
Gas-Fired Steam Generator— Test Report Site C

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

Regulatory and Scientific Affairs

PUBLICATION NUMBER 4712
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PREPARED UNDER CONTRACT BY:

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



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API STAFF CONTACT

Karin Ritter, Regulatory and Scientific Affairs

MEMBERS OF THE PM SOURCE CHARACTERIZATION WORKGROUP

Lee Gilmer, Equilon Enterprises LLC, Stationary Source Emissions Task Force,
Chairperson

Karl Loos, Equilon Enterprises LLC

Miriam Lev-On, BP

Jeff Siegell, ExxonMobil Research and Engineering

GE ENERGY AND ENVIRONMENTAL RESEARCH CORPORATION

PROJECT TEAM MEMBERS

Glenn England, Project Manager

Stephanie Wien, Project Engineer

Bob Zimperman, Field Team Leader

Barbara Zielinska, Desert Research Institute

Jake McDonald, Desert Research Institute

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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 diameters smaller than 2.5 micrometers (PM_{2.5}). There are few existing data regarding emissions and characteristics of fine aerosols from petroleum industry combustion sources, and the information that is available is old. Traditional stationary source air emission sampling methods tend to underestimate or overestimate the contribution of the source to ambient aerosols because they do not properly account for primary aerosol formation, which occurs after the gases leave the stack. This issue was extensively reviewed by the American Petroleum Institute (API) in a recent report (England *et al.*, 1997), which concluded that dilution sampling techniques are more appropriate for obtaining a representative sample from combustion systems. These techniques have been widely used in research studies (Hildemann *et al.*, 1994; McDonald *et al.*, 1998) and use clean ambient air to dilute the stack gas sample and provide 80-90 seconds residence time for aerosol formation prior to sample collection for determination of mass and chemical speciation.

As a result of the API review, a test protocol was developed based on the dilution sampling system described in this report. The dilution sampling protocol was used to collect particulate emissions data from petroleum industry combustion sources, along with emissions data obtained from conventional sampling methods. This test program is designed to provide reliable source emissions data for use in assessing the contribution of petroleum industry combustion sources to ambient PM_{2.5} concentrations. The goals of this test program were to:

- Develop emission factors and speciation profiles for emissions of fine particulate matter, especially organic aerosols; and
- Identify and characterize PM_{2.5} precursor compound emissions.

This test report describes the results of tests performed on a gas-fired steam generator at Site C on October 21, 22 and 25, 1999.

PROJECT OBJECTIVES

The specific objectives of this test were to:

Primary Objectives

- Compare PM_{2.5} mass measured using an in-stack filter and an iced impinger train (EPA Method 201A/202), and mass measured using a dilution tunnel;
- Develop emission factors and speciation profiles for organic aerosols and PM_{2.5} mass;
- Characterize sulfate, nitrate, ammonium, inorganic elements, elemental carbon (EC) and organic carbon (OC) in particulate matter collected on filter media in the dilution sampler;
- Characterize key secondary particle precursors in stack gas samples: volatile organic compounds (VOC) with carbon number of 7 and above; sulfur dioxide (SO₂); and oxides of nitrogen (NO_x); and
- Document the relevant process design characteristics and operating conditions during the test.

Secondary Objective

- Characterize ions (sulfate, nitrate and ammonium), OC, and EC in particulate collected on filter media in stack gas sampling trains.

TEST OVERVIEW

The scope of testing is summarized in Table 1-1. The emissions testing included simultaneous collection and analysis of both in-stack and diluted stack gas samples. All emission samples were collected from the stack of the unit. The samples were analyzed for the compounds listed in Table 1-2. Process data and fuel gas samples were collected during the tests to document operating conditions.

Source Level (In-stack) Samples

In-stack sampling and analysis for filterable (total, PM₁₀ and PM_{2.5}) and condensible particulate matter (CPM), NO_x, oxygen (O₂), carbon dioxide (CO₂), carbon monoxide (CO) and SO₂ was performed using traditional EPA methods. In-stack cyclones and filters were used for filterable particulate matter. Sample analysis was expanded to include OC, EC and organic species on the in-stack quartz filters.

Table 1-1. Overview of Sampling Scope.

Sampling Location	Number of Samples		
	Fuel Gas Header	Stack	Ambient Air
EPA Method 201A/202 train	--	3	--
EPA Method 6 train	--	3	--
Dilution tunnel Teflon [®] filter TIGF/PUF/XAD-4 Quartz filter Tenax	--	3	1
Fuel sample	3	--	--
NO _x , CO, O ₂ , CO ₂	--	Continuous	--
Process monitoring	--	Hourly	--

TIGF - Teflon[®]-impregnated glass fiber filter

PUF - polyurethane foam

XAD-4 - Amberlite[®] sorbent resin

Dilution Stack Gas Samples

Dilution sampling was used to characterize PM_{2.5} including aerosols formed in the near-field plume. The dilution sampler extracted a sample stream from the stack into a mixing chamber, where it was diluted approximately 21:1 with purified ambient air. Because PM_{2.5} behaves aerodynamically like a gas at typical stack conditions, the samples were extracted nonisokinetically. A slipstream of the mixed and diluted sample was extracted into a residence time chamber where it resided for approximately 80 seconds to allow time for low-concentration aerosols, especially organics, to condense and grow. The diluted and aged sample then passed through cyclone separators sized to remove particles larger than 2.5 microns, after which samples were collected on various media: high-purity quartz, Teflon[®] membrane filters (TMF), and Teflon[®]-impregnated glass fiber (TIGF) filters; a polyurethane foam (PUF)/Amberlite[®] sorbent resin (XAD-4)/PUF cartridge to collect gas phase semivolatile organic compounds; and a Tenax cartridge to capture VOCs. Three samples were collected on three sequential test days.

Table 1-2. Summary of Analytical Targets.

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

TMF - Teflon® membrane filter

TIGF - Teflon®-impregnated glass fiber filter

*Carbon number of 7 or greater

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

Process Samples

A sample of the fuel gas burned in the steam generator was collected on each day of testing and analyzed for specific gravity, heating value, and hydrocarbon speciation.

KEY PERSONNEL

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

- Glenn England (GE EER) - Program Manager (949) 859-8851
- Stephanie Wien (GE EER) - Project Engineer (949) 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
- Karin Ritter (API) - API Project Officer (202) 682-8472

Section 2

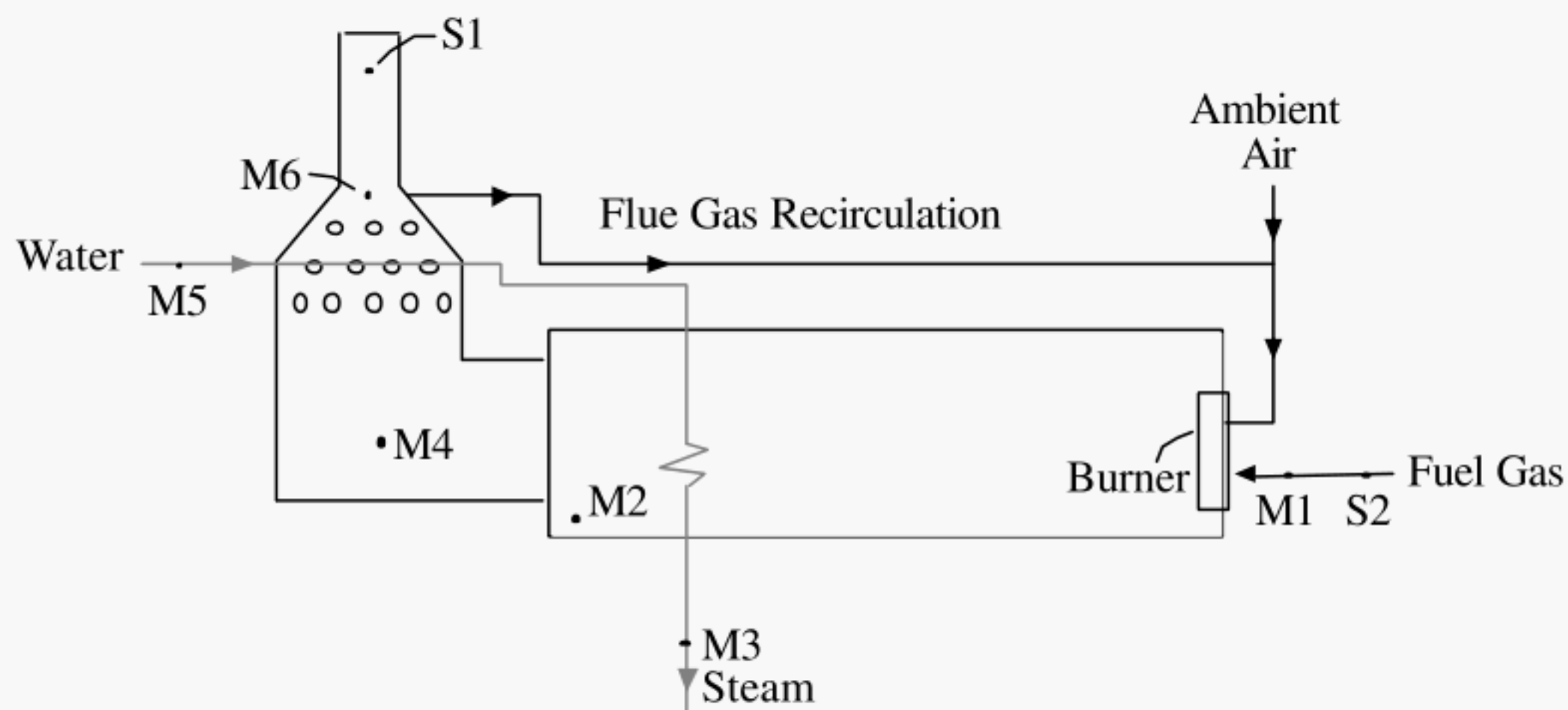
PROCESS DESCRIPTION

The tests were performed on a gas-fired steam generator at Site C. The generator has a maximum heat input of 62.5 MMBtu/hr with an average rate of approximately 50 MMBtu/hr. The unit is an oil field steam generator with a single burner and retrofitted with flue gas recirculation. The generator was designed to fire both crude oil and natural gas, but is now only fired on natural gas. The generator appeared to be in good working condition during the test. Operating conditions during the test are given in Section 4. Process parameters monitored during testing include: burner gas rate; inlet water rate; steam quality; radiant section, steam and stack temperature; and excess oxygen.

SAMPLING LOCATIONS

Figure 2-1 provides an overview of the generator process and the sampling and monitoring locations. Flue gas samples were collected from the stack. The single stack is equipped with a 3 feet by 10.5 feet rectangular sampling platform located approximately 25 feet above the ground, which is accessible via a ladder. There are two 4-inch diameter sampling ports on the stack which are at 45° to one another. The ports are threaded with a 4-inch nipple. The stack diameter at this elevation is 36 inches. The sample ports are located 16 and 29 inches (0.4 and 0.9 diameters) downstream and 104 and 91 inches (2.9 and 2.5 diameters) upstream of flow disturbances. Following velocity and O₂ traverses to check for uniform mixing, all sampling was performed at a single point in the center of the stack to facilitate co-location of the dilution tunnel and EPA Method 201A/202 probes.

Fuel gas samples were collected from the gas supply fuel-sampling manifold. Ambient air samples were collected at ground-level close to the air inlet for the steam generator.



<u>Sampling location</u>	<u>Description</u>	<u>Parameters</u>
S1	Stack	See Table 3-1
S3	Fuel gas feed	
M1	Fuel gas feed	Burner gas rate
M2	Radiant section	Radiant temperature
M3	Steam feed	Steam temperature, steam quality
M4	Radiant section outlet	Excess oxygen
M5	Water feed	Inlet water rate
M6	Stack	Stack temperature

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

Section 3

TEST PROCEDURES

An overview of the sampling and analysis procedures is given in Table 3-1. Figure 3-1 shows the testing chronology for the dilution tunnel and in-stack methods. The time of day for the start and finish of each measurement run is shown on the figure. For example, Method 201A/202 Run 1 began at 09:30 hours and finished at 15:30 hours on Thursday, October 21. Dilution tunnel testing and in-stack testing were performed concurrently. All samples were collected at approximately the same point in the center of the stack; the dilution tunnel and in-stack test method probes were co-located. Testing during Run 3 was halted before the 6-hour sample time due to a process upset. A change in fuel quality caused the oxygen levels in the flue gas to drop, and the unit was not able to automatically adjust to the low levels.

STACK GAS FLOW RATE, MOISTURE CONTENT AND MOLECULAR WEIGHT

An S-type Pitot tube (EPA Method 2) was used to determine the average stack gas velocity and volumetric flow rate. Stack gas molecular weight was calculated in accordance with EPA Method 3. Moisture content of the sample was determined based on weight gain of the impingers used in the Method 201A/202 train according to EPA Method 4. A full velocity traverse of the stack was performed before and after each test to determine total stack gas flow rate.

O₂, CO₂, CO, AND NO_x

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

Table 3-1. Summary of Test Procedures.

Sampling Location	Measurements	Sampling Approach	Sample Analyses	Reference
S1 (Stack)	Total PM, PM10, PM2.5 and composition	In-stack series cyclones and filter	Mass; organic species	U.S. EPA Method 201A (modified)
	Condensible PM and composition	Impingers	Mass (organic and inorganic), sulfate, chloride, nitrate, ammonium, elements	U.S. EPA Method 202 (modified)
	Gaseous PM2.5 Precursors	Continuous	NO _x (O ₂ , CO ₂ , CO also measured)	U. S. EPA Methods 3A/6C/7E/10
		Impingers	SO ₂	U.S. EPA Method 6; SCAQMD Method 6.1
S1 (Stack)	PM2.5 mass and chemical composition	Dilution tunnel and filters	Mass, organic carbon, elemental carbon, elements, sulfate, nitrate, chloride, ammonium	U.S. EPA, 1999a; Hildemann <i>et al.</i> , 1989
	VOC	Dilution tunnel and Tenax	Speciated VOC	Zielinska <i>et al.</i> , 1996; Hildemann <i>et al.</i> , 1989
	SVOC	Dilution tunnel and filter/PUF/XAD-4/PUF	Speciated SVOC	U.S. EPA Method TO13; Hildemann <i>et al.</i> , 1989
S2 (Ground level – ambient air)	PM2.5 and chemical composition	Filters	Mass, organic carbon, elemental carbon, organic species, elements, chloride, sulfate, nitrate, ammonium	U.S. EPA, 1999a
	VOC	Tenax	Speciated VOC	Zielinska <i>et al.</i> , 1996
	SVOC	PUF/XAD-4/PUF	Speciated SVOC	U.S. EPA Method TO13
S3 (Fuel gas feed to generator)	Fuel gas composition	Integrated grab sample (bag or canister)	Hydrocarbon speciation, CHON*, sulfur content and heating value	ASTM D3588-91

* carbon, hydrogen, oxygen, nitrogen

	Time	Generator Stack					Process Samples
		Velocity	Method 201/202	Method 6	CEMS	Dilution Tunnel	Fuel Sample
10/19/99 Tues.	9:00						
	10:00						
	11:00						
	12:00						
	13:00						
	14:00						
	15:00						
	16:00						
	17:00				Stratification		
	18:00				18:26		
	19:00				19:40		
	20:00						
10/21/99 Thurs.	8:00	8:19-8:33	Run 1		Run 1	Run 1	
	9:00		9:30		9:55	9:30	
	10:00			Run 1			
	11:00			11:17	12:00		
	12:00				12:25		12:49
	13:00						
	14:00			14:17	14:27		
	15:00		15:30		14:55-15:30	15:30	
	16:00	16:50					
	17:00	17:17					
	18:00						
10/22/99 Fri.	8:00	8:05-8:31	Run 2	Run 2		Run 2	
	9:00		9:15	9:47		9:15	9:55
	10:00				Run 2		
	11:00			12:47	11:38		
	12:00						
	13:00				13:18		
	14:00				13:49		
	15:00		15:15		15:15	15:15	
	16:00	16:46-17:13					
	17:00						
	18:00						
	19:00						
10/25/99 Mon.	8:00						
	9:00	9:54					
	10:00	10:26	Run 3			Run 3	
	11:00		11:00	Run 3	Run 3	11:00	
	12:00			12:17	12:00		
	13:00						13:31
	14:00				14:28		
	15:00			15:17	15:03		
	16:00		16:20		16:20	16:20	
	17:00						
	18:00	18:25-18:53					
	19:00						

Figure 3-1. Chronology for Gas-Fired Steam Generator Tests (Site C).

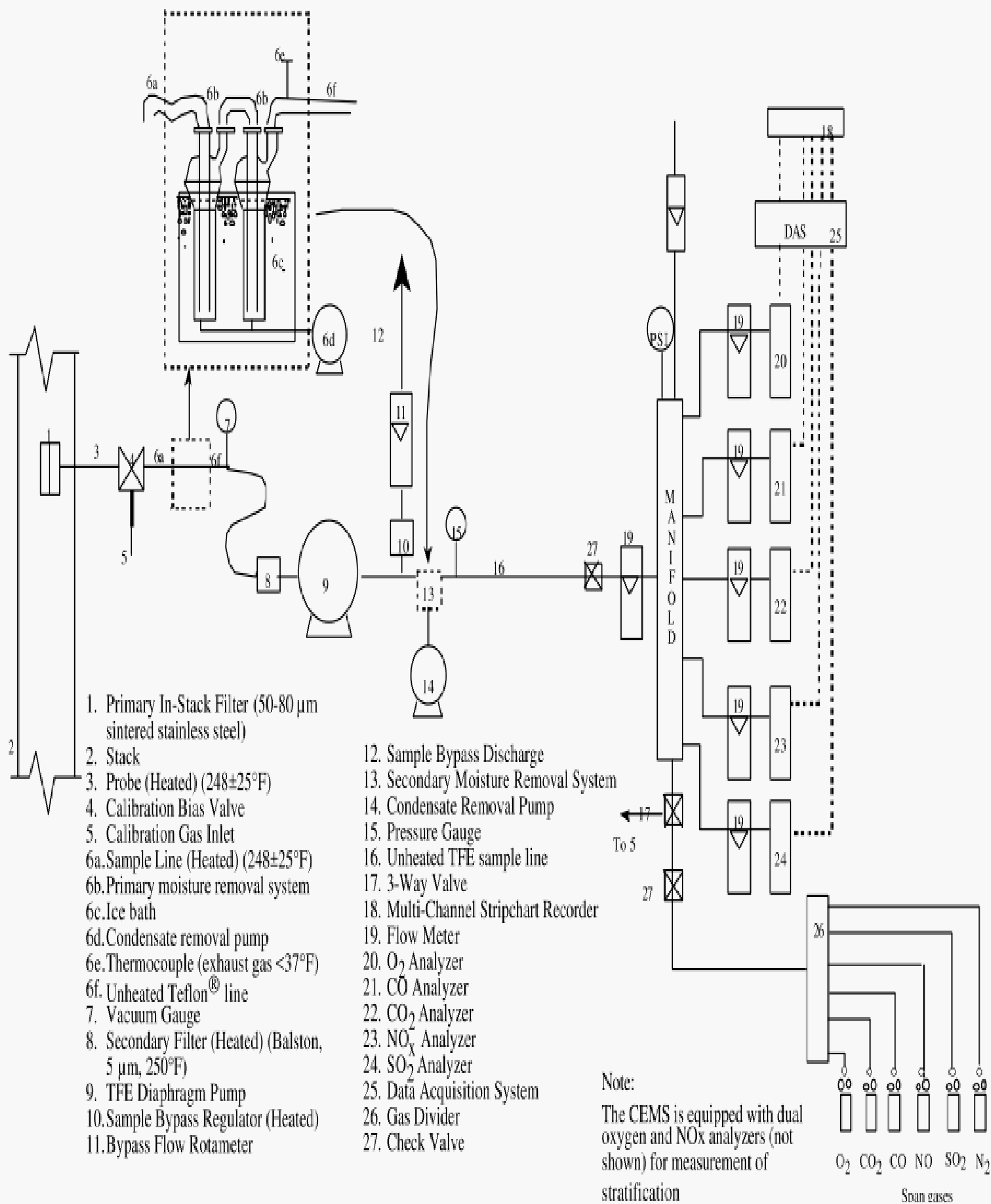


Figure 3-2. Continuous Emissions Monitoring System.

Table 3-2. CEMS Instrumentation Used For Gas-Fired Steam Generator Test (Site C).

Instrument/ Specification	Oxygen (O ₂)	Oxides of Nitrogen (NO _x)	Carbon Monoxide (CO)	Carbon Dioxide (CO ₂)
Instrument Manufacturer	Taylor- Servomex	Thermo- Electron	Thermo- Electron	ACS
Model Number	Model 1400	Model 10AR with molybdenum NO ₂ converter	Model 48H	Model 3300
Detection Principle	Paramagnetism	Chemi- luminescence	Gas filter correlation infrared absorption	Non-dispersive infrared absorption (NDIR)
Units Measured	%	ppmv	ppmv	%
Detection Limit	0.10%	1 ppm	0.5 ppm	0.10%
Ranges Used	0-10	0-100	0-100	0-20

minimum of contact area to avoid loss of the water soluble gas fraction. The condensate was removed with a peristaltic pump through the bottom of the heat exchanger. All components in contact with the sample were constructed of inert materials such as glass, stainless steel, and tetrafluoroethylene (TFE). All components preceding the condenser (probe, sample line, sample bypass regulator, and pump) were heated to 248° F to prevent condensation. The sample was conducted from the chiller outlet through the TFE line to a tertiary filter preceding the sample manifold. Samples were analyzed for O₂ and CO₂ using instrumental methods according to EPA Method 3A. O₂ was measured using a paramagnetic analyzer and CO₂ was measured using a non-dispersive infrared (NDIR) analyzer. Samples were analyzed for NO_x using a low-pressure chemiluminescence analyzer with a molybdenum nitrogen dioxide (NO₂)-to-nitric oxide (NO) converter according to EPA Method 7E. CO was determined using a NDIR analyzer following EPA Method 10.

SULFUR DIOXIDE (SO₂)

A modified version of SCAQMD Method 6.1 was used to measure SO₂ in the stack gas due to expected low concentrations. Flue gas was extracted non-isokinetically and passed through impingers containing hydrogen peroxide. Figure 3-3 shows a schematic of the Method 6 sampling train.

IN-STOCK METHOD TESTS

Total particulate, PM₁₀ and PM_{2.5} filterable at stack temperature were determined using in-stack methods. CPM, defined as the material collected in chilled impingers, also was measured for the in-stack samples.

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

Two in-stack cyclones followed by an in-stack filter (Figure 3-4) were used to measure total particulate and particulate matter with nominal aerodynamic diameters less than or equal to 10 µm (PM₁₀) and 2.5 µm (PM_{2.5}). EPA Method 201A, modified to accommodate the second cyclone, was used following the constant-rate sampling procedure. Sampling time was six hours for each of the three runs. The sample recovery field procedure is summarized in Figure 3-5. Sampling was performed as published except for the following modifications and clarifications:

- A PM₁₀ cyclone and a PM_{2.5} cyclone (Andersen Model Case-PM₁₀ and Case-PM_{2.5}) were attached in series to the filter inlet. Sample recovery procedures were modified accordingly;
- The sample was collected from a single traverse point near the center of the stack to preserve the integrity of the dilution tunnel method comparison. It was assumed that any particulate present was small enough to mix aerodynamically in the same manner as a gas; therefore, the magnitude of the particle concentration profile was assumed to be no greater than the gas concentration profile. Quartz filters were used. The filters were preconditioned in the same manner as those used in the dilution tunnel, as described below; and
- A modified filter assembly was employed in an effort to improve the precision of the gravimetric analysis for low particulate concentration. An o-ring, a filter and a filter support were all placed together in an aluminum foil pouch and weighed as a unit. Post-test all three components were recovered together into the same foil pouch to prevent negative bias due to filter breakage.

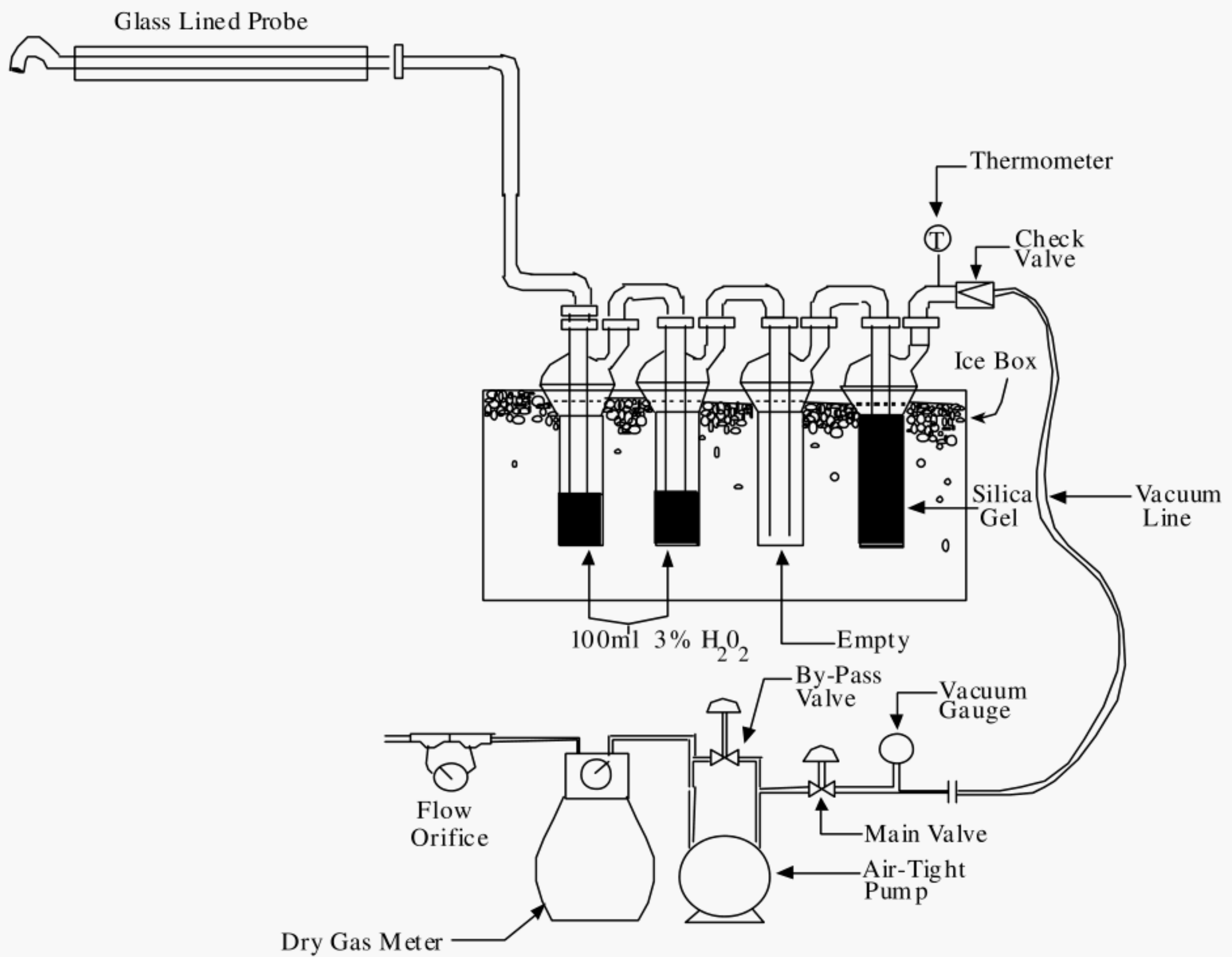
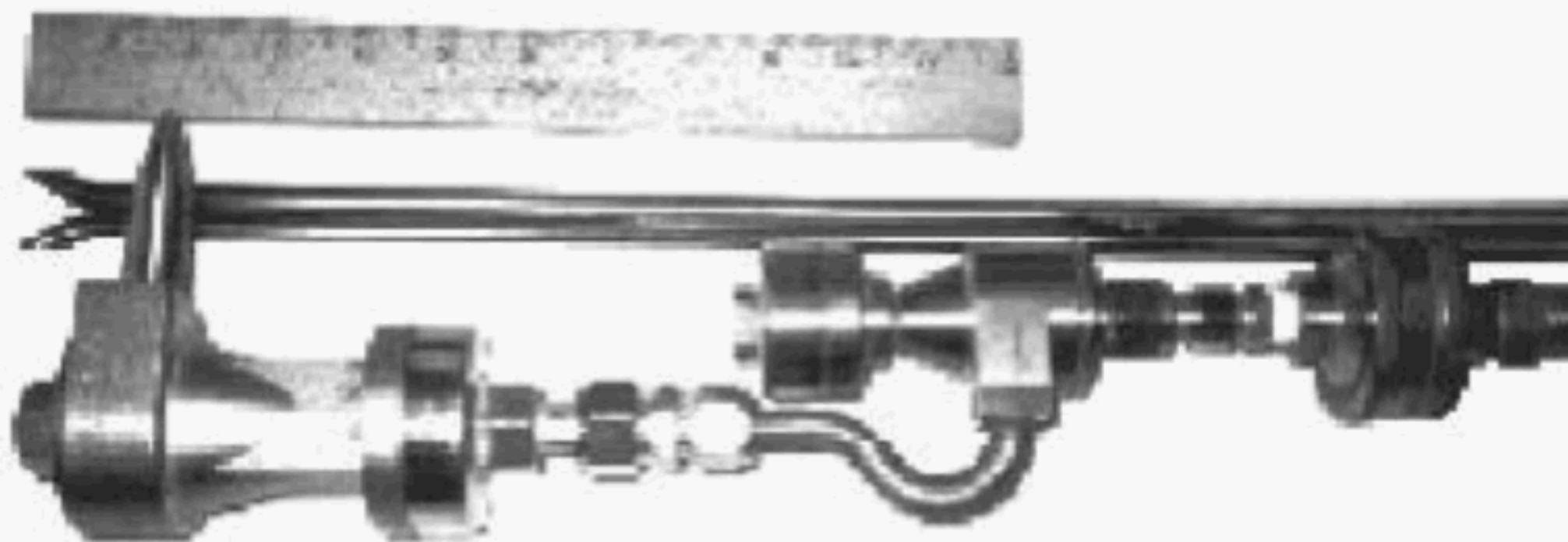
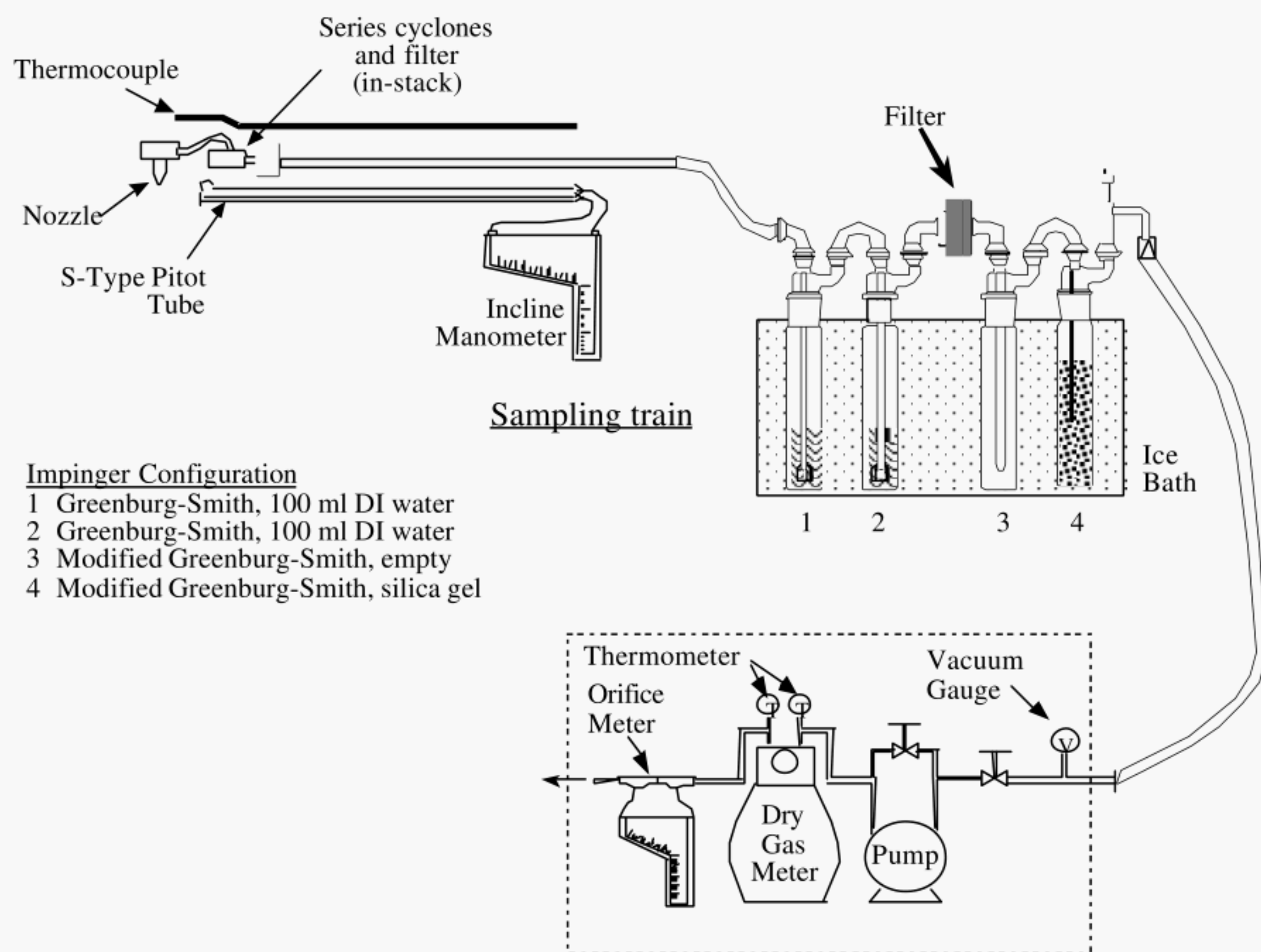


Figure 3-3. Modified SCAQMD Method 6.1 – Sulfur Oxides Sampling Train.



Series cyclone and filter assembly

Figure 3-4. PM10/PM2.5 Train Configuration for Method 201A/202.

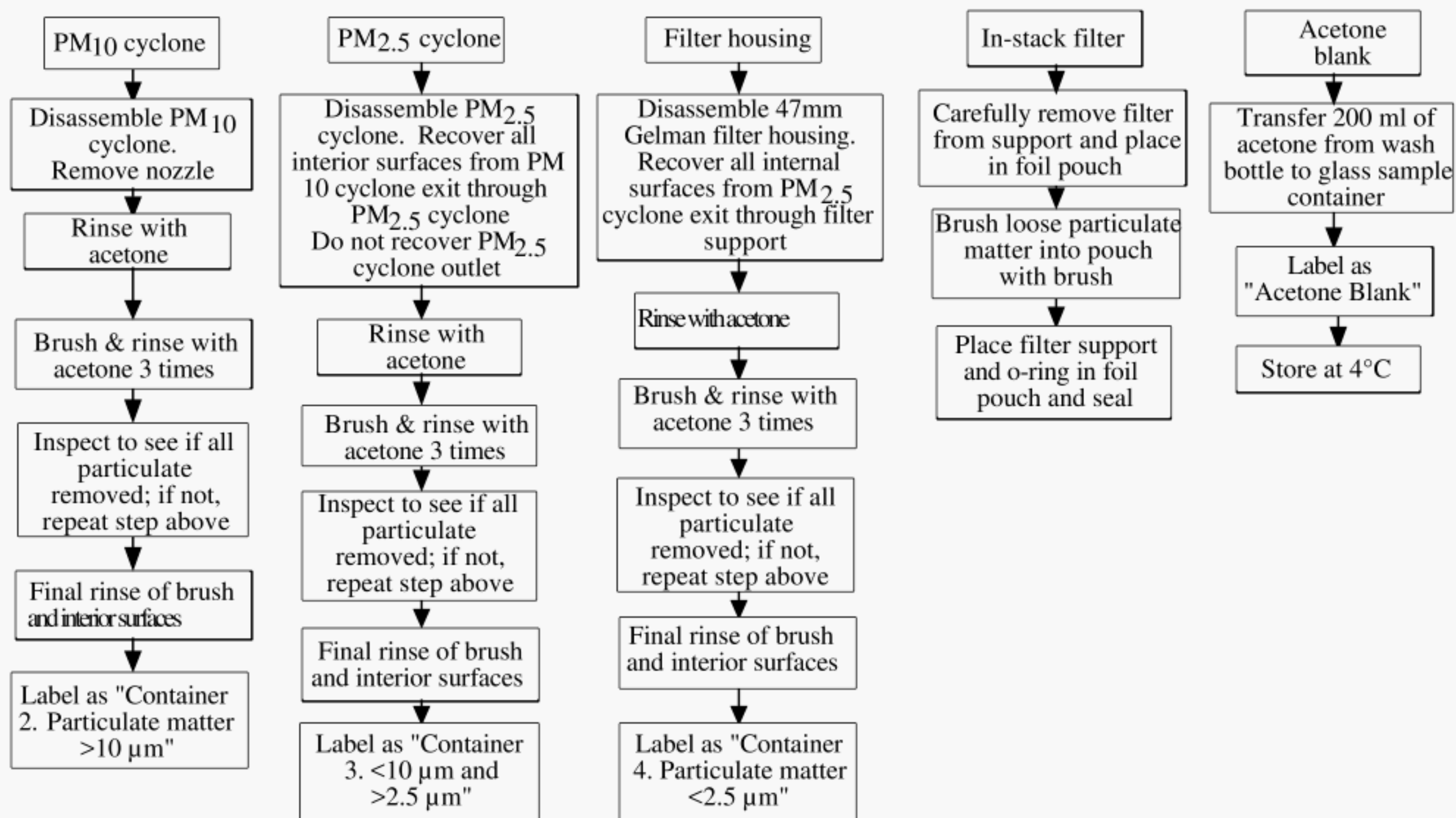


Figure 3-5. Method 201A (Modified) Sample Recovery Procedure.

The particulate mass collected in the two cyclones and on the filter was determined gravimetrically (Figure 3-6). The filters (Pallflex No. 51575) were weighed before and after testing on an analytical balance with a sensitivity of 10 micrograms. In an effort to improve the accuracy and precision of the gravimetric results, the filters, filter support and Viton O-ring seals were weighed together to minimize post-test loss of filter matter during sample recovery. Pre- and post-test weighing was performed after drying the filters in a dessicator for a minimum of 72 hours; repeat weighings were then performed at a minimum of 6-hour intervals until constant weight was achieved. Probe and cyclone acetone rinses were recovered in glass sample jars for storage and shipment, then transferred to tared Teflon[®] beaker liners for evaporation and weighing. Acetone and filter blanks also were collected and analyzed. See Section 4 for discussion of data treatment.

Subsequent to the planning of these tests, EPA published preliminary method PRE-4, entitled "Test Protocol PCA PM10/PM2.5 Emission Factor and Chemical Characterization Testing" (U.S. EPA, 1999b). This protocol, developed by the Portland Cement Association (PCA), is intended for use by Portland cement plants to measure PM10 and PM2.5 emission factors applicable to a variety of particulate sources. Method PRE-4 describes substantially the same sampling equipment and sample collection procedures used in these tests. The analytical procedures differ in the scope of chemical analyses performed: Method PRE-4 cites Method 202 for measurement of CPM, which includes analyses for inorganic and organic CPM mass, sulfate and chloride only. The analyses performed in these tests go beyond the requirements of Method 202 to further speciate the CPM by analysis for anions, cations, metals and VOCs, as described below.

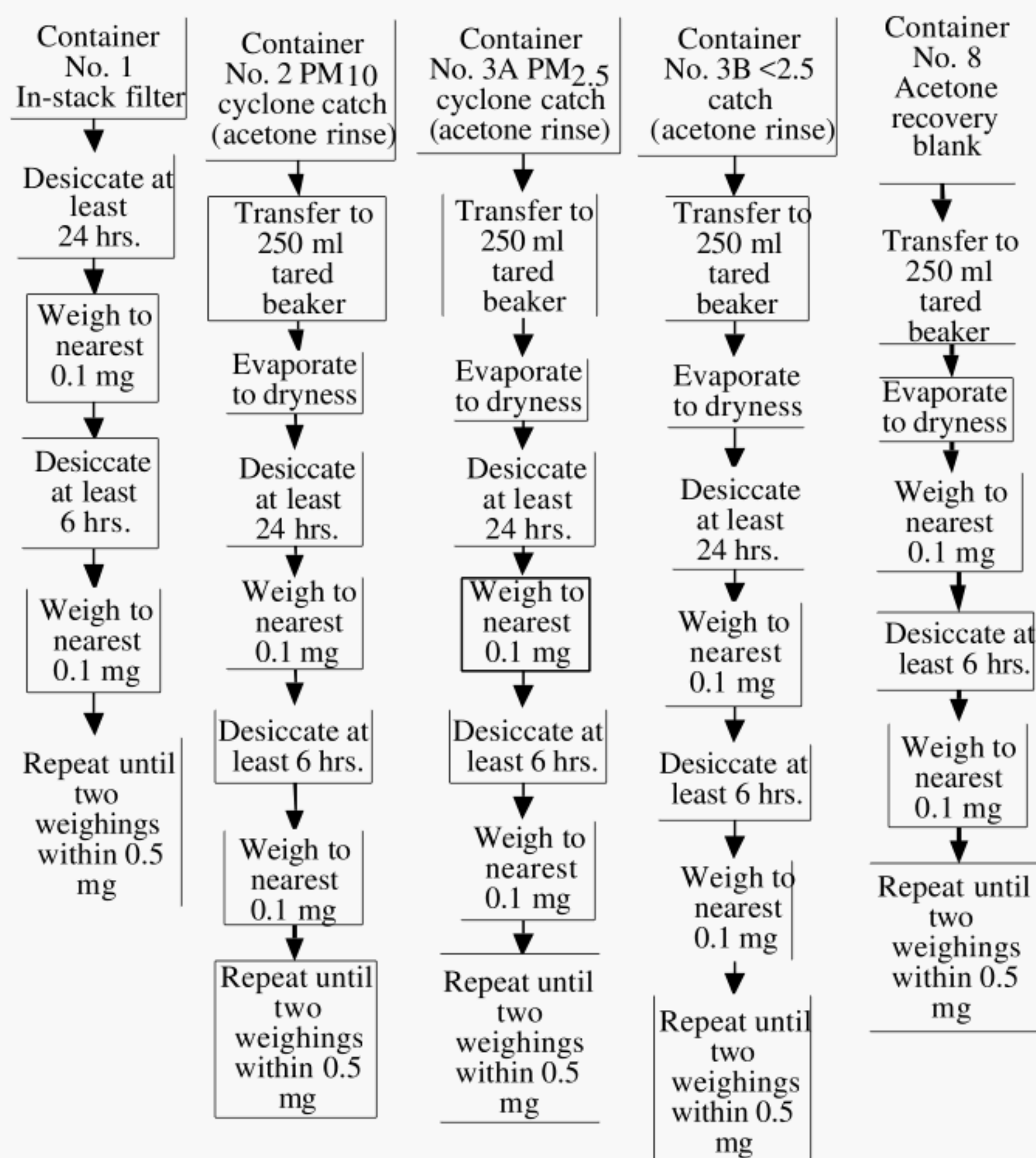


Figure 3-6. Method 201A (Modified) Sample Analysis Procedure.

Condensible Particulate Matter Mass and Chemical Analysis

CPM was determined using EPA Method 202; total sampling time was six hours for all runs. After the in-stack filter, the sample passed through a heated Teflon[®] line to a series of four impingers placed in the ice bath used for the Method 201A train. The first two were standard Greenburg-Smith impingers containing distilled deionized (DI) water. The others were modified Greenburg-Smith impingers; the third was empty for Runs 1 and 2, and contained DI water for Run 3; the fourth contained silica gel. A quartz filter was placed between the second and third impingers to improve capture efficiency for any aerosols that may have passed the first two impingers. At the conclusion of each run the impingers were purged with nitrogen for one hour in an attempt to eliminate dissolved SO₂. The contents of the impingers were recovered with DI water and dichloromethane, as shown in Figure 3-7.

Previous tests (England *et al.*, 2000) have found that a majority of the particulate matter emissions from gas-fired sources consisted of condensible matter. To obtain an optimal understanding of the composition of the material collected in the impingers, a number of complementary analytical procedures were carried out as described below and shown in Figure 3-8:

- Standard Procedure: the protocol defined in Method 202;
- Instrumental Procedure: aliquots of the impinger water catch are removed and analyzed for anions and cations (bromide, chloride, fluoride, nitrate, phosphate and sulfate) by ion chromatography, for ammonium by colorimetry, for volatile organic compounds (VOCs) by GC/MS (SW846 Method 8260), and for metals by digesting the sample in acid and analyzing by ICP/MS; and
- Alternative Procedure: similar to the standard protocol except that the impinger contents are dried without any addition of NH₄OH and no organic extraction with MeCl₂ is performed prior to determination of inorganic CPM by constant weight. The organic fraction is then determined using the results from the analysis in the Standard Procedure in place of the MeCl₂ extraction.

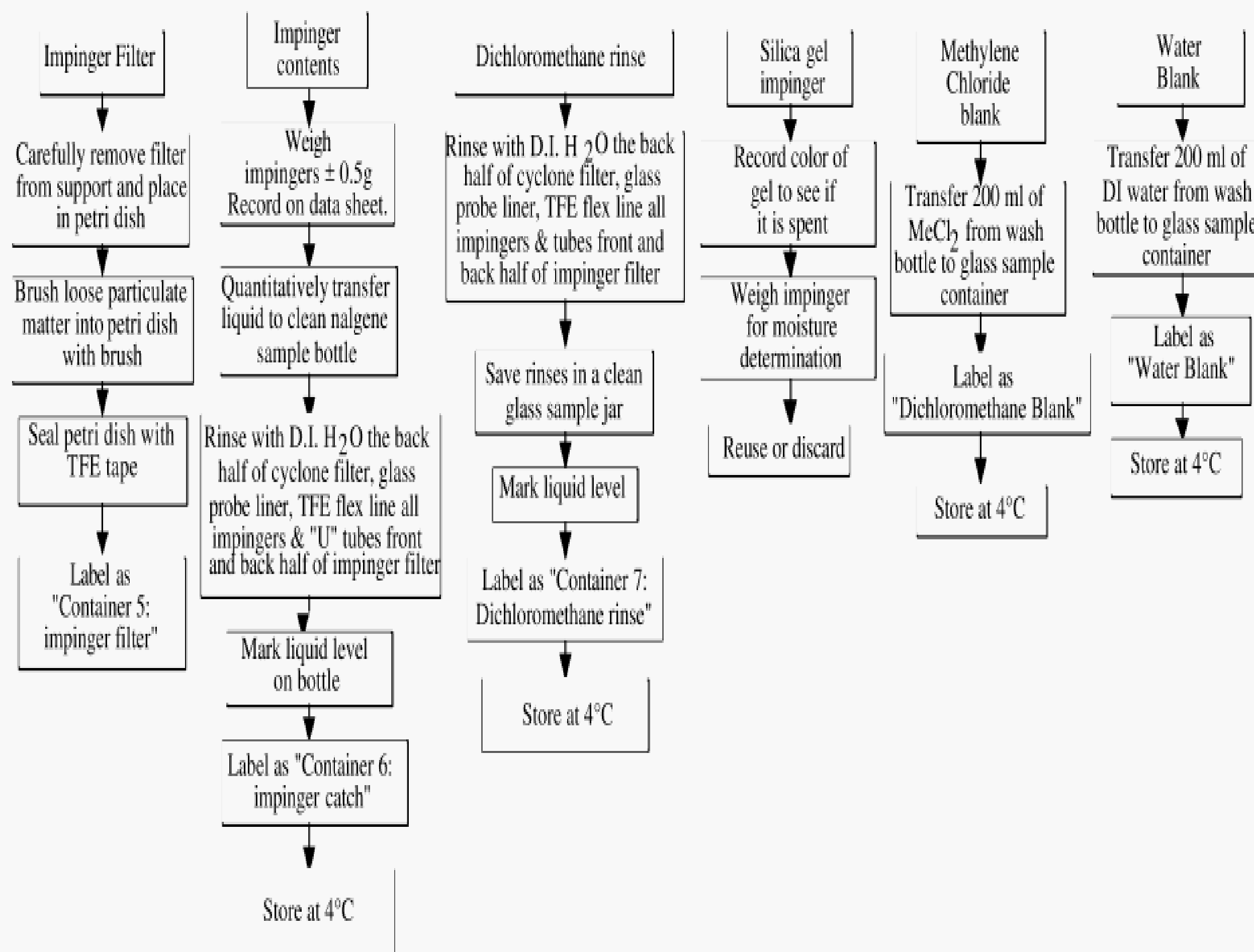


Figure 3-7. Method 202 Sample Recovery Procedure.

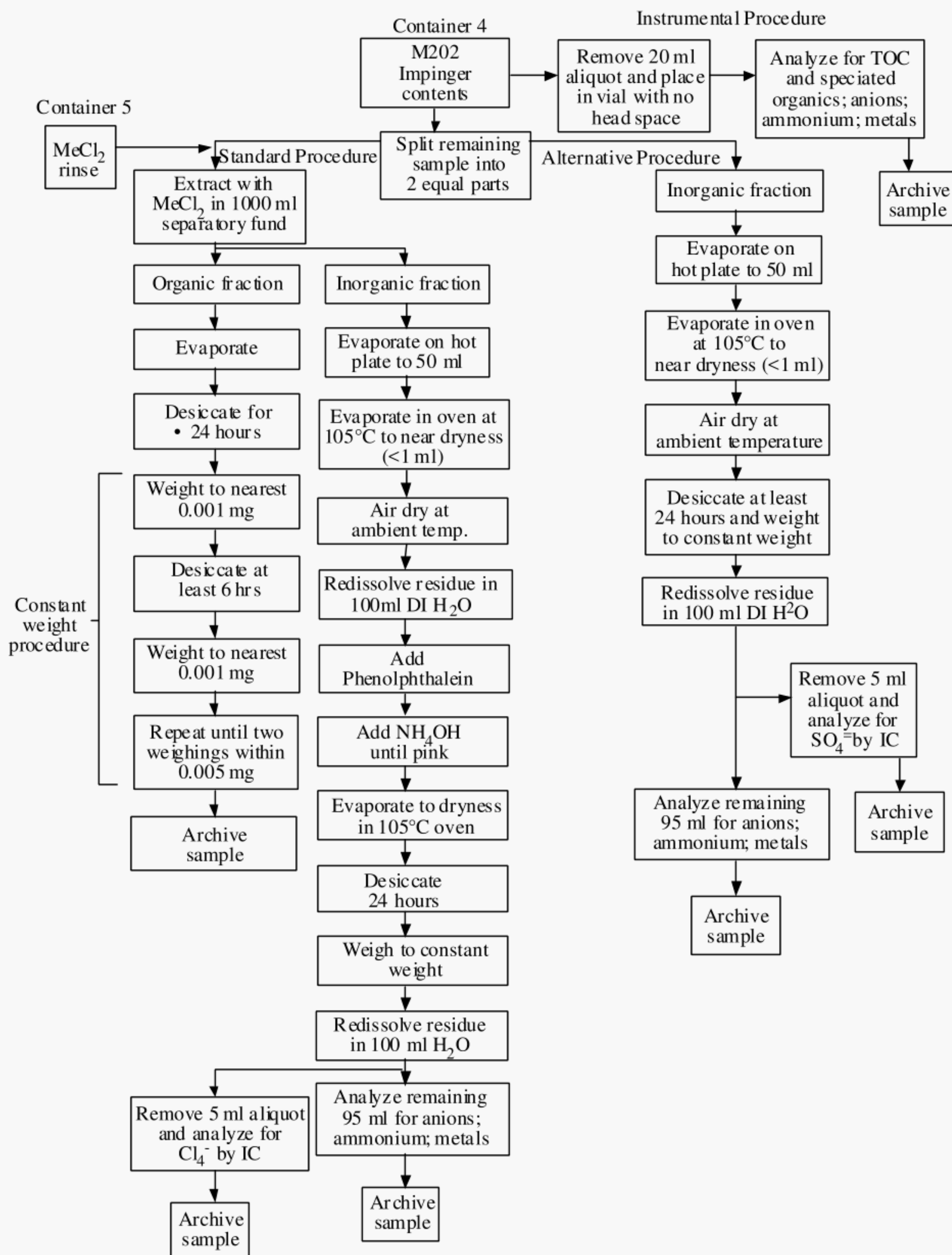


Figure 3-8. Modified Method 202 Sample Analysis Procedure.

DILUTION TUNNEL TESTS

PM_{2.5} mass and chemical speciation in the stack gas was determined using a dilution tunnel (Figure 3-9). A stainless steel probe with a buttonhook nozzle was used to withdraw the stack gas sample at a rate of approximately 20 liters per minute. The sample was transported through a heated copper line into the dilution tunnel. The sample was mixed in the tunnel with purified ambient air under turbulent flow conditions to cool and dilute the sample to near-ambient conditions. The ambient air used for dilution was purified using a high efficiency particulate air (HEPA) filter to remove particulate matter and an activated carbon bed to remove gaseous organic compounds. After passing through a tunnel length equal to 10 tunnel diameters, approximately 50 percent of the diluted sample was withdrawn into a large chamber, where the sample aged for approximately 80 seconds to allow low-concentration aerosols (especially organic aerosols) to fully form. The aged sample was withdrawn through two cyclone separators (each operating at a flow rate of approximately 110 liters per minute) to remove particles larger than 2.5 μm and delivered to the sample collection media (TMF, quartz filter, Tenax cartridge, and TIGF/PUF/XAD-4/PUF cartridge). The sample flow rate through the probe was monitored using a venturi flow meter and thermocouple. The venturi velocity head was measured continuously during the test with a Magnehelic[®] gauge. An S-type Pitot tube with electronic pressure transducer and thermocouple were used to monitor the velocity in the stack. The thermocouples and pressure transducers were connected to a laptop computer data acquisition system. The dilution airflow and backpressure were adjusted to maintain the target dilution ratio and sample flow rates. Total sampling time for each test run was six hours.

A dilution ratio of approximately 40:1 was originally planned, based on the prior work of Hildemann *et al.* (1989). Hildemann selected this ratio both to cool the sample and to ensure complete mixing between the sample and dilution air prior to the residence time chamber takeoff. For these tests, flow rates were set in the field to achieve a target dilution ratio of approximately 20:1 to improve minimum detection limits since very low concentrations of the target substances were anticipated. Hildemann's results suggest that mixing between the sample and the dilution air begins to degrade at a dilution ratio of approximately 10:1.

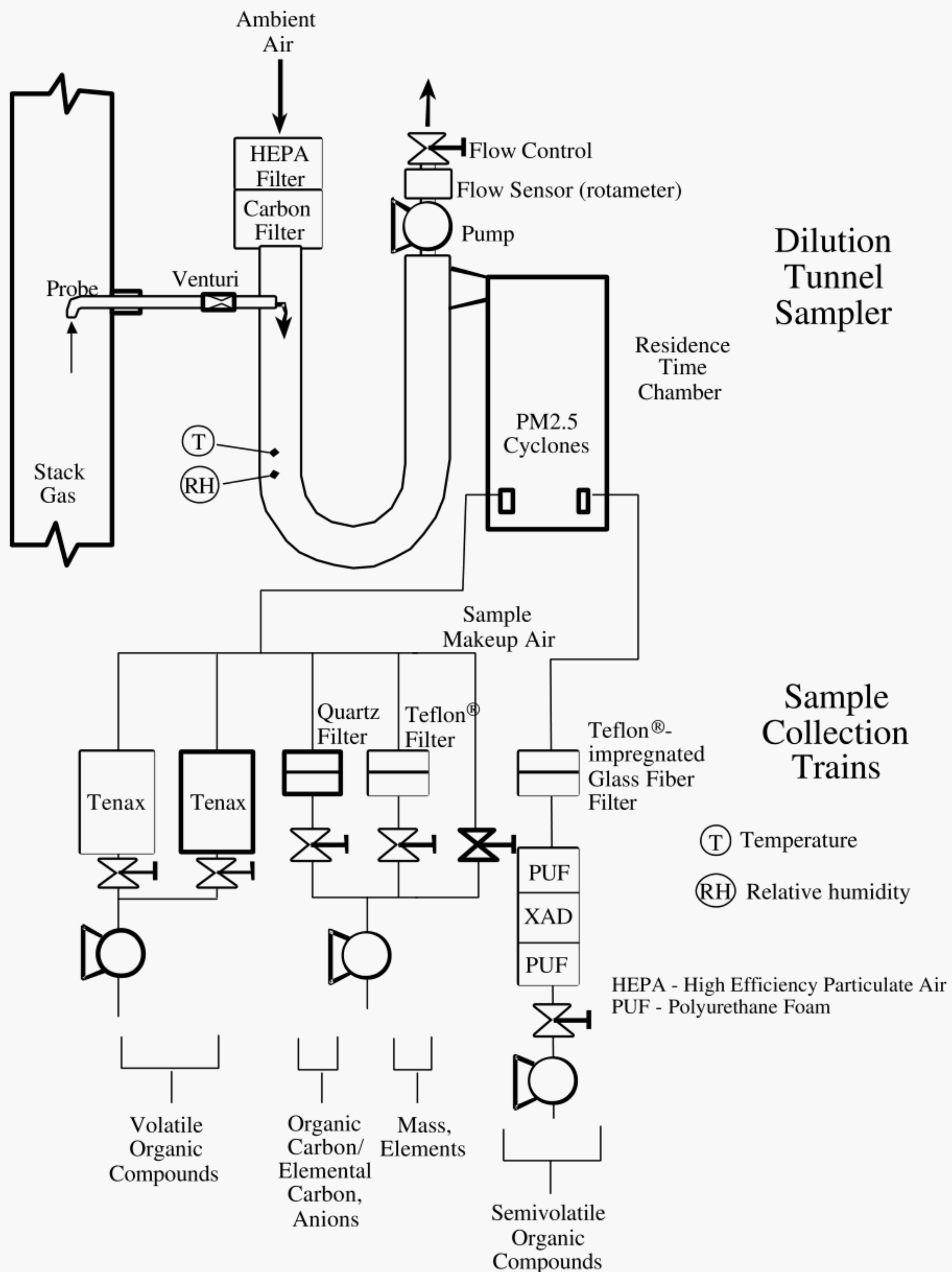


Figure 3-9. Dilution Tunnel Sampling System.

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 3-9.

PM2.5 Mass

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

Elements

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

A Kevex Corporation Model 700/8000 ED-XRF analyzer with a side-window, liquid-cooled, 60 kilo electron volts (keV), 3.3 milliamp rhodium anode x-ray tube and secondary fluorescers was used. The silicon detector had an active area of 30 square millimeters, with a system resolution better than 165 electron volts (eV). The analysis was controlled, spectra were acquired, and

elemental concentrations were calculated by software on a microcomputer, which was interfaced to the analyzer. Five separate XRF analyses were conducted on each sample to optimize the detection limits for the specified elements. The filters were removed from their petri slides and placed with their deposit sides downward into polycarbonate filter cassettes. A polycarbonate retainer ring kept the filter flat against the bottom of the cassette. The cassettes were loaded into a carousel in the x-ray chamber. The sample chamber was evacuated to 10^{-3} Torr. A computer program controlled the positioning of the samples and the excitation conditions. Complete analysis of 16 samples under five excitation conditions required approximately 6 hours.

Sulfate, Nitrate, and Chloride

Samples for determining water-soluble Cl, nitrate (NO_3^-), and $\text{SO}_4^{=}$ 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 valve to achieve the desired flow rate.

Each quartz-fiber filter was cut in half, and one filter half was placed in a polystyrene extraction vial with 15 ml of DI water. The remaining half was used for determination of OC and EC as described below. The extraction vials were capped and sonicated for 60 minutes, shaken for 60 minutes, then aged overnight to assure complete extraction of the deposited material. After extraction, these solutions were stored under refrigeration prior to analysis. The unanalyzed filter half was archived in the original petri slide. Cl, NO_3^- , and $\text{SO}_4^{=}$ were measured with a Dionex 2020i ion chromatograph (IC). Approximately 2 ml of the filter extract was injected into the ion chromatograph.

Organic and Elemental Carbon

Quartz fiber filters were used to collect samples for determination of OC and EC mass (see above). The filters were heated in air for at least three hours at approximately 900°C prior to use. Pre-acceptance testing was performed on each lot of filters. Filters with levels exceeding 1.5 micrograms per square centimeter ($\mu\text{g}/\text{cm}^2$) of OC and $0.5 \mu\text{g}/\text{cm}^2$ of EC were refired or rejected. Pre-fired filters were sealed and stored in a freezer prior to preparation for field sampling.

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

Volatile Organic Compounds

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

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

Semivolatile Organic Compounds

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

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

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

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

Section 4

TEST RESULTS

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

PROCESS OPERATING CONDITIONS

Generator operating conditions during testing are summarized in Table 4-2. The process generator operated at close to its normal firing rate corresponding to approximately 70 percent of full firing capacity. The stack gas temperature averaged approximately 270°F. Excess O₂ measured at the furnace outlet by plant instrumentation was 1.3 to 1.5 percent.

The average fuel higher heating value (HHV) during each test was calculated from fuel gas grab sample analysis results (Table 4-3). The average heat input to the process generator during the test is the product of the average fuel-gas flow rate and the average fuel HHV. The average heat input was used to convert in-stack emission rates (lb/hr) to emission factors (lb/MMBtu), which are presented in Section 5. H₂S concentration in the fuel gas, as determined from grab sample analysis, was less than the detection limit of 1 part per million by volume (ppmv).

PRELIMINARY TEST RESULTS

Preliminary tests were conducted to establish a single point in the stack for sample collection. The O₂ and NO_x concentration profiles were measured by traversing the CEMS probe across the stack, while alternating every other point to the center point. The data from the center point readings were used to correct the spatial traverse results for temporal variations. The deviation from the average concentration for NO_x was determined to be less than ten percent. Under the

Table 4-1. Approximate In-Stack Detection Limits Achieved for Gas-Fired Steam Generator Tests (Site C).

Substance	Dilution Tunnel mg/dscm	In-stack methods mg/dscm	Substance	Dilution Tunnel mg/dscm	In-stack methods mg/dscm	Substance	Dilution Tunnel mg/dscm	In-stack methods mg/dscm	Substance	Dilution Tunnel mg/dscm	In-stack methods mg/dscm
Total PM mass	--	2.5E-03	Sr	3.9E-05	--	2-methylnaphthalene	7.1E-05	2.1E-06	Benzo(b)chrysene	2.2E-06	5.3E-07
PM10 mass	--	2.5E-03	Ti	1.0E-04	--	2-methylphenanthrene	2.2E-06	1.1E-06	Benzo(b+j+k)fluoranthene	1.1E-06	1.6E-06
PM2.5 mass	2.8E-03	2.5E-03	Tl	8.9E-05	--	2-phenylnaphthalene	1.1E-06	2.1E-06	Benzo(c)phenanthrene	1.2E-05	5.3E-07
Ag	4.3E-04	--	U	8.2E-05	--	3,6-dimethylphenanthrene	5.3E-05	2.1E-06	Benzo(e)pyrene	6.9E-06	5.8E-06
Al	3.6E-04	--	V	8.9E-05	--	3-methylbiphenyl	2.5E-04	9.5E-06	Benzo(ghi)perylene	6.7E-06	5.3E-07
As	5.7E-05	--	Y	4.6E-05	--	4-methylbiphenyl	2.1E-05	1.6E-06	Benzonaphthothiophene	2.2E-06	4.2E-06
Au	1.1E-04	--	Zn	3.9E-05	--	4-methylpyrene	2.2E-06	1.6E-06	Bibenzene	2.8E-03	1.3E-05
Ba	1.9E-03	--	Zr	6.1E-05	--	4H-cyclopenta(def)phenanthrene	0.0E+00	1.6E-06	Biphenyl	7.5E-05	2.1E-06
Br	3.6E-05	--	SO4=	4.1E-03	--	5+6-methylchrysene	0.0E+00	3.5E-05	C-dimethylphenanthrene	3.7E-05	2.1E-06
Ca	1.6E-04	--	NO3-	4.1E-03	--	7-methylbenz(a)anthracene	6.9E-06	2.1E-06	C-methylphenanthrene	3.1E-05	1.1E-06
Cd	4.3E-04	--	NH4+	--	--	7-methylbenzo(a)pyrene	7.9E-06	1.3E-04	C-trimethylnaphthalene	9.0E-06	4.2E-06
Cl	3.6E-04	--	Cl-	4.1E-03	--	9,10-dihydrobenzo(a)pyrene	3.4E-06	5.3E-07	Cholestane	3.0E-04	1.3E-04
Co	3.1E-05	--	OC	3.1E-02	2.9E-03	9-anthraldehyde	3.0E-05	4.2E-06	Chrysene	2.2E-06	2.1E-06
Cr	6.8E-05	--	EC	7.2E-03	6.8E-04	9-fluorenone	1.5E-04	1.6E-06	Coronene	6.7E-06	5.3E-07
Cu	3.9E-05	--	1+2-ethylnaphthalene	1.4E-04	2.1E-06	9-methylanthracene	5.2E-05	2.1E-06	D-dimethylphenanthrene	3.4E-05	2.1E-06
Fe	5.4E-05	--	1,2,8-trimethylnaphthalene	6.7E-06	5.3E-07	A-dimethylphenanthrene	5.3E-05	2.1E-06	D-MePy/MeFl	1.1E-06	1.6E-06
Ga	6.8E-05	--	1,2-dimethylnaphthalene	7.8E-05	9.5E-06	A-methylfluorene	1.2E-04	4.2E-06	Dibenz(ah+ac)anthracene	6.7E-06	5.3E-07
Hg	9.3E-05	--	1,3+1,6+1,7-dimethylnaphthalene	2.6E-04	2.7E-06	A-methylphenanthrene	5.4E-05	1.1E-06	Dibenzofuran	7.0E-05	1.1E-06
In	4.6E-04	--	1,4+1,5+2,3-dimethylnaphthalene	1.1E-04	2.7E-06	A-methylpyrene	1.1E-06	1.6E-06	E-dimethylphenanthrene	1.7E-05	2.1E-06
K	2.2E-04	--	1,4,5-trimethylnaphthalene	1.1E-04	2.1E-06	A-trimethylnaphthalene	2.1E-06	5.1E-05	E-MePy/MeFl	1.1E-06	1.6E-06
La	2.2E-03	--	1,4-chrysenequinone	5.6E-06	5.3E-07	Acenaphthene	2.9E-05	1.6E-06	E-trimethylnaphthalene	1.1E-06	4.2E-06
Mg	0.0E+00	--	1,7-dimethylphenanthrene	3.7E-05	2.1E-06	Acenaphthenequinone	6.7E-06	3.7E-06	F-trimethylnaphthalene	1.1E-06	4.2E-06
Mn	5.7E-05	--	1,8-dimethylnaphthalene	7.8E-05	9.5E-06	Acenaphthylene	1.2E-04	2.7E-06	Fluoranthene	2.2E-06	2.1E-06
Mo	9.6E-05	--	1-ethyl-2-methylnaphthalene	2.2E-06	1.6E-06	Anthracene	1.1E-06	6.4E-06	Fluorene	1.4E-04	5.3E-06
Na	0.0E+00	--	1-MeFl+C-MePy/Fl	1.8E-05	4.2E-06	Anthraquinone	0.0E+00	9.5E-06	Indeno[123-cd]pyrene	6.7E-06	5.3E-07
Ni	3.2E-05	--	1-methylfluorene	7.4E-05	3.1E-05	Anthrone	6.1E-05	5.3E-07	J-trimethylnaphthalene	9.0E-06	2.1E-06
P	1.1E-04	--	1-methylnaphthalene	4.3E-05	2.1E-06	B-dimethylphenanthrene	3.7E-05	2.1E-06	Naphthalene	1.1E-03	2.1E-06
Pb	3.9E-04	--	1-methylphenanthrene	2.5E-05	5.3E-07	B-MePy/MeFl	1.1E-06	1.6E-06	Perinaphthenone	1.1E-03	1.1E-06
Pd	2.0E-04	--	1-methylpyrene	9.0E-06	1.6E-06	B-methylfluorene	7.4E-05	3.1E-05	Perylene	2.2E-06	5.8E-06
Rb	3.6E-05	--	1-phenylnaphthalene	5.6E-06	5.0E-05	B-methylphenanthrene	1.2E-05	1.1E-06	Phenanthrene	9.0E-06	1.2E-05
S	1.8E-04	--	2,3,5+1-trimethylnaphthalene	3.4E-06	1.6E-06	B-trimethylnaphthalene	1.1E-06	3.2E-06	Pyrene	4.5E-06	4.2E-06
Sb	6.4E-04	--	2,4,5-trimethylnaphthalene	9.0E-06	5.3E-07	Benz(a)anthracene	6.7E-06	2.1E-06	Retene	6.7E-05	4.2E-06
Se	4.3E-05	--	2,6+2,7-dimethylnaphthalene	1.2E-04	2.7E-06	Benz(a)anthracene-7,12	4.2E-05	5.3E-07	Xanthone	4.5E-06	1.5E-05
Si	2.2E-04	--	2-ethyl-1-methylnaphthalene	1.9E-04	4.2E-06	Benzanthrone	1.0E-05	3.7E-06	Volatile Organic Compounds	3.0E-02	--
Sn	6.1E-04	--	2-methylbiphenyl	1.8E-04	9.5E-06	Benzo(a)pyrene	6.7E-06	1.6E-06			

Table 4-2. Process Operating Conditions (Site C).

Parameter	Units	21-Oct-99	22-Oct-99	25-Oct-99
Excess Oxygen	%	1.4	1.5	1.3
Radiant Temperature	°F	1488	1497	1500
Steam Temperature	°F	499	502	501
Stack Temperature	°F	252	257	254
Burner Gas Rate	scfh	49174	49336	49897
Inlet Water Rate	Bbls	3186	3185	3185
Steam Quality	%	52	55	55
HHV (1)	Btu/ft ³	892	884	886
Heat Input (2)	MMBtu/hr	44	44	44

(1) Obtained from fuel analysis.

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

Table 4-3. Fuel Gas Analysis for Gas-Fired Steam Generator Tests (Site C).

	Units	21-Oct-99	22-Oct-99	25-Oct-99	Average
Specific Gravity	None	0.74	0.75	0.76	0.75
Net Btu	Btu/cu. ft.	806	799	801	802
Gross Btu	Btu/cu. ft.	892	884	886	887
Oxygen	Mol %	2.69	2.77	2.48	2.65
Nitrogen	Mol %	11.6	12.4	11.8	11.9
Carbon Dioxide	Mol %	6.92	7.08	7.79	7.26
Hydrogen	Mol %	ND	ND	ND	ND
Carbon Monoxide	Mol %	ND	ND	ND	ND
Hydrogen Sulfide (1)	Mol %	ND	ND	ND	ND
Methane	Mol %	70.4	69.2	69.3	69.6
Ethane	Mol %	5.48	5.59	5.58	5.55
Propane	Mol %	2.22	2.16	2.3	2.23
Isobutane	Mol %	0.21	0.22	0.21	0.21
Normal Butane (C4)	Mol %	0.32	0.3	0.27	0.30
Isopentane	Mol %	0.09	0.1	0.11	0.10
Normal Petane (C5)	Mol %	0.06	0.06	0.1	0.07
Hexanes Plus	Mol %	0.06	0.14	0.07	0.09
Total		100	100	100	100

(1) Total sulfur in fuel gas was below detection limit of 1 ppm.

ND – not detected

conditions of these tests, fine particles are expected to mix like a gas. It is assumed that the magnitude of any fine-particle concentration profile that may have existed is similar to the gas concentration profile. Therefore, all samples were collected at a point near the center of the stack. A velocity profile was developed by traversing the stack with the pitot probe before and after each test. The resulting average velocity profile was used to correct the velocities measured at the center during sampling to the overall stack average velocity.

STACK GAS CONDITIONS AND FLOW RATE

A summary of the stack conditions during testing is presented in Table 4-4. Stack gas temperature during the tests averaged 269-276°F. The O₂ concentration at the stack averaged 1.3 to 1.5 percent (dry basis) during the tests, approximately the same as at the furnace outlet (Table 4-2). The CO₂ and moisture concentrations are approximately consistent with the carbon and hydrogen contents of the fuel gas.

Table 4-4. Average Stack Conditions (Site C).

Parameter	Units	Run 1	Run 2	Run 3
Date		21-Oct-99	22-Oct-99	25-Oct-99
Stack Temperature	°F	269	273	276
O ₂ (dry basis)	%v	1.5	1.5	1.3
CO ₂ (dry basis)	%v	12	12	12
Moisture	%v	18	18	18
Velocity	ft/s	31	32	32
	m/s	9.4	9.6	9.7
Flow Rate	acfm	12,400	12,700	12,800
	dscfm	7,200	7,300	7,400
	dscmm	205	208	209

CO, NO_x, AND SO₂ EMISSIONS

NO_x and SO₂ are precursors of secondary particulate matter. Average NO_x concentrations (corrected to 3 percent O₂, dry basis) were 30.6-31.5 ppmv and 0.4 to 0.5 ppmv, respectively (Table 4-5). The data were corrected for analyzer drift and bias. Average SO₂ concentrations were 0.8-1.0 ppmv (Table 4-6). The SO₂ concentration is higher than would be expected based on the measured H₂S concentration in the fuel gas, assuming total conversion to SO₂.

Table 4-5. CEMS Data (Site C).

	Run Number	1	2	3
	Date	21-Oct-99	22-Oct-99	25-Oct-99
	Time Period	09:55 - 15:30	11:38 - 15:15	12:00 - 16:20
CO	ppm (dry, as measured)	3.9	4.3	7.4
	ppm (dry, 3% O ₂)	3.6	4.0	6.8
	lb/hr	0.2	0.2	0.4
NO _x	ppm (dry, as measured)	31.5	32.9	30.6
	ppm (dry, 3% O ₂)	29.1	30.5	27.9
	lb/hr	2.6	2.7	2.5

Table 4-6. Method 6 Results (Site C).

Parameter	Units				Average	RSD
Run Number	-	1	2	3		
Date	-	21-Oct-99	22-Oct-99	25-Oct-99		
Time Period	-	11:17-14:17	9:47-12:47	12:17-15:17		
SO ₂ concentration in sample	ppmv	0.83	0.97	0.77	0.86	12%
	lb/hr	0.10	0.12	0.10	0.11	11%

RSD - relative standard deviation

Low CO is an indicator of good combustion performance. CO concentration was consistently near zero during all tests, except for a process upset that occurred at the end of Run 3. A change in fuel quality caused the oxygen levels in the flue gas to drop, and the unit was not able to automatically adjust to the low levels. As a result, one-minute average CO readings increased to greater than 100 ppmv (above the upper range of the analyzer scale). Approximately fifteen minutes after the start of the upset, the test was halted forty minutes short of the planned end-time to avoid adversely impacting the results. No discoloration was observed on the filters.

IN-STACK AND IMPINGER METHOD RESULTS

Particulate Mass

Filterable particulate matter (FPM). FPM results as measured by Method 201A are presented in Table 4-7. Total FPM, which includes all particulate collected in the in-stack nozzle/cyclone assembly and on the in-stack filter, ranged from 0.06 to 0.

Table 4-7. Filterable Particulate Matter (EPA Method 201A) Results (Site C).

Parameter	Units	Results (1)				
Run Number	-	1	2	3	Average	RSD
Date	-	21-Oct-99	22-Oct-99	25-Oct-99		
Total FPM	mg/dscm	< 0.30	< 0.11	< 0.06	< 0.16	79%
	lb/hr	< 8.0E-3	< 3.0E-3	< 1.8E-3	< 4.3E-3	78%
FPM <10 μ m	mg/dscm	< 0.20	< 0.11	< 0.06	< 0.12	56%
	lb/hr	< 5.4E-3	< 3.0E-3	< 1.8E-3	< 3.4E-3	54%
FPM <2.5 μ m	mg/dscm	ND	< 0.11	ND	< 0.11	n/a
	lb/hr	ND	< 3.0E-3	ND	< 3.0E-3	n/a

<-one or more, but not all, constituents are less than the detection limit

n/a-not applicable; two or more runs not detected

ND-not detected

RSD-relative standard deviation

(1) All filter net weights were negative and set to zero for calculations (detection limit = 0.01 mg)

30 mg/dscm. FPM < 10 micrometers, which includes the portion of total FPM collected downstream of the PM10 cyclone, was 0.06 to 0.20 mg/dscm. FPM < 2.5 micrometers, which includes the portion of FPM collected downstream of the PM2.5 cyclone and on the in-stack filter, was below detection limits for Runs 1 and 3; Run 2 was 0.11 mg/dscm. These in-stack concentrations correspond to total weight gains in the sampling train of 0.2 to 1 milligrams (mg), with uncorrected net weights in each fraction of 0.3 to 1.3 mg. The net weight gain on the filters was negative for all runs. These negative weights were caused by weight loss from the Viton o-rings, which were weighed along with the filters in order to avoid loss of filter pieces during sample recovery and analysis. This result reflects the extremely low particulate loading in the stack.

The reported particulate result for each run is attributed entirely to the acetone rinses. The total net weight gain in the field blank train was below detection limits when corrected for the acetone blank. Although the balance used to obtain mass loadings has an analytical resolution of 10 micrograms, these results suggest that the particulate mass loading at the stack in these tests may be near or below the practical limits of the overall method.

Condensible Particulate Matter (CPM). Since there has been much comment on the analytical procedures used to establish levels of CPM collected in the Method 202 impingers, three separate procedures, as described in Section 3, were utilized to analyze their contents. The results are summarized in Table 4-8.

Table 4-8. Condensible Particulate Matter (Method 202) Results (Site C).

Parameter	Units	Value				
Run Number	-	1	2	3	Average	RSD
Date	-	21-Oct-99	22-Oct-99	25-Oct-99		
Inorganic CPM (Standard Procedure) (1)	mg/dscm lb/hr	0.7 1.9E-2	0.5 1.2E-2	1.3 3.7E-2	0.83 2.3E-2	55% 56%
Inorganic CPM (Alternative Procedure)	mg/dscm lb/hr	2.4 6.4E-2	2.7 7.4E-2	5.8 1.6E-1	3.6 9.9E-2	52% 53%
Organic CPM	mg/dscm lb/hr	0.62 1.7E-2	0.46 1.3E-2	1.3 3.5E-2	0.78 2.1E-2	54% 55%
Sulfate (as SO ₄ ⁻) in Impingers (Instrumental Procedure)	mg/dscm lb/hr	1.2 3.4E-2	1.5 4.1E-2	1.7 4.6E-2	1.5 4.0E-2	15% 15%
Sulfate (as SO ₄ ⁻) in Impingers (Standard Procedure)	mg/dscm lb/hr	0.11 2.9E-3	0.29 7.8E-3	0.29 7.9E-3	0.23 6.2E-3	47% 47%
Sulfate (as SO ₄ ⁻) in Impingers (Alternative Procedure)	mg/dscm lb/hr	1.1 2.9E-2	1.6 4.3E-2	1.6 4.3E-2	1.4 3.8E-2	22% 22%
Total CPM (Standard Procedure) (2) (corrected for NH ₄ ⁺ and H ₂ O)	mg/dscm lb/hr	1.6 4.3E-2	< 0.91 2.5E-2	3.2 8.8E-2	1.9 5.2E-2	61% 62%
Dichloromethane Recovery Blank (Standard Procedure)	mg/dscm	0.3				
Water Recovery Blank (Standard Procedure)	mg/dscm	1.0				
Water Recovery Blank (Alternative Procedure)	mg/dscm	0.3				

RSD-relative standard deviation

CPM-condensible particulate matter

<-one or more, but not all, constituents are less than the detection limit

(1) Standard Procedure: all steps for M202 analysis followed, including titration and organic extraction;

Alternative Procedure: titration and organic extraction not performed

(2) Total CPM not corrected for reagent blank mass. Run 2 back-half filter weight was below detection limits.

Standard Procedure. The average total CPM, which is the sum of the evaporated organic extract and the inorganic residue and corrected for addition of NH₄OH, is 1.9 mg/dscm. The total inorganic mass is 0.83 mg/dscm, 27 percent of which is accounted for by sulfate, with a concentration of 0.23 mg/dscm. This sulfate concentration is determined from the resuspended inorganic residue. The average organic CPM concentration is 0.78 mg/dscm. This result is higher than previous tests on a gas-fired boiler and gas-fired heater that had organic CPM concentrations of 0.6 and 0.2 mg/dscm, respectively.

CPM concentration was approximately 17 times greater than FPM2.5 on average. On average, approximately 44 percent of the CPM was found in the inorganic fraction, while 41 percent was found in the organic fraction (the remaining mass is accounted for by the back-half filter and was not characterized). The inorganic and organic CPM results are somewhat variable from run to run, with standard deviations equal to 55 and 54 percent of the average result, respectively. CPM results have not been corrected for dichloromethane and water recovery blank results due to unusually high water reagent blank masses (for Runs 1 and 2 of the Standard Procedure, the water blank weight exceeded the inorganic CPM weight). The Standard Procedure data are corrected for ammonium ion retained and combined water released in the acid base titration, as described in Method 202. Further discussion of the data is provided in Section 7.

Alternative Procedure. The average inorganic CPM concentration is 3.6 mg/dscm, approximately four times higher than that determined by the Standard Method. This concentration is not corrected for NH_4OH because none was added. No total CPM value is provided for the Alternative Procedure because the organic extraction was not performed on this portion of the sample. The average sulfate concentration, as determined by analysis of the resuspended inorganic residue, is 1.4 mg/dscm accounting for approximately 39 percent of the inorganic CPM.

Instrumental Procedure. The Method 202 impinger catch was also analyzed prior to any handling by removing an aliquot from the impinger catch and DI water rinse. The average $\text{SO}_4^{=}$ concentration of the raw impinger contents is 1.5 mg/dscm. Sulfate mass, expressed as sulfate ion, varied according to the fraction analyzed, and is discussed further in Section 7. The sample analyzed prior to Method 202 analysis and the Alternative Procedure numbers agree very well (1.5 versus 1.4 mg/dscm, respectively), while the Standard Procedure results are almost an order of magnitude lower (0.23 mg/dscm). The raw impinger contents were also analyzed for additional cations, anions, and metals, the results of which are shown in Table 4-9 and labeled “Pre-202.”

Table 4-9. Speciation (mg/dscm) of Back-Half Impinger Catch (Site C).

Ion	Run 1 (mg/dscm)			Run 2 (mg/dscm)			Run 3 (mg/dscm)			Average (mg/dscm)			RSD (%)		
	Pre-202	Std	Alt	Pre-202	Std	Alt	Pre-202	Std	Alt	Pre-202	Std	Alt	Pre-SO2	Std	Alt
Sulfate (as SO ₄ ²⁻)	1.09E+0	2.36E-2	9.44E-1	1.40E+0	2.71E-1	1.41E+0	1.52E+0	2.74E-1	1.50E+0	1.3E+00	1.9E-01	1.3E+00	16	76	31
Na	9.61E-1	5.61E-2	1.53E-1	8.03E-1	1.00E-1	1.47E-1	2.94E+0	3.72E-1	1.63E+0	1.6E+00	1.8E-01	6.4E-01	76	97	162
Chloride	ND	1.80E-2	8.26E-3	ND	1.53E-2	ND	3.12E+0	3.91E-1	1.63E-2	< 3.1E+00	1.4E-01	< 1.2E-02	n/a	153	46
K	< 2.57E+0	< 5.90E-2	< 5.90E-2	< 2.71E+0	< 5.89E-2	< 5.89E-2	< 2.79E+0	< 6.52E-2	< 6.52E-2	< 2.7E+00	< 6.1E-02	< 6.1E-02	4	6	7
Ca	< 5.19E-1	1.30E-2	4.78E-2	< 5.40E-1	2.71E-2	4.01E-2	< 5.67E-1	3.06E-2	5.28E-2	< 5.4E-01	2.4E-02	4.7E-02	4	40	8
Ammonium (as NH ₄ ⁺)	3.89E-2	< 2.95E-3	8.85E-3	ND	1.65E-2	2.24E-2	ND	< 3.26E-3	5.35E-3	< 3.9E-02	< 7.6E-03	1.2E-02	n/a	102	20
Mg	< 1.30E-1	3.54E-3	8.85E-3	< 1.37E-1	9.43E-3	7.66E-3	< 1.40E-1	8.48E-3	5.74E-3	< 1.4E-01	7.1E-03	7.4E-03	4	44	30
Nitrate (as N)	ND	ND	5.84E-3	ND	5.48E-3	ND	ND	7.17E-3	1.96E-2	ND	< 6.3E-03	< 1.3E-02	n/a	19	76
P	< 7.53E-2	< 3.54E-3	< 3.54E-3	< 1.20E-1	< 3.53E-3	< 3.53E-3	< 1.67E-1	< 3.91E-3	< 3.91E-3	< 1.2E-01	< 3.7E-03	< 3.7E-03	38	6	7
Tl	< 1.53E-1	< 3.54E-3	< 3.54E-3	< 1.62E-1	< 3.53E-3	< 3.53E-3	< 1.67E-1	< 3.91E-3	< 3.91E-3	< 1.6E-01	< 3.7E-03	< 3.7E-03	4	6	7
Fluoride	2.00E-1	ND	7.08E-3	ND	3.65E-3	ND	ND	ND	ND	< 2.0E-01	< 3.7E-03	< 7.1E-03	n/a	n/a	n/a
Zn	3.38E-2	1.18E-3	8.85E-3	5.12E-2	4.36E-3	1.00E-2	4.54E-2	2.54E-3	6.13E-3	4.3E-02	2.7E-03	8.3E-03	20	59	23
Al	1.17E-1	< 1.77E-3	1.06E-2	< 8.58E-2	< 1.77E-3	7.07E-3	1.22E-1	< 1.96E-3	2.28E-3	< 1.1E-01	< 1.8E-03	6.7E-03	18	6	89
Pb	< 5.19E-2	< 1.18E-3	< 1.18E-3	< 5.40E-2	< 1.18E-3	< 1.18E-3	< 5.67E-2	< 1.30E-3	< 1.30E-3	< 5.4E-02	< 1.2E-03	< 1.2E-03	4	6	7
Co	< 2.60E-2	< 5.90E-4	< 5.90E-4	< 2.77E-2	< 5.89E-4	< 5.89E-4	< 2.84E-2	1.63E-3	1.24E-2	< 2.7E-02	< 9.4E-04	< 4.5E-03	5	64	184
Cu	< 1.30E-2	< 2.95E-4	5.72E-3	< 1.37E-2	1.30E-3	2.95E-3	2.16E-2	9.78E-4	2.35E-3	< 1.6E-02	< 8.6E-04	3.7E-03	30	60	65
Ag	< 2.60E-2	< 5.90E-4	< 5.90E-4	< 2.77E-2	< 5.89E-4	< 5.89E-4	< 2.84E-2	< 6.52E-4	< 6.52E-4	< 2.7E-02	< 6.1E-04	< 6.1E-04	5	6	7
Fe	< 2.60E-2	< 5.90E-4	1.12E-2	< 2.77E-2	< 5.89E-4	8.25E-3	2.84E-2	< 6.52E-4	3.65E-3	< 2.7E-02	< 6.1E-04	7.7E-03	5	6	69
Mo	< 2.60E-2	< 5.90E-4	< 5.90E-4	< 2.77E-2	< 5.89E-4	< 5.89E-4	< 2.84E-2	< 6.52E-4	< 6.52E-4	< 2.7E-02	< 6.1E-04	< 6.1E-04	5	6	7
Ni	< 2.60E-2	< 5.90E-4	1.00E-3	< 2.77E-2	< 5.89E-4	< 5.89E-4	< 2.84E-2	< 6.52E-4	< 6.52E-4	< 2.7E-02	< 6.1E-04	< 7.5E-04	5	6	33
Mn	< 1.53E-2	< 3.54E-4	1.95E-3	< 1.62E-2	< 3.53E-4	5.89E-4	< 1.67E-2	< 3.91E-4	4.89E-4	< 1.6E-02	< 3.7E-04	1.0E-03	4	6	102
V	< 1.30E-2	< 2.95E-4	< 2.95E-4	< 1.37E-2	< 2.95E-4	< 2.95E-4	< 1.40E-2	< 3.26E-4	< 3.26E-4	< 1.4E-02	< 3.1E-04	< 3.1E-04	4	6	7
Cr	< 1.04E-2	< 2.36E-4	< 2.36E-4	< 1.09E-2	< 2.36E-4	< 2.36E-4	< 1.12E-2	< 2.61E-4	< 2.61E-4	< 1.1E-02	< 2.4E-04	< 2.4E-04	4	6	7
Cd	< 8.57E-3	< 1.95E-4	3.60E-4	< 9.00E-3	< 1.94E-4	< 1.94E-4	< 9.36E-3	< 2.15E-4	2.35E-4	< 9.0E-03	< 2.0E-04	< 2.6E-04	4	6	34
Sr	5.97E-3	1.00E-4	1.95E-4	4.43E-3	1.71E-4	1.71E-4	6.52E-3	1.37E-4	2.15E-4	5.6E-03	1.4E-04	1.9E-04	19	26	7
Ba	7.53E-2	< 5.90E-5	5.90E-4	9.69E-2	< 5.89E-5	8.25E-4	1.57E-1	1.04E-4	8.48E-4	1.1E-01	< 7.4E-05	7.5E-04	39	35	24
Be	< 2.60E-3	< 5.90E-5	< 5.90E-5	< 2.77E-3	< 5.89E-5	< 5.89E-5	< 2.84E-3	< 6.52E-5	< 6.52E-5	< 2.7E-03	< 6.1E-05	< 6.1E-05	5	6	7
Bromide	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	n/a	n/a	n/a
ortho-phosphate (as P)	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	n/a	n/a	n/a

< - one or two runs are below limit of quantitation (Detection limit x 3.33)
n/a-not applicable; two or more runs not detected
ND-not detected
Pre-202 - Analysis done on aliquot of impinger solution before analysis by Method 202
Std - Analysis done per Method 202
Alt - Modified Method 202: no organic extraction or ammonium hydroxide titration performed

Additionally, the resuspended inorganic residues of the Standard and Alternative Procedures were analyzed for a broader range of elements and ions by a different lab in order to more fully speciate the inorganic CPM. These results are presented in Table 4-9 alongside the results of the Instrumental Procedure analysis. $\text{SO}_4^{=}$, Na, Cl and K are the four most abundant compounds in the inorganic CPM fraction for all three procedures.

Standard Procedure. $\text{SO}_4^{=}$, Na, Cl and K account for an average of 0.6 mg/dscm, or 68 percent, of the inorganic CPM mass as presented in Table 4-8. The remaining 23 elements and ions that were detected account for an average of 0.07 mg/dscm, or 8 percent, of the average inorganic CPM mass. Twenty-four percent of the inorganic CPM mass remains unaccounted for by the speciated analysis.

Alternative Procedure. $\text{SO}_4^{=}$, Na, Cl and K account for an average of 2 mg/dscm, which is approximately 56 percent of the inorganic CPM mass as presented in Table 4-8. The remaining constituents account for an additional 4 percent, leaving approximately 40 percent of the inorganic CPM mass unspciated.

Although the results of all three procedures do not match quantitatively, the additional analysis qualitatively confirms that $\text{SO}_4^{=}$ is the dominant compound in the inorganic residue. Chloride is also present in significant amounts. It is believed the majority of $\text{SO}_4^{=}$, and perhaps Cl, found in the impinger contents is an artifact resulting from gaseous SO_2 and hydrogen chloride (HCl) in the stack gas. These results and issues are discussed in more detail in Section 7.

OC and EC

OC and EC were determined on in-stack filters. Analysis for SVOCs was not performed, due to the small amount of organic carbon found on the filters. OC and EC were undetected on the in-stack filters for two of the three runs, which is consistent with their very clean visual appearance. Results are presented in Table 4-10.

Table 4-10. OC/EC as Measured on the In-Stack Filters (Site C).

Parameter	Units	Value				
Run Number	-	1	2	3	Average	RSD
Date	-	21-Oct-99	22-Oct-99	25-Oct-99		
Organic Carbon	mg/dscm	5.0E-3	ND	ND	5.0E-3	n/a
	lb/hr	1.4E-4	ND	ND	1.4E-4	n/a
Elemental Carbon	mg/dscm	2.3E-3	ND	ND	2.3E-3	n/a
	lb/hr	6.3E-5	ND	ND	6.3E-5	n/a
Total Carbon	mg/dscm	7.4E-3	ND	ND	7.4E-3	n/a
	lb/hr	2.0E-4	ND	ND	2.0E-4	n/a

n/a-not applicable; two or more runs not detected

ND-not detected

RSD-relative standard deviation

DILUTION TUNNEL RESULTS

Particulate Mass

PM_{2.5} mass measurements using the dilution tunnel include both solid aerosols that are directly emitted and those that condense under simulated stack plume conditions in the residence chamber. The dilution tunnel determines only the PM_{2.5} fraction of particulate emissions. Results from these measurements show that PM_{2.5} concentrations and emission rates average 0.09 mg/dscm and 0.0025 lb/hr, respectively, with a relative standard deviation of 70 percent, based on Teflon[®] filter weight (Table 4-11). These results are approximately 22 times lower than the sum of FPM_{2.5} and CPM measured by EPA Methods 201A and 202. PM_{2.5} concentration measured in the steam-generator stack gas was approximately equal to the concentration measured in the ambient air.

Table 4-11. Dilution Tunnel PM_{2.5} Results (Site C).

	Units	Results					
Run Number	-	1	2	3	Average	RSD	Ambient
Date	-	21-Oct-99	22-Oct-99	25-Oct-99			19-Oct-99
PM _{2.5}	mg/dscm	1.6E-1	8.8E-2	2.7E-2	9.0E-2	71%	8.0E-2
	lb/hr	4.2E-3	2.4E-3	7.5E-4	2.5E-3	70%	n/a

n/a-not applicable

RSD- relative standard deviation

The concentration of PM_{2.5} using the dilution tunnel is approximately equal to FPM <2.5 micrometers measured using Method 201A and a factor of 20 lower than CPM measured using Method 202. CPM is normally included in regulatory definitions of PM₁₀. These emission measurements are strongly method dependent because the dilution tunnel replicates conditions experienced by the stack emissions as they mix with the atmosphere more accurately than Method 202. Due to suspected artifacts associated with Method 202, it is believed the dilution tunnel results are more representative of the true primary PM_{2.5} emissions.

Sulfate, Chloride, and Nitrate

Quartz filters were analyzed for SO₄⁼, Cl⁻, and NO₃⁻ ion. Of these, NO₃⁻ had the highest average concentration at 0.0068 mg/dscm, followed by SO₄⁼ at 0.0063 mg/dscm; Cl⁻ was below detection limits for all runs (Table 4-12). SO₄⁼ was detected in only one of three runs at approximately 2 times the lower method detection limit. All ions in the field blank were present below detectable levels (see Section 6 for additional discussion of blanks).

Table 4-12. Dilution Tunnel Sulfate, Nitrate, and Chloride Results (Site C).

Parameter	Units	Value					
Run Number	-	1	2	3	Average	RSD	Ambient
Date	-	21-Oct-99	22-Oct-99	25-Oct-99			19-Oct-99
Sulfate	mg/dscm	6.3E-3	ND	ND	6.3E-3	n/a	4.3E-3
	lb/hr	1.7E-4	ND	ND	1.7E-4	n/a	n/a
Nitrate	mg/dscm	7.2E-3	6.0E-3	7.2E-3	6.8E-3	10%	5.6E-3
	lb/hr	1.9E-4	1.6E-4	2.0E-4	1.9E-4	10%	n/a
Chloride	mg/dscm	ND	ND	ND	ND	n/a	4.6E-4
	lb/hr	ND	ND	ND	ND	n/a	n/a

n/a - not applicable

ND - not detected

RSD- relative standard deviation

The quartz filters used for these measurements have the potential for a positive SO₄⁼ bias. However, at the low SO₂ concentrations present in the stack gas the artifact probably is not significant for these tests. The average SO₄⁼ concentration from the dilution tunnel is approximately 1/40 of the average concentration reported above for Method 202. This difference lends further support to the possibility of a significant sampling artifact in Method 202 due to gaseous SO₂ in the stack gas.

Concentrations of sulfate, nitrate and ammonium measured in the stack gas are within an order of magnitude of the concentrations measured in the ambient air. Chloride was detected in the ambient sample at levels close to the detection limit, but not in the field samples.

OC, EC and Organic Species

OC and EC were measured on quartz filters from the dilution tunnel. OC concentration ranged from 0.29 to 0.52 mg/dscm. EC was detected in two runs at concentrations of 0.012 and 0.018 mg/dscm (Table 4-13). OC accounts for more than 97 percent of the total carbon mass. Average elemental carbon concentrations measured in the stack gas are within an order of magnitude of the ambient sample concentration; the average OC concentration is slightly more than an order of magnitude greater than the ambient concentration. The high concentration of OC in the field samples relative to the PM_{2.5} mass may be due to the tendency for adsorption of VOCs onto quartz filters when VOC concentrations are high. Organic carbon on the field blank filter is more than an order of magnitude lower than the average concentration in the stack gas samples; elemental carbon in the field blank was below detection limits (see Section 6 for additional discussion of blank results).

Table 4-13. OC/EC as Measured by the Dilution Tunnel (Site C).

Parameter	Units	Value					
Run Number	-	1	2	3	Average	RSD	Ambient
Date	-	21-Oct-99	22-Oct-99	25-Oct-99			19-Oct-99
Organic Carbon	mg/dscm	0.52	0.31	0.29	0.37	34%	3.0E-2
	lb/hr	1.4E-2	8.4E-3	8.0E-3	1.0E-2	33%	n/a
Elemental Carbon	mg/dscm	1.8E-2	1.2E-2	ND	1.5E-2	30%	6.7E-3
	lb/hr	4.9E-4	3.2E-4	ND	4.0E-4	29%	n/a
Total Carbon	mg/dscm	0.53	0.31	0.29	0.38	36%	3.7E-2
	lb/hr	1.4E-2	8.4E-3	8.0E-3	1.0E-2	35%	n/a

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

Volatile organic carbon tends to adsorb to quartz filters in a situation where there are high amounts of VOCs. This may explain the observed enrichment of OC relative to the measured mass seen here.

SVOCs were determined on the combined TIGF/PUF/XAD-4/PUF cartridge used with the dilution tunnel. This method determines both particulate and vapor phase SVOCs together. All

SVOCs detected were present in the stack gas at low levels (Table 4-14). Some of the SVOCs detected in the stack also were detected in the ambient air. Bibenzene is the most abundant SVOC in the dilution tunnel samples with an average concentration of 0.0061 mg/dscm. Most of the average SVOC stack gas concentrations are a factor of ten greater than the ambient air concentration, with the minimum being a factor of 5.

Tenax sorbent was used to collect VOCs. The analysis focused only on VOCs with a carbon number greater than seven since these are believed to be the most significant precursors for secondary organic aerosols. N-undecane was the most abundant VOC detected during sampling, with an average concentration of 0.0069 mg/dscm (Table 4-15). N-nonane was the second most abundant on average (0.0068 mg/dscm). In general, the average VOC concentration in the stack gas was within a factor of approximately one to twenty times the ambient air concentration. Concentrations of 1,2,3-trimethylbenzene, 1,2,4-trimethylbenzene, decanal, octanal, and sec-butylbenzene were all lower in the field samples than in the ambient sample.

All compounds in the field blank were below detection limits (see Section 6 for additional discussion of results).

Elements

Element concentrations were determined by XRF analysis of the TMFs used in the dilution tunnel. On average, Si, Fe, Ca, Al, Cu, and S are the most abundant elements in the stack gas (Table 4-16). The S results are within a factor of 4 of the dilution tunnel $\text{SO}_4^{=}$ results presented earlier, as expected. Na and Mg results are considered semi-quantitative because of analytical limitations. Ag, Au, Ba, Cd, Ga, Hg, In, La, Mo, Pd, Sb, Sn, Tl, U and Y were below detectable levels for all three sample runs. All concentrations in the ambient samples are within an order of magnitude of the average sample concentration. Pb, V, Br, As, Zr, Rb, and Se were detected in the ambient sample but not in the sample runs. Cr, Mg, Mn and S concentrations are higher in the ambient air than in the stack gas.

All compounds detected in the field blank were present at insignificant levels (see Section 6 for further details).

Table 4-14. Semi-Volatile Organic Compound Results, as Measured by the Dilution Tunnel (mg/dscm) (Site C).

Parameter	Value						
Run Number	1	2	3	Average	RSD	Ambient	MDL
Date	21-Oct-99	22-Oct-99	25-Oct-99		(%)	19-Oct-99	
Bibenzene	7.6E-3	4.5E-3	3.9E-4	4.2E-3	87	ND	1.3E-4
Naphthalene	3.0E-3	6.5E-4	ND	1.8E-3	91	2.5E-4	5.1E-5
1,3+1,6+1,7-dimethylnaphthalene	4.8E-3	2.2E-4	6.9E-5	1.7E-3	158	4.6E-5	1.2E-5
1-methylnaphthalene	2.4E-3	1.1E-4	ND	1.2E-3	129	6.1E-5	2.0E-6
2-methylnaphthalene	1.8E-3	1.3E-4	ND	9.9E-4	123	7.3E-5	3.3E-6
2-methylphenanthrene	2.7E-3	1.7E-4	4.4E-5	9.7E-4	154	1.3E-5	1.1E-7
2,3,5+I-trimethylnaphthalene	2.1E-3	8.8E-5	2.4E-5	7.2E-4	160	1.3E-5	1.6E-7
A-methylphenanthrene	1.8E-3	2.1E-4	6.7E-5	6.9E-4	139	1.1E-5	2.5E-6
Phenanthrene	1.7E-3	2.7E-4	5.1E-5	6.8E-4	133	2.0E-5	4.2E-7
B-trimethylnaphthalene	1.7E-3	9.1E-5	2.6E-5	5.9E-4	156	1.4E-5	5.3E-8
1,4+1,5+2,3-dimethylnaphthalene	1.5E-3	1.4E-4	3.1E-5	5.7E-4	147	1.4E-5	5.4E-6
3-methylbiphenyl	9.8E-4	1.2E-4	ND	5.5E-4	111	ND	1.2E-5
2,6+2,7-dimethylnaphthalene	1.5E-3	9.9E-5	2.8E-5	5.5E-4	153	2.5E-5	5.7E-6
E-trimethylnaphthalene	1.5E-3	1.3E-4	2.2E-5	5.4E-4	150	8.2E-6	5.3E-8
C-trimethylnaphthalene	1.4E-3	9.1E-5	1.8E-5	4.9E-4	154	1.1E-5	4.2E-7
J-trimethylnaphthalene	1.2E-3	7.0E-5	6.5E-6	4.2E-4	158	5.3E-6	4.3E-7
Anthracene	7.5E-4	4.9E-7	ND	3.8E-4	141	3.7E-5	0.0E+0
1,4,5-trimethylnaphthalene	7.3E-4	6.9E-6	ND	3.7E-4	139	ND	5.0E-6
2-methylbiphenyl	7.6E-4	2.9E-4	1.4E-5	3.5E-4	107	ND	8.4E-6
C-dimethylphenanthrene	8.9E-4	1.3E-4	2.5E-5	3.5E-4	136	4.6E-6	1.8E-6
9-fluorenone	7.4E-4	2.2E-4	8.5E-5	3.5E-4	99	9.9E-6	7.1E-6
C-methylphenanthrene	6.6E-4	ND	1.8E-5	3.4E-4	134	2.6E-6	1.5E-6
A-trimethylnaphthalene	6.1E-4	2.3E-5	ND	3.1E-4	131	1.6E-6	1.0E-7
2,4,5-trimethylnaphthalene	6.2E-4	ND	4.7E-6	3.1E-4	139	1.1E-6	4.2E-7
1,2-dimethylnaphthalene	9.0E-4	2.4E-5	5.3E-6	3.1E-4	165	4.5E-6	3.7E-6
1+2-ethylnaphthalene	7.7E-4	1.1E-4	8.3E-6	3.0E-4	139	1.1E-5	6.8E-6
F-trimethylnaphthalene	6.7E-4	1.4E-4	1.4E-5	2.7E-4	127	1.0E-5	5.0E-8
4-methylbiphenyl	4.2E-4	1.2E-4	ND	2.7E-4	79	6.1E-6	1.0E-6
Fluorene	6.5E-4	9.4E-5	7.7E-6	2.5E-4	139	1.0E-5	6.4E-6
Fluoranthene	4.0E-4	2.4E-4	4.8E-5	2.3E-4	78	6.6E-6	1.1E-7
Pyrene	4.5E-4	1.2E-4	1.7E-5	1.9E-4	116	4.9E-6	2.1E-7
1,7-dimethylphenanthrene	4.9E-4	7.1E-5	1.8E-6	1.9E-4	141	1.9E-6	1.8E-6
Biphenyl	3.2E-4	3.4E-5	ND	1.8E-4	114	9.4E-6	3.6E-6
D-dimethylphenanthrene	3.1E-4	3.8E-5	ND	1.7E-4	110	ND	1.6E-6
1-methylphenanthrene	5.0E-4	4.5E-6	1.2E-5	1.7E-4	165	2.7E-6	1.2E-6
1-ethyl-2-methylnaphthalene	3.8E-4	1.5E-5	1.8E-6	1.3E-4	162	2.1E-6	1.1E-7
A-dimethylphenanthrene	3.0E-4	8.0E-5	1.1E-5	1.3E-4	116	ND	2.5E-6
4-methylpyrene	2.5E-4	1.3E-4	6.5E-6	1.3E-4	94	8.0E-7	1.1E-7
9-anthraldehyde	3.2E-4	2.1E-5	3.8E-5	1.3E-4	133	3.4E-6	1.4E-6
B-methylpyrene/methylfluorene	1.2E-4	ND	ND	1.2E-4	n/a	1.2E-6	5.3E-8
3,6-dimethylphenanthrene	2.9E-4	6.8E-5	7.7E-6	1.2E-4	123	ND	2.5E-6
A-methylfluorene	2.0E-4	5.9E-5	1.2E-5	9.2E-5	109	ND	5.6E-6
1-methylpyrene	8.9E-5	9.2E-5	ND	9.0E-5	2	ND	4.2E-7
E-dimethylphenanthrene	2.1E-4	4.9E-5	8.3E-6	9.0E-5	120	1.8E-6	8.0E-7
B-dimethylphenanthrene	8.9E-5	ND	ND	8.9E-5	n/a	ND	1.8E-6

Table 4-14. Semi Volatile Organic Compound Results, as Measured by the Dilution Tunnel (mg/dscm) (Site C) (continued).

Parameter	Value						
Run Number	1	2	3	Average	RSD	Ambient	MDL
Date	21-Oct-99	22-Oct-99	25-Oct-99		(%)	19-Oct-99	
Acenaphthene	1.3E-4	2.6E-5	ND	7.9E-5	95	ND	1.4E-6
1,8-dimethylnaphthalene	1.7E-4	2.8E-5	7.1E-6	7.0E-5	130	4.3E-6	3.7E-6
Acenaphthylene	1.4E-4	5.3E-5	1.1E-5	6.7E-5	96	ND	5.5E-6
1,2,8-trimethylnaphthalene	1.2E-4	3.0E-6	ND	6.4E-5	135	ND	3.2E-7
Retene	1.8E-4	8.4E-6	4.1E-6	6.3E-5	156	ND	3.2E-6
2-ethyl-1-methylnaphthalene	8.8E-5	1.7E-5	ND	5.3E-5	96	ND	8.8E-6
Xanthone	1.2E-4	1.5E-5	6.0E-7	4.5E-5	143	7.0E-7	2.1E-7
Chrysene	4.6E-5	1.5E-5	2.0E-5	2.7E-5	60	2.4E-6	1.1E-7
D-methylpyrene/methylfluorene	1.7E-5	4.6E-5	2.4E-6	2.2E-5	101	4.8E-7	5.3E-8
Benzo(b+j+k)fluoranthene	1.9E-5	2.9E-5	1.4E-5	2.1E-5	36	2.6E-6	5.3E-8
Benz(a)anthracene	1.4E-5	2.2E-5	ND	1.8E-5	32	3.8E-6	3.2E-7
Benzo(c)phenanthrene	4.2E-6	2.8E-5	ND	1.6E-5	105	ND	5.8E-7
C-methylpyrene/methylfluorene	ND	1.5E-5	ND	1.5E-5	n/a	3.4E-7	5.3E-8
Benzo(e)pyrene	6.3E-6	3.0E-5	5.3E-6	1.4E-5	100	3.6E-7	3.3E-7
7-methylbenz(a)anthracene	ND	1.1E-5	ND	1.1E-5	n/a	ND	3.3E-7
B-methylphenanthrene	ND	1.1E-5	ND	1.1E-5	n/a	ND	5.8E-7
Benzonaphthothiophene	1.5E-5	5.9E-6	ND	1.0E-5	59	5.6E-7	1.1E-7
A-methylpyrene	1.6E-5	4.5E-6	ND	1.0E-5	78	ND	5.3E-8
5+6-methylchrysene	3.6E-6	1.3E-5	ND	8.2E-6	79	ND	0.0E+0
Perylene	ND	4.5E-6	ND	4.5E-6	n/a	9.2E-7	1.1E-7
1-methylfluorene+C-methylpyrene/fluorene	ND	ND	ND	ND	n/a	ND	8.5E-7
9-methylanthracene	ND	ND	ND	ND	n/a	1.7E-5	2.4E-6
Benzo(a)pyrene	ND	ND	ND	ND	n/a	ND	3.2E-7
Benzo(b)chrysene	ND	ND	ND	ND	n/a	ND	1.1E-7
Benzo(ghi)perylene	ND	ND	ND	ND	n/a	ND	3.2E-7
Coronene	ND	ND	ND	ND	n/a	ND	3.2E-7
Dibenz(ah+ac)anthracen	ND	ND	ND	ND	n/a	ND	3.2E-7
Indeno[123-cd]pyrene	ND	ND	ND	ND	n/a	ND	3.2E-7
Perinaphthenone	ND	ND	ND	ND	n/a	ND	5.2E-5

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

ND- not detected

MDL- method detection limit

RSD- relative standard deviation

Table 4-15. Volatile Organic Compound (VOC) Results (Site C).

Parameter	Value					
Units	mg/dscm				%	mg/dscm
Run Number	1	2	3	Average	RSD	Ambient
Date	21-Oct-99	22-Oct-99	25-Oct-99			19-Oct-99
n-undecane	8.6E-3	1.1E-2	8.9E-4	6.9E-3	78	4.8E-4
n-nonane	8.3E-3	1.1E-2	1.4E-3	6.8E-3	72	4.6E-4
m- & p-xylenes	6.8E-3	8.9E-3	8.4E-4	5.5E-3	76	4.0E-3
n-decane	5.1E-3	6.7E-3	8.4E-4	4.2E-3	72	4.8E-4
n-dodecane	4.3E-3	5.7E-3	7.3E-4	3.6E-3	71	7.7E-4
n-hexadecene	3.6E-3	4.7E-3	6.3E-4	3.0E-3	71	1.2E-4
n-tetradecane	3.4E-3	4.5E-3	6.9E-4	2.8E-3	68	2.0E-4
o-xylene	3.1E-3	4.0E-3	3.2E-4	2.5E-3	78	1.5E-3
n-pentadecane	2.7E-3	3.6E-3	1.0E-3	2.5E-3	53	1.9E-4
n-octadecane	2.7E-3	3.6E-3	9.3E-4	2.4E-3	56	6.7E-5
Ethyl Benzene	2.9E-3	3.8E-3	6.5E-5	2.2E-3	86	1.2E-3
n-heptadecene	2.3E-3	3.1E-3	8.6E-4	2.1E-3	54	9.4E-5
o-ethyltoluene	1.6E-3	2.1E-3	ND	1.9E-3	19	3.5E-4
1,3,5 trimethylbenzene	2.3E-3	3.0E-3	2.4E-4	1.8E-3	78	5.3E-4
n-tridecane	1.9E-3	2.5E-3	4.8E-4	1.7E-3	64	4.5E-4
Styrene	1.9E-3	2.5E-3	3.2E-4	1.6E-3	72	1.2E-4
1,2,4 trimethylbenzene	1.9E-3	2.5E-3	2.2E-4	1.5E-3	77	1.6E-3
p-ethyltoluene	1.8E-3	2.4E-3	1.9E-4	1.5E-3	78	4.5E-4
Nonanal	1.1E-3	1.4E-3	1.3E-3	1.2E-3	13	2.2E-4
n-eicosane	1.1E-3	1.5E-3	1.1E-3	1.2E-3	16	3.5E-5
2-methyl Octane	1.5E-3	1.9E-3	1.9E-4	1.2E-3	75	5.7E-4
2-propyltoluene	6.4E-4	8.4E-4	1.9E-3	1.1E-3	61	1.5E-4
m-ethyltoluene	1.1E-3	1.5E-3	1.9E-4	9.2E-4	71	4.5E-4
undecene-1	7.7E-4	1.0E-3	ND	8.9E-4	19	6.7E-5
n-nonadecane	9.0E-4	1.2E-3	8.6E-5	7.2E-4	79	4.0E-5
Nonene-1	2.8E-4	3.6E-4	1.1E-3	5.9E-4	79	2.8E-4
n-propylbenzene	6.4E-4	8.4E-4	4.3E-5	5.1E-4	82	1.2E-4
Dodecene	3.2E-4	4.2E-4	ND	3.7E-4	19	3.6E-4
Trans-butylbenzene	2.6E-4	3.4E-4	ND	3.0E-4	19	2.2E-4
1,2,4,5-tetramethylbenzene	2.6E-4	3.4E-4	ND	3.0E-4	19	1.4E-4
1,2,3,5-tetramethylbenzene	2.6E-4	3.4E-4	ND	3.0E-4	19	1.4E-4
1,2,3 trimethylbenzene	2.4E-4	3.1E-4	ND	2.7E-4	19	3.4E-4
p-isopropyltoluene	2.4E-4	3.1E-4	ND	2.7E-4	19	5.0E-5
m-isopropyltoluene	3.2E-4	4.2E-4	6.5E-5	2.7E-4	68	3.1E-5
iso-butylbenzene	1.5E-4	2.0E-4	4.3E-4	2.6E-4	58	ND
sec-butylbenzene	1.7E-4	2.2E-4	ND	2.0E-4	19	2.7E-4
1,2,3,4-tetramethylbenzene	1.5E-4	2.0E-4	ND	1.7E-4	19	4.0E-5
Decanal	1.3E-4	1.7E-4	ND	1.5E-4	19	4.2E-4
1-decene	1.1E-4	1.4E-4	ND	1.2E-4	19	5.6E-5
Methylstyrene	8.6E-5	1.1E-4	ND	9.9E-5	19	7.9E-5
Octanal	6.4E-5	8.4E-5	1.1E-4	8.5E-5	26	1.4E-4

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

RSD-relative standard deviation.

ND-not detected.

Table 4-16. Elements, as Measured by the Dilution Tunnel (Site C).

Parameter	Value						
Units	mg/dscm				%	mg/dscm	
Run Number Date	1 21-Oct-99	2 22-Oct-99	3 25-Oct-99	Average	RSD	Ambient 19-Oct-99	MDL (2)
Si	1.3E-2	9.9E-3	7.2E-3	9.9E-3	27	5.3E-3	2.2E-4
Fe	6.6E-3	4.2E-3	4.0E-3	4.9E-3	30	2.7E-3	5.4E-5
Ca	4.6E-3	2.7E-3	2.0E-3	3.1E-3	45	2.6E-3	1.6E-4
Al	3.8E-3	2.6E-3	2.3E-3	2.9E-3	26	1.5E-3	3.6E-4
Cu	2.1E-3	1.0E-3	1.6E-3	1.6E-3	34	9.2E-4	3.9E-5
S	1.8E-3	1.2E-3	1.1E-3	1.4E-3	28	1.6E-3	1.8E-4
Na (1)	1.2E-3	1.8E-3	1.1E-3	1.4E-3	25	ND	0.0E+0
K	2.0E-3	1.1E-3	6.8E-4	1.3E-3	54	8.6E-4	2.2E-4
Cl	8.0E-4	5.0E-4	ND	6.5E-4	33	3.8E-4	3.6E-4
Zn	1.2E-3	2.3E-4	2.2E-4	5.4E-4	102	4.8E-4	3.9E-5
P	3.0E-4	ND	3.6E-4	3.3E-4	12	5.1E-5	2.0E-4
Mn	7.0E-4	6.5E-5	9.0E-5	2.9E-4	126	1.2E-3	5.7E-5
Ti	3.8E-4	ND	1.5E-4	2.6E-4	62	2.1E-4	1.0E-4
Cr	1.5E-4	ND	ND	1.5E-4	n/a	1.7E-4	6.8E-5
Mg (1)	ND	3.4E-5	1.7E-4	1.0E-4	96	7.0E-4	0.0E+0
Ni	6.3E-5	7.7E-5	ND	7.0E-5	14	1.3E-5	3.2E-5
Sr	6.0E-5	ND	ND	6.0E-5	n/a	1.5E-5	3.9E-5
Co	ND	ND	5.1E-5	5.1E-5	n/a	ND	3.1E-5
Pb	ND	ND	ND	ND	n/a	2.7E-4	1.1E-4
V	ND	ND	ND	ND	n/a	1.9E-5	8.9E-5
Br	ND	ND	ND	ND	n/a	1.4E-5	3.6E-5
As	ND	ND	ND	ND	n/a	6.0E-6	5.7E-5
Zr	ND	ND	ND	ND	n/a	5.4E-6	6.1E-5
Rb	ND	ND	ND	ND	n/a	3.6E-6	3.6E-5
Se	ND	ND	ND	ND	n/a	3.3E-6	4.3E-5
Ag	ND	ND	ND	ND	n/a	ND	4.3E-4
Au	ND	ND	ND	ND	n/a	ND	1.1E-4
Ba	ND	ND	ND	ND	n/a	ND	1.9E-3
Cd	ND	ND	ND	ND	n/a	ND	4.3E-4
Ga	ND	ND	ND	ND	n/a	ND	6.8E-5
Hg	ND	ND	ND	ND	n/a	ND	9.3E-5
In	ND	ND	ND	ND	n/a	ND	4.6E-4
La	ND	ND	ND	ND	n/a	ND	2.2E-3
Mo	ND	ND	ND	ND	n/a	ND	9.6E-5
Pd	ND	ND	ND	ND	n/a	ND	3.9E-4
Sb	ND	ND	ND	ND	n/a	ND	6.4E-4
Sn	ND	ND	ND	ND	n/a	ND	6.1E-4
Tl	ND	ND	ND	ND	n/a	ND	8.9E-5
U	ND	ND	ND	ND	n/a	ND	8.2E-5
Y	ND	ND	ND	ND	n/a	ND	4.6E-5

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

(2) Method detection limit for Runs 1-3 (dilution ratio 21:1). Ambient sample MDLs are smaller due to 1:1 dilution ratio.

MDL- method detection limit

ND- not detected

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

RSD- relative standard deviation

Section 5

EMISSION FACTORS AND SPECIATION PROFILES

Emission factors were determined by dividing the emission rate, in lb/hr, by the measured heat input, in MMBtu/hr, to give pounds per million British thermal unit (lb/MMBtu). Heat input is the product of the measured fuel flow rate and the average fuel heating value (based on fuel grab sample analysis). Average emission factors were determined by averaging detected data.

Undetected data were excluded.

UNCERTAINTY

An uncertainty analysis was performed to determine the 95 percent confidence interval and to estimate the upper limit of the measured emission factor and the mass speciation results (ASME, 1990). In the tables that follow, the reported results, the total uncertainty, and a 95 percent confidence upper bound are given for each of the substances of interest. The total uncertainty represents the 95 percent confidence interval based on a two-tailed Student "t" distribution. The 95 percent confidence upper bound estimate is based on the single-tailed Student "t" distribution at the 95 percent confidence level.

EMISSION FACTORS

Table 5-1 presents emission factors for primary emissions, including filterable and condensable particulate mass, and elements and ions as measured on the dilution tunnel filters. FPM includes all particulate captured in the in-stack cyclones, probe and filter. Inorganic, organic, and total CPM have been corrected in accordance with Method 202 guidelines. The average emission factor for total PM_{2.5} (including CPM) measured using in-stack methods is 22 times higher than the emission factor for PM_{2.5} by the dilution tunnel. As discussed previously in Section 4, this is believed to be due to sampling and analytical artifacts associated with the CPM measurement method. Therefore, the emission factor derived from the dilution tunnel results is considered the most reliable.

Table 5-2 presents emission factors for OC, EC, total carbon, and SVOCs as measured by the dilution tunnel. SVOC emission factors are low. The average sum of all SVOCs equals 2.2×10^{-5}

Table 5-1. Primary Emissions – Particulate Mass and Elements (Site C).

Substance		Emission Factor (lb/MMBtu)	Uncertainty (%)	95% Confidence Upper Bound (lb/MMBtu)
Particulate Mass	CPM (organic)	4.8E-4	136	9.4E-4
	CPM (inorganic-Standard Procedure)	5.2E-4	137	1.0E-3
	CPM (inorganic-Alternative Procedure)	2.3E-3	131	4.3E-3
	Total CPM (Standard Procedure)	1.2E-3	154	2.4E-3
	Total Filterable PM (in-stack method)	9.7E-5	196	2.3E-4
	Filterable PM10 (in-stack method))	7.7E-5	139	1.5E-4
	Filterable PM2.5 (in-stack method)	7.0E-5	n/a	n/a
Elements (dilution tunnel)	PM2.5 (Dilution Tunnel)	5.6E-5	177	1.2E-4
	Si	6.2E-6	70	9.2E-6
	Fe	3.1E-6	75	4.7E-6
	Ca	1.9E-6	112	3.4E-6
	Al	1.8E-6	67	2.7E-6
	Cu	9.8E-7	86	1.6E-6
	S	8.7E-7	70	1.3E-6
	K	7.9E-7	134	1.5E-6
	Na	7.0E-7	65	1.0E-6
	Cl	4.0E-7	295	1.0E-6
	Zn	3.3E-7	253	9.0E-7
	P	2.1E-7	110	3.2E-7
	Mn	1.8E-7	314	5.6E-7
	Ti	1.6E-7	557	6.1E-7
	Cr	9.3E-8	n/a	n/a
	Ni	4.4E-8	131	7.3E-8
	Mg	4.3E-8	332	1.4E-7
	Sr	3.7E-8	n/a	n/a
	Co	3.2E-8	n/a	n/a
Ions (dilution tunnel)	Chloride	ND	n/a	n/a
	Nitrate	4.2E-6	30	5.2E-6
	Sulfate	3.9E-6	n/a	n/a

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

Table 5-2. Primary Emissions – Carbon and SVOCs (Site C).

Substance	Average (lb/MMBtu)	Uncertainty (%)	95% Confidence Upper Bound (lb/MMBtu)
Organic Carbon	2.3E-4	87	3.7E-4
Elemental Carbon	9.2E-6	270	2.2E-5
Total Carbon	2.4E-4	90	3.8E-4
Semi-Volatile Organic Compounds (dilution tunnel)			
Bibenzene	2.6E-6	217	6.4E-6
Naphthalene	1.1E-6	814	5.7E-6
1,3+1,6+1,7-dimethylnaphthalene	1.0E-6	394	3.8E-6
1-methylnaphthalene	7.7E-7	1156	5.2E-6
2-methylnaphthalene	6.1E-7	1107	4.0E-6
2-methylphenanthrene	6.0E-7	383	2.2E-6
2,3,5-I-trimethylnaphthalene	4.5E-7	398	1.7E-6
A-methylphenanthrene	4.2E-7	346	1.4E-6
Phenanthrene	4.2E-7	332	1.4E-6
B-trimethylnaphthalene	3.7E-7	389	1.3E-6
1,4+1,5+2,3-dimethylnaphthalene	3.5E-7	366	1.2E-6
3-methylbiphenyl	3.4E-7	1000	2.0E-6
2,6+2,7-dimethylnaphthalene	3.4E-7	382	1.2E-6
E-trimethylnaphthalene	3.3E-7	373	1.2E-6
C-trimethylnaphthalene	3.0E-7	383	1.1E-6
J-trimethylnaphthalene	2.6E-7	392	9.5E-7
1,4,5-trimethylnaphthalene	2.3E-7	1247	1.6E-6
2-methylbiphenyl	2.2E-7	266	6.2E-7
C-dimethylphenanthrene	2.2E-7	338	7.1E-7
9-fluorenone	2.2E-7	246	5.8E-7
C-methylphenanthrene	2.1E-7	1202	1.5E-6
A-trimethylnaphthalene	1.9E-7	1179	1.3E-6
2,4,5-trimethylnaphthalene	1.9E-7	1252	1.4E-6
1,2-dimethylnaphthalene	1.9E-7	411	7.3E-7
1+2-ethylnaphthalene	1.8E-7	346	6.2E-7
F-trimethylnaphthalene	1.7E-7	316	5.3E-7
4-methylbiphenyl	1.7E-7	707	7.6E-7
Anthracene	1.5E-7	1269	1.1E-6
Fluorene	1.5E-7	347	5.2E-7
Fluoranthene	1.4E-7	194	3.3E-7
Pyrene	1.2E-7	290	3.6E-7
1,7-dimethylphenanthrene	1.2E-7	351	3.9E-7
Biphenyl	1.1E-7	1029	6.7E-7
D-dimethylphenanthrene	1.1E-7	991	6.3E-7
1-methylphenanthrene	1.1E-7	411	4.0E-7
1-ethyl-2-methylnaphthalene	8.1E-8	404	3.0E-7
A-dimethylphenanthrene	8.1E-8	288	2.4E-7
4-methylpyrene	8.0E-8	236	2.1E-7

Table 5-2. Primary Emissions – Carbon and SVOCs (Site C) (continued).

Substance	Average (lb/MMBtu)	Uncertainty (%)	95% Confidence Upper Bound (lb/MMBtu)
9-anthraldehyde	7.9E-8	332	2.6E-7
B-methylpyrene/methylfluorene	7.7E-8	n/a	n/a
3,6-dimethylphenanthrene	7.6E-8	306	2.3E-7
A-methylfluorene	5.7E-8	272	1.6E-7
1-methylpyrene	5.6E-8	36	7.2E-8
E-dimethylphenanthrene	5.6E-8	299	1.7E-7
B-dimethylphenanthrene	5.5E-8	n/a	n/a
Acenaphthene	4.9E-8	851	2.6E-7
1,8-dimethylnaphthalene	4.3E-8	324	1.4E-7
Acenaphthylene	4.1E-8	239	1.1E-7
1,2,8-trimethylnaphthalene	3.9E-8	1212	2.8E-7
Retene	3.9E-8	388	1.4E-7
2-ethyl-1-methylnaphthalene	3.3E-8	864	1.7E-7
Xanthone	2.8E-8	357	9.5E-8
Chrysene	1.7E-8	152	3.4E-8
D-methylpyrene/methylfluorene	1.4E-8	252	3.7E-8
Benzo(b+j+k)fluoranthene	1.3E-8	92	2.1E-8
Benz(a)anthracene	1.1E-8	290	2.8E-8
Benzo(c)phenanthrene	1.0E-8	940	5.7E-8
C-methylpyrene/methylfluorene	9.7E-9	n/a	n/a
Benzo(e)pyrene	8.6E-9	251	2.3E-8
7-methylbenz(a)anthracene	7.2E-9	n/a	n/a
B-methylphenanthrene	7.2E-9	n/a	n/a
Benzonaphthothiophene	6.4E-9	535	2.3E-8
A-methylpyrene	6.2E-9	706	2.8E-8
5+6-methylchrysene	5.2E-9	713	2.4E-8
Perylene	2.8E-9	n/a	n/a
1-methylfluorene+C-methylpyrene/fluorene	ND	n/a	n/a
9-methylanthracene	ND	n/a	n/a
Benzo(a)pyrene	ND	n/a	n/a
Benzo(b)chrysene	ND	n/a	n/a
Benzo(ghi)perylene	ND	n/a	n/a
Coronene	ND	n/a	n/a
Dibenz(ah+ac)anthracene	ND	n/a	n/a
Indeno[123-cd]pyrene	ND	n/a	n/a
Perinaphthenone	ND	n/a	n/a
Sum of All SVOCs	1.5E-5		

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

lb/MMBtu, comprising approximately 10 percent of the total organic carbon. Dibenzene has the highest value, with an emission factor of 3.8×10^{-6} lb/MMBtu. Since the dilution tunnel samples are expected to collect SVOCs which condense in the plume, these results are useful for receptor modeling purposes.

Emission factors for VOCs with carbon number greater than seven are presented in Table 5-3. All VOCs are present at extremely low levels, with n-undecane and n-nonane being the most abundant (4.3×10^{-6} lb/MMBtu, each).

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

PM_{2.5} SPECIATION PROFILES

Dilution Tunnel

The speciation profile for PM_{2.5}, based on dilution tunnel results, is given in Table 5-5. This table includes all results from the ED-XRF analysis of the dilution tunnel Teflon[®] filters, the ion analysis of the dilution tunnel quartz filters and the OC/EC analysis of the dilution tunnel quartz filters. The mass fractions presented are the ratio of the emission factor of the emitted compound over the sum of the species emission factors.

The average emission factor for the sum of species (2.6×10^{-4} lb/MMBtu) is approximately 5 times greater than the average emission factor for total PM_{2.5} mass (5.6×10^{-5} lb/MMBtu, measured gravimetrically). This difference is most likely due to the bias associated with the different analytical methods used to determine the speciation of the mass versus the gravimetric analysis used to measure total PM_{2.5} mass. In addition, two different types of filters were used: Teflon[®] filters were used for the elemental analysis and particulate mass, while quartz filters were used for OC/EC analysis and ionic analysis. It is possible that variations in particle deposition occurred between the different filters, resulting in a bias. Inhomogeneous deposition on the filter could also cause a bias. The OC/EC analysis and ion analysis each take only part of the filter for analysis, and the total mass on the filter is normalized assuming that this mass is evenly distributed over the collection area.

Table 5-3. Secondary Organic Aerosol Precursors (VOCs) (Site C).

Substance	Average (lb/MMBtu)	Uncertainty (%)	95% Confidence Upper Bound (lb/MMBtu)
1,2,3 trimethylbenzene	1.7E-7	172	3.2E-7
1,2,3,4-tetramethylbenzene	1.1E-7	172	2.0E-7
1,2,3,5-tetramethylbenzene	1.8E-7	172	3.5E-7
1,2,4 trimethylbenzene	9.6E-7	193	2.2E-6
1,2,4,5-tetramethylbenzene	1.8E-7	172	3.5E-7
1,3,5 trimethylbenzene	1.1E-6	195	2.7E-6
1-decene	7.7E-8	172	1.5E-7
2-methyl Octane	7.5E-7	188	1.7E-6
2-propyltoluene	7.1E-7	155	1.5E-6
Decanal	9.2E-8	172	1.7E-7
Dodecene	2.3E-7	172	4.4E-7
Ethyl Benzene	1.4E-6	216	3.5E-6
iso-butylbenzene	1.6E-7	147	3.3E-7
m- & p-xylenes	3.4E-6	190	7.9E-6
m-ethyltoluene	5.7E-7	178	1.3E-6
m-isopropyltoluene	1.7E-7	172	3.7E-7
Methylstyrene	6.2E-8	172	1.2E-7
n-decane	1.9E-6	180	4.2E-6
n-dodecane	2.6E-6	179	5.9E-6
n-eicosane	2.2E-6	48	3.1E-6
n-heptadecene	7.7E-7	136	1.5E-6
n-hexadecene	1.3E-6	178	2.9E-6
n-nonadecane	4.5E-7	197	1.1E-6
n-nonane	4.3E-6	180	9.5E-6
n-octadecane	1.5E-6	141	3.0E-6
n-pentadecane	1.5E-6	134	3.0E-6
n-propylbenzene	3.2E-7	204	7.6E-7
n-tetradecane	1.8E-6	171	3.9E-6
n-tridecane	1.0E-6	162	2.2E-6
n-undecane	4.3E-6	195	1.0E-5
Nonanal	7.8E-7	42	1.0E-6
Nonene-1	3.7E-7	198	8.7E-7
o-ethyltoluene	1.2E-6	172	2.2E-6
o-xylene	1.5E-6	195	3.6E-6
Octanal	5.3E-8	69	8.0E-8
p-ethyltoluene	9.2E-7	195	2.2E-6
p-isopropyltoluene	1.7E-7	172	3.2E-7
sec-butylbenzene	1.2E-7	172	2.3E-7
Styrene	1.0E-6	180	2.2E-6
Trans-butylbenzene	1.8E-7	172	3.5E-7
undecene-1	5.5E-7	172	1.0E-6

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

Table 5-4. Secondary Particulate Precursors – NO_x and SO₂ (Site C).

Substance	Average (lb/MMBtu)	Uncertainty (%)	95% Confidence Upper Bound (lb/MMBtu)
SO ₂	2.4E-3	35	3.0E-3
NO _x	0.06	67	0.09

Table 5-5. Speciation Profile for Primary Emissions – Dilution Tunnel Results (Site C).

Substance	Average Mass Fraction (1) (%)	Uncertainty (%)	95% Confidence Upper Bound (%)
OC	87	125	163
EC	3.5	417	11
Si	2.3	113	4.2
Nitrate	1.6	94	2.7
Sulfate	1.5	n/a	n/a
Fe	1.2	117	2.1
Ca	0.72	144	1.4
Al	0.69	112	1.2
Cu	0.37	124	0.69
S*			
Na*			
K	0.30	161	0.63
Cl	0.15	434	0.49
Zn	0.13	269	0.36
P	0.08	337	0.21
Mn	0.07	327	0.22
Ti	0.06	642	0.26
Cr	0.04	n/a	n/a
Ni	0.02	344	0.05
Mg*			
Sr	0.01	n/a	n/a
Co	0.01	n/a	n/a
Total	100		

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

(1) Mass fraction is emission factor of species divided by emission factor of sum of species. Average speciated mass was greater than average total PM_{2.5} mass measured on the dilution tunnel filter.

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

Figure 5-1 shows the data presented in Table 5-5. The overwhelming majority of the mass (87 percent) is composed of organic carbon, with elemental carbon being the next most abundant constituent (3.5 percent). As stated before, the OC mass may be biased high due to adsorption of VOCs onto the filters. Compounds with all runs below detectable levels are not included in the figure. Sulfur, sodium, and magnesium were all measured at detectable levels, but are not included in the sum of species, and are therefore not included in the figure.

Organic Aerosols

Table 5-6 shows the organic aerosol speciation profile, expressed as a mass fraction. This mass fraction is determined by dividing the average emission factor of the emitted quantity by the average emission factor of total organic carbon, both in units of lb/MMBtu. The speciated organic carbon, measured as SVOCs, accounts for approximately 10 percent of the total organic carbon. The data from Table 5-6 are shown in Figure 5-2. As can be seen on the figure, the most abundant fraction of the speciated organic aerosol is bibenzene (1.5 percent), followed by 1,3+1,6+1,7-dimethylnaphthalene (0.9 percent).

Method 201A/202

Table 5-7 shows the speciation profile of the PM_{2.5} mass as measured by Method 201A/202 for the Standard Method results. Mass fraction is the ratio of the measured quantity to the total PM_{2.5} mass (filterable and condensible particulate). In this table, total condensible particulate has been subdivided into its respective organic and inorganic fractions for illustrative purposes. Inorganic condensible particulate has been further subdivided to show the amount of PM_{2.5} mass accounted for by sulfate.

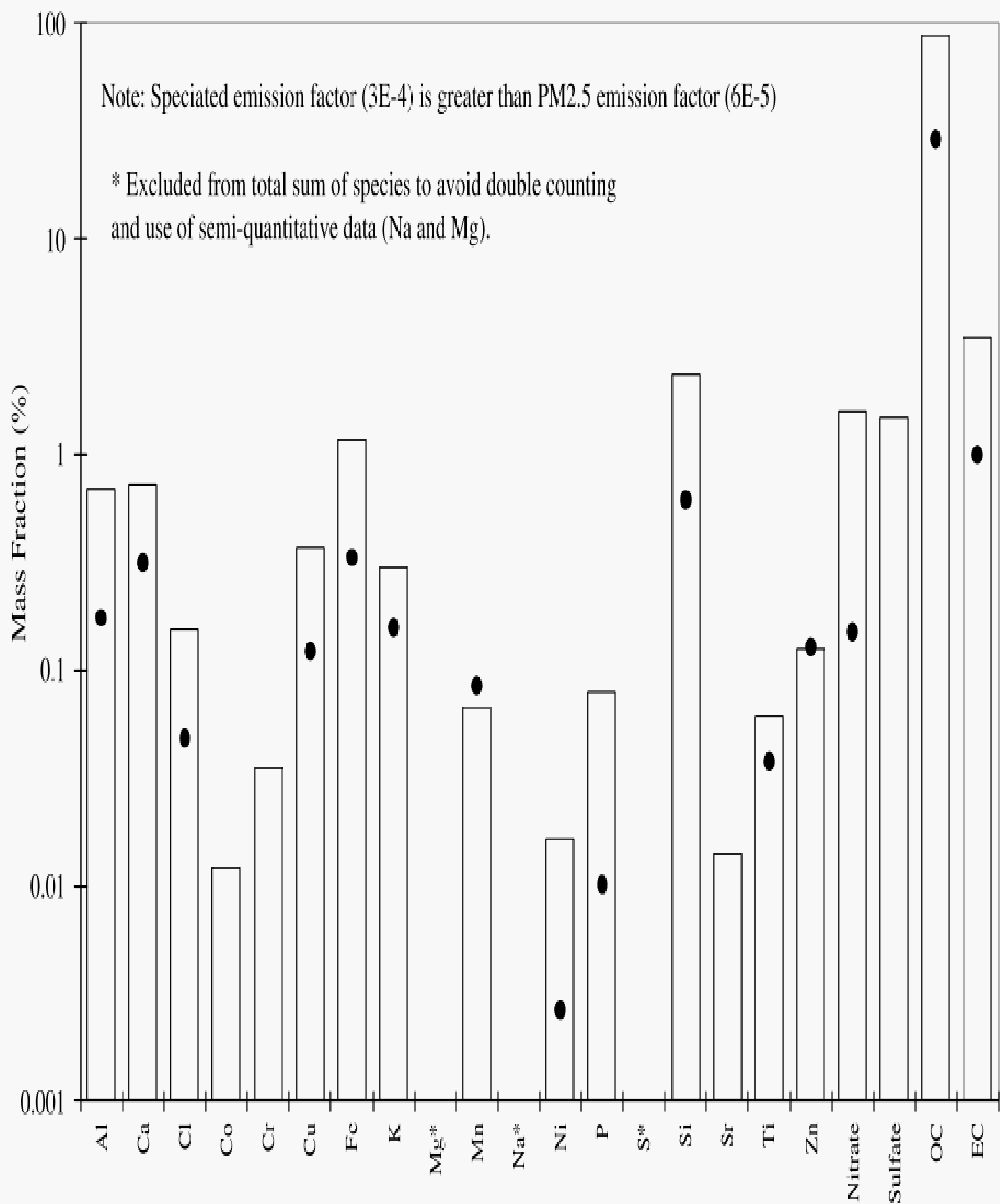


Figure 5-1. PM2.5 Speciation, as Measured by the Dilution Tunnel (Site C).

Table 5-6. Organic Aerosol Speciation Profile (Site C).

Substance	Average Mass Fraction (1) (%)	Uncertainty (%)	95% Confidence Upper Bound (%)
Bibenzene	1.03	234	2.68
Naphthalene	0.39	871	2.10
1,3+1,6+1,7-dimethylnaphthalene	0.34	404	1.28
1-methylnaphthalene	0.25	1196	1.74
2-methylnaphthalene	0.20	1149	1.34
2-methylphenanthrene	0.20	393	0.73
Phenanthrene	0.15	343	0.49
A-methylphenanthrene	0.15	357	0.50
2,3,5-I-trimethylnaphthalene	0.15	407	0.55
B-trimethylnaphthalene	0.12	399	0.45
1,4+1,5+2,3-dimethylnaphthalene	0.12	376	0.43
3-methylbiphenyl	0.11	1047	0.71
2,6+2,7-dimethylnaphthalene	0.11	392	0.41
E-trimethylnaphthalene	0.11	383	0.40
C-trimethylnaphthalene	0.10	393	0.37
J-trimethylnaphthalene	0.09	402	0.32
2-methylbiphenyl	0.08	280	0.24
9-fluorenone	0.08	261	0.23
C-dimethylphenanthrene	0.07	349	0.25
1,4,5-trimethylnaphthalene	0.07	1284	0.53
C-methylphenanthrene	0.07	1241	0.48
1+2-ethylnaphthalene	0.06	356	0.22
A-trimethylnaphthalene	0.06	1218	0.44
1,2-dimethylnaphthalene	0.06	420	0.24
4-methylbiphenyl	0.06	771	0.29
2,4,5-trimethylnaphthalene	0.06	1289	0.45
F-trimethylnaphthalene	0.06	328	0.19
Fluoranthene	0.06	213	0.14
Fluorene	0.05	357	0.18
Anthracene	0.05	1306	0.36
Pyrene	0.04	303	0.13
1,7-dimethylphenanthrene	0.04	361	0.14
Biphenyl	0.04	1074	0.23
D-dimethylphenanthrene	0.04	1037	0.22
1-methylphenanthrene	0.03	420	0.13
4-methylpyrene	0.03	251	0.08
A-dimethylphenanthrene	0.03	301	0.09
9-anthraldehyde	0.03	343	0.09
3,6-dimethylphenanthrene	0.03	318	0.09

Table 5-6. Organic Aerosol Speciation Profile (Site C) (continued).

Substance	Average Mass Fraction (1) (%)	Uncertainty (%)	95% Confidence Upper Bound (%)
1-ethyl-2-methylnaphthalene	0.03	413	0.10
B-methylpyrene/methylfluorene	0.02	n/a	n/a
1-methylpyrene	0.02	310	0.06
A-methylfluorene	0.02	286	0.06
E-dimethylphenanthrene	0.02	312	0.06
B-dimethylphenanthrene	0.02	n/a	n/a
Acenaphthene	0.02	905	0.09
Acenaphthylene	0.02	254	0.04
1,8-dimethylnaphthalene	0.02	336	0.05
Retene	0.01	398	0.05
1,2,8-trimethylnaphthalene	0.01	1250	0.09
2-ethyl-1-methylnaphthalene	0.01	918	0.06
Xanthone	0.009	368	0.03
Chrysene	0.007	175	0.02
D-methylpyrene/methylfluorene	0.006	267	0.02
Benzo(b+j+k)fluoranthene	0.006	126	0.01
C-methylpyrene/methylfluorene	0.005	n/a	n/a
Benz(a)anthracene	0.005	423	0.02
Benzo(c)phenanthrene	0.005	989	0.03
Benzo(e)pyrene	0.004	265	0.01
7-methylbenz(a)anthracene	0.004	n/a	n/a
B-methylphenanthrene	0.004	n/a	n/a
5+6-methylchrysene	0.002	777	0.01
Benzonaphthothiophene	0.002	617	0.01
A-methylpyrene	0.002	770	0.01
Perylene	0.001	n/a	n/a

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

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

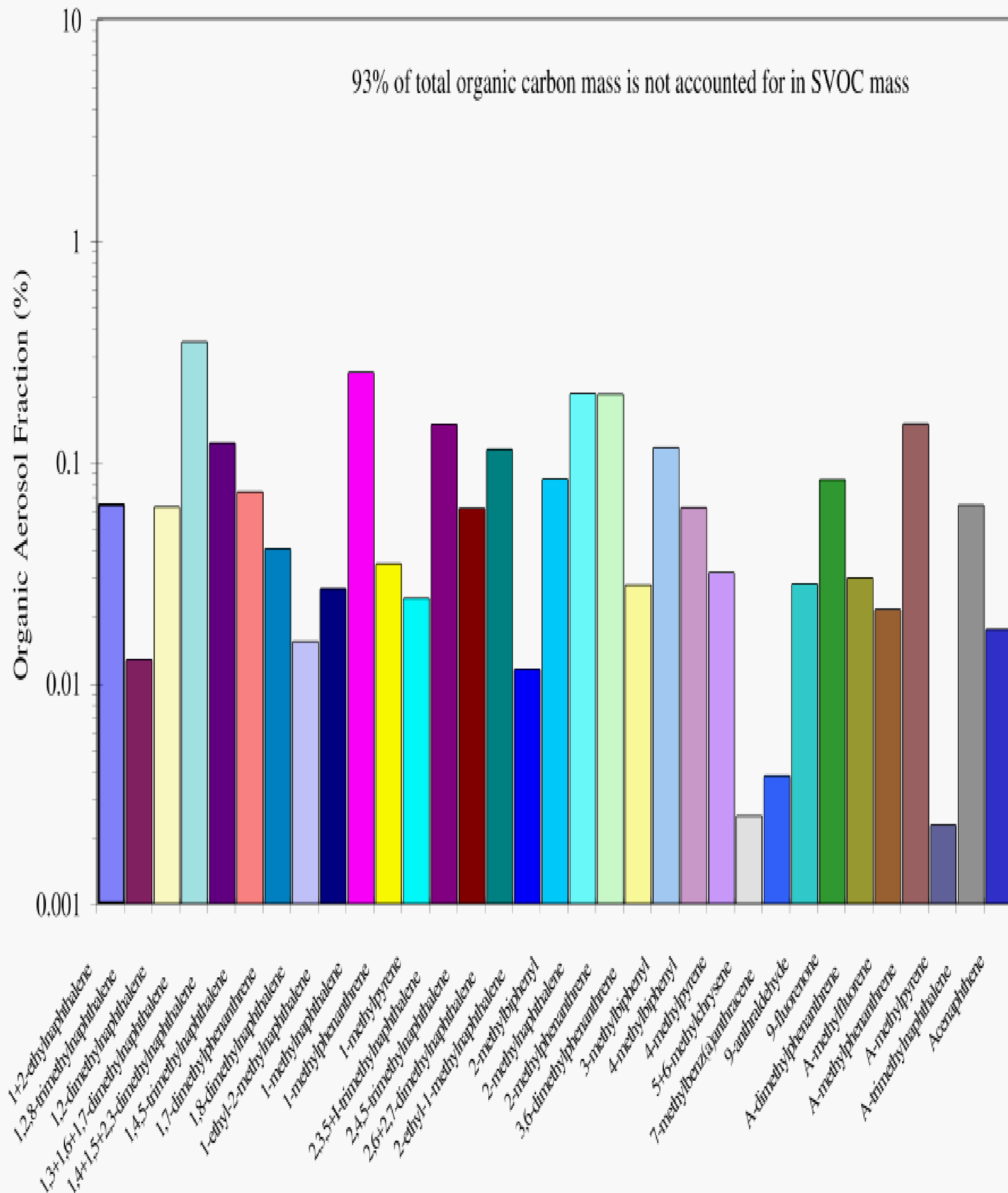


Figure 5-2. Organic Aerosol Speciation (Site C).

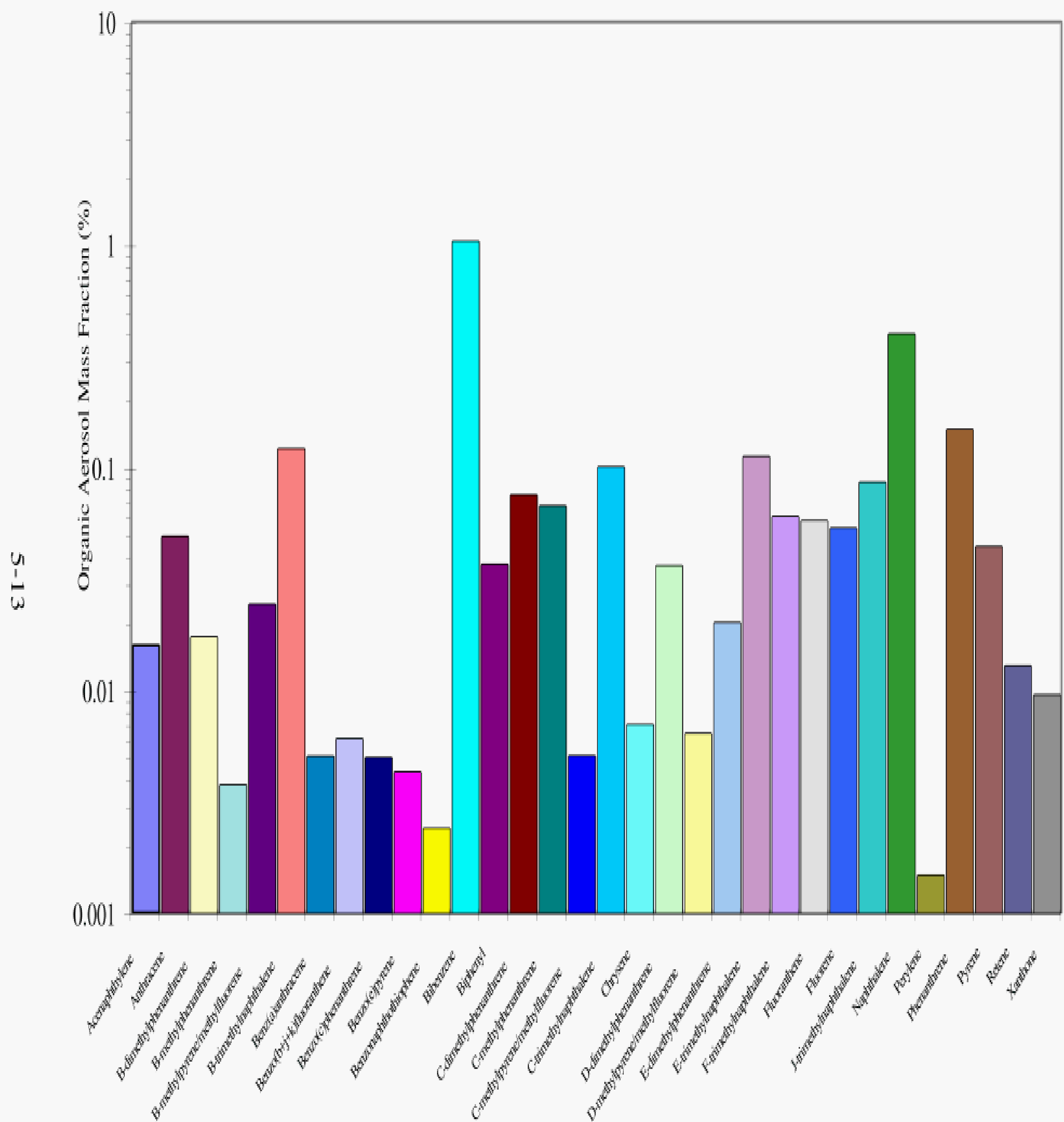


Figure 5-2. Organic Aerosol Speciation (Site C) (continued).

Table 5-7. Speciation Profile for PM2.5 Measured by Method 201A/202 (Site C).

Substance	Average Mass Fraction (1) (%)	Uncertainty (%)	95% Confidence Upper Bound (%)
Standard Method			
Filterable PM2.5	3.6	n/a	n/a
Total Condensible PM	96	259	266
Organic CPM	41	248	110
Inorganic CPM	43	249	117
- Sulfate (as SO ₄ ⁼)	15	239	39
Total	100		

(1) Mass fraction is percent of total PM2.5 (filterable and condensible).

The data from Table 5-7 are shown in Figure 5-3. As can be seen from the figure, nearly all of the PM2.5 mass comes from CPM (96 percent). The inorganic/organic CPM split is approximately equal, with slightly more mass accounted for in the inorganic fraction.

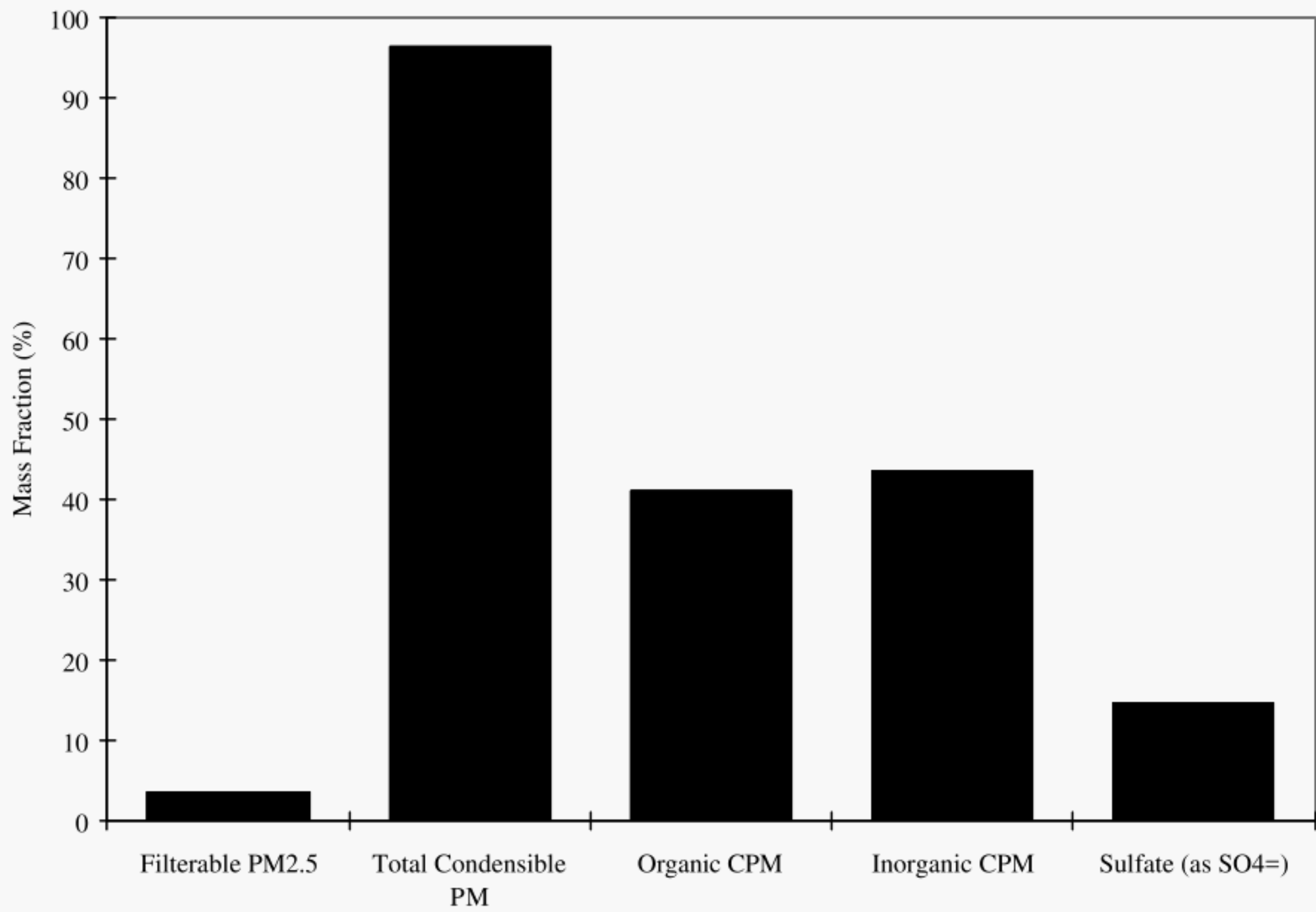


Figure 5-3. Method 201/202 PM2.5 Mass Speciation Profile (Site C).

Section 6

QUALITY ASSURANCE

SAMPLE STORAGE AND SHIPPING

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

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

Upon receipt of samples at the lab, those requiring refrigeration were stored at 4°C (nominal). Samples were stored and shipped in a manner to prevent breakage.

DILUTION TUNNEL FLOWS

Flow rates through the dilution tunnel sample collection media were determined by averaging the flow rates measured before testing commenced and after sampling was completed. The flow rates were measured by connecting a rotameter to each sampling media unit pre- and post-test and recording the flow; the rotameter was not in place during sampling. Results from the pre- and post-test flow checks are presented in Table 6-1. The Teflon[®] and quartz filter flow rates were equal for all runs. Pre- and post-test flow rates were generally consistent.

GRAVIMETRIC ANALYSIS

Dilution Tunnel Filters

Prior to testing, unused filters were stored for at least one month in a controlled environment, followed by one week of equilibration in the weighing environment, to achieve stable filter tare weights. New and used filters were equilibrated at 20 ±5°C and a relative humidity of 30 ±5 percent for a minimum of 24 hours prior to weighing. Weighing was performed on a Cahn 31 electro-microbalance with ±1 microgram sensitivity. The electrical charge on each filter was neutralized by exposure to a polonium source for 30 seconds prior to the filter being placed on the balance pan. The balance was calibrated with a 20 mg Class M weight and the tare was set

Table 6-1. Pre- and Post-Test Flow Checks for the Dilution Tunnel

Pre-test flow	Post-test flow	Average	% Difference
Teflon [®] /Quartz filter flow (scfh)			
42	42	42	0%
42	42	42	0%
42	42	42	0%
PUF/XAD (scfh)			
242	242	242	0%
242	242	242	0%
242	242	242	0%
Tenax A (scfh)			
110	115	113	-5%
110	115	113	-5%
110	110	110	0%
Tenax B (scfh)			
110	110	110	0%
110	130	120	-18%
110	110	110	0%

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 $\pm 5 \mu\text{g}$, the balance was recalibrated. If the difference exceeded $\pm 15 \mu\text{g}$, the balance was recalibrated and the previous 10 samples were reweighed. One hundred percent of initial weights and at least 30 percent of exposed weights were checked by an independent technician and samples were reweighed if these check-weights did not agree with the original weights within $\pm 0.015 \text{ mg}$. Pre- and post-weights, check weights and reweights (if required) were recorded on data sheets, and directly entered into a database via an RS232 connection.

In-Stack Filters

The balance was calibrated daily with two "S" type weights in the range of the media being weighed (5 and 10 g) and the tare was set prior to weighing each batch of filters. If the results of these performance tests had deviated by more than $\pm 1 \text{ mg}$, the balance would have been recalibrated. A recalibration was not required. If consecutive sample weights deviated by more than $\pm 0.5 \text{ mg}$, the sample was returned to the desiccator for at least 6 hours before reweighing. Pre- and post-weights, check weights, and reweights (if required) were recorded on data sheets. Table 6-2 presents the results of the methylene chloride, water and acetone rinse blanks. The acetone blank values were used to correct the EPA Method 201A particulate data.

Results of the filter blank weights are also presented in Table 6-2. All Method 201A in-stack filter weights were negative and treated as a zero in calculations. It is believed that the Viton o-rings lost weight due to heating in the stack, resulting in a negative bias.

Table 6-2. Filter and Reagent Blank Results.

Sample	Mass (mg)
Method 202 Water Recovery Blank	3.5
Method 202 Dichloromethane Recovery Blank	1.0
Method 201A Acetone Recovery Blank	0.6
Cyclone Filter Blank	ND (1)
Dilution Tunnel Filter Blank	ND (2)

1- Weight was negative.

2- Detection limit of balance = 0.001 mg.

An analysis of the acetone rinse blanks is presented in Table 6-3. The particulate mass detection limit was calculated as three times the standard deviation of the results of the field blank acetone rinses and the acetone recovery blank. The resulting detection limit of approximately 0.4 mg further indicates that the filterable particulate levels at the generator were near detection limits. Therefore, the filterable particulate data from Method 201A are presented in Section 5 for qualitative purposes only.

Table 6-3. Results from Acetone Blank Rinses.

Sample Fraction	Mass (mg)
PM10 cyclone catch rinse	0.39
PM2.5 cyclone catch rinse (2.5-10 μm)	0.49
<PM2.5 rinse (<2.5 μm)	0.33
Recovery Blank	0.6
Detection Limit (3*standard deviation)	0.4

ELEMENTAL (XRF) ANALYSIS

Three types of XRF standards were used for calibration, performance testing, and auditing: 1) vacuum-deposited thin-film elements and compounds (supplied by Micromatter, Deer Harbor, WA); 2) polymer films; and 3) NIST thin-glass films. The vacuum deposit standards cover the largest number of elements and were used as calibration standards. The polymer film and NIST standards were used as quality control standards. Standards from the National Institute of

Standards and Technology (NIST) are the definitive standard reference material, but are only available for the species Al, Ca, Co, Cu, Mn, and Si (SRM 1832) and Fe, Pb, K, Si, Ti, and Zn (SRM 1833). A separate Micromatter thin-film standard was used to calibrate the system for each element.

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

Results from the field blank are presented in Table 6-4. Only phosphorous, silicon and sodium were present at detectable levels. Concentrations in the field blank were at least an order of magnitude less than concentrations in the stack samples. The concentration of phosphorous in the field blank was within an order of magnitude of the ambient concentration.

Table 6-4. XRF Elemental Analysis Field Blank Results.

Element	mg/dscm
Phosphorous	1.2E-5
Silicon	1.9E-5
Sodium	8.1E-5

ORGANIC AND ELEMENTAL CARBON ANALYSIS

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

Known amounts of American Chemical Society (ACS) certified reagent-grade crystal sucrose and KHP were committed to TOR as a verification of the organic carbon fractions. Fifteen different standards were used for each calibration. Widely accepted primary standards for elemental and/or organic carbon are still lacking. Results of the TOR analysis of each filter were entered into the DRI database.

Results of the field blank are presented in Table 6-5. Only organic carbon was present above detection limits on the dilution tunnel and in-stack filter blanks. Organic carbon on the in-stack field blank filter is within a factor of two of the average stack-gas sample concentration. Organic carbon on the dilution tunnel field blank filter is more than an order of magnitude lower than the average stack-gas sample concentration.

Table 6-5. Organic and Elemental Carbon Field Blank Results.

	OC (mg/dscm)	EC (mg/dscm)
In-Stack Field Blank	3.5E-3	ND
Dilution Tunnel Field Blank	5.3E-3	ND

SULFATE, NITRATE, AND CHLORIDE ANALYSIS

The primary standard solutions containing NaCl, NaNO₃, and (Na)₂SO₄ were prepared with reagent grade salts that were dried in an oven at 105 °C for one hour and then brought to room temperature in a desiccator. These anhydrous salts were weighed to the nearest 0.10 mg on a routinely calibrated analytical balance under controlled temperature (approximately 20 °C) and relative humidity (±30 percent) conditions. These salts were diluted in precise volumes of DI water. Calibration standards were prepared at least once 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 µg/ml for each of the analysis species. Calibration curves were performed weekly. Chemical compounds were identified by matching the retention time of each peak in the unknown sample with the retention times of peaks in the chromatograms of the standards. A DI water blank was analyzed after every 20 samples and a calibration standard was analyzed after every 10 samples. These quality control checks verified the baseline and calibration, respectively. Environmental Research Associates (ERA, Arvada, CO) standards were used daily

as an independent quality assurance (QA) check. These standards (ERA Wastewater Nutrient and ERA Mineral WW) were traceable to NIST simulated rainwater standards. If the values obtained for these standards did not coincide within a pre-specified uncertainty level (typically three standard deviations of the baseline level or ± 5 percent), the samples between that standard and the previous calibration standards were reanalyzed.

After analysis, the printout for each sample in the batch was reviewed for the following: 1) proper operational settings; 2) correct peak shapes and integration windows; 3) peak overlaps; 4) correct background subtraction; and 5) quality control sample comparisons. When values for replicates differed by more than ± 10 percent or values for standards differed by more than ± 5 percent, samples before and after these quality control checks were designated for reanalysis in a subsequent batch. Individual samples with unusual peak shapes, background subtractions, or deviations from standard operating parameters were also designated for reanalysis.

All ions in the field blank were below detection limits.

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 pre-cleaned XAD-4 resin, and approximately 10 percent of the precleaned TIGF filters and PUF plugs were checked for purity by solvent extraction and GC/MS analysis of the extracts. The PUF plugs and XAD-4 resins were assembled into glass cartridges (10 g of XAD between two PUF plugs), wrapped in hexane-rinsed aluminum foil and stored in a clean freezer prior to shipment to the field.

Prior to extraction, the following deuterated internal standards were added to each filter-sorbent pair:

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

Calibration curves for the GC/MS/MID quantification were made for the molecular ion peaks of the PAH and all other compounds of interest using the corresponding deuterated species (or the deuterated species most closely matched in volatility and retention characteristics) as internal standards. NIST Standard Reference Material (SRM) 1647 (certified PAH), with the addition of deuterated internal standards and compounds not present in the SRM, was used to make calibration solutions. Three concentration levels for each analyte were employed, and each calibration solution was injected twice. After the three-level calibration was completed, a standard solution was injected to perform calibration checks. If deviation from the true value exceeded 20 percent, the system was recalibrated. The mass selective detector (MSD) was tuned daily for mass sensitivity using perfluorotributylamine.

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

Results from the field blank are presented in Table 6-6. Compounds below detection limits in the field blank are not included in the table. All compounds have an average sample concentration that is at least an order of magnitude greater than the field blank concentration.

Table 6-6. PUF/XAD Field Blank and Replicate Results (mg/dscm).

Compound	Field Blank (1)	MDL (1)
2,3,5-I-trimethylnaphthalene	1.7E-7	1.6E-7
2-methylbiphenyl	1.8E-5	8.4E-6
2-methylphenanthrene	1.3E-6	1.1E-7
4-methylbiphenyl	5.7E-6	1.0E-6
Anthracene	9.5E-7	0.0E+0
Benz(a)anthracene	5.5E-7	3.2E-7
E-trimethylnaphthalene	6.0E-7	5.3E-8
F-trimethylnaphthalene	4.3E-7	5.0E-8
Fluoranthene	5.0E-7	1.1E-7
Naphthalene	9.8E-5	5.1E-5
Phenanthrene	8.8E-7	4.2E-7
Pyrene	7.9E-7	2.1E-7

MDL- Method detection limit

1- Assumed sample volume of approximately 40 m³.

VOC ANALYSIS

Calibration curves were performed weekly. Volatile organic compounds were identified by matching the response factors of each unknown sample with the response factors of the standards. Tenax cartridges spiked with a mixture of paraffinic (in the C9-C20 range) and aromatic (C4, C5, and C6 benzenes) hydrocarbons were periodically analyzed by GC/FID to verify quantitative recovery from the cartridges. Three to five different concentrations of the HC standard and one zero standard were injected, and the response factors obtained. If the percent difference of the response factor from the mean was more than 5 percent, the response factors were corrected before proceeding with the analysis.

All compounds in the Tenax field blank were below detection limits.

CEMS ANALYSIS

The instruments generally were calibrated at a minimum at the beginning, middle, and end of the test day, with more frequent calibration and zero drift checks if necessary. Test results were corrected for any drift in excess of the method specifications (generally ± 3 percent).

INORGANIC RESIDUE ANALYSIS

A reagent blank was analyzed in the same manner as the field samples, as described in Section 3.

The results are presented in Table 6-7.

Table 6-7. Method 202 Water Reagent Blank Results (mg/dscm).

Compound	Pre-202	Std	Alt
Fluoride	ND	3.38E-3	ND
Bromide	ND	ND	ND
Chloride	ND	1.69E-2	5.25E-2
Nitrate (as N)	ND	1.06E-2	ND
ortho-phosphate (as P)	ND	ND	ND
Sulfate (as SO ₄ ⁼)	ND	ND	2.63E-2
Ammonium (as NH ₄ ⁺)	ND	< 3.13E-3	< 3.13E-3
Al	< 4.50E-2	< 1.88E-3	< 1.88E-3
Ba	5.49E-3	< 6.25E-5	< 6.25E-5
Be	< 1.41E-3	< 6.25E-5	< 6.25E-5
Cd	< 4.64E-3	< 2.06E-4	< 2.06E-4
Ca	< 2.81E-1	< 1.25E-2	1.25E-2
Cr	< 5.63E-3	< 2.50E-4	< 2.50E-4
Co	< 1.41E-2	< 6.25E-4	< 6.25E-4
Cu	< 7.04E-3	< 3.13E-4	7.51E-4
Fe	< 1.41E-2	< 6.25E-4	6.25E-4
Pb	< 2.81E-2	< 1.25E-3	< 1.25E-3
Mg	< 7.04E-2	5.38E-3	< 3.13E-3
Mn	< 8.30E-3	< 3.75E-4	< 3.75E-4
Mo	< 1.41E-2	< 6.25E-4	< 6.25E-4
Ni	< 1.41E-2	< 6.25E-4	< 6.25E-4
P	< 8.30E-2	< 3.75E-3	< 3.75E-3
K	< 1.39E+0	< 6.25E-2	< 6.25E-2
Ag	< 1.41E-2	< 6.25E-4	< 6.25E-4
Na	3.59E-1	5.57E-2	7.51E-2
Sr	< 1.41E-3	1.56E-4	1.56E-4
Tl	< 8.30E-2	< 3.75E-3	< 3.75E-3
V	< 7.04E-3	< 3.13E-4	< 3.13E-4
Z	< 7.04E-3	1.13E-3	1.88E-3

< - one or two runs are below limit of quantitation (Detection limit x 3.33)

ND - not detected

Pre-202 - Analysis done on aliquot of impinger solution before analysis by M202

Std - Analysis done per Method 202

Alt - Modified Method 202: no organic extraction or ammonium hydroxide titration performed

Section 7

DISCUSSION AND FINDINGS

PM 2.5 emissions from a natural gas-fired steam generator measured by the dilution tunnel technique were found to be more than 20 times less than that measured by conventional in-stack methods (Methods 201A/202). In fact, PM 2.5 concentrations found in the stack emissions were approximately equal to those measured concurrently in nearby ambient air.

Dilution tunnel sampling is designed to capture filterable matter and any aerosols that condense under simulated stack plume conditions. Stack gas is cooled to ambient temperature, typically 70-88°F in these tests, and samples are then collected from the diluted air mass. Conventional in-stack methods are designed to collect particles that are filterable at the stack temperature, along with capturing those likely to condense in ambient air, by collecting them in a series of aqueous impingers placed in an ice bath. The gas temperature leaving the impingers is typically 55-65°F; thus, both systems cool the sample gas to similar final temperatures. However, the in-stack methods cool the sample rapidly without dilution by quenching the gas sample in water maintained at near freezing temperature, while the dilution tunnel cooled the sample more slowly by mixing it with ambient air. Since aerosol condensation mechanisms depend on temperature, concentration, residence time, and other factors, it is not surprising that the results of the two methods differ. However, mechanistic variations alone cannot account for the magnitude of the difference observed in these tests.

As shown in Table 5-1, filterable PM 2.5 measured by the in-stack method (7.7 E-5 lb/MMBtu) agrees quite well with the dilution tunnel value of 5.6 E-5 lb/MMBtu . In fact, 96% of the mass found by Method 201A/202 was contained in the condensible fraction collected in the impingers. This is similar to what was found in earlier tests on gas-fired units (England et al., 2000). A review of those data led us to suspect the validity of the conventionally obtained data on condensibles, and to initiate a more extensive analysis of this fraction in this study than that prescribed by Method 202. Most of the inorganic CPM mass appears to be composed of sulfate, sodium, and chloride (Figure 7-1), with about 23% of unknown composition. The large sulfate

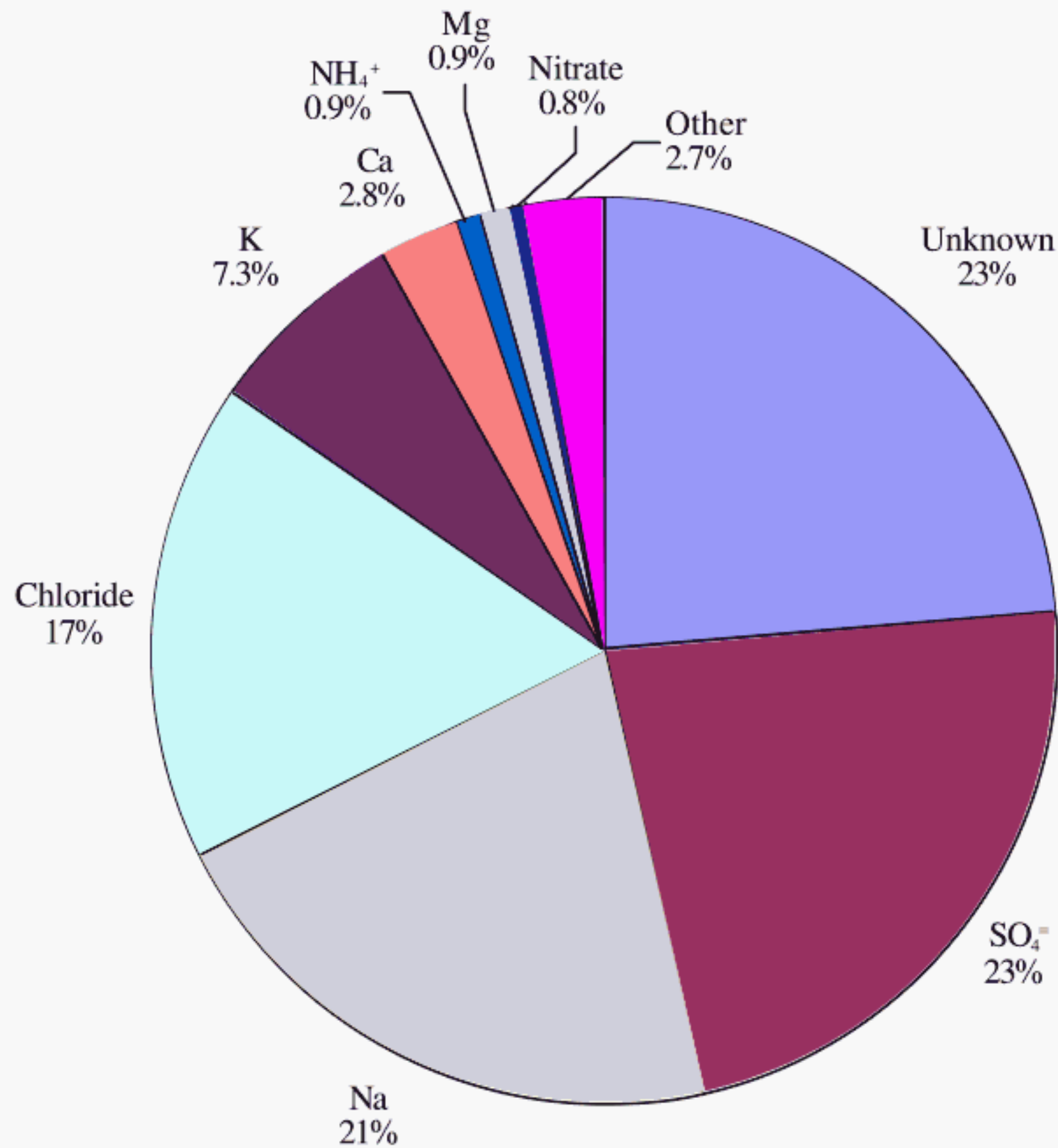


Figure 7-1. Inorganic CPM Residue Speciation Results.

content is unexpected since the sulfur content of the fuel gas was very low (< 1 ppm H₂S), and SO₂ stack emissions averaged over the three days testing were only about 1 ppm. The extensive instrumental analysis (discussed in Section 4) of the impinger solutions does not find any significant levels of either metals or organic compounds. Table 7-1 presents a comparison of the sulfate measurements, expressed as sulfate ion in mg/dscm.

Table 7-1. Comparison of Sulfate Measurements (mg/dscm).

	Run 1	Run 2	Run 3	Average
Impinger aliquot (M202)	1.25	1.52	1.70	1.49
Method 202 residue	0.11	0.29	0.29	0.23
Mod. Method 202 residue	1.06	1.60	1.58	1.41
Dilution tunnel	0.006	ND	ND	0.01
Ambient (1)	0.004	--	--	0.004
SO ₂ by Method 6 (as SO ₄ ²⁻)	3.33	3.88	3.06	3.42
S in fuel (as SO ₄ ²⁻)	1.28	1.26	1.27	1.27

(1) One ambient sample taken on separate day.

The levels in the impinger aliquot and the modified Method 202 residue (Alternative Procedure as described in Section 3) agree very well with each other and account for approximately one-third to one-half of the SO₂ (as SO₄²⁻) measured by Method 6; the sulfate measured in the Standard Method 202 residue are much lower, accounting for approximately 7 percent of the SO₂ (as SO₄²⁻) measured by Method 6. Compared to the measured SO₂ value, the sulfate levels measured by the dilution tunnel account for approximately 0.2 percent of the SO₂ in the flue gas and are on the order of those measured in the ambient sample.

The formation of artifact sulfate caused by SO₂ absorption in the aqueous solutions appears likely. Both SO₂ and oxygen are soluble in water and the dissolved H₂SO₃ can slowly oxidize to sulfate. This is implicitly recognized by Method 202 which recommends purging the impingers with nitrogen (air is also acceptable) to minimize this bias. Method 202 also provides the option of omitting the post test purge if the pH of the impingers is above 4.5, and while the pH of the impingers met this criterion in our test, we performed the nitrogen purge anyway. However, earlier studies of systems having SO₂ levels of approximately 2000 ppm show that these artifacts occur in spite of post-test purging (Filadelfia and McDaniel, 1996).

In the absence of any documented reports to evaluate artifact formation at low SO₂ concentrations, a laboratory scale study was conducted evaluating potential bias at these concentrations (details in Appendix A). The experiments passed simulated combustion gas containing representative amounts of O₂, CO₂, N₂, NO_x, and SO₂ through Method 202 impinger trains. No condensable substances were added. Tests were performed both with and without

post-test nitrogen purges for 1-hour and 6-hour sampling runs for mixtures containing 0, 1, and 10 ppm SO₂.

Significant amounts of sulfate, proportional to the SO₂ concentration in the gas, were found to be present in impingers that had not been purged. However, while the post-test purge definitely reduced the sulfate concentrations, it did not eliminate artifact formation. Purging was less efficient for the 6-hour runs relative to the 1-hour runs, indicating that most of the SO₂ oxidation occurs within this period. This clearly shows that the sulfate, and hence most of the condensible particulate collected by Method 202 in our field test results, comes from this mechanism of artifact sulfate formation from dissolved SO₂.

While the procedures of Method 202 consistently found measured amounts of organic condensibles present, the fact that we were unable to detect any organics in these solutions using instrumental analysis leads us to believe that these are also artifacts. The absence of any blank controls in this method, along with the possibility of contamination during the complex handling procedures, also supports this.

Recently Corio and Sherwell (2000) reviewed emissions data collected from fossil fuel-fired units by Method 201A/202 and raised the question of artifact formation. Table 7-2 presents some of their data (Lakewood Cogeneration and Kamite Milford units) along with data collected by the API PM 2.5 program for refinery gas-fired sources (Sites A, B, and C). These data compare results from the filterable and condensible particulate fractions, along with the composition of CPM, for a natural gas-fired boiler and several natural gas-fired turbines.

As can be seen in Table 7-2, the CPM data from Site C presented in this report are comparable to data collected at other gas-fired combustion units. However, the filterable fraction is at the low end of the range of values.

Table 7-2. Comparison of Data from Corio and Sherwell (2000) and API PM2.5 Program.

Source	Unit Type	Filterable PM		Condensible PM		Makeup of CPM	
		lb/MMBtu	% of Total PM10	lb/MMBtu	% of Total PM10	Inorganic Fraction (% of Total CPM)	Organic Fraction (% of Total CPM)
Lakewood Cogeneration	Natural Gas-fired Boiler	0.0019	46	0.0022	54	0.0015 (66)	0.00076 (34)
Lakewood Cogeneration - Unit #1	Natural Gas-fired Turbine	0.00021	14	0.0012	86	0.0010 (81)	0.00023 (19)
Lakewood Cogeneration - Unit #2	Natural Gas-fired Turbine	0.00052	33	0.0011	67	0.00084 (78)	0.00024 (22)
Kamine Milford ¹	Natural Gas-fired Turbine	0.0132	56	0.0105	44	0.0045 (43)	0.0060 (57)
Kamine Milford ²	Natural Gas-fired Turbine	0.0015	12	0.0112	88	0.0067 (60)	0.0045 (40)
Kamine Milford ³	Natural Gas-fired Turbine	0.0012	10	0.0107	90	0.0079 (74)	0.0028 (26)
Kamine Milford ⁴	Natural Gas-fired Turbine	0.0014	12	0.0100	88	0.0066 (66)	0.0034 (34)
Site A	Refinery Gas-fired Boiler	0.00016	2	0.0097	98	0.0091 (94)	0.00064 (6)
Site B	Refinery Gas-fired Process Heater	0.00064	12	0.0046	88	0.0048 (97)	0.00024 (3)
Site C	Natural Gas-fired Steam Generator	0.00008	6	0.0012	94	0.00052 (44) ⁵	0.00048 (41) ⁵

¹ Steam injection (SI) on, waste heat recovery boiler (WHRB) off.

² SI off, WHRB off.

³ SI on, WHRB on.

⁴ SI off, WHRB on.

⁵ Remaining CPM mass accounted for by back-half filter and was not characterized.

The particulate emission factors obtained using the Method 201A/202 trains are in good agreement with those found in the EPA's AP-42 emission factor database (EPA, 1998) for natural gas-fired external combustion devices (Table 7-3). Since the EPA results were obtained using the same method, a similar bias is likely in those data. While the condensible fraction is somewhat higher for this test (Site C) than that reported in AP-42 (94% vs. the 75% in AP-42), this could be due to problems encountered with the negative bias found in the filterable particulate measurements. Nevertheless, the semi-quantitative agreement of our results with those presented in the EPA database provides additional confidence in the validity of the results found here.

Table 7-3. Comparison of EPA AP-42 Database and API PM2.5 Program Data.

Source	Unit Type	Total PM10 lb/MMBtu	Filterable PM		Condensible PM	
			lb/MMBtu	% of Total PM10	lb/MMBtu	% of Total PM10
AP-42	Natural Gas Combustion	0.0075	0.0019	25	0.0056	75
Site A	Refinery Gas-fired Boiler	0.0099	0.00016	2	0.0097	98
Site B	Refinery Gas-fired Process Heater	0.0052	0.00064	12	0.0046	88
Site C	Natural Gas-fired Steam Generator	0.0013	0.00008	6	0.0012	94

These filterable PM results show that traditional source testing methods such as EPA Method 202 probably overestimate particulate mass emissions by erroneously determining high levels of condensible particulate sulfate. In addition, this method may also overestimate the condensible organic fraction. For the filterable mass collected, all filter weights were negative, most likely due to weight loss from the Viton o-rings weighed along with the filters. This modified weighing procedure is described in Section 3, and was developed to avoid negative biases like those encountered during the tests. These low weights indicate that the actual mass collected on these filters was at, or below, the practical limits of the method as practiced in these tests. Because dilution tunnels provide conditions that more closely simulate true atmospheric condensation conditions, as compared to impinger condensation, results obtained by this technique are more representative of the actual particulate emissions from gas-fired combustion sources such as this boiler.

POTENTIAL EMISSIONS MARKER SPECIES

The results obtained using the dilution tunnel are believed to provide the best representation of the chemical species present in the stack gas emissions. Ions, carbon, and other elements were detected in both stack and ambient air samples. A comparison of the observed concentrations of these species in ambient and stack samples can provide an indication of which species are considered good markers of natural gas combustion for this source.

Cr, Mg, Mn, and S concentrations are higher in the ambient air sample than for the in-stack sample (Figure 7-2), therefore, it is questionable whether these species originate from the combustion process. As, Br, Pb, Rb, Se, V, Zr, and Cl, were detected in ambient air but not in stack emissions (n.b., the detection levels for in-stack samples are approximately 6 times higher than those for ambient air samples). Other species cannot reliably be distinguished because their in-stack concentrations are within a factor of ten from the minimum method detection limits (Figure 7-3); these include: Al, Cl, Co, Cr, K, Mn, Ni, P, S, Sr, Ti, sulfate, nitrate, and EC. The average concentrations of all other species except OC are within a factor of ten of their respective ambient air concentrations. Subtraction of the ambient from in-stack concentrations and ignoring species found near detection limits provides an indication of which species can be considered to be emissions markers. The resulting emissions profile (Figure 7-4) suggests that these are OC, Si, and Fe.

The uncertainty of several of these values is large, as reflected in the high standard deviations, casting doubt on any of the species being definitively used as an emissions marker. The sum of the species shown in Figure 7-4 comprises 1300% of the PM 2.5 mass; this is most likely due to enrichment of OC on the filters from the volatile organics present in the stack gas. Without inclusion of OC, the remaining compounds account for 35% of the PM 2.5 mass. Other compounds were present at lower levels, but the low concentrations and high or unknown standard deviations associated with these suggest that they may not be reliable markers.

Another potentially useful marker for source emissions is the organic emissions profile. All of the SVOCs detected were present at low concentrations. Most SVOCs measured by the dilution tunnel, and present at detectable levels, were found at concentrations 10 times greater than ambient levels. Total SVOCs accounts for approximately 10% of the OC measured by the dilution tunnel indicating the presence of unspciated organics. This large difference is at least partly due to the difference in analytical methods since the TOR method defines OC somewhat arbitrarily, as well as by the presence of organics that are not quantifiable by the methods used in this study.

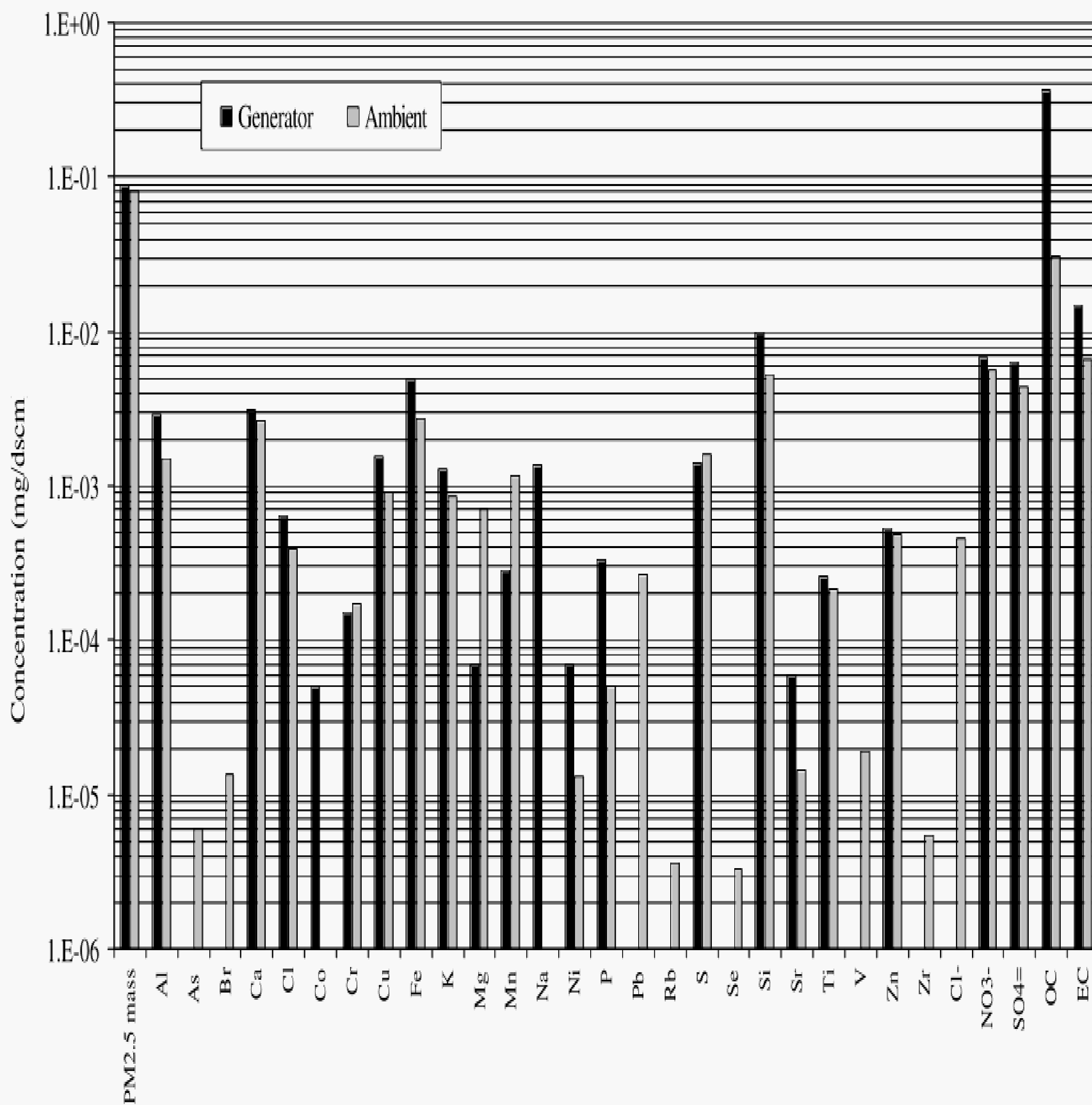


Figure 7-2. Mass Speciation for Dilution Tunnel Ambient and Stack Samples (Site C).

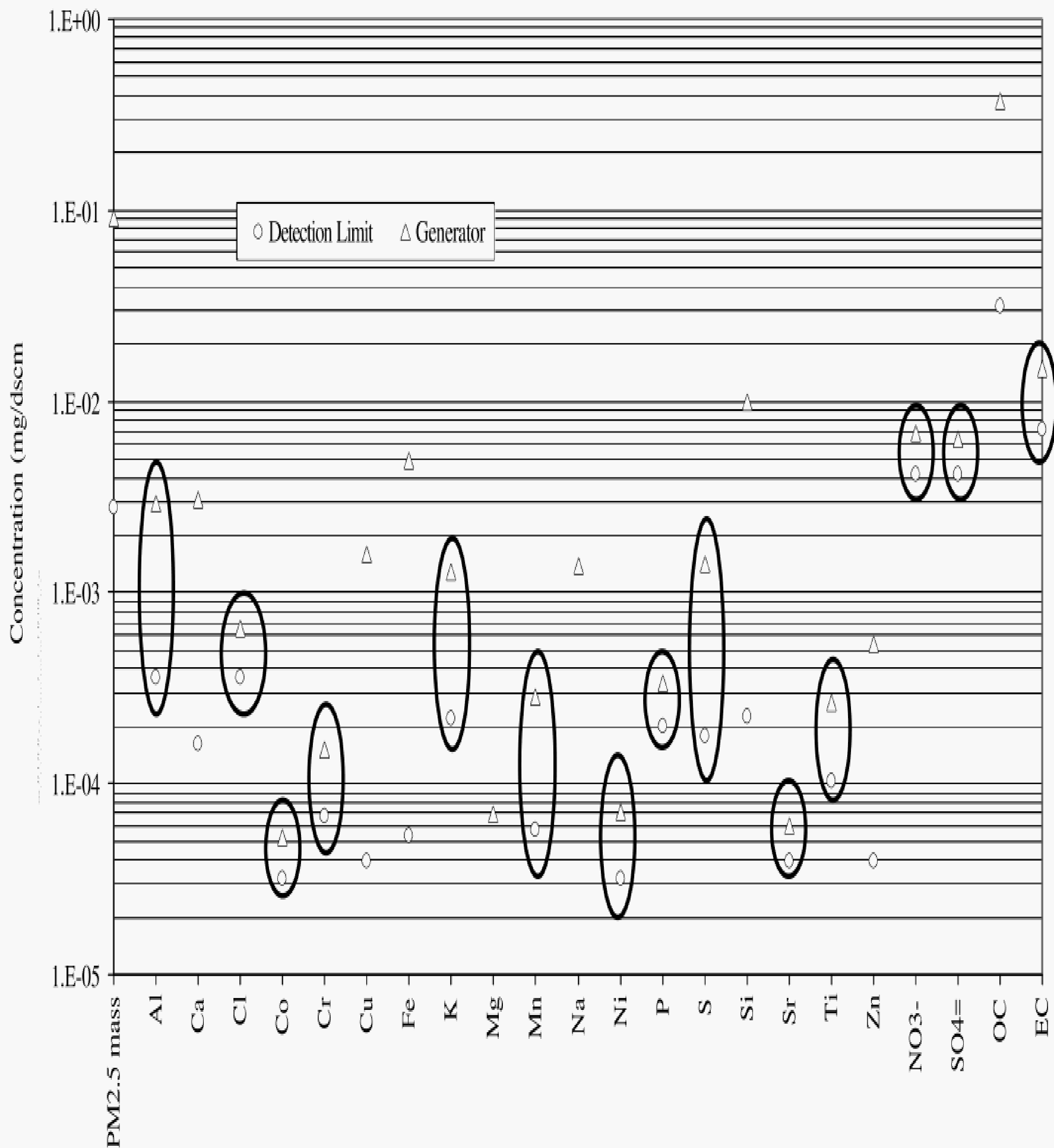


Figure 7-3. Comparison of Average Sample Concentration and Detection Limits (Site C).

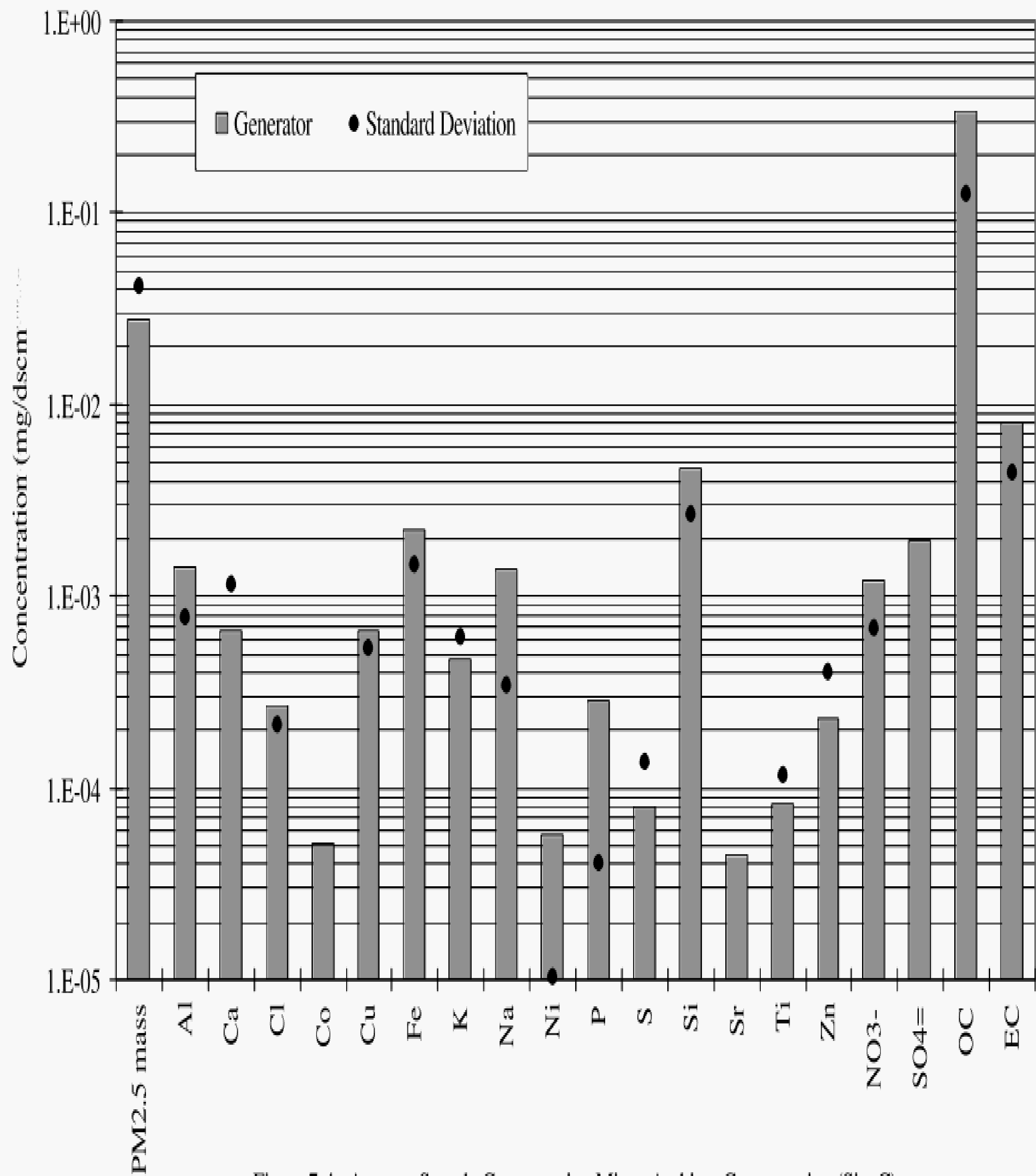


Figure 7-4. Average Sample Concentration Minus Ambient Concentration (Site C).

SVOC measurements were also planned for the in-stack filters in order to estimate the particle-bound SVOCs while using the dilution tunnel data to measure the condensed and gaseous fraction. However, the total OC levels were so low that it was decided that SVOCs would be present below detection limits and not provide meaningful results.

SVOC and OC emissions found for the steam generator were about an order of magnitude higher than those found at the refinery gas-fired process heater (Site B) studied earlier in the API PM_{2.5} project (Table 7-4). VOC emissions were within an order of magnitude of the refinery gas-fired boiler, but an order of magnitude less than those from the refinery gas-fired process heater.

Table 7-4. Average Organic Aerosol Emission Factor Comparison (lb/MMBtu).

Source	Unit Type	Organic Carbon	Elemental Carbon	Total Carbon	Sum of All SVOCs	Sum of All VOCs
Site A	Refinery Gas-fired Boiler	1.5E-4	9.4E-5	2.5E-4	4.1E-6	1.6E-4
Site B	Refinery Gas-fired Process Heater	2.8E-5	1.9E-5	3.4E-5	6.6E-7	4.0E-4
Site C	Natural Gas-fired Steam Generator	2.3E-4	9.2E-6	2.4E-4	1.5E-5	4.1E-5

Elevated levels of organic compounds in the stack samples as compared to levels detected in the blank and the ambient air indicate that potential marker species are more likely to be found within the volatile and semivolatile organic compounds. For the steam generator, almost all SVOCs were at least 10 times greater than levels in the ambient air, and none were within 10 times the levels in the field blank. In particular, 1,3+1,6+1,7-dimethylnaphthalene, 1-methylnaphthalene, and bibenzene were present at elevated concentrations relative to the other SVOCs, and might be potential marker species. However, motor vehicles and wood smoke are also predominant sources of dimethylnaphthalenes and methylnaphthalenes; previous ambient air studies done in the general geographic area of Site C indicate that vegetative biomass burning was a significant contributor to ambient PM levels (Chow and Watson, 1998). Because the ambient air was only sampled on one day, it is possible that elevated levels of these compounds were present in the ambient air during source sampling that were not present when the ambient

sample was taken. In addition, the relative concentrations of these compounds may not be unique enough to clearly distinguish this source from other external combustion sources.

Volatile organic species found at levels significantly different to the ambient air include n-nonane and n-undecane, which may be potential marker species. More comparison to existing speciation profiles is necessary to gauge the uniqueness of the profile produced by this test. In addition, further testing of similar sources is recommended to provide a more robust basis for the emission factors and speciation profiles described herein.

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