
Gas Fired Boiler—Test Report Refinery Site A

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

Regulatory and Scientific Affairs

PUBLICATION NUMBER 4703
JULY 2001

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PREPARED UNDER CONTRACT BY:

GE ENERGY AND ENVIRONMENTAL RESEARCH CORPORATION
18 MASON
IRVINE, CA 92618



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API STAFF CONTACT

Karin Ritter, Regulatory and Scientific Affairs

MEMBERS OF THE PM SOURCE CHARACTERIZATION WORKGROUP

Lee Gilmer, Equilon Enterprises LLC, Stationary Source Emissions Research Committee, Chairperson

Karl Loos, Equilon Enterprises LLC

Jeff Siegell, ExxonMobil Research and Engineering

GE ENERGY AND ENVIRONMENTAL RESEARCH CORPORATION

PROJECT TEAM MEMBERS

Glenn England, Project Manager

Stephanie Wien, Project Engineer

Bob Ziperman, Field Team Leader

Barbara Zielinska, Desert Research Institute

Jake McDonald, Desert Research Institute

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EXECUTIVE SUMMARY

In 1997, the United States Environmental Protection Agency (EPA) promulgated new ambient air standards for particulate matter smaller than 2.5 micrometers in diameter (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aerosols from petroleum industry combustion sources, and the limited information that is available is incomplete and outdated.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 condensable aerosols), especially organic aerosols from gas-fired combustion devices; and
- Identify and characterize secondary particulate (i.e., particulate formed via reaction of stack emissions in the atmosphere) precursor emissions.

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

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

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

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

Emission factors for semivolatile organic species are presented in Table E-2. The sum of semivolatile organic species is approximately three percent of the organic carbon. Emission factors for secondary particulate precursors (NO_x, 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 species concentrations that are within a factor of 10 of the ambient air concentration are indicated on the table by an asterisk (*).

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

The main findings of these tests are:

- Particulate mass emissions from the boiler were extremely low, consistent with levels expected for gaseous fuel combustion.
- Two methods for determining the average emission factor for primary PM_{2.5} mass gave results which differed in magnitude by a factor of 27: 0.000358 lb/MMBtu using the dilution tunnel; and 0.00974 lb/MMBtu using conventional in-stack methods for filterable and condensible particulate.
- Sampling and analytical artifacts principally caused by gaseous SO₂ in the stack gas were shown to produce a relatively large positive bias in condensible particulate as measured by conventional in-stack methods. Most of the difference between the dilution tunnel and conventional method results can be explained by these measurement artifacts. The results using conventional EPA methods are nominally consistent with published EPA emission factors for external combustion of natural gas (U. S. EPA, 1998). Therefore, the published EPA emission factors derived from tests using similar measurement methods also may be positively biased.
- Chemical species accounting for 74 percent of the measured PM_{2.5} mass were quantified.
- Organic and elemental carbon comprise 68 percent of the measured primary PM_{2.5} mass.
- Sulfates, iron, copper, chloride, and smaller amounts of other elements account for another 6 percent of the measured PM_{2.5} mass.
- Less than 26 percent of the measured PM_{2.5} mass is unspciated.
- 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 Refinery Boiler.

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

* <10x ambient

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

B <10x blank

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

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

Substance		Emission Factor (lb/MMBtu)	Uncertainty (%)	95% Confidence Upper Bound (lb/MMBtu)
Semivolatile Organic Compounds (Dilution Tunnel/ PUF/XAD)	Phenanthrene	1.03E-06	94	1.71E-06
	Perinaphthenone	3.78E-07	134	7.29E-07
	Fluoranthene	2.83E-07	136	5.49E-07
	Biphenyl	2.49E-07	372	8.78E-07
	Pyrene	1.99E-07	126	3.72E-07
	Cholestane B	1.91E-07	75	2.94E-07
	Coronene*	1.80E-07	62	2.64E-07
	Fluorene*	1.11E-07	76	1.72E-07
	Naphthalene*	1.04E-07	544	3.88E-07
	Anthracene	7.83E-08	112	1.39E-07
	Acenaphthylene	6.04E-08	283	1.77E-07
	Acenaphthenequinone B	5.48E-08	136	1.06E-07
	B-methylphenanthrene	5.10E-08	113	9.14E-08
	2-methylnaphthalene*	4.44E-08	159	9.31E-08
	1,4+1,5+2,3-dimethylnaphthalene*	4.41E-08	n/a	n/a
	3-methylbiphenyl*	4.41E-08	125	8.24E-08
	1,3+1,6+1,7-dimethylnaphthalene*	4.06E-08	140	8.00E-08
	Anthraquinone* B	4.00E-08	64	5.90E-08
	9-methylanthracene	3.66E-08	n/a	n/a
	2-methylphenanthrene*	3.55E-08	150	7.22E-08
	A-methylphenanthrene*	3.34E-08	145	6.70E-08
	Benzanthrone* B	3.22E-08	56	4.59E-08
	2-phenylnaphthalene	3.13E-08	126	5.86E-08
	Xanthone B	3.10E-08	n/a	n/a
	9-fluorenone	2.82E-08	n/a	n/a
	Benzo(b+j+k)fluoranthene*	2.78E-08	58	4.00E-08
	1-methylnaphthalene*	2.77E-08	169	5.99E-08
	Benz(a)anthracene*	2.51E-08	137	4.88E-08
	Benzo(b)chrysene*	2.39E-08	56	3.40E-08
	1-methylpyrene+C-methylpyrene/fluorene	2.36E-08	188	4.63E-08
	Benz(a)anthracene-7,12* B	2.17E-08	65	3.20E-08
	4H-cyclopenta(def)phenanthrene B	2.07E-08	97	3.49E-08
	2,6+2,7-dimethylnaphthalene*	1.99E-08	122	3.69E-08
	7-methylbenzo(a)pyrene (1)	1.94E-08	75	2.98E-08
	Chrysene* B	1.84E-08	71	2.79E-08
	F-trimethylnaphthalene*	1.84E-08	264	4.28E-08
	C-dimethylphenanthrene*	1.82E-08	315	5.72E-08
	Dibenzofuran*	1.80E-08	66	2.68E-08
	B-dimethylphenanthrene	1.76E-08	238	3.88E-08
	1,2-dimethylnaphthalene*	1.68E-08	n/a	n/a
	1+2-ethylnaphthalene*	1.65E-08	214	3.44E-08
	C-methylphenanthrene*	1.57E-08	79	2.45E-08
	Acenaphthene*	1.55E-08	63	2.27E-08
	E-trimethylnaphthalene*	1.54E-08	297	4.64E-08
	1-phenylnaphthalene (1)	1.17E-08	126	2.20E-08
	Anthrone* B	1.17E-08	69	1.76E-08
	D-dimethylphenanthrene	1.17E-08	76	1.81E-08
	E-dimethylphenanthrene*	1.14E-08	445	3.67E-08

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

Substance		Emission Factor (lb/MMBtu)	Uncertainty (%)	95% Confidence Upper Bound (lb/MMBtu)
	B-methylfluorene	1.13E-08	n/a	n/a
	2,3,5-I-trimethylnaphthalene*	1.13E-08	76	1.75E-08
	C-trimethylnaphthalene*	1.10E-08	76	1.70E-08
	Retene	1.10E-08	144	2.19E-08
	1,4-chrysenequinone* B	1.08E-08	188	2.48E-08
	Benzo(c)phenanthrene*	9.50E-09	99	1.61E-08
	B-trimethylnaphthalene*	9.50E-09	92	1.57E-08
	2-methylbiphenyl (1) B	9.47E-09	n/a	n/a
	A-trimethylnaphthalene*	9.05E-09	84	1.45E-08
	Benzo(ghi)perylene* B	8.87E-09	78	1.38E-08
	1-methylfluorene	8.87E-09	79	1.39E-08
	Benzo(a)pyrene* B	8.75E-09	68	1.31E-08
	1-ethyl-2-methylnaphthalene*	7.99E-09	127	1.51E-08
	3,6-dimethylphenanthrene*	7.80E-09	258	2.16E-08
	Dibenz(ah+ac)anthracene* B	7.33E-09	79	1.15E-08
	A-dimethylphenanthrene*	7.04E-09	662	3.02E-08
	4-methylbiphenyl* B	6.60E-09	141	1.30E-08
	B-methylpyrene/methylfluorene	6.57E-09	230	1.69E-08
	A-methylfluorene	6.38E-09	n/a	n/a
	Indeno[123-cd]pyrene* B	6.15E-09	70	9.31E-09
	4-methylpyrene*	6.09E-09	202	1.45E-08
	2,4,5-trimethylnaphthalene*	5.13E-09	140	1.01E-08
	1,7-dimethylphenanthrene*	4.70E-09	105	8.16E-09
	9,10-dihydrobenzo(a)pyrene* B	4.56E-09	94	7.59E-09
	Benzo(e)pyrene B	4.22E-09	116	7.64E-09
	D-methylpyrene/methylfluorene	4.19E-09	143	8.34E-09
	1,2,8-trimethylnaphthalene*	3.83E-09	123	7.12E-09
	9-anthraldehyde (1) B	3.69E-09	400	1.11E-08
	5+6-methylchrysene (1)	3.51E-09	133	6.75E-09
	Benzonaphthothiophene	3.19E-09	100	5.43E-09
	Perylene B	3.01E-09	117	5.47E-09
	A-methylpyrene B	2.11E-09	175	4.65E-09
	E-methylpyrene/methylfluorene*	1.25E-09	246	3.35E-09
	Sum of All SVOCs	4.06E-06		

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

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

* <10x ambient

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

B <10x blank

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

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

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

* <10x detection limit, ambient = ND

(1) <10x blank

B <10x detection limit, blank = ND

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

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

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

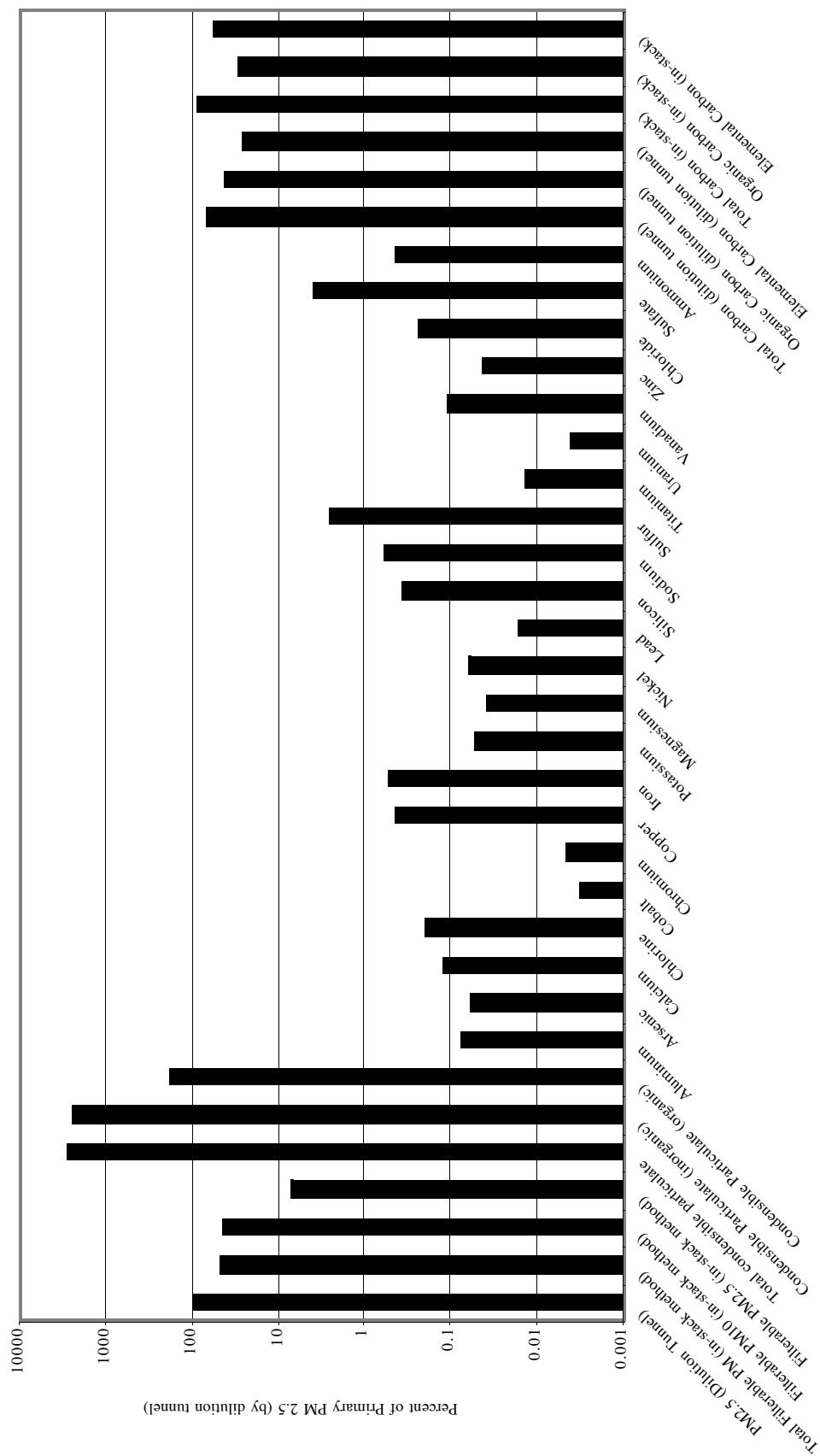


Figure E-1. Speciation Profile for Primary Particulate Emissions from Gas-Fired Boiler (Refinery Site A).

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 that occurs after the gases leave the stack. This issue was extensively reviewed by API in a recent report (England et al., 1997), which concluded that dilution sampling techniques are more appropriate for obtaining a representative sample from combustion systems. These techniques have been widely used in research studies (Hildemann et al., 1994; McDonald et al., 1998), and use clean ambient air to dilute the stack gas sample and provide 80-90 seconds residence time for aerosol formation prior to sample collection for determination of mass and chemical speciation.

As a result of the API review, a test protocol was developed based on the dilution sampling system described in this report, which was then used to collect particulate emissions data from petroleum industry combustion sources, along with emissions data obtained from conventional sampling methods. This test program is designed to provide reliable source emissions data for use in assessing the contribution of petroleum industry combustion sources to ambient 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 boiler at Refinery Site A on July 14-20, 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 collection and analysis of both in-stack and diluted stack gas samples. All emission samples were collected from the stack of the unit. An ambient air sample also was collected. The samples were analyzed for the compounds listed in Table 1-2. Boiler process data and fuel gas samples were collected during the tests to document operating conditions.

Source Level (In-stack) Samples

In-stack sampling and analysis for filterable (total, PM₁₀ and 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 Location	Number of Samples at each Sampling Location		
	Fuel Gas Header	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	6	--	--
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 6:1 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 where it resided for approximately 80 seconds to allow time for low-concentration aerosols, especially organics, to condense and grow. The diluted and aged sample then passed through cyclone separators sized to remove particles larger than 2.5 microns, after which samples were collected on various media: high-purity quartz, Teflon[®] membrane filter (TMF), and Teflon[®]-impregnated glass fiber (TIGF) filters; a polyurethane foam (PUF)/Amberlite[®] sorbent resin (XAD-4)/PUF cartridge to collect gas phase semivolatile organic compounds; and a Tenax cartridge to VOCs. Three samples were collected on three sequential test days.

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		
Condensible 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®

*Carbon number of 7 or greater

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

Process Samples

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

KEY PERSONNEL

Energy and Environmental Research Corporation, a General Electric company, (GE-EER) had primary responsibility for the test program. Key personnel involved in the tests were:

- Glenn England (GE-EER) - Program Manager (949) 859-8851
- Stephanie Wien (GE-EER) - Project Engineer (949) 552-1803
- Bob 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

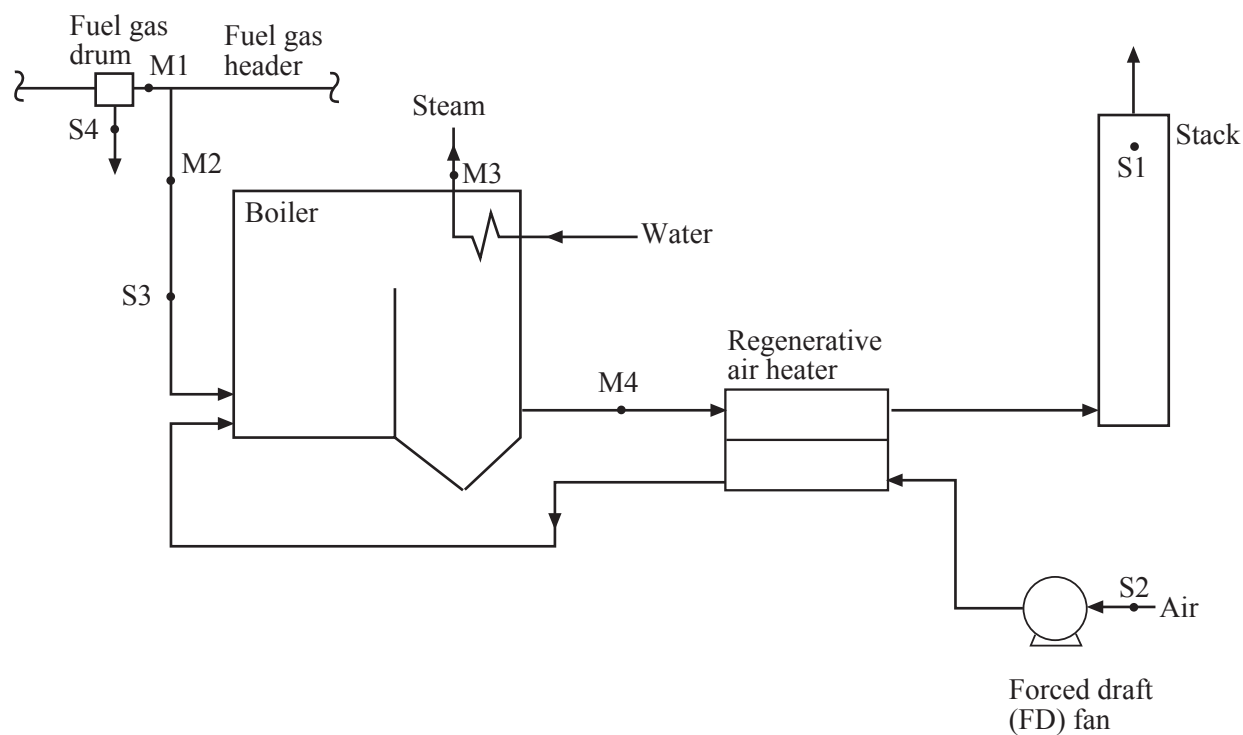
The tests were performed on a gas-fired boiler at Refinery Site A. The boiler has a capacity of 550,000 pounds of steam per hour, corresponding to a firing rate of approximately 650 million British thermal units per hour (MMBtu/hr). The furnace is corner-fired (tangential) with two elevations of conventional gas burners at each corner. It is a forced draft unit with a regenerative air preheater. The boiler is fired with refinery process gas. The unit is not equipped with air pollution controls for NO_x, SO₂ or particulate. The boiler appeared to be in good working condition during the test. Boiler load normally varies depending upon refinery steam demand and availability of steam from other sources. Operating conditions during the test are given in Section 4. Process operating parameters monitored during testing include: fuel gas flow rate, specific gravity, heating value and hydrogen sulfide (H₂S) content; steam flow rate and temperature; and excess oxygen at the boiler outlet.

SAMPLING LOCATIONS

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

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

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



Process Monitoring Station	Description	Parameters
M1	Fuel gas header	Specific gravity, H ₂ S, Btu
M2	Fuel gas feed line	Flow rate
M3	Main steam header	Flow rate, temperature, pressure
M4	Boiler flue gas outlet	Flue gas temperature, O ₂
Sampling Locations		
S1	Stack	See Table 3-1
S2	FD fan inlet	
S3	Fuel gas feed	
S4	Fuel gas drum condensate knockout	

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

Section 3

TEST PROCEDURES

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

STACK GAS FLOW RATE, MOISTURE CONTENT AND MOLECULAR WEIGHT

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

O₂, CO₂, CO, NO_x AND SO₂

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

Table 3-1. Summary of Test Procedures

Sampling Location	Measurements	Sampling Approach	Sample Analyses	Reference
Stack S1	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
Stack (Dilution Tunnel) S1	PM2.5 and chemical composition	Filters	Mass, organic carbon, elemental carbon, organic species, sulfate, nitrate, chloride, ammonium	U.S. EPA, 1999a Hildemann et al., 1989
	VOC	Tenax	Speciated VOC	Zielinska et al., 1996
	SVOC	PUF/XAD-4/PUF	Speciated SVOC	U.S. EPA Method TO13
Ambient Air (Forced Draft Fan Inlet) S2	PM2.5 and chemical composition	Filters	Mass, organic carbon, elemental carbon, organic species, sulfate, nitrate, chloride, 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
Fuel gas feed to heater (S3)	Fuel gas composition	Integrated grab sample (bag or canister)	Hydrocarbon speciation and heating value	ASTM D3588; U.S. EPA Method 19
Fuel gas knockout drum (S4)	Liquid hydrocarbons	Composite grab sample	Ultimate analysis (C, H, N, S, O, ash), hydrocarbon speciation	ASTM D3176; U.S. EPA Method 19 (or equivalent)

	Time	Boiler Stack				
		Velocity	Method 201/202	CEMS	Dilution Tunnel	Fuel Gas Samples
7/14/1998 Tue	9:00					
	10:00					
	11:00					
	12:00					
	13:00					
	14:00					
	15:00					
	16:00					
	17:00					
	18:00	Preliminary	Moisture			
7/15/1998 Wed	19:00	18:52	18:42			
	20:00	19:53	19:27			
	9:00					* Grab
	10:00					
	11:00			Stratification		
	12:00			12:11		
	13:00	Pre-test		13:18		
	14:00	14:27				
	15:00	14:56				
	16:00		R1 / 16:24	R1 / 16:24		
	17:00					
7/16/1998 Thurs	18:00					* Grab
	19:00			18:58		
	20:00			20:05		
	21:00			21:34		
	22:00		22:24			
	9:00					
	10:00		R2 / 10:10	R2 / 10:22		
	11:00					
	12:00			12:56		
	13:00			13:51		
	14:00			15:22		
	15:00		16:10			
	16:00					
	17:00					
	18:00					
	19:00					
	20:00					
	21:00					

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

	Time	Boiler Stack					
		Velocity	Method 201A/202	CEMS	Dilution Tunnel	Fuel Gas Samples	
7/17/1998 Fri	8:00		R3 / 8:15		Ambient / 8:30	* Grab	
	9:00			R3 / 9:14			
	10:00			11:12			
	11:00		11:47				
	12:00		14:15	14:16			
	13:00						
	14:00				16:30		
	15:00						
	16:00						
	17:00						
7/18/1998 Sat	9:00					* Grab	
	10:00						
	11:00						
	12:00			1 DT / 12:45	1 DT / 12:45		
	13:00						
	14:00						
	15:00			15:22*			
	16:00			16:27			
	17:00						
	18:00			18:48	18:48		
19:00							
7/19/1998 Sun	8:00					* Grab	
	9:00						
	10:00						
	11:00			2 DT / 11:35	2 DT / 11:35		
	12:00						
	13:00						
	14:00			14:33*			
	15:00			14:54			
	16:00						
	17:00			17:30	17:30		
18:00							
19:00							
7/20/1998 Mon	8:00			3 DT / 8:45	3 DT / 8:45	* Grab	
	9:00						
	10:00						
	11:00			11:22*			
	12:00			11:45			
	13:00						
	14:00			Post-test	14:45		14:45
	15:00			15:56			
	16:00			16:14			
	17:00						

DT - Dilution tunnel testing run

*Run interrupted for calibration check

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

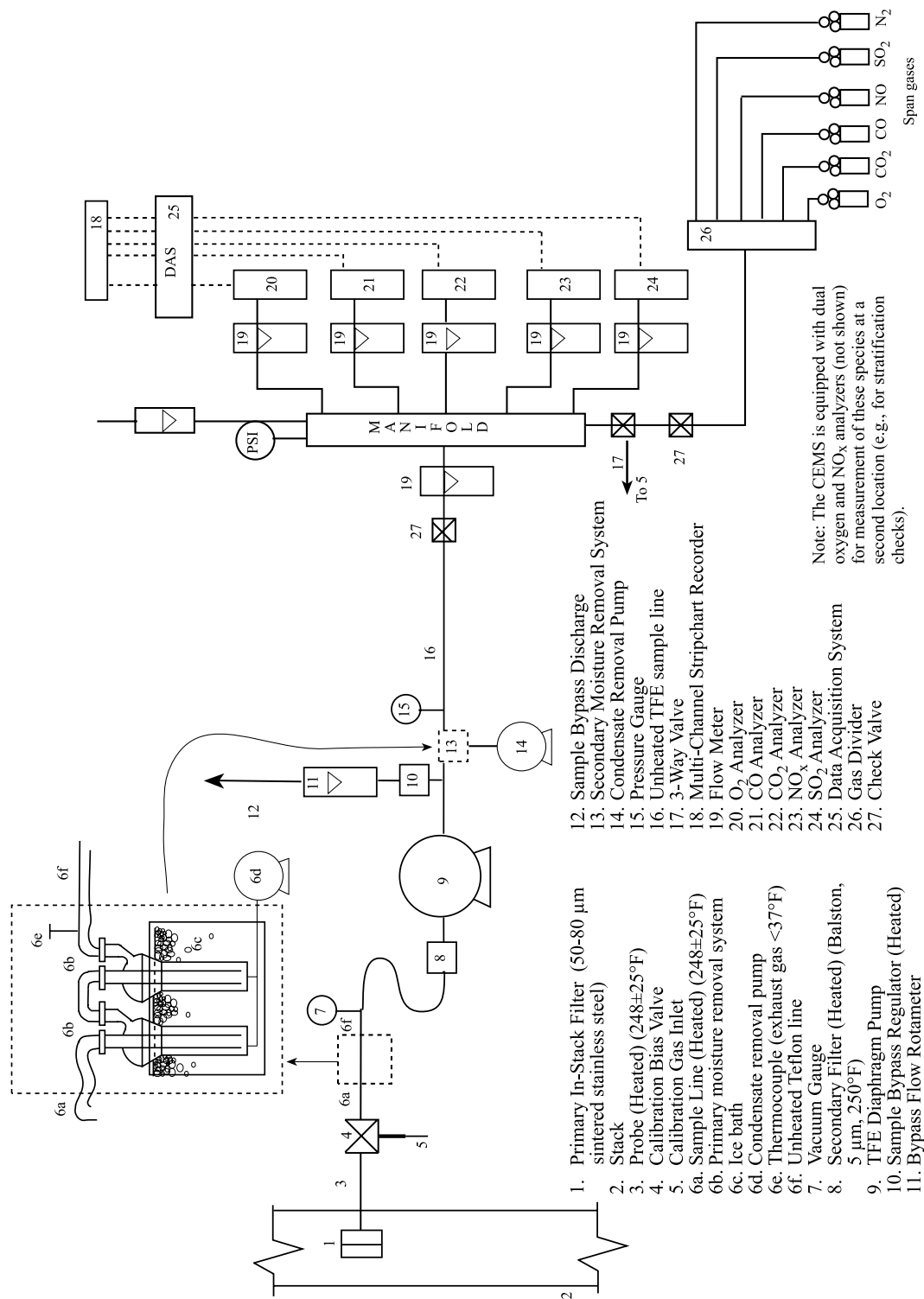


Figure 3-2. CEMS Schematic.

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

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

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

IN-STACK METHOD TESTS

Total particulate, PM10 and PM2.5 filterable at stack temperature were determined using in-stack 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 μm (PM10) and 2.5 μm (PM2.5). EPA Method 201A, modified to accommodate the second cyclone, was used following the constant-rate sampling procedure. Sampling time was six hours for each of the three runs. The sample recovery field procedure is summarized in Figure 3-4. Sampling was performed as published except for the following modifications and clarifications:

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

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

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