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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
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PREPARED UNDER CONTRACT BY:

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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 (PM_{2.5}). Source emissions data are needed to assess the contribution of petroleum industry combustion sources to ambient PM_{2.5} concentrations for receptor modeling and PM_{2.5} 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aerosols from petroleum industry combustion sources, and the limited information that is available is incomplete and outdated.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, SO₂, 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.

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 PM_{2.5} 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 PM_{2.5} mass were quantified.
- Organic and elemental carbon comprise 49% of the measured primary PM_{2.5} mass.
- Sulfate, ammonium, chloride and nitrate together account for approximately 32% of the measured PM_{2.5} mass; sulfate alone accounts for approximately 22%.
- Cobalt, calcium, silicon, copper, zinc, iron, aluminum and lanthanum account for approximately 17% of the measured PM_{2.5} 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.

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

Substance		Flag	Emission Factor (lb/MMBtu)	Uncertainty (%)	95 % Confidence Upper Bound (lb/MMBtu)
Particulate Mass	Condensible Particulate (inorganic)		4.8E-3	201	1.1E-2
	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)	B	2.2E-4	62	3.1E-4
	PM2.5 (in-stack method)	(2)	4.8E-3		
Elements	PM2.5 (Dilution Tunnel)	*	5.4E-5	309	1.7E-4
	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

* <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.

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

	Substance	Flag	Emission Factor (lb/MMBtu)	Uncertainty (%)	95 % Confidence Upper Bound (lb/MMBtu)
Dilution Tunnel	Coronene	*, B	1.6E-7	189	3.6E-7
	2-methylbiphenyl	*, B	8.3E-8	n/a	n/a
	3-methylbiphenyl	*, B	5.7E-8	n/a	n/a
	Phenanthrene	*	5.2E-8	65	7.6E-8
	9-fluorenone	(1), (2)	4.9E-8	n/a	n/a
	2-methylnaphthalene	*, B	4.5E-8	n/a	n/a
	C-methylphenanthrene		4.3E-8	n/a	n/a
	Acenaphthenequinone	B	3.9E-8	235	8.6E-8
	Fluoranthene		3.8E-8	279	1.1E-7
	A-methylfluorene	(1), (2)	3.6E-8	75	5.5E-8
	1-methylnaphthalene	*, B	2.6E-8	n/a	n/a
	1-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	*, B	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-trimethylnaphthalene	*	6.3E-9	82	1.0E-8
	Anthracene	*, B	5.9E-9	167	1.3E-8
	F-trimethylnaphthalene	*	5.1E-9	149	1.0E-8
	Indeno[123-cd]pyrene	*, B	5.0E-9	247	1.1E-8
	Benzo(a)pyrene	*, B	4.7E-9	221	9.9E-9
	Benzo(ghi)perylene	*, B	4.6E-9	189	1.1E-8
	7-methylbenzo(a)pyrene	*, B	4.5E-9	422	1.4E-8
	E-trimethylnaphthalene	*	4.4E-9	123	8.2E-9
	1-methylphenanthrene	(1)	4.1E-9	535	1.5E-8
	Chrysene	*, B	4.0E-9	140	8.0E-9
	4-methylpyrene	B	3.8E-9	138	7.4E-9
	Benz(a)anthracene	*, B	3.8E-9	250	1.0E-8
	Anthraquinone	(1), B	3.7E-9	n/a	n/a
	1-ethyl-2-methylnaphthalene	*, B	3.1E-9	186	7.2E-9
	1,7-dimethylphenanthrene	(1)	3.0E-9	170	5.7E-9
	B-methylpyrene/methylfluorene		2.9E-9	624	1.2E-8
	E-methylpyrene/methylfluorene	*	2.8E-9	935	1.6E-8
	9,10-dihydrobenzo(a)pyrene	*, B	2.8E-9	208	6.7E-9
	9-anthraldehyde	(1), B	2.6E-9	n/a	n/a
	1,4-chrysenequinone	*, B	2.5E-9	166	5.3E-9

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

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

* <10x ambient

B <10x blank

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

Substance			Emission Factor (lb/MMBtu)	Uncertainty (%)	95 % Confidence Upper Bound (lb/MMBtu)
Dilution Tunnel	Benzonaphthothiophene	*, B	2.4E-9	n/a	n/a
	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
	Perylene	*, 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-10
	Sum of All SVOCs		6.6E-7	--	--
In-Stack 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	--	--

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

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

* <10x ambient

B <10x blank

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

Substance		Emission Factor (lb/MMBtu)	Uncertainty (%)	95 % Confidence Upper Bound (lb/MMBtu)
Gases	SO ₂	1.1E-3	81	1.7E-3
	NO _x	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
	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†	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

* <10x ambient

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

B <10x blank

† unidentified long-chain hydrocarbon

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

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	

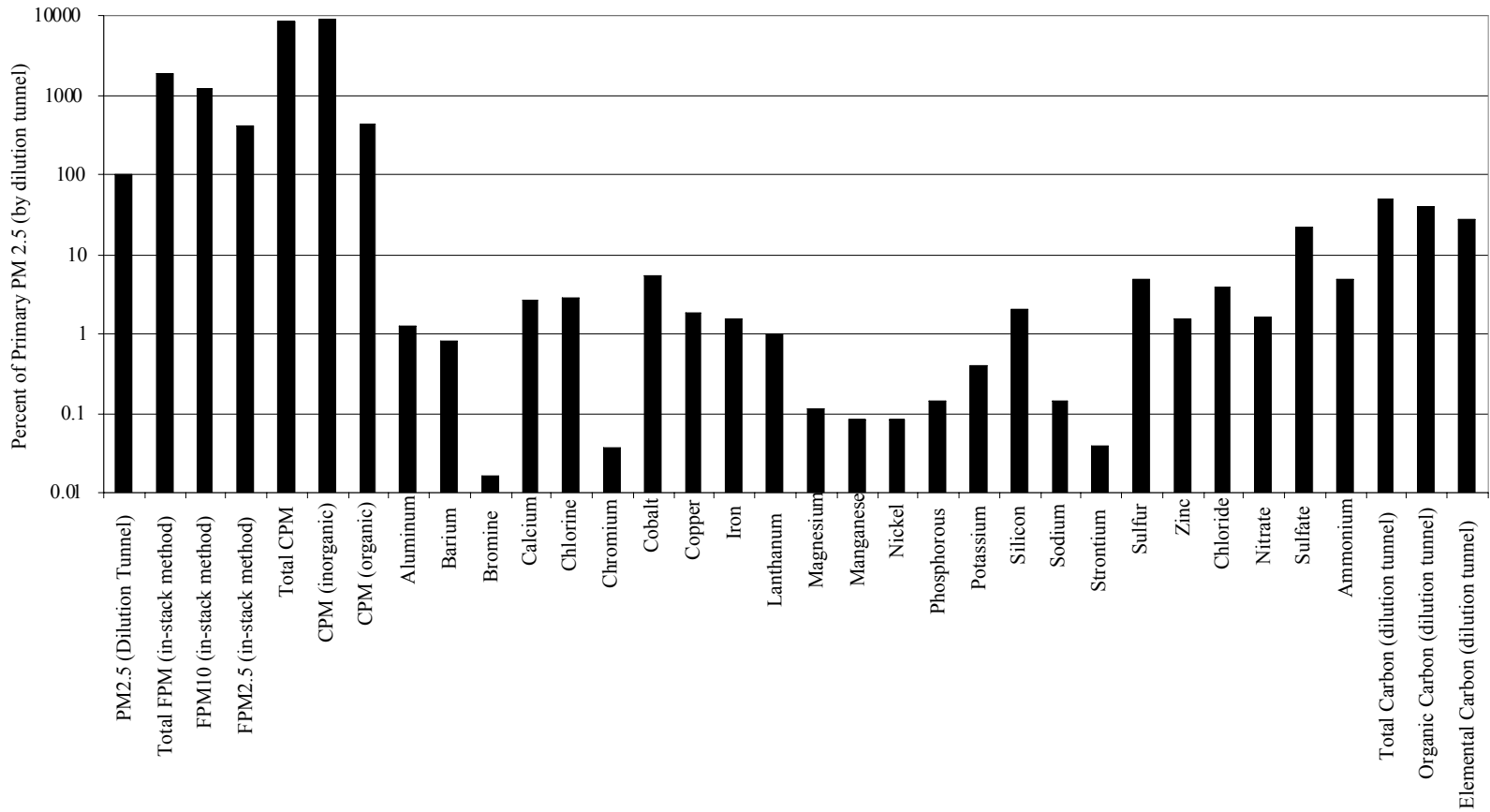


Figure E-1. Speciation profile for primary particulate emissions from gas-fired process heater (Refinery Site B).

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 (PM_{2.5}). 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 PM_{2.5} 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 PM_{2.5} 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 PM_{2.5} 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 PM_{2.5} 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 PM_{2.5}) 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.

Table 1-1. Overview of Sampling Scope.

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 Teflon [®] filter TIGF/PUF/XAD-4 Quartz filter Tenax	--	3	1
Fuel sample	3	--	--
NO _x , SO ₂ , CO, O ₂ , CO ₂	--	continuous	--
Process monitoring	--	continuous	--

TIGF=Teflon[®]-impregnated glass fiber filter

PUF=polyurethane foam

XAD-4 = Amberlite[®] sorbent resin

Dilution Stack Gas Samples

Dilution sampling was used to characterize PM_{2.5} 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 PM_{2.5} 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.

Table 1-2. Summary of Analytical Targets.

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

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 Zipperman (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

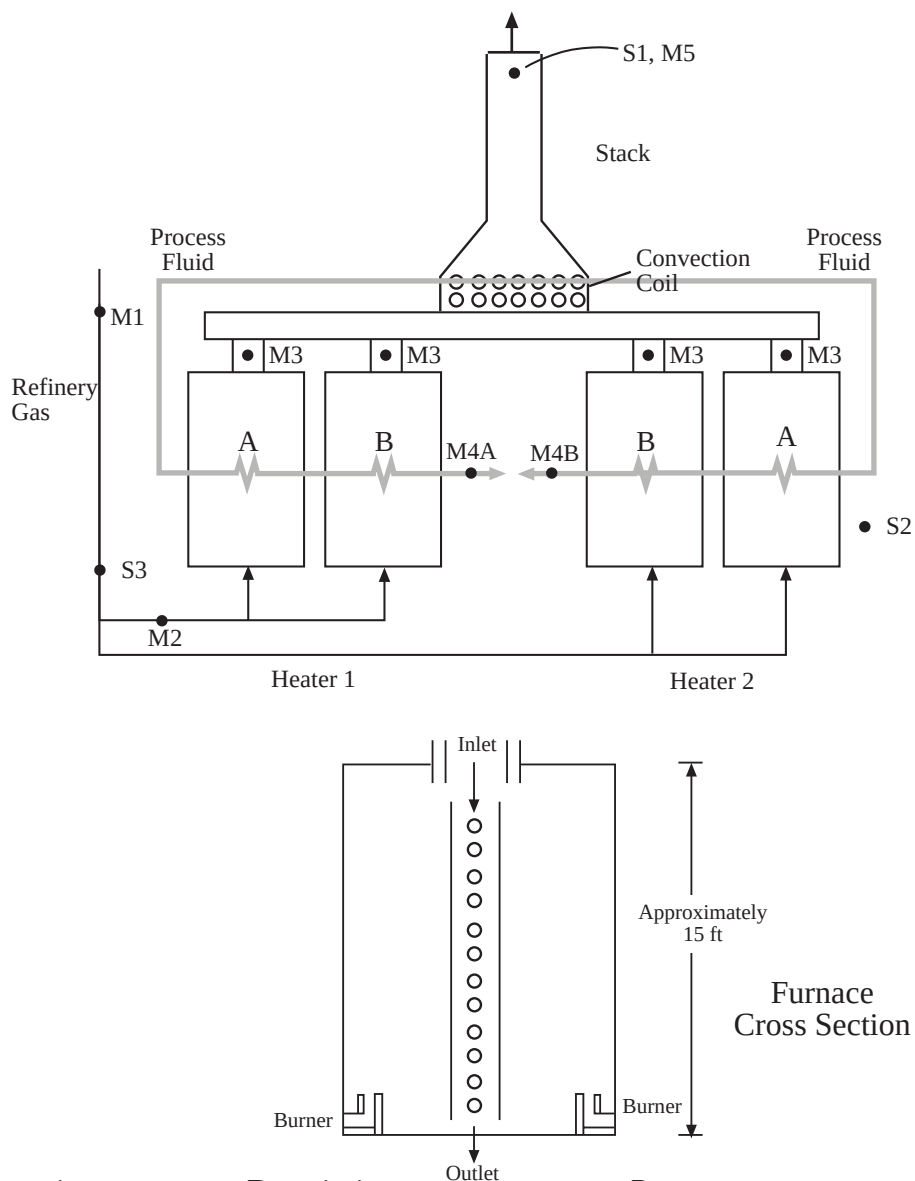
PROCESS DESCRIPTION

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 O₂ 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.



<u>Sampling location</u>	<u>Description</u>	<u>Parameters</u>
S1	Stack	See Table 4-1
S2	Ground level	
S3	Fuel gas feed	
M1	Fuel gas header	Specific gravity, H ₂ S, Btu content
M2A, M2B	Fuel gas feed	Fuel gas flow rate
M3	Heater flue gas outlet	Excess oxygen
M4A, M4B	Process fluid feed	Process fluid flow rate, process fluid outlet temperature
M5	Stack	Flue gas temperature

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

Table 3-1. Summary of Test Procedures.

Sampling Location	Measurements	Sampling Approach	Sample Analyses	Reference
S1 (Stack)	Total PM, PM10, PM2.5 and composition	In-stack series cyclones and filter	Mass; organic species	U.S. EPA Method 201A (modified)
	PM composition	In-stack filter	Organic carbon, elemental carbon	U. S. EPA Method 17 (modified)
	Condensible PM and composition	Impingers	Mass (organic and inorganic), sulfate, chloride, nitrate, ammonium, elements	U.S. EPA Method 202 (modified)
	Gaseous PM2.5 Precursors	Continuous	SO ₂ and NO _x (O ₂ , CO ₂ , CO also measured)	U. S. EPA Methods 3A/6C/7E/10
S1 (Stack)	PM2.5 mass and chemical composition	Dilution tunnel and filters	Mass, organic carbon, elemental carbon, elements, sulfate, nitrate, chloride, ammonium	U.S. EPA, 1999a; Hildemann et al., 1989
	VOC	Dilution tunnel and Tenax	Speciated VOC	Zielinska et al., 1996; Hildemann et al., 1989
	SVOC	Dilution tunnel and filter/PUF/XAD-4/PUF	Speciated SVOC	U.S. EPA Method TO13; Hildemann et al., 1989
S2 (Ground Level Ambient Air)	PM2.5 and chemical composition	Filters	Mass, organic carbon, elemental carbon, organic species, elements, chloride, sulfate, nitrate, ammonium	U.S. EPA, 1999a
	VOC	Tenax	Speciated VOC	Zielinska et al., 1996
	SVOC	PUF/XAD-4/PUF	Speciated SVOC	U.S. EPA Method TO13
S3 (Fuel gas feed to heater)	Fuel gas composition	Integrated grab sample (bag or canister)	Hydrocarbon speciation and heating value	ASTM D3588
S4 (Fuel gas knockout drum)	Liquid hydrocarbons	Composite grab sample	Ultimate Analysis (C, H, N, S, O, ash), hydrocarbon speciation	ASTM D3176

Date	Time	Heater Stack					Process Samples	Ambient Air
		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	P/10:58-11:23						
	12:00			R1/12:45				
	13:00	R1/13:59	R1/13:51		R1/13:50	R1/13:50		
	14:00							
	15:00							
	16:00						15:52 - 16:22	
	17:00							
	18:00						17:30 - 18:00	
	19:00	19:51	19:51	19:41	19:50	19:50		
	20:00	P/20:30-21:03						
	21:00							
10/14/98 Wednesday	9:00	P/8:58 - 9:25						
	10:00	R2/10:41	R2/10:41	R2/10:46	R2/10:40	R2/10:40		
	11:00							
	12:00						13:35 - 14:05	
	13:00							
	14:00							
	15:00							
	16:00	16:41	16:41	16:39	16:40	16:40		
	17:00	P/17:14-17:45						
	18:00							
	19:00							
10/15/98 Thursday	8:00	P/8:15-8:49						
	9:00							
	10:00							
	11:00	R3/11:26	R3/11:26	R3/11:28	R3/11:30	R3/11:25		
	12:00							
	13:00							
	14:00						15:42 - 16:12	
	15:00				16:45			
	16:00							
	17:00	17:26	17:26	17:22		17:25		
	18:00	P/18:20-19:04						
	19:00							
	20:00							
	21:00							
10/16/98 Friday	8:00							
	9:00							9:25
	10:00							
	11:00							
	12:00							
	13:00							
	14:00							15:25
	15:00							

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).

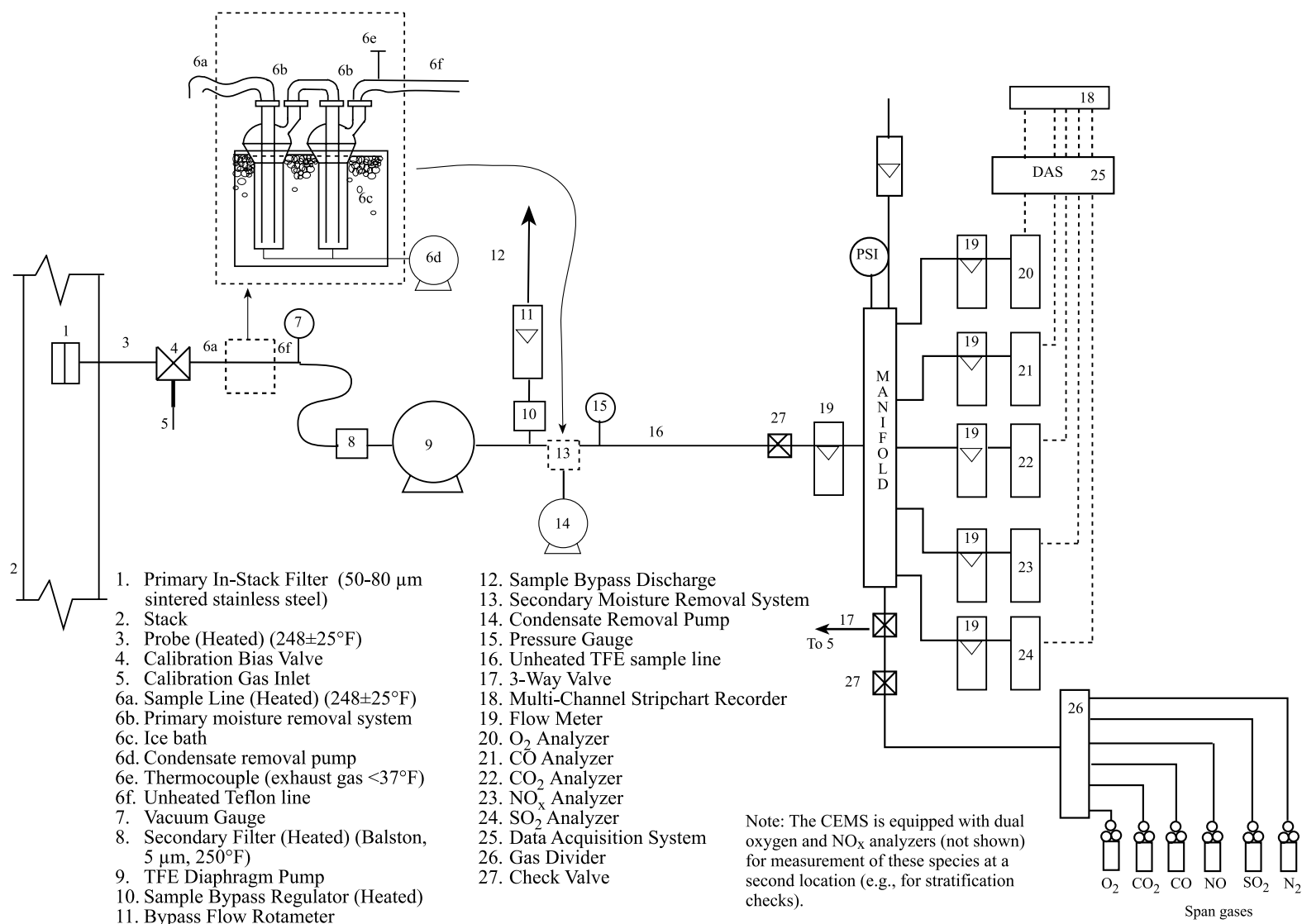


Figure 3-2. Continuous Emissions Monitoring System.