1 0E-8
	Anthracene	* B	5.9E-9	167	1.0E 0
	F-trimethylnanhthalene	, D *	5.1E-9	149	1.5E 0 1.0E-8
	Indeno[123-cd]nyrene	* B	5.0E-9	247	1.0E 0
	Benzo(a)nyrene	* B	4.7E-9	221	9.9F-9
	Benzo(ghi)pervlene	, D * В	4.7E 9 4.6E-9	189	1.1E-8
	7-methylbenzo(a)nyrene	, D * R	4 5F-9	422	1 4F-8
	F trimethylpenbthalono	, D *	$\frac{1}{4}$	123	9 2E 0
	1 mothylphonenthrone	(1)	4.4D-9	525	0.2L-9 1.5E 9
	Chrysona		4.1E-9 4.0E 0	140	
	A mothylayrana	, р	4.0E-9 2.0E 0	140	0.0E-9 7 4E 0
	H-meury pyrene Donz(a) on throanna	а а * р	3.0E-9 2.0E 0	130	1 0E 0
	Anthroquinono	, D	J.0E-7 2.7E 0	230 n/o	1.0E-0
	Anun ayunone		3./E-9 2.1日 0	10 <i>4</i>	
	1 -curyi-2-meuryinaphunatene	$\begin{bmatrix} T, B \\ (1) \end{bmatrix}$	3.1E-9	180	7.2E-9
	1, /-anneuryipnenanurrene		3.0E-9	1/0	3.7世-9
	B-memyipyrene/metnyimuorene	<u>ي</u>	2.9E-9	624	1.2E-8
	E-methylpyrene/methylfluorene	*	2.8E-9	935	1.6E-8
	9,10-dinydrobenzo(a)pyrene	*, B	2.8E-9	208	6./E-9
	9-anthraldehyde	(1), B	2.6E-9	n/a	n/a
	1,4-cnrysenequinone	^°, B	2.5E-9	166	5.3E-9

Table E-2. Summary of Semi-volatile Organic Species Emission Factors for Gas-Fired Process Heater.

(1) <10x detection limit, another = N
(2) <10x detection limit, blank = ND
* <10x ambient
B <10x blank

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	Substance		Emission Factor (lb/MMBtu)	Uncertainty (%)	95 % Confidence Upper Bound (lb/MMBtu)
Dilution	Benzonaphthothiophene	*, B	2.4E-9	n/a	n/a
Tunnel	1-methylfluorene+C-methylpyrene/methylfluorene	(1), B	2.1E-9	338	5.7E-9
	1-phenylnaphthalene	(1), B	2.1E-9	n/a	n/a
	Benzo(c)phenanthrene	(1), B	1.6E-9	234	4.3E-9
	Pervlene	*, B	1.5E-9	262	3.5E-9
	4H-cyclopenta(def)phenanthrene	*, B	1.3E-9	98	2.2E-9
	Benzo(e)pyrene	*, B	1.2E-9	790	5.9E-9
	5+6-methylchrysene	*	9.6E-10	265	2.7E-9
	1-methylpyrene	(1), B	7.9E-10	n/a	n/a
	D-methylpyrene/methylfluorene	(1), (2)	5.1E-10	136	9.9E-10
	2-phenylnaphthalene	*, B	2.5E-10	168	4.6E-1 <u>0</u>
	Sum of All SVOCs		6.6E-7		
In-Stack	1,2,8-trimethylnaphthalene		7.2E-10	n/a	n/a
Filter	1,4-chrysenequinone	*	2.5E-9	n/a	n/a
	2,6+2,7-dimethylnaphthalene	*	6.8E-9	n/a	n/a
l	2-methylphenanthrene	*	1.4E-9	n/a	n/a
	4-methylbiphenyl	*	1.9E-9	n/a	n/a
	Benzo(a)pyrene	*	2.6E-9	266	6.0E-9
	Benzo(b)chrysene	*	2.6E-9	266	6.0E-9
	Biphenyl	*	7.7E-9	n/a	n/a
ļ	Sum of All SVOCs		1.0E-8		

Table E-2 (continued). Summary of Semi-volatile Organic Species Emission Factors for Gas-Fired Process Heater.

(1) <10x detection limit, ambient=ND
 (2) <10x detection limit, blank = ND
 * <10x ambient

B <10x blank

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				95 % Confidence
		Emission Factor	Uncertainty	Upper Bound
Substance		(lb/MMBtu)	(%)	(lb/MMBtu)
Gases SO ₂		1.1E-3	81	1.7E-3
	NOx	1.7E-1	81	2.7E-1
Volatile	1+7 hexadecene	1.9E-4	226	4.9E-4
Organic	1.2.3.4-tetramethylbenzene (1)	4.4E-7	n/a	n/a
Compounds	1.2.4 trimethylbenzene *	1.3E-6	57	1.9E-6
	1.3.5 trimethylbenzene *	4.3E-7	n/a	n/a
	1.3-dichlorobenzene *	1.2E-6	185	2.7E-6
	1-methylnaphthalene *	5.2E-7	n/a	n/a
	2-methyl octane *	1.2E-6	325	3.2E-6
	2-methylnaphthalene *	5.2E-7	n/a	n/a
	3-methyl octane *	4.1E-7	170	7.7E-7
	Acetophenone	6.6E-5	278	1.9E-4
	Benzaldehvde *	4.2E-5	216	1.0E-4
	Benzofuran	1.5E-6	312	4.0E-6
	Benzonitrile	1.6E-5	295	4.7E-5
	Biphenyl	7.6E-7	n/a	n/a
	c12 hydrocarbon 1† (1)	4.3E-6	96	7.3E-6
	c12 hydrocarbon 2† (1)	1.2E-6	426	3.9E-6
	c12 hydrocarbon 3† (1)	3.5E-6	540	1.3E-5
	c12 hydrocarbon 4† (1)	1.5E-6	461	5.0E-6
	c13 hydrocarbon 1†	3.6E-6	703	1.6E-5
	c14 hydrocarbon 1†	1.3E-6	191	3.1E-6
	Ethyl benzene *	9.8E-7	62	1.4E-6
	m- & p-xylenes *	3.1E-6	82	5.0E-6
	m-ethyltoluene *	7.4E-7	54	1.0E-6
	n-decane *	4.8E-7	337	1.3E-6
	n-dodecane *	8.5E-7	244	1.9E-6
	n-eicosane	9.9E-7	362	2.8E-6
	n-heptadecene	9.6E-7	382	2.8E-6
	n-hexadecene	1.5E-6	n/a	n/a
	n-nonadecane	2.0E-6	702	8.9E-6
	n-nonane *	9.8E-7	151	2.0E-6
	n-octadecane	1.0E-6	344	2.8E-6
	n-pentadecane *	9.7E-7	189	2.2E-6
	n-propylbenzene *	3.1E-7	184	5.9E-7
	n-tetradecane *	1.4E-6	159	2.9E-6
	n-tridecane	2.5E-6	313	7.8E-6
	n-undecane	4.3E-6	504	1.5E-5
	Naphthalene *	9.3E-7	388	2.7E-6
	Nonanol *	3.2E-7	n/a	n/a
	o-ethyltoluene *	3.4E-7	185	6.6E-7
	o-xylene *	1.4E-6	55	2.0E-6
	p-ethyltoluene *	3.4E-7	59	4.9E-7
	Phenol	2.8E-5	295	8.4E-5
	Styrene	3.8E-6	145	7.6E-6

Table ES-3. Summary of Secondary Particulate Precursor Emission Factors for Gas-Fired Refinery Process Heater.

* <10x ambient</p>

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

B <10x blank

† unidentified long-chain hydrocarbon

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Antimony	Acenaphthylene
Arsenic	B-methylfluorene
Cadmium	Bibenzene
Gallium	Biphenyl
Gold	Cholestane
Indium	D-dimethylphenanthrene
Lead	Dibenzofuran
Mercury	E-dimethylphenanthrene
Molybdenum	Fluorene
Palladium	J-trimethylnaphthalene
Rubidium	Naphthalene
Selenium	Perinaphthenone
Silver	Retene
Thallium	Xanthone
Tin	1-methylindan
Titanium	2-methylindan
Uranium	1,2,3-trimethylbenzene
Vanadium	1,2,3,5-tetramethylbenzene
Yttrium	1,2,4,5-tetramethylbenzene
Zirconium	2-methylindan
1+2-ethylnaphthalene	Cyclohexanone
1,2-dimethylnaphthalene	Dimethyloctane
1,4+1,5+2,3-dimethylnaphthalene	Dodecene
1,4,5-trimethylnaphthalene	Indan
1,8-dimethylnaphthalene	Indene
2,4,5-trimethylnaphthalene	m-isopropyltoluene
2-ethyl-1-methylnaphthalene	Nonene-1
3,6-dimethylphenanthrene	o-isopropyltoluene
7-methylbenz(a)anthracene	p-isopropyltoluene
A-methylphenanthrene	t-hydroxybutyltoluene
A-methylpyrene	Undecene-1
Acenaphthene	

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



Figure E-1. Speciation profile for primary particulate emissions from gas-fired process heater (Refinery Site B).

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, which 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. The dilution sampling protocol was 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 process heater at Refinery Site B on October 13, 14 and 15, 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 simultaneous collection and analysis of both in-stack and diluted stack gas samples. All emission samples were collected from the stack of the unit. The samples were analyzed for the compounds listed in Table 1-2. Heater 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.

Sampling Test Methods	Number of Samples at Each Sampling Location				
	Fuel Gas Heater	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	3				
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 13:1 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 into a residence time chamber 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 capture VOCs. Three samples were collected on three sequential test days.

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	In-Stack				Dilution Tunnel				
		Quartz			Quartz	TIGF/			
Parameters	Cyclones	Filter	Impingers	Gases	Filter	XAD-4	TMF	Tenax	Gases
Total PM mass	X	Х							
PM10 mass	Х	Х							
PM2.5 mass	Х	Х					X		
Condensible			v						
particulate mass			Λ						
Sulfate			Х		Х				
Chloride			Х		X				
Ammonium			Х		Х				
Nitrate			Х		X				
Elements			Х				X		
Organic carbon		Х			X				
Elemental carbon		Х			X				
Semivolatile organic compounds		X				X			
Volatile organic compounds*								Х	
NO _x				Х					
SO_2				Х					
СО				X					
O_2				Х					
CO ₂				Х					
Moisture or relative			x						x
humidity									Λ
Velocity				X					
Temperature				X					X

Table 1-2. Summary of Analytical Targets.

TMF = Teflon[®] membrane filter

TIGF = Teflon[®]-impregnated glass fiber filter

*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 process heater 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

GE Energy and Environmental Research Corporation (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 process heater at Refinery Site B. The heater has a maximum firing rate of 114 MMBtu/hr with a typical rate of approximately 70 MMBtu/hr. The unit is made up of 4 box-type heaters, with 30 burners on each side in an opposed fired configuration (60 per box), vented to a common stack. Each furnace is radiant-wall fired, and all four share one common convection coil. The heater is fired on refinery fuel gas and is a low temperature duty design with a typical furnace temperature of approximately 1500°F. The unit is not equipped with air pollution controls for NO_x, SO₂ or particulate. The heater appeared to be in good working condition during the test. Operating conditions during the test are given in Section 4. Process parameters monitored during testing include: fuel gas flow rate, specific gravity, heating value and H₂S content; process fluid flow rate; process fluid outlet temperature; excess oxygen; and burners in service (in or out).

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 360-degree sampling platform located 100 feet above the ground, which is accessible via a ladder. There are four threaded 4-inch diameter sampling ports with 4-inch pipe nipples welded to the stack, located orthogonally around the circumference approximately 52 inches above the platform. The stack diameter at this elevation is 74.3 inches. The sample ports are located 630 inches (8.5 diameters) downstream and 304 inches (4.1 diameters) upstream of the nearest flow disturbances. Following velocity and O_2 traverses to check for stratification, 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 from the gas supply fuel-sampling manifold. Ambient air samples were collected at near ground level close to the process heater.



Figure 2-1. Heater 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 13:51 hours and finished at 19:51 hours on Tuesday, October 13. Dilution tunnel testing and in-stack testing were performed concurrently. All samples were collected at approximately the same point in the center of the stack; the dilution tunnel and in-stack test method probes were co-located.

STACK GAS FLOW RATE, MOISTURE CONTENT AND MOLECULAR WEIGHT

An S-type Pitot tube (EPA Method 2) was used to determine the average 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 each test to determine total stack gas flow rate.

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 diaphragm pump, and a heated back-pressure regulator to a thermoelectric water condenser. The condenser's heat exchangers are specially designed impingers that separate the condensate from the gas sample with a

	-				
Sampling	Measurements	Sampling	Sample	Reference	
Location		Approach	Analyses		
S1 (Stack)	Total PM, PM10,	In-stack series cyclones and	Mass; organic species	U.S. EPA Method 201A	
	PM2.5 and	filter		(modified)	
	composition				
	PM composition	In-stack filter	Organic carbon, elemental	U. S. EPA Method 17	
			carbon	(modified)	
	Condensible PM and	Impingers	Mass (organic and inorganic),	U.S. EPA Method 202	
	composition		sulfate, chloride, nitrate,	(modified)	
			ammonium, elements		
	Gaseous PM2.5	Continuous	SO_2 and NO_X (O_2 , CO_2 , CO_2	U. S. EPA Methods	
	Precursors		also measured)	3A/6C/7E/10	
S1 (Stack)	PM2.5 mass and	Dilution tunnel and filters	Mass, organic carbon,	U.S. EPA, 1999a; Hildemann	
	chemical composition		elemental carbon, elements,	et al., 1989	
	-		sulfate, nitrate, chloride,		
			ammonium		
				Zielinska et al., 1996;	
	VOC	Dilution tunnel and Tenax	Speciated VOC	Hildemann et al., 1989	
		Dilution tunnel and		U.S. EPA Method TO13;	
	SVOC	filter/PUF/XAD-4/PUF	Speciated SVOC	Hildemann et al., 1989	
S2 (Ground Level -	PM2.5 and chemical	Filters	Mass, organic carbon,	U.S. EPA, 1999a	
Ambient Air)	composition		elemental carbon, organic		
			species, elements, chloride,		
		l	sulfate, nitrate, ammonium		
	VOC	Tenax	Speciated VOC	Zielinska et al., 1996	
	SVOC	PUF/XAD-4/PUF	Speciated SVOC	U.S. EPA Method TO13	
S3 (Fuel gas feed	Fuel gas composition	Integrated grab sample (bag	Hydrocarbon speciation and	ASTM D3588	
to heater)		or canister)	heating value		
S4 (Fuel gas	Liquid hydrocarbons	Composite grab sample	Ultimate Analysis (C, H, N, S,	ASTM D3176	
knockout drum)			O, ash), hydrocarbon		
			speciation		

Table 3-1. Summary of Test Procedures.

			Process Samples	Ambient Air				
Date	Time	Velocity and Moisture	Method 201/202	CEMS	Dilution Tunnel	Method 17	Fuel Sample	Dilution Tunnel
10/13/98 Tuesday	9:00 10:00 11:00 12:00 13:00	P/10:58-11:23 R1/13:59	R1/13:51	R1/12:45	R1/13:50	R1/13:50		
	14:00 15:00 16:00 17:00 18:00 19:00	19.51	19:51	19:41	19:50	19:50	<u>15:52 - 16:22</u> <u>17:30 - 18:00</u>	
	20:00 21:00	P/20:30-21:03	19.51	19.41	19.50	19.50		
10/14/98 Wednesday	9:00 10:00 11:00 12:00 13:00 14:00	P/8:58 - 9:25 R2/10:41	R2/10:41	R2/10:46	R2/10:40	R2/10:40	13:35 - 14:05	
	15:00 16:00 17:00 18:00 19:00	16:41 P/17:14-17:45	16:41	16:39	16:40	16:40		
10/15/98 Thursday	8:00 9:00 10:00 11:00	P/8:15-8:49 R3/11:26	R3/11:26	R3/11:28	R3/11:30	R3/11:25		
	12:00 13:00 14:00 15:00 16:00 17:00	17:26	17:26	17:22	16:45	17:25	15:42 - 16:12	
	18:00 19:00 20:00 21:00	<u>P/18:20-19:04</u>						
10/16/98 Friday	8:00 9:00 10:00 11:00 12:00 13:00 14:00 15:00							9:25

R1=Test Run 1; R2=Test Run 2; R3=Test Run 3; P=Pre- or Post-Test Run; A=Ambient Air Run.

Figure 3-1. Chronology for Gas-Fired Process Heater Tests (Refinery Site B).

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Figure 3-2. Continuous Emissions Monitoring System.
		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-	ACS	Bovar/Western
			Electron		Research
Model Number	Model 1400	Model 10AR with	Model 48H	Model 3300	Model 720 AT2
		molybdenum NO ₂			
		converter			
Detection principal	Paramagnetism	Chemi-	Gas filter	Non-dispersive	Ultraviolet
		luminescence	correlation	infrared	absorption (UV)
			infrared	absorption	
			absorption	(NDIR)	
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. CEMS Instrumentation Used For Gas-Fired Process Heater Test (Refinery Site B).

minimum of contact 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 components in contact with the sample were constructed of inert materials such as glass, stainless steel, and tetrafluoroethylene (TFE). All components preceding the condenser (probe, sample line, sample bypass regulator, and pump) were heated to 248° 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 chemiluminescence analyzer with a molybdenum nitrogen dioxide (NO₂)-to-nitric oxide (NO) converter according to EPA Method 7E. Sulphur 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 μ m (PM10) and 2.5 μ 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; and
- A modified filter assembly was employed in an effort to improve the precision of the gravimetric analysis for low particulate concentration.

The particulate mass collected in the two cyclones and on the filter was determined gravimetrically (Figure 3-5). The filters (Pallflex No. 51575) were weighed before and after testing on an analytical balance with a sensitivity of 10 micrograms. In an effort to improve the accuracy and precision of the gravimetric results, the filters, filter support and metal O-ring seals were weighed together to minimize post-test loss of filter matter during sample recovery. 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 Teflon[®] beaker liners for evaporation and weighing. Acetone and filter blanks also were collected and analyzed. See Section 4 for discussion of data treatment.



Series cyclone and filter assembly





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



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

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Subsequent to the planning of 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 of particulate sources. Method PRE-4 describes substantially the same sampling equipment and sample collection procedures used in these tests. The analytical procedures differ 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, preconditioned in the same manner as those used in the dilution tunnel, was used. 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 concurrently with the Method 201A/202 samples.



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 sample train consisted of 5 impingers in series. The first two impingers contained DI water and were of the standard Greenburg-Smith design. The third and fourth impingers were empty and of the modified Greenburg-Smith design. The fifth impinger, a modified Greenburg-Smith design, contained silica gel.
- A quartz filter was placed between the third and fourth 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;
- 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.



Figure 3-7. Method 202 Sample Recovery Procedure.



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

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.

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 backpressure 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, based on the prior work of Hildemann et al. (1989). Hildemann selected this ratio both to cool the sample and to ensure





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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 target 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 8:1. 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 not have been completely mixed with the dilution air. Based on profiles reported by Hildemann, this could 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 polymethylpentane ringed, 2.0 μ m pore size, TMF (Gelman No. RPJ047) 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 ±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 sodium 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 kilo electron volts (keV), 3.3 milliamp rhodium anode x-ray tube and secondary fluorescers was used. The silicon detector had an active area of 30 square millimeters, with a system resolution better than 165 electron volts (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

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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 (μ g/cm²) of OC and 0.5 μ 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 on 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 polycyclic aromatic hydrocarbons (PAH), and other compounds of interest, was obtained by multiple ion detection (MID).

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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 to SI units. Substances that were not detected in any of the three test runs generally are not listed on the tables. Where shown, undetected data are flagged "ND", treated as zeroes in sums, and excluded from average calculations. The approximate minimum in-stack detection limits achieved for all measured substances are given in Table 4-1.

PROCESS OPERATING CONDITIONS

Heater operating conditions during testing are summarized in Table 4-2. The process heater operated at close to its normal firing rate corresponding to approximately 44 percent of full firing capacity. All burners were in service during the tests. The stack gas temperature averaged approximately 700 °F. Excess O_2 measured at the furnace outlet by plant instrumentation was 5.6 to 7.1 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 the continuous specific gravity monitor. The average heat input to the process heater during the test is the product of the 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. Hydrogen sulfide concentration in the fuel gas, monitored directly by plant instrumentation, was 7.5 to 7.8 parts per million (ppm) by volume.

A process upset occurred during the first test run at approximately 16:00 hours on October 13 while samples were being collected. A hydrogen compressor in another section of the refinery went offline, which caused fuel gas composition, heater operating conditions, and process

	I I							· · ·	J		
	Dilution	In-stack		Dilution	In-stack		Dilution	In-stack		Dilution	In-stack
	Tunnel	methods	0.1.4	Tunnel	methods	0.1.	Tunnel	methods	0.1.	Tunnel	methods
Substance	mg/dscm	mg/dscm	Substance	mg/dscm	mg/dscm	Substance	mg/dscm	mg/dscm	Substance	mg/dscm	mg/dscm
Total PM mass		2.5E-05	Sr Ti	8.5E-00		2-methylnaphthalene	3.3E-00	2.1E-00	Benzo(gm)perylene	3.2E-07	3.3E-07
PMIU mass	 6 0E 04	2.5E-05	11	2.2E-05		2-meinyiphenantinrene	1.1E-07	1.1E-00 2.1E-06	Benzonaphinoiniophene	1.1E-07	4.2E-00
rivi2.5 mass	0.00-04	2.JE-03	11 TT	1.96-05		2-phenymaphinatene 2.6. dimothylphopanthropo	2.5E-06	2.1E-00	Bibbelizelle	2.60.06	2 1E 06
A1	7.75-05		v	1.00-05		3. mothylbinbonyl	1.2E-05	0.5E-06	B.mothylpyrona/mothylfluorona	5.0E-00	1.1E-06
Δs	1.7E-05		v	1.9E-05		4H-cyclopenta(def)phenanthrene	0.0E+00	1.6E-06	B-methylfluorene	3.5E-06	3 1E-05
Au	2.4E-05		Zn	8 5E-06		411-cyclopenta(def)phenanthrene 4-methylbinhenyl	1.0E-06	1.6E-06	B-methylphenanthrene	5.5E-07	1 1E-06
Ba	4 0E-04		2.n 7.r	1 3E-05		4-methylpyrene	1 1E-07	1.6E-06	B-trimethylnanhthalene	5 3E-08	3 2E-06
Br	7.7E-06			9.0E-04		5+6-methylchrysene	0.0E+00	3.5E-05	C-dimethylphenanthrene	1.8E-06	2.1E-06
Ca	3.5E-05		NO3-	9.0E-04		7-methylbenz(a)anthracene	3.3E-07	2.1E-06	Cholestane	1.4E-05	1.3E-04
Cd	9.2E-05		NH4+	9.0E-04		7-methylbenzo(a)pyrene	3.7E-07	1.3E-04	Chrysene	1.1E-07	2.1E-06
a	7.7E-05		CI-	9.0E-04		9.10-dihvdrobenzo(a)pyrene	1.6E-07	5.3E-07	C-methylphenanthrene	1.5E-06	1.1E-06
Co	6.8E-06		OC	6.7E-03	2.9E-03	9-anthraldehyde	1.4E-06	4.2E-06	Coronene	3.2E-07	5.3E-07
Cr	1.5E-05		EC	1.6E-03	6.8E-04	9-fluorenone	7.1E-06	1.6E-06	C-trimethylnaphthalene	4.2E-07	4.2E-06
Cu	8.5E-06		1,2,8-trimethylnaphthalene	3.2E-07	5.3E-07	9-methylanthracene	2.4E-06	2.1E-06	D-dimethylphenanthrene	1.6E-06	2.1E-06
Fe	1.2E-05		1,2-dimethylnaphthalene	3.7E-06	9.5E-06	Acenaphthene	1.4E-06	1.6E-06	Dibenz(ah+ac)anthracene	3.2E-07	5.3E-07
Ga	1.5E-05		1,3+1,6+1,7-dimethylnaphthalene	1.2E-05	2.7E-06	Acenaphthenequinone	3.2E-07	3.7E-06	Dibenzofuran	3.3E-06	1.1E-06
Hg	2.0E-05		1,4,5-trimethylnaphthalene	5.0E-06	2.1E-06	Acenaphthylene	5.5E-06	2.7E-06	D-methylpyrene/methylfluorene	5.3E-08	1.6E-06
In	1.0E-04		1,4+1,5+2,3-dimethylnaphthalene	5.4E-06	2.7E-06	A-dimethylphenanthrene	2.5E-06	2.1E-06	E-dimethylphenanthrene	8.0E-07	2.1E-06
K	4.7E-05		1,4-chrysenequinone	2.7E-07	5.3E-07	A-methylfluorene	5.6E-06	4.2E-06	E-methylpyrene/methylfluorene	5.3E-08	1.6E-06
La	4.8E-04		1,7-dimethylphenanthrene	1.8E-06	2.1E-06	A-methylphenanthrene	2.5E-06	1.1E-06	E-trimethylnaphthalene	5.3E-08	4.2E-06
Mg	0.0E+00		1,8-dimethylnaphthalene	3.7E-06	9.5E-06	A-methylpyrene	5.3E-08	1.6E-06	Fluoranthene	1.1E-07	2.1E-06
Mn	1.2E-05		1+2-ethylnaphthalene	6.8E-06	2.1E-06	Anthracene	0.0E+00	6.4E-06	Fluorene	6.4E-06	5.3E-06
Mo	2.1E-05		1-ethyl-2-methylnaphthalene	1.1E-07	1.6E-06	Anthraquinone	2.9E-06	9.5E-06	F-trimethylnaphthalene	5.0E-08	4.2E-06
Na	0.0E+00		1-methylfluorene+C-methylpyrene/fluorene	8.5E-07	3.1E-05	Anthrone	5.3E-08	5.3E-07	Indeno[123-cd]pyrene	3.2E-07	5.3E-07
Ni	6.9E-06		1-methylfluorene	3.5E-06	3.1E-05	A-trimethylnaphthalene	1.0E-07	5.1E-05	J-trimethylnaphthalene	4.3E-07	2.1E-06
Р	2.3E-05		1-methylnaphthalene	2.0E-06	2.1E-06	B-dimethylphenanthrene	1.8E-06	2.1E-06	Naphthalene	5.1E-05	2.1E-06
Pb	8.5E-05		1-methylphenanthrene	1.2E-06	5.3E-07	Benz(a)anthracene	3.2E-07	2.1E-06	Perinaphthenone	5.2E-05	1.1E-06
Pd	4.3E-05		1-methylpyrene	4.2E-07	1.6E-06	Benz(a)anthracene-7,12	2.0E-06	5.3E-07	Perylene	1.1E-07	5.8E-06
Rb	7.7E-06		1-phenylnaphthalene	2.7E-07	5.0E-05	Benzanthrone	4.8E-07	3.7E-06	Phenanthrene	4.2E-07	1.2E-05
S	3.9E-05		2,3,5+I-trimethylnaphthalene	1.6E-07	1.6E-06	Benzo(a)pyrene	3.2E-07	1.6E-06	Pyrene	2.1E-07	4.2E-06
Sb	1.4E-04		2,4,5-trimethylnaphthalene	4.2E-07	5.3E-07	Benzo(b)chrysene	1.1E-07	5.3E-07	Retene	3.2E-06	4.2E-06
Se	9.2E-06		2,6+2,7-dimethylnaphthalene	5.7E-06	2.7E-06	Benzo(b+j+k)fluoranthene	5.3E-08	1.6E-06	Xanthone	2.1E-07	1.5E-05
Si	4.9E-05		2-ethyl-1-methylnaphthalene	8.8E-06	4.2E-06	Benzo(c)phenanthrene	5.8E-07	5.3E-07	Volatile Organic Compounds	3.0E-02	1.017.100
Sn	1.3E-04		2-methylbiphenyl	8.4E-06	9.5E-06	Benzo(e)pyrene	3.3E-07	5.8E-06	NO, CO		1.2E+00
									SO ₂	/	Z.7E+00

Table 4-1. Approximate In-Stack Detection Limits Achieved for Gas-Fired Process Heater Tests (Refinery B).

Parameter	Units	13-Oct-94	14-Oct-94	15-Oct-94
Fuel Gas Flow Rate - Heater 1	MMscfd	0.60	0.62	0.59
Fuel Gas Flow Rate - Heater 2	MMscfd	0.85	0.77	0.77
Fuel Gas Specific Gravity		0.71	0.75	0.73
Burners In/Out of Service		All in	All in	All in
Process Fluid Flowrate - Heater 1	Mbpd	11	13	13
Process Fluid Flowrate - Heater 2	Mbpd	11	13	12
Process Fluid Outlet Temperature - Heater 1	°F	753	756	752
Process Fluid Outlet Temperature - Heater 2	°F	738	753	749
Stack Gas Temperature	°F	700	700	690
Excess Oxygen - Heater 1A	%	6.5	6.1	4.6
Excess Oxygen - Heater 1B	%	6.4	8.4	7.0
Excess Oxygen - Heater 2A	%	6.7	6.4	5.0
Excess Oxygen - Heater 2B	%	6.9	7.6	6.0
H ₂ S in Fuel Gas	ppmv	7.5	7.8	7.8
Fuel HHV (1)	Btu/scf	1158	1215	1190
Heat Input (2)	MMBtu/hr	70.0	70.1	67.6

Table 4-2. Process Operating Conditions for Gas-Fired Process Heater (Refinery Site B).

(1) Fuel HHV based on fuel gas sample analysis and normalized over the length of the run using the specific gravity of the grab sample and the specific gravity from the continuous process monitor.

(2) Calculated from the fuel HHV and the fuel gas flow rate.

Date	Units	13-Oct-98	14-Oct-98	15-Oct-98
Specific Gravity		0.68	0.74	0.70
Net Btu	Btu/dscf	1025	1093	1051
Gross Btu	Btu/dscf	1127	1200	1154
Hydrogen	Mol %	32.4	28.7	29.2
Oxygen/Argon	Mol %	0.12	0.12	0.11
Nitrogen	Mol %	5.44	5.60	5.33
Carbon Dioxide	Mol %	ND	0.09	0.10
Methane	Mol %	30.6	32.3	34.0
Ethylene	Mol %	4.55	4.66	4.98
Ethane	Mol %	9.95	9.60	9.43
Propane	Mol %	6.36	7.70	5.93
Propene	Mol %	4.48	3.31	4.02
Isobutane	Mol %	2.14	2.82	2.18
Normal Butane	Mol %	3.36	4.05	4.07
1- Butene	Mol %	0.05	ND	0.06
Isopentane	Mol %	0.37	0.97	0.46
C6 and Heavier	Mol %	0.09	0.07	ND

Table 4-3.	Fuel	Gas Anal	ysis foi	Gas-Fired	Process	Heater	Tests (Refiner	y Site B)).
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ND- not detected

demand to fluctuate. Conditions were re-established after approximately 20 minutes at conditions slightly different from those at the start of the run. It was decided to continue sample collection without interruption since the upset occurred during only a small fraction of the total six-hour run time. A second fuel gas sample was taken after the upset had been rectified. The average of both analyses is reported in Table 4-3.

PRELIMINARY TEST RESULTS

Preliminary tests were conducted to establish a single point in the stack for sample collection. The O_2 concentration profile was measured during a previous test program by traversing the CEMS probe across 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. Under the conditions of these tests, fine particles are expected to mix like a gas. It is assumed that the magnitude of any fine particle concentration profile that may have existed is similar to the O_2 concentration profile. Therefore, all samples were collected at a point near the center of the stack. A velocity profile was developed by traversing the stack with the Pitot probe before and after each test. The resulting average 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 conditions during testing is presented in Table 4-4. Stack gas temperature during the tests averaged 674-684°F. The O_2 concentration at the stack averaged 6.9 to 8.6. percent (dry basis) during the tests, slightly higher than at the furnace outlet (Table 4-2). The CO_2 and moisture concentrations are approximately consistent with the carbon and hydrogen contents of the fuel gas.

CO, NO_x, AND SO₂ EMISSIONS

 NO_X and SO_2 are precursors of secondary particulate matter. Average NO_X and SO_2 concentrations (corrected to 3 percent O_2 , dry basis) were 102-104 ppmv and 0.4 to 0.5 ppmv, respectively (Table 4-5). The data were corrected for analyzer drift and bias. The NO_X

Parameter	Units	Run 1	Run 2	Run 3
Date		13-Oct-98	14-Oct-98	15-Oct-98
Stack Temperature	°F	683	684	674
O ₂ (dry basis)	%v	8.6	8.5	6.9
CO ₂ (dry basis)	%v	7.4	7.4	8.4
Moisture	%v	12	12	13
Velocity	ft/sec	33	32	29
	m/sec	10.0	9.8	8.7
Flow Rate	acfm	59,000	56,900	47,500
	dscfm	24,000	22,900	19,300
	dscmm	681	649	546

Table 4-4. Average Stack Gas Parameters for Gas-Fired Process Heater Tests (Refinery Site B).

Table 4-5. NO_X, SO₂, and CO Results for Gas-Fired Process Heater Tests (Refinery Site B).

	Run Number	1	2	3
	Date	10/12/94	10/13/94	10/14/94
	Time Period	13:50 - 19:41	10:46 - 16:39	11:28 - 17:23
CO	ppm (dry, as measured)	0	0	0
	ppm (dry, $3\% O_2$)	0.0	0.0	0.0
	lb/hr	0	0	0
NO _x	ppm (dry, as measured)	70.1	70.7	81.1
	ppm (dry, $3\% O_2$)	102	102	104
	lb/hr	12.1	11.6	11.2
SO ₂ *	ppm (dry, as measured)	0.34	ND (0.3)	0.39
	ppm (dry, $3\% O_2$)	0.49	ND (0.4)	0.50
	lb/hr	0.08	ND (0.07)	0.08

* Detection limit, given in parentheses, equals three times the standard deviation of the zero gas response.

concentration is typical for process heaters without NO_X controls. The SO₂ concentration is nominally consistent with the measured H₂S concentration in the fuel gas, assuming total conversion to SO₂.

Low CO is an indicator of good combustion performance. Carbon monoxide concentration was consistently near zero during all tests, except for the process upset during Run 1. One-minute average CO readings fluctuated between zero and greater than 50 ppmv (above the upper range of the analyzer scale) for approximately 20 minutes during the upset. The absolute value of the

reported CO data may be biased low, since there was a calibration bias of approximately 20-30 percent during the tests possibly caused by sample line artifacts. Carbon monoxide concentration uncorrected for bias or drift was typically in the range of approximately 5-10 ppmv.

IN-STACK AND IMPINGER METHOD RESULTS

Particulate Mass

Filterable particulate matter (FPM) results as measured by Method 201A are presented in Table 4-6. Total FPM, which includes all particulate collected in the in-stack nozzle/cyclone assembly and on the in-stack filter, ranged from 0.81 to 0.91 mg/dscm. FPM < 10 micrometers, which

Table 4-6. Filterable Total Particulate, PM10, and PM2.5 Results for Gas-Fired Process Hear	ter
(Refinery Site B).	

<u> </u>										
Parameter	Units	Results								
Run Number	-	1		2	3	Average	RSD			
Date	-	12-Oct-94		13-Oct-94	14-Oct-94					
Total FPM	mg/dscm	0.81	(1)	0.91	0.83	0.85	6%			
	lb/hr	7.3E-2	(1)	7.8E-2	6.0E-2	7.0E-2	13%			
FPM <10 µm	mg/dscm	0.58	(1)	0.39	0.67	0.54	26%			
	lb/hr	5.2E-2	(1)	3.3E-2	4.8E-2	4.4E-2	22%			
FPM <2.5 μm	mg/dscm	0.26	(1)	0.19	0.22	0.23	16%			
	lb/hr	2.0E-2	(1)	1.3E-2	1.3E-2	1.5E-2	26%			

RSD-relative standard deviation

(1) Filter net weight was negative or below field blank filter net weight, therefore set to zero. (detection limit = 0.01 mg)

includes the portion of total FPM collected downstream of the PM10 cyclone, was 0.39 to 0.67 mg/dscm. FPM < 2.5 micrometers, which includes the portion of FPM collected downstream of the PM2.5 cyclone and on the in-stack filter, was 0.19 to 0.26 mg/dscm. These in-stack concentrations correspond to total weight gains in the sampling train of 3 to 4 milligrams (mg), with uncorrected net weights in each fraction of 0.2 to 1.8 mg. The net weight gain on the filter was slightly negative for Run 2, and net weights for all three runs were below the field blank filter net weight gain. This reflects the extremely low particulate loading in the stack and

possible losses of small filter fragments during sample recovery despite the modified filter assembly described in Section 3. The reported particulate result for each run is attributed almost entirely to the acetone rinses. The total net weight gain in the field blank train was approximately 25 to 30 percent of the sample results. Although an analytical resolution of 10 micrograms was achieved, these 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.

A second in-stack filter test was performed in parallel with the Method 201A train using a slightly different method than that above. The same in-stack filter assembly, minus the PM10 and PM2.5 cyclones, was used. The results (Figure 4-7) indicate particulate mass concentrations approximately half that of the Method 201A results, except for Run 1 which was much lower. The majority of the mass again occurred in the front-half acetone rinse. There is only one acetone rinse catch, compared to three for the Method 201A train, hence the cumulative bias associated with the acetone rinses is less. The difference between these results and the total FPM results presented in Table 4-6 is probably an artifact of the acetone rinse analytical procedure and provides additional insight into the uncertainty in the absolute value of these extremely low particulate concentrations. Run 2 failed the post-test leak check; the sample volume has been corrected according to the procedure given in the method.

Table 4-7. Method 17 Total Particulate Matter Results for Gas-Fired Process Heater (Refinery Site B).

Parameter	Units	Value							
Run Number	-	1	2	3					
Date	-	12-Oct-94	13-Oct-94	14-Oct-94	Average	RSD			
Total FPM	mg/dscm	0.079	(1) 0.43	0.41	0.31	64%			
	lb/hr	7.1E-3	(1) 3.7E-2	3.0E-2	2.5E-2	63%			

RSD- relative standard deviation

(1) Run failed post-test leak check. Sample volume adjusted per Method 17 guidelines.

Table 4-8 presents results for CPM as measured using Method 202. CPM concentration was approximately 12 times greater than FPM on average. The glass sample jars containing the impinger catches and rinses cracked severely during storage due to freezing. Consequently, a small amount of sample may have been lost and glass chips may have contaminated the samples,

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biasing the inorganic CPM results. This may account in part for the large variation in results observed for Run 2. Eighty-seven to nine-nine percent of the CPM was found in the inorganic fraction. The inorganic CPM (and hence the total CPM) results are somewhat variable from run to run, with a standard deviation equal to 79 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. 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 one 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 shown uncorrected.

Parameter	Units				Valu	ie			
Run Number	-		1		2		3	Average	RSD
Date	-		12-Oct-94		13-Oct-94		14-Oct-94		
Inorganic CPM	mg	(1)	9	(1)	34	(1)	10	18	79%
	mg/dscm	(1)	2.1	(1)	7.6	(1)	2.3	4.0	79%
	lb/hr	(1)	0.19	(1)	0.65	(1)	0.16	0.34	82%
Organic CPM	mg		0.80		0.40		1.5	0.90	62%
	mg/dscm		0.18		0.09		0.34	0.20	62%
	lb/hr		1.6E-2		7.7E-3		2.4E-2	1.6E-2	52%
Dichloromethane Recovery Blank	mg				0.6			-	
Water Recovery Blank	mg				1.5				
Sulfate (as SO ₄) in Impingers	mg	(1)	1.7	(1)	4.3	(1)	1.3	2.4	67%
	mg/dscm	(1)	0.39	(1)	0.96	(1)	0.29	0.55	67%
	lb/hr	(1)	3.5E-2	(1)	8.3E-2	(1)	2.1E-2	4.6E-2	70%
Chloride (as NH ₄ Cl)	mg	(1)	6.0	(1)	8.9	(1)	0.66	5.2	80%
	mg/dscm	(1)	1.4	(1)	2.0	(1)	0.15	1.2	80%
	lb/hr	(1)	0.12	(1)	0.17	(1)	0.01	0.10	81%
Total CPM	mg/dscm		1.9		7.2		2.2	3.8	80%
(corrected for NH_4^+ , H_2O , and blanks)	lb/hr		0.17		0.63		0.16	0.32	84%

Table 4-8. Condensible Particulate Matter for Gas-Fired Process Heater (Refinery Site B).

(1) Some amount of sample lost in freezer resulting from broken glass jar. Also broken glass was contained in sample during experiment.

RSD=relative standard deviation

CPM=condensible particulate matter

SO₄⁼=sulfate ion

NH4Cl=ammonium chloride

 NH_4^+ =ammonium ion

H₂O=water

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 14 percent of the total CPM on average. 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 an average of 35 percent of the total CPM, with a large relative standard deviation of 93 percent corresponding to a range of 7 to 70 percent. To confirm these results, the inorganic residue was re-analyzed for a broader range of elements and ions several months after the original analysis. These latter results are inconclusive, since the second analysis showed the sum of $SO_4^{=}$, Cl^{-} and NH_4^{+} account for an average of 4.7 mg/dscm, or 200 percent, of the total CPM (Table 4-9). 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. Sodium, K, and Ca account for an average of 0.39 mg/dscm, or 10 percent, of the total average CPM. The remaining 22 elements and ions that were detected account for an average of 0.09 mg/dscm, or 3 percent, of the average CPM.

Although the uncertainty of the results is large, the second analysis shows Cl^- and SO_4^- to be the dominant compounds in the inorganic residue. This is in qualitative agreement with the first analysis although the relative fraction of Cl^- and SO_4^- appears to be considerably 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 $H_2SO_4^-$ (substituting for water). Both analyses show Cl^- present in significant amounts. 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, the analysis was performed on the EPA Method 17 train

filters. Organic carbon and EC were undetected on the in-stack filters, which is consistent with their very clean visual appearance.

Parameter	Value									
Units				mg/c	lsci	n		%		
Run Number		1		2		3	Average	RSD		
Sulfate		1.6		6.8		2.0	3.5	82		
Ammonium		0.42		2.4		0.57	1.1	98		
Na		2.1E-1		3.1E-1		1.7E-1	2.3E-1	31		
Ca		6.9E-2		1.4E-1		8.2E-2	9.5E-2	37		
K		6.9E-2		6.3E-2		6.8E-2	6.7E-2	4		
Chloride		3.3E-2		4.3E-2		2.9E-3	2.6E-2	79		
Fluoride		2.2E-2		3.0E-2	<	6.8E-4	1.7E-2	86		
Zn		1.7E-2		2.4E-2		3.5E-3	1.5E-2	70		
Mg		1.2E-2		1.4E-2		9.1E-3	1.2E-2	23		
Al		9.1E-3		2.1E-2		4.4E-3	1.2E-2	75		
Nitrate		7.8E-3		1.6E-2	<	6.8E-4	8.2E-3	95		
Fe		1.3E-3		1.2E-2		2.3E-3	5.1E-3	113		
Mn		5.0E-3		3.6E-3		2.5E-3	3.7E-3	34		
Cu		3.5E-3		4.5E-3		2.6E-3	3.5E-3	27		
Ni		2.3E-3		1.7E-3		2.0E-3	2.0E-3	16		
Bromide	<	1.4E-3	<	1.4E-3	<	1.4E-3	1.4E-3	1		
Phosphate		1.4E-3		1.4E-3	<	1.4E-3	1.4E-3	1		
Р	<	9.1E-4	<	9.0E-4	<	9.1E-4	9.1E-4	1		
Tl	<	9.1E-4	<	9.0E-4	<	9.1E-4	9.1E-4	1		
Co		1.2E-3		ND		2.7E-4	7.5E-4	90		
Nitrite		6.9E-4		6.8E-4	<	6.8E-4	6.8E-4	1		
Ag		ND		6.8E-4		ND	6.8E-4	n/a		
Sn		5.0E-4		9.0E-4		5.9E-4	6.7E-4	32		
Ba		4.6E-4		1.1E-3		3.1E-4	6.2E-4	66		
Pb	<	3.2E-4		8.6E-4	<	3.2E-4	5.0E-4	62		
Cd		1.8E-4		6.3E-4		2.9E-4	3.7E-4	64		
Cr		1.1E-4		5.9E-4		1.2E-4	2.7E-4	101		
v	<	7.8E-5	<	7.7E-5	<	7.7E-5	7.7E-5	1		
Be		ND		ND		ND	ND	n/a		
Mo		ND		ND		ND	ND	n/a		

Table 4-9. Analysis of Method 202 Residue for Process Heater Tests (Refinery Site B).

"<"- 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

A few SVOCs were detected on the in-stack filters at very low levels (Table 4-10). Biphenyl was the most abundant substance detected on the in-stack filters; detected in only a single test run at a concentration of 0.000007 mg/dscm. The sum of the detected SVOCs on the in-stack filters is an insignificant fraction of the total in-stack particulate mass.

	·).					
Run Numnber	1	2	3	Average	RSD	MDL
Date	14-Oct-02	15-Oct-02	16-Oct-02			
Biphenyl	ND	ND	7.2E-6	7.2E-6	n/a	2.1E-6
2,6+2,7-dimethylnaphthalene	ND	ND	6.3E-6	6.3E-6	n/a	2.7E-6
Benzo(a)pyrene	2.5E-6	ND	1.8E-6	2.2E-6	23%	1.6E-6
Benzo(b)chrysene	2.5E-6	ND	1.8E-6	2.2E-6	23%	5.3E-7
1,4-chrysenequinone	ND	2.0E-6	ND	2.0E-6	n/a	5.3E-7
4-methylbiphenyl	ND	ND	1.8E-6	1.8E-6	n/a	1.6E-6
2-methylphenanthrene	ND	1.1E-6	ND	1.1E-6	n/a	1.1E-6
1,2,8-trimethylnaphthalene	ND	ND	6.8E-7	6.8E-7	n/a	5.3E-7

Table 4-10. In-Stack Filter Semivolatile Organic Compound Results for Gas-Fired Process Heater (Refinery Site B, mg/dscm).

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

ND- not detected

MDL- method detection limit

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 0.007 to 0.01 mg/dscm with an average of 0.043 mg/dscm (Table 4-11). Precision of the data over the three runs is somewhat poor, with a relative standard deviation (RSD) of 123 percent. These results are nearly 100 times lower than the sum of FPM and CPM measured by EPA Methods 201A and 202. PM2.5 concentration measured in the process heater stack gas (Table 4-12) was only 2.6 times higher than the concentration measured in the ambient air.

	Units	Results							
Run Number	-	1	2	3	Average	RSD			
Date	-	13-Oct-98	14-Oct-98	15-Oct-98					
PM2.5	mg/dscm	1.0E-1	1.9E-2	6.5E-3	4.3E-2	123%			
	lb/hr	9.3E-3	1.6E-3	4.7E-4	3.8E-3	127%			

Table 4-11. Dilution Tunnel PM2.5 Results for Gas-Fired Process Heater (Refinery Site B).

RSD- relative standard deviation

Table 4-12, Ambient Air PM2.5 Results for Refinery Site B.

Parameter	Units	Value
Run Number	-	Ambient
Date	-	16-Oct-98
PM2.5	mg/dscm	1.6E-2

n/a - not applicable

RSD- relative standard deviation

The concentration of PM2.5 using the dilution tunnel is a factor of 5 lower than FPM <2.5 micrometers measured using Method 201A and a factor of 88 lower than CPM measured using Method 202. CPM is normally included in regulatory definitions of PM10. The dilution tunnel and EPA method results clearly indicate 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 $SO_4^{=}$, CI^{-} , NO_3^{-} , and NH_4^{+} ion. Of these, $SO_4^{=}$ had the highest average concentration at 0.012 mg/dscm, followed by NH_4^{+} and CI^{-} at 0.0027 mg/dscm and 0.0021 mg/dscm (Table 4-13). Run 2 results for sulfates are considered not valid due to very high sulfate mass and the presence of an anomalous blue spot observed on the filter in the field. NH_4^{+} and CI^{-} were detected in only two of three runs at levels near the lower method detection limit. Nitrate ion was detected in only one of the three runs at 0.00092 mg/dscm. All ions in the field blank were present below detectable levels (see Section 6 for additional discussion of blanks).

The quartz filters used for these measurements have the potential for a positive $SO_4^{=}$ bias. However, at the low SO_2 concentrations present in the stack gas, the artifact probably is not significant for these tests. The average $SO_4^{=}$ concentration from the dilution tunnel is approximately 1/50 of the average concentration reported above for Method 202. Chloride ion results from the dilution tunnel also are several orders of magnitude lower than Method 202. This difference lends further support to the possibility of a significant sampling artifact in Method 202 due to gaseous SO_2 or HCl in the stack gas.

Parameter	Units		Value									
Run Number	-	1	2	3	Average	RSD	Ambient					
Date	-	14-Oct-02	15-Oct-02	16-Oct-02			17-Oct-02					
Sulfate	mg/dscm	2.1E-2	NV	2.7E-3	1.2E-2	109%	2.6E-3					
	lb/hr	1.9E-3	NV	2.0E-4	1.0E-3	115%	n/a					
Nitrate	mg/dscm	ND	9.2E-4	ND	9.2E-4	n/a	8.7E-4					
	lb/hr	ND	7.9E-5	ND	7.9E-5	n/a	n/a					
Chloride	mg/dscm	3.0E-3	1.3E-3	ND	2.1E-3	57%	ND					
	lb/hr	2.7E-4	1.1E-4	ND	1.9E-4	59%	n/a					
Ammonium	mg/dscm	1.6E-3	3.7E-3	ND	2.7E-3	55%	7.8E-4					
	lb/hr	1.5E-4	3.2E-4	ND	2.3E-4	52%	n/a					

Table 4-13. Dilution Tunnel Sulfate, Nitrate, Chloride and Ammonium Results for Gas-Fired Process Heater (Refinery Site B).

n/a - not applicable

NV- not valid

ND - not detected

RSD- relative standard deviation

Concentrations of sulfate, nitrate and ammonium measured in the stack gas are within an order of magnitude of the concentrations measured in the ambient air. Chloride was not detected in the ambient sample. The mass of sulfate measured on the dilution tunnel filter represents approximately 0.9 percent of the SO_2 in the stack.

OC, EC and Organic Species

OC and EC were measured on quartz filters from the dilution tunnel. Organic carbon concentration ranged from 0.018 to 0.031 mg/dscm. Elemental carbon was detected in only one run at a concentration of 0.015 mg/dscm (Table 4-14). Organic carbon accounts for more than 80 percent of the total carbon mass. Average organic and elemental carbon concentrations

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measured in the stack gas are within an order of magnitude of the ambient sample concentration. Organic carbon on the field blank filter is approximately an order of magnitude lower than the average concentration in the stack gas samples (see Section 6 for additional discussion of blank results).

Table 4-14.	Dilution	Tunnel	Organic	and Eler	nental	Carbon	Results	for C	Gas-Fired	Process
Heater (Refi	inery Site	B).								

Parameter	Units	Value									
Run Number	-	1	2	3	Average	RSD	Ambient				
Date	-	12-Oct-94	13-Oct-94	14-Oct-94			15-Oct-94				
Organic Carbon	mg/dscm	3.1E-2	2.0E-2	1.8E-2	2.3E-2	30%	6.7E-3				
	lb/hr	2.8E-3	1.7E-3	1.3E-3	1.9E-3	39%	n/a				
Elemental Carbon	mg/dscm	1.5E-2	ND	ND	1.5E-2	n/a	4.5E-3				
	lb/hr	1.3E-3	ND	ND	1.3E-3	n/a	n/a				
Total Carbon	mg/dscm	4.6E-2	2.0E-2	1.8E-2	2.8E-2	55%	1.1E-2				
	lb/hr	4.1E-3	1.7E-3	1.3E-3	2.4E-3	63%	n/a				

Note: Average total carbon equals the mean of the sum of organic and elemental carbon; therefore, average total carbon does not equal sum of average organic carbon and elemental carbon due to undetected elemental carbon results in Runs 2 and 3.

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 in the stack gas at extremely low levels (Table 4-15). Many of the SVOCs detected in the stack also were detected in the ambient air. Coronene, which was not detected on the in-stack filters (Table 4-10), is the most abundant SVOC in the dilution tunnel samples with an average concentration of 0.00013 mg/dscm. Most of the average SVOC stack gas concentrations are within a factor of one to five of the ambient air concentration, which suggests these levels in the stack may be indistinguishable from the background levels. Acenaphthenequinone, c-methylphenanthrene, fluoranthene, b-methylphenanthrene 4-methylpyrene and anthrone concentrations are approximately 10 to 26 times their corresponding ambient air concentrations. The average stack gas concentrations of 1,3+1,6+1,7-dimethylnaphthalene, 2,6+2,7-dimethylnaphthalene, 2-methylnaphthalene, 1-methylnaphthalene E-trimethylnaphthalene, 5+6-methylchrysene, B-trimethylnaphthalene, and

Parameter	Value						
Run Number	1	2	3	Average	RSD	Ambient	MDL
Date	13-Oct-98	14-Oct-98	15-Oct-98			16-Oct-98	
Coronene	2.9E-5	2.2E-4	1.5E-4	1.3E-4	73%	4.0E-5	3.2E-7
2-methylbiphenyl	6.4E-5	ND	ND	6.4E-5	n/a	1.2E-5	8.4E-6
3-methylbiphenyl	4.5E-5	ND	ND	4.5E-5	n/a	1.2E-5	1.2E-5
Phenanthrene	4.3E-5	4.9E-5	3.6E-5	4.3E-5	15%	1.3E-5	4.2E-7
9-fluorenone	3.8E-5	ND	ND	3.8E-5	n/a	ND	7.1E-6
2-methylnaphthalene	3.5E-5	ND	ND	3.5E-5	n/a	5.7E-5	3.3E-6
C-methylphenanthrene	3.3E-5	ND	ND	3.3E-5	n/a	1.7E-6	1.5E-6
Acenaphthenequinone	3.5E-5	2.7E-5	ND	3.1E-5	18%	1.2E-6	3.2E-7
Fluoranthene	6.9E-5	1.1E-5	1.1E-5	3.0E-5	110%	2.1E-6	1.1 E-7
A-methylfluorene	3.1E-5	3.5E-5	2.3E-5	3.0E-5	22%	ND	5.6E-6
1-methylnaphthalene	2.0E-5	ND	ND	2.0E-5	n/a	3.2E-5	2.0E-6
B-methylphenanthrene	1.5E-5	3.4E-5	2.8E-6	1.7E-5	91%	1.4E-6	5.8E-7
1-methylfluorene	1.7E-5	ND	ND	1.7E-5	n/a	ND	3.5E-6
1,3+1,6+1,7-dimethylnaphthalene	1.6E-5	ND	ND	1.6E-5	n/a	3.6E-5	1.2E-5
Benzo(b+j+k)fluoranthene	1.4E-6	2.1E-5	1.6E-5	1.3E-5	80%	3.0E-6	5.3E-8
2-methylphenanthrene	5.1E-6	2.1E-5	1.0E-5	1.2E-5	65%	3.5E-6	1.1E-7
B-dimethylphenanthrene	ND	1.5E-5	8.7E-6	1.2E-5	36%	2.2E-6	1.8E-6
C-dimethylphenanthrene	1.2E-5	ND	ND	1.2E-5	n/a	ND	1.8E-6
4-methylbiphenyl	1.9E-5	3.7E-6	ND	1.1E-5	95%	3.6E-6	1.0E-6
Pyrene	1.3E-5	8.6E-6	1.0E-5	1.1E-5	22%	6.4E-6	2.1E-7
Benz(a)anthracene-7,12	2.7E-6	ND	1.7E-5	9.7E-6	103%	ND	2.0E-6
Benzo(b)chrysene	1.9E-6	1.1E-5	1.4E-5	9.1E-6	70%	5.3E-6	1.1E-7
2,6+2,7-dimethylnaphthalene	8.4E-6	ND	ND	8.4E-6	n/a	1.7E-5	5.7E-6
9-methylanthracene	1.3E-5	3.4E-6	ND	8.2E-6	82%	ND	2.4E-6
2,3,5+I-trimethylnaphthalene	1.2E-5	8.0E-6	4.1E-6	7.9E-6	48%	7.8E-6	1.6E-7
C-trimethylnaphthalene	9.3E-6	7.1 E-6	3.5E-6	6.6E-6	44%	5.5E-6	4.2E-7
Benzanthrone	2.3E-6	1.1E-5	6.5E-6	6.4E-6	64%	1.1 E-6	4.8E-7
1,2,8-trimethylnaphthalene	6.4E-6	ND	ND	6.4E-6	n/a	ND	3.2E-7
Anthrone	8.4E-6	4.9E-6	4.8E-6	6.1E-6	34%	6.1E-7	5.3E-8
Dibenz(ah+ac)anthracene	ND	6.4E-6	5.2E-6	5.8E-6	15%	1.7E-6	3.2E-7
A-trimethylnaphthalene	8.2E-6	4.7E-6	3.7E-6	5.6E-6	43%	5.7E-6	1.0E-7
A-dimethylphenanthrene	5.4E-6	ND	ND	5.4E-6	n/a	ND	2.5E-6
B-trimethylnaphthalene	6.6E-6	5.2E-6	3.9E-6	5.2E-6	25%	6.1E-6	5.3E-8
Anthracene	7.8E-6	4.7E-6	1.7 E-6	4.8E-6	64%	1. 0E-6	0.0E+0
Indeno[123-cd]pyrene	ND	4.9E-6	3.7E-6	4.3E-6	20%	1.2E-6	3.2E-7
F-trimethylnaphthalene	6.6E-6	3.9E-6	2.0E-6	4.1E-6	56%	4.1E-6	5.0E-8
Benzo(a)pyrene	ND	3.7E-6	4.6E-6	4.1E-6	16%	1.6E-6	3.2E-7

Table 4-15. Dilution Tunnel SVOC Results for Gas-Fired Process Heater (Refinery Site B, mg/dscm).

Parameter				Value			
Run Number	1	2	3	Average	RSD	Ambient	MDL
Date	13-Oct-98	14-Oct-98	15-Oct-98	_		16-Oct-98	
7-methylbenzo(a)pyrene	ND	2.8E-6	5.2E-6	4.0E-6	43%	1.7E-6	3.7E-7
Benzo(ghi)perylen	6.2E-7	5.8E-6	5.5E-6	4.0E-6	73%	1.4E-6	3.2E-7
E-	5.4E-6	3.2E-6	2.2E-6	3.6E-6	45%	5.1E-6	5.3E-8
Chrysene	1.4E-6	4.9E-6	3.9E-6	3.4E-6	52%	9.5E-7	1.1E-7
1-	4.5E-6	1.9E-6	ND	3.2E-6	57%	ND	1.2E-6
4-methylpyrene	1.4E-6	4.7E-6	3.5E-6	3.2E-6	52%	2.6E-7	1.1E-7
Benz(a)anthracen	8.2E-7	6.7E-6	2.0E-6	3.1E-6	98%	1.2E-6	3.2E-7
Anthraquinone	2.9E-6	ND	ND	2.9E-6	n/a	ND	2.9E-6
1-ethyl-2-	3.7E-6	3.4E-6	4.3E-7	2.5E-6	72%	1.8E-6	1.1E-7
1,7-	2.5E-6	2.4E-6	ND	2.4E-6	3%	ND	1.8E-6
9,10-	2.1E-7	3.9E-6	3.1E-6	2.4E-6	81%	8.4E-7	1.6E-7
B-	1.2E-6	3.4E-6	ND	2.3E-6	67%	ND	5.3E-8
E-	6.2E-7	3.9E-6	ND	2.2E-6	102%	4.6E-7	5.3E-8
9-anthraldehyde	ND	2.1E-6	ND	2.1E-6	n/a	ND	1.4E-6
1,4-	1.4E-6	1.3E-6	3.7E-6	2.1E-6	63%	3.8E-7	2.7E-7
Benzonaphthothiophene	ND	1.9E-6	ND	1.9E-6	n/a	3.3E-7	1.1E-7
1-							
methylpyrene/methylfluoren	2.1E-6	1.3E-6	ND	1.7E-6	33%	ND	8.5E-7
1-phenylnaphthalene	1.6E-6	ND	ND	1.6E-6	n/a	ND	2.7E-7
Benzo(c)phenanthren	6.2E-7	2.8E-6	6.5E-7	1.4E-6	92%	ND	5.8E-7
Perylene	ND	1.5E-6	1.1E-6	1.3E-6	22%	5.4E-7	1.1E-7
Benzo(e)pyrene	ND	4.3E-7	1.7E-6	1.1E-6	86%	6.1E-7	3.3E-7
4H-	1.2E-6	1.3E-6	6.5E-7	1.1E-6	33%	1.2E-6	0.0E+0
5+6-methylchrysene	4.1E-7	1.7E-6	2.2E-7	7.8E-7	105%	1.1E-6	0.0E+0
1-methylpyrene	ND	6.4E-7	ND	6.4E-7	n/a	ND	4.2E-7
D-	2.1E-7	6.4E-7	4.3E-7	4.3E-7	51%	ND	5.3E-8
2-phenylnaphthalene	ND	2.2E-7	2.2E-7	2.2E-7	0%	7.7E-8	5.3E-8
1+2-ethylnaphthalene	ND	ND	ND	ND	n/a	9.3E-6	6.8E-6
1,2-	ND	ND	ND	ND	n/a	3.8E-6	3.7E-6
1,4+1,5+2,3-	ND	ND	ND	ND	n/a	9.0E-6	5.4E-6
2,4,5-	ND	ND	ND	ND	n/a	2.8E-6	4.2E-7
A-	ND	ND	ND	ND	n/a	ND	2.5E-6
Acenaphthene	ND	ND	ND	ND	n/a	1.7E-6	1.4E-6
Biphenyl	ND	ND	ND	ND	n/a	9.7E-6	3.6E-6
Dibenzofuran	ND	ND	ND	ND	n/a	5.4E-6	3.3E-6
Fluorene	ND	ND	ND	ND	n/a	6.9E-6	6.4E-6
J-	ND	ND	ND	ND	n/a	7.9E-7	4.3E-7
Naphthalene	ND	ND	ND	ND	n/a	1.4E-4	5.1E-5

Table 4-15 (continued). Dilution Tunnel SVOC Results for Gas-Fired Process Heater (Refinery Site B, mg/dscm).

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

ND- not detected

MDL- method detection limit

RSD- relative standard

Not for Resale

4H-cyclopenta(def)phenanthrene are less than the detected ambient air concentration. Naphthalene, biphenyl, 1+2-ethylnaphthalene, 1,4+1,5+2,3-dimethylnaphthalene, fluorene, dibenzofuran, 1,2-dimethylnaphthalene, 2,4,5-trimethylnaphthalene, acenaphthene, jtrimethylnaphthalene were detected in the ambient air sample but not in any of the stack gas samples.

Tenax sorbent was used to collect VOCs. The analysis focused only on VOCs with a carbon number greater than 7 since these are believed to be the most significant precursors for secondary organic aerosols. 1+7-hexadecene was the most abundant VOC detected during sampling, with an average concentration of 0.16 mg/dscm (Table 4-16). Acetophenone was the second most abundant on average (0.055 mg/dscm). The substances labeled 'C12 hydrocarbon 1', 'C12 hydrocarbon 2' et cetera, are unidentified long-chain hydrocarbons. In general, the average VOC concentration in the stack gas was within a factor of approximately one to thirty times the ambient air concentration.

During Run 1 the flow through one of the two parallel Tenax traps dropped by more than 80 percent. Consequently, this sample was rejected and the sample from the second Tenax trap was used for analysis. Of the few compounds detected in the field blank, only nonanal was within a factor of ten of the average sample concentration. All other compounds detected in the blank are at least a factor of ten lower than the average sample concentration (see Section 6 for additional discussion of results quality).

Elements

Element concentrations were determined by XRF analysis of the TMFs used in the dilution tunnel. On average, Co, S, Cl, Ca, Si, and Cu are the most abundant elements in the stack gas (Table 4-17). The S results are somewhat lower than expected based on the dilution tunnel SO₄⁼ results presented earlier, but within a factor of two on a mole-for-mole basis. Sodium results are considered semi-quantitative because of analytical limitations. Antimony, As, Cd, Ga, Au, In, Pb, Hg, Mo, Pd, Rb, Se, Ag, Tl, Sn, Ti, Ur, V, Yt and Zr were below detectable levels for all three sample runs. Chlorine, Zn, Cu, and to a lesser degree Sr, P and Ni, are significantly enriched in the

Parameter	Value							
Units		mg/ds		%	mg/dscm			
Run Number	1	2	3	Average	RSD	Ambient		
Date	13-Oct-98	14-Oct-98	15-Oct-98			16-Oct-98		
1+7 hexadecene	9.7E-4	2.8E-1	2.1E-1	1.6E-1	88%	ND		
acetophenone	9.5E-3	1.2E-1	3.2E-2	5.5E-2	110%	3.1E-3		
Benzaldehyde	1.0E-2	6.8E-2	2.8E-2	3.5E-2	84%	4.7E-3		
Phenol	2.4E-3	5.4E-2	1.4E-2	2.3E-2	117%	8.9E-4		
Benzonitrile	1.4E-3	3.0E-2	7.4E-3	1.3E-2	117%	2.6E-4		
n-undecane	ND	2.4E-3	5.3E-3	3.8E-3	53%	1.8E-4		
c12 hydrocarbon 1	3.0E-3	3.0E-3	5.1E-3	3.7E-3	32%	ND		
c13 hydrocarbon 1	ND	1.5E-3	5.0E-3	3.3E-3	76%	5.4E-5		
Styrene	1.4E-3	4.9E-3	3.4E-3	3.2E-3	54%	1.9E-4		
c12 hydrocarbon 3	ND	1.8E-3	4.4E-3	3.1E-3	57%	ND		
m- & p-xylenes	2.5E-3	3.3E-3	2.0E-3	2.6E-3	25%	1.9E-3		
n-tridecane	3.1E-4	9.8E-4	5.5E-3	2.3E-3	124%	1.5E-4		
n-nonadecane	ND	8.3E-4	2.7E-3	1.8E-3	76%	3.2E-5		
c12 hydrocarbon 4	ND	8.9E-4	1.8E-3	1.3E-3	48%	ND		
Benzofuran	ND	1.6E-3	1.1E-3	1.3E-3	29%	3.6E-5		
n-tetradecane	4.0E-4	1.4E-3	1.8E-3	1.2E-3	61%	2.2E-4		
o-xylene	1.3E-3	1.2E-3	1.1E-3	1.2E-3	6%	7.6E-4		
n-hexadecene	ND	1.2E-3	ND	1.2E-3	n/a	1.0E-4		
c14 hydrocarbon1	6.0E-4	7.6E-4	2.2E-3	1.2E-3	74%	3.8E-5		
1,2,4 trimethylbenzene	1.0E-3	1.2E-3	1.2E-3	1.1E-3	9%	7.1E-4		
c12 hydrocarbon 2	ND	7.6E-4	1.4E-3	1.1E-3	44%	ND		
2-methyl octane	8.1E-4	ND	1.3E-3	1.0E-3	31%	1.1E-4		
1.3-dichlorobenzene	5.2E-4	1.8E-3	6.3E-4	9.8E-4	71%	3.4E-4		
n-octadecane	ND	1.1E-3	6.8E-4	8.8E-4	33%	5.4E-5		
n-eicosane	ND	1.1E-3	6.3E-4	8.5E-4	36%	3.1E-5		
n-heptadecene	ND	1.0E-3	6.0E-4	8.2E-4	38%	7.7E-5		
n-nonane	4.3E-4	1.3E-3	7.0E-4	8.2E-4	57%	3.7E-4		
n-pentadecane	2.7E-4	1.5E-3	7.2E-4	8.2E-4	73%	2.1E-4		
Ethyl Benzene	8.5E-4	8.9E-4	6.9E-4	8.1E-4	13%	5.6E-4		
Naphthalene	ND	1.0E-3	5.8E-4	7.9E-4	39%	1.9E-4		
n-dodecane	ND	6.4E-4	8.5E-4	7.5E-4	20%	1.2E-4		
m-ethyltoluene	6.4E-4	6.2E-4	5.8E-4	6.2E-4	5%	5.0E-4		
Biphenvl	ND	6.2E-4	2.3E-4	4.3E-4	64%	3.4E-5		
1-methylnaphthalene	ND	4.3E-4	ND	4.3E-4	n/a	4.9E-5		
2-methylnaphthalene	ND	4.3E-4	ND	4.3E-4	n/a	8.4E-5		
n-decane	ND	5.1E-4	3.2E-4	4.1E-4	33%	2.5E-4		
1.2.3.4-tetramethylbenzene	ND	3.6E-4	ND	3.6E-4	n/a	ND		
3-methyl octane	ND	3.5E-4	3.7E-4	3.6E-4	3%	2.5E-4		
1 3 5 trimethylbenzene	3 4E-4	ND	ND	34E-4	n/a	2.0E-4		
o-ethyltoluene	2.7E-4	ND	3.1E-4	2.9E-4	9%	1.9E-4		
n-ethyltoluene	3.0E-4	3.1E-4	2.5E-4	2.8E-4	11%	2.5E-4		
n-propylhenzene	ND	2.8E-4	2.5E-4	2.7E-4	8%	1.5E-4		
Nonanol	2 5E-4	ND .	ND .	2 5E-4	NA	2 2E-4		
1 2 3 trimethylbenzene	ND	ND	ND	2.5£ 1	n/a	1.6E-4		
1 2 3 5-tetramethylbenzene	ND	ND	ND	n/a	n/a	7.4E-5		
1 2 4 5-tetramethylbenzene	ND	ND	ND	n/a	n/a	7.1E-5 7.4E-5		
1-methylindan		ND	ND	n/a	n/a	9.0F-5		
2-methylindan		ND	ND	n/2	n/a	5.0E-5		
Dodecene		ND	ND	n/a	n/a	4.5E-5		
Indan				n/a	n/a	8.5E-5		
o-isopronyltoluene				n/a	n/a	7 3E-5		
undecene-1	ND	ND	ND	n/a	n/a	3.9E-5		
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Table 4-16. Dilution Tunnel VOC Results for Gas-Fired Process Heater (Refinery Site B).

n/a- not applicable. Less than two runs within detectable limits.

RSD- relative standard deviation.

ND - not detected.

Parameter	Value									
Units		mg/	dscm		%	mg/dso	cm			
Run Number	1	2	3	Average	RSD	Ambient	MDL			
Date	13-Oct-98	14-Oct-98	15-Oct-98	_		16-Oct-98	(2)			
Aluminum	1.4E-3	5.4E-4	1.9E-4	7.0E-4	86%	1.2E-4	7.2E-5			
Barium	ND	4.4E-4	5.4E-4	4.9E-4	13%	1.3E-4	3.8E-4			
Bromine	8.9E-6	ND	ND	8.9E-6	n/a	9.5E-6	7.2E-6			
Calcium	3.5E-3	5.9E-4	3.5E-4	1.5E-3	118%	1.8E-4	3.3E-5			
Chlorine	2.8E-3	ND	2.5E-4	1.5E-3	118%	2.0E-5	7.2E-5			
Cobalt	8.8E-3	1.2E-4	5.1E-5	3.0E-3	168%	ND	6.4E-6			
Chromium	2.0E-5	ND	ND	2.0E-5	n/a	ND	1.4E-5			
Copper	1.4E-3	1.3E-3	5.8E-4	1.1E-3	40%	2.9E-5	8.0E-6			
Iron	2.0E-3	3.7E-4	2.3E-4	8.5E-4	113%	2.1E-4	1.1E-5			
Potassium	4.4E-4	8.6E-5	1.4E-4	2.2E-4	87%	1.3E-4	4.4E-5			
Lanthanum	5.5E-4	ND	ND	5.5E-4	n/a	ND	4.5E-4			
Magnesium	ND	8.6E-5	5.3E-5	6.9E-5	33%	7.4E-5	(1)			
Manganese	4.6E-5	ND	ND	4.6E-5	n/a	5.2E-6	1.2E-5			
Sodium	ND	ND	9.5E-5	9.5E-5	n/a	3.2E-4	(1)			
Nickel	7.9E-5	2.3E-5	4.4E-5	4.8E-5	58%	4.8E-6	6.4E-6			
Phosphorous	8.2E-5	ND	8.5E-5	8.3E-5	3%	7.8E-6	4.1E-5			
Sulfur	6.0E-3	1.1E-3	7.8E-4	2.6E-3	110%	9.1E-4	3.6E-5			
Selenium	ND	ND	ND	ND	n/a	1.9E-6	8.7E-6			
Silicon	2.6E-3	5.4E-4	3.5E-4	1.1E-3	107%	4.0E-4	4.6E-5			
Strontium	2.2E-5	ND	ND	2.2E-5	n/a	1.9E-6	8.0E-6			
Zinc	1.4E-3	1.1E-3	1.2E-4	8.8E-4	78%	2.0E-5	8.0E-6			

Table 4-17. Dilution Tunnel Elemental Results for Gas-Fired Process Heater (Refinery Site B).

(1) No detection limits given. Zeroes treated as non-detect. Data is semi-quantitative.

(2) Method detection limit for Runs 1-3 (dilution ratio 8:1). Ambient sample MDLs are smaller due to 1:1 dilution ratio.

MDL- Method Detection Limit

ND- not detected

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

RSD- relative standard deviation

stack gas samples compared to the ambient air. Selenium was detected in the ambient sample but not in the sample runs. Bromine and Mg concentrations are higher in the ambient air than in the stack gas.

Indium and P were present at detectable levels in the blank, but not in the field samples. Sodium in the field blank was within a factor of ten of the average stack gas concentration. Aluminum and P field blank concentrations are within an order of magnitude of the ambient concentrations. 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

Table 5-1 presents emission factors for primary emissions, including filterable and condensible 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 88 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.

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		Emission		
		Factor		95% Confidence
		lb/MMBtu	Uncertainty	Upper Bound
	Substance		(%)	lb/MMBtu
Particulate	CPM (inorganic)	4.8E-3	201	1.1E-2
Mass	CPM (organic)	2.4E-4	161	4.9E-4
	Total CPM	4.6E-3	209	1.1E-2
	Total Filterable PM (in-stack	1.0E-3	51	1.4E-3
	Filterable PM10 (in-stack	6.4E-4	82	1.0E-3
	Filterable PM2.5 (in-stack	2.2E-4	62	3.1E-4
	PM2.5 (Dilution Tunnel)	5.4E-5	309	1.7E-4
Elements	Aluminum	8.7E-7	218	2.2E-6
(dilution	Barium	5.6E-7	205	1.1E-6
tunnel)	Bromine	1.1E-8	n/a	n/a
	Calcium	1.9E-6	297	5.6E-6
	Chlorine	1.9E-6	1075	1.2E-5
	Chromium	2.6E-8	n/a	n/a
	Cobalt	3.8E-6	421	1.5E-5
	Copper	1.3E-6	110	2.3E-6
	Iron	1.1E-6	284	3.1E-6
	Lanthanum	7.1E-7	n/a	n/a
	Magnesium	8.1E-8	340	2.2E-7
	Manganese	5.9E-8	n/a	n/a
	Nickel	5.9E-8	153	1.2E-7
	Phosphorous	9.8E-8	168	1.8E-7
	Potassium	2.7E-7	221	6.8E-7
	Silicon	1.4E-6	270	4.1E-6
	Sodium	1.0E-7	n/a	n/a
	Strontium	2.8E-8	n/a	n/a
	Sulfur	3.3E-6	278	9.6E-6
	Zinc	1.1E-6	199	2.6E-6
Ions	Chloride	2.7E-6	530	9.8E-6
(dilution	Nitrate	1.1E-6	n/a	n/a
tunnel)	Sulfate	1.5E-5	992	8.9E-5
	Ammonium	3 3E-6	696	1 5E-5

Table 5-1. Particulate Mass, Element and Ion Emission Factors for Gas-Fired Process Heater (Refinery Site B).

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

Table 5-2 presents emission factors for OC, EC, total carbon, and SVOCs. SVOC emission factors are very low. The average sum of all SVOCs equals 6.6×10^{-7} lb/MMBtu, comprising only approximately 2 percent of the total organic carbon. Coronene has the highest value, with an emission factor of 1.6×10^{-7} lb/MMBtu. Since the dilution tunnel samples are expected to

			95% Confidence
	Average	Uncertainty	Upper Bound
Substance	(lb/MMBtu)	(%)	(lb/MMBtu)
Organic Carbon	2.8E-5	89	4.5E-5
Elemental Carbon	1.9E-5	n/a	n/a
Total Carbon	3.4E-5	145	6.8E-5
Semi-Volatile Organic Compounds (dilut	ion tunnel)		
1,2,8-trimethylnaphthalene	8.2E-9	n/a	n/a
1,3+1,6+1,7-dimethylnaphthalene	2.1E-8	n/a	n/a
1,4-chrysenequinone	2.5E-9	166	5.3E-9
1,7-dimethylphenanthrene	3.0E-9	170	5.7E-9
1-ethyl-2-methylnaphthalene	3.1E-9	186	7.2E-9
1-methylfluorene+C-methylpyrene/fluorene	2.1E-9	338	5.7E-9
1-methylfluorene	2.2E-8	n/a	n/a
1-methylnaphthalene	2.6E-8	n/a	n/a
1-methylphenanthrene	4.1E-9	535	1.5E-8
1-methylpyrene	7.9E-10	n/a	n/a
1-phenylnaphthalene	2.1E-9	n/a	n/a
2,3,5+I-trimethylnaphthalene	9.8E-9	130	1.9E-8
2,6+2,7-dimethylnaphthalene	1.1E-8	n/a	n/a
2-methylbiphenyl	8.3E-8	n/a	n/a
2-methylnaphthalene	4.5E-8	n/a	n/a
2-methylphenanthrene	1.4E-8	170	3.1E-8
2-phenylnaphthalene	2.5E-10	168	4.6E-10
3-methylbiphenyl	5.7E-8	n/a	n/a
4-methylbiphenyl	1.4E-8	872	7.6E-8
4-methylpyrene	3.8E-9	138	7.4E-9
4H-cyclopenta(def)phenanthrene	1.3E-9	98	2.2E-9
5+6-methylchrysene	9.6E-10	265	2.7E-9
7-methylbenzo(a)pyrene	4.5E-9	422	1.4E-8
9,10-dihydrobenzo(a)pyrene	2.8E-9	208	6.7E-9
9-anthraldehyde	2.6E-9	n/a	n/a
9-fluorenone	4.9E-8	n/a	n/a
9-methylanthracene	1.0E-8	756	5.0E-8
A-dimethylphenanthrene	6.9E-9	n/a	n/a
A-methylfluorene	3.6E-8	75	5.5E-8
A-trimethylnaphthalene	6.8E-9	118	1.2E-8
Acenaphthenequinone	3.9E-8	235	8.6E-8
Anthrone	7.3E-9	99	1.2E-8
Anthracene	5.9E-9	167	1.3E-8
Anthraquinone	3.7E-9	n/a	n/a
B-dimethylphenanthrene	1.4E-8	361	3.8E-8

 Table 5-2. Carbon and Semi-Volatile Organic Compound Emission Factors for Gas-Fired

 Process Heater (Refinery Site B).

			95% Confidence
	Average	Uncertainty	Upper Bound
Substance	(lb/MMBtu)	(%)	(lb/MMBtu)
B-methylpyrene/fluorene	2.9E-9	624	1.2E-8
B-methylphenanthrene	2.1E-8	233	5.6E-8
B-trimethylnaphthalene	6.3E-9	82	1.0E-8
Benzo(a)pyrene	4.7E-9	221	9.9E-9
Benz(a)anthracene	3.8E-9	250	1.0E-8
Benz(a)anthracene-7,12	1.1E-8	937	6.1E-8
Benzanthrone	7.6E-9	168	1.6E-8
Benzo(b)chrysene	1.0E-8	183	2.3E-8
Benzo(b+j+k)fluoranthene	1.5E-8	205	3.6E-8
Benzo(c)phenanthrene	1.6E-9	234	4.3E-9
Benzo(ghi)perylene	4.6E-9	189	1.1E-8
Benzonaphthothiophene	2.4E-9	n/a	n/a
Benzo(e)pyrene	1.2E-9	790	5.9E-9
C-dimethylphenanthrene	1.5E-8	n/a	n/a
C-methylphenanthrene	4.3E-8	n/a	n/a
C-trimethylnaphthalene	8.1E-9	121	1.5E-8
Chrysene	4.0E-9	140	8.0E-9
Coronene	1.6E-7	189	3.6E-7
D-methylpyrene/fluorene	5.1E-10	136	9.9E-10
Dibenz(ah+ac)anthracene	6.8E-9	213	1.4E-8
E-methylpyrene/fluorene	2.8E-9	935	1.6E-8
E-trimethylnaphthalene	4.4E-9	123	8.2E-9
F-trimethylnaphthalene	5.1E-9	149	1.0E-8
Fluoranthene	3.8E-8	279	1.1E-7
Indeno[123-cd]pyrene	5.0E-9	247	1.1E-8
Perylene	1.5E-9	262	3.5E-9
Phenanthrene	5.2E-8	65	7.6E-8
Pyrene	1.3E-8	76	2.0E-8
Sum of All SVOCs	6.6E-7		
Semi-Volatile Organic Compounds (in-sta	ack filter)		
1,2,8-trimethylnaphthalene	7.2E-10	n/a	n/a
1,4-chrysenequinone	2.5E-9	n/a	n/a
2,6+2,7-dimethylnaphthalene	6.8E-9	n/a	n/a
2-methylphenanthrene	1.4E-9	n/a	n/a
4-methylbiphenyl	1.9E-9	n/a	n/a
Benzo(a)pyrene	2.6E-9	266	6.0E-9
Benzo(b)chrysene	2.6E-9	266	6.0E-9
Biphenyl	7.7E-9	n/a	n/a
Sum of All SVOCs	1.0E-8		

Table 5-2 (continued). Carbon and Semi-Volatile Organic Compound Emission Factors for Gas-Fired Process Heater (Refinery Site B).

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

collect SVOCs which condense in the plume, these results are considered more representative for receptor modeling purposes.

Emission factors for VOCs with carbon number greater than 7 are presented in Table 5-3. All VOCs are present at extremely low levels, with 1+7-hexadecene being the most abundant, (1.9 x 10^{-4} lb/MMBtu).

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

PM2.5 SPECIATION PROFILES

Dilution Tunnel

The speciation profile for PM2.5, based on dilution tunnel results, is given in Table 5-5. This table includes all results from the ED-XRF analysis of the dilution tunnel Teflon[®] filters, 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 for PM2.5 mass.

The average emission factor for the sum of species (8.2x10⁻⁵ lb/MMBtu) is approximately 50 percent greater than the average emission factor for total PM2.5 mass (5.4x10⁻⁵ lb/MMBtu, measured gravimetrically). 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, two different types of filters were used: Teflon[®] filters 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. 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.

			95% Confidence
	Average	Uncertainty	Upper Bound
Substance	(lb/MMBtu)	(%)	(lb/MMBtu)
1+7 hexadecene	1.9E-4	226	4.9E-4
1,2,3 trimethylbenzene	ND	n/a	n/a
1,2,3,4-tetramethylbenzene	4.4E-7	n/a	n/a
1,2,3,5-tetramethylbenzene	ND	n/a	n/a
1,2,4 trimethylbenzene	1.3E-6	57	1.9E-6
1,2,4,5-tetramethylbenzene	ND	n/a	n/a
1,3,5 trimethylbenzene	4.3E-7	n/a	n/a
1,3-dichlorobenzene	1.2E-6	185	2.7E-6
1-methylindan	ND	n/a	n/a
1-methylnaphthalene	5.2E-7	n/a	n/a
2-methyl octane	1.2E-6	325	3.2E-6
2-methylindan	ND	n/a	n/a
2-methylnaphthalene	5.2E-7	n/a	n/a
3-methyl octane	4.1E-7	170	7.7E-7
Acetophenone	6.6E-5	278	1.9E-4
Benzaldehyde	4.2E-5	216	1.0E-4
Benzofuran	1.5E-6	312	4.0E-6
Benzonitrile	1.6E-5	295	4.7E-5
Biphenyl	7.6E-7	n/a	n/a
c12 hydrocarbon 1 (1)	4.3E-6	96	7.3E-6
c12 hydrocarbon 2 (1)	1.2E-6	426	3.9E-6
c12 hydrocarbon 3 (1)	3.5E-6	540	1.3E-5
c12 hydrocarbon 4 (1)	1.5E-6	461	5.0E-6
c13 hydrocarbon 1 (1)	3.6E-6	703	1.6E-5
c14 hydrocarbon 1 (1)	1.3E-6	191	3.1E-6
Cyclohexanone	ND	n/a	n/a
Dimethyloctane	ND	n/a	n/a
Dodecene	ND	n/a	n/a
Ethyl Benzene	9.8E-7	62	1.4E-6
Indan	ND	n/a	n/a
Indene	ND	n/a	n/a
m- & p-xylenes	3.1E-6	82	5.0E-6
m-ethyltoluene	7.4E-7	54	1.0E-6
m-isopropyltoluene	ND	n/a	n/a

Table 5-3. Volatile Organic Compound Emission Factors for Gas-Fired Process Heater (Refinery Site B).

	Average		95% Confidence
	(lb/MMBtu	Uncertainty	Upper Bound
Substance)	(%)	(lb/MMBtu)
n-decane	4.8E-7	337	1.3E-6
n-dodecane	8.5E-7	244	1.9E-6
n-eicosane	9.9E-7	362	2.8E-6
n-heptadecene	9.6E-7	382	2.8E-6
n-hexadecene	1.5E-6	n/a	n/a
n-nonadecane	2.0E-6	702	8.9E-6
n-nonane	9.8E-7	151	2.0E-6
n-octadecane	1.0E-6	344	2.8E-6
n-pentadecane	9.7E-7	189	2.2E-6
n-propylbenzene	3.1E-7	184	5.9E-7
n-tetradecane	1.4E-6	159	2.9E-6
n-tridecane	2.5E-6	313	7.8E-6
n-undecane	4.3E-6	504	1.5E-5
Naphthalene	9.3E-7	388	2.7E-6
Nonanal	3.2E-7	n/a	n/a
Nonene-1	ND	n/a	n/a
o-ethyltoluene	3.4E-7	185	6.6E-7
o-isopropyltoluene	ND	n/a	n/a
o-xylene	1.4E-6	55	2.0E-6
p-ethyltoluene	3.4E-7	59	4.9E-7
p-isopropyltoluene	ND	n/a	n/a
Phenol	2.8E-5	295	8.4E-5
Styrene	3.8E-6	145	7.6E-6
t-hydroxybutyltoluene	ND	n/a	n/a
Undecene-1	ND	n/a	n/a

Table 5-3 (continued). Volatile Organic Compound Emission Factors for Gas-Fired Process Heater (Refinery Site B).

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

(1) Unidentified long-chain hydrocarbon.

Figure 5-1 shows the data presented in Table 5-5. The majority of the mass (34 percent) is composed of organic carbon, with sulfate being the next most abundant constituent (18 percent). The sulfate fraction could be biased high due to potential artifacts associated with the use of quartz filters. Compounds with all runs below detectable levels are not included in the figure. Chloride, sulfur, sodium and magnesium were all measured at detectable levels, but are not included in the sum of species, and are therefore not included in the figure.

			95% Confidence
	Average	Uncertainty	Upper Bound
Substance	(lb/MMBtu)	(%)	(lb/MMBtu)
SO ₂	1.1E-3	81	1.7E-3
NO _x	0.17	81	0.27

Table 5-4. NO_X and SO₂ Emission Factors for Gas-Fired Process Heater (Refinery Site B).

Table 5-5.	PM2.5 S	peciation P	rofile for	r Gas-Fire	ed Process H	leater -	– Dilution	Tunnel Results
(Refinery S	Site B).	-						

	Average Mass		95% Confidence
	Fraction (1)	Uncertainty	Upper Bound
Substance	(%)	(%)	(%)
Aluminum	1.1	291	3.2
Barium	0.68	726	3.2
Bromine	0.01	n/a	n/a
Calcium	2.3	355	7.8
Chlorine	2.4	1281	18
Chromium	0.03	n/a	n/a
Cobalt	4.7	463	19
Copper	1.6	222	4.0
Iron	1.3	343	4.4
Lanthanum	0.9	n/a	n/a
Magnesium*			
Manganese	0.07	n/a	n/a
Nickel	0.07	246	0.2
Phosphorous	0.12	716	0.5
Potassium	0.33	293	1.0
Silicon	1.8	332	5.8
Sodium*			
Strontium	0.03	n/a	n/a
Sulfur*			
Zinc	1.3	278	3.9
Organic Carbon	34	213	100
Elemental Carbon	23	n/a	n/a
Total Carbon*	42	241	135
Sulfate	18	1212	129
Nitrate	1.4	n/a	n/a
Chloride*			
Ammonium	4.1	984	24
Total	100		

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. Average speciated mass was greater than average total PM2.5 mass measured on the dilution tunnel filter.

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



Figure 5-1. PM2.5 Speciation Profile for Gas-Fired Process Heater – Dilution Tunnel Results (Refinery Site B).

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 (filterable and condensible particulate). In this table, blank corrected total condensible particulate has been subdivided into its respective organic and inorganic fractions for illustrative purposes. Inorganic condensible particulate has been further subdivided to show the amount accounted for by sulfate and chloride.

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 (91 percent), a large portion of which is

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unaccounted for by the sulfate and chloride fractions. Future tests will need to more fully speciate this inorganic CPM fraction in order to better understand its composition.

	Average Mass		95%
	Fraction (1)	Uncertainty	Confidence
Substance	(%)	(%)	Upper Bound
Filterable PM2.5	5.6	218	14
Organic CPM	2.9	264	8.0
Inorganic CPM	91	290	271
- Unknown Inorganic CPM	47	(1)	(1)
- Sulfate (as SO_4^{-})	14	271	40
- Chloride (as NH ₄ Cl)	31	293	94
Total	100		

Table 5-6. PM2.5 Speciation Profile for Gas-Fired Process Heater – Method 201A/202 Results(Refinery Site B).

(1) Unknown inorganic CPM is fraction not accounted for by sulfate or chloride.

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 of total organic carbon, both in units of lb/MMBtu. The speciated organic carbon, measured as SVOCs, accounts for approximately 2 percent of the total organic carbon. 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 coronene (0.6 percent), followed by phenanthrene (0.2 percent).



Figure 5-2. PM2.5 Speciation Profile for Gas-Fired Process Heater – Method 201A/202 Results (Refinery Site B).

			95%
	Average Mass		Confidence
	Fraction (1)	Uncertainty	Upper Bound
Substance	(%)	(%)	(%)
1,2,8-trimethylnaphthalene	2.9E-2	n/a	n/a
1,3+1,6+1,7-dimethylnaphthalene	7.6E-2	n/a	n/a
1,4-chrysenequinone	8.8E-3	255	2.4E-2
1,7-dimethylphenanthrene	1.1E-2	717	5.0E-2
1-ethyl-2-methylnaphthalene	1.1E-2	268	3.2E-2
1-methylfluorene+C-methylpyrene/fluorene	7.6E-3	774	3.7E-2
1-methylfluorene	8.0E-2	n/a	n/a
1-methylnaphthalene	9.4E-2	n/a	n/a
1-methylphenanthrene	1.5E-2	878	7.9E-2
1-methylpyrene	2.8E-3	n/a	n/a
1-phenylnaphthalene	7.6E-3	n/a	n/a
2,3,5+I-trimethylnaphthalene	3.5E-2	233	9.1E-2
2,6+2,7-dimethylnaphthalene	3.9E-2	n/a	n/a
2-methylbiphenyl	3.0E-1	n/a	n/a
2-methylnaphthalene	1.6E-1	n/a	n/a
2-methylphenanthrene	5.2E-2	257	1.4E-1
2-phenylnaphthalene	8.9E-4	716	4.1E-3
3-methylbiphenyl	2.1E-1	n/a	n/a
4-methylbiphenyl	5.1E-2	1116	3.4E-1
4-methylpyrene	1.4E-2	238	3.6E-2
4H-cyclopenta(def)phenanthrene	4.6E-3	217	1.1E-2
5+6-methylchrysene	3.4E-3	328	1.1E-2
7-methylbenzo(a)pyrene	1.6E-2	814	8.2E-2
9,10-dihydrobenzo(a)pyrene	9.9E-3	284	2.9E-2
9-anthraldehyde	9.4E-3	n/a	n/a
9-fluorenone	1.7E-1	n/a	n/a
9-methylanthracene	3.7E-2	1028	2.3E-1
A-dimethylphenanthrene	2.5E-2	n/a	n/a
A-methylfluorene	1.3E-1	207	3.1E-1
A-trimethylnaphthalene	2.4E-2	226	6.2E-2
Acenaphthenequinone	1.4E-1	735	6.6E-1
Anthrone	2.6E-2	217	6.6E-2
Anthracene	2.1E-2	255	5.8E-2
Anthraquinone	1.3E-2	n/a	n/a
B-dimethylphenanthrene	4.9E-2	784	2.4E-1

Table 5-7. SVOC Speciation Profile for Gas-Fired Process Heater – Dilution Tunnel Results (Refinery Site B).

			95%
	Average Mass		Confidence
	Fraction (1)	Uncertainty	Upper Bound
Substance	(%)	(%)	(%)
B-methylpyrene/methylfluorene	1.0E-2	935	5.9E-2
B-methylphenanthrene	7.7E-2	303	2.4E-1
B-trimethylnaphthalene	2.3E-2	210	5.5E-2
Benzo(a)pyrene	1.7E-2	731	7.8E-2
Benz(a)anthracene	1.4E-2	316	4.3E-2
Benz(a)anthracene-7,12	3.8E-2	1168	2.6E-1
Benzanthrone	2.7E-2	256	7.5E-2
Benzo(b)chrysene	3.7E-2	266	1.1E-1
Benzo(b+j+k)fluoranthene	5.4E-2	282	1.6E-1
Benzo(c)phenanthrene	5.9E-3	304	1.8E-2
Benzo(ghi)perylene	1.6E-2	270	4.7E-2
Benzonaphthothiophene	8.5E-3	n/a	n/a
Benzo(e)pyrene	4.3E-3	1053	2.7E-2
C-dimethylphenanthrene	5.3E-2	n/a	n/a
C-methylphenanthrene	1.5E-1	n/a	n/a
C-trimethylnaphthalene	2.9E-2	228	7.5E-2
Chrysene	1.4E-2	239	3.8E-2
Coronene	5.6E-1	270	1.6E+0
D-methylpyrene/methylfluorene	1.8E-3	236	4.8E-3
Dibenz(ah+ac)anthracene	2.4E-2	728	1.1E-1
E-methylpyrene/methylfluorene	9.9E-3	1166	6.7E-2
E-trimethylnaphthalene	1.6E-2	229	4.0E-2
F-trimethylnaphthalene	1.8E-2	244	4.9E-2
Fluoranthene	1.4E-1	339	4.5E-1
Indeno[123-cd]pyrene	1.8E-2	739	8.4E-2
Perylene	5.4E-3	744	2.5E-2
Phenanthrene	1.9E-1	204	4.4E-1
Pyrene	4.6E-2	208	1.1E-1

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

1- Mass fraction expressed as a percent of total organic carbon.



Figure 5-3. SVOC Speciation Profile for Gas-Fired Process Heater – Dilution Tunnel Results (Refinery Site B).

Section 6 QUALITY ASSURANCE

SAMPLE STORAGE AND SHIPPING

All samples were stored on-site in an ice chest prior to shipment to the lab for analysis. All of the samples except in-stack and impinger filters were shipped to the lab in an ice chest.

All in-stack (Method 201A and Method 17) and impinger filters (Method 202) were sent to the lab for analysis. The filters were stored in a desiccator at ambient conditions prior to shipment.

Upon receipt of samples at the lab, those requiring refrigeration were stored at 4° C (nominal). Samples were stored and shipped in a manner to prevent breakage, however glass sample jars containing the impinger catch and rinse from the Method 201A/202 trains broke while in storage due to freezing. Loss of sample was minimal but glass chips may have contaminated the samples.

DILUTION TUNNEL FLOWS

Flow rates through the dilution tunnel sample collection media were determined by averaging the flow rates measured before testing commenced and after sampling was completed. Results from the pre- and post-test flow checks are presented in Table 6-1. Flow rates were generally consistent, however during the first run the flow rate through Tenax A dropped by 86 percent. This change could be a result of the flow becoming obstructed by loose Tenax or the flow regulator valve being bumped after the pre-test flow check. The Tenax B flows for this run were within 20 percent of one another, therefore the Tenax A sample was rejected and only the results from the Tenax B sample were used.

GRAVIMETRIC ANALYSIS

Dilution Tunnel Filters

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

Pre-test flow	Post-test flow	Average	% Difference			
	Quartz filter flo	w (scfh)				
85.00	110.00	97.50	-29%			
85.00	83.00	84.00	2%			
85.00	85.00	85.00	0%			
	Teflon®	filter flow (s	cfh)			
85.00	95.00	90.00	-12%			
85.00	83.00	84.00	2%			
85.00	90.00	87.50	-6%			
[PUF/XAD (scfh)				
242.00	242.00	242.00	0%			
242.00	225.00	233.50	7%			
239.00	235.00	237.00	2%			
	Tenax A (se	cfh)				
100.00	14.00	57.00	86%			
100.00	90.00	95.00	10%			
100.00	80.00	90.00	20%			
	Tenax B (scfh)					
100.00	88.00	94.00	12%			
100.00	85.00	92.50	15%			
67.00	81.00	74.00	-21%			

Table 6-1. Pre- and Post-Test Dilution Tunnel Flow Checks for the Gas-Fired Process Heater Tests (Refinery Site B).

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 ± 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 ± 0.015 mg. Pread 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.

In-Stack Filters

The balance was calibrated daily with two "S" type weights in the range of the media being weighed (0.2 and 0.5 g) and the tare was set prior to weighing each batch of filters. If the results of these performance tests had deviated by more than ± 1 mg, the balance would have been recalibrated. A recalibration was not required. If consecutive sample weights deviated by more than ± 0.5 mg, the sample was returned to the desiccator for at least 6 hours before reweighing. Pre- and post-weights, check weights and reweights (if required) were recorded on data sheets. Table 6-2 presents the results of the methylene chloride, water and acetone rinse blanks. These blank values were used to correct the EPA Method 201A/202 and Method 17 particulate data.

Table 6-2. N	/Iethod 2	201A/202	2 Blank	Results
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Sample	Mass (mg)
Method 202 Water Recovery Blank	1.5
Method 202 Dichloromethane Recovery Blank	0.6
Method 201A Acetone Recovery Blank	ND (1)
Cyclone Filter Blank	0.66
Back-half Filter Blank	0.42
Method 17 Filter Blank	0.24
Dilution Tunnel Filter Blank	ND (2)

1- Weight was negative.

2- Detection limit of balance = 0.001 mg

Results of the filter blank weights are also presented in Table 6-2. All Method 201A in-stack filter weights were less than the field blank, with the post-test mass from Run 2 being negative and treated as a zero in calculations. Post-test weights of the back-half filters (Method 202) for Runs 2 and 3 were less than the field blank. Run 1 of the Method 17 filters was less than the field blank. These results indicate that the particulate levels are at or below the detection limits of the method.

An analysis of the acetone rinse blanks is presented in Table 6-3. The particulate mass detection limit was calculated as three times the standard deviation of the results of the field blank acetone rinses and the acetone recovery blank. The resulting detection limit of approximately 2 mg further indicates that the filterable particulate levels at the heater were below detection limits.

Therefore, the filterable particulate data from Methods 201A and 17 are presented in Section 5 for qualitative purposes only.

Table 6-3. Acetone Blank Results for Gas-Fired Process Heater Tests (Refinery Site B).

Sample Fraction	Mass (mg)
PM10 cyclone catch rinse	0.3
PM2.5 cyclone catch rinse (2.5-10 μm)	-1.6
<pm2.5 (<2.5="" rinse="" td="" μm)<=""><td>-0.12</td></pm2.5>	-0.12
Recovery Blank	-0.19
Detection Limit (3*standard deviation)	2

Detection Limit (3*standard deviation)

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 ± 5 percent or when a replicate concentration differed from the original value (when values exceed 10 times the detection limits) by more than ± 10 percent, the samples were reanalyzed. If further tests of standards showed that the system calibration had changed by more than ± 2 percent, the instrument was recalibrated as described above. All XRF results were entered directly into the DRI databases.

Results from the field blank are presented in Table 6-4. Only aluminum, magnesium, phosphorous and sodium were present at detectable levels. In general, concentrations in the field blank were at least an order of magnitude less than concentrations in the stack samples. Sodium in the field blank was within an order of magnitude of the average stack-sample concentration. Aluminum and phosphorous field blank concentrations were within an order of magnitude of the ambient concentrations.

Table 6-4. Blank Results for Elements.

Element	mg/dscm
Aluminum	1.7E-5
Magnesium	4.5E-6
Phosphorous	5.5E-6
Sodium	2.5E-5

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 ± 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. Only organic carbon in the dilution tunnel blank was present above detection limits. Organic carbon on the field blank filter was

approximately an order of magnitude lower than the average concentration in the stack gas samples.

Table 6-5. Organic and Elemental Carbon Blank Results for Gas-Fired Process Heater Tests (Refinery Site B).

	OC (mg/dscm)	EC (mg/dscm)
Field Blank	ND	ND
Dilution Tunnel Field Blank	2.9E-3	ND

SULFATE, NITRATE, CHLORIDE, AND AMMONIUM ANALYSIS

The primary standard solutions containing NaCl, NaNO₃ and (Na)₂SO₄ were prepared with reagent grade salts that 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 ± 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 ± 10 percent, or values for standards differed by more than ± 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. All ions were below detection limits.

Table 6-6.	Ion Blank Results.	

Ion	mg/dscm
Chloride	ND
Sulfate	ND
Nitrate	ND
Ammonium	ND

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]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.

Results from the field blank and replicate analysis are presented in Table 6-7. Compounds below detection limits in the field blank and replicate analyses are not included in the table. The following compounds have an average sample concentration within an order of magnitude of the field blank: 1-ethyl-2-methylnaphthalene, 1-methylfluorene+C-methylpyrene/methylfluorene, 1methylnaphthalene, 1-phenylnaphthalene, 2-methylbiphenyl, 2-methylnaphthalene, 2phenylnaphthalene, 3-methylbiphenyl, 4-methylbiphenyl, 4-methylpyrene, 4Hcyclopenta(def)phenanthrene, 7-methylbenzo(a)pyrene, acenaphthenequinone, anthracene, benzo(a)pyrene, benz(a)anthracene, benzonaphthothiophene, coronene, and pyrene. 1,4chysenequinone, 9,10-dihydrobenzo(a)pyrene, 9-anthraldehyde and anthraquinone benzanthrone, benzo(b)chrysene, benzo(ghi)perylene, benzo(e)pyrene, chrysene dibenz(ah+ac)anthracene, indeno[123-cd]pyrene have concentrations in the field blank that are all greater than the average of the stack samples (within an order of magnitude, in general). Anthrone concentrations in the field blank are one and a half orders of magnitude higher than the average of the stack samples. These results may cause the data for these compounds to have a positive bias. 7methylbenz(a)anthracene, a-methylpyrene, bibenzene, cholestane and xanthone were detected in the field blank but not in the stack samples or the ambient sample.

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.

	Heater Field	Heater Run 1-	Heater Run 1-	
Compound	Blank (1)	Primary (1)	Replicate (1)	MDL(1)
1,2,8-trimethylnaphthalene	4.8E-7	1.1E-6	ND	3.2E-7
1,4,5-trimethylnaphthalene	ND	ND	ND	5.0E-6
1,4-chrysenequinone	2.6E-5	2.5E-5	2.4E-5	2.7E-7
1-ethyl-2-methylnaphthalene	3.3E-7	4.5E-7	6.0E-7	1.1E-7
1-MeFH-C-MePy/Fl	1.5E-6	8.5E-7	1.3E-6	8.5E-7
1-methylfluorene	ND	3.8E-6	ND	3.5E-6
1-methylnaphthalene	3.5E-6	5.9E-6	4.4E-6	2.0E-6
1-methylpyrene	6.5E-7	ND	ND	4.2E-7
1-phenylnaphthalene	5.3E-7	1.0E-6	6.0E-7	2.7E-7
2,3,5+I-trimethylnaphthalene	5.5E-7	1.8E-6	1.7E-6	1.6E-7
2-methylbiphenyl	2.4E-5	2.6E-5	2.5E-5	8.4E-6
2-methylnaphthalene	5.1E-6	8.3E-6	6.0E-6	3.3E-6
2-methylphenanthrene	9.0E-7	6.3E-7	3.6E-6	1.1E-7
2-phenylnaphthalene	1.5E-7	1.8E-7	2.8E-7	5.3E-8
3-methylbiphenyl	1.5E-5	1.9E-5	1.9E-5	1.2E-5
4-methylbiphenyl	8.0E-6	9.5E-6	9.4E-6	1.0E-6
4-methylpyrene	1.2E-6	2.3E-7	ND	1.1E-7
4H-cyclopenta(def)phenanthrene	7.5E-6	7.7E-6	7.7E-6	0.0E+0
5+6-methylchrysene	6.7E-6	5.0E-8	7.5E-8	0.0E+0
7-methylbenz(a)anthracene	1.3E-6	ND		3.3E-7
7-methylbenzo(a)pyrene	1.2E-5	ND	8.3E-7	3.7E-7
9,10-dihydrobenzo(a)pyrene	4.2E-5	3.6E-5	3.7E-5	1.6E-7
9-anthraldehyde	3.0E-5	3.0E-5	3.0E-5	1.4E-6
9-methylanthracene	ND	3.6E-6	ND	2.4E-6
A-methylpyrene	2.3E-6	1.9E-6	2.3E-6	5.3E-8
A-trimethylnaphthalene	1.8E-7	1.0E-6	9.3E-7	1.0E-7
Acenaphthenequinone	2.1E-5	2.4E-5	2.3E-5	3.2E-7
Anthrone	2.3E-4	2.3E-4	2.3E-4	5.3E-8
Anthracene	1.0E-0	1.9E-0	2.0E-0	0.0E+0
D MaDy/MaE1	2.0E-5	1.0E-3	1.0E-J	2.9E-0
D-Mery/Meri		1.3E-/ 2.1E-6		5.3E-8
B-methylphenanthiene		2.1E-0 1.0E-6	3.2E-0 1.1E-6	J.0E-/
B-u interny inapirulaiene Benz(a) anthracene	3.0E-7	1.0E-0 1.8E-6	1.1E-0 1.9E-6	3.3E-8 3.2E-7
Benz(a)anthracene 7.12	4.3L-0	7.7E.6	0.6E.6	3.2E-7 2.0E-6
Benzenthrone	1.0E-5	7.7E-0 7.2E-6	9.0E-0 7.8E-6	2.0E-0 1 9E 7
Benzo(a)pyrene	8.7E-6	7.5E=0 1.0E=6	7.8E-0 1.2E-6	
Benzo(b)chrysene	3.0E-5	1.0E-0 1.0E-6	1.2E-0 3.7E-6	5.2E-7 1.1E-7
Benzo(b+i+k)fluoranthene	2 0F-5	5.8F_7	2.0E-6	53E-8
Benzo(c)phenanthrepe	2.01-5 2.1F_6	5.01-7 ND	2.01-0 ND	5.5E-0
Benzo(e)pyrene	5 7E-6	2 0F-6	2 2F-6	3 3 F_7
Benzo(ghi)pervlene	1 7F-5	6.8F-6	7.2E-0	3.2E-7
Benzonaphthothiophene	2 1F-6	ND	1 3F-7	1 1F-7
Bibenzene	2.11-0 2.2F-4	ND	ND	1 3F-4
Binhenvl	5 0F-6	ND	ND	3 6E-6
	5.01-0			5.0L-0

Table 6-7. SVOC Blank and Replicate Results (mg/dscm).

	Heater Field	Heater Run 1-	Heater Run 1-	
Compound	Blank (1)	Primary (1)	Replicate (1)	MDL (1)
C-dimethylphenanthrene	ND	ND	1.9E-6	1.8E-6
C-methylphenanthrene	ND	4.7E-6	3.6E-6	1.5E-6
C-trimethylnaphthalene	5.0E-7	1.5E-6	1.7E-6	4.2E-7
Cholestane	2.9E-5	ND	ND	1.4E-5
Chrysene	6.6E-6	4.4E-6	4.7E-6	1.1E-7
Coronene	6.5E-5	ND	1.4E-5	3.2E-7
Dibenz(ah+ac)anthracene	2.8E-5	1.7E-5	1.7E-5	3.2E-7
E-MePy/MeFl	ND	7.5E-8	1.0E-7	5.3E-8
E-trimethylnaphthalene	1.0E-7	6.8E-7	6.8E-7	5.3E-8
F-trimethylnaphthalene	ND	8.0E-7	9.3E-7	5.0E-8
Fluoranthene	1.1E-6	8.7E-6	1.6E-6	1.1E-7
Indeno[123-cd]pyrene	1.7E-5	4.6E-6	5.0E-6	3.2E-7
Naphthalene	5.4E-5	5.7E-5	ND	5.1E-5
Perylene	5.7E-6	2.2E-6	2.4E-6	1.1E-7
Phenanthrene	3.1E-6	7.3E-6	7.8E-6	4.2E-7
Pyrene	3.4E-6	4.0E-6	3.9E-6	2.1E-7
Xanthone	6.8E-6	4.7E-6	6.0E-6	2.1E-7

Table 6-7 (continued). SVOC Blank and Replicate Results (mg/dscm).

MDL-Method detection limit

MeFl- Methylfluorene

MePy-Methylpyrene

ND-Not detected

1- Assumed sample volume of 40 m3.

Table 6-8 shows the results of the Tenax field blank. Of the few compounds detected in the field blank, only nonanal was within an order of magnitude of the average sample concentration. All other compounds detected in the blank were at least an order of magnitude less than the average sample concentration.

Table 6-8. VOC Blank Results (mg/dscm).

	Heater Field Blank
Compound	(1)
1+7 hexadecene	4.9E-3
1,3-dichlorobenzene	3.3E-5
Acetophenone	1.6E-4
Benzaldehyde	1.2E-4
Nonanal	7.7E-5
Phenol	4.4E-5
Styrene	5.7E-5

1- Assumed sample volume of 30 m3.

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 ± 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 88 times greater than the PM2.5 mass measured by the dilution tunnel. The PM2.5 mass measured by the dilution tunnel is approximately 3 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.

Ninety-four percent of the mass from in-stack methods was contained in the condensible particulate fraction, approximately 95 percent of which was inorganic (i.e., not extractable in dichloromethane). While sulfate and chloride were 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 appears to be 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 SO_2 in the stack gas. Sulfur dioxide levels in the flue gas averaged approximately 0.3 to 0.4 ppm over the three days of testing at the process

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heater. Compared to this value, the sulfate levels measured by the dilution tunnel accounted for approximately 0.9 percent of the SO_2 in the flue gas, while the levels measured by Method 202 accounted for approximately 39 percent.



Figure 7-1. Method 202 Inorganic Fraction Residue Analysis for Gas-Fired Process Heater Tests (Refinery Site B).

Artifacts from SO₂ absorption in the impingers of the Method 202 train leading to a positive bias in the results have been previously documented for SO₂ concentrations on the order of 2000 ppm (Filadelfia and McDannel, 1996). Sulphur dioxide and O₂ 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 SO_2 bias under the conditions of their study. No literature was found to evaluate if this artifact would be significant at sub-10 ppm SO_2 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 was 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 the 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



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

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were at or below the practical limits of the method as practiced in these tests. Dilution tunnel 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. Bromine, Mg and Na 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 process heater combustion process. Selenium was 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 Cl, Co, Cu and Zn. Chromium, La, P, Sr, and Cl⁻ 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 process heater emissions should be revealed. The resulting emissions profile (Figure 7-5) shows the most significant compounds are $S/SO_4^{=}$, Co, Cl, Ca, Cu, Zn, and Fe. The uncertainty in several of these values is large, as reflected in the high standard deviations. The sum of the species shown in Figure 7-5 account for 165 percent of the PM2.5 mass, which is fair closure considering the large standard



Figure 7-3. In-Stack and Ambient Species Concentrations for Gas-Fired Process Heater – Dilution Tunnel Results (Refinery Site B).



Figure 7-4. Comparison of Species Concentrations to Detection Limits for Gas-Fired Process Heater – Dilution Tunnel Results (Refinery Site B).



Figure 7-5. Mean Species Concentrations and Standard Deviation for Gas-Fired Process Heater Tests – Dilution Tunnel Results (Refinery Site B).

deviations for most substances. Organic carbon and EC account for 54 percent of all the species shown in the figure, with organic carbon dominating. Sulfate accounts for 19 percent. 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.

Another potentially useful marker for source emissions is the organic emissions profile. All of the SVOCs detected were present at extremely low concentrations. A majority of SVOCs measured by the dilution tunnel, and present at detectable levels, were within 10 times the ambient and field blank levels. Thus, the SVOCs contributed by the boiler are largely undistinguishable from the background levels. The sum of all SVOCs accounted for approximately 2 percent of the organic carbon measured by the dilution tunnel. 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 detected SVOCs accounts for only about 2 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).

SECONDARY PM2.5 PRECURSOR EMISSIONS

Secondary precursor emissions considered in this project were NO_X , SO_2 , 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 principal sources of NO_X emissions, since the fuel is usually free of significant fixed nitrogen species. Nitrogen oxide concentration during testing ranged from 102 to 104 ppm (dry,

corrected to 3 percent oxygen), which is in the range expected for gas combustion in this process heater design and operating conditions. Sulphur dioxide concentration averaged 0.3-0.4 ppm during these tests. This is nominally consistent with the measured H_2S 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. The VOCs present are generally characteristic of partially combusted fuel fragments and pyrolysis products which escape complete combustion.
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Appendix A

GLOSSARY

$\mu g/cm^2$	micrograms per square centimeter				
AC	automated colorimetry system				
acfm	actual cubic feet per minute				
ACS	American Chemical Society				
Δα	silver				
Δ1	aluminum				
ΔΡΙ	American Petroleum Institute				
Ag	arsonic				
A SME	American Society of Mechanical Engineers				
	harium				
Da Dr	bramina				
DI Dtu/sof	Divining Dritich thermal units ner standard subic feet				
Diu/sci	Bintisii meninai units per standard cubic toot				
Ca					
CEMS	continuous emissions monitoring system				
C_x	compound containing 'x' carbon atoms				
Cl	chloride ion				
Cl	chlorine				
Co	cobalt				
CO	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				

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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
Ğ-S	Greenburg-Smith
Hg	mercury
H_2S	hydrogen sulfide
HC1	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
Mo	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
\mathbf{NO}_2	muogen ulonide

GLOSSARY

(continued)

NO ₃	nitrate ion
NO _x	oxides of nitrogen
O_2	molecular oxygen
ŌĊ	organic carbon
Р	phosphorus
PAH	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

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

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