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CRITICAL REVIEW OF SOURCE SAMPLING AND ANALYSIS METHODOLOGIES FOR CHARACTERIZING ORGANIC AEROSOL AND FINE PARTICULATE SOURCE EMISSION PROFILES

Health and Environmental Affairs Department Publication Number 344 June 1998





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Critical Review of Source Sampling and Analysis Methodologies for Characterizing Organic Aerosol and Fine Particulate Source Emission Profiles

Health and Environmental Affairs Department

API PUBLICATION NUMBER 344

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ACRONYMS

μm	micrometer (micron)
2-NF	2-Nitrofluoranthene
AAS	atomic adsorption spectrometry
AC	automated chromatography
ΔΡΙ	American Petroleum Institute
ASME	American Society of Mechanical Engineers
ASIVIL	heiling point
b.p.	boung point
BaP	benzolajpyrene
C	centigrade
$C_{15}H_{32}$	n-pentadecane
C,H.	propane
CÅ	California
CaCO.	calcium carbonate
Caltech	California Institute of Technology
CADD	California Air Pesources Board
CARD	Camonia An Resources Board
	catalylic cracking unit
Cl_2	chlorine (molecular)
cm	centimeter
CO	carbon monoxide
CO ₂	carbon dioxide
D.	50 percent cutoff diameter
DHS	Department of Health Services
DNDU	2 4 dipitrophenylhydrazine
	Decert Research Institute
	des standard oubic motor
ascm	ary standard cubic meter
EASA	electrical aerosol size analyzer
EC	elemental carbon
ECD	electron capture detector
EER	Energy and Environmental Research Corporation
EPA	Environmental Protection Agency
ESP	electrostatic precipitator
F	Fahrenheit
FCCU	fluidized catalytic cracking unit
FID	flame ionization detector
	fast
	four transform infrared spectroscopy
FIIK	Tourier transform initiated spectroscopy
g-cm	grams per cubic centimeter
GC/MS	mass spectrometric detector
GC	gas chromatography
H ₂ SO ₄	sulfuric acid
HĒPA	high efficiency particulate air
HEST	high efficiency sampling train
Ho	mercury
hivol	bigh volume
	nitrous acid
	nitulous acid
HNO ₃	
HO ₂	nyaroperoxyi radicai
HPLC	high performance liquid chromatography
HRSG	heat recovery steam generator
IC	ion chromatography
IC engine	internal combustion engine
ICP	inductively coupled plasma
x~1	manan

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ΓΝΔΔ	instrumental neutron activation analysis
K CO	notassium carbonate
$\mathbf{K}_2 \subset \mathbf{U}_3$	liquid chromatography
	liters per minute
ipin ma	miliaram
ing MaCO	minigram momesium corbonate
	magnesium carbonate
MOUDI	microomice uniform deposit impactor
MS No CO	mass spectrometry
Na_2CO_3	socium carbonate
NAAQS	national ambient air quality standards
NaCl	sodium chioride
NaNO ₃	sodium nitrate
NaOH	sodium hydroxide
Ncm	normal cubic meter (O°C)
NDIR	non-dispersive infrared
NEA	Nuclear Environmental Analysis, Inc.
NF	nitrofluoranthene
ng	nanogram
NH,	ammonia
(NH ₄) ₂ SO ₄	ammonium sulfate
NH.HSO.	ammonium bisulfate
NH.NO,	ammonium nitrate
NMHC	non-methane hydrocarbons
NO	nitric oxide
NO.	nitrogen dioxide
NO.	nitrate (ion)
NO ³	oxides of nitrogen
NP	nitronviene
	ozone
ů,	organic carbon
OH OH	hydroxyl (radical)
DAH DAH	polycyclic aromatic hydrocarbons
DAV	polycyclic aromatic ketones
PAN	polycyclic alomatic Actorics
	polycyclic prometic quinones
PAQ	polycyclic alomatic quintines
PLD	polycinormated orphenyls
PIAC	piolon muleeu A-ray emission
	particulate matter equal to or smaller then 10 microns in diameter
PM10	particulate matter equal to or smaller than 10 microns in diameter
PM2.5	particulate matter equal to or smaller than 2.5 microns in diameter
POM	polycyclic organic matter
ppbv	parts per billion (volume)
PSDS	plume simulation dilution sampler
PSVOC	particulate/semi-volatile organic compound sampler
PUF	polyurethane foam
PVC	poly vinyl chloride
RADS	reduced artifact dilution sampler
Re	Reynolds number
ROG	reactive organic gases
SCAQMD	South Coast Air Quality Management District
SCAÒS	Southern California Air Quality Study
SCR	selective catalytic NOx reduction
sec	second
E 4 1	

SFS	sequential filter samplers
SO,	sulfur dioxide
SO ₃	sulfur trioxide
SoČAB	South Coast Air Basin
SOx	oxides of sulfur
SRI	Southern Research Institute
Т	thermal
TA	thermal absorption
TCE	trichloroethylene
TEA	triethanolamine
TMO	thermal manganese oxidation
TOR	thermal/optical reflectance
TOT	thermal/optical transmission
TSP	total suspended particulate
URG	University Research Glassware
UV	ultraviolet
VOC	volatile organic compounds
v/v	volume per volume
WSPA	Western States Petroleum Association
XRF	X-ray fluorescence
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EXECUTIVE SUMMARY

This report presents a critical review of sampling and analysis techniques for characterizing stationary source emissions of organic aerosols, fine particulate matter, and their precursors. This information is intended for use in designing future measurement programs for characterizing emissions from stationary sources which contribute to fine particle concentrations in the atmosphere. The review is based on relevant literature and discussions with technical/scientific experts in academia, industry and the regulatory community. The benefits and drawbacks of various measurement approaches are discussed, and a recommended approach for combustion sources is presented.

BACKGROUND

The recent change in the National Ambient Air Quality Standards (NAAQS) for particulate matter (PM) includes new annual and 24-hour standards for particles 2.5 µm or less in diameter, referred to collectively as PM2.5. The geologic component of PM2.5 is typically 10 percent or less; the balance is typically sulfates, nitrates and carbon (e.g., sulfuric acid, ammonium bisulfate, ammonium nitrate, and organic and elemental carbon). Organic compounds are important components of particulate matter and most of the particulate organic carbon is believed to reside in the fine particle fraction. For example, in an early study of the Los Angeles area, organic compounds constituted approximately 30 percent of the fine particle mass.

Particulate matter may be either directly emitted into the atmosphere (primary particulate) or formed there by chemical reactions and physical transformations (secondary particulate). The majority of primary particulate emissions from combustion are found in the PM2.5 or smaller size range, especially with clean burning fuels such as gas. Sulfates and nitrates are the most common secondary particles, although organic carbon also can result from reaction of volatile organic compounds. The gaseous precursors of most particulate sulfates and nitrates are sulfur dioxide, sulfur trioxide, and oxides of nitrogen. Secondary organic aerosol formation mechanisms are not well understood due to the multitude of precursors involved and the rates of formation which are heavily dependent on meteorological variables and the concentrations of other pollutants. It is believed, however, that atmospheric transformations leading to the formation of secondary aerosol from gas-phase primary organic emissions may be significant in some areas, particularly during the summertime. The chemical composition of PM2.5 strongly suggests combustion devices as the principal source in urban areas.

PETROLEUM INDUSTRY COMBUSTION SOURCES

Petroleum industry combustion devices likely are minor sources of carbonaceous aerosols in ambient fine particulate matter. An estimate of fine carbonaceous aerosol emissions from major sources in the Los Angeles area based on 1982 data showed that emissions from natural and refinery gas combustion (0.5 percent), petroleum industrial processes (0.7 percent), and coke calciners (0.6 percent) comprised a minor but significant fraction (1.8 percent) of total emissions.

Results of direct measurements of organic aerosol emissions from petroleum industry combustion devices are very limited. Petroleum industry combustion devices are found in both upstream (steam generators, heater treaters, reciprocating engines, etc.) and downstream (boilers, process heaters, gas turbines, thermal oxidizers, etc.) operations. Particulate emissions and particle size data from combustion processes indicate that a large fraction - often more than half - of the primary particles are PM2.5. In addition, emissions data from several fluidized catalytic cracking units (FCCUs) indicate primary PM10 emissions from FCCUs dominate total filterable particulate mass, accounting for 67 to 88 percent; primary PM2.5 comprises 40 to 70 percent of primary FCCU particulate emissions.

Volatile and semivolatile organic compounds are believed to be key contributors to secondary and condensable primary aerosols. The source profile of organic compound emissions also provides a powerful method of apportioning the contribution of various emission sources to ambient particle concentrations. Emissions of all organic compounds from petroleum industry combustion sources are not well-characterized. Previous emissions measurements for hazardous air pollutants (air toxics) provide an indication of the potential importance of different sources. For example, tests of petroleum industry combustion sources show that polycyclic aromatic hydrocarbon (PAH) emissions from reciprocating internal combustion engines and asphalt blowing units are approximately an order of magnitude higher than PAH emissions from boilers, process heaters, gas turbines, and coke calciners. Also, although organic hazardous air pollutant emissions data from gas-fired sources show extremely low emissions per unit of gas fired, the sheer quantity of gas fired in refineries could make a measurable if minor contribution to organic fine particulate. However, since hazardous air pollutant/air toxics measurements focus on a small subset of the total spectrum of organic compound emissions, they provide an incomplete picture of organic emissions.

ES-2

TEST METHODS FOR AEROSOL/FINE PARTICULATE CHARACTERIZATION

Development of emission factors for primary particulate and secondary particle precursors requires emissions rates to be measured accurately. Also, the chemical composition of the emissions must be accurately measured to develop speciation profiles. Traditional stationary source sampling methods are capable of providing accurate data for criteria and many hazardous air pollutants, but may not completely characterize the fine particulate matter, especially organic aerosols, which forms as the stack gas mixes and reacts with the atmosphere. This critical review indicates that methods which dilute and age the stack gas sample in a manner roughly simulating stack plume conditions before collection of samples for analysis are better suited for characterizing mobile source particulate emissions. A combination of traditional source stack sampling methods and dilution sampling methods for stationary combustion sources provides the opportunity to develop accurate emission factors/speciation profiles for evaluating the applicability of different fine particulate test methods to various source types. The data also could be used to identify less costly methods of measuring fine particulate emissions for future compliance, if required.

Due to the potential importance of organic aerosol emissions from gas-fired sources, a dilution sampler design developed and used specifically for characterizing organic aerosol emissions is recommended for future testing programs. The dilution sampling system should be designed using the following criteria.

- Dilution ratio: Dilution sampler emissions tests on an oil-fired furnace showed a dependence of aerosol size on dilution ratio, with larger particles resulting from higher dilution ratios and smaller ratios giving a larger number of smaller particles. Obtaining representative aerosol data requires not only uniform concentrations at the sampling point, but mixing in a manner that simulates local condensation conditions as closely as possible. It is recommended that dilution ratios of 40:1 or greater be used.
- Residence time: The characteristic time necessary for formation of secondary aerosol varies from a few seconds to several days, depending on the concentration and volatility of gaseous precursors, availability of primary particles and moisture droplets, sunlight intensity and radical species. It is recommended that the dilution chamber be configured to approximate time scales of actual plume mixing, when possible, and should be adjustable, to allow enough residence time for condensation processes to occur. An after-dilution residence time of at least 60 seconds should be used.

- Particle losses: Significant losses of charged particles to the electrically nonconducting surfaces (e.g., polyvinyl chloride [PVC] and Teflon[®]) of dilution samplers can be significant, and use of conducting surfaces wherever possible and installing charge neutralizers to avoid fine particle loss are recommended. To minimize line losses, sampler designs also should incorporate heated, temperature controlled probes and hoses to prevent condensation prior to mixing with dilution air.
- Sample contamination: Dilution samplers should be constructed of materials which will not dissolve or degrade during solvent rinsing or when exposed to caustic or corrosive stack gases. Use of rubber, plastics, greases or oils upstream of where the samples are collected should be avoided, since these materials may provide a source of organics within the sampler. Dilution air must either be thoroughly conditioned prior to introduction to the sample or pure gas mixtures must be used.
- Flow control and measurement: A reliable, field-verifiable method of flow measurement is important. Venturis and flow orifices are suitable for flow measurement, and are recommended. Since sample collection typically takes several hours, a computer data logger/ flow controller is also recommended.
- Field use: To minimize contamination and facilitate efficient use in the field, samplers should be lightweight, easy to take apart by a two person crew in a short amount of time for recovery and cleaning between sample runs, leak free without relying on greases or silicone and should have a small footprint which fits onto cramped stack platforms.

The dilution sampling technique should be combined with ambient air sampling and analysis methods to characterize fine particulate mass and chemical speciation. This will enhance comparability of source and ambient test measurement results. Traditional source stack sampling methods should be employed for measuring particulate mass, particle size distribution, chemical speciation and secondary particle precursor emissions. This will enhance comparability to previous source test data.

GOALS AND OBJECTIVES FOR FUTURE PROGRAMS

The overall goals of future measurement programs for characterizing stationary combustion source emissions which contribute to ambient fine particle levels should be to:

- Develop emission factors and speciation profiles for emissions of organic aerosols.
- Identify and characterize PM2.5 precursor compound emissions.

ES-4

- Investigate surrogate monitoring parameters for aerosol formation based on in-stack concentrations of commonly measured species.
- Identify a method or methods for routine testing which is potentially inexpensive and relatively easy compared to present methods of dilution sampling.

Organic aerosol emissions and speciation are of special interest to the petroleum industry because of the predominance of natural and process gases as a fuel for process heaters and boilers in U.S. refineries. Organic aerosols are likely to comprise the majority of primary fine particulate emissions from gas-fired sources, and organic carbon is typically a significant fraction of fine particulate matter in the ambient air. Based on a review of the issues governing organic aerosol and fine particulate emissions, the following test objectives were identified to meet these goals:

- (1) Characterize primary aerosol emissions, including mass, size, organic carbon, elemental carbon, and organic species, after dilution and aging of stack emissions to simulate near-field atmospheric aerosol formation mechanisms.
- (2) Characterize in-stack total particulate mass and particle size distribution, including PM2.5.
- (3) Characterize major gaseous PM2.5 precursors, specifically organic compounds (especially those with carbon number of 7 and above), oxides of nitrogen (NO_x) , sulfur dioxide (SO_2) , and ammonia (NH_3) .
- (4) Develop organic speciation profiles from particulate matter collected on the filter media after dilution.
- (5) Provide data that can be related to existing ambient particulate data (i.e., of similar quality and completeness).
- (6) Compare total PM2.5 mass (filterable and condensable) using EPA reference methods and dilution sampling.
- (7) Analyze the in-stack total particulate matter for composition (including elemental carbon, nitrates, sulfate, and ammonium).
- (8) Characterize minor gaseous PM2.5 precursors, specifically sulfur trioxide (SO_3) , sulfuric acid (H_2SO_4) and nitric acid (HNO_3) .

The above objectives may be prioritized for a specific testing program. The Test Protocol should be designed to ensure that the planned measurements are appropriate for achieving the project objectives, that the quality assurance plan is sufficient for obtaining data of known and adequate quality, and that data generated will withstand scrutiny by the scientific and regulatory communities.

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Section 1 INTRODUCTION

The Environmental Protection Agency's (EPA's) decision to revise the NAAQS for particulate matter may have significant impacts on the petroleum industry. The U.S. petroleum industry operates many stationary combustion devices such as process heaters, boilers, flares, fluid catalytic cracking unit regenerators, catalytic reforming unit regenerators, sulfur recovery units, steam generators, heater treaters, coke calciners, thermal oxidizers, stationary internal combustion engines such as gas turbines, and other devices. Most are gas fired, using process gases (refinery gas, casing gas, etc.) or natural gas. A small number of units are fired with distillate or residual oils, petroleum coke (e.g., catalyst regenerators for catalytic cracking units and catalytic reforming units), coal, or other petroleum refining byproducts. Those in urban non-attainment areas such as Los Angeles are almost exclusively gas-fired. Although gas is a relatively clean fuel, due to the target number and variety of gas-fired combustion devices and the range of process gas compositions even gas combustion may have significant potential to emit aerosol-forming organics. Organic aerosols are believed to contribute significantly to ambient particulate concentrations, especially in the very fine (below 2.5 micron) particle size range. Air emissions from combustion devices are important sources of organic aerosols, particulate matter and fine particle precursors.

Existing information regarding emission of organic compounds and aerosols from petroleum industry sources is sparse; therefore, API is conducting a two-phase program to characterize organic aerosol emission profiles for stationary petroleum industry combustion devices. The program also will seek to characterize emissions of other particles and particle precursors that contribute to fine particulate matter in the atmosphere. In Phase 1, the work includes: a critical review of sampling and analysis methodology (the subject of this report); development of an experimental design for characterizing organic aerosol emissions from petroleum industry combustion devices; and development of a test plan for implementation. In Phase 2, the test plan may be implemented.

The design of API's program requires a thorough understanding of the wide variety of available measurement approaches, regulatory agency and industry objectives, experimental design approaches, and combustion device characteristics. It should be noted that measurement of aerosols and aerosol precursors from stationary sources is not common practice; in fact, such

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measurements are presently at the forefront of science and are thus subject to considerable uncertainty. Therefore, caution must be exercised in selecting a particular approach, to ensure that it is capable of achieving the project goals. Differing approaches to such measurements have been taken by various researchers, subject to differing research objectives. Ambient aerosols, especially fine aerosols, are dominated by particles which form after the exhaust gases leave the source stack. Since the mechanisms of aerosol formation are not yet completely known, interpretation of measurement results is subject to considerable uncertainty. This report provides a critical review of sampling and analysis methods to serve as important background for an effective test program design.

REPORT ORGANIZATION

This report is divided into seven sections as follows:

- Section 1 Introduction. General overview of API program.
- Section 2 Background. Provides overview of proposed fine particulate regulations, aerosol formation mechanisms, and past emissions data from petroleum industry combustion sources.
- Section 3 Ambient Air Sampling and Analysis Methods. Overview of methods likely to be modified for dilution sampling.
- Section 4 Traditional Stationary Source Emissions Measurement Methods. Overview of conventional stationary source testing methods relevant to this program.
- Section 5 Aerosol Source Emissions Measurements. Review of dilution sampler designs and previous experience.
- Section 6 Recommendations. Summary of Recommendations for Phase 2.
- Section 7 References. Listing of literature reviewed to develop this report.

Section 2 BACKGROUND

Accurate measurements of organic aerosols and interpretation of test results will require an understanding of aerosol formation processes. Also, EPA's recent action to implement NAAQS for PM2.5 adds to the debate over the contribution of stationary combustion sources to ambient fine particulate concentrations. This section provides a brief overview of EPA's revised particulate standards and a review of ambient aerosol formation processes.

NATIONAL AMBIENT PM2.5 STANDARDS

On July 18, 1997, EPA published revisions to the NAAQS for particulate matter (62 Federal Register 38652). The revisions to the particulate standard were based solely on epidemiological studies without supporting toxicological and human clinical evidence. EPA's revisions include new annual and 24-hour standards for particles 2.5 micrometers (microns or μ m) and smaller in diameter, referred to as PM2.5. Combustion processes are the most likely source of PM2.5.

EPA revised the previous primary (health-based) particulate standards by adding a new annual PM2.5 standard of 15 μ g/m³ and a new 24-hour PM2.5 standard of 65 μ g/m³. EPA is retaining the current annual PM10 standard of 50 μ g/m³, but has revised the form of the current 24-hour PM10 standard of 150 μ g/m³. The previous form of one exceedence has been replaced with a form based on the 99th percentile of 24-hour PM10 concentrations in a year, averaged over 3 years. EPA has also revised its PM monitoring requirements to account for the new standards, including a reference test method for monitoring ambient PM2.5 (discussed later in Section 3). In addition, the sampling frequency for PM10 monitoring has been extended to once in 3 days.

PARTICULATE MATTER IN THE ATMOSPHERE

Particles or particulate matter may be either directly emitted into the atmosphere or formed there by chemical reactions; they are called primary and secondary particles, respectively. The relative importance of primary and secondary particles depends mainly on the geographical location, with its particular mix of emissions, and on the atmospheric chemistry. For example, in areas where wood is burned as heating fuel during the wintertime, most of the particles are primary in nature, whereas during summertime photochemical episodes, a substantial fraction of the particulate matter is attributed to secondary reactions in the atmosphere (Grosjean and Friedlander, 1975). As

shown in Figure 2-1, these particles are formed via several pathways, which are discussed in the sections below.

Particle Size

Atmospheric particles may be solid or liquid, with diameters between approximately 0.002 and 100 μ m (Finlayson-Pitts and Pitts, 1986). Particles with diameters of approximately 0.002 μ m are the smallest size detectable by condensation nuclei counters. The upper end of this range corresponds to the size of fine drizzle or very fine sand. These particles are so large that they do not remain suspended for a significant amount of time and quickly fall out of the atmosphere. The most important particles with respect to atmospheric chemistry, physics, and health effects related issues are in the 0.002-10 μ m range.

Aerosols are defined as relatively stable suspensions of solid or liquid particles in a gas. Thus aerosols differ from particles in that an aerosol includes both the particles and the gas in which they are suspended.

A particle's size affects many of its properties such as volume, mass and settling velocity. Size is expressed in terms of effective diameter, which depends on a physical rather than a geometric property. The most commonly used physical property is the aerodynamic diameter, D_a , which is defined as the diameter of a sphere of unit density (1 g-cm⁻³) which has the same terminal falling speed in air as the particle under consideration (Finlayson-Pitts and Pitts, 1986).

Factors Affecting Ambient Particle Size and Composition

Suspended particles congregate in different sub-ranges according to their method of formation (Whitby *et al.*, 1972). Figure 2-2 (from Chow, 1995) shows the major features of the mass distribution of particle sizes found in the atmosphere. The "nucleation" range (also termed "ultrafine particles") consists of particles with diameters less than approximately 0.08 µm that are emitted directly from combustion sources or that condense from cooled gases soon after emission. The lifetimes of particles in the nucleation range are usually less than 1 hour because they rapidly coagulate with larger particles or serve as nuclei for cloud or fog droplets. This size range is detected only when fresh emission sources are close to a measurement site or when new particles have been recently formed in the atmosphere (Chow, 1995, and references therein).

2-2



Figure 2-1. Fine Particulate Formation Pathways.





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The "accumulation" range consists of particles with diameters between approximately 0.08 and 2 μ m. These particles result from the coagulation of smaller particles emitted from: 1) combustion sources; 2) the condensation of volatile species; 3) gas-to-particle conversion; and 4) finely ground dust particles. The nucleation and accumulation ranges constitute the "fine particle size fraction," and the majority of sulfuric acid, ammonium bisulfate, ammonium sulfate, ammonium nitrate, and organic and elemental carbon is found in this size range. Particles larger than approximately 2 or 3 μ m are called "coarse particles"; they result from grinding activities and are dominated by material of geological origin. Pollen and spores also inhabit the coarse particle size range, as do ground up trash, leaves, and tires. Coarse particles at the low end of the size range also occur when cloud and fog droplets form in a polluted environment, then dry out after having scavenged other particles and gases (Chow, 1995, and references therein).

Particle size fractions commonly measured by air quality monitors are identified in Figure 2-1 by the portion of the size spectrum that they occupy. The mass collected is proportional to the area under the distribution within each size range. The *total suspended particulate* (TSP) size fraction ranges from 0 to approximately 40 μ m, the PM10 fraction ranges from 0 to 10 μ m, and the PM2.5 size fraction ranges from 0 to 2.5 μ m in aerodynamic diameter. No sampling device operates as a step function, passing 100 percent of all particles below a certain size and excluding 100 percent of the particles larger than that size. Instead, the cut-point of a sampling device is the diameter where 50 percent of the particles are collected, so a fraction of those particles larger than the size cut also will be collected.

Figure 2-3 shows calculated residence times in the atmosphere for particle sizes within each size range, based on gravitational settling in stilled and stirred chambers (Hinds, 1982). Particles in the fine particle (PM2.5) size fraction have substantially longer residence times, and therefore greater potential to affect PM concentrations further from emissions sources, than particles with aerodynamic diameters exceeding 2 or 3 μ m. In this regard, fine particles behave more like gases than coarse particles.

Figure 2-2 shows the accumulation range to consist of at least two submodes, which is contrary to many other presentations that show only a single peak in this region. Recent measurements of chemically specific size distributions show these submodes in several different urban areas. John *et al.* (1991) interpreted the peak centered at approximately 0.2 μ m as a "condensation" mode, containing gas-phase reaction products, and the approximately 0.7 μ m peak as a "droplet" mode,



Figure 2-3. Aging Time for Homogeneously Distributed Particles of Different Aerodynamic Diameters in a 100 m Deep Mixed Layer. Gravitational Settling is Assumed for Both Still and Stirred Chamber Models (Hinds, 1982).

resulting from growth by nucleation of particles in the smaller size ranges and by reactions that take place in water droplets. The liquid water content of ammonium nitrate, ammonium sulfate, sodium chloride, and other soluble species increases with relative humidity. This behavior is especially important when relative humidity exceeds 70 percent. When these modes contain soluble particles, their peaks shift toward larger diameters as humidity increases (Chow, 1995, and references therein). The peak of the coarse mode may shift between approximately 6 and 25 μ m. A small shift in the 50 percent cut-point of a PM10 sampler has a large influence on the mass collected because the coarse mode usually peaks near 10 μ m. On the other hand, a similar shift in cut-point near 2.5 μ m has a small effect on the mass collected owing to the low quantities of particles in the 1 to 3 μ m size range (Chow, 1995).

Chemical Composition

Six major components account for nearly all of the PM10 mass in most urban areas: 1) geological material (oxides of aluminum, silicon, calcium, titanium, and iron); 2) organic carbon (consisting of hundreds of compounds); 3) elemental carbon; 4) sulfate; 5) nitrate; and 6) ammonium. Liquid water absorbed by soluble species is also a major component when the relative humidity exceeds approximately 70 percent, but much of this evaporates when filters are equilibrated prior to weighing. Water-soluble sodium and chloride are often found in coastal areas, and certain trace elements are found in areas greatly influenced by industrial sources.

Although total mass measurements depend somewhat on sampling and analysis methods (Chow, 1995), mass concentrations of PM10 and PM2.5 can be reproduced within experimental precision (typically 20-30 percent) by summing the measured concentrations of these six chemical components. Approximately half of PM10 is composed of geological material. However, geological material often constitutes less than approximately 10 percent of the PM2.5 mass concentrations, as most of it is found in the coarse particle size fraction. The majority of sulfuric acid, ammonium bisulfate, ammonium sulfate, ammonium nitrate, and organic and elemental carbon is found in the "fine particle size fraction," PM2.5 size range.

Table 2-1 summarizes the chemical composition of particles directly emitted from several representative emission sources measured in California in 1993 (Watson *et al.*, 1997; Chow, 1995). Although the detailed chemical composition of particles emitted from these sources may differ somewhat in different parts of the country, the table gives a reasonable overview of primary emissions from different sources. It can be seen from this table that organic carbon (OC) and elemental carbon (EC) are important constituents of most of these emissions.

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Source Type	Dominant Particle Size	< 0.1%	0.1 to 1%	1 to 10%	> 10%	
Paved Road Dust	ed Road Dust Coarse Cr, Sr, Pb, Zr		$SO_4^{=}$, Na ⁺ , K ⁺ , P, S, Cl, Mn, Ba, Ti	EC, Al, K, Ca, Fe	OC, Si	
Unpaved Road Dust	Coarse	NO ₃ ⁻ , NH₄ ⁺ , P, Zn, Sr, Ba	SO ₄ ⁼ , NA ⁺ , K ⁺ , P, S, Cl, Mn, Ba, Ti	OC, Al, K, Ca, Fe	Si	
Construction	Coarse	Cr, Mn, Zn, Sr, Ba	SO4 [≠] , K ⁺ , S, Ti	OC, Al, K, Ca, Fe	Si	
Agricultural Soil	Coarse	NO ₃ , NH ₄ ⁺ , Cr, Zn, Sr	$\begin{array}{ccc} SO_4^{=}, NA^+, K^+, \\ S, Cl, Mn, Ba, \\ Ti \end{array} OC, Al, K, Ca, Fe Si \\ \end{array}$		Si	
Natural Soil	Coarse	Cr, Mn, Sr, Zn, Ba	Cl, Na ⁺ , EC, P, S, Cl, Ti	OC, Al, Mg, K, Ca, Fe	Si	
Lake Bed	Lake Bed Coarse Mn, Sr, Ba K		K⁺, Ti	SO₄ ⁺ , Na ⁺ , OC, Al, S, Cl, K, Ca, Fe	Si	
Motor Vehicle Fine Cr, Ni, Y		Cr, Ni, Y	NH₄ ⁺ , Si, Cl, Al, Si, P, Ca, Mn, Fe, Zn, Br, Pb	Cl ⁻ , NO ₃ ⁻ , SO ₄ ⁼ , NH ₄ ⁺ , S	OC, EC	
Vegetative Burning	Fine	Ca, Mn, Fe, Zn, Br, Rb, Pb	NO ₃ ⁻ , SO ₄ ⁼ , NH ₄ ⁺ , Na ⁺ , S	CL ⁻ , K ⁺ , Cl, K	OC, EC	
Residual /Crude Oil Combustion (including fires)	Fine	K ⁺ , OC, Cl, Ti, Cr, Co, Ga, Se	NH₄ ⁺ , Na ⁺ , Zn, Fe, Si	V, OC, EC, Ni	S, SO₄⁼	
Incinerator	Fine	V, Mn, Cu, Ag, Sn	K ⁺ , Al, Ti, Zn, Hg	NO3 ⁻ , Na ⁺ , EC, Si, S, Ca, Fe, Br, La, Pb	$SO_4^{=}$, NH ⁴ , OC, Cl	
Coal-Fired Power Plant	Fine	Cl, Cr, Mn, Ga, As, Se, Br, Rb, Zr	NH₄ ⁺ , P, K, Ti, V, Ni, Zn, Sr, Ba, Pb	SO ₄ [≠] , OC, EC, Al, S, Ca, Fe	Si	
Oil-Fired Power Plant	Fine	V, Ni, Se, As, Br, Ba	Al, Si, P, K, Zn	NH ₄ ⁺ , OC, EC, Na, Ca, Pb	S, SO₄ ⁼	
Smelter Fine	Fine	V, Mn, Sb, Cr, Ti	Cd, Zn, Mg, Na, Ca, K, Se	Fe, Cu, As, Pb	S	
Antimony Roaster	Fine	V, Cl, Ni, Mn	SO₄⁼, Sb, Pb	S	None Reported	
Marine (Natural)	Fine and Coarse	Ti, V, Ni, Sr, Zr, Pd, Ag, Sn, Sb, Pb	Al, Si, K, Ca, Fe, Cu, Zn, Ba, La	NO ₃ ⁻ , SO ₄ ⁼ , OC, EC	Cl-, Na ⁺ , Na, Cl	

Table 2-1. Chemicals in Primary Particles Emitted Directly from Different Emission Sources.

EC = Elemental Carbon

OC = Organic Carbon

Organic compounds are important components of particulate matter, whether in urban, rural, or remote areas. Most of the particulate organic carbon is believed to reside in the fine particle fraction. It has been reported (Gray *et al.*, 1986) that in the Los Angeles area organic compounds constitute approximately 30 percent of the fine particle mass. Rogge *et al.* (1993a) analyzed



Figure 2-4. Mass Balance on the Chemical Composition of Annual Mean Fine Particle Concentrations, 1982, for (a) West Los Angeles and (b) Rubidoux (Riverside), California (Rogge *et al.*, 1993a). atmospheric fine particulate samples collected at four urban locations in southern California in 1982 to quantify individual organic compounds. Figure 2-4 shows the material balances that describe the chemical composition of ambient fine particulate matter for the most western (West Los Angeles) and most eastern (Rubidoux) sampling sites. During the summer photochemical smog season, the prevailing winds are from west to east. Under this meteorological condition, West Los Angeles is often upwind of the city, whereas Rubidoux is far downwind of the metropolitan area. Consequently, the concentrations of total fine particles and the secondary formation products such as nitrates and dicarboxylic acids are higher in Rubidoux than in West Los Angeles.

Rogge *et al.* (1993a) identified and quantified more than 80 individual organic compounds found in the fine particles fraction, including n-alkanes, n-alkanoic acid, one n-alkenoic acid, one nalkanal, aliphatic dicarboxylic acids, aromatic polycarboxylic acids, polycyclic aromatic hydrocarbons (PAH), polycyclic aromatic ketones (PAK), polycyclic aromatic quinones (PAQ), diterpenoid acids and some nitrogen-containing compounds. In general, many of the same organic compounds are found, in different proportions, in direct emissions from various sources, such as diesel and auto exhaust, charbroilers and meat cooking operations, cigarette smoke, biogenic sources, etc. (Rogge, 1993; Rogge *et al.* 1991, 1993b-e).

AEROSOL FORMATION

Primary Particles

Atmospheric concentrations of primary particles are, on average, proportional to the quantities that are emitted. Primary particles are emitted in several size ranges, the most common being less than 1 μ m in aerodynamic diameter from combustion sources and larger than 1 μ m in aerodynamic diameter from dust sources. Particles larger than 10 μ m in aerodynamic diameter usually deposit to the surface within a few hours after being emitted and do not have a large effect on light scattering, unless high winds and turbulence resuspend the particles.

Emission source categories include: 1) major stationary (point) sources (e.g., boilers, process heaters, incinerators, and steam generators); 2) area sources (e.g., fires, wind-blown dust, petroleum extraction operations, meat cooking operations, and residential fuel combustion); 3) mobile sources (e.g., automobiles, buses, trucks, trains, and aircraft); 4) agricultural and ranching activities (e.g., fertilizers, herbicides, tilling operations, and ammonia emissions from livestock); and 5) biogenic sources (e.g., pollen fragments and particulate abrasion products from leaf surfaces).



Figure 2-5. Surface Area Distribution of Particles from the Combustion of Several Organics and from Automobiles and a Candle (from National Research Council, 1979).

Combustion processes (e.g., power plants, incinerators, diesel engines) may produce particles not only in the nucleation range (less than approximately $0.08 \mu m$) but also in the accumulation range. The relative numbers of particles produced in the nucleation range compared to the accumulation range depend on the nature of the combustion process (e.g., fuel, operating conditions) and air emission controls, as well as the conditions of cooling and dilution (Finlayson-Pitts and Pitts, 1986). Partitioning of particulate mass to the condensation and nucleation fractions is affected by the rate of cooling, the relative humidity of the diluting air, and the presence of other particles. Figure 2-5 shows the surface area distribution of particles produced by the combustion of several organic compounds, as well as by automobiles and a burning candle. The area under the curve represents the total particle surface area of the distribution. The "dirtier" flames (e.g., the candle and the acetone flame) produce significant numbers of particles in the accumulation mode, while the cleaner flames produce particles in the nucleation mode.

Secondary Particles: Chemical and Physical Transformation in the Atmosphere

Once released into the atmosphere, primary particle emissions are subjected to dispersion and transport and, at the same time, to various physical and chemical processes that determine their ultimate environmental fate. The role of the atmosphere may be compared in some ways to that of a giant chemical reactor in which materials of varying reactivities are mixed together, subjected to chemical and/or physical processes and finally removed. Primary emissions from various sources such as motor vehicles, residential wood combustion, meat cooking, etc., are very complex mixtures containing thousands of organic and inorganic constituents in the gas and particulate phases. These compounds have different chemical reactivities and are removed by dry and wet deposition processes at varying rates. Some of the gaseous species, by a series of chemical transformations, are converted into particles, forming secondary aerosols. Sulfates and nitrates are the most common secondary particles, though a fraction of organic carbon can also result from volatile organic compounds (VOC) via atmospheric reactions.

Atmospheric gases can also become suspended particles by absorption, solution, or condensation. Several of these mechanisms may operate in series in the process of secondary particle formation. In absorption, gas molecules are attracted to and adhere to existing particles. Sulfur dioxide and many organic gases have an affinity for graphitic carbon (e.g., activated charcoal is often used as a scrubbing agent for these gases), and most graphitic carbon particles in the atmosphere are usually found in association with an organic component. Most gases are somewhat soluble in water, and liquid particles will rapidly become saturated in the presence of sulfur dioxide, nitrogen dioxide,

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and certain organic gases. Many hydrocarbons are emitted at elevated temperatures as a result of incomplete combustion and condense rapidly upon cooling to ambient temperatures. These are usually considered to be primary emissions if the condensation takes place rapidly, within approximately 1 minute of exiting the stack, but the particles formed can be sensitive to changes in temperature and the surrounding gas concentrations.

Chemical transformation and equilibrium processes for inorganic secondary aerosols are complicated, depending on many meteorological and chemical variables, and are not completely understood. Lurmann *et al.* (1988) and Lurmann (1989) summarize the different pathways from gas to particle conversion. Calvert and Stockwell (1983) have studied gas-phase chemistry. Stelson and Seinfeld (1982a; 1982b; 1982c), Russell *et al.* (1983), Russell and Cass (1984; 1986), Bassett and Seinfeld (1983a; 1983b), Saxena *et al.* (1986), Pilinus and Seinfeld (1987) and Wexler and Seinfeld (1992) provide good explanations of the equilibrium between gas and particle species in polluted environments.

The gaseous precursors of most particulate sulfates and nitrates are SO_2 , SO_3 , oxides of nitrogen (NO and NO_2 , the sum of which is designated NO_x) and ammonia. Ambient concentrations of sulfate and nitrate are not necessarily proportional to quantities of emissions since the rates at which they form may be limited by factors other than the concentration of the precursor gas (e.g., photo-chemical reactions). The majority of secondary sulfates are found as a combination of H_2SO_4 , ammonium bisulfate (NH_4HSO_4), and ammonium sulfate ($(NH_4)_2SO_4$). The majority of secondary nitrates in PM10 are found as ammonium nitrate (NH_4NO_3), though a portion of the nitrate is also found in the coarse particle fraction, usually in association with sodium. This is presumed to be sodium nitrate ($NaNO_3$) derived from the reaction of nitric acid with the sodium chloride (NaCl) in sea salt.

Secondary Sulfate Pathways

Sulfur dioxide changes to particulate sulfate through gas- and aqueous-phase transformation pathways. In the gas-phase pathway, sulfur dioxide reacts with hydroxyl radicals in the atmosphere to form hydrogen sulfite. This species rapidly reacts with oxygen and small amounts of water vapor to become sulfuric acid gas. Sulfuric acid gas has a low vapor pressure, and it either condenses on existing particles, nucleates at high relative humidities to form a sulfuric acid droplet or, in the presence of ammonia gas, becomes neutralized as ammonium bisulfate or ammonium sulfate. Though there are other gas-phase pathways, the hydroxyl radical pathway is

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usually the most dominant. Calvert and Stockwell (1983) show a wide range of gas-phase transformation rates from less than 0.01 percent/hr to about 5 percent/hr. The transformation rate appears to be controlled more by the presence or absence of the hydroxyl radical and competing reactions of other gases than by the sulfur dioxide concentration. Hydroxyl radical concentrations are related closely to photochemistry. Gas-phase sulfur dioxide transformation rates are highest during the daytime and drop to less than 0.1 percent/hr at night (Calvert and Stockwell, 1983).

When fogs or clouds are present, SO_2 can be dissolved in a droplet where it experiences aqueous reactions which are much faster than gas-phase reactions. If ozone and hydrogen peroxide are dissolved in the droplet, the sulfur dioxide is quickly oxidized to sulfuric acid. If ammonia is also dissolved in the droplet, the sulfuric acid is neutralized to ammonium sulfate. As relative humidity decreases below 100 percent (i.e., the fog or cloud evaporates), the sulfate particle is present as a small droplet which includes a portion of liquid water. As the relative humidity further decreases below 70 percent, the droplet evaporates and a small, solid sulfate particle remains. The reactions within the fog droplet are very fast, and the rate is controlled by the solubility of the precursor gases. Aqueous transformation rates of sulfur dioxide to sulfate are 10 to 100 times as fast as gas-phase rates.

Secondary Nitrate Pathways

Directly emitted nitric oxide (NO) converts to nitrogen dioxide (NO₂), primarily via reaction with ozone. The principal gas-phase pathways for atmospheric nitrogen dioxide are that: 1) it can change back to nitric oxide in the presence of ultraviolet radiation; 2) it can change to short-lived radical species which take place in other chemical reactions; 3) it can form organic nitrates such as peroxyacetyl nitrate (PAN); or 4) it can oxidize to form nitric acid. The major pathway to nitric acid is reaction with the same hydroxyl radicals which transform sulfur dioxide to sulfuric acid. Nitric acid deposits from the atmosphere fairly rapidly but, in the presence of ammonia, it is neutralized to particulate ammonium nitrate. Calvert and Stockwell (1983) show a wide range of conversion rates for nitrogen dioxide to nitric acid, ranging from less than 1 percent/hr to 90 percent/hr. Though they vary throughout a 24-hour period, these rates are significant during both daytime and nighttime hours, in contrast to the gas-phase sulfate chemistry which is most active during daylight hours. Nitrate is also formed by aqueous-phase reactions in fogs and clouds in a manner analogous to aqueous-phase sulfate formation. Nitrogen dioxide dissolves in a droplet where, in the presence of oxidants, it converts to nitric acid and, in the presence of dissolved ammonia, to ammonium nitrate.

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While ammonium sulfate is a fairly stable compound, ammonium nitrate is not. Its equilibrium with gaseous ammonia and nitric acid is strongly influenced by temperature and relative humidity. Russell *et al.* (1983) show that lower temperatures and higher relative humidities favor the particulate phase of ammonium nitrate. Their sensitivity tests demonstrate that the equilibrium is most sensitive to changes in ambient temperature and gaseous ammonia concentrations. The gas phase is highly favored when ambient temperatures approach or exceed 35 °C, while the particulate ammonium nitrate phase is highly favored when temperatures are less than 15 °C. When gaseous ammonia or nitric acid concentrations are reduced, some of the particulate ammonium nitrate evaporates to regain equilibrium with the gas phase. This phenomenon must be addressed in order to make accurate measurements of particulate nitrate and nitric acid, since ammonium nitrate particles on a filter may disappear during sampling or between sampling and analysis with changes in temperature and gas concentrations.

As noted above, gaseous nitric acid can also react with basic materials such as sodium chloride (from sea salt) and possibly alkaline dust particles. The products of these reactions (e.g., sodium nitrate) are usually stable and are often observed as coarse particles, since the original sea salt or dust was in that size range. Coarse particle nitrate accompanied by sodium and a deficit of chloride is a good indicator that this reaction has taken place.

Sulfur dioxide to particulate sulfate and nitrogen oxide to particulate nitrate reactions compete with each other for available hydroxyl radicals and ammonia. Ammonia is preferentially scavenged by sulfate to form ammonium sulfate and ammonium bisulfate, and the amount of ammonium nitrate formed is only significant when total ammonia exceeds sulfate by a factor of two or more on a mole basis. In an ammonia-limited environment, reducing ammonium sulfate concentrations by one molecule would increase ammonium nitrate concentrations by two molecules. This also implies that sulfur dioxide, oxides of nitrogen, and ammonia must be treated as a coupled system and cannot be dealt with separately. It also implies that reducing sulfur dioxide emissions might actually result in ammonium nitrate increases which exceed the reductions in ammonium sulfate where the availability of ammonia is limited.

Atmospheric water is another important component of suspended particulate matter. The liquid water content of ammonium nitrate, ammonium sulfate, sodium chloride, and other soluble species changes with relative humidity (Charlson *et al.*, 1969; Covert *et al.*, 1972), becoming especially important when relative humidity exceeds 70 percent.

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Table 2-2. Calculated Atmospheric Lifetimes for Gas-Phase Reactions of Selected Gas-Phase	;
Compounds with Atmospherically Important Reactive Species (From Atkinson, 1988, Unless	5
Noted Otherwise).	

Compound	Atmospheric Lifetime Due to Reaction with:				
	OHª	03 [°]	NO ₃ ^c	HO ₂ ^d	hv ^e
NO ₂	2 days	12 hr	1 hr	2 hr	2 min
NO	4 days	1 min	3 min	20 min	-
HNO ₃	180 days	-	-	-	-
SO ₂	26 days	>200 yr	>4x10⁴ yr	>600 yr	-
NH ₃	140 days	-	-	•	-
Propane	19 days	>7,000 yr	-	-	-
n-Butane	9 days	>4,500 yr	9 yr	-	-
n-Octane	3 days	-	3 yr	-	-
Ethylene	3 days	9 days	3 yr	-	-
Propylene	11 hr	1.5 days	15 days	-	-
Acetylene	30 days	6 yr	>14 yr	-	-
Formaldehyde	3 days	>2x10 ⁴ yr	210 days	23 days	4 hr
Acetaldehyde	1 day	>7 yr	50 days	-	60 hr
Benzaldehyde	2 days	-	60 days	-	-
Acrolein	1 day	60 days	-	-	-
Formic acid	50 days	-	-	-	-
Benzene	18 days	600 yr	>16 yr	-	-
Toluene	4 days	300 yr	9 yr	-	-
m-Xylene	11 hr	75 yr	2 yr	-	-
Phenol	10 hr	-	20 min	-	-
Naphthalene	1 day	>80 days	80 days	-	-
2-Methylnaphthalene	5 hr	>40 days	35 days	-	-
2,3-Dimethylnaphthalene	4 hr	>40 days	20 days	-	-
Acenaphthene	2 hr	>30 days	~3 hr	-	-
Acenaphthylene	2 hr	~50 min	13 min	-	-
Phenanthrene	9 hr	-	-	-	-
Anthracene	2 hr	-	-		-
Fluoranthene	6 hr	-	64 days	-	-
Pyrene ^r	6 hr	-	20 days		-

^a For 12-hr average concentration of OH radical of 1 x 10⁶ molecule/cm³.

^b For 24-hr average O_3 concentration of 7 x 10¹¹ molecule/cm³.

^e For 12-hr average NO_3 concentration of 2 x 10⁸ molecule/cm³.

^d For 12-hr average HO₂ concentration of 10⁸ molecule/cm³.

^e For solar zenith angle of 0°.

^f Lifetimes calculated from kinetic data given in Atkinson et al., 1990.

Secondary Organic Aerosols

While the mechanisms and pathways for inorganic secondary particles are fairly well known, those for secondary organic aerosols are not well understood. Hundreds of precursors are involved in these reactions, and the rates at which these particles form are greatly dependent on the concentrations of other pollutants and meteorological variables. Organic compounds present in the gas phase undergo atmospheric transformation through reactions with reactive gaseous species such as OH radicals, NO₃ radicals, or O₃. Table 2-2 gives the calculated atmospheric lifetimes for some selected compounds present in direct gas-phase emissions due to known tropospheric

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chemical removal reactions (from Atkinson, 1988). These lifetimes (i.e., the time for the compound to decay to 1/e or 37 percent of its original concentration) are calculated from the corresponding measured reaction rate constants and the average ambient concentration of the tropospheric species involved. Although the individual rate constants are known to a reasonable degree of accuracy (in general, to within a factor of two), the tropospheric concentrations of these key reactive species are much more uncertain. For example, the ambient concentrations of OH radicals at any given time and/or location are uncertain to a factor of at least 5, and more likely 10 (Atkinson, 1988). In addition, the concentration of OH radicals varies significantly not only diurnally but also with season and latitude due to varying penetration of solar ultraviolet light. The direct measurements by a ¹⁴C-tracer method (Felton *et al.*, 1988) showed maximum midday OH radical concentrations in early to mid-October for pure and polluted air to be, respectively, 2.4x10⁶ and 9.5x10⁶ radicals cm⁻³. Nighttime OH concentrations of less than 2x10⁵ radicals cm⁻³ were measured.

Winter mid-latitude noontime maximum values on the order of approximately 2x10⁶ radicals cm⁻³ are likely (Mount, 1992). The tropospheric diurnally and annually averaged OH radical concentrations are more certain, to possibly a factor of two. For this reason, the calculated lifetimes listed in Table 2-2 are approximate only and are valid for those reactive species concentrations which are listed in the footnotes. However, these data permit one to estimate the contribution of each of these atmospheric reactions to the overall rates of removal of most pollutants from the atmosphere.

As can be seen from Table 2-2, the major atmospheric loss process for most of the direct emission constituents listed is by daytime reaction with OH radicals. For some pollutants, photolysis, reactions with ozone, and reactions with NO₃ radicals during nighttime hours are also important removal routes. For alkanes, the atmospheric lifetimes calculated from the corresponding measured reaction rate constant and the average ambient concentration of OH radicals ranges from approximately 19 days for propane (C_3H_8) to approximately 1 day for n-pentadecane ($C_{15}H_{32}$). For aromatic hydrocarbons, lifetimes range from 18 days for benzene to a few hours for methylnaphthalenes (assuming average 12-hour daylight OH radical concentration of 1x10⁶ molecule cm⁻³).

Although the rate constants for OH radical reactions with most VOCs are known or can be deduced to a reasonable degree of accuracy (see, for example, Atkinson, 1986, 1989), relatively

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few data exist concerning the products of these reactions. The presently existing product data are usually limited to lower molecular weight substrates and gaseous products (Atkinson, 1989). However, for aerosol formation, only the reactions of VOCs with carbon numbers higher than seven (C_7) are important (Grosjean and Seinfeld, 1989), because the products from those having fewer than seven carbon atoms are too volatile to form aerosols under atmospheric conditions. Thus, the products arising from the OH radical-initiated reactions of aromatic, aliphatic, and cyclic saturated and unsaturated hydrocarbons with eight or more carbon atoms are likely to be distributed between the gas and particulate phases and may have an important effect on aerosol concentrations in ambient air. However, the relations between the chemistry of these compounds and the physical processes of aerosol formation are still not well understood.

Particles are formed when gaseous reaction products achieve concentrations which exceed their saturation concentrations. This means that chemical transformations must be rapid enough to increase concentrations faster than they decrease by deposition and atmospheric dilution, and that the saturation concentrations of the products must be lower than those of the gaseous precursors. Grosjean and Seinfeld (1989) outline an empirical model for addressing secondary organic formation and Grosjean (1992) demonstrates this model for reactive organic emissions in the South Coast Air Basin (SoCAB). Fractional conversion factors, based on experimental data taken in smog chamber experiments, relate the aerosol products of selected precursors to the original quantities of those precursors. Applying these factors to chemically speciated emissions inventories provides an approximate estimate of the equivalent emissions of secondary organic particles. Grosjean (1992) shows that these equivalent emissions are comparable to primary emissions from other carbon-containing sources such as motor vehicle exhaust in the Los Angeles area. While this empirical model provides an order-of-magnitude estimate of the VOC impacts on PM10, and while these impacts appear to be significant in southern California, quantitative estimates are very imprecise.

Recently, Odum *et al.* (1997) discussed the atmospheric aerosol-forming potential of whole gasoline vapor. The authors argue that, since the mixture of hydrocarbons that comprise gasoline is representative of the atmospheric distribution of anthropogenic hydrocarbons in an urban airshed, it is of significant interest to determine the atmospheric aerosol-forming potential of whole gasoline vapor. They determined that the aromatic compounds present in fuel (toluene and higher alkylated benzenes) control gasoline vapor secondary organic aerosol formation potential. Thus, it should be possible to model the formation of secondary particulate matter in an urban airshed

based on the aromatic content of the whole gasoline used in this airshed. However, in those urban airsheds where sources other than motor vehicles are important, this approach may not work.

Ultimately, one desires an organic transformation model based on fundamental principles. The structure for such models already exists in photochemical mechanisms which are applied in grid-based models for ozone prediction. Unfortunately, these models are highly simplified with respect to organic chemistry. Ozone mechanisms assign all hydrocarbons to five to eight groups having similar reactive properties. While these groupings have been shown to be effective for ozone, they have little to do with the tendency of reactions to create products which might achieve saturation in the atmosphere. Pandis *et al.* (1992) have divided these groups into sub-groups which are more conducive to aerosol formation and have added reactions for alcohols, pinenes, isoprene, toluene, acetylene, heptane, octene, and nonene. When Pandis *et al.* (1992) modeled the Southern California Air Quality Study (SCAQS) August 27-29, 1987 episode with double the ROG emissions in the SCAQS emissions inventory, they found reasonable comparisons between calculated secondary organic aerosol and that inferred by Turpin and Huntzicker (1991) from time-resolved organic to elemental carbon ratios.

Sources of secondary sulfates and nitrates are fairly easy to identify because there are few primary emitters of these species. The origin of secondary organic particles is more difficult to identify because only organic carbon, and not its chemical constituents, is usually measured and there are many primary emitters of organic material. Gray *et al.* (1986) propose that evidence of secondary organic carbon contributions to suspended particles is found when: 1) the ratio of total (elemental plus organic) to elemental carbon exceeds that in source emissions (which can be as high as 4:1 but is typically between 2:1 and 3:1); 2) ambient ratios of total to elemental carbon are higher in summer and during the afternoon (when the products of photochemistry are most influential); and 3) when the ratio of total to elemental carbon is larger at sites which receive aged aerosol (i.e., downwind sites) than at sites which receive unaged aerosol.

Gray *et al.* (1986) did not find conclusive evidence of secondary organic aerosol formation in the 24-hour speciated samples taken in 1982. Turpin and Huntzicker (1991) did observe total to elemental carbon ratios as high as 5.6 at the Claremont site (CA) on the afternoon of August 28, 1987 and they interpreted a portion of this increase as contributions from secondary organic carbon. Though they monitored organic carbon at 2-hour intervals every day during SCAQS, Turpin and Huntzicker (1991) definitively observed this phenomenon only between June 22 and

28, July 11 and 13, July 25 and 29, and August 27 and 31, 1987. Elevated total to elemental carbon ratios were not found during fall monitoring at Long Beach.

Secondary organic compounds in particulate matter include aliphatic acids, aromatic acids, nitro aromatics, carbonyls, esters, phenols, and aliphatic nitrates (Grosjean, 1992; Grosjean and Seinfeld, 1989). However, these compounds also can be present in primary emissions (see for example Rogge, 1993), so they are not unique tracers for atmospheric transformation processes. It has been reported that, in the presence of NO_x, the OH radical reactions with fluoranthene and pyrene present in the gas phase lead to the formation of specific nitroarene isomers different from those present in the direct emissions (Arey et al., 1986, 1989a; Atkinson et al., 1990; Zielinska et al., 1990). A reaction pathway involving initial OH radical addition to the most reactive ring position has been postulated; for example, addition of OH to the C-3 position for fluoranthene and the C-1 position for pyrene (Pitts et al., 1985), followed by NO₂ addition in the C-2 position. Subsequent elimination of water results in the formation of 2-nitrofluoranthene from fluoranthene and 2-nitropyrene from pyrene. Night-time reactions with the NO₃ radical lead to the same result as the OH radical reaction, nitrofluoranthene and nitropyrene isomers (Zielinska et al., 1986). In contrast, the electrophilic nitration reaction of fluoranthene, or pyrene, involving the NO ion produces mainly 3-nitrofluoranthene from fluoranthene and 1-nitropyrene from pyrene, and these isomers are present in direct emissions from combustion sources.

Generally the same nitro-PAH isomers as those formed from OH radical and NO₃ reactions are observed in ambient air samples (Arey *et al.*, 1987; Atkinson *et al.*, 1988; Zielinska *et al.*, 1989a, 1989b; Ciccioli *et al.*, 1989). For example, ambient particulate matter samples were collected at three sites (Claremont, Torrance, and Glendora) situated in the Los Angeles Basin, with the Claremont and Glendora sites being approximately 30 km and 20 km, respectively, northeast and the Torrance site approximately 20 km southwest of downtown Los Angeles (Arey *et al.*, 1987; Atkinson *et al.*, 1988; Zielinska *et al.*, 1989a, 1989b). The sampling was conducted during two summertime periods (Claremont, September 1985, and Glendora, August 1986) and one wintertime period (Torrance, January-February 1986). Table 2-3 lists the maximum concentrations of nitropyrene (NP) and nitrofluoranthene (NF) isomers observed at these three sites during the daytime and nighttime sampling periods. As can be seen from this table, 1-nitropyrene (1-NP), the most abundant nitroarene emitted from diesel engines, is not the most abundant nitroarene observed in ambient particulate matter collected at three sites heavily impacted by motor vehicle emissions. Of the two nitropyrene isomers present, 2-nitropyrene (2-NP), the

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main nitropyrene isomer formed from the gas-phase OH radical initiated reaction with pyrene, is sometimes more abundant. 2-Nitrofluoranthene (2-NF) was always the most abundant nitroarene observed in ambient particulate matter collected at these three sites and this nitrofluoranthene isomer is not present in diesel and gasoline vehicle emissions. 2-Nitrofluoranthene is the only nitroarene produced from the gas-phase OH radical-initiated and NO₃ reactions with fluoranthene, whereas mainly 3-nitrofluoranthene, and lesser amounts of 1-, 7-, and 8-nitroisomers are present in diesel particulate matter and are produced from the electrophilic nitration reactions of fluoranthene.

Table 2-3. The Maximum Concentrations of Nitrofluoranthene (NF) and Nitropyrene (NP) Isomers Observed at Three South Coast Air Basin Sampling Sites.

Collection Period	Nitroarene Concentration, pg/m ³				
	Claremont ^{a,b}	Glendora ^{c,d}	Torrance ^{a,e}		
2-NF, day	40	350	410		
2-NF, night	1700	2000	750		
3-NF, day	3	ND ^f	~3		
3-NF, night	~3	ND	70		
8-NF, day	2	3	8		
8-NF, night	2	4	50		
1-NP, day	3	15	60		
1-NP, night	10	15	50		
2-NP, day	1	14	50		
2-NP, night	8	32	60		

^aFrom Zielinska et al., 1989b.

^bDaytime sample collected from 1200 to 1800 hr and nighttime sample from 1800 to 2400 hr on 9/13/85.

^cFrom Atkinson et al., 1988.

^dDaytime sample collected from 0800 to 2000 hr on 8/20/86 and nighttime sample from 2000 to 0800 hr on 8/20-21/86.

^eDaytime sample collected from 0500 to 1700 hr on 1/28/86 and nighttime sample from 1700 to 0500 hr on 1/27-28/86.

^fND: none detected.

Figure 2-6 compares the nitroarenes formed from the OH radical-initiated reaction of fluoranthene and pyrene in an environmental chamber (upper trace) with the ambient samples collected at Torrance (lower trace) (from Arey *et al.*, 1989b). It is very unlikely that NO_3 could have been present during the nighttime winter collections in Torrance, given the high level of NO present at sunset. More likely a relatively high level of OH radicals was present due to the measured high

concentration of HNO_2 , which photolyzes to yield OH radicals. This suggests that all isomers observed in Figure 2-6 lower trace), with the exception of 1-nitropyrene, are the product of the OH-radical-initiated reactions of the parent PAH. Direct emissions may account for the 1-nitropyrene (and 3-nitrofluoranthene) observed at relatively low levels in these ambient samples (see Zielinska *et al.*, 1989b, for full discussion of all the molecular weight 247 nitroarenes observed in ambient particles).

The evidence presented above, as well as the observation that 2-nitrofluoranthene has been the most abundant molecular weight 247 nitroarene in ambient samples collected worldwide (Ramdahl *et al.*, 1986), strongly suggests that atmospheric formation from the parent PAH, not the direct automotive emissions, is the major source of these nitroarenes in ambient air. However, under certain sampling conditions, when ambient particulate matter is collected very close to emission sources, the molecular weight 247 nitroarene profile may be different. For example, in urban samples collected during wintertime rush hours at a central square in Rome, Italy, at a height of 1.5 m above street level, 2-NF and 2-NP were not observed (Ciccioli *et al.*, 1989).

Fluoranthene and pyrene, both four-ring PAHs, are distributed between the gas and particle phases under ambient conditions. The distribution of PAH between the gaseous and particulate phases is determined by the vapor pressure of the individual species, by the amount and type of the particulate matter present (adsorption surface available), and by the temperature (Ligocki and Pankow, 1989). For example, during two summertime studies in the Los Angeles basin cited above (Claremont and Glendora), the amounts of pyrene and fluoranthene observed in the gas phase were greater than 80 percent of the total ambient concentrations (Arey *et al.*, 1989b). On the other hand, in samples collected in the heavily traveled Baltimore Harbor Tunnel, approximately 50 percent of total pyrene and fluoranthene concentration was observed in the gas phase (Benner *et al.*, 1989). Coutant and co-workers (Coutant *et al.*, 1988) measured the vapor-phase concentrations of PAH in ambient air samples collected at temperatures of -2 to 29 °C and found the percentages of fluoranthene and pyrene present in the vapor phase to range from 27 to 64 percent and 5 to 80 percent, respectively. Since the OH radical reaction occurs in the gas phase with the nitro-products condensing on the particle phase, the amount of PAH available for reaction is important.

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Figure 2-6. Mass Chromatograms of the Molecular Ion of the Nitrofluorantheses (NF) and Nitropyrenes (NP) Formed from the Gas-Phase Reaction of Fluoranthene and Pyrene with the OH Radicals (Top) and Present in Ambient Particulate Sample Collected at Torrance, California (Bottom).

Therefore, atmospheric transformations leading to the formation of secondary aerosol from gasphase primary organic emissions may be very significant in some areas, particularly during the summertime.

PETROLEUM INDUSTRY COMBUSTION SOURCES

Fired equipment used within the petroleum industry includes a variety of designs depending on the application. Combustion devices are used in both "upstream" (oil exploration and production) and "downstream" (refining, transportation and marketing) operations. Table 2-4 shows an estimate of fine carbonaceous aerosol emissions from major sources within a heavily urbanized area surrounding Los Angeles (Hildemann *et al.*, 1994b). Emissions from natural and refinery gas combustion, petroleum industrial processes, and coke calciners comprise a minor but significant fraction of total 1982 organic aerosol emissions.

Table 2-5 provides a partial list of stationary equipment included in an emissions database for petroleum industry combustion devices (Hansell, 1997). The table does not include all possible air pollution control equipment combinations for each type of combustion device, but does serve to illustrate the variety of equipment and configurations employed within the industry. Only a small fraction of the fired equipment within the U.S. industry is believed to utilize liquid or solid fuels - the vast majority is fired on natural gas or a variety of process gases. Catalytic cracking units, catalytic reforming units, fluid cokers and sulfur recovery units are not strictly defined as fired equipment, but are included in the table since combustion is an integral part of the process leading to air emissions.

Results of direct measurements of organic aerosol emissions from petroleum industry combustion devices are limited. Table 2-6 shows a summary of emissions from oil-fired utility boilers and industrial size watertube boilers, which are roughly similar to boiler designs that would be found at petroleum industry sites. There are limited data available on emissions of other relevant substances which may be precursors to ambient aerosols, such as NO_x , SO_2 , ammonia, VOCs and semivolatile organic compounds (SVOCs). Particulate emissions and particle size data from non-fired petroleum industry processes were reviewed in an earlier study for API (Harris *et al.*, 1982). The data were obtained using EPA Method 5 and in-stack cascade impactors; therefore, total primary particulate emissions are probably underestimated because condensable particles that form after dilution in the plume were not measured. Also shown in Table 2-7 are rough estimates of

Eine gerogal	% of total	Contemporary The of	Notes
carbon emitted	emissions	C used in model ^b	INDIES
(ko/dav) ⁴	CHIIOSICHIS		
(16/04/)	17.3	99.5	
4938	1,10		e.f
1576			e.f.g
	14.4	2.6	- <u></u>
2800			e,f
2635			<u> </u>
5113	16.3	49.2	е
	12.2		
3690		100.5	e,f
891		84.2	e,f
	10.9	0.5	
2343			e,f
1744	i		
1433	3.8		h
	3.4	5.7	
1132			e,f
143	L	<u></u>	
933	2.5		i
900	2.4	2.6	j
857	2.3	51.2	е
808	2.1	100.2	e,f
736	2.0		h
590	1.6	14.5	е
556	1.5	1.7	e
424	1.1		h
394	1.0	1.9	k
	<u> </u>		e,f
32			~
262	<u> </u>		l
278	0.7		h
257	0.7	1.9	k
239	0.6		h
228	0.6		h
212	0.6		h
195	0.5		h
180	0.5	2.6	i
167	0.4		h
	0.4	1.9	
89		A12	e.f
55		1	0
		4	•
825	2.2	<u> </u>	h
	Fine aerosol carbon emitted (kg/day) ^a 4938 1576 2800 2635 5113 3690 891 2343 1744 1433 1132 143 933 900 857 808 736 590 556 424 394 32 262 278 257 239 228 212 195 180 167 89	Fine aerosol carbon emitted $(kg/day)^a$ % of total emissions4938 157617.34938 157614.42800 263514.42800 263512.23690 89110.92343 174410.92343 17443.8933 9332.5900 5902.4857 2.32.3808 552.1736 2.02.0590 50 1.61.5424 2.111.1394 2.62 2.78 2.77 2.57 2.570.7239 2.62 2.78 2.750.6212 0.60.6195 0.50.5180 0.40.489 550.4	$\begin{array}{c c} \hline Fine aerosol carbon emitted (kg/day)^{o'} & \hline C used in modelb C used in mod$

Table 2-4. Apportionment of Carbonaceous Aerosols in South Coast Air Basi	Table 2-4.	Apportionment of	Carbonaceous	Aerosols in South	n Coast Air Basi
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^aAnnual average emissions stated at a daily rate; includes both elemental and organic carbon. ^bTo allow comparison with ambient measurements, contemporary carbon fractions used in model assume that all contemporary carbon was accumulated in 1982; hence, the woodsmoke values differ from those in Table 1. ^cExcept where otherwise noted, values are based on literature survey (6,43). ^dWhile original inventory only considered commercial charbroiling, revised mass emission rates include domestic and commercial frying and charbroiling. ^cFraction of total carbon in fine emissions revised based on the source tests of Hildemann *et al.* (7). ^JFine mass emission rate revised based on the source tests of Hildemann *et al.* (7). ^sNew emission source not included in original inventory. ^hCarbon isotope composition is uncertain. ⁱIntermittant source not included in model due to lack of contributions during the ambient periods sampled in 1982. ^jAssumed to have a carbon isotope composition like that of the heavy-duty diesel truck emissions sample. ^kAssumed to have a carbon isotope composition like that of the distillate oil-fired boiler emissions sample.

Combustion Device	Combustibles	Air Pollution Controls
Asphalt Blowing	Asphalt fumes	Thermal Oxidizer
Boiler	No. 6 fuel oil	None
Boiler	Refinery gas	None
Boiler	Refinery gas	SCR
Catalytic Reforming Unit Regenerator	Petroleum Coke	Caustic spray
CO Boiler	Refinery gas/Off gas	(See FCCU)
Coke Calcining Kiln	Natural gas	Spray Drier/Fabric Filter
Coker, Delayed	?	?
Coker, Fluid	?	?
Flares	Waste gas	None
Fluid Catalytic Cracking Unit Regenerator	Petroleum Coke	Cyclone/CO Boiler/ESP
Fluid Catalytic Cracking Unit Regenerator	Petroleum Coke	Cyclone/ESP
Fluid Catalytic Cracking Unit Regenerator	Petroleum Coke	Cyclone/CO
		Boiler/Scrubber
Gas turbine	Natural gas	None
Gas turbine	Natural gas	SCR
Gas turbine, combined cycle	Natural gas	SCR
Gas turbine, combined cycle	Natural/LP/Refinery	SCR
	gas	
Gas turbine, combined cycle	Natural/Refinery gas	SCR
Gas turbine, combined cycle	Refinery gas	None
Heater	Natural gas	None
Heater	Natural/Refinery gas	None
Heater	Pipeline oil	None
Heater	Refinery gas	Thermal DeNOx
Heater	Refinery gas	None
Heater	Refinery gas	SCR
Heater	Refinery gas	Low-NOx Burners
Heater	Refinery gas	Low-NOx Burners/SCR
Moving Bed Catalytic Cracking Unit	Petroleum Coke	
Regenerator		
Reciprocating ICE, Diesel	Diesel Oil	None
Reciprocating ICE, Diesel	Field gas	None
Reciprocating ICE, Diesel	Natural gas	None
SRU Tail Gas Incinerator	Waste gas	None
Steam Generator	Crude oil	None
Steam Generator	Crude oil	Scrubber
Steam Generator	Natural gas	None
Steam Generator	Natural gas/casing vent	None
	gas	
Thermal Oxidizer	Refinery gas/water	None
	treatment vent gas	
Thermal Oxidizer	Fuel/gasoline vapors	None
Glycol Dehydrator - vent	Ethylene glycol	None
Glycol Dehydrator - vent	Triethylene glycol	None

Table 2-5. Petroleum Industry Stationary Combustion Devices.

Boiler Function	Fuel Type	Burn Conditions	PM _{2.5} ^a (lb/MMBtu)	PM ₁₀ ^a (lb/MMBtu)	Total Filterable Particulate (lb/MMBtu)
Industrial	No. 2 Oil	Baseline Low NOx	0.034 (40%) 0.0234 (35%)	0.034 (40%) 0.0268 (40%)	0.084 0.0670
Industrial	No. 6 Oil	Baseline Low NOx	0.0282 (50%) 0.0039 (40%)	0.0197 (35%) 0.0039 (40%)	0.0564 0.0097

Table 2-6. Summary of Particulate Emissions from Oil-Fired Boilers.

(Derived from Carter et al., 1978)

^aPM_{2.5} and PM₁₀ percentages estimated from reported particle size distributions.

Boiler Function	Fuel Type	Total Filterable Particulate ^b	H_2SO_4	Organic C (lb/MMBtu)	Elemental C (lb/MMBtu)	Total Carbon (lb/MMBtu)
I unotion		(lb/MMBtu)	(lb/MMBtu)	(10/11/12/02)	(10/1/1/10/00)	(10/11/12/12)
Heating	No. 4 Oil	0.025	0.007	3.7E-4	2.1E-3	2.5E-3
	(S=	0.019	0.006	2.2E-4	1.1E-3	1.3E-3
	0.28%)	0.018	0.007	3.3E-4	1.8E-3	2.1E-3
		0.021	0.007	1.7 E -4	1.9E-3	2.1E-3
		0.018	0.006	1.9E-4	3.4E-3	3.6E-3
Utility	No. 6 Oil	0.059	0.005	1.0E-3	2.3E-2	2.4E-2
-	(S=	0.044	0.006	1.0E-3	1.3E-2	1.3E-2
	0.51%)	0.102	0.008	1.3E-3	4.7E-2	4.8E-2
Heating	No. 6 Oil	0.049	0.016	4.1E-4	8.5E-4	1.3E-3
	(S=	0.038	0.027	3.2E-4	2.0E-4	5.1E-4
	0.45%)	0.064	0.044	2.5E-4	1.1E-4	3.6E-4
Utility	No. 6 Oil	0.043	0.010	2.1E-4	1.2E-4	3.3E-4
	(S=	0.028	0.009	1.4E-5	2.6E-5	1.6E-4
	0.53%)	0.030	0.011	2.4E-4	1.1E-4	3.5E-4
Heating	No. 6 Oil	0.069	0.007	1.6E-4	1.8E-3	1.9E-3
Ĭ	(S=	0.027	0.007	9.6E-5	7.9E-4	8.9E-4
	0.57%)	0.025	0.008	8.0E-5	2.0E-4	2.8E-4
	ŕ	0.033	0.010	6.0E-5	3.5E-5	9.5E-5

(Derived from Miller, 1985)

^bAll data are approximate.

primary PM10 and PM2.5 emissions obtained by applying particle size distributions to the total mean particulate mass emissions. Note, there is considerable uncertainty to these estimates; however, the results illustrate that a large fraction — often more than half — of the filterable primary particles are PM2.5.

Recently, the Western States Petroleum Association (WSPA) summarized total particulate and PM10 emissions from several fluidized catalytic cracking units (FCCUs) of differing capacity. Note, the measurements reported in the study include only particulate matter that is filterable at stack (hot) conditions. Particulate emissions from FCCUs stem primarily from catalyst fines

Device	Particulate	Emissions	PM ₁₀	PM _{2.5}
	Range (lb/1000	Mean	· · · · · ·	
	bbl feed)	(lb/1000 bbl	'	(
	<u> </u>	feed)	<u> </u>	!
FCCU with internal cyclones	16.8-1440	303	212	121
FCCU with external cyclones	b	10.3	8.4	4.0
FCCU with CO boiler	10.8-657	245		167
FCCU with ESP	4.1-96.9	47.5	35	27
FCCU with ESP and CO boiler	9.1-150	29.9	108	87
FCCU with CO boiler and scrubber	8.4-10	9.1	8.0	5.8
FCCU with full combustion and SO2 absorbing		43.7		
catalyst	L]	L/	L!	l
Thermofor CCU with no controls		17		-
Thermofor CCU with cyclones	-	18.3	-	
Thermofor CCU with CO boiler		15		
Moving bed CCU		17	<u> </u>	
Fluid coking with internal cyclones	437-523	494	435	222
Fluid coking with scrubber and CO boiler		153	135	69
Fluid coking with ESP and CO boiler	- 1	6.85	6.0	3.1

Table 2-7. Particulate Emissions and Particle Size Data for Selected Non-Fired Refinery Air Emission Sources.^a

^aDerived from Harris et al., 1982.

^b -- Indicates no data available.

entrained in the exhaust gas from the catalyst regenerator, plus condensable particles arising from NH₃ and SO₃ and organics. PM10 comprises the major fraction of total filterable (at stack conditions) particulate emissions from FCCUs - 67 to 88 percent - and varies substantially from refinery to refinery on a mass basis (Table 2-8, Wilkness, 1997). It should be noted that all of the units represented in Table 2-8 are in California and are equipped with high-efficiency particulate emission control devices to meet particulate emission standards which are generally more stringent than for those in other states. Also, since primary particles that form in the plume after emission are excluded, primary PM10 is probably greater than these data suggest.

1 able 2-8. Total Filterable Particulate and Pivin Emissions from FUCUS in Sou
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Refinery	Total Filterat	ole Particulate	Filterabl	e PM ₁₀ ^b
	lb/hr ^a	lb/hr ⁶	lb/hr	%
A	5.54	6.73	4.59	68
В	6.61	7.11	6.2	87
С	5.42	5.8	5.13	88
D	12.95	16.06	10.79	67
E	4.72	4.14	3.58	86

All data are averages of three valid test runs.

^aSouth Coast Air Quality Management District Method 5.2, including probe and filter catch only. Similar to EPA Method 5.

^bEPA Method 201A. Cyclone catch added for total filterable particulate.

Gas-fired sources are seldom tested for particulate emissions because particulate emissions are extremely low and there is typically no regulatory requirement. Table 2-9 presents PM10 emissions results from several boilers and gas turbines firing distillate (No. 2) oil and gas obtained using EPA Methods 201A and 202 (Corio and Sherwell, 1997). Method 201A employs an instack cyclone and filter; Method 202 employs impingers in an ice bath following the Method 201A filter. The condensable (impinger) fraction comprises a significant fraction of total PM10 emissions, and in the case of all but one gas combustion test is greater than the filterable fraction.

		the second s	¥	
Unit Type	Fuel	PM ₁₀ Emissions (lb/hr)		Back Half Percent of Total
		Front Half	Back Half	
Boiler	Gas	0.26	0.31	54
Boiler	No. 2 Oil	0.62	0.63	50
Turbine	Gas	0.22	1.32	86
Turbine	No. 2 Oil	6.05	7.92	57
Turbine	Gas	0.51	1.05	67
Turbine	No. 2 Oil	5.71	9.48	62
Boiler	No. 2 Oil	0.75	1.74ª	70
Boiler	No. 2 Oil	1.04	0.49	32
Turbine	Gas	5.24	4.29 ^b	45
Turbine	Gas	0.56	4.31°	89
Turbine	Gas	0.54	4.63 ^d	90
Turbine	Gas	0.58	4.23°	88
Turbine	Gas	0.15	0.46	75

Table 2-9	FPA Method	201 A/202 Result	s for Oil- and	Gas-Burning	Boilers and Turbines
$I = A \cup I \subset Z^+ Z$.		ZVI AZUZ RESUI	S 101 OH- and	i Gas-Dunning	Doneis and Futomes.

Based on two runs only

^bSteam on, heat recovery steam generator (HRSG) on

Steam off, HRSG off

^dSteam on, HRSG on

Steam off, HRSG on

(Corio and Sherwell, 1997)

Semivolatile organic compounds are believed to be key contributors to secondary and condensable primary aerosols. Existing data for emissions of SVOCs from petroleum industry sources are generally limited to PAH emissions data, obtained primarily from testing of sources in California. PAH are usually defined as a subset of 16 to 19 substances for which source test methods are validated. Emissions of PAH plus a small number of other SVOCs, expressed as polycyclic organic matter (POM), are summarized in Figure 2-7 for selected petroleum industry sources (Hansell, 1997). Note, the range of emissions indicated on the figure is not necessarily representative of the entire population of such devices, since the results include anywhere from one to several sources. The figure shows that reciprocating IC engines have the highest average POM emissions, on the order of 0.1 lb per million Btu of gas fired, with asphalt blowing (one unit) a close second. POM emissions from several boilers, process heaters, gas turbines, and one coke calciner are approximately an order of magnitude lower.

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Total POM Emissions

Figure 2-7. Emissions of POM from Selected Petroleum Industry Combustion Devices (Hansell, 1997).

Section 3 AMBIENT AIR SAMPLING AND ANALYSIS METHODS

Most methods of organic aerosol source emission measurement involve diluting the stack gas and subsequently sampling the diluted gas using ambient air methods. Therefore, a brief review of ambient air measurement methodologies is provided in this section. For a more detailed discussion see Chow (1995), Watson and Chow (1994), Zielinska and Fujita (1994), and references therein.

AMBIENT PARTICULATE SAMPLING METHODS

Aerosol samples are most often acquired by drawing ambient air through filter material using a pump, with subsequent quantification of particle mass and its chemical components by off-site laboratory analysis. Although this is by no means the only option, it is the most highly developed measurement principle, and the only one that is currently applicable to the quantification of a wide variety of chemical components in suspended particles. When the filter is impregnated with an absorbing solution, or when the filter material has specific gas-absorbing properties, quantitative measures of gases as well as particle phases are possible.

The particle sampling systems that have achieved U.S. EPA reference or equivalence status for PM10 compliance monitoring involve sampling onto filter media (Code of Federal Regulations, 1988). Reference methods require equilibration and weighing of the filter in a laboratory, while equivalent methods allow the in situ determination of particle mass by beta-ray attenuation or by an inertial microbalance (Chow, 1995). A more detailed examination of the specifications for reference or equivalence designation shows that the relevant variables in sampler design are: 1) properties of the size-selective inlet and sampler surfaces; 2) filter media and filter holders; and 3) flow movement and control. Several options are available for measuring each of these variables.

Size-Selective Inlets

Size-selective inlets define the particle size fraction being sampled. Air is drawn through these inlets to remove particles that exceed a specified aerodynamic diameter prior to exposure of the filter to the air stream. Inlets are characterized by sampling effectiveness curves that show the fraction of spherical particles of unit density which penetrate the inlet as a function of their aerodynamic diameters. Sampling effectiveness curves are summarized by their 50 percent cutpoints (d_{50} , the diameter at which half of the particles pass through the inlet and the other half are deposited in the inlet), and by their slopes (the square root of the particle diameter ratios for inlet

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penetrations at 16 percent and 84 percent, $[d_{16}/d_{84}]^{0.5}$). These curves are determined by presenting particles of known diameter to the inlet and measuring the concentrations before and after passage through the inlet. The principles of operation for different size-selective inlets include direct impaction, virtual impaction, cyclonic flow, selective filtration, and elutriation (Chow, 1995). Impaction inlets consist of a set of circular or rectangular jets positioned above an impaction plate. The impactor dimensions are chosen such that particles smaller than the desired cut-point follow the streamlines as they bend at the impaction plate, while the larger particles with sufficient inertia depart from the streamlines and impact against the plate. The virtual impactor operates on a similar principle, with the exception that the impaction surface is replaced by an opening which directs the larger particles to one sampling substrate while the smaller particles follow the streamlines to another substrate. Cyclones employ tangential inlets which impart a circular motion to the gas, resulting in a centripetal force on the particles that moves them toward the walls. Those particles reaching the tube wall either adhere to it, often with the help of an oil or grease coating, or drop into a "hopper" at the bottom of the collection device. Selective filtration uses the uniform pore size and known sampling effectiveness of etched polycarbonate filters manufactured by Corning CoStar (formerly Nuclepore Corporation) to collect large particles on a pre-filter and pass smaller particles to a backup filter. Elutriator inlets draw air into a stilled-air chamber surrounding an open duct which leads to the filter. When the upward velocity due to flow through the inlet exceeds the particle settling velocity, that particle penetrates the inlet. When the settling velocity exceeds the upward velocity, the particle is not transmitted.

Denuders are often used as part of, or immediately behind, size-selective inlets to remove gases that might interfere with the aerosol measurement, or to quantify the concentrations of gases that are precursors to secondary aerosols (Chow, 1995, and references therein). Denuders take advantage of the fact that gas molecules diffuse through air much more rapidly than small particles. Denuder surfaces are made of or coated with substances that absorb the gases of interest. When properly coated, the denuder surfaces can be washed and the solvent analyzed for the absorbed gases. Denuder geometries can be rectangular, cylindrical, or annular; the annular designs provide the highest gas collection efficiency so their lengths can be minimized. When the walls of the denuder are coated with substances that absorb the gases, the denuders can be washed and the extract can be submitted for chemical analysis. This method is often used to measure nitric acid, sulfur dioxide, and ammonia gases along with suspended particles. These gases are common precursors to secondary sulfate and nitrate compounds.

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Filter Media and Filter Holders

Particle sampling filters consist of a tightly woven fibrous mat or of a plastic membrane that has been penetrated by microscopic pores. No single filter medium is appropriate for all desired analyses, and it is often necessary to sample on multiple substrates when chemical characterization is desired. Several characteristics are important to the selection of filter media for compliance measurements. They are:

- Particle sampling efficiency: filters should remove more than 99 percent of suspended particles drawn through them, regardless of particle size or flow rate.
- Mechanical stability: filters should lie flat in the sampler, remain in one piece, and provide a good seal with the sampling system to eliminate leaks; a brittle filter material may flake and negatively bias mass measurements.
- Chemical stability: filters should not chemically react with the deposit, even when submitted to strong extraction solvents, and they should not absorb gases that are not intended to be collected.
- Temperature stability: filters should retain their porosity and structure in the presence of temperatures typical of the sampled airstream and of the analysis methods.
- Blank concentrations: filters should not contain significant and highly variable concentrations of the chemicals which are being sought by analysis (each batch of the unexposed filters should be examined for blank concentration levels prior to field sampling).
- Flow resistance and loading capacity: filters should allow sufficient amounts of air to be drawn through them to satisfy the flow rate requirements of the inlet and to obtain an adequate deposit.
- Cost and availability: filters should be consistently manufactured and available at reasonable cost.

Filters require representative chemical analyses, or "acceptance testing," when the deposits they acquire are intended for chemical characterization. In addition, some filters require pre-treatment before sampling. Quartz-fiber filters can be baked at high temperatures (greater than 500 °C) prior to acceptance testing to remove adsorbed organic vapors. Nylon-membrane filters, used to collect nitric acid and total particulate nitrate, absorb nitric acid over time and need to be tested and/or cleaned prior to use. Filters intended for organic compound analyses need to be cleaned by extraction with proper solvents.

Cellulose-fiber and quartz-fiber filters can be soaked in solutions of gas-absorbing chemicals prior to sampling to collect HNO_3 , NH_3 , SO_2 , and NO_2 (Chow, 1995 and references therein). Sulfuric acid, oxalic acid, phosphoric acid, sodium carbonate, and citric acid have been used as active agents in the sampling of ammonia. Potassium carbonate and sodium carbonate with glycerin impregnating solutions have been used for collecting sulfur dioxide, nitric acid, and organic acids. The carbonate in the impregnating solution presents interferences to certain analytical techniques. Sodium chloride solutions have been used for nitric acid collection. Triethanolamine (TEA) has been used as an absorbent for NO_2 . The TEA is usually mixed with glycol or glycerin to improve its absorbing capacity.

To minimize contamination, filters can be loaded into and unloaded from filter holders in a clean laboratory environment rather than in the field.

Flow Measurement, Control, and Movement

As noted above, size-selective inlets require flow rates to be held within close tolerances in order to maintain the desired cut-point. While manual flow control is adequate when filters do not load appreciably, most modern sampling devices use some form of feedback to adjust the pressure drop or pump speed to compensate for increasing flow resistance during sampling. Volumetric and mass flow controls and critical orifices are commonly used as flow control devices (Chow, 1995 and references therein). Pump capacities and power requirements must be matched to the flow resistance of the filters, the flow control method, inlet flow rate requirements, and available power.

FILTER ANALYSIS METHODS

<u>Mass</u>

Gravimetric analysis is used almost exclusively to obtain mass measurements of filters in a laboratory environment. Gravimetry determines the net mass by weighing the filter before and after sampling with a balance in a temperature- and relative-humidity-controlled environment. The main interference in gravimetric analysis of filters results from electrostatic charges, which induce non-gravimetric forces between the filter and the balance. The charge can be removed from most filter material by exposure to a low-level radioactive source prior to and during weighing. Accurate gravimetric analyses require the use of filters with low dielectric constants, high filter integrity, and inertness with respect to absorbing water vapor and other gases. Equilibration at low temperatures and relative humidities effectively removes liquid water associated with the particle

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deposit, but some particles may volatilize if they are exposed to ambient air for more than a day or two. While balances with ± 100 mg sensitivities are adequate for high-volume samples, special electro-balances with sensitivities as low as $\pm 1 \mu g$ are needed for medium- and low-volume samples. These sensitive balances require isolation from vibration and air currents. Balances placed in laminar flow hoods with filtered air minimize contamination of filters from particles and gases in laboratory air. Ammonia produced by human breathing and cleaning solvents can neutralize acidic species that might have been captured on the filters. Equilibration temperatures and relative humidities should be kept at the low end of the 15 to 30 °C and 20 to 45 percent ranges in the PM10 performance standard to minimize volatilization and aerosol liquid water biases (Chow, 1995 and references therein).

Elements

X-Ray fluorescence (XRF) and proton induced x-ray emission (PIXE) spectroscopy quantify the concentrations of elements with atomic numbers ranging from 11 (sodium) to 92 (uranium). In addition to providing a large number of chemical concentrations, neither XRF nor PIXE requires sample preparation or extensive operator time after it is loaded into the analyzer. Filters remain intact after analysis and can be used for additional analyses by other methods. Inductively coupled plasma (ICP) and instrumental neutron activation analysis (INAA) are not as commonly applied to aerosol samples as XRF and PIXE owing to their greater expense. ICP requires destruction of the filter, and INAA wads up the filter and makes it radioactive. These analyses are useful in certain applications owing to lower detection limits for some species used in source apportionment studies. Atomic absorption spectrophotometry (AAS) is useful for a few elements, but it requires too great a dilution of the sample to be an effective technique when many different elements are to be measured (Chow, 1995 and references therein).

<u>Ions</u>

Ionic species are those that are soluble in water. Ions are important constituents of secondary aerosol and can often be used to distinguish among pollution sources, as in the case of soluble potassium for wood smoke. Several simple ions, such as sodium, magnesium, potassium, and calcium, are best quantified by AAS. Polyatomic ions, such as sulfate, nitrate, ammonium, and phosphate, must be quantified by other methods such as ion chromatography (IC) and automated colorimetry (AC). Simple ions, such as chloride, may also be measured by these methods along with the polyatomic ions. Some of these methods can be adapted to separately quantify metal ions with different valence states, such as iron and chromium, that may have distinct effects on human

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health. When the aerosol deposit is suspected of being acidic, its hydrogen ion content can be determined by a pH electrode or by microtitration (Chow, 1995 and references therein).

Carbon Measurements

Three classes of carbon are commonly measured in aerosol samples collected on quartz fiber filters: 1) organic, volatilized, or non-light absorbing carbon; 2) elemental or light-absorbing carbon; and 3) carbonate carbon. Carbonate carbon (e.g., K_2CO_3 , Na_2CO_3 , $MgCO_3$, $CaCO_3$) can be determined on a separate filter section by measurement of the carbon dioxide (CO₂) evolved upon acidification (Chow, 1995 and references therein).

Many methods have been applied to the separation of organic and elemental carbon in ambient and source particulate samples. Comparisons among the results of the majority of these methods show that they yield comparable quantities of total carbon in aerosol samples, but the distinctions between organic and elemental carbon are quite different (Chow, 1995 and references therein). "Organic carbon" and "elemental carbon" are operational definitions rather than fundamental chemical quantities. "Elemental carbon" generally refers to particles that appear black and are also called "soot," "graphitic carbon" or "black carbon." Chow *et al.* (1993) documented several variations of thermal (T), thermal/optical reflectance (TOR), thermal/optical transmission (TOT), and thermal manganese oxidation (TMO) methods for organic and elemental carbon. The TOR and TMO methods have been most commonly applied in aerosol studies in the United States.

Speciated Organic Compounds

The most common method used for analysis of particulate matter collected on filters for speciated organic compounds is the extraction of a filter with a suitable organic solvent (or combination of solvents), followed by the analysis of the extract by gas chromatography (GC) combined with mass spectrometry (MS) or with other specific detectors. Combined GC/Fourier transform infrared (FTIR)/MS techniques or high performance liquid chromatography (HPLC)/MS techniques are also used.

Direct chemical analysis of the entire extractable fraction of particulate matter is not always possible because a large number of compounds of different polarity is present. The separation of particulate organic matter (POM) into various fractions according to chemical functionalities is a common preliminary step to chemical identification of individual compounds. Open-column liquid chromatography (LC) and liquid-liquid separation procedures have been the most widely

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used fractionation methods (Lee and Schuetzle, 1983). Open-column LC is very often followed by normal-phase HPLC, if the identification of less abundant components is required.

ORGANIC GAS SAMPLING AND ANALYSIS METHODS

Organic gases are emitted from many naturally occurring biogenic and geogenic sources, as well as from anthropogenic sources, such as petroleum refining, oil and gas production, agricultural burning, industrial processes, and motor vehicles. Most of these compounds are highly reactive in the atmosphere: some undergo chemical transformations in the troposphere, contributing to ozone and organic aerosol formation; some are transported into the stratosphere and contribute to the destruction of the ozone layer; many are toxic to living organisms. Organic compounds exhibit a wide range of volatility and are hence distributed in the atmosphere between the gas and particle phases. Compounds having a saturated vapor pressure at 25 °C of greater than 10⁻¹ mm Hg are generally classified as VOC (U.S. EPA, 1988) and are present entirely in the gas phase. Compounds with a saturated vapor pressure at 25 °C of less than 10⁻⁷ mm Hg are generally called SVOC (U.S. EPA, 1988) and are distributed between the gas and particle phases. Compounds having a saturated vapor pressure at 25 °C of less than 10⁻⁷ mm Hg are generally called SVOC (U.S. EPA, 1988) and are distributed between the gas and particle phases. Compounds having a saturated vapor pressure at 25 °C of less than 10⁻⁷ mm Hg are nonvolatile and are predominantly adsorbed on particles (U.S. EPA, 1988). Different sampling techniques are required for the quantitative collection of VOC, SVOC, and nonvolatile organics.

Methods for organic gas sampling include collection of whole air or preconcentration of samples on chemically selective and nonselective adsorbents (Rudolph *et al.*, 1990). Each sampling methodology includes the following steps: 1) selection and preparation of sampling media; 2) the actual sampling process; and 3) the transport and storage of the collected samples. The selection of the optimal sampling method for target compounds (or a class of compounds) depends greatly on the physicochemical nature of these compounds and their expected concentrations in air — sample volumes must be compatible with the sensitivity of the analysis method, and the expected behavior of the targeted compounds during each step of the sampling process must be carefully considered.

Whole-Air Sampling

Sampling of whole air with containers of defined volume has been successfully employed for volatile compounds of low polarity. This method has two main limitations: 1) the sample volume is limited to a few liters which, for low compound concentrations encountered in ambient air, may be insufficient for analysis purposes; and 2) sample stability during storage is sometimes in doubt due to adsorption on (or desorption from) container walls and chemical reactions between

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compounds. However, the recent development of very sensitive analytical methods for organic compound analysis (for example, ion trap GC/MS) and more information available on the stability of major classes of volatile organic compounds in stainless steel canisters have made this method of sampling very popular (Zielinska and Fujita, 1994, and references therein). Containers typically used for VOC collection in whole air include flexible plastic bags (such as Teflon[®], Tedlar[®], Mylar[®], etc.), glass bulbs, stainless steel SUMMA[®] canisters, and glass-lined SUMMA[®] canisters.

Stainless steel canisters as sample containment vessels offer several advantages over other containers for whole-air sampling. The interior surfaces of the canisters are conditioned by the SUMMA[®] process, a proprietary treatment that passivates the internal surfaces of the canister to minimize surface reactivity. This process allows stable storage for many of the compounds of interest. The canisters can be used repeatedly for many years, however their thorough cleaning prior to sampling is essential. The U.S. EPA recommended method of canister cleaning (EPA Method TO-14 and the EPA document "Technical Assistance Document for Sampling and Analysis of Ozone Precursors," [U.S. EPA, 1991]) involves repeated evacuation and pressurization of canisters with humidified zero air.

A variety of sampling systems are employed for whole-air ambient VOC collection (Zielinska and Fujita, 1994, and references therein). Selection of the sampling device is dictated by the ultimate sampling goals. If only a "grab sample" is needed, no sampling device is necessary for stainless steel canisters. Since canisters are shipped to the field under a vacuum, a grab sample can be obtained by manually opening the canister valve. In most cases whole-air samples are integrated over a specific period of time, and an automated mode of operation is required. In this case ambient air is drawn into a sampling train that consists of an evacuated canister and upstream components that serve to regulate the rates and duration of air sampling. In the simplest design, the differential pressure between the atmosphere and the evacuated canister causes flow into the system. A mass flow controller or a critical orifice placed in-line regulates the flow rate. This system is sometimes called subatmospheric sampling (EPA Method TO-14), since the canister pressure after sampling is below or at atmospheric pressure. The most common method of canister sampling is pressurized sampling, i.e., collection of a whole-air sample in a canister with the aid of a pump regulated by a mechanical or electronic flow controller to achieve a final canister pressure above atmospheric pressure. In both the subatmospheric and pressurized systems the

flow rate and sample duration must be matched in order to maintain constant flow during the sampling period.

The whole air samples are typically analyzed for VOC using high resolution capillary gas chromatography with flame ionization detector and electron capture detector (GC/FID/ECD) or mass spectrometric detector (GC/MS) after cryogenic sample concentration in a freeze-out loop packed with deactivated glass beads. A sample aliquot (100-1000 ml) is transferred from the canister to an evacuated vessel of known volume through a loop immersed in liquid oxygen or argon. The exact sample volume is determined from the pressure change of the vessel, using the Ideal Gas Law. The trap is then flash-heated with hot (approximately 95 °C) water and switched via a rotary valve to transfer the condensed non-methane hydrogen compounds (NMHC) into the gas chromatograph for analysis. The detection limit for the canister sampling method is generally in the range of 0.1-1 ppbv. Alternatively, a preconcentration system, composed of a series of solid adsorbent cartridges, is used for sample preconcentration.

Preconcentration Methods

Due to generally low concentrations of organic compounds in ambient air, one of the most widely used methods for sampling of gaseous constituents is their preconcentration either on a suitable solid adsorbent or, if the constituent is reactive, in an absorbing solution contained in a bubbler or impinger or coated on some solid porous support. Cryogenic concentration of VOC in an empty tube or a tube filled with glass beads and cooled by liquid oxygen or argon is also employed, especially in connection with gas chromatography by EPA Methods TO-3, TO-12, and TO-14 (U.S. EPA, 1988).

A number of solid adsorbents are available commercially (Zielinska and Fujita, 1994, and references therein). Porous polymers, such as Tenax-GC (or TA), XAD resins, and polyurethane foam, have found wide application in organic gas sampling (see, for example, EPA Methods TO-1 and TO-13). Tenax-GC (and recently Tenax-TA) is the most popular porous polymer sorbent, mainly because of its high thermal stability (up to 350 °C), and hence low bleed on thermal desorption (Brown and Purnell, 1979), and extremely low affinity to water vapor. The main disadvantages of Tenax-GC are its relatively poor capacity for more volatile compounds (i.e., those with boiling points [b.p.] less than 80 °C) and the possibility of chemical reactions occurring during sampling in the presence of some reactive gases and during thermal desorption (Pellizzari *et al.*, 1984; Walling *et al.*, 1986; Zielinska *et al.*, 1986). Other types of sorbents, such as various

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types of charcoal, carbon molecular sieves (e.g., Carbosieve and Carboxen offered by Supelco, Inc., or Carbosphere offered by Altech Associates, Inc.) and other carbon-based sorbents are also widely used, especially for more volatile, lower molecular weight compounds. However, due to their high surface activity, chemical reactions may occur during storage and desorption of the samples (Rudling *et al.*, 1986).

The selection of a proper adsorbent for a given application depends mainly on the following factors (Namiesnik, 1988): (1) the volume of an air sample which can be passed through the sorbent without breakthrough of the compounds of interest; (2) stability of target analytes on the sorbent during sampling, storage, and desorption; (3) any background signals due to the sorbent; (4) affinity of the sorbent for water; (5) efficiency of desorption of collected compounds; and (6) the enrichment factor.

All solid adsorbents must be cleaned prior to use. The cleaning procedure depends on the type of adsorbent. Carbon-based adsorbents require only heating under nitrogen flow for several hours at approximately 400 °C (EPA Method TO-2), whereas porous polymers are usually extracted with organic solvent(s) prior to heating. For example, Tenax-GC is cleaned by sequential Soxhlet extraction with methanol and n-pentane (EPA Method TO-1) or in a 6/4 (v/v) acetone/hexane mixture (Atkinson *et al.*, 1988) and then thermally conditioned for four hours by heating at 280 °C under a nitrogen purge. XAD resins and polyurethane foam have low thermal stability and cannot be conditioned thermally. They require complex cleaning procedures (Chuang *et al.*, 1987; Offerman *et al.*, 1990).

Solvent extraction or thermal desorption is used for solid adsorbent sample analysis. Thermal desorption is preferred over solvent extraction, since it avoids the dilution of an enriched sample with a solvent; it allows the entire amount of a collected sample to be injected at once into a gas chromatographic column, thus providing maximum sensitivity. The detection limit for the thermal desorption method depends on the volume of air sampled through a solid adsorbed cartridge; for approximately 40L it is generally in the range of 0.1-1 ppbv.

Selective Methods of Compound Preconcentration

The classical example of a selective preconcentration method for organic gas sampling is the collection of carbonyl compounds by their derivatization with 2,4 dinitrophenylhydrazine (DNPH). The acid-catalyzed derivatization of carbonyls proceeds by nucleophilic addition of the DNPH to a

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C=O bond, followed by 1,2-elimination of water to form 2,4-dinitrophenylhydrazone. The DNPH-hydrazones, formed during sampling, are non-volatile and remain on the sampling medium, which is usually either a reagent-impregnated cartridge or an impinger charged with the reagent solution. The yellow to deep-orange colored DNPH-hydrazones have ultra violet (UV) absorption maxima in the 360-375 nm range and can be analyzed by the HPLC method coupled with UV detection; this method offers very high selectivity and sensitivity of analysis. Another example of a selective preconcentration method for organic gas collection is the collection of gaseous organic acids by NaOH or Na_2CO_3 -coated filters or solid adsorbents (Zielinska and Fujita, 1994, and references therein).

Semi-Volatile Compounds

The distribution of SVOCs between the gas and particle phases is determined not only by the equilibrium vapor pressure of the individual species, but also by the amount and type of particulate matter present (how much adsorption surface is available), and by the temperature (Ligocki and Pankow, 1989). For example, the factor of approximately 10⁷ in the range of vapor pressures of PAH is reflected in the fact that, at equilibrium and ambient temperature, naphthalene exists almost entirely in the gas phase, while BaP, other five-ring PAH, and higher-ring PAH are predominantly adsorbed on particles. The intermediate three- and four-ring PAH are distributed between the two phases. However, the vapor pressures of these intermediate PAH can be significantly reduced by their adsorption on various types of surfaces. Because of this phenomenon, the amount and type of particulate matter present play an important role, together with temperature, in the gas-particle partitioning of SVOCs.

The partitioning of SVOC between gas and particle phases has received much attention (Ligocki and Pankow, 1989; Cotham and Bidleman, 1992; Lane *et al.*, 1992; Kaupp and Umlauf, 1992; Pankow, 1992). Most estimates of partitioning have relied on high volume (hivol) sampling, using a filter to collect particles followed by a solid adsorbent trap, such as polyurethane foam (PUF), Tenax, or XAD-2, to collect the gaseous portion of SVOC (c.f., Kaupp and Umlauf, 1992, and Foreman and Bidleman, 1990, and references therein). However, the pressure drop behind a hivol sampler or cascade impactor suggests the possibility of the occurrence of artifacts due to volatilization during the sampling process (Coutant *et al.*, 1988). Such volatilization (sometimes called blowoff) would cause the underestimation of the particle-phase concentrations of organics. On the other hand, adsorption of gaseous substances on deposited particles, or on the filter material itself, a process driven by the lowered vapor pressure over the sorbed material, would lead to

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overestimation of the particle-phase fraction (Bidleman *et al.*, 1986; Ligocki and Pankow, 1989; McDow and Huntzicker, 1990). It has been shown (Kaupp and Umlauf, 1992) that the hivol sampling approach, although not totally free from adsorption and desorption artifacts, produces reliable results. The maximum differences observed between hivol filter-solid adsorbent sampling and impactor sampling (the latter believed to be less susceptible to these sampling artifacts) did not exceed a factor of two.

There is good theoretical and experimental evidence that use of a diffusion denuder technique significantly improves measurements of gas-particle phase partitioning (Coutant *et al.*, 1988, 1989, 1992; Lane *et al.*, 1988). However, the reliability of presently existing denuders for investigation of atmospheric partitioning of nonpolar SVOC needs to be improved, as suggested by contradictions in published field data (c.f., Kaupp and Umlauf, 1992, and references therein). A new, improved sampler has been introduced (Gundel *et al.*, 1992) which uses a proprietary XAD-4-coated tube for vapor collection, followed by filter collection of organic aerosol particles and a sorbent bed to quantitatively retain desorbed (blownoff) organic vapors. Preliminary results from the use of this device look very promising for direct measurements of the phase distribution of semivolatile organic aerosol constituents.

The methods of analysis for SVOC are the same as those used for analysis of particulate matter collected on filters for speciated organic compounds, i.e., extraction with suitable organic solvent (or combination of solvents), followed by analysis of the extract by gas chromatography combined with mass spectrometry or with other specific detectors. The SVOC detection limit for a hivol sampling, using a filter followed by a solid adsobernt, and subsequent GC/MS analysis, is on the order of 0.1 ng/m³ for approximately 100 m³ of air sampled.

Section 4

TRADITIONAL STATIONARY SOURCE EMISSION MEASUREMENTS

Stationary source test methods are designed to characterize pollutants present in the exhaust gas at the point of emission to the atmosphere. While similar in many respects to ambient air methods, source-level sampling and analysis methods also have many differences, mainly to account for higher pollutant concentrations and interferences from background gases (e.g., combustion products) which are present at much higher concentrations than in ambient air samples.

Source level sampling (undiluted) for substances such as particulate and SVOCs may be included in the test program to characterize aerosol precursors, gain insight into organic aerosol formation, and/or develop surrogate monitoring parameters for aerosols. Partitioning of SVOCs into the aerosol and gaseous phases could be determined by comparing results of SVOC measurements made at the stack and in a dilution sampler. For example, simultaneous measurements of VOC and SVOC in diluted and undiluted samples from the stack of a coal-fired power plant (Sverdrup *et al.*, 1995) indicated possible enrichment of SVOC species between the stack and diluted sample; conversely, single-ring aromatic VOC compounds were depleted in the dilution samples compared to the stack. It is tempting to relate the depletion of these compounds to the enrichment of multiple ring SVOC compounds within the dilution process, despite the variability of the results. This result is unexpected but conceivable, particularly among the oxygenated, nitrated, and halogenated compounds. Given the presence of oxides of nitrogen, hydrogen chloride, hydrogen fluoride and the addition of excess oxygen, such results suggest a variety of gas phase and heterogeneous reactions may occur within the dilution chamber.

Table 4-1 lists commonly used source-level reference test methods for characterizing particulate, organic, metallic, ammonia, and other emissions relevant to this program. The test methods can be divided into two types according to sampling principle: manual sampling and continuous sampling. In manual sampling, a sample is extracted from the exhaust stack and collected in the sampling equipment, transported to a laboratory and subsequently analyzed in the lab. Test results may not be known for a period of time ranging from hours to weeks, depending on laboratory turnaround time. In continuous sampling, the sample is extracted and continuously fed to on-site analyzers, yielding real-time or near real-time results. Analytical principles cover the full spectrum of laboratory techniques, from simple gravimetric and titrimetric analysis to complex solvent extractions with tandem gas chromatography-mass spectrometry. In Table 4-1 only the reference tests for gases, labelled as continuous emissions monitors under the sampling principle heading, are continuous sampling methods. All other tests listed in Table 4-1 involve manual sampling.

4-1

Measurement Group	Sampling Principle	Reference	Analytical Principle	Reference
Particulate matter	Heated out-of-stack	EPA Method 5 ^b	Gravimetric	Ibid.
(filterable)	filter			
Particulate matter	Heated out-of-stack	EPA Method 5B ^b	Gravimetric	Ibid.
(filterable non-	filter			
sulfuric acid)				
Particulate matter	Heated out-of-stack	EPA Method 5F ^b	Gravimetric/IC	Ibid.
(filterable non-	filter/impingers			
sulfate)				
Particulate Matter	In-Stack Filter	EPA Method 17 ^b	Gravimetric	Ibid.
(Filterable)				
Particulate matter	Heated filter with	EPA Method 202 ^c	Methylene chloride	Ibid.
(condensable)	ice bath impinger		extraction with	
	collection		gravimetric analysis	
Formaldehyde,	DNPH impingers	EPA Method 0011 ^a	HPLCUV	Ibid.
acetaldehyde	(derivitization)			
NH3	Heated in-stack	EPA Method 206	IC	Ibid.
	filter with H ₂ SO ₄			
	impingers			
Volatile organic	Preconcentration	EPA Method 0031 ^a	Purge-And-Trap	EPA Methods 5041 ^a and
compounds	(Tenax [®])		HRGC/LRMS	8260ª
	Tedlar [®] Bag	EPA Method 0040 ^a	GC/MS	EPA Method 8240 ^a
			GC/FID (On-Site)	EPA Method 18°
Semivolatile organic	Preconcentration	EPA Method 0010 ^a	Solvent Extraction/	EPA Method 8270 ^a
compounds	(XAD-2) and H_2O		HRGC/LRMS	
	Impingers			
Trace metals	Heated out-of-stack	EPA Method 29 ^b		
	filter with		ICAP	EPA Method 6010 ^e
	HNO_3/H_2O_2 and		CVAAS	EPA Method 7470 and
	KMnO₄ impingers		GFAAS	7471°
				EPA Method 7000 Series
Particle size	Cascade impactor	EPA Method 201A ^c	Gravimetric	Ibid.
distribution (PM10				
and PM2.5)				
O ₂	Continuous	EPA Method 3A ^b	Paramagnetic	Ibid.
со	emissions monitors	EPA Method 10°	NDIR	
CO ₂		EPA Method 3A ^o	NDIK	
NO		EPA Method /E	NDUV	
SU ₂		EPA Method OC		
		EFA Mictiou 25A		Thid
Gas Flow Rate	S-Type Pitot Tube	EPA Method 1-3	Grovingstrig	
II Moisture	Condensation	EPA Memod 4	Gravimeuric	1010.

Table 4-1. Flue Gas Source Sampling and Analytical Methods.

^aTest Methods for Evaluating Solid Waste, Physical/Chemical Methods. EPA SW-846, Third Edition, 1986, as amended by Updates I (July, 1992), II (September, 1994), IIA (August, 1993), and IIB (January, 1995). ^bAppendix A, Part 60, Code of Federal Regulations, Title 40. ^cAppendix M, Part 51, Code of Federal Regulations, Title 40.

PARTICULATE EMISSIONS

The specific test method selected for measuring particulate source emissions can have a strong effect on the test results. Filterable particulate matter and condensable particulate matter form the two basic definitions of particulate. Using an in-stack filter according to EPA Method 17, particles which are solid or condensed at the stack temperature are captured on the filter (Method 17 was the first EPA reference test method developed, based on ASME test Method 17). The sample is extracted from the stack isokinetically to minimize over- or under-sampling of large particles that do not follow gas streamlines. The glass or quartz fiber filters typically have a minimum initial efficiency of 99.95 percent for 0.3 µm diameter dioctyl phthalate smoke particles; as a cake of particles accumulates on the filter during sampling, this efficiency probably increases and the diameter of particles passing through the filter decreases. Some of the stack gas constituents, such as SO₃, NH₃, HCl and Cl₂, may condense or react with each other and/or the filter materials at sampling temperatures. Therefore, the amount of particulate captured depends on the stack temperature, which itself may vary with process conditions and sampling location. EPA Method 5 employs a filter external to the stack heated to a constant temperature, typically 250°F, which allows particulate to be defined independent of the stack gas temperature. The EPA Method 5 sampling equipment is illustrated in Figure 4-1. The filterable particulate catch is determined by recovering the material deposited in the probe and any transfer lines upstream of the filter, in addition to the material trapped on the filter. The total filterable particulate mass is then determined gravimetrically. For some sources, filterable particulate may be further defined as non-sulfate and non-sulfuric acid by raising the filter temperature to 320°F to prevent acid condensation (EPA Method 5B), or by extracting the filterable particulate and analyzing it to determine sulfate content (EPA Method 5F).

"Condensable particulate" in stationary source air emissions is usually defined as the amount of material collected in a series of iced impingers downstream of an in-stack filter. This includes both fine particles which pass through the filter and gases which condense at the ice bath temperature. The simplest analytical procedure involves evaporating the impinger liquid after sampling and determining the mass of residue gravimetrically. This procedure may be subject to substantial artifacts that do not occur in atmospheric processes, especially for sources with ammonia and chlorides present in the sample. Some methods incorporate procedures which attempt to prevent such artifacts. For example, in EPA Method 202, the impinger solutions are purged with nitrogen immediately following sampling to minimize artifact reactions, and the impinger solutions are extracted with methylene chloride before being taken to dryness and weighed to determine condensable particulate mass. Impinger condensation methods neither completely eliminate

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Figure 4-1. EPA Method 5 Particulate Matter Sampling Train.

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artifacts nor accurately simulate the chemistry and physics of atmospheric plume dilution, typically leading to overestimation of particulate which condenses in the atmosphere and to changes in the particulate characteristics. In California's South Coast Air Quality Management District (SCAQMD) Method 5.1 sampling train, the stack gas is extracted isokinetically through an unheated nozzle and probe assembly, and is bubbled through a train of impingers immersed in an ice bath. A glass fiber filter is placed between the third and fourth impingers, after the collection of condensable particulate. Particulate captured by the filter is determined by desiccating then weighing the filter; the probe and impingers are recovered with dichloromethane and the organic and aqueous fractions separated, dried and weighed. Artifacts of this method may be more significant in some cases since now sulfates, nitrates and chlorides present on the particles captured in the liquid solutions may react in addition to those in the gas-phase. SCAQMD Method 5.2 employs a heated glass fiber filter upstream of an impinger train containing deionized water. Total particulate mass, determined gravimetrically, is defined as the sum of the mass collected from the probe, filter, washings and impingers after removal of uncombined water. It is clear from the variety of methods that "condensable particulate" may be defined in a number of different ways, none of which may represent the true contribution to ambient aerosols.

PARTICLE SIZE DISTRIBUTION AND PM10

Aerodynamic particle size distribution in stationary source emissions is usually determined using cyclone separators or cascade impactors. Cascade impactors can separate particles from approximately 0.005 µm (Fernandez de la Mora, 1990) to 50 µm (Vanderpool et al., 1987). Several different designs of cascade impactors are commonly used, depending on the application. Normally, in-stack impactors are used for source sampling to avoid artifacts due to particle losses and condensation/reaction described previously. Ex-situ cascade impactors such as the microorifice uniform deposit impactor (MOUDI) design are generally not used for this reason. The MOUDI is an eight-stage cascade impactor which collects ultrafine particles as small as 0.056 um uniformly over the surface of the impaction plate by rotating it relative to the nozzles during sampling (Marple et al., 1991). Brinks impactors are generally used when particle loading is moderately high. Brinks impactors are similar to virtual impactors, with a single jet impinging on a substrate in each stage. Andersen or University of Washington (Pilat) Mark III impactors are usually used for low particulate loadings. They employ multiple slots or jets, respectively, in each stage. In-stack cascade impactors typically have eight stages of size segregation from about 1 to 10 microns including a total backup filter. For very high particle loading, series cyclones are used for determining particle size distribution. These employ one to five cyclones of decreasing D50 arranged in series, followed by a backup filter. Both in-stack and out-of-stack designs are available commercially.

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PM10 emissions from stationary sources are usually determined using either cyclones or cascade impactors. EPA Method 201 employs an in-stack cyclone with a D_{50} of 10 µm, followed by an in-stack backup filter. PM10 is defined as the material recovered after the cyclone. EPA Method 201 employs recirculation of sample gas into the cyclone, enabling the sampling rate through the nozzle to be varied in order to maintain isokinetic sampling conditions. For example, when traversing the stack or during process variations, the flow rate through the cyclone is kept at a constant level to maintain constant D_{50} . Based on terminal settling velocity, particles smaller than about 100 µm should follow gas streamlines well at the velocities (approximately 50 ft/sec) typically found in stationary source stacks. Therefore, errors due to non-isokinetic sampling for PM10 are likely to be small. EPA Method 201A is similar to EPA Method 201, but employs constant-rate sampling and hence allows use of either a cyclone or a cascade impactor. Since sampling rate is constant, isokinetic sampling can only be accomplished on an average basis with appropriate nozzle size selection. If stack gas velocity varies while sampling, the dwell time at each point or condition is varied to ensure a representative integrated sample. Either of these methods may be combined with EPA Method 202 to determine condensable particulate by adding iced impingers downstream of the filter. Condensable particulate matter measured in this manner is sometimes included in regulatory definitions of PM10.

There are a number of potential sampling artifacts associated with the above particle size measurements. Filter substrates must be chosen carefully and preconditioned if necessary to prevent formation of solids, e.g., sulfates. If the loading on a particular stage becomes excessive, particles may "bounce" to the next stage leading to an oversampling bias in the smaller particle mass. Fortunately, these are well-documented in the test literature and appropriate steps can be taken to minimize them.

An inherent limitation of the above techniques is their inability to provide real-time particle sizing data during a sampling event. Various light scattering techniques for particle sizing have been developed which have the significant advantages of being non-invasive and providing real-time results (Swithenbank *et al.*, 1975; Samuelson *et al.*, 1984). For example, a non-invasive, polarization ratio and angular scattering particle size spectrometer has been developed and applied to stationary sources and ambient air monitoring with encouraging results (Holve, 1996). However, accurate light scattering techniques in this small particle size range have long been a major challenge to instrument manufacturers especially for submicron light absorbing particles (Garvey and Pinnick, 1983; Clark *et al.*, 1986). While potentially useful diagnostic techniques,

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they have not yet gained general acceptance within the regulatory community for particle size determination. Also, light scattering techniques characterize physical particle diameter rather than aerodynamic diameter; this may be of less relevance to potential health effects especially when non-spherical and irregular particles of non-ideal density are present. Researchers have developed many potentially useful methods of characterizing particle size. Optical particle counting using optical or scanning electron microscopy has been used to characterize physical particle size on filter substrates (Cass, 1997). In addition to impactors and cyclones, aerodynamic diameter of particle suspensions extracted from the stack can be measured in the laboratory using electrical aerosol analyzers, diffusion batteries, condensation nuclei counters, and aerodynamic sieves (Friedlander, 1977). There is some question as to how well these methods produce results which represent the state of the particles in the stack; hence, their use has not been accepted widely by the regulatory community.

The methods described above for PM10 have been used for measuring PM2.5 emissions from stationary sources; in fact, cyclones with D_{50} of 2.5 µm are commercially available, and 2.5 µm is within the range characterized by most commercial cascade impactors. EPA has indicated it is presently contemplating minor modifications to these methods for PM2.5 emission measurements (Logan, 1997). However, only a small fraction of ambient PM2.5 is believed to be due to particles present in the hot stack gases of most stationary sources so it is unlikely this approach will provide an appropriate characterization of emissions. In particular, both primary and secondary organic aerosols will not be accurately characterized with these methods.

PM2.5 PRECURSORS

Several substances known to be precursors of ambient PM2.5 are best characterized using source test methods. Important PM2.5 precursors include NO_X , SO_2 , SO_3 , ammonia, and organic compounds (primarily semivolatile organics). Some volatile trace metals (e.g., mercury and selenium) also may be gases in the stack which later condense in the atmosphere, and these have been the subject of recent tests on hazardous waste combustors (Stevens, 1997).

Semivolatile Organic Compounds

SVOC emissions from stationary sources are measured using a variation of the EPA Method 5 train. Figure 4-2 illustrates the sampling equipment arrangement for EPA Method 0010, a common example of this technique. The equipment is similar to that for EPA Method 5 except that materials in contact with the sample are either glass or Teflon[®], and a condenser and sorbent

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Figure 4-2. EPA Method 0010 Sampling Train for SVOCs.

trap are added between the filter and the impingers. A porous polymeric resin (XAD-2) is used as the sorbent material. The method and materials are effective for compounds with boiling points greater than 100 °C. A sample of effluent gas is withdrawn isokinetically from a source. Particulate is collected on a filter and gas-phase SVOCs are trapped in the sorbent module. The SVOCs are extracted from the probe and filter, sorbent module, impingers and various solvent recovery rinses using methylene chloride and, if necessary, toluene. The exact procedure varies depending on the specific target compounds for each test. SVOC analysis is by gas chromatography/mass spectrometry (GC/MS). The probe and filter ("front half") and sorbent module and impingers ("back half") can be analyzed separately to yield particulate-phase and gasphase SVOCs; however, it is widely suspected that adsorption of organics on the filter and filter cake during sampling clouds the results of this analysis. In addition, the partitioning between particulate and gas phase measured at stack temperatures will significantly underestimate how much of the SVOCs will be in the particle phase under ambient temperatures. EPA Method 0010 has been subjected to a rigorous method evaluation program for most of the organic compounds considered by EPA to be hazardous air pollutants (Jackson et al., 1996). Table 4-2 lists individual SVOCs which have been evaluated and whether each meets EPA's criteria for acceptance. Other SVOCs useful for characterizing primary and secondary organic aerosol precursors may be determined with this method; however, the accuracy of the method has not been demonstrated. Reliable application of this method requires a thorough quality assurance plan specific to each test and close attention to test and quality control procedures. SO₂, HCl and Cl₂ have been reported to be potential interferents if present in sufficient concentrations. Naphthalene contamination is a common sampling artifact; however, this should not pose a significant problem for the proposed program since naphthalene is not expected to contribute significantly to organic aerosols.

There are a small number of equivalent methods which rely on essentially the same principles but which differ in the details of sampling, analytical, and quality control procedures. For example California Air Resources Board (CARB) Methods 428 and 429 for characterization of dioxins/furans and PAH/PCB, respectively, are very similar to EPA Method 0010 and yield similar results.

Ammonia

Ammonia is an important precursor leading to ammonium sulfate and ammonium chloride, which have been identified in PM2.5 samples. Ammonia from stationary sources can be measured using draft EPA Method 206 using the sampling equipment illustrated in Figure 4-3. This method

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Semivolaile Organic	Mean	Meets	Meets EPA	Semivolaile Organic	Mean	Meets	Meets EPA	
Compound	Recovery	Method 301	QAQC	Compound	Recovery	Method 301	QAQC	
		Acceptance	Handbook			Acceptance	Handbook	
		Criteria? ³	Acceptance Criteria? ⁴			Criteria? ³	Acceptance Criteria? ⁴	
Acids				Neutrals ²				
Di-n-butyl phthalate	46 ± 54%	٥N	No	styrene oxide	0.5 ± 1481%	No	No	
bis(2-ethylhexyl) phthalate	$48 \pm 23\%$	No	No	phthalic anhydride	5.3 ± 144%	No	°Z	
m-/p-cresol ⁷	69 ± 14%	°N	Yes	methoxychlor	$73 \pm 19\%$	No ⁷	Yes	
dimethyl phthalate	82 ± 17%	No	Yes	toluene	76 ± 11%	No ⁷	Yes	
phenol	89 ± 9%	Yes	Yes	<u>m-/p-xylene</u>	79 ± 12%	Yes	Yes	
Q-cresol	$90 \pm 15\%$	Yes	Yes	quinoline ⁵	$80 \pm 19\%$	Yes	Yes	_
2,4-dinitrophenol	111 ± 31%	Yes	Yes	sytrene	$84 \pm 10\%$	Yes	Yes	
4-nitrophenol	$114 \pm 31\%$	Yes	Yes	Q-xylene	85 ± 11%	Yes	Yes	
4,6-dinitro- <u>o</u> -cresol	122 土 14%	Yes	Yes	1,4-dioxane	87±11%	Yes	Yes	
Bases ¹				cumene	88 ± 11%	Yes	Yes	
quinone	$2 \pm 438\%$	No	No	ethylbenzene	89 ± 12%	Yes	Yes	
hexamethylposphoramide	$14 \pm 118\%$	No	No	parathion	$89 \pm 28\%$	Yes	Yes	
trifluralin	$27 \pm 41\%$	°Z	No	isophorone	93 ± 12%	Yes	Yes	
dimethylaminoazo-benzene	$31 \pm 51\%$	No No	No	acetophenone	$96 \pm 12\%$	Yes	Yes	_
3,3'-dimethoxybenzidine	$37 \pm 38\%$	°N No	No No	napthalene	96±11%	Yes	Yes	_
Q-anisidine	$39 \pm 39\%$	°Ž	No	dibenzofuran	$100 \pm 12\%$	Yes	Yes	_
Q-toluidine	$56 \pm 30\%$	°Ž	Yes	dichlorvos	$101 \pm 18\%$	Yes	Yes	_
benzidine	$65 \pm 119\%$	°N N	No	DDE	102 ± 15%	Yes	Yes	
N,N,-dimethylaniline	$67 \pm 24\%$	°Ž	Yes	4-nitrobiphenyl	102 ± 14%	Yes	Yes	_
aniline	$70 \pm 24\%$	°N0	Yes	heptachlor	103 ± 12%	Yes	Yes	
4,4'-methylene bis(2-	$89 \pm 36\%$	Yes	Yes	l biphenyl	103 ± 12%	Yes	Yes	_
chloroaniline)			:	lindane	$104 \pm 12\%$	Yes	Yes	_
3,3'-dimethylbenzidine	92 ± 44%	Yes	Yes	nitrobenzene	$109 \pm 12\%$	Yes	Yes	_
N,N,diethylaniline	$95 \pm 19\%$	Yes	Yes	2,4-dinitrotoluene	$109 \pm 12\%$	Yes	Yes	_
carbaryl	99 ± 19%	Yes	Yes	methyl isobutyl ketone	112±11%	Yes	Yes	_
ethyl carbamate	103 ± 14%	Yes	Yes	chlordane	142 ± 16%	Yes'	Yes	_
caprolactam	114 ± 12%	Yes	Yes					
N-nitrosomorpholine	$116 \pm 12\%$	Yes	Yes					
N-nitrosodimethyl-amine	$117 \pm 13\%$	Yes	Yes					_
propoxur	$123 \pm 12\%$	Yes	Yes					
2-actylaminofluorene	$147 \pm 23\%$	No	Yes					
Values represent the mean from	ten complete q	uad sampling run	is with dynamic s	piking, two spiked trains and	d two unspiked t	rains. ² Values re	cpresent the mean	
from twenty complete duad same	UING TIINS WILD	UVDAMIC SDIKING	two sniked trains	t and two incrited traine	Jentral compound	de ware chibad u	with both the Arid	

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and the Bases, and all neutral data are included in the composite values. ³EPA Method 301 acceptance criteria include recovery of 70-130%, with a precision 550% relative standard deviation and a correction factor between 0.70 and 1.30. ⁴ EPA QA/QC Handbook acceptance criteria include recovery of 50-150%, with a precision \leq 50% relative standard deviation. ⁴ Quinoline was placed in Neutral solution rather than Basic solution because of confusion of name with quinone. ⁹ Listed together in the table because of chromatographic coelution. ⁷ The correction factors (CF) for toluene and methoxychlor were 1.31 and 1.40; the CF for chlordane was 0.71, however, this was due to high variability of the unspiked trains.



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employs a heated in-stack filter to avoid conversion of gaseous ammonia in the stack gas to solid ammonia sulfates or salts, or vice versa. Gaseous ammonia is trapped in a series of impingers containing dilute sulfuric acid solution. The samples are analyzed using ion chromatography. Other methods of measuring ammonia have been developed using similar impinger absorption techniques but alternative analytical methods such as colorimetric and ion specific electrode techniques. Recently, continuous analyzers for ammonia have been applied to stationary sources with varying success; while promising, these are not yet generally accepted by the regulatory community.

NO_x and SO₂

 NO_x and SO_2 emissions are precursors to nitrate and sulfate in aerosols. Emissions of NOx and SO_2 can be characterized by a variety of manual and continuous techniques; however, continuous techniques are generally preferred because of simplicity and assurance of obtaining valid data. Figure 4-4 illustrates a typical continuous emissions monitoring system. Samples are extracted from the flue gas, dried, and filtered before being introduced to the gas analyzers. EPA Methods 6C and 7E are generally employed for measuring SO_2 and NO_x emissions using chemiluminescence and non-dispersive ultraviolet absorption spectroscopy analyzers, respectively. The EPA methods specify criteria for system design, performance, and quality assurance/quality control procedures (calibration, drift, bias, etc.).

<u>SO</u>3

Sulfur trioxide is often present in flue gas when SO_2 is present. In coal-fired power plants, for example, SO_3 is typically present at 0.25 to one percent of the SO_2 concentration. SO_3 has been measured in the stack gas from catalytic cracking units, cokers, and reformers. SO_3 is difficult to measure accurately in the presence of SO_2 by modified EPA Method 5-type techniques; hence controlled condensation techniques are generally used. This method involves high-temperature filtration of the sample to remove solid particles, followed by cooling of the sample to a temperature below the H_2SO_4 dew point, but above the moisture dew point, and subsequent filtration to remove condensed acid mist (Figure 4-5). The sample is then rinsed from the sampling apparatus and analyzed by conventional titrimetric or ion chromatographic techniques.

Elemental Analysis

Elements which may be characterized in the API program include carbon, sulfur and selected trace metals. Elemental carbon and other elements can be measured on the filters from particulate sampling via EPA Methods 5 or 17. For regulatory purposes, stationary source trace metal emissions are typically measured using manual sampling techniques similar to those described above. EPA Method 29 is validated for 17 trace metals including mercury, arsenic and selenium; many other metals also may be determined with suitable modifications. EPA Method 101A is specific to mercury measurements. The sampling equipment is generally similar to that described above, with a heated out-of-stack filter and capture of volatile metals in iced impinger solutions. Samples are analyzed for metals using inductively coupled plasma emission and/or atomic spectrometry. Other methods also exist which are not currently recognized by the regulatory community but which have potential for easier measurements. For example, the high-efficiency sampling train (HEST) method employs an in-stack filter with stacked quartz fiber and impregnated carbon filters to capture and segregate particulate-phase and vapor-phase metals, which are subsequently measured using x-ray fluorescence (Cooper, 1994). This has the potential capability to measure a wide range of elements with a vastly simplified analytical procedure compared to EPA Method 29.



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Figure 4-4. Continuous Emissions Monitoring System.

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Section 5

AEROSOL SOURCE EMISSIONS MEASUREMENTS

Traditional stationary source air emission sampling methods tend to underestimate or overestimate the contribution of the source to ambient aerosols because they do not account for aerosol formation which occurs after the gases leave the stack (see discussion in Section 2). Based on the probable mechanisms controlling aerosol formation and growth, techniques which dilute the stack gas to simulate atmospheric aerosol formation mechanisms would therefore seem the best approach for characterizing organic aerosols. This section of the report discusses dilution sampling approaches and dilution sampler design criteria, and provides details on several recent designs.

DILUTION SAMPLING VERSUS TRADITIONAL APPROACHES

Methods of characterizing the total contribution have centered around two basic approaches:

- Collection of condensable particulate in iced impingers using traditional source air emission sampling methods; and
- Simulation of conditions resulting in aerosol formation experienced in the plume from the stack by diluting the sample and subsequently analyzing the sample using ambient air methods.

The use of iced impingers to collect condensable particulate matter and potential artifacts of using this technique were discussed previously in Section 4. Table 5-1 compares total particulate emission results obtained using dilution sampling and EPA Method 5 for three different combustion sources (Heinsohn *et al.*, 1980). EPA Method 5 results are shown both with and without analysis of the impingers for condensable particulate. The results from dilution sampling produced higher total particulate concentrations than EPA Method 5 in four of six tests, even when the condensable particulate collected in the impingers is included. In one of the glass tank tests, the difference between dilution and Method 5 results is quite dramatic. However, the balance of total particulate dilution sampling results range from -9 to 18 percent of the EPA Method 5 results (including impingers), with the greatest differences associated with lowest absolute particulate concentrations. These differences are generally small and might be considered within the accuracy of Method 5.

Source	Test	Dilution sampler (mg/Ncm)	EPA Method 5 (mg/Ncm)		
			Including impingers	Excluding impingers	
Coal-fired boiler	1	495.6	462.1	407.6	
Glass melt tank	6 (ESP on)	71.7	45.8	38.9	
	7 (ESP off)	351.7	331.8	323.6	
Lime kiln	12	116.2	126.6	111.0	
	13	99.4	83.8	70.0	
	14	139.0	140.3	123.6	

Table 5-1. Comparison of Total Particulate Concentration Using Dilution Sampling Versus EPA Method 5.

(Heinsohn et al., 1980)

The total particulate including the condensable fraction of the Method 5 results ranged from 2 to 20 percent higher than the filterable fraction alone. When one looks just at carbonaceous material associated with the fine particle fraction, however, the results are dramatically different. As seen in Figure 5-1, a comparison of fine organic carbon emissions from an oil-fired industrial boiler showed a dilution sampling system collected 7 to 16 times as much organic aerosol as the filterable fraction of a modified EPA Method 5 train using hot filtration of particulate (Hildemann *et al.*, 1989). Referring to Figure 2-1 presented previously, the difference is most likely attributable to the fact that organic compounds in the emissions do not partition into the aerosol phase until post-stack cooling allows nucleation, condensation and accumulation mechanisms to occur.

Dilution sampling also yields different results than source sampling for specific SVOCs. Tests on two coal-fired utility boilers using stack and dilution methods showed some accumulation of individual PAHs on solid particles in the diluted samples - PAH/SVOC concentrations determined by dilution sampling were six times higher than parallel sampling using EPA Method 0010 - but results were not definitive because absolute concentrations were extremely low (U.S. Department of Energy, 1994). As seen in Table 5-2, concentrations of 19 individual PAH obtained using dilution sampling on a diesel engine were up to 30 times higher than results obtained by simultaneous sampling using CARB Method 429 for all substances except naphthalene, which was lower (Lindner and Wall, 1995). The apparent formation of PAH during dilution may be caused by gas-phase conversion or condensation of volatile and reactive organics present in diesel exhaust. Because nucleation and condensation mechanisms occur in the plume, a change in mean particle size would be expected as the stack gases dilute and cool. For example, in tests of coalfired boilers mean particle size decreased from approximately 5 µm, measured at the stack using





Figure 5-1. Organic Carbon Collected by Filtration vs. Dilution Sampling Procedure for Distilled Oil-Fired Industrial Boiler.

РАН	ng/d	Ratio (dilution sampling to Method 429)		
	Dilution Sampling (corrected)	CARB Method 429		
2 Rings				
Naphthalene	305362	697253	0.44	
2-Methylnaphthalene	528436	423154	1.2	
<u>3 Rings</u>				
Acenaphthylene	212344	22417	9.5	
Acenaphthene	122842	15541	9.5	
Fluorene	557851	46679	12	
Phenanthrene	1855405	86112	22	
Anthracene	262352	8721	30	
4 Rings		•		
Fluoranthene	62608	7476	8.4	
Ругепе	105296	11474	9.2	
Benzo[a]anthracene	19553	1672	12	
Chrysene	20878	2700	7.7	
5 Rings				
Benzo[b]fluoranthene	9665	2712	3.6	
Benzo[k]fluoranthene	6300	783	8.0	
Benzo[e]pyrene	9081	1449	6.3	
Benzo[a]pyrene	11377	1049	11	
Perylene	3081	217	14	
Dibenzo[a,h]anthracene	1083	214	5.1	
6 Rings				
Indeno[1,2,3-c,d]pyrene	4548	1816	2.5	
Benzo[g,h,i]pervlene	7756	2408	3.2	

Table 5-2. Comparison of PAH Emissions from a Diesel Engine Using CARB Method 429 and Dilution Sampling.

in-stack cascade impactors, to less than 1 μ m, measured in diluted samples (U.S. Department of Energy, 1996; Heinsohn *et al.*, 1980).

Based on the above considerations, it is apparent that traditional source test methods and dilution sampling methods produce significantly different aerosol emission mass, size and speciation results, especially for the organic components. Therefore, based on the mechanisms controlling aerosol formation and growth, dilution sampling techniques would provide the best approach for characterizing organic aerosols. The following section reviews designs of dilution sampling systems previously employed to characterize stationary source emissions.

EVOLUTION OF DILUTION SAMPLER DESIGNS

Dilution samplers can be grouped into two categories:

- Static, or constant-volume dilution samplers; and
- Dynamic dilution samplers.

Constant-volume dilution sampling has become the standard technique for measuring particulate emissions from mobile sources (ISO, 1994). Static dilution chambers also have been applied to characterize stationary source emissions. For example, atmospheric effects including clouds, rain, and UV-induced photochemical reaction recently were simulated in a transportable chamber and sampling apparatus during tests to characterize mercury species transformations and fate in coalfired boiler plumes (Prestbo, 1997). DYNAMIC dilution SYSTEMS have been adopted by most researchers instead of static dilution approaches, because, due to long time constants (several hours to days) it is not feasible to simulate photochemical aerosol formation.

Investigators have been using dynamic dilution samplers to simulate physico-chemical processes in exhaust plumes for more than 20 years. Most early dynamic dilution systems for stack sampling were designed for dilution of stack gases to ambient temperature and particle concentrations to facilitate primary particle mass and size determinations by devices designed for ambient service. Condensation of fine aerosol mists or fumes is seen as an interferant in these systems; hence some system components, such as absorbent banks which remove condensed fumes, are not applicable to characterization of secondary aerosols.

Both in-stack and extractive dynamic dilution techniques have been used in past designs, primarily for characterizing aerosol mass and size distribution. Figure 5-2 illustrates several early designs used primarily for characterizing aerosol mass and size distribution. Bradway and Cass (1975) used an extractive technique for sampling at a gas-fired power plant which employed a cyclone preseparator to remove large particles (greater than 15 μ m) before dilution. Such large particles probably do not remain entrained in the plume and can distort the aerosol formation process; they also present orifice and capillary tube clogging problems. Bradway and Cass took several approaches to diluting the sample, including an air ejector, a capillary tube system and a pump system. The first two were used to achieve dilution ratios up to approximately 12:1, while the pump system was used for higher dilution (up to 375:1). Particle sizing was accomplished using a condensation nuclei counter and a diffusion-denuder.



Figure 5-2. Early Dilution Sampling Methods.

Large particles were also removed in the particle sizing dilution system described by Ensor *et al.* (1975) using an in-stack impactor sized to cut particles larger than 2.7 μ m. Moisture was removed from the stack gas in a diffusional dryer prior to entering a three-stage dilution system. Stack gas flows were measured by venturi meters, and dilution air flows by orifice plates. Flow control was accomplished by manipulating dilution air control valves; dilution was determined as the ratio of total flow to stack gas flow.

Schmidt *et al.* (1976) used a two-stage system in which the first stage of dilution occurred instack, downstream of a precutting cyclone, to reduce the possibility of submicron aerosol fume; the second stage occurred out of stack. Flow through the precutting cyclone was measured using a venturi at the cyclone outlet. The dilution ratio was determined by dividing total flow rate by sample flow through the cyclone venturi. This system was equipped with a single charge neutralization device downstream of the dilution chamber to minimize electrostatic particle losses. Charge neutralization is potentially a critical issue for some sources, especially those which use electrostatic precipitators for dust emissions control (e.g., FCCUs).

Baladi and Stultz (1977) employed an in-stack single stage dilution system with eductors to achieve controlled turbulent mixing between the sample and dilution air. A portion of the sample flow through a large particle precutter was drawn through an eductor by a vacuum induced by pumping dilution air into the eductor. The sample flow and the dilution streams intersect at right angles, causing turbulent mixing before passing through a straight section producing laminar flow. A 5-millicurie Kr-85 radioactive source equilibrated the diluted aerosol charge before particles were sized using an optical counter and diffusion battery. The advantages of this system are its compactness, and the ability of the pressure-induced sampling and mixing principle to produce a diluted sample at atmospheric pressure; however, under low dilution conditions fume condensation is likely. Calvert used a single-stage dilution system with an in-stack cascade impactor for large particle removal (Ensor *et al.*, 1975). To minimize surface particle loss, this system employed a PO-210 alpha source to neutralize particle charge. A rotameter metering system was employed for dilution flows; the system did not address premature fume or acid condensation.

Felix *et al.* (1981) incorporated PO-210 charge neutralization in two locations, upstream of an outof-stack cyclone and in the dilution chamber. An optional bank of SO_x absorbers was included to eliminate acid mists prior to dilution. Highly turbulent mixing conditions were created by

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introducing cooled, desiccated dilution air through perforations in a cone; stack gas was injected through the cone's apex. Sample and dilution air flow rates and dilution ratio were adjusted using two bleed valves on the dilution air pump; manipulation of the valves changed the pressure in the diluter which in turn set the sampling rate. Gross changes in sample flow were accomplished by changing orifice meters. Particle sizing was achieved using an optical particle counter, an electrical aerosol size analyzer (EASA) and a condensation nuclei counter. Particles penetrating to the sizing instrumentation were resolved at a lower size limit of 0.01 μ m and an upper size limit of 2.0 μ m; particles smaller than 0.01 μ m were lost by diffusion and electrostatic attraction and those larger than 2.0 μ m were lost by and impaction and settling. Particle losses was determined by passing three sizes (0.822 μ m, 1.091 μ m, and 2.02 μ m) of polystyrene latex monodisperse aerosols through the dilution sampler and measuring concentrations at the inlet to the sampling probe and at a sample take-off port after dilution. For dilutions greater than 40:1, no significant losses were found for the 1.091 and 2.02 μ m particles. At 14:1 dilution 25 percent of the 1.091 and 2.02 μ m particles were given for the smallest (0.822 μ m) particles. Particle loss to surfaces became significant as the dilution ratio dropped below about 50:1.

CURRENT DILUTION SAMPLER DESIGNS

Dilution sampling has been applied to the development of source profiles or "fingerprints" which are used in source apportionment and receptor modeling studies (Schauer *et al.*, 1996). These , systems have aimed to replicate atmospheric aerosol formation processes, and retain rather than eliminate condensable aerosols. Most systems use the same sampling and aerosol size fractionation techniques as ambient air samplers, thus eliminating biases introduced by using different reference methods for source and ambient sample collection. The ideal source sampling method would allow for chemical and physical transformations of source emissions to occur prior to sample collection. Lacking this ideal, the sampling would at least quantify the precursors of the receptor profile so that a theoretically or empirically derived transformation could be applied. Methods used to sample source emissions include: 1) hot exhaust sampling; 2) diluted exhaust sampling; 3) plume sampling from airborne platforms; 4) ground-based sampling of single-source dominated air; and 5) grab sampling and resuspension.

This section deals with diluted exhaust sampling methodologies. Dilution stack sampling is the only practical alternative for the extraction of industrial stack effluents. Dilution sampling systems for stacks vary with respect to dilution ratios, dilution air filtration, sampler materials, particle size fractionation, and sampling substrates. In general, dilution samplers draw hot exhaust gases into a

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chamber where they are mixed with filtered ambient air. After an aging period, the particles are drawn through a size-selective inlet and onto the substrates. Multiple substrates for different chemical analyses are obtained simultaneously or via sequential sampling of the same gas stream. Houck *et al.* (1982) have developed such a system which draws the diluted sample through a virtual impactor to provide particle size fractionation. McCain and Williamson (1984) performed tests on this sampler which showed losses of large particles owing to inertial impaction and electrostatic charging. They recommended design changes to minimize these losses and these changes have been implemented in later designs. Also, polyvinyl chloride (PVC) piping was used in the original Houck design which would be likely to adsorb organic species during sampling as well as desorbing phthalate esters and other components of the PVC formulation. A later version of this dilution sampler (Cooper, 1992) eliminated the use of plastic.

Hildemann *et al.* (1989, 1991) described the first dilution sampler designed specifically for organic particulate matter characterization. The dilution system suitable for collecting organic aerosol samples for detailed organic analyses by GC and GC/MS technique has to fulfill certain requirements (Hildemann *et al.*, 1989). It cannot contain any plastic or rubber materials that may leach organics into the system and that would prevent thorough cleaning of the system between different tests to avoid cross-contamination. It should allow for relatively large sample size to facilitate detailed chemical analysis of organic compounds. The dilution sampler should also simulate atmospheric transformation as closely as possible; it should allow for dilution and cooling of the emissions to ambient temperature. To minimize particle and vapor losses onto the walls, the dilution tunnel diameter should be as large as possible and the flow rates in the system should be adequately chosen. Yet the system should be portable, relatively light and compact, so that it can be transported to and assembled on the sampling platform of some industrial stacks.

Table 5-3 lists the main features of several published dilution sampler designs (adapted from Hildemann *et al.*, 1989). Most of these systems are not designed for the long residence times, on the order of one minute, required to complete organic aerosol formation. Only the Caltech/DRI design and perhaps the University Research Glassware (URG) design have been created expressly with this in mind. The last column of this table presents the main features of the recently constructed DRI dilution sampler, the most recent in the evolution of dilution samplers based on the Caltech design. These designs are discussed in more detail below.

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	Carpenter Design	NEA ^a Design	SRI ^b Design	CalTech ^c Design	URG ^d Design	California ARB ^e Design	DRI ^f Design
Tunnel diameter (cm)	30	10	21	15	8	15	15
Diameter of effective mixing length	12 - 15D	29D	6D	10D	80D	12D	18D
Residence time (s)	1.3	1 - 3	6.2	2 - 180	5-40	1-5	80 typically)
Dilution ratio	Typically 8 - 25 x (up to 100 x)	>20 x	25 x	Typically 40x (25x to 100x)	20:1-40:1	10:1-50:1	Typically 40x (25x to 50x)
Reynolds number	47,000	11,000- 23,000	2800	10,000		10,000	9,000 (at 40x dilution ratio)
Tunnel material	Stainless steel	PVC	Plexigl as and Teflon [®]	Stainless steel and Teflon [®]	Teflon [®] - coated glass and aluminum	Teflon [®] - coated stainless steel	Stainless steel and Teflon [®]
Portability?	No	Yes	Yes	Yes	Yes	Yes	Yes
References	Carpenter (1978)	Houck et al. (1982)	Smith et al. (1982)	Hildemann et al. (1989)	URG (1996)	Wall (1996)	(Lindner and Wall, 1995)

Table 5-3. Features of Published Dilution Sampler Designs (adapted from Hildemann et al., 1989).

*Nuclear Environmental Analysis, Inc. *Southern Research Institute *California Institute of Technology d'University Research Glassware Inc. *California Air Resources Board

^fDesert Research Institute

Caltech System

A dilution stack sampler designed by Cass and Hildemann *et al.* (1989; 1991) specifically to characterize organic aerosols is illustrated in Figure 5-3. The system is constructed entirely of stainless steel and Teflon[®] to prevent contamination artifacts and facilitate solvent rinsing between sample runs. Stack gas is extracted through an isokinetic nozzle and 10-µm cyclone, and flows at a high sample flow rate through a heated probe to a dilution chamber, where it is injected in a cross-flow pattern to a high efficiency particulate air (HEPA)- and activated carbon-filtered dilution air stream. Initial mixing is turbulent, with a Reynolds number (Re) of approximately 10,000. After following the dilution tunnel for 10 tunnel diameters, 20 percent of the diluted stream is



Figure 5-3. Caltech Dilution Sampling System Design (Hildemann et al., 1989).

withdrawn into a residence time chamber, where the sample is aged prior to extraction of analytical samples. Residence time is approximately 40-60 seconds, to allow condensation processes to go to completion prior to sample collection. Twelve sampling ports at the bottom of the residence time chamber allow parallel sample extraction. PM10 samples can be captured by sampling the diluted exhaust directly, while fine aerosol is sampled by equipping each of the 12 ports with cyclone separators of different sizes and sampling downstream from the separators. Flow through each of the sampling filters is measured using a ± 1 percent calibrated rotameter before and after each experiment. During sampling events, the flow of sample gas is measured using a venturi meter, and flows of dilution air and total exhaust are measured using calibrated orifice plates and Magnahelic differential pressure gauges.

Complete mixing of the dilution and sample streams was demonstrated in the laboratory by injecting nitric oxide through the sample inlet line and measuring concentrations at two cross-sections upstream of the residence time chamber. At dilution ratios of 28:1 and 55:1, NO concentrations were uniform, indicating complete mixing. Non-uniformity of NO concentrations across these sections was detected at a dilution ratio of 21:1, indicating incomplete mixing below this point. Particle losses in the sampler were also evaluated, by passing monodisperse ammonium fluorescein aerosols through the sampler and recovering the surfaces with ammonium hydroxide. Recovered samples were analyzed using absorption spectrometry; 93 percent of particles 1 μ m in diameter and 85 percent of 2 μ m diameter were captured on the filters. Losses of 20 to 30 percent were observed for 2.5 to 5 μ m diameter particles. Losses were highest in the inlet line and venturi.

Cass and Hildemann have extensively applied this system to characterize organic aerosols from a variety of sources including industrial boilers, fireplaces, diesel engines, gas-fired appliances, and meat cooking operations. The sampler is vapor degreased prior to use at each source by washing larger parts with trichloroethylene (TCE) and wrapping all open ends with aluminum foil; this is followed by heat treatment with flowing purified air at 70 °C. Smaller parts are sonicated in methanol and hexane. Prior to use in the field, the system is leak checked at 2500 Pa vacuum; a leak rate of less than 0.1 percent of the total system flow is acceptable. System blanks are collected prior to sampling by running dilution air through the system for several hours, to detect ambient organics, TCE residue, or contaminants introduced during storage and transport.

Desert Research Institute System

The recently completed DRI dilution system is based on the design described by Hildemann et al. (1989). Figure 5-4 shows the schematic diagram of this system. A sample stream of 20–30 liters per minute (lpm) is withdrawn from the stack through a heated stainless steel line to a 15 cm diameter dilution tunnel; the sample inlet also contains a thermocouple for monitoring stack temperature. The sample is mixed in the tunnel with dilution air under turbulent flow conditions to cool and dilute the sample to near ambient conditions. Ambient air, filtered through a HEPA filter (to remove particulate matter) and an activated carbon bed (to remove gas-phase organics) is used for dilution at ratios from 25- to 50-fold (typically 40-fold dilution is used). The dilution flow is provided and monitored via a hi-vol blower. An S-type pitot tube is used to monitor the stack flow and the sample flow rate is measured using a Venturi meter. Both the sample line and Venturi are heated to stack temperature. After passing through a tunnel length equal to 18 times the tunnel diameter, a portion of the diluted sample enters a large stainless steel chamber for additional residence time (on the order of 80 seconds). A relative humidity sensor is used to warn if conditions too closely approach water saturation. Two independent samples are drawn through cyclone separators with a cut-off diameter of 2.5 μ m, each operating at 113 lpm and collected using a filter sampler (for inorganic species) and a fine particulate/semi-volatile organic compound sampler (PSVOC) for organic species. The residence chamber has additional ports for sampling gas-phase species by sorbent cartridges or other methods that are appropriate to the species of interest.

Temperature and flow rate sensors and data loggers continuously record the temperature of ambient air, stack, sampling line, dilution chamber, residence chamber, stack flow, and relative humidity in the residence chamber. Two portable computers record the data to tables and time-series plot in real time.

The sampler is constructed entirely from stainless steel and Teflon[®] to prevent contamination artifacts and to facilitate cleaning between runs. A thorough rinsing with organic solvents followed by vapor degreasing with tetrachloroethylene and heating over a minimum 24-hour period up to 160 °C with clean air flowing through the system, is used to clean the entire dilution system between different tests. Following cleaning, the entire system is leak-checked by pressurizing with helium up to 5 psi and monitoring the pressure drop over a 24-hour period. Also, after cleaning and before the test, blank samples are collected.



Figure 5-4. Schematic Diagram of the DRI Dilution System.

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The system is relatively portable, compact, and can be easily disassembled and re-assembled by two persons. Figure 5-5 shows the DRI dilution system on a sampling platform during wood combustion tests.

Nuclear Environmental Analysis. Inc. (NEA) System

The plume simulation dilution sampler (PSDS) was designed by Houck and Cooper (1982) to simulate the effects of plume dilution and cooling on stack emissions, and to develop PM10 source profiles to be used in chemical mass balance receptor modeling studies. An early version of this system was critically reviewed by EPA (McCain and Williamson, 1983) in response to concerns that particles were being lost in the system, and generating results that were too low relative to ambient concentrations of aerosols. Particle surface losses were evaluated by introducing monodisperse ammonium fluorescein aerosols into the system, then recovering the entire sampler using dilute ammonium hydroxide. Serious particle losses in the inlet components (45 percent loss of 2 µm particles in the hose) were identified at a flow rate of 74 liters/min. After installing a large particle precollector, reducing the length of the inlet hose to five feet, and lowering the sample flow rate to 14 liters per minute, fine particle losses less than 5 percent were observed. After a period of field use and system modifications, electrostatic particle losses were evaluated and found to be significant: at a sample flow rate of 14 liters per minute, 2 µm charged particles penetrated to the sample collection device (filter) with an efficiency of 64 percent, versus 88 percent penetration efficiency for a 2 µm aerosol neutralized by PO-210 strips. The EPA study suggested that electrostatic deposition problems could be largely avoided if only electrically conducting components were used throughout the system.

The current-generation PSDS shown in Figure 5-6 was applied to a field testing program at a coalfired power plant in 1994 to allow comparison of plume-cooled emissions to hot stack (undiluted) emissions. All of the surfaces in the sampler in contact with the gas are Teflon[®], Viton[®], or stainless steel. The sample is withdrawn from the stack isokinetically through a conventional Method 5 buttonhook nozzle, sized on-site with no in-stack particle removal, and transferred to the dilution chamber through a heated tube. The dilution stream is a dry, cryogenically pure 79 percent N₂-21 percent O₂ mixture, delivered pre-mixed to the test facility in compressed gas tube trailers. The dilution gas is activated carbon filtered and HEPA filtered prior to injection to the dilution chamber. Targeted dilute sample gas conditions are near ambient temperatures and less than 30 percent relative humidity, after 2 seconds residence time. A dilution chamber residence time of 2 seconds is considered appropriate to provide adequate condensation and equilibration of analytes

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Figure 5-5. Dilution Tunnel Sampler on Top of Test Shed.

and to minimize artifact formation due to acidic condensate on sample substrates. Major adjustments to the system residence time are made by reconfiguring the dilution chamber.

Dilution ratios and flow rates are determined on a source-specific basis, and correlated to the dilution chamber pressure using a spreadsheet provided by the manufacturer. Adjustments to the dilution chamber pressure, and subsequently the sample flow, dilution ratio and residence time, are made by throttling the positive pressure dilution air source. The chamber pressure-flow relationship is calibrated off-site as an integrated unit.

Particulate samples are collected onto an 8-inch by 10-inch quartz filter for mass and appropriate chemical analyses, while particle sizing is done through a parallel port in a cascade impactor. In the Battelle study, gas phase samples were collected from a manifold downstream of the particulate collection section using the back half of hot stack gas reference method sampling trains. Due to the low concentrations of particulate after dilution, particulate samples were collected for the duration of a test day, typically 8-10 hours. The cascade impactor was operated for 2 days to capture enough sample.

Comparison of diluted versus undiluted analytical results (hot stack gas sampling was conducted in parallel) showed considerable enrichment of PAH/SVOC in the dilution system; dilution sampler levels averaged six times higher than undiluted samples for all analytes. The dioxin/furan results were dominated by non-detects and showed considerable variability, particularly the PSDS samples. Aldehydes showed enrichment in formaldehyde and depletion in acetaldehyde; this is inconsistent with previous test program results, which showed enrichment for all aldehydes. Variation among samples was considerable with standard deviations ranging from 60-150 percent of the average. VOC data agreed reasonably well, considering the relatively high PSDS detection limits and the variability in the data. Other analytes (elements and ammonia/cyanide) showed a high degree of uncertainty.

Potential limitations of the PSDS for petroleum industry combustion source testing include: 1) indirect method of controlling flows and dilution ratio: this flow could introduce error to the final sample results due to differences in the field pressure drop characteristics relative to those in the calibration laboratory; 2) short residence time; and 3) bulk (single port sampling was conducted in the Battelle study; traversing was prohibited by the size and configuration of the PSDS and peripherals).

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<u>URG System</u>

The dilution sampler illustrated in Figure 5-7 is manufactured by URG of Chapel Hill, North Carolina. The design is based on earlier work by Houck (1982) and Stevens (1997) aimed at obtaining source signatures for receptor model validations. The current sampler is intended to simulate condensation and coagulation reactions on a 20-30 second time scale, which is considered sufficient time to simulate plume effects one-quarter to one-half mile downwind of sources. Internal surfaces are Teflon[®]-coated glass and Teflon[®]-coated aluminum. After extraction through an in-stack cyclone, the sample passes through a heated probe and is injected through a venturity nozzle into a mixing chamber. Dilution air is injected radially from a bottled or purified air source upstream of the mixing chamber, where it follows the chamber walls before passing through holes drilled in a concentric circle around the heated sample probe. Stack sample flowing at 1 to 2 liters per minute is thus mixed in a coflow arrangement with dilution air at approximately 40 liters per minute. System residence time is 20-30 seconds, and can be extended by adding more sections onto the sampler upstream of the sample collection point.

A sampling manifold at the back end of the sampler allows the attachment of up to ten ambient air sampling arrays (filters/sorbent modules/denuders), which are chosen based on analytes of interest. Each sampler is equipped with its own pump; each pump adds approximately 10 liters per minute of total flow through the system. System flows are controlled by adjusting valves connected to the sampling pumps and varying the size of dilution air orifice plates.

Limitations of the URG dilution sampler include a dearth of available data to evaluate its performance, especially with respect to organics speciation, though new data collected in 1996 at four incinerators in Florida may be made available. Leak check difficulties in past testing have required the use of silicone rubber sealants between the sampler sections, which may pose sample contamination problems. Finally, the means for adjusting the dilution ratio (changing orifice plates) and residence time (adding sampler sections) could result in considerable down time in field applications. The URG system has recently been applied by EPA to a cement kiln and incinerator burning hazardous waste and to a municipal waste incinerator (Stevens, 1997). The focus of the measurements was on inorganics and particulates; some effort to characterize organics was made but a full suite of measurements was not performed. Results of these tests should be available in the future.



Figure 5-7. URG Dilution Sampling System Design (URG, 1996).

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Southern Research Institute (SRI) System

The SRI system (Figure 5-8) was designed for EPA to quantify aerosols resulting from homogeneous condensation of acid vapors, metal vapors and organics in combustion plumes. This system was recently employed during air toxic emissions testing at a coal fired power plant (U.S. Department of Energy, 1994). Interior surfaces are glass and Teflon[®]-coated aluminum to prevent sample contamination. An 8-µm cyclone is mounted at the inlet end of the probe to minimize fouling of the sample flow orifice; stack gas is then passed through heated probes and a Method 5 filter to remove primary particles before entering the dilution chamber at the apex of a perforated cone. Dilution is provided by ambient air which has been cooled, dried, activated carbon filtered, and particle filtered; the dilution air circuit employs a bypass leg around the particle filter to provide a source of condensation nuclei if needed. Dilution air that is characterized by high levels of small-scale turbulence and low net swirl. This behavior results in a flat velocity profile at the dilution chamber exit.

Sample and dilution air flows are established by the exhaust pump and are regulated with valves in the dilution air inlet and exhaust branches. A heated orifice located at the apex of the perforated cone is used to measure sample flow rate and total volume. A total flow orifice meter is located just upstream of the exhaust. The SRI system's maximum dilution ratio is 20:1, corresponding to a chamber residence time of one to two seconds. Optimal dilution is set to provide high enough stack gas flows relative to dilution air flows for sufficient sample mass collection, with enough dilution to cool to ambient temperature and prevent condensation of moisture droplets in the sampler.

A condensables filter spanning the dilution chamber is used to capture condensed particulate matter at ambient temperature. In recent tests, gas phase samples were collected from the dilution sampler using hot stack gas reference method sampling trains; target analytes included metals, acid gases and organics (U.S. Department of Energy, 1994). Most of the analytical results did not agree with parallel hot stack gas sampling using manual methods; many of the analytes were below minimum detectable concentrations. Use of the diluter for measuring metals concentrations that were low even before dilution produced data with a high degree of uncertainty and many apparent contradictions to the results for direct sampling. In addition, though the system appears to be lightweight and portable, significant difficulties were encountered in maneuvering the SRI



Figure 5-8. SRI Dilution Sampling System Design (U. S. Department of Energy, 1994a).

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system at stack level once assembled. Cramped stack conditions prevented maneuvering the diluter in and out of the ports, limiting the ability to perform representative sampling. Recovery rinses of the sampler were completed once per day instead of after every run (since complete disassembly of the sampler was necessary for solvent rinsing) due to time constraints and concerns about breakage.

Enhancements to the SRI system for application to petroleum industry sources would include removal of the Method 5 filter upstream of the dilution chamber and elimination of the dilution air filtering bypass, to provide a stack source of fine primary particles. The highly turbulent mixing chamber is qualitatively different mixing than that in an actual plume. Improvements to the portability of the system at stack level would facilitate representative (traversing) sampling.

California Air Resources Board System

The reduced artifact dilution sampler (RADS), illustrated in Figure 5-9, was designed to characterize condensable species which form at the exit of a combustion stack, and has been applied in the Department of Health Services (DHS) laboratory to characterize gaseous and aerosol PAH emissions from diesel engines (Wall, 1997; Lindner and Wall, 1995; Wall, 1994). All chamber materials are PVC with Teflon[®] liners which can withstand solvent rinsing between uses. No sealants or lubricants are used; connections are all Swagelok with Teflon[®] ferrules. The sample is extracted from the stack isokinetically without primary particle removal, passes through a heated inlet line and is injected in cross-flow into a flowing stream of purified dilution air. (Ambient PAH is removed from the dilution air by filtration in a polyurethane foam cartridge.) Mixing is turbulent, with Reynolds numbers greater than 10,000; smoke visualization tests have shown uniform mixing between sample and dilution streams. The diluted stream flows through 10 diameters to develop flow before entering the sampling section. The dilution ratio is adjustable from 10:1 to 50:1; at 35:1 dilution, the dilution chamber residence time is 1.5 seconds, while at 10:1 dilution, the residence time is 5 seconds.

Dilution and sample flow rates in the RADS are controlled by microprocessor using mass flow controllers. Several "reduced artifact sampling trains" may be installed in parallel downstream of the dilution chamber; each is equipped with a variable cut size cyclone to remove large particles upstream of the sample media, followed by a denuder, a 5-inch Teflon[®] filter to capture particulate, and a 6-inch diameter PUF cartridge for absorption of gaseous PAH. Microprocessor flow control allows the dilution ratio to be maintained at a constant level irrespective of the number of cyclones installed for sample collection.



Figure 5-9. California ARB Dilution Sampling System (Wall, 1996).

The sampling probe and inlet lines are heated and temperature controlled to a maximum temperature of 500 °F to avoid premature condensation. Past research on PAH wall losses when sampling diesel exhaust has shown approximately 10 percent loss in the probe and heated hose, and 3 percent loss in the dilution tunnel. Loss percentages were calculated by dividing the PAH recovered from each sampler component by the total PAH, where the total is the sum of that recovered from sampler surfaces plus the PAH deposited on filters. PAH emissions from a 500 kW diesel generator were found to be enhanced in the dilution system from three to ten times the levels detected in a parallel Method 5-type sampling train, with the greatest enhancement in medium molecular weight PAH compounds.

CONSIDERATIONS FOR PETROLEUM INDUSTRY SOURCE TESTS Portability

All of the systems used previously suffer from being relatively heavy and bulky for ready use on petroleum industry stack platforms. Most researchers forgo traversing the stack due to the size of the units. The DRI design is the most evolved of the various systems reviewed in detail, and considerable effort was made to improve its size, weight, and ease of assembly/disassembly. Nevertheless, the system weighs approximately 250 pounds, has a footprint of approximately 3 feet square, and stands approximately 6 feet tall. It is not clear whether a smaller, more portable system could be designed based on the same principles and still achieve all the desired characteristics. There appear to be fundamental considerations limiting the minimum size achievable while avoiding significant particle losses and collecting sufficient sample volume for analysis. Also, if a major change in design were made, comparability to the body of existing test data generated with this equipment by researchers at DRI and Caltech might be questionable. Development and validation of a new system would doubtless be costly and time-consuming. It should also be noted that modifying a facility's stack (sampling platform, ports, etc.) may be very expensive as well.

Sample Collection

Each of the dilution samplers considered in this study is equipped with a multi-port sample collection manifold downstream of the dilution chamber, to which sampling media and a sample pump are attached during field use. Ambient air sampling and analysis methods described in Section 3 are used to allow comparability of data to ambient aerosol data. At least 0.5 mg of recoverable sample is necessary to perform organics speciation using GC/MS; owing to the often low in-stack organics concentrations and to the dilution process, collection of enough sample mass

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to overcome analytical detection limits is a key concern. The minimum practical dilution ratio should be chosen to maximize mass accumulation on the filter media. Sampling media should also be selected to avoid artifact problems which obscure true organic aerosol concentrations: adsorption of organic vapors on filters and collected particulate matter (positive artifact), volatilization of collected particulate matter (negative artifact), as well as chemical reaction of collected particulate species with reactive gases during sampling.

Figure 5-10 shows a typical sample collection scheme (Gray *et al.*, 1986). A vacuum pump is used to draw 25 to 30 liters per minute of sample through a fine particle cyclone. Sample flow splits downstream of the cyclone and is passed through several filtering media, arranged in parallel, with substrates specific to the analytes of interest. Quartz fiber filters are used for organic and elemental carbon determinations, and for organics speciation by GC/MS; Teflon[®] filters are used for ionic species.

Sampling Media Selection

Filtering and sorbent media to be used in this program will be chosen based on their ability to capture secondary aerosols and their precursors. Many compound classes that are present in emissions from combustion sources exhibit a wide range of volatility and are distributed between the gas and particle phases. Volatile organic compounds with carbon numbers greater than seven and semi-volatile organics (for example aliphatic and aromatic hydrocarbons, polycyclic aromatic hydrocarbons) are expected to be present in both phases. The use of a filter for particles and a solid adsorbent for gases is necessary to account for the total concentrations of these species in the diluted samples. Contamination resulting from gaseous organics in the ambient air can be eliminated in dilution samplers by using HEPA and activated carbon filters to preclean the dilution air. PAH compounds may react on glass fiber filters (Daisey *et al.*, 1986); Teflon[®] or Teflon[®]-coated glass fiber filters are preferred for their relative chemical inertness. Particulate organic carbon concentrations have been observed to vary with sampling conditions such as face velocity, sampling period duration, and filter type; such variations are caused at least in part by adsorption of organic vapors by filter media.

Backup filters have been installed downstream of quartz fiber filters to evaluate artifact formation. In emissions testing of a boiler fired on No. 2 fuel oil, Hildemann *et al.* (1989) installed a second quartz fiber filter downstream of a quartz fiber filter, and found that the organic carbon mass

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Figure 5-10. Typical Sampling Protocol (Grey et al., 1986).

collected on the downstream filter averaged 18 percent of the fine organic aerosol mass collected on the upstream filter. Similarly, Cadle et al. (1983) discovered OC on backup filters as high as 15 percent of the concentration on front filters. These results suggest that quartz fiber filters intended to adsorb organic aerosols also adsorb gaseous organics. Also, filtration alone cannot quantify the magnitude of the sampling artifacts since the sorption processes (adsorption of gaseous organics and volatilization of particulate organics) compete with each other. Fitz (1990) used a quartz fiber lined annular denuder upstream of a quartz fiber filter to evaluate organic sampling artifacts, and concluded that the OC concentration on backup filters should be subtracted from that on front filters to yield more accurate ambient organic particle concentrations. Use of a denuder upstream of the filter media to eliminate positive artifact formation is suggested where possible (Fitz, 1990). In past test programs DRI has applied its Fine Particulate/Semivolatile Organic Compound Sampler, equipped with a size-selective inlet, to the collection of semi-volatile organics. A variety of backup solid adsorbents have been used to collect gaseous SVOC and those SVOC which are volatilized off the filter during sampling. Zaranski et al. (1991) performed SVOC sample collection using polyurethane foam-granular adsorbent sandwich cartridges. Good collection efficiencies for naphthalene using either Tenax-GC or XAD resins have been reported. DRI has successfully used PUF/XAD-4/PUF cartridges for collection of semivolatile compounds (including naphthalene) in the several ambient and source emissions monitoring programs. VOC can be sampled by using solid adsorbent cartridges, such as Tenax-GC or Tenax-TA.

Inorganic species, including primary sulfate, nitrate and metals can also be sampled from the dilution tunnel, using a filter sampler. Sequential filter samplers (SFS) with various filter media can be used to sample for PM10 mass, PM2.5 mass, sulfate and nitrate ions, elements, and organic and elemental carbon (OC/EC). The SFS, using a Sierra-Andersen or SA-2541 medium-volume PM10 inlet, has been designated by EPA as a PM10 reference method in the State of Oregon. The SFS can be configured with two channels for simultaneous measurement of mass, ions, elements and OC/EC. Channel 1 consists of a Teflon[®] membrane filter followed downstream by a quartz fiber filter. The Teflon[®] membrane filter removes particles for mass and elemental analyses. The quartz fiber backup filter is intended to quantify organic vapor adsorption which has been found to interfere with organic carbon measurements. Channel 2 of the PM2.5 SFS consists of a quartz fiber filter is submitted to ion and carbon analyses. The NaCl impregnated cellulose fiber filter allows the magnitude of volatilized particle nitrate to be determined and added to the nitrate measurement on the front filter to obtain total PM2.5 particulate nitrate.

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Section 6

RECOMMENDATIONS

TEST OBJECTIVES

Recommended technical objectives for future test programs to characterize fine particulate emissions from stationary combustion sources should be to:

- 1) Characterize primary aerosol emissions, including mass, size, organic carbon, elemental carbon, and organic species, after dilution and aging of stack emissions to simulate near-field atmospheric aerosol formation mechanisms.
- 2) Characterize in-stack total particulate mass and particle size distribution, including PM2.5.
- 3) Characterize major gaseous PM2.5 precursors, specifically organic compounds (especially compounds of carbon $[C_7]$ and above), oxides of nitrogen (NO_x), sulfur dioxide (SO₂), and ammonia.
- 4) Develop organic speciation profiles from particulate matter collected on the filter media after dilution.
- 5) Provide data that can be related to existing ambient particulate data (i.e., of similar quality and completeness).
- 6) Compare total particulate mass (filterable and condensable) using EPA reference methods and dilution sampling.
- 7) Analyze the in-stack total particulate matter for composition (including elemental carbon, nitrates, sulfate, and ammonium).
- 8) Characterize minor gaseous PM2.5 precursors, specifically sulfur trioxide (SO_3) , sulfuric acid (H_2SO_4) and nitric acid (HNO_3) .

The above objectives may be prioritized for individual test programs, but should include as primary objectives at least objectives 1 through 4.

TEST METHODOLOGY

Based on a critical review of sampling and analysis techniques for characterizing fine particulate matter, especially organic aerosols, a methodology combining traditional stationary source sampling methods and dilution sampling techniques is recommended for future testing programs.

Since there is no generally accepted method for accurately measuring PM2.5 at this writing, the initial thrust of a future program should include evaluating and comparing different methods. This critical review strongly suggests that dilution sampling techniques combined with ambient air collection and analysis methods will provide a more accurate characterization of fine particulate emissions than existing EPA stationary source methods. In particular, a comparative study of PM2.5 mass loading and composition based on evolving dilution sampling/ambient air analysis techniques and traditional EPA source sampling methods for size- and phase-segregated particulate matter (e.g., EPA Method 201A, EPA Method 202) is needed. Methods should be evaluated over a range of in-stack conditions (e.g., high versus low solid particulate loadings, different levels of condensable sulfates) representing different source types. An evaluation of organic sampling methods also is recommended. In particular, a comparison of ambient air collection and analysis methods for volatile and semivolatile organic compounds combined with dilution sampling techniques and source-level sampling methods (e.g., EPA Method 0031, EPA Method 0010) is needed. The results of the method comparison study then could be used to define the applicability of different methods to various source types for future tests. It also would facilitate linking results from future tests to existing source emission and ambient air test data (e.g., air toxics source emissions databases, ambient PM2.5 monitoring network data).

Figure 6-1 illustrates a recommended test approach combining dilution and traditional source sampling methods that would accomplish the objectives stated at the beginning of this section. In this approach, PM2.5 mass and composition would be characterized using two different methods: a modified version of EPA's stationary source methods for PM10 and condensable particulate emissions, and a dilution sampling technique with ambient air collection and analysis methods. To facilitate method comparison, sampling probes would be co-located in the source stack to eliminate potential differences caused by concentration and flow gradients in the stack. The samples collected with the two sample trains would be characterized for PM2.5 mass, elemental and organic carbon, organic species, elemental composition, sulfates, nitrates, and ammonium. Traditional source sampling methods would be applied for measuring in-stack volatile and semivolatile organic compounds, for comparison to samples collected from the dilution sampler using ambient air methods. Traditional stationary source sampling methods also would be applied to collect other secondary particulate precursors (ammonia, SO₃, NO_x, and SO₂) and to characterize the total instack particle size distribution.

6-2



Figure 6-1. Overview of Recommended Measurements for Characterizing Emissions of Fine Particulate, Especially Organic Aerosols, and Its Precursors from Combustion Devices.

6-3

Dilution sampling for characterizing stationary source emissions is currently a research tool that has been widely used in the scientific community but which has not been adopted by EPA for regulatory purposes. Several different dilution sampler designs were identified in the critical review, which generally share several common elements. A stack gas sample is typically withdrawn from the stack, sometimes through a cyclone separator to remove large particles, before being transported through a heated sample line to a dilution tunnel. In the dilution tunnel, the stack gas is mixed with dilution air under turbulent flow conditions and cooled via dilution to near-ambient temperature and concentrations. Purified ambient air or bottled gas mixtures have been used at dilution ratios ranging from 25:1 to 500:1. The completely mixed and diluted stack gas sample is passed to a sampling manifold at the back end of the mixing chamber where the pollutant samples are captured on various filter and sorbent media before being exhausted. The methods of sample collection and analysis usually resemble those used for ambient air measurements.

Since a standard method for dilution sampling of stationary sources is not presently available, this is an area that should be developed in future test programs. Hildemann et al. (1989) developed several critical design criteria for dilution samplers intended for evaluating organic aerosols: (1) mixing chambers should simulate the cooling and dilution that stack gases experience as they disperse in the atmosphere; (2) sufficient residence time should be provided for condensation of aerosols upstream of the sample collection point (typically 60 seconds or more after mixing is completed); (3) vapor and particle losses to the surfaces of the sampler should be minimized by avoiding flow constrictions while still allowing for control of dilution and stack gas streams; and (4) contamination and other sampling artifacts should be avoided. Contamination can be avoided by building the sampler from organically inert materials, and designing the system such that mild heat treatment and solvent rinsing between uses are possible. Sample collection for particulateand gas-phase organic matter should be designed to minimize artifacts. In addition, dilution samplers designed for field use should be lightweight and portable, and should have a small footprint to allow use on small sampling platforms. Due to the importance of organic aerosols for petroleum industry tests, it is recommended that dilution samplers incorporating the above criteria be used for future testing programs. More specific recommendations for dilution sampler design and operation based on these criteria are provided below.

6-4
Dilution Ratio

Mixing between stack gases and the ambient atmosphere is a function of stack temperature and local meteorology. In a quiescent environment, mixing may take place slowly, in turbulent eddies at the interface between the flowing plume and the ambient air, while under windy conditions mixing is more rapid and cross-flowing. None of the samplers reviewed allows for adjustable geometry of dilution or sample injection to match local plume conditions. Most systems attempt to qualitatively simulate plume processes by dilution and turbulent mixing sufficient to match the temperature at the sampling point to ambient conditions. Several of the designs promote highly turbulent mixing which achieves a rapid reduction in temperature and uniform concentrations but which may not lead to aerosol formation representative of actual plume conditions. Conversely, mixing chamber geometries which do not provide for high turbulence may not lead to representative aerosol concentrations at the sample extraction point. Smith et al. (1982) reported that dilution sampler emissions tests on an oil-fired furnace showed a dependence of aerosol size on dilution ratio, with larger particles resulting from higher dilution ratios and smaller particles resulting from smaller ratios. It is clear that obtaining representative aerosol data requires not only uniform concentrations at the sampling point, but also mixing in a manner that simulates local conditions governing nucleation, coagulation and condensation as closely as possible. It is recommended that dilution ratios of 40:1 or greater be used, to minimize particle losses on the dilution sampler surfaces and to adequately simulate aerosol formation processes that occur in the near-field plume.

Residence Time

The characteristic time necessary for formation of secondary aerosol varies from a few seconds to several days, depending on the concentration and volatility of gaseous precursors, availability of primary particles and moisture droplets, sunlight intensity and radical species. For the purpose of characterizing combustion source emissions of secondary aerosols, atmospheric formation processes can be roughly grouped into those occurring in the time scale of the plume dispersion, and those dependent on diurnal cycles of sunlight intensity and availability of radical species on an urban scale. Since the focus of the current study is to better understand secondary aerosol formation sources, photochemical reaction pathways occurring in the atmosphere beyond the plume are excluded.

Theoretical predictions of the time necessary for condensation to occur in a dilution sampler may exceed the 1-2 seconds of residence time provided in most dilution samplers, especially for

6-5

cleaner-burning sources, like those using natural gas, which generate limited amounts of primary particulate matter under hot stack conditions (Hildemann *et al.*, 1989). The characteristic time necessary for homogeneous and heterogeneous condensation of aerosols depends on parameters specific to the source tested and local meteorology. Estimated requirements for dilution chamber residence time range from 1-2 seconds to several minutes (Hildemann *et al.*, 1989), depending on the degree of supersaturation of vapors and the availability of primary particles to serve as condensation nuclei. A single "target" response time may be misleading in light of these conditions. Instead, it is recommended that the dilution chamber be configured to approximate time scales of actual plume mixing, when possible, and should be adjustable, to allow enough residence time for condensation processes to occur. Based on estimated condensation times for conditions typical of combustion sources, the dilution sampler should provide a residence time of at least 60 seconds after dilution and mixing are complete.

Particle Losses

Particles may adhere to sampler surfaces after displacement by gravitational, inertial, diffusional or electrostatic attraction mechanisms. Maintaining isokinetic sampling both in-stack and at the sample aliquot extraction points within the sampler also is important. One approach is to provide variable size tubes to match the sample extraction rate and the gross flow through the dilution tunnel (Houck *et al.*, 1982). Diffusion and electrostatic attraction to sampler surfaces are probably more important loss mechanisms for fine particulate than non-isokinetic sampling, since inertial and gravitational mechanisms are insignificant in this size range (Felix *et al.*, 1981; McCain and Williamson, 1983). Losses of charged particles to the electrically non-conducting surfaces (e.g., PVC and Teflon[®]) of dilution samplers can be significant. Use of conducting surfaces and installation of charge neutralizers to avoid fine particle loss is recommended wherever possible.

The greatest particle losses usually occur in probes, inlet lines and flow metering devices. Felix (1981) reported that at a sampling rate of 1 liter/minute, a sample line removed $0.005 \,\mu\text{m}$ particles by diffusion at a rate of 8 percent of the instantaneous concentration per foot of sample line; short probes and high sample flow rates into the dilution chamber were therefore recommended. To minimize line losses, the dilution sampler design also should incorporate heated, temperature controlled probes and hoses to prevent condensation prior to mixing with dilution air. As discussed previously, dilution ratios of 40:1 or greater, particle charge neutralization (especially for sources which employ electrostatic precipitators to control particulate emissions), avoiding the use

of electrically non-conducting materials for construction, and elimination of flow obstructions in the probe also will reduce particle losses in the system

Sample Contamination

Concentrations of individual species are typically near detection limits for most volatile and semivolatile organics even at the source level. When diluted at 10 or 25 to one, quantification is even more difficult and encourages the use of high-volume sampling techniques. Several investigators have reported a minimum sample mass accumulation for organic speciation of between 0.5 and 3 mg on Teflon[®] membrane filters (Hildemann *et al.*, 1989; Houck *et al.*, 1982; Stevens, 1997). Contamination of the dilution train from previously sampled organics may therefore be significant if present; provision should be made for thorough decontamination through the use of stainless steel and minimal amounts of Teflon[®] (subject to electrostatic losses discussed above) materials that can be completely solvent-rinsed prior to each use. Dilution samplers should be constructed of materials which will not dissolve or degrade during solvent rinsing or when exposed to caustic or corrosive stack gases. Use of rubber, plastics, greases or oils upstream of where the samples are collected is to be avoided, since these materials may provide a source of organics within the sampler.

Background levels of organics in the ambient air may be significant; comparable levels of toluene in the ambient air and stack have been observed in sampling at coal-fired power plants (McGrath *et al.*, 1994). Therefore, the dilution air must either be thoroughly conditioned prior to introduction to the sample or pure gas mixtures must be used. The latter approach is comparatively expensive; filtration has provided acceptable blanks in previous applications. Care must be taken to avoid other sources of contamination, e.g., from heating tapes used to wrap probes and lines which have been shown to release toluene and benzene if local hot spots develop.

Flow Control and Measurement

Field adjustable dilution and/or stack gas flows are useful for varying residence times in the dilution chamber to site-specific sampling conditions. In addition, accurate flow rate and/or sample volume data must be available to correctly report in-stack concentrations from sample mass collected after dilution. Many dilution samplers rely on laboratory calibration curves relating sample and dilution stream pressure drops to volumetric flow through the system. In field application, flow obstructions within the sampler may arise due to particle accumulation, changed fittings, sublimation of Teflon[®] components from overheating, line kinking, etc. These

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occurrences reduce the accuracy of the flow data determined via differential pressure-flow calibration curves, and the overall quality of the sampling effort. Therefore a reliable, field-verifiable method of flow measurement is important. Most researchers have found venturis and flow orifices suitable for flow measurement, therefore these are recommended. Since sample collection typically takes several hours, a computer data logger/ flow controller also is recommended.

Field Use

Contamination and background interferences also present significant challenges to dilution samplers. To minimize contamination and facilitate efficient use in the field, samplers should be easy to take apart for recovery and cleaning between sample runs, and must be leak free without relying on greases or silicone. The system should be lightweight and modular to allow set-up and take-down by a two person crew in a short amount of time, and should have a small footprint that fits onto cramped stack platforms.

Section 7

REFERENCES

Arey, J., B. Zielinska, R. Atkinson, A.M. Winer, T. Ramdahl and J.N. Pitts, Jr. (1986). The formation of nitro-PAH from the gas-phase reactions of fluoranthene and pyrene with the OH radical in the presence of NO_x . *Atmospheric Environment*. 20: 2339-2345.

Arey, J., B. Zielinska, R. Atkinson and A.M. Winer (1987). Polycyclic aromatic hydrocarbon and nitroarene concentrations in ambient air during a wintertime high NO_x episode in the Los Angeles basin. *Atmospheric Environment.* 21: 1437-1444.

Arey J., B. Zielinska, R. Atkinson and S.M. Aschmann (1989a). Nitroarene products from the gas-phase reactions of volatile polycyclic aromatic hydrocarbons with the OH radical and N_2O_5 . *International Journal of Chemical Kinetics*. 21: 775-799.

Arey, J., R. Atkinson, B. Zielinska and P.A. McElroy (1989b). "Diurnal concentrations of volatile polycyclic aromatic hydrocarbons and nitroarenes during a photochemical air pollution episode in Glendora, California." *Environ. Sci. Technol.*, 23, 321-327.

Atkinson, R. (1986). "Kinetics and mechanisms of the gas-phase reactions of the hydroxyl radical with organic compounds under atmospheric conditions." *Chem. Rev.*, 86, 69.

Atkinson, R., J. Arey, A.M. Winer and B. Zielinska (1988). "A survey of ambient concentrations of selected polycyclic aromatic hydrocarbons (PAH) at various locations in California." Final Report, prepared under Contract No. A5-185-32, for the California Air Resources Board, Sacramento, CA, by Statewide Air Pollution Research Center, University of California, Riverside, CA.

Atkinson, R. (1989). "Kinetics and mechanisms of the gas-phase reactions of the hydroxyl radical with organic compounds." *J. Phys. Chem. Ref. Data*, Monograph, 1, 1.

Atkinson, R., J. Arey, B. Zielinska and S.M. Aschmann (1990). "Kinetics and nitro-products of the gas-phase OH and NO_3 radical-initiated reactions of naphthalene-d₈, fluoranthene-d₁₀ and pyrene." *Int. J. Chem. Kinet.*, 22, 999-1014.

Baladi, E.Y. and R.C. Stultz, "A Dynamic Sampling-Dilution System for Use in Conjunction with Fine Particle Counters in a Source. Presented at the 70th Annual Meeting, Air Pollution Control Association, Toronto, Canada, Paper 77-21.1, (June 1977).

Bassett, M., and J.H. Seinfeld (1983a). "Atmospheric equilibrium model of sulfate and nitrate aerosols." *Atmos. Environ.*, 17, 2237-2252.

Bassett, M., and J.H. Seinfeld (1983b). "Atmospheric equilibrium model of sulfate and nitrate aerosols -- ii. Particle size analysis." *Atmos. Environ.*, 18, 1163-1170.

Benner, B.A., G.E. Gordon and S.A. Wise (1989). "Mobile sources of atmospheric PAH: A roadway tunnel study." *Environ. Sci. Technol.*, 23, 1269-1278.

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Bidleman, T.F., W.N. Billings, and W.T. Foreman (1986). "Vapor-particle partitioning of semivolatile organic compounds: Estimates from field collections." *Environ. Sci. Technol.*, 20, 1038-1043.

Bradway, R. M. and R. W. Cass (1975). "Fractional efficiency of a utility boiler baghouse, Nucla Generating Plant." EPA 600-2-75-013a, U.S. Environmental Protection Agency, Research Triangle Park, NC.

Brown, R.H., and C.J. Purnell (1979). "Collection and analysis of trace organic vapour pollutants in ambient atmospheres." J. Chromatog., 178, 79-90.

Cadle, S.H., Groblicki, P.J., and Mulawa, P.A. (1983). "Problems in the sampling and analysis of carbon particulate." *Atmospheric Environment*, 17: 593-600.

Calvert, J.G., and W.R. Stockwell (1983). "Acid generation in the troposphere by gas-phase chemistry." *Environ. Sci. Technol.*, 17, 428A-443A.

Carpenter, K.A. (1978). Master's Thesis, Michigan Technological University.

Carter, W.A., H.J. Buening, and S.C. Hunter (1978). "Emission reduction on two industrial boilers with major combustion modifications." EPA-600/7-78-099a, U.S. Environmental Protection Agency, Research Triangle Park, NC.

Cass, G.R., P.M. Boone, and E.S. Macias (1982). In <u>Particulate Carbon: Atmospheric Life Cycle</u>. Wolff, G.T. And R.L. Klimisch eds., Plenum Press: New York, pp. 207-240. Charlson, R.J., N.C. Ahlquist, H. Selvidge and P.B. MacCready (1969). "Monitoring of atmospheric aerosol parameters with the integrating nephelometer." J. Air Poll. Control Assoc., 19, 937-942.

Chow, J.C., J.G. Watson, L.C. Pritchett, W.R. Pierson, C.A. Frazier and R.G. Purcell (1993). "The DRI thermal/optical reflectance carbon analysis system: Description, evaluation and applications in U.S. air quality studies." *Atmos. Environ.*, 27A, 1185-1201.

Chow, J.C. (1995). "Measurement methods to determine compliance with ambient air quality standards for suspended particles." J. Air & Waste Manage. Assoc., 45: 320-382.

Chuang, J.C., S.V. Hannan and N.K. Wilson (1987). "Field comparison of polyurethane foam and XAD-2 resin for air sampling for polynuclear aromatic hydrocarbons." *Environ. Sci. Technol.*, 21, 798.

Ciccioli, A., A. Cecinato, E. Brancaleoni, R. Draisci and A. Liberti (1989). "Evaluation of nitrated PAH in anthropogenic emission and air samples." *Aerosol Sci. Technol.*, 10, 296-310.

Cooper, J. and R. Peltier (1992). "Simultaneous particulate and vapor-phase stack sampling for toxic species using plume simulating dilution sampling with zero background air." Presented to U.S. Department of Energy, Pittsburgh Energy Technology Center.

Cooper, J. *Hazardous element sampling train (HEST) update*. Presented at the meeting of Stationary Source Sampling and Analysis for Air Pollutants, XVIII, Palm Coast Florida, April 29, 1994.

Corio, L. A. and J. Sherwell (June 1997). "In-Stack condensable particulate matter measurement and permitting issues." Air and Waste Management Association 90th Annual Meeting and Exhibition, Toronto.

Cotham, W.E., and T.F. Bidleman (1992). "Laboratory investigations of the partition of organochlorine compounds between the gas phase and atmospheric aerosols on glass fiber filters." *Environ. Sci. Technol.*, 26, 469-478.

Coutant, R.W., L. Brown, J.C. Chuang, R.M. Riggin and R.G. Lewis (1988). "Phase distribution and artifact formation in ambient air sampling for polynuclear aromatic hydrocarbons." *Atmos. Environ.*, 22, 403-409.

Coutant, R.W., P.J. Callahan, M.R. Kuhlman and R.G. Lewis (1989). "Design and performance of a high-volume compound annular denuder." *Atmos. Environ.*, 23, 2205-2211.

Coutant, R.W., P.J. Callahan and J.C. Chuang (1992). "Efficiency of silicone-grease-coated denuders for collection of polynuclear aromatic hydrocarbons." *Atmos. Environ.*, 26, 2831-2834.

Covert, D.S., R.J. Charlson and N.C. Ahlquist (1972). "A study of the relationship of chemical composition and humidity to light scattering by aerosols." *J. Appl. Meteorol.*, 11, 968-976.

Daisey, J.M., J.L. Cheney, and P.J. Lioy (1986). "Profiles of organic particulate matter emissions from air pollution sources: Status and needs for receptor source apportionment modeling." *J. Air Poll. Control Assoc.*, Vol. 36, no. 1: 17-33.

Ensor, D. S., B. S. Jackson, S. Calvert and C. Lake, "Evaluation of a particulate scrubber on a coal-fired utility boiler." EPA 600/2-75-074, U.S. Environmental Protection Agency, Research Triangle Park, NC (1975).

Felix, L.G., R.L. Merritt, J.D. McCain, and J. W. Ragland (1981). "Sampling and dilution system design for measurement of submicron particle size and concentration in stack emissions aerosols." *TSI Quarterly*, 7: 3-12.

Felton, C.C., J.C. Sheppard and M.J. Campbell (1988). "Measurements of the diurnal OH cycle by a ¹⁴C-tracer method." *Nature*, 335, 53-55.

Fernandez de la Mora, J., S. V. Hering, N. Rao, and P. H. McMurry (1990). J. Aerosol Sci. 21:169-187.

Fields, P. G. and S. M. Roe, "Assessing the significance of secondary organic aerosol contributions to regional particulate inventories." E. H. Pechan Associates, citation unknown.

Finlayson-Pitts, B.J., and J.N. Pitts, Jr. (1986). <u>Atmospheric Chemistry: Fundamentals and</u> <u>Experimental Techniques</u>. John Wiley & Sons, New York, NY.

Fitz, Dennis R. (1990). "Reduction of the positive organic artifact on quartz filters." Aerosol Science and Technology, 12: 142-148.

Foreman, W.T., and T.F. Bidleman (1990). "Semivolatile organic compounds in the ambient air of Denver, Colorado." *Atmos. Environ.*, 24A, 2405-2416.

Friedlander, S.K. (1977). Smoke, Dust and Haze. John Wiley & Sons, Inc., New York, New York.

Garvey, D.M., and R.G. Pinnick (1983). "Response characteristics of the particle measuring systems active scattering aerosol spectrometer probe (ASASP-X)", *Aerosol Sci. Technol.*, 2: 477-488.

Gray, H.A. (1986). "Control of atmospheric fine primary carbon particle concentrations." Ph.D. Thesis; available as EQL Report 23; Environmental Quality Laboratory, California Institute of Technology, Pasadena, CA.

Gray, H.A., G.R. Cass, J.J. Huntzicker, E.K. Heyerdahl, and J.A. Rau (1986). "Characteristics of atmospheric organic and elemental carbon particle concentrations in Los Angeles." *Environ. Sci. Technol.*, 20: 580-589.

Grosjean, D., and S.K. Friedlander (1975). "Gas-particle distribution factors for organic and other pollutants in the Los Angeles atmosphere." J. Air Pollut. Assoc., 25, 1038.

Grosjean, D., and J.H. Seinfeld (1989). "Parameterization of the formation potential of secondary organic aerosols." *Atmos. Environ.*, 23: 1733-1747.

Grosjean, D. (1992). "In situ organic aerosol formation during a smog episode: Estimated production and chemical functionality." *Atmos. Environ.*, 26A, 953-963.

Gundel, L.A., R.K. Stevens, J.M. Daisey, V. Lee and K.R.R. Mahanama (1992). "Annular denuders for sampling semi-volatile polycyclic aromatic hydrocarbons and other organic species." Presented at the 11th Annual Meeting, American Association for Aerosol Research, San Francisco, CA, October 12-16.

Hansell, D. and England, G. Energy and Environmental Research Corporation (1997). "Development of Toxic Emission Factors for Petroleum Industry Combustion Sources". American Petroleum Institute, Washington, D.C.

Harris, G. E. and L. A. Rohlack (December 1982). "Particulate emissions from non-fired sources in petroleum refineries: A review of existing data." American Petroleum Institute, Particulates Task Force (by Radian).

Heinsohn, R.J., J.W. Davis, and K.T. Knapp (1980). "Dilution source sampling system." *Environ. Sci. Technol.*, 14: 1205-1209.

Hildemann, L.M., G.R. Cass, and G.R. Markowski (1989). "A dilution stack sampler for organic aerosol emissions: Design, characterization and field tests." *Aerosol Sci. Technol.*, 10, 193-204.

Hildemann, L. M., G.R. Markowski, G.R. Cass (1991a). "Chemical composition of emissions from urban sources of fine organic aerosol." *Environ. Sci. Technol.*, 25, 4.

Hildemann, L.M., M.A. Mazurek, and G.R. Cass (1991b). "Quantitative characterization of urban sources of organic aerosol by high-resolution gas chromatography." *Environ. Sci. Technol.*, 25, 7.

Hildemann, L. M., G. R. Markowski, M. C. Jones, and G. R. Cass (1991c). "Submicrometer aerosol mass distributions of emissions from boilers, fireplaces, automobiles, diesel trucks, and meat-cooking operations." *Environ. Sci. Technol.*, 14:138-152.

Hildemann, L. M., M. A. Mazurek, G. R. Cass, and B. R. T. Simoneit (1994a). "Seasonal trends in Los Angeles ambient organic aerosol observed by high-resolution gas chromatography." *Aerosol Sci. and Technol.* 20:303-317.

Hildemann, L. M., D. B. Klinedinst, G. A. Klouda, and L. A. Currie, and G. R. Cass (1994b). "Sources of urban contemporary carbon aerosol." *Environ. Sci. Technol.*, Vol 28, No. 9.

Hinds, W.C. (1982). In <u>Aerosol Technology: Properties, Behavior, and Measurement of Airborne</u> <u>Particles</u>, New York: Wiley, pp. 28-37.

Holve, D.J. (1996). Personal communication. Insitec Measurement Systems, San Ramon, CA.

Houck, J.E., J.A. Cooper and E.R. Larson. Dilution sampling for chemical receptor source fingerprinting. Paper No. 82-61M.2, presented at 75th Annual Meeting of the Air Pollution Control Association, New Orleans, LA, (June 20-25, 1982).

International Standards Organization (1994). ISO 8178.

Jackson, M. D., J. F. McGaughey, R. G. Merrill, J. T. Bursey (1996). "Method evaluation study: The application of SemiVOST to the nonhalogenated semivolatile organic compounds from the Clean Air Act Amendments." Proceedings of the International Specialty Conference on Measurement of Toxic and Related Air Pollutants, Research Triangle Park, NC, Air and Waste Management Association, VIP-64.

John, W., W. Winklmayr, and H.C. Wang (1991). "Particle deagglomeration and reentrainment in a PM10 sampler." *Aerosol Sci. Technol.*, 14: 165-176.

Kaupp, H., and G. Umlauf (1992). "Atmospheric gas-particle partitioning of organic compounds: Comparison of sampling methods." *Atmos. Environ.*, 26A, 2259-2267.

Lane, D.A., N.D. Johnson, S.C. Barton, G.H.S. Thomas and W.H. Schroeder (1988). "Development and evaluation of a novel gas and particle sampler for chlorinated organic compounds in ambient air." *Environ. Sci. Technol.*, 22, 941-947.

Lane, D.A., N.D. Johnson, M.J.J. Hanley, W.H. Schroeder and D.T. Ord (1992). "Gas- and Particle-Phase Concentrations of a-hexachlorocyclohexane, g-hexachlorocyclohexane and Hexachlorobenzene in Ontario Air." *Environ. Sci. Technol.*, 26, 126-132.

Lanier, W.S. (May 1997). Personal communication. Energy and Environmental Research Corporation, 1001 Aviation Parkway, Morrisville, NC.

Lee, F.S.C., and D. Schuetzle (1983). "Sampling, extraction and analysis of PAH from internal combustion engines." <u>Handbook of Polycyclic Aromatic Hydrocarbons</u>, Chapter II, A. Bjeorseth, ed., Marcel Dekker, New York, NY.

Ligocki, M., and J.F. Pankow (1989). "Measurements of the gas/particle distributions of atmospheric organic compounds." *Environ. Sci. Technol.*, 23, 75-83.

Lindner, G. and S. Wall (1995). "Comparison of PAH emissions determined by ARB Method 429 and a dilution sampling (DS) method." Unpublished presentation to Engineering Foundation Conference on Stationary Source Sampling and Analysis for Air Pollutants XIX, San Diego (March 1995).

Logan, T. Personal Communication. Emission Measurement Center, U.S. Environmental Protection Agency, (March 1997).

Lurmann, F., J. Collins and J. Coyner (1988). "Development of a chemical transformation submodel for annual PM10 dispersion modeling." Report No. P-E146-002, prepared for the South Coast Air Quality Management District, El Monte, CA, by Environmental Research and Technology, Camarillo, CA.

Lurmann, F. (1989). "A review of PM10 air quality models." In <u>Transactions: Receptor Models</u> in <u>Air Resources Management</u>, J.G. Watson, ed. Air & Waste Management Association, Pittsburgh, PA, pp. 461-474.

Marple, V.A., K.L. Rubow, and S.M. Behm (1991). A Microorifice Uniform Deposit Impactor (Moudi): Description, Calibration, and Use. *Aerosol Science and Technol*.ogy. 14: 434-446.

McCain, J.D., and A.D. Williamson (1983). Development and evaluation of dilution probes used for sampling to determine source signatures. EPA 600/3-84-045, U.S. Environmental Protection Agency, Research Triangle Park, NC.

McDow, S.R. and J.J. Huntzicker (1990). Vapor adsorption artifact in the sampling of organic aerosol: Face velocity effects. *Atmospheric Environment*. 24A: 2563-2572.

McGrath, T.M., G.C. England, D. Hansell, B. Springsteen, M. Boddy, W. Oberg, and L. Pooler (1994). "Assessment of Toxic Emissions from a Coal-Fired Power Plant Utilizing an ESPs: Final Report." DOE Contract DE-AC22-94PC93252, Energy and Environmental Research Corporation, Irvine, CA.

Miller, S.E. (1985). "Measurement of sulfur and carbon species emissions from oil-fired commercial and institutional boilers." EPA/600/3-85/030, U.S. Environmental Protection Agency, Research Triangle Park, NC.

Mount, G.H. (1992). "The measurement of tropospheric OH by long path absorption: 1. Instrumentation." J. Geophys. Res., 97: 2427-2444.

Namiesnik, J. (1988). Preconcentration of gaseous organic pollutants in the atmosphere. *Talanta*. 35: 567-587.

National Research Council (1979). Airborne Particles. University Park Press, Baltimore, MD.

Odum, J.R., T.P.W. Jungkamp, R.J. Griffin, R.C. Flagan and J.H. Seinfeld (1997). The atmospheric aerosol-forming potential of whole gasoline vapor. *Science*. 276: 96-99.

Offerman, F.J., S.A. Loiselle, J.M. Daisey, A.T. Hodgson, and L.A. Gundel (1990). "Sampling, analysis and data validation of indoor concentrations of polycyclic aromatic hydrocarbons (PAH)." Final Report, prepared under Contract No. A732-106, for California Air Resources Board, Sacramento, CA.

Pandis, S.N., R.A. Harley, G.R. Cass and J.H. Seinfeld (1992). "Secondary aerosol formation and transport." *Atmos. Environ.*, 26: 2269-2282.

Pankow, J.F. (1992). "Application of Common Y-Intercept Regression Parameters for Log Kp vs 1/T for Predicting Gas-Particle Partitioning in the Urban Environment." *Atmos. Environ.*, 26A:2489-2497.

Pellizzari, E., B. Demian, and K. Krost (1984). "Sampling of organic compounds in the presence of reactive inorganic gases with Tenax GC." Anal. Chem., 56, 793-798.

Pitts, J.N., Jr., J.A. Sweetman, B. Zielinska, A.M. Winer, and R. Atkinson (1985). "Determination of 2-nitrofluoranthene and 2-nitropyrene in ambient particulate organic matter: Evidence for atmospheric reactions." *Atmos. Environ.*, 19, 1601-1608.

Prestbo, E. J. Personal communication. Frontier Geosciences, Seattle, WA (June 1997).

Rogge, W.F., L.M. Hildemann, M.A. Mazurek and G.R. Cass (1991). "Sources of fine organic aerosol 1. Charbroilers and meat cooking operations." *Environ. Sci. Technol.*, 25, 1112-1125.

Rogge, W.F. (1993). "Molecular tracers for sources of atmospheric carbon particles: measurements and model predictions." Ph.D. Dissertation, California Institute of Technology, Pasadena, CA.

Rogge, W.F., M.A. Mazurek, L.M. Hildemann, G.R. Cass and B.R.T. Simoneit (1993a). "Quantification of urban organic aerosols at a molecular level: Identification, abundance and seasonal variation." *Atmos. Environ.*, 27, 1309-1330.

Rogge, W.F., L.M. Hildemann, M.A. Mazurek and G.R. Cass (1993b). "Sources of fine organic aerosol. 2. Noncatalyst and catalyst-equipped automobiles and heavy-duty diesel trucks." *Environ. Sci. Technol.*, 27, 636-651.

Rogge, W.F., L.M. Hildemann, M.A. Mazurek, G.R. Cass and B.R.T. Simoneit (1993c). "Sources of fine organic aerosol. 3. Road dust, tire debris, and organometallic brake lining dust: Roads as sources and sinks." *Environ. Sci. Technol.*, 27, 1892-1904.

Rogge, W.F., L.M. Hildemann, M.A. Mazurek, G.R. Cass and B.R.T. Simoneit (1993d). "Sources of fine organic aerosol. 4. Particulate abrasion products from leaf surfaces of urban plants." *Environ. Sci. Technol.*, 27, 2700-2711.

Rogge, W.F., L.M. Hildemann, M.A. Mazurek, G.R. Cass and B.R.T. Simoneit (1993e). "Sources of fine organic aerosol. 5. Natural gas home appliances." *Environ. Sci. Technol.*, 27, 2736-2744.

Rudling, J., E. Bjorkholm, and B.O. Lundmark (1986). "Storage stability of organic solvents adsorbed on activated carbon." Ann. Occup. Hyg., 30, 319-327.

Rudolph, J., K.P. Müller, and R. Koppmann (1990). "Sampling of organic volatiles in the atmosphere at moderate and low pollution levels." *Analytical Chimica Acta*, 236, 197-211.

Russell, A.G., G.J. McRae and G.R. Cass (1983). "Mathematical modeling of the formation and transport of ammonium nitrate aerosol." *Atmos. Environ.*, 17, 949-964.

Russell, A.G., and G.R. Cass (1984). "Acquisition of regional air quality model validation data for nitrate, sulfate, ammonium ion and their precursors." *Atmos. Environ.*, 18, 1815-1827.

Russell, A.G., and G.R. Cass (1986). "Verification of a mathematical model for aerosol nitrate and nitric acid formation and its use for control measure evaluation." *Atmos. Environ.*, 20, 2011-2025.

Saxena, P., A.B. Hudischewskyj, C. Seigneur and J.H. Seinfeld (1986). "A comparative study of equilibrium approaches to the chemical characterization of secondary aerosols." *Atmos. Environ.*, 20, 1471-1483.

Schauer, J. J., W. F. Rogge, L. M. Hildemann, M. A. Mazurek and G. R. Cass (1996). "Source apportionment of airborne particulate matter using organic compounds and tracers." *Atmos. Environ.* 30,22:3837-3855.

Schmidt, E. W., J. A. Gieseke, and J. M. Allen (1976). "Size distribution of fine particulate emissions from a coal-fired power plant." *Atmospheric Environment*. 10(12): 1065-1069.

Smith, W. B., K.M. Cushing, J.W. Johnson, C.T. Parsons, A.D. Williamson, and R.R. Wilson, Jr. (1982) "Sampling and data handling methods for inhalable particulate sampling." EPA-600/7-82-036, U.S. Environmental Protection Agency, Research Triangle Park, NC.

Stelson, A.W., and J.H. Seinfeld (1982a). "Relative humidity and temperature dependence of the ammonium nitrate dissociation constant." *Atmos. Environ.*, 16, 983-992.

Stelson, A.W., and J.H. Seinfeld (1982b). "Relative humidity and pH dependence of the vapor pressure of ammonium nitrate-nitric acid solutions at 25 °C." *Atmos. Environ.*, 16, 993-1000.

Stelson, A.W., and J.H. Seinfeld (1982c). "Thermodynamic prediction of the water activity, NH_4NO_3 dissociation constant, density and refractive index for the NH_4NO_3 - $(NH_4)_2SO_4$ - H_2O system at 25 °C." Atmos. Environ., 16, 2507-2514.

Stevens, R. K. (February 1997). Personal communication. Florida Department of Environmental Protection, c/o U.S. EPA, MD-47, Research Triangle Park, NC.

Sverdrup, G. M., J. C. Chuang, L. Slivon, A. R. McFarland, J. A. Cooper, R. W. Garber, B. S. Smith (1995). "Comparison of the chemical composition of fly ash particles collected in the plume and stack of a coal-fired power plant." For Battelle, Columbus Operations.

Turpin, B.J., and J.J. Huntizicker (1991). "Secondary formation of organic aerosol in the Los Angeles Basin: A descriptive analysis of organic and elemental carbon concentrations." *Atmos. Environ*, 25A: 207-215.

URG Corporation (1996). "Operating Manual, Model URG-3000R Large Source Dilution Sampling System."

U.S. Department of Energy (May 1996). "Characterization of toxic emissions from two coalfired utility boilers operating at different combustion intensities." Final Report, Contract No. DE-AC22-91PC90366.

U.S. Department of Energy (June 1994). "Characterizing toxic emissions from a coal-fired power plant demonstrating the AFGD ICCT Project and a plant utilizing a dry scrubber/baghouse system: Final report, Springerville Generating Station Unit No. 2." Pittsburgh Energy Technology Center, DOE/PC/93254.

U.S. Department of Energy (June 1994). "A study of toxic emissions from a coal-fired power plant - Niles Station Boiler No. 2." Pittsburgh Energy Technology Center, DOE/PC/93251-T1 (DE94016050).

U.S. EPA (1988). "Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air". EPA/600/4-89/017. U.S. Environmental Protection Agency, Research Triangle Park, NC.

U.S. EPA (1991). "Technical Assistance Document for Sampling and Analysis of Ozone Procursors". EPA/600-8-91/215. U.S. Environmental Protection Agency, Research Triangle Park, NC.

Vanderpool, R. W., D. A. Lundgren, V. A. Marple and K. L Rubow (1987). Aerosol Sci. Technol. 7:177-185.

Wall, S. (February 1997). Personal Communication. California Air Resources Board.

Wall, S. M. (1994). "Application of a new integrated sampling method to the measurement of PAH in diesel combustion aerosols." International Aerosol Research Assembly/American Association for Aerosol Research, Fourth International Aerosol Conference, Los Angeles.

Wall, S. M. (1996). "Improved methods for PAH combustion source sampling." Final Report, California Air Resources Board Contract A932-098, NTIS PB97148746.

Walling, J.F., J.E. Bumgarner, D.J. Driscol, C.M. Morris, A.E. Riley, and L.H. Wright (1986). "Apparent reaction products desorbed from Tenax used to sample ambient air." *Atmos. Environ.*, 20, 52-57.

Watson, J.G., and J.C. Chow (1994). "Particle and gas measurements on filters." <u>Environmental</u> <u>Sampling for Trace Analysis</u>, Chapter 6, B. Markert, ed., VCH Publishers, Inc., New York, NY.

Watson, J.G., J.C. Chow, C.F. Rogers, D. DuBois, C. Cahill (1997). "Analysis of historical PM10 and PM2.5 measurements in Central California." Draft report prepared for California Regional Particulate Air Quality Study, Sacramento, CA, by Desert Research Institute, Reno, NV.

Wexler, A.S., and J.H. Seinfeld (1992). "Analysis of aerosol ammonium nitrate: Departures from equilibrium during SCAQS." *Atmos. Environ.*, 26(A), 579-591.

Whitby, K.T., R.B. Husar, and B.Y. Li (1972). "The aerosol size distribution of Los Angeles smog." J. Colloid Interface Sci., 39, 177-179.

Wilkness, R.R. (March 1997). Personal communication and enclosures. Western States Petroleum Association, Glendale, CA.

Zaranski, M.T., G.W. Patton, L.L. McConnell, and T.F. Bidleman (1991). "Collection of nonpolar organic compounds from ambient air using polyurethane foam-granular adsorbent sandwich cartridges." *Anal. Chem.*, 63: 1228-1232.

Zielinska, B., J. Arey and R. Atkinson (1990). "The atmospheric formation of nitroarenes and their occurrence in ambient air." Proceedings of the Fourth International Conference on N-Substituted Aryl Compounds: Occurrence, Metabolism and Biological Impact of Nitroarenes, Cleveland, OH, 15-19 July 1989, P.C. Howard et al., eds., Plenum Press, New York, pp. 73-84.

Zielinska, B., J. Arey, R. Atkinson, T. Ramdahl, A.M. Winer, and J.N. Pitts, Jr. (1986). "Reaction of dinitrogen pentoxide with fluoranthene." J. Am. Chem. Soc., 108, 4126-4132.

Zielinska, B., J. Arey, R. Atkinson and P.A. McElroy (1989a). "Formation of methylnitronaphthalenes from the gas-phase reactions of 1- and 2-methylnaphthalene with OH radicals and N_2O_5 and their occurrence in ambient air." *Environ. Sci. Technol.*, 23, 723-729.

Zielinska, B., J. Arey, R. Atkinson, and A.M. Winer (1989b). "The nitroarenes of molecular weight 247 in ambient particulate samples collected in Southern California." *Atmos. Environ.*, 23, 223-229.

Zielinska, B., and E. Fujita (1994). "Organic Gas Sampling." <u>Environmental Sampling for Trace</u> <u>Analysis</u>, Chapter 7. B. Markert, ed., VCH Publishers, Inc., New York, NY.

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