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

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Test Report: Fluidized Catalytic Cracking Unit at a Refinery (Site A)

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

Regulatory and Scientific Affairs

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MARCH 2002

PREPARED UNDER CONTRACT BY:
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EXECUTIVE SUMMARY

In 1997, EPA promulgated new ambient air standards for particulate matter smaller than 2.5 micrometers (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aerosols from petroleum industry combustion sources, and the limited information that is available is incomplete and outdated.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 a refinery fluid catalytic cracking unit (FCCU). The FCCU tested is a partial combustion unit with a process capacity of 47,000 barrels per day. The CO-rich offgas from the regenerator is combusted with refinery process gas in a process heater, which preheats the FCCU process feed. The process heater flue gases pass through an electrostatic precipitator to recover catalyst fines, which also reduces particulate emissions. The unit has no controls for NO_x or SO₂ emissions. The FCCU was operating at approximately 94 percent of capacity and the flue gas temperature at the stack was approximately 579°F during the tests.

The tests included comparison of a dilution tunnel research test method for sample collection and traditional methods used 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;

however, existing regulatory methods for condensible aerosols may have significant bias problems for some source types and analytical options are limited.

In addition to a standard EPA particulate sampling train, hot and cold cascade impactors were used to measure particle size distribution. Ammonia (by EPA Method 206) and sulfur trioxide (by controlled condensation) emissions also were measured.

The results of these tests demonstrated that the test protocol developed by API could be applied successfully to refinery sources. The results also were used to refine the test protocol leading to lower costs for future tests. Emission factors for primary particles including: total particulate mass, PM₁₀ (mass of particles smaller than 10 micrometers), and PM_{2.5}; elements; ionic species; sulfuric acid; and organic and elemental carbon are presented in Table E-1. Emission factors are expressed in pounds of pollutant per thousand pounds of coke burned in the regenerator. The tables include only those substances that were detected in at least one of the three test runs. The uncertainty and upper 95 percent confidence bound also are presented. Emission factors for semivolatile organic species that comprise organic carbon are presented in Table E-2. The sum of semivolatile organic species totals approximately three percent of the organic carbon. Emission factors for secondary particulate precursors (NO_x, SO₂, volatile organic species, and ammonia) are presented in Table E-3. 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 also 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 with concentrations within a factor of 10 of the measured ambient air concentration are indicated on the table by an asterisk (*).

The primary particulate matter results presented in Table E-1 also may be expressed as a PM_{2.5} speciation profile, which is the mass fraction of each species contributing to the total PM_{2.5} mass. The speciation profile is presented in Figure E-1.

Table E-1. Summary of Primary Particulate Emission Factors for FCCU.

	Substance	Average Emission Factor (lb/1000 lb coke burned)	Uncertainty (%)	95% Confidence Upper Bound (lb/1000 lb coke burned)
Particulate Mass	CPM (inorganic)	0.51	279	1.5
	CPM (organic)	4.7E-3	160	0.01
	Total CPM (blank corrected)	0.51	281	1.5
	Total FPM (in-stack method)	0.50	69	0.74
	Filterable PM10 (in-stack method)	0.47	72	0.71
	Filterable PM2.5 (in-stack method)	0.44	72	0.65
	PM2.5 (Dilution Tunnel)	0.11	68	0.16
Elements	Aluminum	3.9E-3	80	6.1E-3
	Antimony	8.5E-5	80	1.3E-4
	Barium	2.0E-5	49	2.7E-5
	Bromine *	3.3E-7	54	4.6E-7
	Calcium	1.3E-4	73	1.9E-4
	Chromium	4.3E-5	60	6.1E-5
	Cobalt	7.9E-6	146	1.6E-5
	Copper	4.6E-4	375	1.6E-3
	Gallium	2.3E-6	142	4.5E-6
	Iron	9.2E-4	80	1.4E-3
	Lanthanum	8.5E-4	80	1.3E-3
	Lead	9.7E-6	74	1.5E-5
	Manganese	1.6E-5	78	2.5E-5
	Molybdenum	9.3E-6	84	1.5E-5
	Nickel	2.1E-4	74	3.2E-4
	Potassium	7.7E-5	70	1.1E-4
	Rubidium	6.9E-7	48	9.2E-7
	Selenium	5.9E-7	61	8.4E-7
	Silicon	6.8E-3	78	1.0E-2
	Strontium	8.1E-6	79	1.3E-5
	Sulfur	1.3E-3	124	2.4E-3
	Thallium	6.1E-7	n/a	n/a
	Tin	3.5E-6	n/a	n/a
	Titanium	4.2E-4	83	6.5E-4
	Uranium	8.1E-7	254	1.8E-6
	Vanadium	4.1E-4	87	6.6E-4
	Yttrium	1.0E-6	118	1.8E-6
	Zinc	3.3E-5	57	4.6E-5
	Zirconium	7.6E-6	78	1.2E-5
Ions	Chloride	2.0E-4	71	3.0E-4
	Nitrate	ND	n/a	n/a
	Sulfate	9.7E-2	72	1.5E-1
	Ammonium	8.9E-4	82	1.4E-3
Sulfuric Acid	SO ₃ (as H ₂ SO ₄)	1.4	92	2.3
Carbon	Organic Carbon (dilution tunnel)	9.9E-4	53	1.4E-3
	Elemental Carbon (dilution tunnel) *	2.0E-4	n/a	n/a
	Total Carbon (dilution tunnel)	1.1E-3	52	1.5E-3
	Organic Carbon (in-stack) B	1.5E-4	66	2.2E-4
	Elemental Carbon (in-stack)	3.2E-5	153	6.6E-5
	Total Carbon (in-stack) B	1.8E-4	77	2.8E-4

* <10x ambient

B <10x blank

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

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

Table E-2. SVOC Emission Factors for FCCU.

Substance		Average Emission Factor (lb/1000 lb coke burned)	Uncertainty (%)	95% Confidence Upper Bound (lb/1000 lb coke burned)
Semivolatile Organic Compounds (Dilution Tunnel, PUF/XAD)	1+2-ethylnaphthalene *	5.4E-7	1037	3.4E-6
	1,2,8-trimethylnaphthalene *	3.2E-8	580	1.2E-7
	1,2-dimethylnaphthalene *	2.1E-7	n/a	n/a
	1,3+1,6+1,7-dimethylnaphthalene *	6.1E-7	285	1.8E-6
	1,4+1,5+2,3-dimethylnaphthalene *	6.2E-7	n/a	n/a
	1,4-chrysenequinone * B	2.0E-7	178	4.5E-7
	1,7-dimethylphenanthrene *	5.2E-8	348	1.4E-7
	1-ethyl-2-methylnaphthalene	9.8E-8	122	1.8E-7
	1-MeFl+C-MePy/Fl	2.0E-7	n/a	n/a
	1-methylfluorene *	3.9E-7	1033	2.4E-6
	1-methylnaphthalene * B	1.9E-7	176	4.3E-7
	1-phenylnaphthalene B	8.7E-8	706	3.9E-7
	2,3,5+1-trimethylnaphthalene *	2.3E-7	59	3.3E-7
	2,4,5-trimethylnaphthalene *	8.0E-8	89	1.3E-7
	2,6+2,7-dimethylnaphthalene *	4.0E-7	220	9.9E-7
	2-methylbiphenyl (1) B	5.7E-7	332	1.5E-6
	2-methylnaphthalene *	3.1E-7	177	5.8E-7
	2-methylphenanthrene *	4.7E-7	75	7.2E-7
	2-phenylnaphthalene	1.5E-7	162	3.3E-7
	3,6-dimethylphenanthrene *	1.1E-7	565	4.0E-7
	3-methylbiphenyl *	9.3E-7	167	1.7E-6
	4-methylbiphenyl *	4.6E-7	n/a	n/a
	4-methylpyrene *	1.8E-7	227	4.6E-7
	4H-cyclopenta(def)phenanthrene B	1.4E-7	281	4.2E-7
	5+6-methylchrysene	1.2E-6	148	2.5E-6
	7-methylbenz(a)anthracene	1.0E-7	261	2.8E-7
	7-methylbenzo(a)pyrene	6.9E-7	70	1.0E-6
	9,10-dihydrobenzo(a)pyrene *	1.4E-7	157	2.9E-7
	9-anthraldehyde (1) B	5.0E-8	n/a	n/a
	9-fluorenone	2.1E-6	n/a	n/a
	A-dimethylphenanthrene *	3.9E-8	326	1.0E-7
	A-methylfluorene (1)(2)	2.4E-7	167	4.5E-7
	A-methylphenanthrene *	4.0E-7	55	5.6E-7
	A-methylpyrene B	8.4E-8	1014	5.1E-7
	A-trimethylnaphthalene *	1.4E-7	112	2.6E-7
	Acenaphthene *	7.9E-8	288	2.3E-7
	Acenaphthenequinone B	3.2E-7	290	9.6E-7
	Acenaphthylene (1)(2)	1.8E-7	744	8.6E-7
	Anthracene	2.5E-6	n/a	n/a
	Anthraquinone	7.3E-7	292	2.2E-6
	Anthrone * B	1.3E-7	63	1.9E-7
	B-dimethylphenanthrene	2.5E-7	182	4.8E-7
	B-MePy/MeFl *	8.1E-8	326	2.6E-7
	B-methylfluorene (1)(2)	1.8E-7	n/a	n/a
	B-methylphenanthrene	3.9E-7	66	5.8E-7
	B-trimethylnaphthalene *	1.4E-7	82	2.3E-7
	Benz(a)anthracene	1.0E-6	172	2.2E-6
	Benz(a)anthracene-7,12 B	6.9E-7	82	1.1E-6
	Benzanthrone	1.1E-6	71	1.7E-6
	Benzo(a)pyrene	3.4E-7	79	5.3E-7
	Benzo(b)chrysene *	8.9E-7	90	1.5E-6
	Benzo(b+j+k)fluoranthene	2.1E-6	107	3.7E-6
	Benzo(c)phenanthrene *	1.6E-7	87	2.6E-7
	Benzo(e)pyrene	5.5E-7	71	8.4E-7
	Benzo(ghi)perylene B	2.9E-7	101	4.9E-7
	Benzonaphthothiophene	9.6E-8	90	1.6E-7

Table E-2 (Cont'd). SVOC Emission Factors for FCCU.

Substance		Average Emission Factor (lb/1000 lb coke burned)	Uncertainty (%)	95% Confidence Upper Bound (lb/1000 lb coke burned)
Semivolatile Organic Compounds (Dilution Tunnel, PUF/XAD)	Bibenzene (1) B	1.2E-5	n/a	n/a
	Biphenyl *	1.6E-7	513	5.5E-7
	C-dimethylphenanthrene *	3.9E-7	972	2.3E-6
	C-methylphenanthrene *	2.6E-7	133	5.0E-7
	C-trimethylnaphthalene *	1.6E-7	75	2.5E-7
	Cholestane B	2.1E-6	69	3.2E-6
	Chrysene	1.1E-6	80	1.7E-6
	Coronene	7.3E-6	64	1.1E-5
	D-dimethylphenanthrene (1)(2)	1.8E-7	279	5.2E-7
	D-MePy/MeFl	4.0E-8	615	1.6E-7
	Dibenz(ah+ac)anthracene B	2.6E-7	112	4.6E-7
	Dibenzofuran *	1.9E-7	185	4.3E-7
	E-dimethylphenanthrene *	2.1E-7	589	8.3E-7
	E-MePy/MeFl *	2.5E-8	945	1.4E-7
	E-trimethylnaphthalene	7.7E-8	72	1.2E-7
	F-trimethylnaphthalene *	1.8E-7	92	3.0E-7
	Fluoranthene	1.9E-6	95	3.2E-6
	Fluorene *	9.3E-7	150	1.9E-6
	Indeno[123-cd]pyrene B	2.4E-7	82	3.8E-7
	Naphthalene *	8.3E-6	123	1.5E-5
	Perinaphthenone (1)(2)	4.0E-6	166	8.5E-6
	Perylene B	1.4E-7	75	2.1E-7
	Phenanthrene *	6.9E-6	217	1.7E-5
	Pyrene	1.5E-6	99	2.6E-6
	Retene (1)(2)	3.0E-7	185	6.7E-7
	Xanthone B	2.3E-7	n/a	n/a
	Sum of All SVOCs	7.3E-5		
Semi- Volatile Organic Compounds (in-stack filter)	1,4-chrysenequinone	1.9E-8	314	4.8E-8
	1-ethyl-2-methylnaphthalene	9.3E-8	n/a	n/a
	2,6+2,7-dimethylnaphthalene	1.0E-7	n/a	n/a
	2-methylphenanthrene	3.5E-8	n/a	n/a
	4-methylbiphenyl	4.6E-8	n/a	n/a
	9,10-dihydrobenzo(a)pyrene	7.7E-9	n/a	n/a
	A-methylfluorene	8.9E-8	n/a	n/a
	A-methylpyrene	7.7E-8	509	2.7E-7
	Benz(a)anthracene-7,12	7.7E-9	n/a	n/a
	Benzo(a)pyrene	5.4E-8	n/a	n/a
	Benzo(b)chrysene	9.6E-9	298	2.4E-8
	Benzo(c)phenanthrene	7.7E-9	n/a	n/a
	Bibenzene	1.3E-6	n/a	n/a
	Biphenyl	8.1E-8	574	3.1E-7
	Cholestane	2.8E-6	412	8.6E-6
	Dibenzofuran	4.2E-8	717	1.9E-7
	Naphthalene	3.8E-7	106	6.5E-7
	Perinaphthenone	1.0E-7	1042	6.2E-7
	Sum of All SVOCs	1.9E-6		

† MePy = methylpyrene

MeFl = methylfluorene

* <10x ambient

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

B <10x blank

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

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

Table E-3. Summary of Secondary Particulate Precursor Emission Factors for FCCU.

Substance		Average Emission Factor (lb/1000 lb coke burned)	Uncertainty (%)	95% Confidence Upper Bound (lb/1000 lb coke burned)
Gases	SO ₂	26	80	41
	NO _x	4.1	80	6.5
	Ammonia	3.6E-3	70	5.4E-3
Volatile Organic Compounds	1,2,4-trimethylbenzene *	4.6E-5	100	7.9E-5
	1-hexadecene	7.7E-5	n/a	n/a
	1-methylnaphthalene *	1.1E-5	n/a	n/a
	2-methylnaphthalene *	1.1E-5	n/a	n/a
	2-methyloctane *	2.6E-5	122	4.9E-5
	3-methyloctane (1)(2)	3.4E-5	n/a	n/a
	7-hexadecene (1)(2)	2.6E-5	n/a	n/a
	Acetophenone *	4.6E-4	59	6.6E-4
	Benzaldehyde *	4.7E-4	83	7.4E-4
	Benzonitrile	6.6E-5	259	1.5E-4
	Butylated hydroxytoluene	2.1E-3	97	3.6E-3
	Decane *	2.1E-5	1003	1.2E-4
	Dodecane *	3.0E-5	n/a	n/a
	Eicosane	9.3E-6	n/a	n/a
	Ethylbenzene *	4.7E-5	208	1.1E-4
	Heptadecane *	2.2E-5	101	3.8E-5
	Hexadecane	3.2E-5	120	5.9E-5
	m- & p-xylenes *	1.3E-4	206	3.2E-4
	m-ethyltoluene *	3.9E-5	508	1.4E-4
	Naphthalene (1)(2)	1.6E-5	n/a	n/a
	Nonadecane (1)(2)	1.1E-5	371	3.2E-5
	Nonane	1.3E-4	n/a	n/a
	o-xylene *	5.3E-5	202	1.3E-4
	Octadecane	2.0E-5	87	3.3E-5
	p-ethyltoluene*	2.3E-5	n/a	n/a
	Phenol *	1.5E-4	96	2.5E-4
	Propylbenzene *	1.0E-5	706	4.5E-5
	Styrene *	7.6E-5	74	1.2E-4
	Tetradecane *	1.7E-5	91	2.8E-5
	Tridecane *	1.1E-5	171	2.4E-5
	Undecane *	2.6E-5	138	5.0E-5

* <10x ambient

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

B <10x blank

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

Table E-4. Substances of Interest Not Detected in Stack Emissions from FCCU.

Arsenic
 Cadmium
 Chlorine
 Gold
 Indium
 Magnesium
 Mercury
 Palladium
 Phosphorus
 Silver
 Sodium
 Nitrate
 1,8-dimethylnaphthalene
 1,4,5-trimethylnaphthalene
 1-methylphenanthrene
 1-methylpyrene
 2-ethyl-1-methylnaphthalene
 9-methylantracene
 J-trimethylnaphthalene
 1,3,5-trimethylbenzene
 1,2,3-trimethylbenzene
 1-methylindan
 1-nonene
 1-undecene
 2-methylindan
 Biphenyl
 Cyclohexanone
 Dimethyloctane
 Dodecene
 Indan
 Indene
 m-isopropyltoluene
 Nonanal
 o-ethyltoluene
 o-isopropyltoluene
 p-isopropyltoluene
 Pentadecane

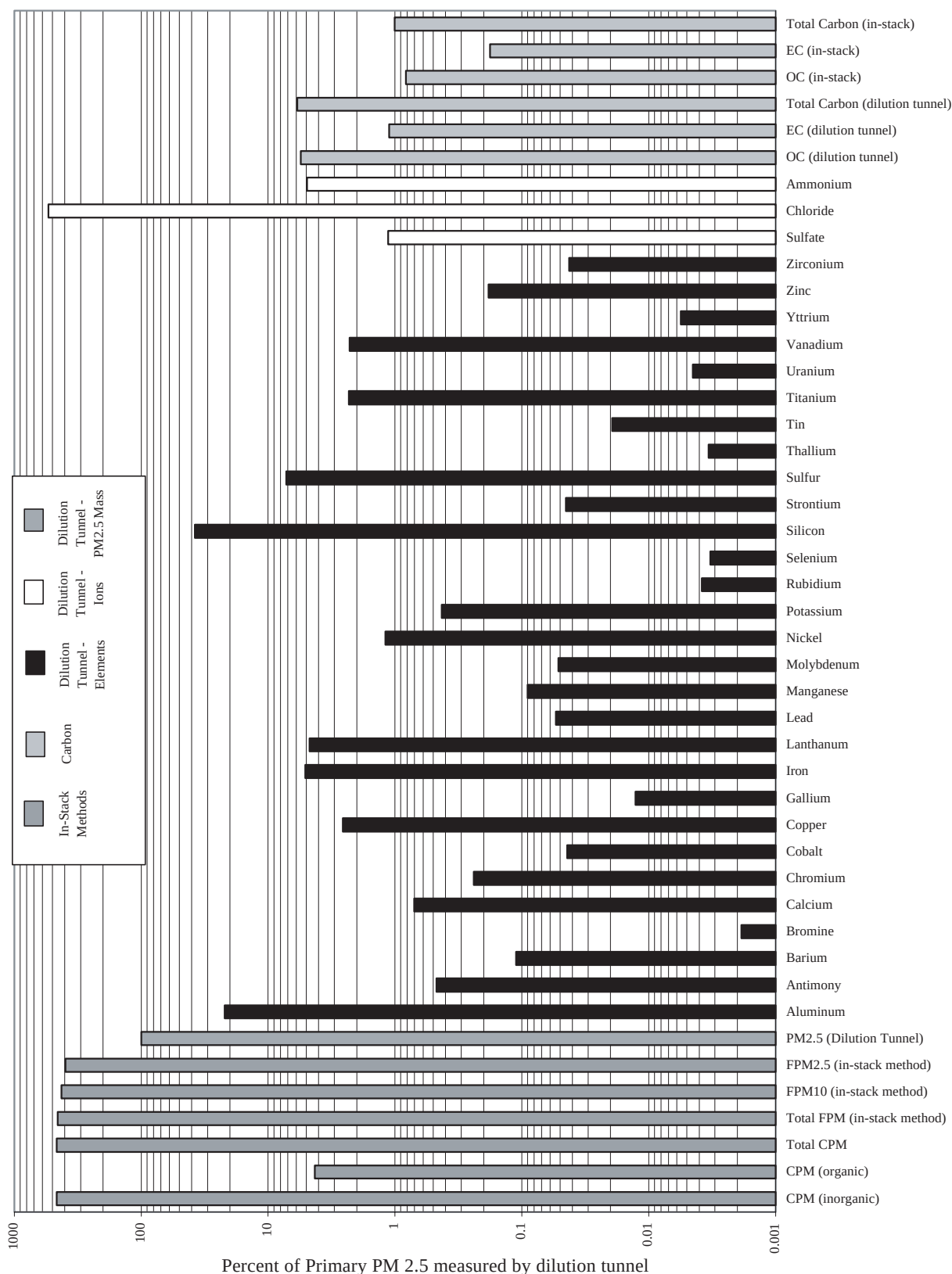


Figure E-1. Primary Particulate Speciation Profile.

FINDINGS

The key findings of these tests are:

- Traditional in-stack/impinger method (Method 201A and controlled condensation) results are considered the best representation of actual filterable and condensible particulate mass emissions from the FCCU, respectively.
- The dilution tunnel test protocol is capable of chemically speciating a much broader range of substances (including many inorganic and organic hazardous air pollutants) comprising PM_{2.5} emissions than traditional in-stack/impinger methods. Dilution tunnel results are considered the best representation of PM_{2.5} speciation, compared to traditional in-stack/impinger methods.
- PM_{2.5} emissions from this FCCU were 24 percent filterable particulate matter and 76 percent condensible particulate matter (based on Method 201A and controlled condensation results, respectively).
- PM_{2.5} (including sulfuric acid mist) comprises 97 percent to the total particulate emissions from the FCCU.
- PM_{2.5} mass emissions measured by the dilution tunnel are biased low due to deposition of solid particles in the probe, sample line, venturi, and other components upstream of the filter. For mass emission measurements applied to FCCUs, further development of the dilution tunnel and test methodology is needed to reduce unaccounted particle losses in the sampling system.
- PM_{2.5} emissions from the FCCU at this refinery are composed principally of catalyst fines, sulfur trioxide (at stack temperatures) and sulfuric acid.
- SO₂ and NO_x comprise the majority of PM_{2.5} precursor emissions from this FCCU.
- Emissions of speciated organic compounds, including several hazardous air pollutants, are extremely low, with only a few compounds significantly exceeding background levels or minimum detection limits.
- Potential chemical markers for FCCU emissions include silicon, aluminum, iron, lanthanum, titanium, vanadium and nickel.
- Despite uncertainties associated with some measurements, these results represent a very comprehensive and useful characterization of FCCU emissions.

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 (μm), also referred to as 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 some sources 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, which have been widely used in research studies (Hildemann et al., 1994; McDonald et al., 1998), 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 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 test report describes the results of tests performed on a fluidized catalytic cracking unit (FCCU) at Refinery Site A on July 22-July 29, 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 iced impinger train (EPA Method 201A/202) and PM_{2.5} mass measured using a dilution tunnel;
- Develop emission factors and speciation profiles for organic aerosols and PM_{2.5} mass;
- Characterize sulfate ($\text{SO}_4^{=}$), nitrate (NO_3^-), ammonium (NH_4^+), chloride (Cl^-) elemental carbon (EC) and organic carbon (OC) in particulate matter collected on filter media after stack gas dilution;
- Characterize semivolatile organic compounds (SVOC) in stack gas samples after dilution;
- Characterize key gaseous secondary particle precursors in stack gas samples: volatile organic compounds (VOC) with carbon number of 7 and above; sulfur dioxide (SO_2); sulfur trioxide (SO_3); ammonia (NH_3); and oxides of nitrogen (NO_x);
- Document the relevant process design characteristics and operating conditions during the test.

Secondary Objectives

- Characterize ions ($\text{SO}_4^{=}$, NO_3^- , NH_4^+ and Cl^-), OC, and EC in particulate collected on filter media in stack gas sampling trains;
- Characterize the size distribution of solid and condensable particles at stack conditions.

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

Table 1-1. Overview of Sampling Scope for FCCU (Refinery Site A).

Sampling Location	Number of Samples				
	ESP Hopper	Regenerator Inlet	Regenerator Outlet	Stack	Ambient Air
EPA Method 201A/202 train	--	--	--	3	--
EPA Method 206 train	--	--	--	3	--
Controlled condensation train	--	--	--	3	--
Dilution tunnel	--	--	--	3	1
Teflon filter					
TIGF/PUF/XAD-4					
Quartz filter					
Tenax					
Composited grab sample	3	3	3	--	--
Continuous emissions monitoring (NO _x , SO ₂ , CO, O ₂ , CO ₂)	--	--	--	continuous	--
Process monitoring	--	--	--	continuous	--

TIGF = Teflon-impregnated glass fiber filter.

PUF = polyurethane foam.

XAD = Amberlite XAD-4 resin.

analyzed for the compounds listed in Table 1-2. FCCU process data, electrostatic precipitator (ESP) hopper fines, and spent and regenerated catalyst fines 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}) particulate matter, condensable particulate matter (CPM), NH₃, SO₃, NO_x, oxygen (O₂), carbon dioxide (CO₂), carbon monoxide (CO) and SO₂ were 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 1-2. Summary of Analytical Targets for FCCU Tests (Refinery A).

Parameters	In-Stack					Dilution Tunnel				
	Cascade Impactors	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						
Particle size distribution	X									
Sulfate				X		X				
Chloride				X		X				
Ammonium						X				
Nitrate						X				
Elements								X		
Organic carbon			X			X				
Elemental carbon			X			X				
Semivolatile organic compounds			X				X			
Volatile organic compounds									X	
Ammonia				X						
SO ₃				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

TIGF = Teflon-impregnated glass fiber filter.

PUF = polyurethane foam.

XAD = Amberlite XAD-4 resin.

Dilution Stack Gas Samples

Dilution sampling was used to characterize PM2.5 including aerosols formed in the near-field plume from the stack. The dilution sampler extracted a sample stream from the stack into a mixing chamber, where it was diluted approximately 18:1 with purified ambient air. Because PM2.5 behaves aerodynamically like a gas at typical stack conditions, the samples were

extracted non-isokinetically. A slipstream of the mixed and diluted sample was drawn into a 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 (TMF), and Teflon[®]-impregnated glass fiber (TIGF) filters; a polyurethane foam (PUF)/ Amberlite[®] sorbent resin (XAD-4)/PUF cartridge to collect gas-phase SVOC; and a Tenax cartridge to collect VOC. Three samples were collected on three sequential test days.

A single sample run was performed on ambient air at the refinery 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 ESP fines from the ESP hopper was collected on each day of particulate testing and analyzed for elements. Spent catalyst and regenerated catalyst samples were collected from the regenerator inlet and outlet, respectively, on each day of particulate testing and subsequently analyzed for combustion properties.

KEY PERSONNEL

GE Energy and Environmental Research Corporation (GE EER) had primary responsibility for conducting 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) 859-8851;
- 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;

- Irving Crane (ExxonMobil Research and Engineering) - API Work Group Co-Chairman (973) 765-6800;
- Karin Ritter (API) - API Project Officer (202) 682-8472.

Section 2

PROCESS DESCRIPTION

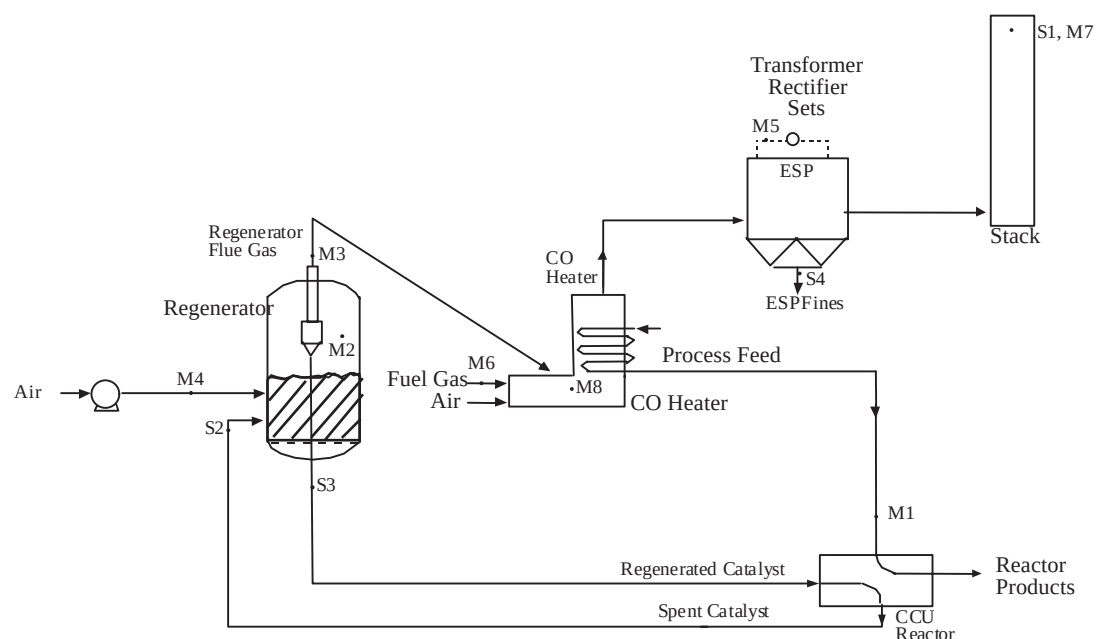
The tests were performed on a FCCU at Refinery Site A. The FCCU has a capacity of 47,000 barrels (bbl)/day and is equipped with a CO heater and an ESP (Figure 2-1). The regenerator air is oxygen-enriched. The CO heater is fired by refinery process gas and has a refractory-lined furnace with a single row of burners along the front wall. The CO regenerator off gas is introduced into the furnace close to the burners through ports in the roof of the furnace. The ESP is equipped with NH_3 conditioning and humidification systems for enhanced performance; however, these are not required under all operating conditions and neither was in service during these tests. The FCCU, CO heater, and ESP appeared to be in good working order during the tests. Operating conditions during the test are given in Section 4. FCCU, CO heater, and ESP operating parameters were monitored during testing.

SAMPLING LOCATIONS

Flue gas samples were collected from the stack. The unit has a 230-foot vertical stack with a 360-degree sampling platform located 120 feet from the ground, accessible via a ladder. There are four 4-inch diameter sampling ports spaced evenly around the stack's circumference. The stack diameter at sampling location is 124 inches. The sample ports are located 60 feet (6 diameters) downstream from the nearest flow disturbance and 72 feet (7 diameters) below the top of the stack. The normal flue gas temperature at the sampling location is approximately 550 degrees Fahrenheit ($^{\circ}\text{F}$). All sampling was performed at a single point in the stack to facilitate comparison between the dilution tunnel and EPA methods.

ESP hopper catalyst fines samples were collected during each run by diverting a small amount from the hopper conveyer belt into a 55-gallon drum. A half-liter dipper was used to remove a representative sample from the barrel at the end of the test run. Spent catalyst fines and regenerated catalyst fines were collected from taps located at the regenerator inlet and outlet, respectively, three times during each run and composited into one sample.

An ambient air sample was collected at near ground level at the refinery.



Sampling Locations	Description	Process Monitoring Station	Description	Parameters
S1	Stack	M1	Process Feed	Feed flow rate
S2	Regenerator inlet	M2	Regenerator	Coke burn rate, catalyst recirculation rate, pressure
S3	Regenerator outlet See Table 4-1	M3	Regenerator outlet	O ₂ , CO, temperature
S4	ESP hopper inlet	M4	Regenerator air inlet	Regenerator air flow rate, O ₂ enrichment rate
		M5	Electrostatic precipitator	ESP current
		M6	Fuel gas feed	CO heater fuel gas flow rate
		M7	CO heater stack	O ₂ , CO ₂ , Opacity
		M8	CO heater	North and South firebox temperature

Figure 2-1. FCCU 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, in-stack measurements and process sampling. 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 11:35 hours and finished at 17:35 hours on Monday, July 27. Sampling using the dilution tunnel and in-stack methods was performed simultaneously with co-located sample probes at a single point at the center of the stack (see Section 4 for selection process).

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 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 O₂ concentration profile deviated 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[®] tubing 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 second (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 minimize loss of the water soluble gas fraction. The condensate was removed with a peristaltic pump through the bottom of the heat exchanger. All

Table 3-1. Summary of Test Procedures.

Sampling Location	Measurements	Sampling Approach	Sample Analyses	Reference
Stack (In-Situ) S1	Total PM, PM10, PM2.5 and composition	In-stack series cyclones and filter	Mass (dry and after heated), organic carbon, elemental carbon, organic species	U.S. EPA Method 201A (modified)
	Particle size distribution	Hot and cold cascade impactors	Mass	U.S. EPA Method 201A (modified)
	Condensible PM and composition	Impingers	Mass (organic and inorganic), sulfate, chloride	U.S. EPA Method 202 (modified)
	Ammonia	In-stack filter and impingers	Mass, ammonium	U.S. EPA Method 206
	SO ₃	Impingers	SO ₃ , SO ₂	Controlled condensation method
	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, 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
Ambient Air (Ground Level)	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
ESP hopper inlet (S4)	ESP fines	Composite grab sample	Elements	U.S. EPA SW-846 6010B
Regenerator inlet (S2)	Spent catalyst	Composite grab sample	Ultimate Analysis (C, H, N, O), moisture, ash, calorific content	ASTM D3286, D4239, D5142, D5373
Regenerator outlet (S3)	Regenerated catalyst	Composite grab sample	Ultimate Analysis (C, H, N, O), moisture, ash, calorific content	ASTM D3286, D4239, D5142, D5374

	Time	FCCU Stack							Process Samples				
		Velocity and Moisture	Method 201/202	CEMS	Dilution Tunnel	Controlled Condensate	Ammonia and Particulate	Cold Cascade Impactor	Hot Cascade Impactor	ESP Hopper Composite	Spent Catalyst	Regenerated Catalyst	Soot Blowing
7/17/98 Fri.	9:00												
	10:00												
	11:00												
	12:00												
	13:00												
	14:00	14:35											
	15:00	15:10											
	16:00												
	17:00												
7/21/98 Tues.	9:00												
	10:00												
	11:00												
	12:00												
	13:00												
	14:00	14:12-14:50											
	15:00												
	16:00												
	17:00												
7/22/98 Wed.	9:00												
	10:00						R1 / 10:05						
	11:00						11:05						
	12:00						R2 / 12:30						
	13:00						13:30						
	14:00												
	15:00						R3 / 14:58						
	16:00						15:58						
	17:00												
7/23/98 Thurs.	9:00												
	10:00												
	11:00												
	12:00												
	13:00								13:53				
	14:00						Preliminary / 14:10	Blank					
	15:00							15:07					
	16:00						16:40						
	17:00												

Figure 3-1. Chronology for Testing at FCCU (Refinery Site A).

	Time	FCCU Stack							Process Samples													
		Velocity and Moisture	Method 201/202	CEMS	Dilution Tunnel	Controlled Condensation	Ammonia and Particulate	Cold Cascade Impactor	Hot Cascade Impactor	ESP Hopper Composite	Spent Catalyst	Regenerated Catalyst	Soot Blowing									
7/24/98 Fri.	8:00			Strat. / 8:30																		
	9:00													R1 / 11:25								
	10:00			9:43											12:25							
	11:00			R1										R2 / 13:20								
	12:00													14:20								
	13:00			R2										R3 / 15:05								
	14:00													16:05								
	15:00			R3																		
	16:00																					
	17:00																					
18:00																						
19:00																						
7/27/98 Mon.	9:00																					
	10:00													R1 / 11:35	R1 / 11:34	R1 / 11:35						
	11:00																					
	12:00																					
	13:00																R1 / 13:15	R1 / 13:15		13:11	13:11	
	14:00																		14:10- 14:40			
	15:00														15:09		15:15	15:15		15:15	15:15	
	16:00														15:33				16:15- 16:30			
	17:00													Post-test	17:35	17:41	17:35				17:04	17:04
	18:00													18:16- 18:42								
19:00																						
7/28/98 Tues.	8:00	8:30- 8:42	R2 / 8:17		R2 / 8:17																	
	9:00		R2 / 9:17	R2 / 10:35	R2 / 10:36									11:00- 11:30	11:00	11:00						
	10:00																					
	11:00																11:43					
	12:00																12:15					
	13:00														13:30- 14:00	13:00	13:00					
	14:00	14:17	14:15	14:17																		
	15:00	15:05- 15:22																				
	16:00																					
	17:00																					
18:00																						
19:00																						
7/29/98 Wed.	8:00	8:10- 8:30																				
	9:00	R3 / 9:11												R3 / 10:10	R3 / 9:11							
	10:00																					
	11:00															R3 / 10:55	R3 / 10:55	10:00- 10:30	10:00	10:00		
	12:00																					
	13:00															12:10	12:10		12:00	12:00		
	14:00																	13:30- 14:00	13:30	13:30		
	15:00	15:43 - 15:55												15:11	15:10	15:11						
	16:00	16:15 - 16:22																				
	17:00																					
18:00																						
19:00																						

Figure 3-1 (Continued) Chronology for Testing at FCCU (Refinery Site A).

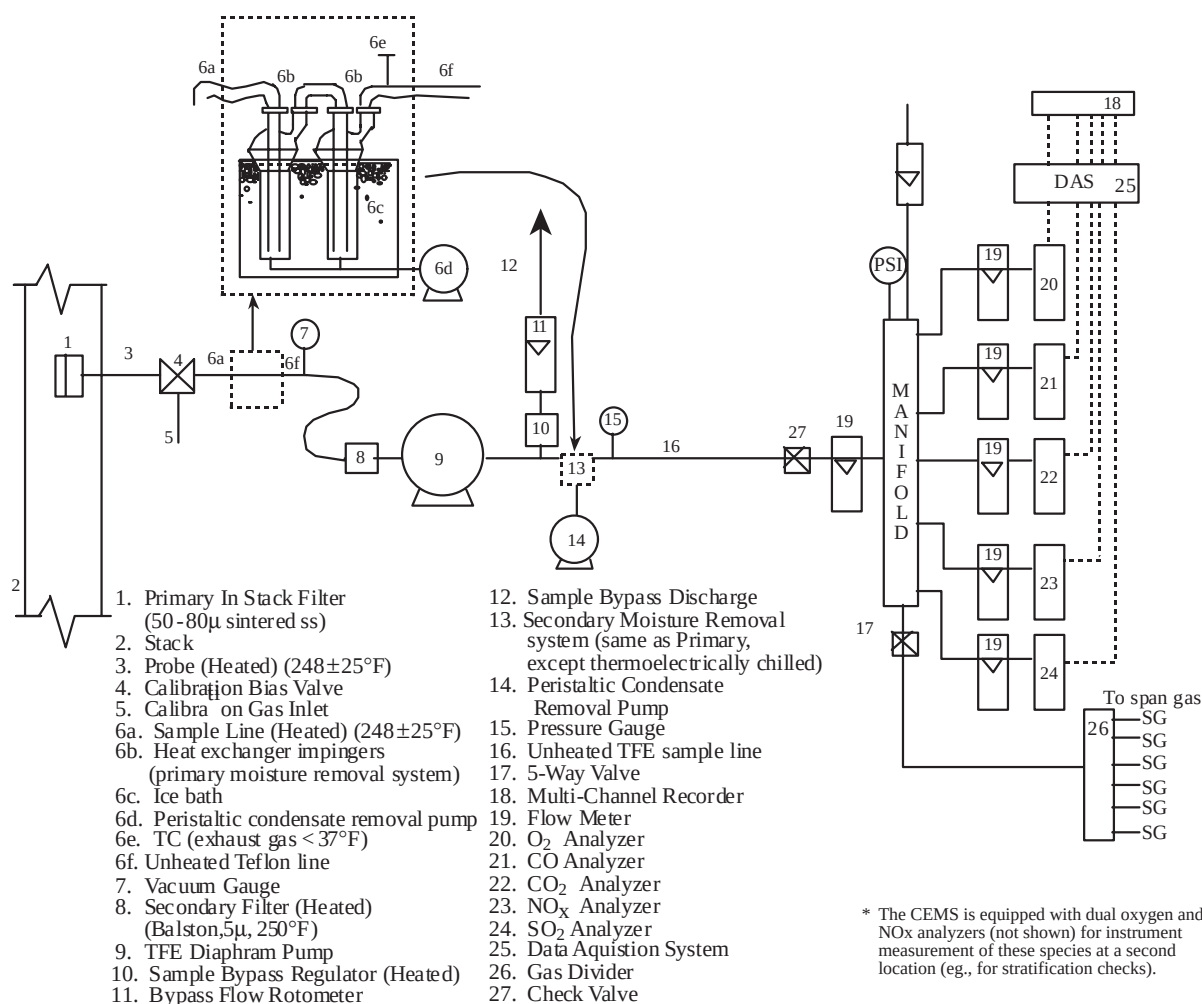


Figure 3-2. Continuous Emissions Monitoring System.

contact 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 TFE tubing to a tertiary filter preceding the sample manifold. Samples were analyzed for O₂ and CO₂ using instrumental methods according to EPA Method 3A. O₂ 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. SO₂ was determined in the sample using a non-dispersive ultraviolet (NDUV) analyzer according to EPA Method 6C. CO was determined using a NDIR analyzer following EPA Method 10.

Table 3-2. Continuous Emissions Monitoring System Instrumentation.

Parameter	Manufacturer	Model	Serial Number	Detection Principal	Units	Minimum Detection Limit	Range
Oxygen (O ₂)	Taylor-Servomex	Model 1400	14203.9	Paramagnetism	%	0.10%	0-25
Oxides of Nitrogen (NO _x)	Thermo- Electron	Model 10AR with molybdenum NO ₂ -NO converter	1420701499	Chemi-luminescence	ppmv	1 ppm	0-1000
Carbon Monoxide (CO)	Thermo- Electron	Model 48H	25252219	Gas Filter Correlation	ppmv	0.5 ppm	0-100
Carbon Dioxide (CO ₂)	ACS	Model 3300	8P0001T	Non-dispersive Infra-red absorption (NDIR)	%	0.10%	0-20
Sulfur Dioxide (SO ₂)	Bovar/ Western Research	Model 720 AT2	89721AT273991	Non-dispersive Ultraviolet Absorption (NDUV)	ppmv	1 ppm	0-1000

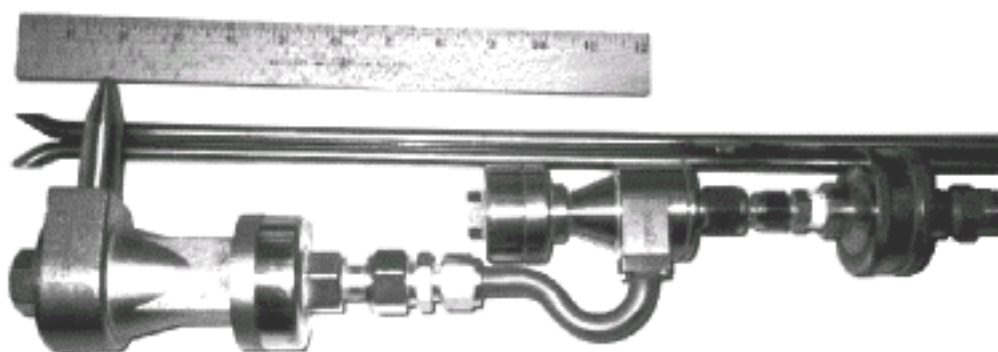
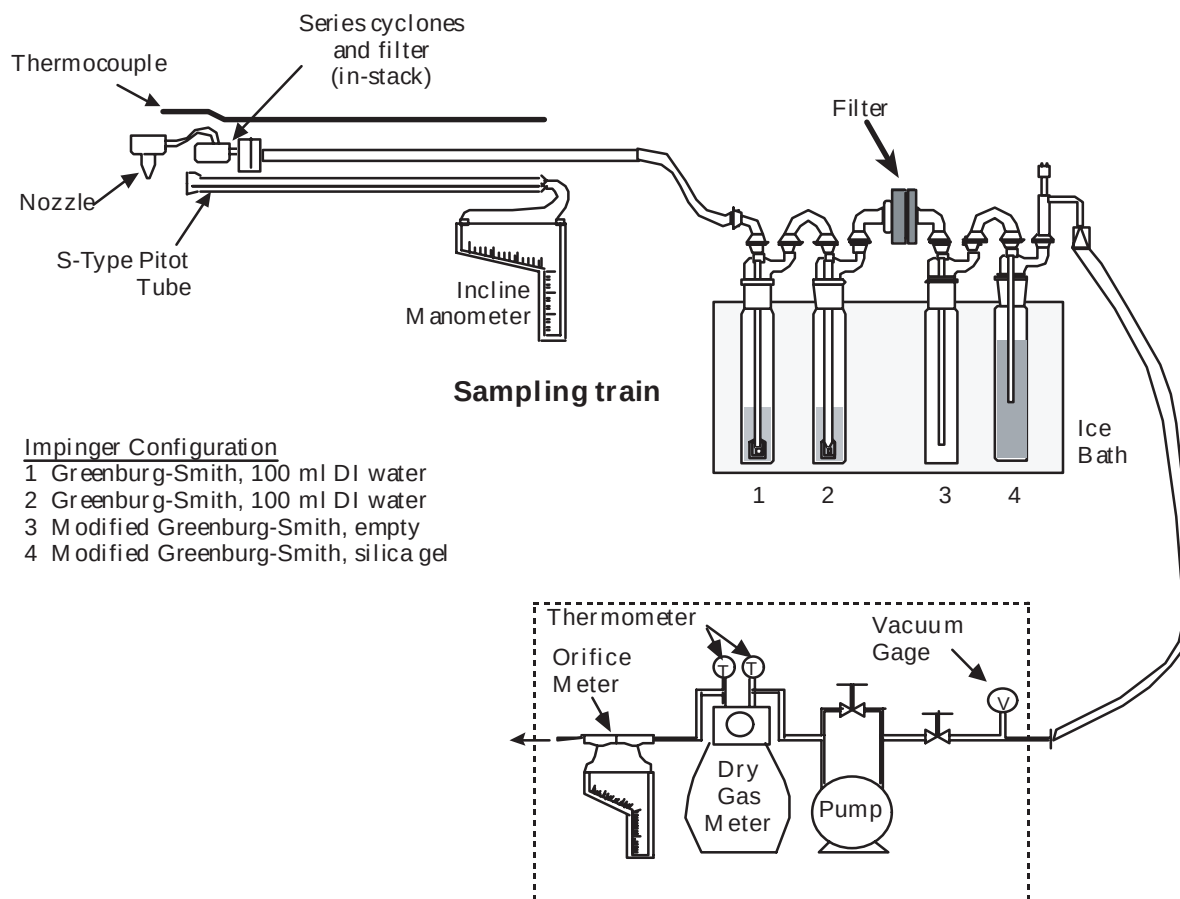
IN-STACK METHOD TESTS

Total particulate, particulate matter with aerodynamic diameter smaller than 10 µm (PM₁₀) and PM_{2.5} filterable at stack temperature, were determined using in-stack methods. Solid and condensible particle size distribution was measured using cascade impactors. CPM, defined as the material collected in chilled impingers after in-stack filtration, also was measured for the in-stack samples. NH₃ and SO₃ concentrations were measured using extractive methods.

In-Stack Total Filterable PM, PM₁₀ and PM_{2.5}

Two in-stack cyclones followed by an in-stack filter (Figure 3-3) were used to measure total particulate mass, PM₁₀ and PM_{2.5}. 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 according to the methods as published except for the following modifications and clarifications:

- A PM₁₀ cyclone and a PM_{2.5} cyclone (Andersen Model Case-PM₁₀ and Case-PM_{2.5}) were attached in series to the filter inlet. Sample recovery procedures were modified accordingly;



Series cyclone and filter assembly

Figure 3-3. EPA Method 201A (Modified)/202 Sampling Train.

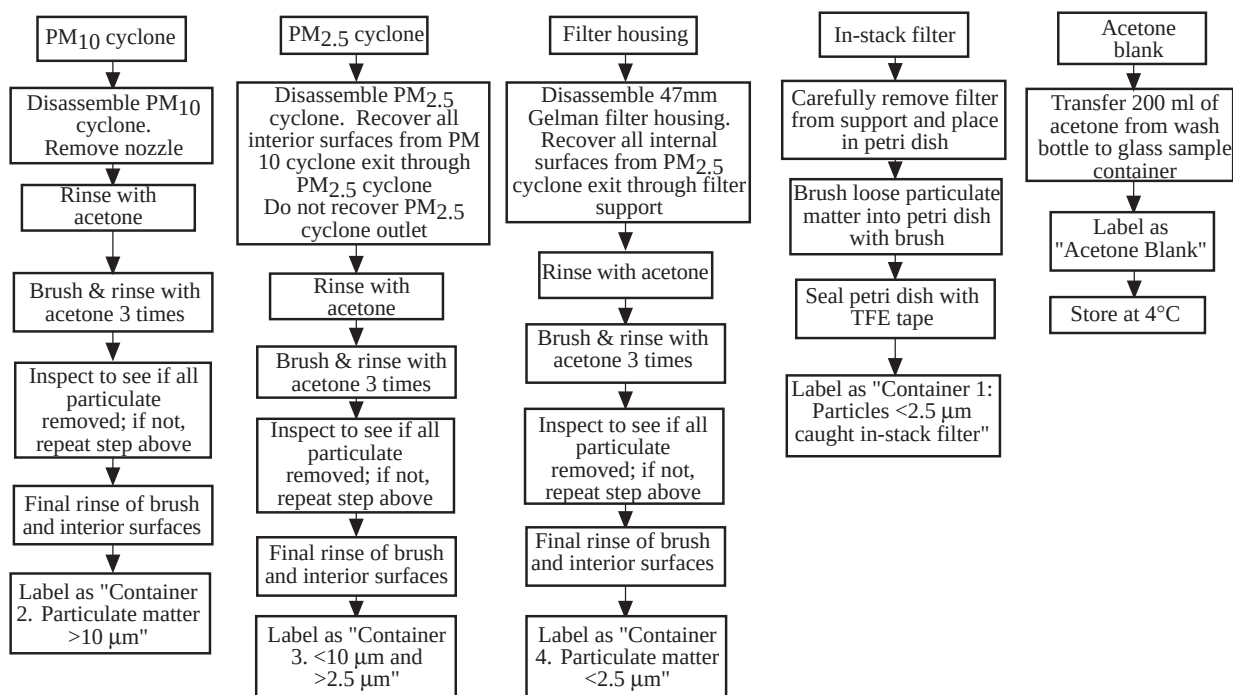


Figure 3-4. EPA Method 201A (Modified) Sample Recovery Procedure.

- Samples were collected from a single traverse point in 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 then repeat weighings were 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.

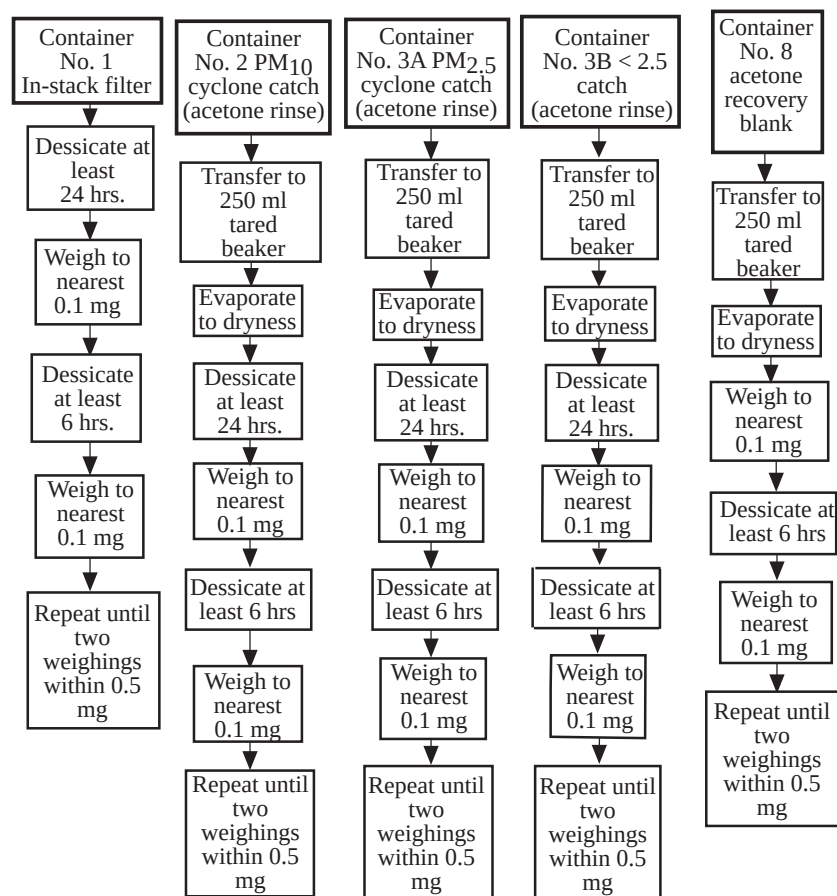


Figure 3-5. Method 201A (Modified) Sample Analysis Procedure.

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