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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** 

API PUBLICATION 4713 MARCH 2002

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#### EXECUTIVE SUMMARY

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aerosols from petroleum industry combustion sources, and the limited information that is available is incomplete and outdated.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

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

This report presents results of a pilot project to evaluate the test protocol on a 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<sub>x</sub> or SO<sub>2</sub> emissions. The FCCU was operating at approximately 94 percent of capacity and the flue gas temperature at the stack was approximately  $579^{\circ}F$  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 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;

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 PM2.5; 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 totals approximately three percent of the organic carbon. Emission factors for secondary particulate precursors (NO<sub>x</sub>, SO<sub>2</sub>, 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 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.

		Average		95% Confidence
		Emission Easter		Jonar Bound
		(lh/1000 lh asla	Uncertainty (%)	(lb/1000 lb asla
	Substance	(10/1000 10 Coke		(ID/IOOU ID COKE
Deutienlate		o 51	270	burned)
Particulate	CPM (inorganic)	0.51	279	1.5
Mass	CPM (organic)	4./E-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 $H_2SO_4$ )	1.4	92	2.3
Carbon	Organic Carbon (dilution tunnel)	9.9E-4	53	1.4E-3
Carbon	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
ļ	L'our curoon (in suich) D	1.01 7	, ,	2.01 -

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

\* <10x ambient

B <10x blank

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

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

		Avorago		05% Confidence
		Emission Easter		Junnar Dound
		Emission Factor	Uncertainty (%)	Upper Bound
	Substance	(Ib/1000 lb coke	• • •	(Ib/1000 lb coke
		5 4E 7	1027	
Semivolatile	1+2-ethylnaphthalene *	5.4E-7	1037	3.4E-0
Organic	1,2,8-uimeuiyinapinnalene *	5.2E-0 2.1E-7	580	1.2E-7
Compounds	1,2-dimethylnaphthalene *	2.1E-7	n/a 205	п/а 1 ог с
(Dilution	1,3+1,6+1,7-dimethylnaphthalene *	6.1E-7	285	1.8E-0
Tunnel,	1,4+1,5+2,3-dimethylnaphthalene *	6.2E-7	n/a	n/a
PUF/XAD)	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+I-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-nhenvlnanhthalene	1.5E-7	162	3 3E-7
	3 6-dimethylphenanthrene *	1.5E 7 1.1E-7	565	4.0E-7
	2 mothylbinhonyl *	0.2E 7	167	4.0E-7
	4 methylbinhenyl *	9.3E-7	107	1.7E-0
	4-methyloipnenyi *	4.0E-7	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 8F-7	744	8.6E-7
	$\Delta$ nthracene	2.5E.6	n/9	0.0E-7
	Anthraquinone	2.5E-0 7 2E 7	11/a 202	11/a 2 2E 4
	Anthrono * D	1.3E-/	292 62	2.2E-0 1.0E-7
	Anurrone * B	1.3E-/	03	1.9E-/
	B-dimethylphenanthrene	2.5E-7	182	4.8E-7
	B-MePy/MeF1 *	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+i+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	84F-7
	Benzo(ghi)pervlene B	2.9E-7	101	4.9F-7
	Benzonanhthothionhana	9.6E 8	00	1.6E 7
	Benzonaphiniouniophene	9.0E-ð	90	1.0E-/

## Table E-2. SVOC Emission Factors for FCCU.

		Average		95% Confidence
		Emission Factor	TT	Upper Bound
		(lb/1000 lb coke	Uncertainty (%)	(lb/1000 lb coke
	Substance	burned)		burned)
Semivolatile	Bibenzene (1) B	1.2E-5	n/a	n/a
Organic	Biphenyl *	1.6E-7	513	5.5E-7
Compounds	C-dimethylphenanthrene *	3.9E-7	972	2.3E-6
(Dilution	C-methylphenanthrene *	2.6E-7	133	5.0E-7
Tunnel,	C-trimethylnaphthalene *	1.6E-7	75	2.5E-7
PUF/XAD)	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-	1,4-chrysenequinone	1.9E-8	314	4.8E-8
Volatile	1-ethyl-2-methylnaphthalene	9.3E-8	n/a	n/a
Organic	2,6+2,7-dimethylnaphthalene	1.0E-7	n/a	n/a
Compounds	2-methylphenanthrene	3.5E-8	n/a	n/a
(in-stack	4-methylbiphenyl	4.6E-8	n/a	n/a
filter)	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		

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

† 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

--^,,,,,,,-^--,,,,,,,,,,,,,,,

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		Average		95% Confidence
		Emmision		Upper Bound
		Factor (lb/1000	Uncertainty (%)	(lb/1000 lb coke
	Substance			burned)
Gases	SO <sub>2</sub>	26	80	41
	NO <sub>x</sub>	4.1	80	6.5
	Ammonia	3.6E-3	70	5.4E-3
Volatile	1,2,4-trimethylbenzene *	4.6E-5	100	7.9E-5
Organic	1-hexadecene	7.7E-5	n/a	n/a
Compounds	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

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

\* <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-methylanthracene 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



Percent of Primary PM 2.5 measured by dilution tunnel

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 PM2.5 emissions than traditional in-stack/impinger methods. Dilution tunnel results are considered the best representation of PM2.5 speciation, compared to traditional in-stack/impinger methods.
- PM2.5 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).
- PM2.5 (including sulfuric acid mist) comprises 97 percent to the total particulate emissions from the FCCU.
- PM2.5 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.
- PM2.5 emissions from the FCCU at this refinery are composed principally of catalyst fines, sulfur trioxide (at stack temperatures) and sulfuric acid.
- SO<sub>2</sub> and NO<sub>X</sub> comprise the majority of PM2.5 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.

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## 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 PM2.5. There are few existing data regarding emissions and characteristics of fine aerosols from petroleum industry combustion sources, and such information that is available is fairly old. Traditional stationary source air emission sampling methods tend to underestimate or overestimate the contribution of 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 PM2.5 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 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 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 PM2.5 mass measured using an in-stack filter and iced impinger train (EPA Method 201A/202) and PM2.5 mass measured using a dilution tunnel;
- Develop emission factors and speciation profiles for organic aerosols and PM2.5 mass;
- Characterize sulfate (SO<sub>4</sub><sup>=</sup>), nitrate (NO<sub>3</sub><sup>-</sup>), ammonium (NH<sub>4</sub><sup>+</sup>), chloride (Cl<sup>-</sup>) 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<sub>2</sub>); sulfur trioxide (SO<sub>3</sub>); ammonia (NH<sub>3</sub>); and oxides of nitrogen (NO<sub>X</sub>);
- Document the relevant process design characteristics and operating conditions during the test.

## Secondary Objectives

- Characterize ions (SO<sub>4</sub><sup>=</sup>, NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup> and Cl<sup>-</sup>), OC, and EC in particulate collected on filter media in stack gas sampling trains;
- Characterize the size distribution of solid and condensible 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

			Number of Samp	les	
Sampling Location	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	

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

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 PM2.5) particulate matter, condensible particulate matter (CPM), NH<sub>3</sub>, SO<sub>3</sub>, NO<sub>x</sub>, oxygen (O<sub>2</sub>), carbon dioxide (CO<sub>2</sub>), carbon monoxide (CO) and SO<sub>2</sub> 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.

	In-Stack			Dilutior	ı Tunn	el				
	Cascade		Quartz			Quartz	TIGF/			
Parameters	Impactors	Cyclones	Filter	Impingers	Gases	Filter	XAD-4	TMF	Tenax	Gases
Total PM mass		Х	Х							
PM10 mass		Х	Х							
PM2.5 mass		Х	Х					Х		
Condensible particulate mass				Х						
Particle size distribution	Х									
Sulfate				Х		Х				
Chloride				Х		Х				
Ammonium						Х				
Nitrate						Х				
Elements								Х		
Organic carbon			Х			Х				
Elemental carbon			Х			Х				
Semivolatile organic compounds			Х				Х			
Volatile organic compounds									Х	
Ammonia				Х						
SO3				Х						
NO <sub>x</sub>					Х					
SO <sub>2</sub>					Х					
СО					Х					
O <sub>2</sub>					Х					
CO <sub>2</sub>					Х					
Moisture or relative humidity				Х						Х
Velocity					Х					
Temperature					Х					Х

## Table 1-2. Summary of Analytical Targets for FCCU Tests (Refinery A).

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<sup>®</sup> membrane (TMF), and Teflon<sup>®</sup>-impregnated glass fiber (TIGF) filters; a polyurethane foam (PUF)/ Amberlite<sup>®</sup> 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<sub>3</sub> 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 Farenheit (°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.



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.

#### O<sub>2</sub>, CO<sub>2</sub>, CO, NO<sub>x</sub> AND SO<sub>2</sub>

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 O<sub>2</sub> 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<sup>®</sup> 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

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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 <sub>3</sub>	Impingers	SO <sub>3</sub> , SO <sub>2</sub>	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

Table 3-1. Summary of Test Procedures.

		FCCU Stack							Process Samples				
	Time	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	9:00												
Fri.	10:00												
	11:00												
	12:00												
	13:00												
	14:00	14:35											
	15:00	15:10											
	16:00												
7/01/00	17:00												
//21/98	9:00												
Tues.	10:00												
	12.00												
	13.00												
	14:00	14:12-14:50											
	15:00												
	16:00												
	17:00												
7/22/98	9:00												
Wed.	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						
7/22/00	17:00												
1/23/98	9:00												
I nurs.	10:00												
	12.00												
	12.00								13.53				
	14.00							Preliminary / 14·10	Blank				
	15:00								15:07				
	16:00							16:40	10.07				
	17:00												

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

		FCCU Stack									Process Samples				
	Time	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 9:00 10:00 11:00 12:00 13:00 14:00 15:00 16:00 17:00 18:00 19:00			Strat. / 8:30   9:43 R1   R2   R3 	-	R1 / 11:25 12:25 R2 / 13:20 14:20 R3 / 15:05 16:05									
7/27/98 Mon.	9:00 10:00 11:00 12:00 13:00 14:00 15:00 16:00 17:00 18:00 19:00	Post-test 18:16- 18:42	R1 / 11:35	R1 / 11:34   15:09 15:33 17:41	R1 / 11:35			R1 / 13:15   15:15	R1 / 13:15   15:15	14:10- 14:40 16:15- 16:30	13:11 15:15 17:04	13:11 15:15 17:04	Not done this test		
7/28/98 Tues.	8:00 9:00 10:00 11:00 12:00 13:00 14:00 15:00 16:00 17:00 18:00 19:00	8:30- 8:42	R2 / 8:17	R2 / 9:17   11:43 12:15   14:15	R2 / 8:17			R2 / 10:35   12:05	R2 / 10:36   12:05	11:00- 11:30 13:30- 14:00	9:00 11:00 13:00	9:00 11:00 13:00	8:30   10:30 12:30   14:30		
7/29/98 Wed.	8:00 9:00 10:00 11:00 12:00 13:00 14:00 15:00 16:00 17:00 18:00 19:00	8:10- 8:30 15:43 - 15:55 16:15 - 16:22	R3/9:11	R3 / 10:10	R3 / 9:11			R3 / 10:55   12:10	R3 / 10:55   12:10	10:00- 10:30 13:30- 14:00	10:00 12:00 13:30	10:00 12:00 13:30	10:05 11:45 13:40 15:20		

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  $O_2$  and  $CO_2$  using instrumental methods according to EPA Method 3A.  $O_2$  was measured using a paramagnetic analyzer and  $CO_2$  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 (NO<sub>2</sub>)-to-nitric oxide (NO) converter according to EPA Method 7E. SO<sub>2</sub> 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.

			a · 1			Minimum	
_			Serial	Detection		Detection	
Parameter	Manufacturer	Model	Number	Principal	Units	Limit	Range
Oxygen (O <sub>2</sub> )	Taylor-Servomex	Model 1400	14203.9	Paramagnetism	%	0.10%	0-25
Oxides of Nitrogen (NO <sub>x</sub> )	Thermo- Electron	Model 10AR with molybdenum NO <sub>2</sub> - 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 <sub>2</sub> )	ACS	Model 3300	8P0001T	Non-dispersive Infra-red absorption (NDIR)	%	0.10%	0-20
Sulfur Dioxide (SO <sub>2</sub> )	Bovar/ Western Research	Model 720 AT2	89721AT27 3991	Non-dispersive Ultraviolet Absorption (NDUV)	ppmv	1 ppm	0-1000

Table 3-2. Continuous Emissions Monitoring System Instrumentation.

#### **IN-STACK METHOD TESTS**

Total particulate, particulate matter with aerodynamic diameter smaller than 10  $\mu$ m (PM10) and PM2.5 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 instack samples. NH<sub>3</sub> and SO<sub>3</sub> concentrations were measured using extractive methods.

#### 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 mass, PM10 and 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 according to the methods 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;




Series cyclone and filter assembly

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

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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.

# Particle Size Distribution

Cascade impactors were used for measuring particle size distribution (Figure 3-6). Eight-stage Andersen Mark IV impactors were used according to the manufacturer's instructions. High-purity quartz substrates were used to minimize  $SO_4^=$  artifacts. The measurements were performed according to EPA Method 201A except for the following modifications and clarifications:

- Two cascade impactors, one at stack temperature and one cooled, were used to quantify the size distribution of solid and condensible particulate matter. The hot impactor was at stack temperature, approximately 590°F, and the cooled impactor was cooled to a temperature below the sulfuric acid dew point. The actual acid dew point was estimated to be approximately 311°F for the SO<sub>3</sub> and H<sub>2</sub>O concentrations measured during these tests. The cooled impactor was maintained at approximately 200°F;
- The lower temperature cascade impactor was cooled using an in-stack aircooled cooling jacket surrounding the probe. A two foot probe extension between the pre-cyclone and the first impactor stage was used so that the cascade impactor could be located out of the stack, surrounded by a heating jacket to maintain a constant temperature. An equivalent probe extension was used on the hot impactor to maintain comparability, but the hot impactor was located entirely within the stack. The impactors are illustrated in Figure 3-5;
- Samples were collected isokinetically from a single point to preserve comparability among the different methods.

Each cascade impactor yielded the acetone rinse from the precutter plus high-purity quartz fiber substrates for each stage of the impactor. Tare weights for substrates were performed using a marked foil container, and the samples were recovered into and returned to the laboratory in the same containers to prevent loss of particulate matter. The samples were dried in a desiccator, then weighed. The acetone rinse was analyzed in the same manner as the in-stack cyclone samples.

# Condensible Particulate Matter Mass and Chemical Analysis

CPM was determined using EPA Method 202. After the in-stack filter, the sample passed through a heated Teflon<sup>®</sup> line to a series of impingers placed in an ice bath used for the Method





Figure 3-6. Hot and Cooled Cascade Impactor Train Configurations.

201A train. The contents of the impingers were recovered with distilled deionized (DI) water and dichloromethane (Figure 3-7). The samples were analyzed in the laboratory according to the method, including optional analyses for  $SO_4^{=}$  and Cl<sup>-</sup> (Figure 3-8). The method was performed as published except for the following modifications and clarifications:



Figure 3-7. Method 202 Sample Recovery Procedure.

- The impinger train consisted of 5 impingers for Runs 1 and 2 and six for Run 3. The first two impingers contained DI water, the third was empty, the fourth contained 30 percent hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) to scrub acid gas for protection of the metering equipment and pumps, and the fifth contained silica gel. The impinger setup deviated from the standard method due to unexpected glassware breakage. For Runs 1 and 3 the first impinger was a standard Greenburg-Smith (G-S) design and for Run 2 it was a modified G-S design. For Runs 2 and 3 the second impinger was a standard G-S design and for Run 1 it was a modified G-S design. The third impinger was a modified G-S design for Runs 2 and 3 and a standard G-S design for Run 1. The H<sub>2</sub>O<sub>2</sub> impinger was a modified G-S design for Run 3. For Run 3 an additional empty modified G-S impinger was added between the second and third impingers to prevent the captured moisture from carrying over into the quartz filter;
- A quartz filter was placed between the second and third impingers for Runs 1 and 2 and between the two empty impingers for Run 3 to improve capture efficiency and capture any aerosols that may have passed through the first two impingers, as described in the method as an optional procedure;
- The Method 202 impinger trains were purged with ambient air for one hour after the test;



Figure 3-8. Method 202 Sample Analysis Procedure.

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- Total sampling time for all runs was six hours;
- An aliquot of the impingers was analyzed for SO<sub>4</sub><sup>=</sup> by ion chromatography, as described in the method as an optional procedure;
- The first inorganic fraction drying step was finished at ambient temperature in a dessicator, as described in the method as an optional procedure;
- Ammonium hydroxide (NaOH) was added to the inorganic fraction during analysis to stabilize SO<sub>4</sub><sup>=</sup> and Cl<sup>-</sup> compounds, as described in the method;
- The inorganic fraction final residue was analyzed for Cl<sup>-</sup> by ion chromatography, as described in the method as an optional procedure.

See Section 4 for discussion of data treatment.

# SO<sub>3</sub> and NH<sub>3</sub>

EPA Method 206 was used to determine emissions of NH<sub>3</sub>. The sample passed through an instack filter followed by an impinger train (Figure 3-9). The method was performed as published except for the following modifications and clarifications:

- The impinger train (5 impingers total) was configured as follows for all three runs: impingers 1, 3, 4 and 5 were modified G-S type, and impinger 2 was a standard G-S type. Impingers 1 and 2 contained 100 ml each of a 0.1 normal sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) solution, impinger 3 was empty, impinger 4 contained 100 ml of a 30 percent H<sub>2</sub>O<sub>2</sub> solution, and impinger 5 contained silica gel;
- The sample was collected isokinetically from a single point to allow simultaneous sampling using reference methods and dilution sampling.

The impinger contents were analyzed for  $NH_4^+$  by colorimetry in the same manner as described above.



Impinger Specifications

- 1 Greenburg-Smith, 100 ml 0.1N H<sub>2</sub>SO<sub>4</sub>
- 2 Greenburg-Smith, 100 ml 0.1N H<sub>2</sub>SO<sub>4</sub>
- 3 Modified Greenburg-Smith, Empty
- 4 Modified Greenburg-Smith, Silica Gel

Figure 3-9. Illustration of Draft EPA Method 206 Sampling Train Assembly.

The controlled condensation technique was used to measure the SO<sub>3</sub> concentration in the flue gas. The sampling train is shown in Figure 3-10. The method for this system is described in the document "Process Measurement Procedures, Sulfuric Acid Emissions," February 1977 (EPA IERL by TRW, Contract No. 68-02-2165 Task No. 13). The method was performed as published except for the following modifications and clarifications:



Impinger Configuration

- Modified Greenburg-Smith, 100 ml 10% H<sub>2</sub>O<sub>2</sub>
  Greenburg-Smith, 100 ml 10% H<sub>2</sub>O<sub>2</sub>
- 3 Modified Greenburg-Smith, Empty
- 4 Modified Greenburg-Smith, silica gel

Figure 3-10. Controlled Condensation Sampling Train Configuration.

 $SO_2$  was collected in impingers after the controlled condensation train. The impingers were charged as follows: Impingers 1 and 2 contained 20 ml of 30 percent  $H_2O_2$  solution, impinger 3 was empty, and impinger 4 contained silica gel.

### DILUTION TUNNEL TESTS

PM2.5 mass and chemical speciation of the stack gas particulate were determined using a dilution tunnel (Figure 3-11). A stainless steel probe with a buttonhook nozzle was used to withdraw the stack gas sample at a rate of approximately 10 liters per minute. The sample was transported through a heated copper line into the dilution tunnel. The sample was mixed in the tunnel with purified ambient air under turbulent flow conditions to cool and dilute the sample to near-ambient conditions. The ambient air used for dilution was filtered through a high efficiency particulate air (HEPA) filter to remove particulate matter and an activated carbon bed to remove gaseous organic compounds. After passing through a tunnel length equal to 10 tunnel diameters, approximately 60 percent of the diluted sample was withdrawn into a large chamber, where the sample aged for approximately 80 seconds to allow low-concentration aerosols (especially organic aerosols) to fully form. The aged sample was withdrawn through two cyclone separators (each operating at a flow rate of approximately 110 liters per minute) to remove particles larger



Figure 3-11. Dilution Tunnel Sampling System.

than 2.5 µm and delivered to the sample collection media (TMF, quartz filter, Tenax cartridge, and TIGF/PUF/XAD-4/PUF cartridge). The sample flow rate through the probe was monitored using a venturi flow meter and thermocouple. The venturi velocity head was measured continuously during the test with a Magnehelic® gage. An S-type Pitot tube with electronic pressure transducer and thermocouple were used to monitor the velocity in the stack. The thermocouples and pressure transducers were connected to a laptop computer data acquisition system. The dilution airflow and backpressure were adjusted to maintain the target dilution ratio and sample flow rates. Total sampling time for each test run was six hours.

A dilution ratio of approximately 40:1 was originally planned, consistent with the prior work of Hildemann et al. (1989). Hildemann selected this ratio both to cool the sample and to ensure complete mixing between the sample and dilution air prior to the residence time chamber takeoff. For these tests, flow rates were set in the field to achieve a dilution ratio of approximately 15:1 for the first run, and increased to approximately 30:1 for Runs 2 and 3 due to high particulate loading. During a post-test calibration of the sample probe venturi it was discovered that the actual dilution ratio during testing was approximately 9:1 for Run 1 and 18:1 for Runs 2 and 3. Hildemann's results suggest that mixing between the sample and the dilution air begins to degrade below a dilution ratio of approximately 10:1. Therefore, the sample drawn into the residence time chamber may have been incompletely mixed with the dilution air. Based on profiles reported by Hildemann, this may produce a slight (estimated 10-20 percent) positive bias in the reported emission factors for Run 1, but should not significantly affect chemical speciation profiles.

A single ambient air sample was collected using the dilution tunnel. The dilution tunnel setup was modified by removing the sample probe and attaching a special inlet adapter in place of the HEPA and charcoal filters. The ambient air sample was drawn into the tunnel without dilution through the special inlet adapter. The sampling period was increased to eight hours to improve minimum detection limits. The same sampling media were used as described below and in Figure 3-11.

### PM2.5 Mass

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

### **Elements**

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

A Kevex Corporation Model 700/8000 ED-XRF analyzer with a side-window, liquid-cooled, 60 keV, 3.3 milliamp rhodium anode x-ray tube and secondary fluorescers was used. The silicon detector had an active area of 30 mm<sup>2</sup>, with a system resolution better than 165 eV. The analysis was controlled, spectra were acquired, and elemental concentrations were calculated by software on a microcomputer which was interfaced to the analyzer. Five separate XRF analyses were conducted on each sample to optimize the detection limits for the specified elements. The filters were removed from their petri slides and placed with their deposit sides downward into polycarbonate filter cassettes. A polycarbonate retainer ring kept the filter flat against the bottom of the cassette. The cassettes were loaded into a carousel in the x-ray chamber. The sample chamber was evacuated to  $10^{-3}$  Torr. A computer program controlled the positioning of

the samples and the excitation conditions. Complete analysis of 16 samples under five excitation conditions required approximately 6 hours.

## Sulfate, Nitrate, Chloride and Ammonium

Samples for determining water-soluble  $Cl^-$ ,  $NO_3^-$ ,  $SO_4^-$  and  $NH_4^+$  were collected on quartz fiber filters. The flow rate through the filter holder was set prior to sample collection and checked after sample collection by placing a calibrated rotameter on the outlet of the holder and setting the position of the needle value to achieve the desired flow rate.

Each quartz-fiber filter was cut in half, and one filter half was placed in a polystyrene extraction vial with 15 ml of DI water. The remaining half was used for determination of OC and EC as described below. The extraction vials were capped and sonicated for 60 minutes, shaken for 60 minutes, then aged overnight to assure complete extraction of the deposited material. After extraction, these solutions were stored under refrigeration prior to analysis. The unanalyzed filter half was archived in the original petri slide. Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, and SO<sub>4</sub><sup>=</sup> were measured with a Dionex 2020i ion chromatograph (IC). Approximately 2 ml of the filter extract was injected into the ion chromatograph.

A Technicon TRAACS 800 Automated Colorimetric System (AC) was used to measure  $NH_4^+$  concentrations by the indolphenol method. Each sample was mixed with reagents and subjected to appropriate reaction periods before submission to the colorimeter. Beer's Law relates the liquid's absorbency to the amount of the ion in the sample. A photomultiplier tube measured this absorbency through an interference filter which is specific to  $NH_4^+$ . Two ml of extract in a sample vial were placed in a computer-controlled autosampler. Technicon software operating on a microcomputer controlled the sample throughput, calculated concentrations, and recorded data.

# Organic and Elemental Carbon

Quartz fiber filters were used to collect samples for determination of OC and EC mass (see above). The filters were heated in air for at least three hours at approximately 900 degrees Centigrade (°C) prior to use. Pre-acceptance testing was performed on each lot of filters. Filters with levels exceeding 1.5 micrograms per square centimeter ( $\mu$ g/cm<sup>2</sup>) of OC and 0.5  $\mu$ g/cm<sup>2</sup> of

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EC were refired or rejected. Pre-fired filters were sealed and stored in a freezer prior to preparation for field sampling.

The thermal/optical reflectance (TOR) method was used to determine OC and EC on the quartz filters. The TOR method is based on the principle that different types of carbon-containing particles are converted to gases under different temperature and oxidation conditions. The TOR carbon analyzer consists of a thermal system, an FID and an optical system. Carbon evolved from the sample is converted and measured as methane by the FID. Reflected light is continuously monitored throughout the analysis cycle. The negative change in reflectance is proportional to the degree of pyrolytic conversion of carbon that takes place during OC analysis. After  $O_2$  is introduced, the reflectance increases rapidly as the light-absorbing carbon burns off the filter. The carbon measured after the reflectance attains the value it had at the beginning of the analysis cycle is defined as EC.

### Volatile Organic Compounds

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

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

### Semivolatile Organic Compounds

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

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

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

The samples were isotopically spiked, extracted in dichloromethane, and concentrated prior to analysis. Sample extracts were analyzed by the electron impact (EI) gas chromatography/mass spectrometric (GC/MS) technique, using a Hewlett-Packard 5890 gas chromatograph (GC) equipped with a model 7673A Automatic Sampler and interfaced to a model 5970B Mass Selective Detector (MSD). To assist in the unique identification of individual compounds, selected samples were analyzed by combined gas chromatography/Fourier transform infrared/mass spectrometry (GC/IRD/MSD) technique, i.e., using the Fourier transform infrared detector to aid mass spectrometric identification. Quantification of polyaromatic hydrocarbon (PAH), and other compounds of interest, was obtained by multiple ion detection (MID).

### Section 4

## TEST RESULTS

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

# PROCESS OPERATING CONDITIONS

FCCU and CO heater operating conditions are summarized in Table 4-2. The FCCU feed rate ranged from approximately 93 to 95 percent of full capacity during the tests. During particulate tests (July 27, 28 and 29), coke burn rate averaged 355 tons per day, and CO and O<sub>2</sub> concentration in the regenerator off gas averaged 5.45 percent and 0.05 percent, respectively. CO heater fuel gas firing rate was approximately 115 million British thermal units per hour (MMBtu/hour) during these tests (based on typical fuel gas gross heating value of approximately 1080 British thermal units per standard cubic foot (Btu/scf), determined from previous tests at the refinery). The FCCU, CO heater and ESP were operating normally during the tests; no upsets or unusual conditions were noted. Sootblowing in the CO heater convective section was intentionally suspended during Run 1 to assess the contribution of sootblowing.

The average measured emission rates (lb/hr) during each test were converted to emission factors in pounds per thousand pounds of coke burned (lb/1000 lb coke burned) by dividing the emission rate by the average coke burn rate for each test.

### PRELIMINARY TEST RESULTS

Preliminary tests were conducted to establish a single point in the stack for sample collection. The O<sub>2</sub> concentration profile was measured by traversing the CEMS probe across the stack,

# Table 4-1. Detection Limits for Target Compounds.

	Dilution	In-stack	· · · · · · · · · · · · · · · · · · ·	Dilution	In-stack	· · · · · · · · · · · · · · · · · · ·	Dilution	In-stack		Dilution	In-stack
	Tunnel	methods	1 1	Tunnel	methods		Tunnel	methods		Tunnel	methods
Substance	mg/dscm	mg/dscm	Substance	mg/dscm	mg/dscm	Substance	mg/dscm	mg/dscm	Substance	mg/dscm	mg/dscm
Total PM mass	· '	2.6E-04	Sr	2.7E-05		2-methylnaphthalene	3.3E-06	2.1E-06	Benzo(ghi)perylene	3.2E-07	5.3E-07
PM10 mass	i '	2.6E-04	1 Ti	7.1E-05	'	2-methylphenanthrene	1.1E-07	1.1E-06	Benzonaphthothiophene	1.1E-07	4.2E-06
PM2.5 mass	2.4E-05	2.6E-04	TI	6.1E-05	'	2-phenylnaphthalene	5.3E-08	2.1E-06	Bibenzene	1.3E-04	1.3E-05
Ag	2.9E-04	[ <u> </u>	U	5.6E-05	'	3,6-dimethylphenanthrene	2.5E-06	2.1E-06	Biphenyl	3.6E-06	2.1E-06
Al	2.4E-04	1 !	l v	6.1E-05	'	3-methylbiphenyl	1.2E-05	9.5E-06	B-MePy/MeFl	5.3E-08	1.6E-06
As	3.9E-05	1 !	Y	3.2E-05	'	4H-cyclopenta(def)phenanthrene	0.0E+00	1.6E-06	B-methylfluorene	3.5E-06	3.1E-05
Au	7.5E-05	1 !	Zn	2.7E-05	'	4-methylbiphenyl	1.0E-06	1.6E-06	B-methylphenanthrene	5.8E-07	1.1E-06
Ba	1.3E-03	1 !	Zr	4.1E-05	'	4-methylpyrene	1.1E-07	1.6E-06	B-trimethylnaphthalene	5.3E-08	3.2E-06
Br	2.4E-05	1 !	SO4=	3.7E-05	· · · ·	5+6-methylchrysene	0.0E+00	3.5E-05	C-dimethylphenanthrene	1.8E-06	2.1E-06
Ca	1.1E-04	1 1	NO3-	3.7E-05	'	7-methylbenz(a)anthracene	3.3E-07	2.1E-06	Cholestane	1.4E-05	1.3E-04
Cd	2.9E-04	1 1	NH4+	3.7E-05	'	7-methylbenzo(a)pyrene	3.7E-07	1.3E-04	Chrysene	1.1E-07	2.1E-06
Cl	2.4E-04	1 !	Cl-	3.7E-05	'	9,10-dihydrobenzo(a)pyrene	1.6E-07	5.3E-07	C-methylphenanthrene	1.5E-06	1.1E-06
Co	2.1E-05	1 !	OC	2.8E-04	3.0E-03	9-anthraldehyde	1.4E-06	4.2E-06	Coronene	3.2E-07	5.3E-07
Cr	4.6E-05	1 1	EC	6.3E-05	6.9E-04	9-fluorenone	7.1E-06	1.6E-06	C-trimethylnaphthalene	4.2E-07	4.2E-06
Cu	2.7E-05	1 !	1,2,8-trimethylnaphthalene	3.2E-07	5.3E-07	9-methylanthracene	2.4E-06	2.1E-06	D-dimethylphenanthrene	1.6E-06	2.1E-06
Fe	3.7E-05	1 !	1,2-dimethylnaphthalene	3.7E-06	9.5E-06	Acenaphthene	1.4E-06	1.6E-06	Dibenz(ah+ac)anthracene	3.2E-07	5.3E-07
Ga	4.6E-05	1 1	1,3+1,6+1,7-dimethylnaphthalene	1.2E-05	2.7E-06	Acenaphthenequinone	3.2E-07	3.7E-06	Dibenzofuran	3.3E-06	1.1E-06
Hg	6.3E-05	1 !	1,4,5-trimethylnaphthalene	5.0E-06	2.1E-06	Acenaphthylene	5.5E-06	2.7E-06	D-MePy/MeFl	5.3E-08	1.6E-06
In	3.2E-04	1 1	1,4+1,5+2,3-dimethylnaphthalene	5.4E-06	2.7E-06	A-dimethylphenanthrene	2.5E-06	2.1E-06	E-dimethylphenanthrene	8.0E-07	2.1E-06
K	1.5E-04	1 1	1,4-chrysenequinone	2.7E-07	5.3E-07	A-methylfluorene	5.6E-06	4.2E-06	E-MePy/MeFl	5.3E-08	1.6E-06
La	1.5E-03	1 1	1,7-dimethylphenanthrene	1.8E-06	2.1E-06	A-methylphenanthrene	2.5E-06	1.1E-06	E-trimethylnaphthalene	5.3E-08	4.2E-06
Mg	0.0E+00	1 !	1,8-dimethylnaphthalene	3.7E-06	9.5E-06	A-methylpyrene	5.3E-08	1.6E-06	Fluoranthene	1.1E-07	2.1E-06
Mn	3.9E-05	1 !	1+2-ethylnaphthalene	6.8E-06	2.1E-06	Anthracene	0.0E+00	6.4E-06	Fluorene	6.4E-06	5.3E-06
Mo	6.6E-05	1 !	1-ethyl-2-methylnaphthalene	1.1E-07	1.6E-06	Anthraquinone	2.9E-06	9.5E-06	F-trimethylnaphthalene	5.0E-08	4.2E-06
Na	0.0E+00	1 !	1-MeFl+C-MePy/Fl	8.5E-07	4.2E-06	Anthrone	5.3E-08	5.3E-07	Indeno[123-cd]pyrene	3.2E-07	5.3E-07
Ni	2.2E-05	1 !	1-methylfluorene	3.5E-06	3.1E-05	A-trimethylnaphthalene	1.0E-07	5.1E-05	J-trimethylnaphthalene	4.3E-07	2.1E-06
Р	1.4E-04	1 !	1-methylnaphthalene	2.0E-06	2.1E-06	B-dimethylphenanthrene	1.8E-06	2.1E-06	Naphthalene	5.1E-05	2.1E-06
Pb	7.3E-05	1 !	1-methylphenanthrene	1.2E-06	5.3E-07	Benz(a)anthracene	3.2E-07	2.1E-06	Perinaphthenone	5.2E-05	1.1E-06
Pd	2.7E-04	1 !	1-methylpyrene	4.2E-07	1.6E-06	Benz(a)anthracene-7,12	2.0E-06	5.3E-07	Perylene	1.1E-07	5.8E-06
Rb	2.4E-05	1 - 1	1-phenylnaphthalene	2.7E-07	5.0E-05	Benzanthrone	4.8E-07	3.7E-06	Phenanthrene	4.2E-07	1.2E-05
S	1.2E-04	1 - 1	2,3,5+I-trimethylnaphthalene	1.6E-07	1.6E-06	Benzo(a)pyrene	3.2E-07	1.6E-06	Pyrene	2.1E-07	4.2E-06
Sb	4.4E-04	1 - 1	2,4,5-trimethylnaphthalene	4.2E-07	5.3E-07	Benzo(b)chrysene	1.1E-07	5.3E-07	Retene	3.2E-06	4.2E-06
Se	2.9E-05	1 - 1	2,6+2,7-dimethylnaphthalene	5.7E-06	2.7E-06	Benzo(b+j+k)fluoranthene	5.3E-08	1.6E-06	Xanthone	2.1E-07	1.5E-05
Si	1.5E-04	!	2-ethyl-1-methylnaphthalene	8.8E-06	4.2E-06	Benzo(c)phenanthrene	5.8E-07	5.3E-07	Volatile Organic Compounds	3.0E-02	
Sn	4.1E-04	<u> </u>	2-methylbiphenyl	8.4E-06	9.5E-06	Benzo(e)pyrene	3.3E-07	5.8E-06	NO, CO		1.3E+00
									SO <sub>2</sub>		2.9E+00

	1100035 L			<i>ite 11)</i> .
Parameter	Monitoring Station	Units		
Date			22-Jul-98	23-Jul-98
Feed Flow Rate	M1	Mbbl/day	45.0	45.0
Coke Burn Rate	M2	tons/day	351	346
Catalyst Recirculation Rate		tons/min	26.7	27.5
Stripping Steam Flow		Mlb/hr		
Regenerator Outlet O2	M3	Vol%	0.05	0.06
Regenerator Outlet CO	M3	Vol%	4.94	5.18
Regenerator Bed Temperature	M2	°F	1298	1291

M2

M4

M5

M5

M6

M7

M8

M8

psig

Mscfm

Mscfm

kV

Amps

MMscfd

Vol%

°F

°F

9.38

65.9

3.10

---

Regenerator Pressure

Regenerator Air Flow Rate

CO Heater Fuel Gas Flow

CO Heater Stack Gas Oxygen

CO Heater Firebox, N. Side

CO Heater Firebox, S. Side

Regenerator Air O2 Enrichment Rate

Electrostatic Precipitator, Voltage

Electrostatic Precipitator, Current

Table 4-2. FCCU Process Data (Refinery	<sup>v</sup> Site A).
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while simultaneously measuring  $O_2$  with a second system at a single point in the stack. The data from the second system were used to correct the spatial traverse results for temporal variations. The point-to-point deviation from the mean concentration was determined to be less than 10 percent (Table 4-3). Under the conditions of these tests, the majority of particles in the flue gas are expected to behave approximately like a gas (i.e., the Stokes number for particles smaller than about 100 microns is low enough that the particles should follow gas streamlines). It is assumed that the magnitude of any fine particle concentration profile that may have existed is similar to the  $O_2$  concentration profile. Therefore, the center of the stack was selected as the single point for sample collection. A velocity profile was developed by traversing the stack with a Pitot probe. The resulting velocity profile was used to correct the velocities measured at the center during sampling to the overall stack average velocity.

Value

26-Jul-98

43.8

362

28.0

0.06

5.31

1288

9.42

66.5

2.89

---

27-Jul-98

44.0

358

28.2

91.2

0.06

5.64

1278

9.41

66.2

2.86

139

191

2.59

1.60

1754

1428

28-Jul-98

44.0

356

27.9

88.4

0.05

5.71

1278

9.40

66.1

2.85

132

195

2.43

1.64

1741

1383

29-Jul-98

44.0

351 27.2

84.6

0.05

5.01

1286

9.36

65.0

3.11

110

190

2.61

1.66

1712

1350

25-Jul-98

43.6

364

28.2

0.05

5.47

1288

9.41

66.4

2.91

24-Jul-98

44.0

366

28.6

82.7

0.06

5.71

1284

9.41

66.0

3.17

---

2.08

1.71

1693

1325

9.40

65.7

3.13

---

### STACK CONDITIONS AND FLOW RATE

The average stack gas temperature during particulate tests (July 27, 28 and 29) was 580 to 590°F (Table 4-4). The  $O_2$  concentration at the stack was 1.5 to 1.8 percent (dry basis) during the tests. The stack gas moisture content averaged 17 to 18 percent. The measured stack gas flow rate was very stable from day to day, ranging from 108,000 to 115,000 dry standard cubic feet per minute (dscfm) during the particulate tests. The stack gas flow rate during controlled condensation tests

	24-Jul-98					
	Ref point:	Point 4 of Port 1				
Port	Traverse	Distance from the	Sampling Time	O <sub>2</sub> CEMS Conc.	O <sub>2</sub> ref Conc.	Normalized
	Point	stack wall (inches)	(hhmm)	(%)*	(%)**	$O_2 (\%)^{***}$
1	4	40.5	8:30	1.42	1.48	1.36
	3	24.3	8:34	1.45	1.50	1.37
	2	13.2	8:38	1.53	1.59	1.37
	1	4	8:42	1.57	1.63	1.37
2	4	40.5	8:50	1.58	1.60	1.40
	3	24.3	8:54	1.53	1.58	1.38
	2	13.2	8:58	1.41	1.43	1.40
	1	4	9:02	1.10	1.17	1.34
3	4	40.5	9:11	1.89	1.90	1.41
	3	24.3	9:15	1.89	1.87	1.44
	2	13.2	9:19	1.80	1.82	1.40
	1	4	9:23	1.78	1.76	1.44
4	4	40.5	9:31	1.65	1.60	1.46
	3	24.3	9:35	1.60	1.56	1.46
	2	13.2	9:39	1.56	1.54	1.44
	1	4	9:43	1.64	1.60	1.46
			Maximum	1.89	1.90	1.46
			Minimum	1.10	1.17	1.34
			Average	1.59	1.60	1.41
			Stratification	0.50	0.46	9.20%

Table 4-3. Stratification Test Results for FCCU (Refinery Site A).

\* this probe was traversed

\*\* this probe remained stationary

\*\*\*traverse  $O_2$  normalized for variations in  $O_2$  measured by stationary probe

Table 4-4. Stack Summary for FCCU (Refinery Site A).

	Stack								
Date	Temperature	O <sub>2</sub>	CO <sub>2</sub>	Moisture	Veloc	ity		Flow Rate	
Units	°F	%v, dry	%v, dry	%v	ft/sec	m/sec	acfm	dscfm	dscmm
21-Jul-98	577				52.3	15.9	269,440	111,252	3,151
21-Jul-98	580				52	16	269,000	111,000	3,200
22-Jul-98	564			17.4	50.5	15.4	260,420	109,148	3,091
22-Jul-98	560			20	51	15	260,000	109,000	3,100
24-Jul-98	574	1.68	18.2	16.8				* 111,412	* 3,155
24-Jul-98	570	1.7	18	17				* 111,000	* 3,200
27-Jul-98	588	1.50	18.2	17.3	54.5	16.6	280,702	114,913	3,254
27-Jul-98	590	1.5	18	17	54	17	281,000	115,000	3,300
28-Jul-98	586	1.54	19.2	17.2	54.2	16.5	280,863	113,972	3,228
28-Jul-98	590	1.5	19	17	54	17	281,000	114,000	3,200
29-Jul-98	583	1.75	18.5	18.5	51.8	15.8	270,168	107,776	3,052
29-Jul-98	580	1.8	19	18	52	16	270,000	108,000	3,100

\* Average flow rate from all runs at the FCCU.

on July 24 was not measured. Therefore, the flow rate was estimated by averaging the results of all runs.

### CO, NO<sub>x</sub> AND SO<sub>2</sub> EMISSIONS

 $NO_X$  and  $SO_2$  are precursors of secondary particulate matter. Average  $NO_X$  and  $SO_2$  concentrations (corrected to 3 percent  $O_2$ , dry basis) were 134-157 parts per million by volume (ppmv) and 557-806 ppmv, respectively, corrected to 3 percent  $O_2$  and dry basis (Table 4-5). The  $NO_X$  concentration is higher than would be expected from natural gas combustion most likely due to the oxidation of gaseous fixed nitrogen species (e.g., NO, NH<sub>3</sub>, hydrogen cyanide) evolved from nitrogen in the coke during catalyst regeneration.  $SO_2$  emissions reflect the sulfur content of heavy feed to the FCCU.  $SO_2$  emissions varied considerably from run. This was caused by changes in FCCU feed from day to day due to other process variations within the refinery.

CO is an indicator of combustion efficiency and regenerator offgas destruction efficiency within the CO heater. CO concentration was low during all tests, indicating excellent combustion and destruction efficiency, with average test results ranging from approximately 0 to 4 ppmv (corrected to 3 percent  $O_2$ , dry basis).

				CO			NOX		SO <sub>2</sub>			
Date	Run No.	Time Period	O <sub>2</sub> (%)	ppm (dry, as measured)	ppm (dry, 3% O <sub>2</sub> )	kg/hr	ppm (dry, as measured)	ppm (dry, 3% O <sub>2</sub> )	kg/hr	ppm (dry, as measured)	ppm (dry, 3% O <sub>2</sub> )	kg/hr
	SO3 by CCS - Run 1	11:25-12:25	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
7/24/98	SO3 by CCS - Run 2	13:20-14:20	1.51	2.83	2.61	0.63	150	138	54	878	811	440
	SO3 by CCS - Run 3	15:05-16:05	1.84	0.51	0.48	0.11	164	154	60	858	806	430
7/27/98	M201/202- Run 1	11:35-17:34	1.50	4.31	3.98	0.99	146	134	55	603	557	320
	Cascade- Run 1	13:15-15-15	1.40	0.97	0.89	0.22	171	157	65	764	701	400
7/28/98	M201/202- Run 2	09:17-14:15	1.54	0	0	0	170	157	62	794	734	400
	Cascade- Run 2	10:35-12:05	1.37	0	0	0	167	153	65	796	730	430
7/29/98	M201/202- Run 3	10:10-15-10	1.75	3.05	2.85	0.65	143	134	50	706	660	340
	Cascade- Run 3	10:55-12:10	1.78	2.80	2.62	0.62	147	138	54	701	657	360

Table 4-5. NO<sub>X</sub>, SO<sub>2</sub> and CO Test Results for FCCU (Refinery Site A).

n/a - data not available

### IN-STACK AND IMPINGER METHOD RESULTS

### Particulate Mass

Total filterable particulate mass (FPM), which includes all particulate collected in the in-stack nozzle/cyclones assembly and on the in-stack filter; ranged from 29 to 44 milligrams per dry standard cubic meter (mg/dscm), with an average of 36 mg/dscm (Table 4-6). The results are corrected for acetone blanks (see Section 3), which were insignificant compared to the uncorrected sample results. The result for Run 1 is approximately 26 percent lower than the average of those for Runs 2 and 3 (although the difference does not lie outside the 95 percent confidence interval of the Run 2/Run 3 results and hence the difference is not statistically significant). This could indicate the effect of sootblower operation in the convective pass of the CO heater to control the buildup of catalyst fines on heat transfer surfaces. Sootblowing was intentionally suspended for Run 1 so that particulate emissions due to sootblowing could be assessed. Since sootblower operating cycles are generally left somewhat to the discretion of the operating staff, these results enable emissions for different sootblowing cycles to be estimated.

Parameter	Parameter Units			Value						
Run Number	-	1	2	3						
Date	-	27-Jul-98	28-Jul-98	29-Jul-98	Average	RSD				
Gas Temperature	°F	581	579	572	577	1%				
Isokinetic	%	92	97	103	97	6%				
Total FPM	mg/dscm	29	44	35	36	20%				
	lb/hr	13	18	14	15	18%				
FPM <10 μm	mg/dscm	27	42	32	34	22%				
	lb/hr	12	17	13	14	20%				
	% of total	92	95	92	93	2%				
FPM <2.5 μm	mg/dscm	25	39	30	31	22%				
	lb/hr	11	16	12	13	19%				
	% of total	87	89	85	87	2%				

Table 4-6. Filterable Particulate Matter (Method 201A) for FCCU (Refinery Site A).

RSD- Relative standard deviation

FPM smaller than  $10 \,\mu\text{m}$  - i.e., filterable PM10 or FPM10 - includes the portion of FPM collected downstream of the PM10 cyclone. FPM10 ranges from 27 to 42 mg/dscm with an

average of 34 mg/dscm. Comparing these results to the total FPM results shows that 91 to 95 percent of the total FPM is smaller than 10  $\mu$ m. Run 1 results are lower than Run 2 and Run 3 results by approximately the same proportion as total FPM results.

FPM2.5 includes the portion of FPM collected downstream of the PM2.5 cyclone. FPM2.5 ranges from 25-39 mg/dscm (average 30 mg/dscm) and is lower for Run 1 than Runs 2 and 3. Comparing these results to the total FPM results shows that 86 to 89 percent of the total FPM is smaller than 2.5  $\mu$ m.

Condensable particulate matter (CPM), as measured by EPA Method 202, ranged from 6.3 to 85 mg/dscm with an average of 37 mg/dscm (Table 4-7). The mass of CPM accounts for 51 percent of total FPM and 54 percent of FPM2.5, on average. The variation from run to run was significant, with a relative standard deviation about the mean of 111 percent. Effectively, all of the CPM is contained in the inorganic fraction. On average,  $SO_4^{=}$  and Cl<sup>-</sup> (as ammonium salts, which is the form most likely to be present in the analytical residue since ammonium hydroxide is added during sample analysis) can account for 38 percent of the inorganic CPM. Most of this fraction is sulfate. The individual run results are highly variable; for example,  $SO_4^{=}$  mass (as ammonium sulfate) exceeds inorganic CPM mass in Run 1 by nearly a factor of two,, and in Run 3 accounts for only 18 percent of the inorganic CPM. Cl<sup>-</sup> trends similarly to inorganic CPM, i.e., Cl<sup>-</sup> is 11 times higher in Run 3 compared to Run 1, while inorganic CPM is 13 times higher in Run 3 compared to Run 1. This suggests the possibility of a relationship between CPM and chlorides; however, the amount of Cl<sup>-</sup> is only 3 percent of total inorganic CPM. The variability of the CPM data can be attributed to the inorganic fraction, but the source of the variation is not readily explained by variation in SO<sub>4</sub><sup>=</sup> and Cl<sup>-</sup> results from the Method 202 train.

### Particle Size Distribution

Particle size distribution was measured using cooled and hot cascade impactors. The difference in mass between the two impactor sets is intended to indicate  $H_2SO_4$  mist since the cooled impactor is below the  $H_2SO_4$  dew point and the hot one is above the  $H_2SO_4$  decomposition temperature. The total particulate mass concentration in the cooled impactors was 3 to 87

Parameter	Units			Value		
Run Number	-	1	2	3		
Date	-	27-Jul-98	28-Jul-98	29-Jul-98	Average	RSD
	mg	26	80	326	144	111%
Inorganic CPM	mg/dscm	6.7	21	85	38	111%
	lb/hr	3.0	8.6	34	15	109%
	mg	0.5	2.1	1	1	62%
Organic CPM	mg/dscm	0.13	0.56	0.34	0.34	62%
	lb/hr	0.06	0.23	0.13	0.14	60%
Dichloromethane Recovery Blank	mg			1.1		
Water Recovery Blank	mg			1.3		
Sulfate $(SO_4^{=})$	mg/dscm	9.7	10	9.3	9.8	6%
	lb/hr	4.2	4.3	3.7	4.1	8%
Chloride (Cl <sup>-</sup> )	mg/dscm	0.13	0.34	1.5	0.64	111%
	lb/hr	0.06	0.14	0.58	0.26	108%
Total CPM	mg/dscm	6.3	21	85	37	111%
(corrected for $NH_4^+$ and $H_2O$ )	lb/hr	2.8	8.6	34	15	109%
Total Particulate (CPM)	mg/dscm	35	65	119	73	58%
	lb/hr	16	26	47	30	55%
PM10 (including CPM)	mg/dscm	33	63	116	71	60%
	lb/hr	15	26	46	29	56%
PM2.5 (including CPM)	mg/dscm	32	60	114	69	61%
	lb/hr	14	24	45	28	58%

Table 4-7. Condensable Particulate Emissions for FCCU (Refinery Site A).

RSD-relative standard deviation

percent higher than for the hot impactors, with an average difference of 35 percent (Tables 4-8 and 4-9). The results of the third hot impactor run are skewed by a large catch in the preimpactor. This appears to indicate a problem with the measurement, although no error in the sampling or analysis procedures could be traced. If the average preimpactor catch from Runs 1 and 2 are substituted for Run 3, the overall results are much more consistent and the average total particulate concentration is in fair agreement with the Method 201A results (48 mg/dscm versus 36 mg/dscm). The average total particulate mass loading in the cooled impactor set compares favorably to the sum of the Method 201A and Method 202 results (68 mg/dscm versus 73 mg/dscm). It should be noted that the cascade impactor results are based on much shorter sampling times than the Method 201A/202 results (two hours compared to six hours), and this could contribute to the inconsistency between the methods especially considering the large variability in run to run results.

For the cooled impactors, 91 percent of the particle mass is smaller than 10  $\mu$ m and 64 percent is smaller than 2.5  $\mu$ m, on average. 85 percent of the particle mass is smaller than 10  $\mu$ m and 66 percent is smaller than 2.5  $\mu$ m, on average, in the hot impactors. If the average of the Run 1 and 2 preimpactor catches is substituted for the anomalous result in Run 3, the PM10 and PM2.5 fractions in the hot impactor are 93 and 72 percent, respectively (Figure 4-1). A significant increase in the mass of particles smaller than 1  $\mu$ m is apparent for the cooled impactors, which is consistent with condensation of H<sub>2</sub>SO<sub>4</sub> on the very fine particles that comprise most of the particle surface area and nucleation of ultrafine particles.

The particle volume distributions indicate a distinctly bimodal size distribution in the cooled impactor data (Figure 4-2), with the majority of the particle volume accounted for in the less than 2.5- $\mu$ m range. This could be explained by agglomeration of small particles in the less than 2.5  $\mu$ m range to form larger particles in the second mode above 10  $\mu$ m, since condensation of H<sub>2</sub>SO<sub>4</sub> on the surface of particles will increase their "stickiness." The majority of particle volume in the hot cascade impactors is in the under 1- $\mu$ m range, and a more pronounced drop off in the volume of larger diameter particles.

### OC, EC, and SVOCs (In-Stack Filters)

OC and EC measured on the in-stack filters (Table 4-10) were present at very low concentrations. Carbon on the in-stack filters represents an insignificant amount of the total FPM measured on in-stack filters (presented earlier in Table 4-6). Several SVOCs were detected but at very low concentrations (Table 4-11). Of these, most were detected in only one of the three tests. Cholestane is the most abundant substance identified on the in-stack filters, with an average concentration of  $2.0 \times 10^{-4}$  mg/dscm. Bibezene is the second most abundant, with an average concentration of  $9.5 \times 10^{-5}$  mg/dscm. Naphthalene is the only SVOC measured at a concentration more than a factor of 10 above detection limits (in two runs) and the only SVOC detected in all three tests.

Table 4-8. Particle Size Distribution from the Cooled Cascade Impactor at FCCU (Refinery Site A).

Run 1		61.2 mg/dscm	27-Jul-98
Impactor Temp.:	186°F		
		Net	Cumulative
Stage Number	d50	Weight	percent < d50
	(µm)	(mg)	(%)
Preimpactor	14.8	0.20	
0	14.8	2.23	95.8
1	10.0	1.55	93.2
2	6.8	1.53	90.6
3	4.7	1.11	88.7
4	3.0	5.17	79.8
5	1.51	14.34	55.3
6	0.93	5.87	45.3
7	0.64	2.97	40.2
Back up Filter		23.48	
	TOTAL	58.45	

Run 2		77.6 mg/dscm	28-Jul-98	
Impactor Temp.: 1	83°F			
		Net	Cumulative	
Stage Number	d50	Weight	percent < d50	
	(µm)	(mg)	(%)	
Preimpactor	14.8	0.1		
0	14.8	3.78	93.0	
1	10.1	2.21	89.0	
2	6.8	2.45	84.6	
3	4.7	2.04	80.9	
4	3.0	4.89	72.1	
5	1.51	12.53	49.4	
6	0.93	5.44	39.6	
7	0.64	3.97	32.4	
Back up Filter		17.95		
	TOTAL	55.36		

Run 3		65.8 mg/dscm	29-Jul-98
Impactor Temp.:	211°F		
		Net	Cumulative
Stage Number	d50	Weight	percent < d50
	(µm)	(mg)	(%)
Preimpactor	14.8	1.4	
0	14.8	1.73	91.9
1	10.0	0.84	89.7
2	6.8	1.7	85.3
3	4.6	1.16	82.3
4	3.0	4.57	70.4
5	1.50	14.3	33.4
6	0.93	3.97	23.1
7	0.64	2.17	17.4
Back up Filter		6.72	
	TOTAL	38.56	

(1) d50 of preimpactor is used for Stage 0.

Run 1		53.8 mg/dscm	27-Jul-98
Impactor Temr	o.: 593°F	U	
		Net	Cumulative
Stage Number	d50	Weight	percent < d50
0	(µm)	(mg)	(%)
Preimpactor	13.8	2.2	
0	13.8	0.98	93.6
1	9.1	0.86	91.9
2	6.2	1.63	88.6
3	4.2	2.08	84.5
4	2.7	3.88	76.7
5	1.36	7.84	61.0
6	0.85	8.44	44.1
7	0.58	6.28	31.6
Back up Filter		15.76	
^	TOTAL	49.95	
Run 2		41.5 mg/dscm	28-Jul-98
Impactor Temr	.: 586⁰F		20 0 41 90
impuetor remp		Net	Cumulative
Stage Number	d50	Weight	percent < d50
Stuge Humber	(IIm)	(mg)	(%)
Preimpactor	13.6	0.2	
0	13.6	1.08	95 7
1	9.0	1.00	91.5
2	61	1.17	87.5
3	4.2	13	83.2
4	2.7	3.09	72.7
5	1 34	7.22	48.4
6	0.84	6.93	25.1
7	0.57	476	9.0
, Back up Filter		2.68	
Buck up I liter	TOTAL	29.68	
		(2.0. /1	a 20 J 1 00
Run 3		63.8 mg/dscm	29-Jul-98
Impactor Temp	b.: 582°F		<u> </u>
	150	Net	Cumulative
Stage Number	d50	Weight	percent < d50
	(µm)	(mg)	(%)
Preimpactor	13.9	10.3	
0	13.9	-0.05	71.5
1	9.2	0.38	70.5
2	6.3	0.7	68.5
3	4.3	0.77	66.4
4	2.8	3.13	57.7
5	1.38	6.94	38.5
6	0.86	7.74	17.0
7	0.58	4.87	3.4
Back up Filter		1.24	
	TOTAL	36.02	1

Table 4-9. Particle Size Distribution for the Hot Cascade Impactor at FCCU (Refinery Site A).

\*Preimpactor d50 used for Stage 0.



Figure 4-1. In-Stack Particle Size Distribution for FCCU (Refinery Site A).

4-12

-^....



Figure 4-2. ParticleVolume Distribution for FCCU (Refinery Site A).

Parameter	Units				Average	RSD
Run Number	-	1	2	3		
Date	-	27-Jul-98	28-Jul-98	29-Jul-98		
Organic	mg/dscm	1.2E-2	1.1E-2	8.5E-3	1.0E-2	18%
Carbon	lb/hr	5.4E-3	4.3E-3	3.4E-3	4.4E-3	23%
Elemental	mg/dscm	3.7E-3	1.7E-3	1.3E-3	2.2E-3	59%
Carbon	lb/hr	1.6E-3	7.0E-4	5.1E-4	9.5E-4	64%

Table 4-10. Organic and Elemental Carbon Results for the FCCU (Refinery Site A), as Measured on the In-Stack Filter (Method 201A).

RSD- Relative standard deviation

Table 4-11. SVOC Results for Method 201A Filters at the FCCU (Refinery Site A) (mg/dscm).

				Average	RSD	MDL
Run Number	1	2	3			
Date	27-Jul-98	28-Jul-98	29-Jul-98			
1,4-chrysenequinone	ND	1.59E-06	1.039E-06	1.32E-6	30%	5.30E-7
1-ethyl-2-methylnaphthalene	6.43E-6	ND	ND	6.43E-6	n/a	1.59E-6
2,6+2,7-dimethylnaphthalene	6.97E-6	ND	ND	6.97E-6	n/a	2.65E-6
2-methylphenanthrene	2.41E-6	ND	ND	2.41E-6	n/a	1.06E-6
4-methylbiphenyl	3.22E-6	ND	ND	3.22E-6	n/a	1.59E-6
9,10-dihydrobenzo(a)pyrene	ND	5.31E-07	ND	5.31E-7	n/a	5.30E-7
A-methylfluorene	6.17E-6	ND	ND	6.17E-6	n/a	4.24E-6
A-methylpyrene	7.51E-6	ND	3.377E-06	5.44E-6	54%	1.59E-6
Benz(a)anthracene-7,12	5.36E-7	ND	ND	5.36E-7	n/a	5.30E-7
Benzo(a)pyrene	3.75E-6	ND	ND	3.75E-6	n/a	1.59E-6
Benzo(b)chrysene	5.36E-7	7.96E-07	ND	6.66E-7	28%	5.30E-7
Benzo(c)phenanthrene	5.36E-7	ND	ND	5.36E-7	n/a	5.30E-7
Bibenzene	ND	ND	9.533E-05	9.53E-5	n/a	1.33E-5
Biphenyl	8.04E-6	3.18E-06	ND	5.61E-6	61%	2.12E-6
Cholestane	ND	1.41E-04	2.60E-04	2.00E-4	42%	1.30E-4
Dibenzofuran	4.56E-6	1.33E-06	ND	2.94E-6	78%	1.06E-6
Naphthalene	3.03E-5	3.34E-05	1.507E-05	2.63E-5	37%	2.12E-6
Perinaphthenone	1.26E-5	1.33E-06	ND	6.96E-6	114%	1.06E-6

MDL- Method detection limit

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

ND- not detected

RSD- Relative standard deviation

### SO3 and NH3

 $SO_3$  and  $NH_3$  are secondary particle precursors.  $SO_3$  was measured at an average concentration of 25 ppmv in the stack (Table 4-12). The  $SO_3$  concentration represents approximately 2.9 percent of the  $SO_2$  concentration.  $SO_3$  combines with water to form  $H_2SO_4$  at stack gas temperature below the  $H_2SO_4$  dew point. For the conditions of these tests, the  $H_2SO_4$  dew point is estimated to be approximately  $311^{\circ}F$ . The mass flow rate of  $SO_3$  expressed as  $H_2SO_4$ averaged 41 lb/hr. This is very close to the average CPM emission rate of 38 lb/hr presented earlier in Table 4-7.  $NH_3$  averaged approximately 0.4 ppmv and the mass emission rate was insignificant (Table 4-13). Note the  $NH_3$  flue gas conditioning system for the ESP was not operated during these tests. Higher  $NH_3$  emissions may occur when the system is operated.

Table 4-12. Controlled Condensation Train Results for the FCCU (Refinery Site A).

Parameter	Units	Value							
Run Number	-	1	2	3					
Date	-	24-Jul-98	24-Jul-98	24-Jul-98	Average	RSD (%)			
SO <sub>3</sub>	ppmv	29	29	16	25	32%			
SO <sub>3</sub>	lb/hr	41	40	22	34	31%			
$SO_3$ (as $H_2SO_4$ )	lb/hr	49	48	26	41	31%			

RSD = standard deviation

Table 4-13. EPA Method 206 Ammonia Train Results for the FCCU (Refinery Site A).

	Units				Average	RSD
Run Number	-	1	2	3		
Date	-	22-Jul-98	22-Jul-98	22-Jul-98		
Impinger catch (dry basis):						
Ammonium (as NH <sub>4</sub> )	mg/dscm	0.35	0.30	0.18	0.28	31%
Ammonium (as NH <sub>4</sub> )	lb/hr	0.14	0.12	0.08	0.11	29%
Ammonia concentration in stack gas	ppmv	0.46	0.41	0.24	0.37	31%

RSD- Relative standard deviation

# DILUTION TUNNEL RESULTS

# Particulate Mass

The dilution tunnel used for these tests is designed to characterize only fine particles. PM2.5 mass averaged 7.8 mg/dscm during these tests, with a relative standard deviation of 20 percent

(Table 4-14). This is approximately 11 percent of the sum of FPM2.5 and CPM measured using the in-stack methods and 25 percent of the FPM2.5 alone. Lower CPM in the dilution tunnel is expected due to the effect of dilution on the aerosol formation rate.

	Units				Average	RSD	
Run Number	-	1	2	3			Ambient
Date	-	27-Jul-98	28-Jul-98	29-Jul-98			
PM2.5	mg/dscm	6.5	7.4	9.5	7.8	20%	2.0E-2
	lb/hr	2.8	3.1	3.8	3.3	16%	n/a

Table 4-14. Dilution Tunnel PM2.5 Results for the FCCU (Refinery Site A).

n/a- not applicable

RSD- Relative standard deviation

In Run 1, two parameters were intentionally changed: CO heater sootblowing was suspended during testing; and dilution ratio in the dilution tunnel was reduced. Comparing the results in Tables 4-14 and 4-6, the filterable PM2.5 concentrations for Run 1 are lower than the average of Runs 2 and 3 by approximately the same percentage (albeit the difference is not statistically significant in either case). SO<sub>3</sub> by controlled condensation, and hence the majority of true CPM, was relatively constant (at least compared to CPM variability in Table 4-7) from run to run. If the difference between Run 1 and the average of Runs 2 and 3 is assumed to be FPM attributed solely due to sootblowing, then the results could indicate that the variation in dilution ratio had little effect on aerosol condensation in the dilution tunnel. However, any effect of either sootblowing or dilution ratio is difficult to distinguish from the variability of all the results.

The difference between the results in Tables 4-14 and 4-7 also indicates the potential for losses of solid fine particles in the sample probe/dilution tunnel components prior to the filter. In the current version of the dilution tunnel test protocol, recovery of sample from the probe, venturi, walls of the dilution tunnel, residence time chamber and the various transfer lines is not performed because of the difficulty of the task. At the completion of the final test run, the probe venturi was inspected and visible deposits were noted. It was decided to rinse the probe and venturi with acetone. The rinse was dried and analyzed gravimetrically. Using the average of the Method 201A and hot in-stack cascade impactor results to estimate the fraction of the rinse

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attributable to PM2.5, then dividing the result by the total sample volume drawn through the probe for all three runs, yields an average PM2.5 concentration of 6.0 mg/dscm associated with the rinse. This represents 43 percent of the total PM2.5 recovered in the dilution tunnel. The total PM2.5 recovered from the dilution tunnel represents 55 percent of the FPM2.5 measured with the in-stack methods.

The results indicate that further development of the dilution tunnel equipment and procedures is required to assure more reliable mass results for these sample conditions. Future tests on sources with significant filterable particulate should include a procedure for pre-cleaning and recovery of the sample probe and venturi, and possibly other components, for each test run. The impact of particle losses prior to the filter on chemical speciation profiles has not been quantified. Chemical speciation and particle size analysis of the probe rinse also should be considered, especially  $SO_4^{=}$ . To obtain reliable ion results may require the probe/venturi to be rinsed with water initially, with analysis of the water for ions/anions, followed by acetone for the final rinse. Also, heating the probe above the stack temperature may help to reduce thermophoretic deposition of particles in the probe and venturi.

The single ambient air sample yielded a PM2.5 concentration of 0.020 mg/dscm, which is negligible compared to the concentration in the stack.

# $\underline{SO_4^{=}, NO_3^{-}, Cl^{-} and NH_4^{+}}$

The most abundant ion was  $SO_4^=$ , with a mean concentration of 6.8 mg/dscm (Table 4-15). NH<sub>4</sub><sup>+</sup> and Cl<sup>-</sup> were detected at much lower concentrations of 0.063 and 0.014 mg/dscm, respectively. Average NH<sub>4</sub><sup>+</sup> measured with the dilution tunnel was lower than gaseous NH<sub>3</sub> measured by the in-stack method by a factor of approximately four (mole basis). NO<sub>3</sub><sup>-</sup> was below the minimum detection limits in all three runs. The amount of SO<sub>4</sub><sup>=</sup> found on the quartz filters is similar to the total mass of PM2.5 found on the Teflon membrane filters. Sulfate mass, which should be a factor of three higher than elemental sulfur mass, is in poor agreement with elemental sulfur measured on the Teflon membrane filter by XRF (discussed later in this section). This indicates that the sulfate results and/or the PM2.5 mass results may not be reliable. Data and procedures were checked, but no errors were found. The results might be

	Units				Average	RSD	
Run Number	-	1	2	3			Ambient
Date	-	27-Jul-98	28-Jul-98	29-Jul-98			
Sulfate	mg/dscm	7.1	8.1	5.2	6.8	22%	4.4E-3
	lb/hr	3.0	3.5	2.1	2.9	25%	n/a
Nitrate	mg/dscm	ND	ND	ND	ND	n/a	7.6E-4
	lb/hr	ND	ND	ND	ND	n/a	n/a
Chloride	mg/dscm	1.6E-2	1.6E-2	1.1E-2	1.4E-2	21%	ND
	lb/hr	7.1E-3	6.7E-3	4.4E-3	6.0E-3	24%	n/a
Ammonium	mg/dscm	4.7E-2	6.1E-2	8.0E-2	6.3E-2	27%	1.5E-3
	lb/hr	2.0E-2	2.6E-2	3.2E-2	2.6E-2	23%	n/a

Table 4-15. Dilution Tunnel Sulfate, Nitrate, Chloride and Ammonium Results for the FCCU.

n/a- not applicable; only one run above detection limit

ND- not detected

RSD- Relative standard deviation

explained by known artifacts associated with the quartz filters due to high SO<sub>2</sub> concentration in the stack gas (the quartz can catalyze SO<sub>2</sub> oxidation to SO<sub>4</sub><sup>=</sup>). Sulfate results are discussed further in Section 7.

# OC, EC and Organic Species

Total carbon detected on the dilution tunnel filters is dominated by OC, which comprises 90 percent of the total carbon on average (Table 4-16). EC was below detection limits in Runs 2 and 3. OC/EC mass is not significant compared to the total PM2.5 mass. Compared to the instack results, OC/EC results from the dilution tunnel are six times higher. This could reflect condensation of organics on the dilution tunnel filter. However, considering that the concentrations are so low, any significance attached to this difference may not be warranted.

VOCs with carbon number greater than 7 are believed to be secondary organic aerosol precursors. Therefore, the sampling and analytical procedures used in these tests did not include quantification of lower carbon number VOCs such as benzene. Several VOCs were detected at very low concentrations – approximately 0.2 to 17 parts per billion by volume (ppbv) – in at least one of the three test runs (Table 4-17). Butylated hydroxytoluene was the most abundant

	Units				Average	RSD	
Run Number	-	1	2	3			Ambient
Date	-	27-Jul-98	28-Jul-98	29-Jul-98			
Organic	mg/dscm	6.5E-2	6.7E-2	7.8E-2	7.0E-2	10%	1.0E-2
Carbon	lb/hr	2.8E-2	2.9E-2	3.1E-2	2.9E-2	6%	n/a
Elemental	mg/dscm	1.4E-2	ND	ND	1.4E-2	n/a	2.4E-3
Carbon	lb/hr	6.0E-3	ND	ND	6.0E-3	n/a	n/a

Table 4-16. Organic and Elemental Carbon Results for the FCCU (Refinery Site A), as Measured by the Dilution Tunnel.

n/a- not applicable; only one run above detection limit ND- not detected

RSD- Relative standard deviation

VOC, detected in all three runs, with an average concentration of 0.15 mg/dscm (17 ppbv). Benzaldehyde was the second most abundant at  $3.3 \times 10^{-2}$  mg/dscm (7 ppbv). VOCs detected in the stack were higher than in the ambient air sample, but generally within a factor of ten of the ambient concentration.

SVOCs were detected at extremely low levels (Table 4-18), from approximately 0.1 to 2 parts per trillion by volume (pptv). Concentrations of many target substances were near or below the minimum detection limits, defined as 3 times the standard deviation of replicate analysis. Bibenzene was the most abundant substance detected during testing, with an average concentration of  $1.38 \times 10^{-3}$  mg/dscm (approximately 2 pptv), however, the concentration present in the stack sample is approximately equal to the concentration detected in the field blank so this measurement probably does not represent actual emissions. The average concentrations of 1,3+1,6+1,7-dimethylnaphthalene, 1+2-ethylnaphthalene, 1,2-dimethylnaphthalene, 1methylnaphthalene, 2,3,5+I-trimethylnaphthalene, 2,4,5-trimethylnaphthalene, 2,6+2,7dimethylnaphthalene, 2-methylnaphthalene, a-dimethylphenanthrene, e-trimethylnaphthlene, atrimethylnaphthalene in the stack samples are lower than their concentrations in the ambient air.

				Average	RSD	
Run Number	1	2	3			Ambient
Date	27-Jul-98	28-Jul-98	29-Jul-98			17-Jul-98
1,2,4-trimethylbenzene	2.40E-3	4.54E-3	2.83E-3	3.26E-3	35	1.68E-3
1-hexadecene	ND	5.30E-3	ND	5.30E-3	n/a	ND
1-methylnaphthalene	ND	ND	8.30E-4	8.30E-4	n/a	3.41E-4
2-methylnaphthalene	ND	ND	8.30E-4	8.30E-4	n/a	5.47E-4
2-methyloctane	9.19E-4	2.24E-3	2.45E-3	1.87E-3	44	2.40E-4
3-methyloctane	ND	ND	2.47E-3	2.47E-3	n/a	ND
7-hexadecene	ND	1.78E-3	ND	1.78E-3	n/a	ND
Acetophenone	3.46E-2	3.37E-2	2.76E-2	3.20E-2	12	3.77E-3
Benzaldehyde	4.28E-2	2.70E-2	2.88E-2	3.29E-2	26	5.49E-3
Benzonitrile	5.28E-3	3.84E-3	ND	4.56E-3	22	2.60E-4
Butylated hydroxytoluene	1.66E-1	9.53E-2	1.93E-1	1.52E-1	33	1.24E-2
Decane	3.19E-4	2.56E-3	ND	1.44E-3	110	5.67E-4
Dodecane	ND	2.10E-3	ND	2.10E-3	n/a	4.16E-4
Eicosane	ND	6.41E-4	ND	6.41E-4	n/a	ND
Ethylbenzene	1.13E-3	6.28E-3	2.47E-3	3.29E-3	81	1.20E-3
Heptadecane	1.16E-3	1.35E-3	2.19E-3	1.57E-3	35	2.10E-4
Hexadecane	1.52E-3	3.38E-3	1.87E-3	2.26E-3	44	2.15E-4
m-& p-xylenes	3.28E-3	1.76E-2	6.98E-3	9.30E-3	80	#N/A
m-ethyltoluene	ND	3.76E-3	1.70E-3	2.73E-3	53	1.10E-3
Naphthalene	ND	ND	1.18E-3	1.18E-3	n/a	ND
Nonadecane	ND	9.97E-4	5.83E-4	7.90E-4	37	ND
Nonane	ND	8.90E-3	ND	8.90E-3	n/a	7.61E-4
o-xylene	1.42E-3	7.00E-3	2.70E-3	3.71E-3	79	1.38E-3
Octadecane	9.74E-4	1.69E-3	1.66E-3	1.44E-3	28	1.19E-4
p-ethyltoluene	ND	1.60E-3	ND	1.60E-3	n/a	4.50E-4
Phenol	7.77E-3	1.43E-2	9.29E-3	1.05E-2	33	2.35E-3
Propylbenzene	3.19E-4	1.07E-3	ND	6.93E-4	76	3.46E-4
Styrene	4.56E-3	4.88E-3	6.73E-3	5.39E-3	22	2.20E-3
Tetradecane	8.19E-4	1.55E-3	1.29E-3	1.22E-3	30	2.58E-4
Tridecane	3.28E-4	1.34E-3	6.71E-4	7.78E-4	66	2.73E-4
Undecane	7.46E-4	2.26E-3	2.45E-3	1.82E-3	51	4.77E-4

Table 4-17. Dilution Tunnel VOC Results for the FCCU (Refinery Site A) (mg/dscm).

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

ND- not detected

RSD- relative standard deviation
				Average	RSD		MDL
Run Number	1	2	3	Ŭ	(%)	Ambient	
Date	27-Jul-98	28-Jul-98	29-Jul-98			17-Jul-98	
1+2-ethylnaphthalene	ND	ND	3.95E-5	3.95E-5	n/a	4.5E-5	6.8E-6
1,2,8-trimethylnaphthalene	1.25E-6	ND	3.28E-6	2.27E-6	64	8.4E-7	3.2E-7
1,2-dimethylnaphthalene	ND	ND	1.55E-5	1.55E-5	n/a	1.6E-5	3.7E-6
1,3+1,6+1,7-dimethylnaphthaler	1.25E-5	1.76E-5	1.01E-4	4.39E-5	114	1.8E-4	1.2E-5
1,4+1,5+2,3-dimethylnaphthaler	ND	ND	4.51E-5	4.51E-5	n/a	4.1E-5	5.4E-6
1,4-chrysenequinone	8.47E-6	8.81E-6	2.63E-5	1.45E-5	70	2.2E-6	2.7E-7
1,7-dimethylphenanthrene	4.49E-6	ND	2.83E-6	3.66E-6	32	2.6E-6	1.8E-6
1-ethyl-2-methylnaphthalene	6.23E-6	1.02E-5	4.22E-6	6.88E-6	44	5.1E-6	1.1E-7
1-MeFl+C-MePy/Fl	1.37E-5	ND	ND	1.37E-5	n/a	ND	8.5E-7
1-methylfluorene	ND	ND	2.82E-5	2.82E-5	n/a	3.6E-6	3.5E-6
1-methylnaphthalene	3.74E-6	1.48E-5	2.26E-5	1.37E-5	69	1.8E-4	2.0E-6
1-phenylnaphthalene	2.74E-6	9.27E-6	ND	6.01E-6	77	ND	2.7E-7
2,3,5+I-trimethylnaphthalene	1.40E-5	1.81E-5	1.64E-5	1.62E-5	13	2.5E-5	1.6E-7
2,4,5-trimethylnaphthalene	3.74E-6	6.96E-6	6.11E-6	5.60E-6	30	7.1E-6	4.2E-7
2,6+2,7-dimethylnaphthalene	ND	1.76E-5	3.90E-5	2.83E-5	53	8.2E-5	5.7E-6
2-methylbiphenyl	4.81E-5	3.06E-5	ND	3.94E-5	31	ND	8.4E-6
2-methylnaphthalene	ND	2.04E-5	2.30E-5	2.17E-5	9	2.6E-4	3.3E-6
2-methylphenanthrene	2.94E-5	2.78E-5	4.23E-5	3.32E-5	24	1.7E-5	1.1E-7
2-phenylnaphthalene	6.48E-6	1.85E-5	7.52E-6	1.08E-5	62	5.2E-7	5.3E-8
3,6-dimethylphenanthrene	4.23E-6	ND	1.08E-5	7.52E-6	62	3.5E-6	2.5E-6
3-methylbiphenyl	6.60E-5	6.35E-5	ND	6.48E-5	3	1.9E-5	1.2E-5
4-methylbiphenyl	ND	3.20E-5	ND	3.20E-5	n/a	6.0E-6	1.0E-6
4-methylpyrene	6.23E-6	6.03E-6	2.63E-5	1.29E-5	91	1.7E-6	1.1E-7
4H-cyclopenta(def)phenanthren	2.24E-6	5.11E-6	2.35E-5	1.03E-5	112	6.5E-7	0.0E+0
5+6-methylchrysene	1.02E-4	3.29E-5	1.30E-4	8.83E-5	57	1.0E-6	0.0E+0
7-methylbenz(a)anthracene	5.98E-6	4.63E-7	1.55E-5	7.32E-6	104	ND	3.3E-7
7-methylbenzo(a)pyrene	5.46E-5	5.29E-5	3.85E-5	4.87E-5	18	3.1E-6	3.7E-7
9,10-dihydrobenzo(a)pyrene	1.62E-5	4.65E-6	8.92E-6	9.92E-6	59	1.1E-6	1.6E-7
9-anthraldehyde	3.49E-6	ND	ND	3.49E-6	n/a	ND	1.4E-6
9-fluorenone	ND	1.44E-4	ND	1.44E-4	n/a	ND	7.1E-6
A-dimethylphenanthrene	ND	ND	2.83E-6	2.83E-6	n/a	3.4E-6	2.5E-6
A-methylfluorene	1.72E-5	ND	1.69E-5	1.71E-5	1	ND	5.6E-6
A-methylphenanthrene	2.52E-5	2.78E-5	3.05E-5	2.78E-5	10	1.1E-5	2.5E-6
A-methylpyrene	1.25E-6	ND	1.08E-5	6.03E-6	112	1.5E-7	5.3E-8
A-trimethylnaphthalene	5.73E-6	1.07E-5	1.41E-5	1.02E-5	41	2.2E-5	1.0E-7
Acenaphthene	1.49E-6	2.31E-6	1.32E-5	5.65E-6	115	1.2E-5	1.4E-6
Acenaphthenequinone	1.49E-6	1.48E-5	5.31E-5	2.31E-5	116	1.6E-6	3.2E-7
Acenaphthylene	5.48E-6	ND	2.07E-5	1.31E-5	82	ND	5.5E-6
Anthrone	ND	ND	9.40E-6	9.40E-6	n/a	1.1E-6	5.3E-8
Anthracene	4.06E-4	9.32E-5	2.82E-5	1.76E-4	115	4.1E-6	0.0E+0
Anthraquinone	5.46E-5	5.57E-5	4.28E-5	5.10E-5	14	4.8E-6	2.9E-6
B-dimethylphenanthrene	1.82E-5	1.62E-5	ND	1.72E-5	8	ND	1.8E-6
B-MePy/MeFl	2.49E-6	4.63E-7	1.46E-5	5.84E-6	131	6.3E-7	5.3E-8
B-methylfluorene	ND	ND	1.27E-5	1.27E-5	n/a	ND	3.5E-6
B-methylphenanthrene	3.26E-5	2.46E-5	2.58E-5	2.77E-5	16	ND	5.8E-7
B-trimethylnaphthalene	7.23E-6	1.25E-5	1.08E-5	1.02E-5	27	2.3E-5	5.3E-8
Benzo(a)pyrene	1.94E-5	4.13E-5	1.08E-5	2.38E-5	66	1.3E-6	3.2E-7

Table 4-18. Dilution Tunnel SVOC Results for the FCCU (Refinery Site A) (mg/dscm).

				Average	RSD		MDL
Run Number	1	2	3		(%)	Ambient	
Date	27-Jul-98	28-Jul-98	29-Jul-98			17-Jul-98	
Benz(a)anthracene	7.60E-5	5.06E-5	8.83E-5	7.16E-5	27	3.3E-6	3.2E-7
Benz(a)anthracene-7,12	5.03E-5	3.76E-5	5.78E-5	4.86E-5	21	4.2E-6	2.0E-6
Benzanthrone	7.75E-5	6.08E-5	1.01E-4	7.99E-5	26	7.1E-6	4.8E-7
Benzo(b)chrysene	7.35E-5	7.14E-5	4.13E-5	6.21E-5	29	3.9E-6	1.1E-7
Benzo(b+j+k)fluoranthene	1.40E-4	9.69E-5	2.14E-4	1.50E-4	39	3.8E-6	5.3E-8
Benzo(c)phenanthrene	9.72E-6	8.81E-6	1.50E-5	1.12E-5	30	1.9E-6	5.8E-7
Benzo(ghi)perylene	2.34E-5	2.09E-5	1.60E-5	2.01E-5	19	1.2E-6	3.2E-7
Benzonaphthothiophene	8.72E-6	4.17E-6	7.52E-6	6.80E-6	35	6.7E-7	1.1E-7
Benzo(e)pyrene	4.19E-5	2.60E-5	4.93E-5	3.91E-5	31	3.8E-7	3.3E-7
Bibenzene	8.04E-4	ND	ND	8.04E-4	n/a	ND	1.3E-4
Biphenyl	6.72E-6	ND	1.55E-5	1.11E-5	56	1.6E-5	3.6E-6
C-dimethylphenanthrene	6.72E-6	ND	4.93E-5	2.80E-5	107	6.3E-6	1.8E-6
C-methylphenanthrene	8.23E-6	2.04E-5	2.63E-5	1.83E-5	50	6.8E-6	1.5E-6
C-trimethylnaphthalene	1.02E-5	1.44E-5	9.87E-6	1.15E-5	22	1.8E-5	4.2E-7
Cholestane	1.23E-4	1.79E-4	1.49E-4	1.51E-4	19	ND	1.4E-5
Chrysene	8.20E-5	5.47E-5	9.30E-5	7.66E-5	26	4.5E-6	1.1E-7
Coronene	5.44E-4	5.59E-4	4.26E-4	5.10E-4	14	3.0E-5	3.2E-7
D-dimethylphenanthrene	2.74E-6	2.83E-5	6.57E-6	1.25E-5	110	ND	1.6E-6
D-MePy/MeFl	1.49E-6	ND	4.22E-6	2.86E-6	68	1.5E-7	5.3E-8
Dibenz(ah+ac)anthracene	2.62E-5	1.58E-5	1.27E-5	1.82E-5	39	1.2E-6	3.2E-7
Dibenzofuran	5.98E-6	9.74E-6	2.44E-5	1.34E-5	73	1.9E-5	3.3E-6
E-dimethylphenanthrene	8.23E-6	ND	2.21E-5	1.52E-5	65	2.0E-6	8.0E-7
E-MePy/MeFl	2.99E-6	ND	4.77E-7	1.74E-6	103	8.4E-7	5.3E-8
E-trimethylnaphthalene	4.23E-6	6.50E-6	5.63E-6	5.45E-6	21	2.0E-5	5.3E-8
F-trimethylnaphthalene	8.23E-6	1.53E-5	1.55E-5	1.30E-5	32	1.9E-5	5.0E-8
Fluoranthene	8.75E-5	1.75E-4	1.43E-4	1.35E-4	33	8.6E-6	1.1E-7
Fluorene	4.86E-5	1.07E-4	3.90E-5	6.48E-5	57	2.0E-5	6.4E-6
Indeno[123-cd]pyrene	2.09E-5	1.67E-5	1.27E-5	1.68E-5	25	1.1E-6	3.2E-7
Naphthalene	6.36E-4	8.07E-4	2.99E-4	5.81E-4	45	1.7E-4	5.1E-5
Perinaphthenone	2.55E-4	1.13E-4	4.75E-4	2.81E-4	65	ND	5.2E-5
Perylene	1.02E-5	1.16E-5	7.52E-6	9.78E-6	21	5.2E-7	1.1E-7
Phenanthrene	2.95E-4	9.52E-4	2.02E-4	4.83E-4	85	4.9E-5	4.2E-7
Pyrene	6.50E-5	1.34E-4	1.25E-4	1.08E-4	35	5.7E-6	2.1E-7
Retene	1.25E-5	1.21E-5	3.90E-5	2.12E-5	73	ND	3.2E-6
Xanthone	ND	ND	1.64E-5	1.64E-5	n/a	ND	2.1E-7

Table 4-18. (Cont'd) Dilution Tunnel SVOC Results for the FCCU (Refinery Site A) (mg/dscm).

MDL- Method detection limit

ND- not detected

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

RSD - relative standard deviation

The concentrations of 1,4-chrysenequinone, 9,10-dihydrobenzo(a)pyrene, 9-anthraldehyde, and anthrone in the stack samples are all lower than the concentrations detected in the field blank.

## **Elements**

Si (0.48 mg/dscm) and Al (0.28 mg/dscm) were the most abundant elements found on the filters, consistent with the use of an alumina-silica based catalyst in the FCCU (Table 4-19). Ca, Cu, Fe, La, Ni, S, Ti, and V were present at intermediate concentrations relative to the other elements detected. La, Ni, and V are probably good markers for this source since they are present in the feed and/or catalyst. As, Cd, Au, In, Hg, Pd, P, and Ag concentrations were all below detectable levels in the stack sample, and are not listed in the table. Cl and Mg were detected in the ambient sample but not in the stack samples.

## PROCESS SAMPLES

## ESP Fines

Al and Si were the two most abundant elements (Table 4-20), consistent with the results from the dilution tunnel filters. Recovery of some trace metals was hampered by interference of high Al levels. Method blank, method spike and duplicate analysis results are presented in Section 6.

# Spent and Regenerated Catalyst Samples

Regenerated and spent catalyst samples were collected and analyzed for fuel content to characterize coke burnoff. The carbon content was reduced from an average of 0.60 percent by weight in the spent catalyst down to 0.21 percent in the regenerated catalyst (Tables 4-21 and 4-22). The carbon content of the spent catalyst in the second run is suspect because it is lower than that for the regenerated catalyst. Excluding Run 2 raises the average carbon content to 0.86 weight percent. This also is more consistent with the coke burn rate reported by process controls.

				Average	RSD	Ambient
Run Number	1	2	3		(%)	
Date	27-Jul-98	28-Jul-98	29-Jul-98			
Aluminum	2.6E-1	2.2E-1	3.6E-1	2.8E-1	26	3.6E-4
Antimony	5.2E-3	5.0E-3	7.8E-3	6.0E-3	26	ND
Barium	1.3E-3	1.4E-3	1.5E-3	1.4E-3	5.6	ND
Bromine	2.3E-5	2.1E-5	2.6E-5	2.4E-5	11	2.3E-6
Calcium	8.2E-3	7.5E-3	1.1E-2	9.0E-3	22	6.8E-4
Chlorine	ND	ND	ND	ND	n/a	1.0E-5
Chromium	2.5E-3	3.3E-3	3.3E-3	3.0E-3	15	2.3E-6
Cobalt	9.1E-4	4.2E-4	3.4E-4	5.5E-4	56	ND
Copper	8.8E-4	8.8E-2	8.0E-3	3.2E-2	150	1.5E-4
Gallium	1.7E-4	7.2E-5	2.5E-4	1.6E-4	54	ND
Iron	8.1E-2	4.8E-2	6.4E-2	6.4E-2	26	4.9E-4
Lanthanum	5.4E-2	4.8E-2	7.7E-2	6.0E-2	26	ND
Lead	8.6E-4	6.0E-4	5.8E-4	6.8E-4	23	1.3E-5
Magnesium	ND	ND	ND	ND	n/a	6.9E-5
Manganese	1.0E-3	9.2E-4	1.5E-3	1.1E-3	25	1.3E-5
Molybdenum	4.5E-4	7.0E-4	8.1E-4	6.5E-4	28	ND
Nickel	1.4E-2	1.3E-2	1.9E-2	1.5E-2	23	7.4E-6
Potassium	5.2E-3	4.5E-3	6.7E-3	5.4E-3	21	1.7E-4
Rubidium	4.9E-5	4.6E-5	5.0E-5	4.8E-5	3.9	8.4E-7
Selenium	4.1E-5	3.5E-5	4.8E-5	4.2E-5	16	ND
Silicon	4.5E-1	3.8E-1	6.1E-1	4.8E-1	25	1.1E-3
Strontium	5.2E-4	4.6E-4	7.4E-4	5.7E-4	26	3.6E-6
Sulfur	4.3E-2	1.2E-1	1.1E-1	9.1E-2	46	1.2E-3
Thallium	ND	4.2E-5	ND	4.2E-5	n/a	ND
Tin	2.4E-4	ND	ND	2.4E-4	n/a	ND
Titanium	2.8E-2	2.2E-2	3.8E-2	2.9E-2	28	3.6E-5
Uranium	4.9E-5	ND	6.7E-5	5.8E-5	22	ND
Vanadium	2.5E-2	2.3E-2	3.9E-2	2.9E-2	30	1.9E-5
Yttrium	6.7E-5	4.2E-5	1.0E-4	7.1E-5	44	ND
Zinc	2.2E-3	2.1E-3	2.7E-3	2.3E-3	13	6.6E-5
Zirconium	4.8E-4	4.4E-4	7.0E-4	5.4E-4	25	2.8E-6

Table 4-19. Dilution Tunnel Elemental Results for the FCCU (Refinery Site A) (mg/dscm).

RSD- Relative standard deviation

n/a- not applicable; one or fewer runs above detection limits

Compound	MDL	Run 1	Run 2	Run 3	Average	RSD
Mercury	0.04	ND	ND	ND	ND	n/a
Aluminum	3	48000	83000	46000	59000	35%
Antimony	3	620	560	610	600	5.4%
Barium	0.1	9	13	7.8	9.9	27%
Beryllium	0.1	3.5	4.5	3.5	3.8	15%
Cadmium	0.2	0.5	< 2.0*	0.5	0.67	43%
Calcium	20	< 200	< 200	ND	100	0.0%
Chromium	0.4	87	95	85	89	5.9%
Cobalt	1	44	48	42	45	6.8%
Copper	0.6	41	46	35	41	14%
Iron	1	3600	3700	3100	3500	9.2%
Lead	2	ND	< 20	ND	10	n/a
Magnesium	5	41	98	49	63	49%
Manganese	0.5	19	17	16	17	8.8%
Molybdenum	1	57	54	53	55	3.8%
Nickel	1	1800	1800	1600	1700	6.8%
Phophorous	6	510	490	500	500	2.0%
Potassium	100	300	1500	440	750	87%
Selenium	10	ND	< 100	ND	50	n/a
Silicon	10	240000	250000	230000	240000	4.2%
Silver	1	1.5	< 10	1.4	2.6	2.7%
Sodium	10	2000	2300	2000	2100	8.2%
Strontium	0.1	2	< 1.0	2.7	1.7	29%
Sulfur	10	11000	11000	11000	11000	0.0%
Thallium	6	< 60	< 60	< 60	30	0.0%
Tin	5	< 50	< 50	< 50	25	0.0%
Titanium	5	6100	6500	6100	6200	3.7%
Vanadium	0.5	4600	4700	4300	4500	4.6%
Zinc	0.5	270	270	230	260	8.9%
Zirconium	5	59	70	62	64	8.9%

Table 4-20. Elemental Analysis of ESP Fines from the FCCU (Refinery Site A) (mg/kg).

MDL- Method detection limit

ND- not detected (less than MDL)

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

RSD- relative standard deviation

\* Concentrations expressed as < X were taken to be half of X in calculations

(eg., < 2.0 taken as 1.0 in calculations)

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	Units	Run 1	Run 2	Run 3		
		Regenerated	Regenerated	Regenerated		
		catalyst	catalyst	catalyst	Average	RSD
Total moisture	%	0.36	0.26	0.28	0.3	18%
Carbon	%	0.2	0.2	0.22	0.21	5.6%
Hydrogen	%	< 0.01	< 0.01	< 0.01	0.005	0.0%
Nitrogen	%	0.19	0.03	0.03	0.08	111%
Sulfur	%	0.01	0.01	0.01	0.01	0.0%
Ash	%	99.17	99.26	99.3	99.24	0.1%
Oxygen (diff.)	%	0.06	0.23	0.15	0.15	58%
Calorific content	Btu/lb	ND	ND	120	120	n/a
Moisture and ash free						
calorific content	Btu/lb	ND	ND	28572	28572	n/a

Table 4-21. Regenerated Catalyst Fines Analysis Results.

< - Less than reporting limit. One half of reporting limit used in calculations

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

ND- not detected

RSD- relative standard deviation

	Units	Run 1	Run 2	Run 3		
		Spent	Spent	Spent	1	
		catalyst	catalyst	catalyst	Average	RSD
Total moisture	%	0.48	0.84	0.36	0.56	45%
Carbon	%	0.89	0.09	0.83	0.60	74%
Hydrogen	%	0.01	< 0.01	< 0.01	0.007	0.0%
Nitrogen	%	0.03	< 0.01	0.02	0.02	55%
Sulfur	%	0.02	0.02	0.02	0.02	0.0%
Ash	%	98.16	97.6	98.35	98.04	0.4%
Oxygen (diff.)	%	0.41	1.43	0.41	0.75	79%
Calorific content	Btu/lb	ND	ND	97	97	n/a
Moisture and ash free						
calorific content	Btu/lb	ND	ND	7519	7519	n/a

Table 4-22. Spent Catalyst Fines Analysis Results.

 $<\,$  - Less than reporting limit. One half of reporting limit used in calculations

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

ND- not detected

RSD- relative standard deviation

#### Section 5

# EMISSION FACTORS AND SPECIATION PROFILES

Emission factors and chemical speciation profiles are presented in this section. Emission factors were determined by dividing the measured emission rate, in lb/hr, by the process coke burn rate, in tons/day (with appropriate units conversions), to yield pollutant emissions in units of lb/1000 lb coke burned. These units are considered the most appropriate for combustion-generated pollutants from FCCUs, given the wide range of process design and operating variables that may affect catalyst coking for a given feed. Emission factors given in EPA's AP-42 emission factor compilation are in units of pounds per thousand barrels of fresh feed (lb/10<sup>3</sup> bbl). To convert results of these tests to lb/10<sup>3</sup> bbl, multiply lb/1000 lb coke burned by 16.1. Speciation profiles were determined by dividing the emission factor of a substance by the sum of emission factors for all detected substances, yielding the mass fraction of each substance.

The average emission factor, total uncertainty, and 95 percent confidence upper bound were calculated for each substance of interest. The total uncertainty represents the 95 percent confidence interval (including cumulative bias associated with individual measurements needed to determine emission and process rates, and precision of the replicate measurements), based on a two-tailed Student "t" distribution. The 95 percent confidence upper bound estimate is based on the single-tailed Student "t" distribution at the 95 percent confidence level (ASME, 1998).

# IN-STACK AND IMPINGER METHOD RESULTS

Table 5-1 presents emission factors derived from the in-stack and impinger method results. FPM includes all particulate captured in the in-stack cyclones, probe and filter. Inorganic and organic CPM results presented in Table 5-1 have not been individually corrected for water and methylene chloride blanks; however, the total CPM has been blank-corrected in accordance with Method 202. The in-stack filter SVOC results can be interpreted to represent SVOCs that are filterable or adsorb on the filter at stack temperature.

Table 5-2 shows the PM2.5 mass speciation profile based on the Method 201A/202 results, expressed as a fraction of total PM2.5 mass (FPM plus CPM). FPM and CPM each comprise

	<b>Emission Factor</b>	<b>T</b> T , · ,	95% Confidence
Compound	(lb/1000 lb coke	Uncertainty	Upper Bound (lb/1000
_	burned)	(%)	lb coke burned)
Condensable particulate (inorganic)	0.51	279	1.5
Chlorides (as Cl <sup>-</sup> )	0.013	84	0.021
Sulfates (as SO <sub>4</sub> =)	0.14	79	0.21
Condensable particulate (organic)	4.7E-3	160	0.01
Condensable particulate (total)*	0.51	281	1.5
Filterable PM2.5	0.44	72	0.65
Filterable PM10	0.47	72	0.71
Total Filterable Particulate	0.50	69	0.74
Filterable PM2.5 + CPM	0.95	117	1.70
$SO_3$ (as $H_2SO_4$ )	1.4	92	2.3
Organic Carbon	1.5E-4	66	2.2E-4
Elemental Carbon	3.2E-5	153	6.6E-5
Total Carbon	1.8E-4	77	2.8E-4
Semivolatile 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
NO <sub>x</sub>	4.1	80	6.5
$SO_2$	26	80	41
NH <sub>3</sub>	3.6E-3	70	5.4E-3

Table 5-1. Emission Factors – In-Stack and Impinger Methods.

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

\*blank corrected

	Average	Uncertainty	95% Confidence
Compound	Mass Fraction	(%)	Upper Bound
	(%)		(Mass Fraction, %)
Filterable PM2.5 <sup>1</sup>	46	129	87
Condensable particulate (total) <sup>1</sup>	54	300	164
Sulfates (as $SO_4^{=}$ ) <sup>1</sup>	15	133	28
Chlorides (as Cl <sup>-</sup> ) <sup>1</sup>	0.92	136	1.8
Organic Carbon*	1.6E-2	198	3.7E-2
1,4-chrysenequinone	0.013	746	0.06
1-ethyl-2-methylnaphthalene	0.063	n/a	n/a
2,6+2,7-dimethylnaphthalene	0.068	n/a	n/a
2-methylphenanthrene	0.024	n/a	n/a
4-methylbiphenyl	0.031	n/a	n/a
9,10-dihydrobenzo(a)pyrene	0.005	n/a	n/a
A-methylfluorene	0.060	n/a	n/a
A-methylpyrene	0.052	847	0.27
Benz(a)anthracene-7,12	0.005	n/a	n/a
Benzo(a)pyrene	0.037	n/a	n/a
Benzo(b)chrysene	0.007	739	0.03
Benzo(c)phenanthrene	0.005	n/a	n/a
Bibenzene	0.891	n/a	n/a
Biphenyl	0.055	888	0.30
Cholestane	1.9	793	9.4
Dibenzofuran	0.029	986	0.17
Naphthalene	0.254	215	0.63
Perinaphthenone	0.068	1242	0.49
Elemental Carbon	3.4E-3	242	9.0E-3
Total Carbon	1.9E-2	203	4.5E-2

Table 5-2. PM2.5 Speciation Profile – In-Stack and Impinger Methods.

 $n\!/\!a$  - not applicable. Detected in only one run.

\*Organic species are expressed as a fraction of the organic carbon.

<sup>1</sup>Percentage of PM2.5 mass based on Method 201A + Method 202 results (see Table 4-7).

approximately half of the total mass (Figure 5-1). Fifteen percent of the total mass is sulfate and 0.9 percent is chloride; however, these results may be subject to errors as discussed in the following paragraphs. Individual SVOC species are expressed as a fraction of OC. Cholestane is the most abundant, and comprises 1.9 percent of the OC mass (Figure 5-2).

5-4

Not for Resale







Figure 5-1. PM2.5 Speciation Profile – In-Stack and Impinger Methods.

## DILUTION TUNNEL RESULTS

Emission factors for PM2.5 mass, elements and ions from the dilution tunnel results (Table 5-3) differ from those obtained using in-stack and impinger methods. The average emission factor for total (filterable plus condensible) PM2.5 mass based on the Method 201A/202 results is approximately nine times higher than the emission factor for PM2.5 as measured by the dilution tunnel. The reason for this discrepancy could not be positively determined based on these test results. It is likely that Method 202 results are biased high due to known artifacts from SO<sub>3</sub> and SO<sub>2</sub> in the flue gas (Filadelphia and McDannel, 1996). Also, the dilution tunnel PM2.5 mass results are biased low due to deposition of solid particles upstream of the filter. The mass of deposited particles recovered from the dilution tunnel probe, sample line and venturi at the end of all three runs is significant relative to the filter catch (see Sections 6 and 7 for additional discussion). Any additional particles deposited in the tunnel and residence time chamber were not quantified. Because of this bias due to loss of solid particles in the dilution tunnel system, the total PM2.5 mass emission factor from the dilution tunnel should not be used.

 $SO_4^{=}$  based on IC analysis of the quartz filters is much greater than expected based on S by XRF analysis of the Teflon membrane filters. Controlled condensation results show H<sub>2</sub>SO<sub>4</sub> present in significant quantities relative to  $SO_4^{=}$  on the quartz filters. Since the XRF analysis is conducted under high vacuum, any free H<sub>2</sub>SO<sub>4</sub> present on the filters would be expected to vaporize. Therefore, the results are consistent with the majority of  $SO_4^{=}$  being present as H<sub>2</sub>SO<sub>4</sub>.

The sum of individual species is approximately three percent greater than the average emission factor for total PM2.5 mass. This slight difference could be attributed to differences in sampling and analytical methods used to determine the speciation of the mass versus the gravimetric analysis used to measure total PM2.5 mass. Two different types of filters were used: Teflon filters were used for the elemental analysis and particulate mass, while quartz filters were used for OC/EC and ionic species determination. Possible explanations for this difference include: variations in particle deposition between the different filters; non-uniform deposition on the filter (the OC/EC analysis and ion analysis each take only part of the filter for analysis, and the total mass on the filter is normalized assuming that this mass is evenly distributed over the collection

	Emission Factor	T	95% Confidence
Compound	(lb/1000 lb coke	Uncertainty	Upper Bound (lb/1000
_	burned)	(%)	lb coke burned)
PM2.5 mass*	0.11	68	0.16
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
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

Table 5-3. Emission Factors – Dilution Tunnel (Mass, Elements and Ions).

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

\*Presented for method comparison purposes only. Do not use (see text).

area); different response to analytes and interferents for different analytical methods; and potential positive bias on the quartz filters due to SO<sub>2</sub>.

The mass fractions of elements, ions and carbon relative to the total mass of all substances are given in Table 5-4. Only detected substances are considered. Total carbon (because it is defined as the sum of EC and OC) and S (because  $SO_4^{=}$  by IC analysis is included) results are excluded from the sum.

Eighty-five percent of the PM2.5 mass is  $SO_4^{=}$  (expressed as a fraction of the sum of individual species in Table 5-4), with Si (6 percent) and Al (3.5 percent) being the next most abundant (Figure 5-3). This agrees qualitatively with the in-stock filter (Method 201A) and controlled condensation results, which indicate sulfuric acid (expressed as sulfate) accounts for 76 percent of PM2.5 mass. The elemental analysis results are expressed as pure element rather than the higher oxide form. Expressing elemental results as higher oxides reduces the significance of S in the total and results in minor changes in the rest of the species profile. Based on the controlled condensation results, the large  $SO_4^{=}$  fraction is probably present as H<sub>2</sub>SO<sub>4</sub>. If S and  $SO_4^{=}$  are neglected, Si, Al, Fe, La, and V dominate the particulate composition. V is a contaminant present in the FCCU feed. The elemental results are similar in overall composition to the ESP fines results presented in Section 4. Since FCCU catalysts typically are supported on silica-alumina substrates, and since Fe and La are known catalysts, these results show that the vast majority of the emitted solid particles are catalyst fines. Compounds that were undetected in all three runs, are redundant with other compounds, or are not considered quantitative results are not included in the figure.

SVOC emission factors (Table 5-5), which represent both the solid and vapor phase, are all very low. Table 5-6 presents emission factors for SVOCs expressed as a fraction of OC. The sum of speciated SVOCs ( $6x10^{-5}$  lb/1000 lb coke burned) accounts for only about 7 percent of the total OC. The SVOC speciation profile (Figure 5-4) shows that the most abundant compound is bibenzene (1.2 percent), followed by naphthalene (0.8 percent).

Emission factors for secondary organic aerosol precursors, i.e., VOC with carbon number greater than seven, are presented in Table 5-7. Butylated hydroxytoluene is the most prevalent, with an emission factor of  $2.1 \times 10^{-3}$  lb/1000 lb coke burned.

			95% Confidence Upper
Compound	Average Mass Fraction	Uncertainty (%)	Bound (Mass Fraction,
1	(1)(%)	5 ( )	%)
Aluminum	3.5E+0	204	8.3E+0
Antimony	7.5E-2	204	1.8E-1
Barium	1.8E-2	194	4.1E-2
Bromine	2.9E-4	195	6.9E-4
Calcium	1.1E-1	201	2.7E-1
Chromium	3.8E-2	197	8.9E-2
Cobalt	7.0E-3	238	1.8E-2
Copper	4.1E-1	419	1.6E+0
Gallium	2.0E-3	235	5.3E-3
Iron	8.1E-1	204	1.9E+0
Lanthanum	7.5E-1	204	1.8E+0
Lead	8.6E-3	201	2.0E-2
Manganese	1.4E-2	203	3.4E-2
Molybdenum	8.2E-3	206	2.0E-2
Nickel	1.9E-1	202	4.5E-1
Potassium	6.8E-2	200	1.6E-1
Rubidium	6.1E-4	194	1.4E-3
Selenium	5.2E-4	197	1.2E-3
Silicon	6.0E+0	203	1.4E+1
Strontium	7.1E-3	204	1.7E-2
Sulfur*	1.1E+0	225	2.9E+0
Thallium	5.4E-4	n/a	n/a
Tin	3.1E-3	n/a	n/a
Titanium	3.7E-1	205	8.8E-1
Uranium	7.2E-4	723	3.3E-3
Vanadium	3.6E-1	207	8.7E-1
Yttrium	8.9E-4	222	2.2E-3
Zinc	2.9E-2	196	6.8E-2
Zirconium	6.7E-3	203	1.6E-2
Sulfate	85	201	203
Nitrates	ND	n/a	n/a
Chloride	1.8E-3	200	4.3E-1
Ammonium	7.8E-1	205	1.9E+0
Organic Carbon	8.8E-1	195	2.0E+0
Elemental Carbon	1.8E-1	n/a	n/a
Total Carbon*	9.4E-1	195	2.2E+0
Total	100		

Table 5-4. PM2.5 Speciation Profile – Dilution Tunnel (Elements, Ions and Carbon).

n/a- not applicable; detected in only one run.

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

\*These compounds are not included in the sum of species since they are redundant with other measurements.



Figure 5-3. PM2.5 Speciation Profile – Dilution Tunnel Methods.

5-9

			95% Confidence
	Emission Factor	Uncertainty	Upper Bound
Compound	(lb/1000 lb coke	(%)	(lb/1000 lb coke
	burned)	(70)	(10/1000 10 COKe
Organic Carbon	9 9E-4	53	1 4E-3
Elemental Carbon	2 0F-4	n/a	n/a
Total Carbon	1 1E-3	52	1 5E-3
1+2-ethylnaphthalene	5 4F-7	1037	3 4F-6
1 2 8-trimethylnanhthalene	3.4E 7	580	1.4E 0
1.2-dimethylnaphthalene	2.1E-7	n/a	n/a
1 3+1 6+1 7-dimethylnanhthalene	6 1E-7	285	1 8F-6
1,3+1,5+1,7-dimethylnaphthalene	6.2E-7	203 n/a	n/a
1 A_chrysenequinone	0.2E-7 2.0E-7	178	17a 15E-7
1,7-cm yschequillone	2.0L-7 5.2E.8	248	4.3L-7 1 AE 7
1, /-dimetry prenantinene	J.2E-0	122	1.4L-7 1.9E 7
1 MoEl+C MoDy/El	9.0E-0	122 n/a	1.0L-/
1-MEFITC-MEFy/Fi	2.0E-7	1022	
1-methylnuorene	5.9E-7	1033	2.4E-0
1 - methymaphthalene	1.9E-/	1/0	4.3E-/ 2.0E.7
1-pnenyinaprinalene	8./E-8	/06	3.9E-7
2,3,5+1-trimethyinaphthalene	2.3E-/	59	3.3E-/
2,4,5-trimethylnaphthalene	8.0E-8	89	1.3E-/
2,6+2,/-dimethylnaphthalene	4.0E-7	220	9.9E-7
2-methylbiphenyl	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	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	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	2.4E-7	167	4.5E-7
A-methylphenanthrene	4.0E-7	55	5.6E-7
A-methylpyrene	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	3.2E-7	290	9.6E-7
Acenaphthylene	1.8E-7	744	8.6E-7
Anthracene	2.5E-6	n/a	n/a

Table 5-5. Emission Factors – Dilution Tunnel (Carbon and SVOC).

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

· · · · ·			
	Emission Factor		95% Confidence
Compound	(lb/1000 lb coke	Uncertainty	Upper Bound
Compound	(10/1000 to coke	(%)	(lb/1000 lb coke
	ourned)		burned)
Anthraquinone	7.3E-7	292	2.2E-6
Anthrone	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	1.8E-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	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	2.9E-7	101	4.9E-7
Benzonaphthothiophene	9.6E-8	90	1.6E-7
Bibenzene	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	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	1.8E-7	279	5.2E-7
D-MePy/MeFl	4.0E-8	615	1.6E-7
Dibenz(ah+ac)anthracene	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	2.4E-7	82	3.8E-7
Naphthalene	8.3E-6	123	1.5E-5
Perinaphthenone	4.0E-6	166	8.5E-6
Perylene	1.4E-7	75	2.1E-7
Phenanthrene	6.9E-6	217	1.7E-5
Pyrene	1.5E-6	99	2.6E-6
Retene	3.0E-7	185	6.7E-7
Xanthone	2.3E-7	n/a	n/a

Table 5-5. (Continued) Emission Factors – Dilution Tunnel (Carbon and SVOC).

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

	Awara a Maga		050/ Confidence
Compound	Erection (1)	Uncertainty	93% Confidence
Compound	$r_{1}$	(%)	(Mass Erection 9/)
1 - 2 - other large left a large	(%)	1020	(Mass Fraction, %)
1+2-ethylnaphthalene	0.055	1238	0.39
1,2,8-trimethyinaphthalene	0.003	892	0.02
1,2-dimethylnaphthalene	0.022	n/a	n/a
1,3+1,6+1,7-dimethylnaphthalene	0.061	341	0.20
1,4+1,5+2,3-dimethylnaphthalene	0.063	n/a	n/a
1,4-chrysenequinone	0.021	259	0.06
1,7-dimethylphenanthrene	0.005	761	0.02
1-ethyl-2-methylnaphthalene	0.010	224	0.03
1-MeFl+C-MePy/Fl	0.020	n/a	n/a
1-methylfluorene	0.039	1235	0.28
1-methylnaphthalene	0.019	257	0.05
1-phenylnaphthalene	0.009	978	0.05
2,3,5+I-trimethylnaphthalene	0.023	197	0.05
2,4,5-trimethylnaphthalene	0.008	207	0.02
2,6+2,7-dimethylnaphthalene	0.040	289	0.12
2-methylbiphenyl	0.057	754	0.27
2-methylnaphthalene	0.031	700	0.14
2-methylphenanthrene	0.047	202	0.11
2-phenylnaphthalene	0.016	248	0.04
3,6-dimethylphenanthrene	0.011	882	0.06
3-methylbiphenyl	0.094	697	0.42
4-methylbiphenyl	0.046	n/a	n/a
4-methylpyrene	0.018	295	0.05
4H-cyclopenta(def)phenanthrene	0.014	338	0.05
5+6-methylchrysene	0.125	239	0.33
7-methylbenz(a)anthracene	0.010	321	0.03
7-methylbenzo(a)pyrene	0.070	200	0.17
9,10-dihydrobenzo(a)pyrene	0.014	245	0.04
9-anthraldehyde	0.005	n/a	n/a
9-fluorenone	0.209	n/a	n/a
A-dimethylphenanthrene	0.004	752	0.02
A-methylfluorene	0.024	697	0.11
A-methylphenanthrene	0.040	195	0.09
A-methylpyrene	0.008	1219	0.06
A-trimethylnaphthalene	0.014	218	0.04
Acenaphthene	0.008	344	0.03
Acenaphthenequinone	0.032	345	0.11
Acenaphthylene	0.018	1006	0.11
Anthrone	0.254	n/9	n/a
Anthracene	0.073	347	0.25
Anthraquinone	0.013	198	0.03

Table 5-6. PM2.5 Speciation Profile – Dilution Tunnel (SVOC).

Speciated SVOCs represent approximately 7% of total organic carbon.

(1) Relative to organic carbon by TOR analysis.

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

	Average Mass		05% Confidence
Compound	Fraction (1)	Uncertainty	95% Confidence
Compound	(%)	(%)	(Mass Erection %)
D dimethylphenenthrone	(%)	701	(Mass Flaction, %)
	0.023	276	0.11
B-Mery/Meri	0.008	570	0.05
	0.018	n/a	n/a
B-methylphenanthrene	0.040	199	0.09
B-trimethylnaphthalene	0.015	205	0.03
Benz(a)anthracene	0.102	254	0.28
Benz(a)anthracene-7,12	0.069	205	0.17
Benzanthrone	0.114	201	0.27
Benzo(a)pyrene	0.034	204	0.08
Benzo(b)chrysene	0.089	208	0.22
Benzo(b+j+k)fluoranthe	0.213	216	0.53
Benzo(c)phenanthrene	0.016	207	0.04
Benzo(e)pyrene	0.056	201	0.13
Benzo(ghi)perylene	0.029	213	0.07
Benzonaphthothiophene	0.010	208	0.02
Bibenzene	1.163	n/a	n/a
Biphenyl	0.016	849	0.08
C-dimethylphenanthrene	0.039	1184	0.27
C-methylphenanthrene	0.026	230	0.07
C-trimethylnaphthalene	0.016	202	0.04
Cholestane	0.215	200	0.51
Chrysene	0.109	204	0.26
Coronene	0.730	198	1.7
D-dimethylphenanthrene	0.018	336	0.06
D-MePy/MeFl	0.004	914	0.02
Dibenz(ah+ac)anthracene	0.026	218	0.07
Dibenzofuran	0.019	263	0.05
E-dimethylphenanthrene	0.021	897	0.12
E-MePy/MeFl	0.002	1162	0.02
E-trimethylnaphthalene	0.008	201	0.02
F-trimethylnaphthalene	0.019	209	0.05
Fluoranthene	0.193	210	0.47
Fluorene	0.093	240	0.25
Indeno[123-cd]pyrene	0.024	205	0.06
Naphthalene	0.836	224	2.1
Perinaphthenone	0.397	251	1.1
Perylene	0.014	202	0.03
Phenanthrene	0.696	287	2.1
Pyrene	0.154	212	0.38
Retene	0.030	263	0.08
Xanthone	0.023	n/a	n/a

# Table 5-6. (Continued) PM2.5 Speciation Profile – Dilution Tunnel (SVOC).

Speciated SVOCs represent approximately 7% of total organic carbon.

(1) Relative to organic carbon by TOR analysis.

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



Mass Fraction (%)

Figure 5-4. PM2.5 Speciation Profile – Dilution Tunnel Methods (SVOC).

Compound	Emission Factor (lb/1000 lb coke	Uncertainty (%)	95% Confidence Upper Bound (lb/1000 lb coke
	burned)		burned)
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 <b>-</b> 5	n/a	n/a
2-methyloctane	2.6E-5	122	4.9E-5
3-methyloctane	3.4E-5	n/a	n/a
7-hexadecene	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	1.6E <b>-</b> 5	n/a	n/a
Nonadecane	1.1E <b>-</b> 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

Table 5-7. Emission Factors – Dilution Tunnel (VOC C7+).

n/a- Not applicable. Only one run within detectable limits.

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## Section 6

# QUALITY ASSURANCE

# DILUTION TUNNEL QA/QC RESULTS

# **Dilution Tunnel Flows**

Flow rates through the dilution tunnel sample collection media were determined by averaging the flow rate measured before testing commenced and after sampling was completed. Results from the pre- and post-test flow checks are presented in Table 6-1. Most post-test flow rates are within 20 percent of their respective pre-test flow rate values. In some cases, the post-test flow rate check is significantly lower or higher than the pre-test check (quartz filter Run 1, Teflon filter runs 1 and 2). This could indicate a bias in the calculated sample volume, since it is not known how the flow rate varied during actual sampling. It is recommended that future tests incorporate flow rate monitoring (e.g., rotameters) so that media flow rates can be monitored and adjusted continually during the test.

# Blank Results - Dilution Tunnel

Blank results for dilution tunnel methods are presented in Table 6-2. Only compounds with concentrations above the minimum detection limit are shown. In, Mg and P were present at detectable levels in the Teflon filter field blank, but not in the stack samples. 1,4-chrysenequinone, 9-anthraldehyde, and anthrone were detected in the TIGF/PUF/XAD field blank at levels greater than in the stack samples. 1,2,3-trimethylbenzene was detected in the Tenax field blank but not in any of the samples. All other compounds detected in the field blank were not found at levels of concern relative to the stack samples.

# **QA Checks – Dilution Tunnel Particulate Mass**

Upon completion of the third dilution tunnel run, the probe, sample line, and venturi were rinsed with acetone to recover particles that may have accumulated there during the three test runs. The rinses were evaporated and weighed in two fractions:

- Probe and sample line: 89.3 mg
- Venturi: 16.4 mg

Run	Pretest (scfh)	Post Test (scfh)	Average	% Difference		
Quartz Filter Flow (scfh)						
1	85.00	48.00	66.50	44%		
2	85.00	90.00	87.50	-6%		
3	85.00	85.00	85.00	0%		
	Teflor	n Filter Flow (scfh	)			
1	85.00	72.00	78.50	15%		
2	85.00	98.00	91.50	-15%		
3	85.00	85.00	85.00	0%		
	Mak	te Up Flow (scfh)				
1	240.00	150.00	195.00	38%		
2	242.00	250.00	246.00	-3%		
3	242.00	225.00	233.50	7%		
	PU	JF/XAD (scfh)				
1	240.00	220.00	230.00	8%		
2	242.00	239.00	240.50	1%		
3	242.00	235.00	238.50	3%		
	Tena	ax Tube A (slpm)				
1	0.10	0.10	0.10	-1%		
2	0.10	0.11	0.11	-10%		
3	0.10	0.10	0.10	0%		
	Tena	ax Tube B (slpm)				
1	0.10	0.10	0.10	2%		
2	0.10	0.11	0.10	-6%		
3	0.10	0.10	0.10	3%		

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

Dividing the total weight (105.7) by the total sample volume drawn through the probe during all three tests (approximately 13.7 dscm) yields a total particulate concentration of 7.7 mg/dscm. Using the average of the Method 201A results (PM2.5 equals 87 percent of total FPM) and the hot cascade impactor results (PM2.5 equals 69 percent of total PM) to estimate the fraction that is PM2.5 (PM2.5 equals 78 percent of total PM) yields PM2.5 equal to 6.0 mg/dscm. Adding the PM2.5 loading on the dilution tunnel Teflon filters of 7.8 mg/dscm, this represents PM2.5 losses of 43 percent in the probe, sample line and venturi. Comparing the sum of the Teflon filter and probe/sample line/venturi catches (13.8 mg/dscm) to the Method 201A results. Based on these

Sample Type	Blank Type	Media/Analysis		Mass (mg)
Dilution Tunnel	Field Blank	Teflon filter/Mass	mg/dscm	5.4E-4
Dilution Tunnel	Field Blank	Teflon filter/Aluminum	mg/dscm	2.1E-5
Dilution Tunnel	Field Blank	Teflon filter/Indium	mg/dscm	1.6E-5
Dilution Tunnel	Field Blank	Teflon filter/Magnesium	mg/dscm	4.6E-5
Dilution Tunnel	Field Blank	Teflon filter/Phosphorus	mg/dscm	7.0E-6
Dilution Tunnel	Field Blank	Teflon filter/Silicon	mg/dscm	8.8E-6
Dilution Tunnel	Field Blank	Teflon filter/Sulfur	mg/dscm	5.7E-6
Dilution Tunnel	Field Blank	Quartz filter/OC	mg/dscm	5.5E-3
Dilution Tunnel	Field Blank	Quartz filter/EC	mg/dscm	7.7E-6
Dilution Tunnel	Field Blank	Quartz filter/Chloride	mg/dscm	6.0E-5
Dilution Tunnel	Field Blank	Quartz filter/Nitrate	mg/dscm	ND
Dilution Tunnel	Field Blank	Quartz filter/Sulfate	mg/dscm	3.2E-5
Dilution Tunnel	Field Blank	Quartz filter/Ammonium	mg/dscm	3.4E-5
Dilution Tunnel	Field Blank	TIGF/PUF/XAD/1,4-chrysenequinone	mg/dscm	2.46E-5
Dilution Tunnel	Field Blank	TIGF/PUF/XAD/1-MeFl+C-MePy/Fl	mg/dscm	1.00E-6
Dilution Tunnel	Field Blank	TIGF/PUF/XAD/1-methylnaphthalene	mg/dscm	2.43E-6
Dilution Tunnel	Field Blank	TIGF/PUF/XAD/1-phenylnaphthalene	mg/dscm	7.00E-7
Dilution Tunnel	Field Blank	TIGF/PUF/XAD/2,3,5+I-trimethylnaphthalene	mg/dscm	4.75E-7
Dilution Tunnel	Field Blank	TIGF/PUF/XAD/2-methylbiphenyl	mg/dscm	1.46E-5
Dilution Tunnel	Field Blank	TIGF/PUF/XAD/2-phenylnaphthalene	mg/dscm	2.25E-7
Dilution Tunnel	Field Blank	TIGF/PUF/XAD/4-methylbiphenyl	mg/dscm	7.68E-6
Dilution Tunnel	Field Blank	TIGF/PUF/XAD/4H-cyclopenta(def)phenanthrene	mg/dscm	7.50E-6
Dilution Tunnel	Field Blank	TIGF/PUF/XAD/9,10-dihydrobenzo(a)pyrene	mg/dscm	3.63E-5
Dilution Tunnel	Field Blank	TIGF/PUF/XAD/9-anthraldehyde	mg/dscm	2.95E-5
Dilution Tunnel	Field Blank	TIGF/PUF/XAD/A-methylpyrene	mg/dscm	2.25E-6
Dilution Tunnel	Field Blank	TIGF/PUF/XAD/Acenaphthenequinone	mg/dscm	2.00E-5
Dilution Tunnel	Field Blank	TIGF/PUF/XAD/Anthracene	mg/dscm	9.50E-7
Dilution Tunnel	Field Blank	TIGF/PUF/XAD/Anthraquinone	mg/dscm	1.46E-5
Dilution Tunnel	Field Blank	TIGF/PUF/XAD/Anthrone	mg/dscm	2.30E-4
Dilution Tunnel	Field Blank	TIGF/PUF/XAD/B-trimethylnaphthalene	mg/dscm	2.00E-7
Dilution Tunnel	Field Blank	TIGF/PUF/XAD/Benz(a)anthracene	mg/dscm	1.58E-6
Dilution Tunnel	Field Blank	TIGF/PUF/XAD/Benz(a)anthracene-7,12	mg/dscm	6.40E-6
Dilution Tunnel	Field Blank	TIGF/PUF/XAD/Benzanthrone	mg/dscm	6.78E-6
Dilution Tunnel	Field Blank	TIGF/PUF/XAD/Benzo(a)pyrene	mg/dscm	9.25E-7
Dilution Tunnel	Field Blank	TIGF/PUF/XAD/Benzo(b)chrysene	mg/dscm	1.63E-6
Dilution Tunnel	Field Blank	TIGF/PUF/XAD/Benzo(b+j+k)fluoranthene	mg/dscm	4.25E-7
Dilution Tunnel	Field Blank	TIGF/PUF/XAD/Benzo(e)pyrene	mg/dscm	2.18E-6
Dilution Tunnel	Field Blank	TIGF/PUF/XAD/Benzo(ghi)perylene	mg/dscm	6.68E-6
Dilution Tunnel	Field Blank	TIGF/PUF/XAD/Bibenzene	mg/dscm	2.45E-4
Dilution Tunnel	Field Blank	TIGF/PUF/XAD/C-trimethylnaphthalene	mg/dscm	5.50E-7
Dilution Tunnel	Field Blank	TIGF/PUF/XAD/Cholestane	mg/dscm	2.26E-5
Dilution Tunnel	Field Blank	TIGF/PUF/XAD/Chrysene	mg/dscm	4.18E-6
Dilution Tunnel	Field Blank	TIGF/PUF/XAD/Dibenz(ah+ac)anthracene	mg/dscm	1.69E-5
Dilution Tunnel	Field Blank	TIGF/PUF/XAD/Fluoranthene	mg/dscm	3.00E-7
Dilution Tunnel	Field Blank	TIGF/PUF/XAD/Indeno[123-cd]pyrene	mg/dscm	4.60E-6
Dilution Tunnel	Field Blank	TIGF/PUF/XAD/Perylene	mg/dscm	2.20E-6
Dilution Tunnel	Field Blank	TIGF/PUF/XAD/Phenanthrene	mg/dscm	1.80E-6
Dilution Tunnel	Field Blank	TIGF/PUF/XAD/Pyrene	mg/dscm	2.25E-6
Dilution Tunnel	Field Blank	TIGF/PUF/XAD/Xanthone	mg/dscm	7.18E-6

Table 6-2. Blank Results for Dilution Methods.

Sample Type	Blank Type	Media/Analysis		Mass (mg)
Dilution Tunnel	Field Blank 1	Tenax/1,2,3-trimethylbenzene	mg/dscm	ND
Dilution Tunnel	Field Blank 1	Tenax/Acetophenone	mg/dscm	3.1E-4
Dilution Tunnel	Field Blank 1	Tenax/Benzaldehyde	mg/dscm	2.1E-4
Dilution Tunnel	Field Blank 1	Tenax/Decane	mg/dscm	6.3E-5
Dilution Tunnel	Field Blank 1	Tenax/Styrene	mg/dscm	ND
Dilution Tunnel	Field Blank 2	Tenax/1,2,3-trimethylbenzene	mg/dscm	3.0E-5
Dilution Tunnel	Field Blank 2	Tenax/Acetophenone	mg/dscm	5.3E-4
Dilution Tunnel	Field Blank 2	Tenax/Benzaldehyde	mg/dscm	4.8E-4
Dilution Tunnel	Field Blank 2	Tenax/Decane r		5.6E-5
Dilution Tunnel	Field Blank 2	Tenax/Styrene	mg/dscm	ND
Dilution Tunnel	Field Blank 3	Tenax/1,2,3-trimethylbenzene	mg/dscm	ND
Dilution Tunnel	Field Blank 3	Tenax/Acetophenone	mg/dscm	6.1E-4
Dilution Tunnel	Field Blank 3	Tenax/Benzaldehyde mg/dsc		3.8E-4
Dilution Tunnel	Field Blank 3	Fenax/Decane mg/dscm		5.8E-5
Dilution Tunnel	Field Blank 3	Tenax/Styrene	mg/dscm	2.7E-4

Table 6-2. (Continued) Blank Results for Dilution Methods.

ND=not detected; MeFl- methylfluorene; MePy- methylpyrene

results, its probable that additional losses occurred in the dilution tunnel itself. Therefore, the dilution tunnel PM2.5 mass concentration and emission factors are probably significantly biased low (on the order of 43 percent) due to unrecovered solid particle losses in the dilution tunnel.

It is recommended that in future tests:

- Losses in all parts of the tunnel upstream of the Teflon filters should be characterized.
- The probe, sample line, and venturi (as a minimum) should be recovered by acetone rinse after each test and analyzed gravimetrically. The samples also should be analyzed for elements and ions.
- Consider adding an in-stack PM2.5 cyclone so that all particles deposited in the probe, sample line, venturi, and other parts of the dilution tunnel are known to be PM2.5.

# Precision – Dilution Tunnel

Replicate SVOC analysis was performed to determine the precision of results (Table 6-3). All but a few SVOCs were repeatable within 20% of the original value. Those SVOCs with significantly poor repeatability were present near the minimum detection limits; thus the lack of precision for these results is insignificant.

	Sample	Replicate	Relative Percent
Compound	(mg/dscm)	(mg/dscm)	Difference
1+2-ethylnaphthalene	ND	ND	
1.2.8-trimethylnaphthalene	1.2E-6	1.0E-6	20%
1,2-dimethylnaphthalene	ND	ND	
1.3+1.6+1.7-dimethylnaphthalene	ND	ND	
1.4+1.5+2.3-dimethylnaphthalene	ND	ND	
1.4.5-trimethylnaphthalene	2.1E-5	2.3E-5	-5.8%
1.4-chrysenequinone	2.4E-4	2.5E-4	-2.2%
1.7-dimethylphenanthrene	ND	ND	
1,8-dimethylnaphthalene	ND	ND	
1-ethyl-2-methylnaphthalene	5.0E-6	6.0E-6	-20%
1-MeFl+C-MePy/Fl	ND	ND	
1-methylfluorene	3.7E-6	ND	
1-methylnaphthalene	3.3E-5	3.2E-5	3.7%
1-methylphenanthrene	3.2E-6	2.7E-6	15%
1-methylpyrene	ND	ND	
1-phenylnaphthalene	1.3E-5	1.2E-5	7.7%
2,3,5+I-trimethylnaphthalene	1.4E-5	1.4E-5	-1.8%
2,4,5-trimethylnaphthalene	3.0E-6	3.7E-6	-25%
2,6+2,7-dimethylnaphthalene	7.0E-6	1.2E-5	-71%
2-ethyl-1-methylnaphthalene	2.8E-5	2.6E-5	10%
2-methylbiphenyl	1.7E-4	1.6E-4	3.1%
2-methylnaphthalene	2.8E-5	3.6E-5	-25%
2-methylphenanthrene	1.5E-5	1.5E-5	-3.3%
2-phenylnaphthalene	1.1E-5	1.2E-5	-6.5%
3,6-dimethylphenanthrene	ND	ND	
3-methylbiphenyl	1.1E-4	1.1E-4	-0.2%
4-methylbiphenyl	8.4E-5	9.4E-5	-11%
4-methylpyrene	5.0E-7	3.2E-6	-550%
4H-cyclopenta(def)phenanthrene	8.0E-5	7.7E-5	3.4%
5+6-methylchrysene	1.4E-5	1.8E-5	-29%
7-methylbenz(a)anthracene	ND	ND	
7-methylbenzo(a)pyrene	5.5E-6	2.8E-5	-418%
9,10-dihydrobenzo(a)pyrene	3.6E-4	3.6E-4	-0.3%
9-anthraldehyde	3.0E-4	2.9E-4	0.5%
9-fluorenone	2.8E-5	1.1E-4	-302%
9-methylanthracene	3.5E-6	ND	
A-dimethylphenanthrene	ND	ND	
A-methylfluorene	2.8E-5	2.7E-5	1.8%
A-methylphenanthrene	1.1E-5	1.5E-5	-30%
A-methylpyrene	2.3E-5	2.1E-5	6.6%
A-trimethylnaphthalene	5.2E-6	5.7E-6	-10%
Acenaphthene	1.7E-6	1.7E-6	0%
Acenaphthenequinone	2.1E-4	2.1E-4	-0.2%
Acenaphthylene	ND	ND	
Anthracene	6.4E-5	6.0E-5	7.0%
Anthraquinone	1.6E-4	1.7E-4	-8.7%
Anthrone	2.3E-3	2.3E-3	0.1%

Table 6-3. Replicate Analysis Results for Dilution Tunnel (SVOCs).

	Sample	Replicate	Relative Percent
Compound	(mg/dscm)	(mg/dscm)	Difference
B-MePv/MeFl	1.5E-6	2.5E-7	83%
B-methylfluorene	ND	ND	
B-methylphenanthrene	1.0E-5	1.3E-5	-26%
B-trimethylnaphthalene	9.7E-6	8.7E-6	10%
Benz(a)anthracene	2.4E-5	4.3E-5	-79%
Benz(a)anthracene-7.12	7.9E-5	8.4E-5	-5.6%
Benzanthrone	7.9E-5	1.0E-4	-27%
Benzo(a)pyrene	1.2E-5	3.1E-5	-168%
Benzo(b)chrysene	2.6E-5	5.5E-5	-113%
Benzo(b+j+k)fluoranthene	2.6E-5	5.6E-5	-113%
Benzo(c)phenanthrene	4.2E-6	6.5E-6	-53%
Benzo(e)pyrene	2.4E-5	3.6E-5	-46%
Benzo(ghi)perylene	7.2E-5	7.8E-5	-8.0%
Benzonaphthothiophene	2.5E-7	2.2E-6	-800%
Bibenzene	1.3E-3	1.2E-3	7.7%
Biphenyl	2.5E-5	2.4E-5	4.0%
C-dimethylphenanthrene	ND	ND	
C-methylphenanthrene	6.5E-6	1.1E-5	-69%
C-trimethylnaphthalene	1.2E-5	1.3E-5	-13%
Cholestane	5.2E-4	3.2E-4	38%
Chrysene	7.0E-5	7.1E-5	-1.4%
Coronene	1.3E-4	3.0E-4	-138%
D-dimethylphenanthrene	1.6E-5	1.5E-5	6.2%
D-MePy/MeFl	7.5E-7	ND	
Dibenz(ah+ac)anthracene	1.7E-4	1.8E-4	-2.8%
Dibenzofuran	7.2E-6	6.5E-6	10%
E-dimethylphenanthrene	ND	ND	
E-MePy/MeFl	5.0E-7	ND	
E-trimethylnaphthalene	4.0E-6	3.5E-6	13%
F-trimethylnaphthalene	7.0E-6	8.2E-6	-18%
Fluoranthene	1.0E-4	9.7E-5	3.5%
Fluorene	7.1E-5	6.7E-5	5.7%
Indeno[123-cd]pyrene	4.9E-5	5.5E-5	-12%
J-trimethylnaphthalene	1.0E-6	ND	
Naphthalene	8.7E-4	7.7E-4	12%
Perinaphthenone	7.3E-5	1.4E-4	-88%
Perylene	2.3E-5	2.8E-5	-22%
Phenanthrene	5.6E-4	5.3E-4	6.2%
Pyrene	9.7E-5	9.4E-5	2.8%
Retene	7.5E-6	6.5E-6	13%
Xanthone	4.8E-5	5.7E-5	-20%

Table 6-3. (Continued) Replicate Analysis Results for Dilution Tunnel (SVOCs).

ND = not detected; MeFl = Methylfluorene; MePy = Methylpyrene

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# IN-STACK AND IMPINGER METHOD QA/QC RESULTS

Blank results for in-stack and impinger methods are summarized in Table 6-4. The net weight of the in-stack filter field blank was slightly negative (less than zero) indicating a slight loss of the brittle and fibrous quartz filter material during sample handling. Dichloromethane, water and acetone recovery blanks were used to correct the EPA Method 201A/202 particulate mass as prescribed in the methods. For the Run 1 stack sample, the measured organic CPM is less than the mass measured in the methylene chloride reagent blank. OC and EC blanks were well below the level of concern.

Sample Type	Blank Type	Description	Units	Mass (mg)
EPA 202	Recovery Blank	Water	mg	1.3
EPA 202	Recovery Blank	Dichloromethane	mg	1.1
EPA 201A	Recovery Blank	Acetone	mg	0.4
EPA 201A	Field Blank	In-stack Quartz Filter	mg	<0
EPA 201A	Field Blank	PM10 Cyclone Acetone Wash	mg	0.5
EPA 201A	Field Blank	PM2.5 Cyclone Acetone Wash	mg	1.5
EPA 201A	Field Blank	<pm2.5 connector="" rinse<="" td=""><td>mg</td><td>0.3</td></pm2.5>	mg	0.3
EPA 201A	Field Blank	OC	mg/dscm	4.1E-3
EPA 201A	Field Blank	EC	mg/dscm	ND

Table 6-4. Blank Results for In-Stack and Impinger Methods.

ND = not detected

The various acetone blanks in these tests always show a small amount of material. The lower detection limits of an analytical method are frequently defined as three times the standard deviation for concentrations at or near zero. Taking the four acetone rinse results (three field blank rinses plus the recovery rinse), the resulting detection limit for the acetone rinse gravimetric procedure using this definition is approximately 1.7 mg in each fraction. Stack sample acetone rinses ranged from 5.8 to 26.1 mg, except for the <PM2.5 connector rinse from Run 1, which was 0.3 mg. The Method 201A field blanks accounted for 5 to 15 percent of the total particulate mass. The sum of the detection limits for the three acetone rinse fractions is 11 to 34 percent of the measured total mass in the stack samples. The results indicate that the total particulate emissions are very low, only somewhat greater than the capability of the test method.

#### **CEMS** Analysis

The response of the CO analyzer to  $CO_2$  was determined prior to testing, and the results demonstrated no  $CO_2$  bias in the CO results. The instruments generally were calibrated at a minimum at the beginning, middle, and end of the test day, with more frequent calibration and zero drift checks if necessary. Test results were corrected for any drift in excess of the method specifications (generally  $\pm 3$  percent).

## PROCESS SAMPLE QA/QC RESULTS

A method blank and a blank spike were performed during elemental analysis of the ESP hopper samples. In addition, duplicate analysis and method spikes were performed on the sample from Run 1 at the FCCU. Only Al, Ba, Fe and Si were detected in the blanks (Table 6-5) at levels insignificant relative to the actual samples.

# ANALYTICAL QA/QC PROCEDURES

A brief summary of general laboratory QA/QC procedures employed during these tests is provided below.

## Particulate Mass

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

						R1-FCCU	
	Method	Blank			R1-FCCU	Matrix	R1-FCCU
	Blank	Spike	Blank Spike	R1-FCCU	Duplicate	Spike	Matrix Spike
Element	(mg/kg)	(mg/kg)	(% Recovery)	(mg/kg)	(mg/kg)	(mg/kg)	(% Recovery)
Mercury	ND	1	100	ND	ND	1.1	110
Aluminum	4	220	110	48000	40000	42000	-
Antimony	ND	540	110	620	-	NS	-
Barium	0.2	110	110	9	9.7	16	69*
Beryllium	ND	52	100	3.5	3.5	48	89
Cadmium	ND	53	110	0.5	0.5	46	90
Calcium	ND	1100	110	<200	-	NS	-
Chromium	ND	110	110	87	86	180	94
Cobalt	ND	110	110	44	44	140	94
Copper	ND	110	110	41	36	130	92
Iron	4	1300	110	3600	3200	4500	94
Lead	ND	110	110	ND	ND	64	66*
Magnesium	ND	1200	110	41	48	180	12*
Manganese	ND	110	110	19	17	73	55*
Molybdenum	ND	54	110	57	58	110	100
Nickel	ND	54	110	1800	1800	1800	150**
Phosphorous	ND	530	110	510	510	1000	97
Potassium	ND	1100	100	300	380	750	41
Selenium	ND	52	110	ND	ND	38	91
Silicon	51	85	35	240000	-	NS	-
Silver	ND	54	110	1.5	1.7	48	92
Sodium	ND	1100	110	2000	1700	2200	37**
Strontium	ND	53	110	2	2.2	4.2	4.2*
Sulfur	ND	110	97	11000	11000	12000	320**
Thallium	ND	110	110	<60	-	NS	-
Tin	ND	100	100	<50	-	NS	-
Titanium	ND	110	110	6100	5900	6200	200**
Vanadium	ND	53	110	4600	4500	4600	200**
Zinc	ND	220	110	270	270	430	83
Zirconium	ND	110	110	59	53	160	100

Table 6-5. QA Results for ESP Fines Analysis.

ND- Not detected (less than MDL)

NS - Not spiked

"-" - Not analyzed

\* Poor recovery because of inter-element interference with high aluminum

\*\* Native metal levels too high to accurately determine spike recoveries

and post-weights, check weights and reweights (if required) were recorded on data sheets as well as being directly entered into a database via an RS232 connection.

### Elemental (XRF) Analysis

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

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

#### Organic and Elemental Carbon Analysis

The TOR system was calibrated by analyzing samples of known amounts of methane,  $CO_2$ , and potassium hydrogen phthalate (KHP). The FID response was compared to a reference level of methane injected at the end of each sample analysis. Performance tests of the instrument calibration were conducted at the beginning and end of each day's operation. Intervening samples were reanalyzed when calibration changes of more than  $\pm 10$  percent were found.

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

standards were used for each calibration. Widely accepted primary standards for EC and/or OC are still lacking. Results of the TOR analysis of each filter were entered into the laboratory database.

## Sulfate, Nitrate, Chloride and Ammonium Analysis

The primary standard solutions containing sodium chloride (NaCl), sodium nitrate (NaNO<sub>3</sub>) and sodium sulfate ((Na)<sub>2</sub>SO<sub>4</sub>) were prepared with reagent grade salts which were dried in an oven at 105 °C for one hour and then brought to room temperature in a desiccator. These anhydrous salts were weighed to the nearest 0.10 mg on a routinely calibrated analytical balance under controlled temperature (approximately 20°C) and relative humidity ( $\pm$ 30 percent) conditions.

These salts were diluted in precise volumes of distilled deionized (DI) water. Calibration standards were prepared at least once within each month by diluting the primary standard solution to concentrations covering the range of concentrations expected in the filter extracts and stored in a refrigerator. The calibration concentrations prepared were at 0.1, 0.2, 0.5, 1.0, and 2.0  $\mu$ g/ml for each of the analysis species. Calibration curves were performed weekly. Chemical compounds were identified by matching the retention time of each peak in the unknown sample with the retention times of peaks in the chromatograms of the standards. A DI water blank was analyzed after every 20 samples and a calibration standard was analyzed after every 10 samples. These quality control checks verified the baseline and calibration, respectively. Environmental Research Associates (ERA, Arvada, CO) standards were used daily as an independent quality assurance (QA) check. The standards (ERA Wastewater Nutrient and ERA Mineral WW) were traceable to NIST simulated rainwater standards. If the values obtained for these standards did not coincide within a pre-specified uncertainty level (typically three standard deviations of the baseline level or ±5 percent), the samples between that standard and the previous calibration standards were reanalyzed.

After analysis, the printout for each sample in the batch was reviewed for the following: 1) proper operational settings; 2) correct peak shapes and integration windows; 3) peak overlaps; 4) correct background subtraction; and 5) quality control sample comparisons. When values for replicates differ by more than  $\pm 10$  percent or values for standards differ by more than  $\pm 5$  percent, samples before and after these quality control checks are designated for reanalysis in a

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subsequent batch. Individual samples with unusual peak shapes, background subtractions, or deviations from standard operating parameters are also designated for reanalysis.

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

## SVOC Analysis

Prior to sampling, the XAD-4 resin was Soxhlet extracted with methanol, followed by dichloromethane, each for 24 hours. The cleaned resin was dried in a vacuum oven heated to 40°C and stored in sealed glass containers in a clean freezer. The PUF plugs were Soxhlet extracted with acetone, followed by 10 percent diethyl ether in hexane. The TIGF filters were cleaned by sonification in dichloromethane for 30 minutes followed by another 30-minute sonification in methanol. Then they were dried, placed in aluminum foil, and labeled. Each batch of precleaned XAD-4 resin and approximately 10 percent of the precleaned TIGF filters and PUF plugs were checked for purity by solvent extraction and GC/MS analysis of the extracts. The PUF plugs and XAD-4 resins were assembled into glass cartridges (10 g of XAD between two PUF plugs), wrapped in hexane-rinsed aluminum foil and stored in a clean freezer prior to shipment to the field.

Prior to extraction, deuterated internal standards were added to each filter-sorbent pair (Table 6-6). Calibration curves for the GC/MS/MID quantification were made for the molecular ion peaks of the PAH and all other compounds of interest using the corresponding deuterated species (or the deuterated species most closely matched in volatility and retention characteristics) as internal standards. NIST Standard Reference Material (SRM) 1647 (certified PAH), with the addition of deuterated internal standards and compounds not present in the SRM, was used to make calibration solutions. Three concentration levels for each analyte were employed, and each calibration solution was injected twice. After the three-level calibration was completed, a

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

Table 6-6. Internal Standards for SVOC Analysis.

standard solution was injected to perform calibration checks. If deviation from the true value exceeded 20 percent, the system was recalibrated. The MSD was tuned daily for mass sensitivity using perfluorotributylamine.

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

# **VOC Analysis**

Calibration curves were performed weekly. VOCs were identified by matching the response factors of each unknown sample with the response factors of the standards. Tenax cartridges spiked with a mixture of paraffinic (in the C<sub>9</sub>-C<sub>20</sub> range) and aromatic (C<sub>4</sub>, C<sub>5</sub>, and C<sub>6</sub> benzenes) hydrocarbons were periodically analyzed by GC/FID to verify quantitative recovery from the cartridges. Three to five different concentrations of the hydrocarbon standard and one zero standard were injected, and the response factors obtained. If the percent difference of the

response factor from the mean was more than 5 percent, the response factors were corrected before proceeding with the analysis.

# SAMPLE STORAGE AND SHIPPING

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


### Section 7 DISCUSSION AND FINDINGS

#### PRIMARY PM2.5 MASS EMISSIONS

EPA Methods 201A and 202 collect filterable and condensible particles separately and on different media (on a filter and in impinger solutions, respectively), whereas the dilution tunnel captures filterable particles plus any aerosols that condense under simulated plume conditions together on the same filter. The in-stack/impinger and dilution tunnel measurements gave very different results for PM2.5 mass. The in-stack/impinger methods yield a total (filterable plus condensible) PM2.5 mass concentration that is 8.8 times greater than that from the dilution tunnel. Several known and potential reasons for this difference were identified, with biases likely in both test methods.

Foremost, solid particle deposits that were recovered from the dilution tunnel probe, sample line, and venturi at the conclusion of the final test run indicate significant solid particle deposition in these parts of the sampling system. When included with the Teflon filter results, these deposits represent approximately 43 percent of the total particulate concentration measured by the dilution tunnel. Deposits in the tunnel itself and residence time chamber were not recovered. Visual inspection of these components did not indicate a large amount of deposits; however, the relatively large amount of surface area in these components could make even light deposits potentially significant. Some minor pitting of the stainless steel dilution tunnel surface was noted near the probe entry point, which probably indicates a slight amount of H<sub>2</sub>SO<sub>4</sub> condensation. Therefore, the EPA Method 201A results are considered more representative of filterable PM2.5 mass emissions.

Another potential explanation lies in the measurement of condensible particles. Fifty-one percent of the total PM mass from Methods 201A/202 is accounted for by the condensible particulate fraction, essentially all of which is inorganic CPM. SO<sub>3</sub> (or H<sub>2</sub>SO<sub>4</sub>) concentration by controlled condensation is approximately 25 ppmv, on average. This corresponds to approximately 2.9 percent of the measured SO<sub>2</sub> in the flue gas. The total CPM by Method 202 and the H<sub>2</sub>SO<sub>4</sub> by controlled condensation yield very similar mass results (38 lb/hr vs. 41 lb/hr, respectively), indicating H<sub>2</sub>SO<sub>4</sub> likely accounts for all of the CPM emissions. The Method 202

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results show only 27 percent of the total CPM as  $SO_4^=$  (36 percent as  $(NH_4)_2SO_4$ ) and 1.7 percent as Cl<sup>-</sup>. The balance of the inorganic CPM is unspeciated by Method 202. The  $SO_4^=$  analysis is performed on the raw impinger sample prior to sample preparation; therefore, this may not represent the  $SO_4^=$  content of the actual residue that is gravimetrically analyzed for mass. Because the Method 202 analytical procedure (see Figure 3-5) is complex and H<sub>2</sub>SO<sub>4</sub> can be troublesome during sample analysis, the CPM mass and/or  $SO_4^=$  reported by Method 202 may be subject to significant errors. In future tests, it is recommended that the inorganic residue be fully speciated to determine its composition directly. This would eliminate ambiguity regarding the CPM composition and allow more direct comparison to the dilution tunnel and other results.

Expressed as  $H_2SO_4$ , the mass emission rate of  $SO_3$  by controlled condensation is 14 times greater than  $SO_4^{=}$  by the dilution tunnel. Potential explanations for this difference include: not all the  $SO_3$  may be converted to  $H_2SO_4$  in the dilution tunnel; unaccounted losses of  $H_2SO_4$  in the dilution tunnel; reduced condensation of  $H_2SO_4$  under dilute conditions; artifacts from  $SO_2$  that may be oxidized to  $SO_3$  on the controlled condensation train quartz filter, biasing those results high; or other potential sampling and analytical artifacts. No data other than anecdotal evidence were found to support  $SO_2$  artifacts in the controlled condensation train; hence these results are considered valid. It is expected from fundamental considerations that less  $H_2SO_4$  will condense in diluted samples (or in the atmosphere) than in undiluted samples; thus, part or all of the discrepancy is expected and normal. In the atmosphere, all the  $SO_3$  eventually is expected to form  $H_2SO_4$ ; however, the  $H_2SO_4$  may partition in the atmosphere to liquid (by dissolving into existing cloud/rain droplets) droplets or to solid particles (e.g., ammonium sulfate). Therefore, the fraction of the emitted  $H_2SO_4$  that contributes to condensible airborne particulate matter must be estimated through the use of air quality models. Since the partitioning to solid and liquid particles is unknown, a conservative approach is to consider all the emitted  $SO_3/H_2SO_4$  as CPM.

Another potential positive bias in the CPM measurement by Method 202 exists due to artifact  $SO_4^{=}$  formation arising from  $O_2$  and  $SO_2$  absorption and subsequent  $SO_2$  oxidation in the water impingers. This artifact is fairly well documented by others at high  $SO_2$  concentrations (Filadelfia et al., 1996). Recent results (Wien and England, 2001) indicate that the long sampling

times used during these tests probably increase the extent of the artifact due to longer contact time in solution. Compared to the amount of  $SO_3/H_2SO_4$ , the  $SO_2$  artifact is not considered significant in these tests.

Based on these results, the Method 201A and controlled condensation results are considered the best representation of actual FPM and CPM mass emission factors, respectively. Further development of the dilution tunnel and test methodology should address means to reduce unaccounted particle losses in the system. The average particulate emission factor observed during these tests are at the very low end of the range reported by EPA (EPA, 1995).

#### PARTICLE SIZE DISTRIBUTION

Particle size distribution measurements using cascade impactors and series cyclones in-stack are in qualitative agreement. At stack temperature, 93 percent of the solid particles are smaller than 10  $\mu$ m, and 72 (hot cascade impactors) to 87 (cyclones) percent are smaller than 2.5  $\mu$ m.

The cooled (temperature below acid dew point) cascade impactor results and total (FPM plus CPM) particulate mass by Method 201A/202 are in qualitative agreement. They indicate a strongly bimodal particle size distribution, with the majority of the particle volume accounted for in the PM2.5 fraction. Compared to the hot cascade impactor results, a sharp increase in the mass of particles smaller than 1  $\mu$ m is apparent in the cooled cascade impactor. This is consistent with condensation of H<sub>2</sub>SO<sub>4</sub> on the surfaces of the smaller particles and subsequent agglomeration.

#### SPECIATION OF PRIMARY PM2.5 EMISSIONS

Although PM2.5 mass emission factors determined using the dilution tunnel are biased significantly low, the dilution tunnel results are considered to best represent total primary PM2.5 (FPM2.5 plus CPM) chemical speciation, with the exception of  $SO_4^=$  for reasons discussed above. Since the majority of the emitted filterable particles appears to be catalyst fines, and since there is no evidence to indicate the losses of particles in the dilution tunnel upstream of the sampling media are size or species dependent, the dilution tunnel speciation results are assumed valid. However, future tests should be directed at confirming this assumption.

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Examining the speciation of the dilution tunnel samples, the most abundant species is  $SO_4^{=}$  (Figure 7-1), accounting for approximately 85 percent of the total PM2.5 mass. This agrees qualitatively with the in-stack filter (Method 201A) and controlled condensation method results, which indicate 76 percent of the PM2.5 mass is accounted for by sulfate. The next most abundant are Si (6 percent) and Al (3.5 percent) which is consistent with the composition of the FCCU catalyst substrate. Neglecting S (see earlier discussions), Fe, La, Cu, Ti, V and Ni are the next most abundant, present at very low concentrations. La, Fe and Ti are known to catalyze certain reactions and may be active elements in the FCCU catalyst. The standard deviation for the Cu results exceeds the mean, which indicates a large degree of uncertainty for this result. V and Ni probably originate in the FCCU feed and become bound to the catalyst during the cracking process. These elements may serve as effective markers in source apportionment studies. Qualitatively, the elemental profile is similar to the ESP fines composition reported earlier (see Table 4-20). With the exception of  $SO_4^{=}$ , the elemental profile compares qualitatively well with speciation profiles reported by EPA in the SPECIATE database (EPA, 2001). Concentrations of the 11 metals considered by EPA to be HAPs (Sb, As, Be, Cd, Cr, Co, Pb, Mn, Hg, Ni, Se) are either extremely low or undetected in the stack gas.

The test results indicate that concentrations of OC, EC and SVOC are very low, within a factor of ten of the analytical detection limits or the field blank levels in most cases. OC accounts for 0.8 percent of the total PM2.5 mass as measured by the dilution tunnel, and comprises approximately 85 percent of the total particulate carbon. OC is approximately 83 percent of total particulate carbon and approximately 0.03 percent of the total filterable particulate mass by Method 201A. SVOCs detected were present only at extremely low concentrations. For example, benzo[a]pyrene was present at concentrations of approximately 3 to 4 pptv. These levels compare quite well with results of 2 to 10 pptv reported for natural gas combustion following good combustion practices (England et al., 2001). One half of the SVOCs detectable in the dilution tunnel samples are within 10 times the ambient level and one fifth are within 10 times the field blank levels. Thus, the contribution of the FCCU to SVOC in the ambient air is considered practically negligible. In-stack filters also were used to analyze for SVOCs, but very few SVOC are above detection limits. These results suggest that most of the SVOCs detected with the dilution tunnel are present in the vapor phase at stack temperatures and therefore not captured on the in-stack filter. Note, the dilution tunnel sampling approach is designed to





Figure 7-1. Average Concentrations of Detected Substances in the FCCU Stack Gas (FCCU, Refinery Site A).

capture both vapor- and condensed-phase SVOCs, whereas the in-stack filter collects only SVOCs that condense at stack temperature or adsorb on the filter.

The mass balance between total PM2.5 and speciated mass provides a general indication of the overall data quality. Expressed in elemental form, the sum of individual species mass (except Cl<sup>-</sup>, Mg, Na, and S, which are excluded as explained in Section 5) is comparable (within 5 percent) to the gravimetrically measured PM2.5 mass on the Teflon filter. Although this agreement is considered excellent, it is also somewhat fortuitous since many of the elements are expected to be in higher oxide form (e.g., Si and Al present as SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>). These have higher molecular weights than the elemental forms. Assuming all the elements are present as higher oxides, the sum of individual species is approximately three times the PM2.5 mass measured gravimetrically. The true degree of closure is probably somewhere in between these results. The sum of all SVOCs accounts for only 7 percent of the OC measured by the dilution tunnel. This is probably a consequence of the extremely low concentrations of individual SVOC species and the vastly different analytical techniques used for determining OC and SVOCs. Incomplete speciation of OC is commonly encountered in other studies for the same reasons.

To further evaluate the quality of the speciation data, the concentrations of various substances can be compared with their respective concentrations in the ambient air and with their analytical detection limits. With the exception of Br and Cl<sup>-</sup>, all of the elements and ions detected in the stack gas were present at concentrations significantly (i.e., more than a factor of 10) higher than their respective concentrations in the ambient air (Figure 7-2). Elemental Cl (by XRF), which was not detected in the stack gas but was detected in the ambient air, and Cl<sup>-</sup> (by IC) are not in good agreement. Cl<sup>-</sup> was detected in both the stack gas and ambient air, but at very low levels that are not significantly different. Cl/ Cl<sup>-</sup> concentrations are extremely low in any case. Both OC and EC are slightly elevated in the stack gas relative to the ambient air, again at low levels that may not be significantly different. Slightly less than one third of the elements and ions detected in the stack gas (Ba, Br, Ga, Rb, Se, Sn, Tl, U, Y, Cl<sup>-</sup>), are OC and EC are present at levels within a factor of 10 of their respective detection limits (Figure 7-3). Therefore, the qualitative uncertainty associated with these results is somewhat greater than that for the other substances detected.

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Figure 7-2. Comparison of Average Sample Concentration and Detection Limits (FCCU, Refinery Site A).



Figure 7-3. Comparison of Stack and Ambient Air Results (FCCU, Refinery Site A).

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Despite the seemingly large uncertainties in the data, the overall confidence in speciation results should be considered high because PM2.5 mass closure within a factor of two or three is still good given all the known and potential errors in the sampling and analysis procedures.

#### PM2.5 PRECURSOR EMISSIONS

PM2.5 precursors characterized in these tests include NO<sub>X</sub>, SO<sub>2</sub>, NH<sub>3</sub>, and VOCs with carbon number greater than seven. SO<sub>2</sub>, and to a lesser extent NO<sub>X</sub>, comprise almost the entire mass emission of PM2.5 precursors. Less than one half ppm of NH<sub>3</sub> was measured, near the minimum detection limit of the method used. The NH<sub>3</sub> (by impinger method) results are approximately four times higher than the NH<sub>4</sub><sup>+</sup> (by dilution tunnel) results, on an equivalent molar basis. If present in the stack gas, gaseous NH<sub>3</sub> and aerosol H<sub>2</sub>SO<sub>4</sub> are expected to react almost instantaneously to form (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, a solid at ambient temperature. Since a large excess of SO<sub>3</sub> for this reaction was measured by controlled condensation, the difference in NH<sub>3</sub> and NH<sub>4</sub><sup>+</sup> results provides further support for reduced H<sub>2</sub>SO<sub>4</sub> formation under dilute sample conditions in the dilution tunnel (discussed earlier). 31 VOCs with carbon number greater than 7 were detected in the stack samples but at very low concentrations. Most of the detected VOCs are considered fuel fragments or products of incomplete combustion. A few VOCs considered HAPs were detected at low concentrations generally close to background or detection levels, including benzaldehyde, ethylbenzene, xylenes and a small number of others.

#### FINDINGS

Summarizing the key findings of these tests:

- Traditional in-stack/impinger method (Method 201A and controlled condensation) results are considered the best representation of actual FPM and CPM 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 HAPs) comprising PM2.5 emissions than traditional in-stack/impinger methods. Dilution tunnel results are considered the best representation of PM2.5 speciation, compared to traditional in-stack/impinger methods.

- PM2.5 emissions from this FCCU during these tests were 43 percent FPM and 57 percent CPM (based on Method 201A and controlled condensation results, respectively).
- PM2.5 (including H<sub>2</sub>SO<sub>4</sub> as CPM) comprises 94 percent of the total particulate emissions from the FCCU.
- PM2.5 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.
- PM2.5 emissions from the FCCU at this refinery are composed principally of catalyst fines, SO<sub>3</sub> (at stack temperatures) and H<sub>2</sub>SO<sub>4</sub>.
- SO<sub>2</sub> and NO<sub>X</sub> comprise the majority of PM2.5 precursor emissions.
- Emissions of speciated organic compounds, including several HAPs, are extremely low, with only a few compounds significantly exceeding background levels or minimum detection limits.
- Potential chemical markers for FCCU emissions include Si, Al, Fe, La, Ti, V and Ni.
- Despite uncertainties associated with some measurements, these results represent a very comprehensive and useful characterization of FCCU emissions.

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## Appendix A

## GLOSSARY

$(Na)_2SO_4$	sodium sulfate				
$(NH_4)_2SO_4$	ammonium sulfate				
<	less than reporting limit				
°F	degrees Fahrenheit				
μg	microgram				
$\mu g/cm^2$	micrograms per square centimeter				
μm	micrometer				
AC	automated colorimetry system				
acfm	actual cubic feet per minute				
ACS	American Chemical Society				
Ag	silver				
Al	aluminum				
API	American Petroleum Institute				
As	arsenic				
ASME	American Society of Mechanical Engineers				
Au	gold				
Ba	barium				
bbl	barrel (crude oil)				
Br	bromine				
Btu/scf	British thermal units per standard cubic foot				
Ca	calcium				
Cd	cadmium				
CEMS	continuous emissions monitoring system				
Cl	chloride ion				
Cl	chlorine				
CO	carbon monoxide				
Co	cobalt				
$CO_2$	carbon dioxide				
CPM	condensible particulate matter				
Cr	chromium				
Cu	copper				
C <sub>x</sub>	compound containing 'x' carbon atoms				
DI	distilled deionized				
DRI	Desert Research Institute				
dscfm	dry standard cubic feet per minute				
dscmm	dry standard cubic meters per minute				
EC	elemental carbon				
ED-XRF	energy dispersive x-ray fluorescence				
EER	GE Energy and Environmental Research Corporation				
EI	electron impact				
EPA	Environmental Protection Agency				
ERA	Environmental Research Associates				

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# GLOSSARY

## (continued)

ESP	electrostatic precipitator
FCCU	fluid catalytic cracking unit
Fe	iron
FID	flame ionization detection
FPM	filterable particulate matter
ft/sec	feet per second
FTIR	Fourier transform infrared detection
Ga	gallium
GC	gas chromatography
GC/IRD/MSD	gas chromatography/infrared detector/mass selective detector
GC/MS	gas chromatography/mass spectrometry
GE EER	General Electric Energy and Environmental Research Corporation
GE	General Electric
gr/100dscf	grains per hundred dry standard cubic feet
G-S	Greenburg-Smith
H <sub>2</sub> S	hvdrogen sulfide
$H_2SO_4$	sulfuric acid
HC1	hydrochloric acid
НЕРА	high efficiency particulate air
Hg	mercurv
HHV	higher heating value
IC	ion chromatography
In	indium
K	potassium
КНР	potassium hydrogen phthalate
La	lanthanum
$\frac{10}{1000}$ lb	pounds per thousand pounds
lb/hr	pounds per hour
lb/MMBtu	pounds of pollutant per million British thermal units of gas fired
m/sec	meters per second
Mg	magnesium
mg	milligram
mg/dscm	milligrams per dry standard cubic meter
MID	multiple ion detection
Mlb/hr	thousand pounds per hour
MMBtu/hr	million British thermal units per hour
Mn	manganese
Мо	molybdenum
MSD	mass spectrometric detector
MSD/FTIR	mass selective detector/Fourier transform infrared detection
n/a	not applicable
Na	sodium
Na <sub>2</sub> CO <sub>3</sub>	sodium carbonate
<u> </u>	

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# GLOSSARY

## (continued)

NaCl	sodium chloride
NaHCO <sub>3</sub>	sodium bicarbonate
NaNO <sub>3</sub>	sodium nitrate
NaOH	sodium hydroxide
ND	not detected
NDIR	non-dispersive infrared
NDUV	non-dispersive ultraviolet
NH <sub>3</sub>	ammonia
NH4 <sup>+</sup>	ammonium ion
Ni	nickel
NIST	National Institute of Standards and Technology
NO	nitric oxide
$NO_2$	nitrogen dioxide
NO <sub>3</sub> <sup>-</sup>	nitrate ion
NO <sub>x</sub>	oxides of nitrogen
NS	not spiked
$O_2$	molecular oxygen
°C	degrees celsius
OC	organic carbon
°F	degrees Farenheit
Р	phosphorus
РАН	polycyclic aromatic hydrocarbon
Pb	lead
PCA	Portland Cement Association
Pd	palladium
PM	particulate matter
PM10	particulate with aerodynamic diameter less than 10 micrometers
PM2.5	particulate with aerodynamic diameter less than 2.5 micrometers
ppbv	parts per billion by volume
ppmv	parts per million by volume
pptv	parts per trillion by volume
psig	pounds per square inch (gauge)
PUF	polyurethane foam
QA	quality assurance
Rb	rubidium
RSD	relative standard deviation
S	sulfur
Sb	antimony
Se	selenium
Si	silicon
SI	Systeme Internationale
Sn	tin
$SO_2$	sulfur dioxide

### GLOSSARY (continued)

$SO_3$	sulfur trioxide
$SO_4^{=}$	sulfate ion
Sr	strontium
SRM	standard reference material
SVOC	semivolatile organic compound
TFE	tetrafluoroethylene
Ti	titanium
TIGF	Teflon-impregnated glass fiber
T1	thallium
TMF	Teflon-membrane filter
TOR	thermal/optical reflectance
U	uranium
V	vanadium
VOC	volatile organic compound
XAD-4	Amberlite® sorbent resin (trademark)
XRF	x-ray fluorescence
Y	yttrium
Zn	zinc
Zr	zirconium

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## Appendix B

## SI CONVERSION FACTORS

	English (US) units	Х	Factor	=	<u>SI units</u>
Area:	$1 \text{ ft}^2$	X	9.29 x 10 <sup>-2</sup>	=	$m^2_2$
	l 1n <sup>2</sup>	Х	6.45	=	cm <sup>2</sup>
Flow Rate:	1 gal/min	х	6.31 x 10 <sup>-5</sup>	=	m <sup>3</sup> /s
	1 gal/min	Х	6.31 x 10 <sup>-2</sup>	=	L/s
Length <sup>.</sup>	1 ft	x	0 3048	=	m
8	1 in	X	2.54	=	cm
	1 yd	X	0.9144	=	m
Mass <sup>.</sup>	1 lb	x	$4.54 \times 10^2$	=	g
	1 lb	X	0.454	=	8 kg
	1 gr	X	0.0648	=	g
Volume:	$1 \text{ ft}^3$	х	28.3	=	L
	$1 \text{ ft}^3$	х	0.0283	=	$m^3$
	1 gal	х	3.785	=	L
	1 gal	х	3.785 x 10 <sup>-3</sup>	=	$m^3$
	1 bbl	Х	159.0	=	L
Temperature	°F-32	X	0.556	=	°C
-	°R	Х	0.556	=	K
<b>D</b>	D		1055 1		<b>x</b> 1
Energy	Btu	Х	1055.1	=	Joules
Power	Btu/hr	х	0.29307	=	Watts

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