DEVELOPMENT OF FINE PARTICULATE EMISSION FACTORS AND SPECIATION PROFILES FOR OIL AND GAS-FIRED COMBUSTION SYSTEMS

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

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Chang, O.M.C. and England, G.C., "Development of Fine Particulate Emission Factors and Speciation Profiles for Oil and Gas-fired Combustion Systems, Update: Critical Review of Source Sampling and Analysis Methodologies for Characterizing Organic Aerosol and Fine Particulate Source Emission Profiles."

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

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Prepared for:
National Petroleum Technology Office
National Energy Technology Laboratory
U.S. Department of Energy
(DOE Contract No. DE-FC26-00BC15327)

Gas Research Institute
California Energy Commission
New York State Research and Development Authority
(GRI Contract No. 8362)

American Petroleum Institute
(API Contract No. 00-0000-4303)

Draft (Revision 0): February 2003
Final (Revision 1) February 12, 2004

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ACKNOWLEDGEMENTS

The following people are recognized for their contributions of time and expertise during this study and in the preparation of this report:

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Marla Mueller, California Energy Commission
Dr. Paul Drayton, Gas Research Institute
Karin Ritter, American Petroleum Institute
Barry Liebowitz, New York State Energy Research and Development Authority
Janet Joseph, New York State Energy Research and Development Authority

FOREWORD

In 1997, the United States Environmental Protection Agency (EPA) promulgated new National Ambient Air Quality Standards (NAAQS) for particulate matter, including for the first time particles with aerodynamic diameter smaller than 2.5 micrometers (PM2.5). PM2.5 in the atmosphere also contributes to reduced atmospheric visibility, which is the subject of existing rules for siting emission sources near Class 1 areas and new Regional Haze rules. There are few existing data regarding emissions and characteristics of fine aerosols from oil, gas and power generation industry combustion sources, and the information that is available is generally outdated and/or incomplete. Traditional stationary source air emission sampling methods tend to underestimate or overestimate the contribution of the source to ambient aerosols because they do not properly account for primary aerosol formation, which occurs after the gases leave the stack. These deficiencies in the current methods can have significant impacts on regulatory decision-making. For example, siting of new gas-fired power plants in California has been delayed due to PM10 emission estimates that may be positively biased due to these deficiencies in the current methods. The current program was jointly funded by the U.S. Department of Energy National Petroleum Technology Office (DOE/NPTO), California Energy Commission CEC), Gas Research Institute (GRI), New York State Energy Research and Development Authority (NYSERDA) and the American Petroleum Institute (API) to provide improved measurement methods and reliable source emissions data for use in assessing the contribution of oil, gas and power generation industry combustion sources to ambient PM2.5 concentrations. More accurate and complete emissions data generated using the methods developed in this program will enable more accurate source apportionment and source receptor analysis for PM2.5 NAAQS implementation and streamline the environmental assessment of oil, gas, and power production facilities.

The goals of this program were to:

- Develop emission factors and speciation profiles for emissions of fine particulate matter, especially organic aerosols, for use in source-receptor and source apportionment analysis;

- Identify and characterize PM2.5 precursor compound emissions that can be used in source-receptor and source apportionment analysis; and

- Develop improved dilution sampling technology and test methods for PM2.5 mass emissions and speciation measurements, and compare results obtained with dilution and traditional stationary source sampling methods.

This report is part of a series of progress, topical and final reports presenting the findings of the program.

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EXECUTIVE SUMMARY

This report is an update of a 1997 report entitled "Critical Review of Source Sampling and Analysis Methodologies for Characterizing Organic Aerosol and Fine Particulate Source Emission Profiles" (England et al., 1997). The original review and this update are intended for use in designing measurement programs for characterizing emissions from stationary sources which contribute to fine particle concentrations in the atmosphere. This update incorporates findings from a review of recent literature and discussions with technical/scientific experts in academia, industry, institutions 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 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 sulfate, 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.

The US EPA (2003) has issued a report, based on 2000 data, indicating the relative contribution of different source categories to the ambient PM10 and PM2.5 loading. The majority of PM10 ambient loading was attributed to fugitive dust emissions (60%) with industrial processes and fuel combustion contributing 5% and 4% respectively. Fugitive dust emissions were also the largest contributor to PM2.5 ambient loading. In the PM2.5 size range, Industrial processes and Fuel combustion were responsible for 12% and 10% of the ambient loading.

OIL, GAS AND POWER GENERATION INDUSTRY COMBUSTION SOURCES

Industrial and power generation 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.

Data from direct measurements of organic aerosol emissions from oil, gas and power generation industry combustion equipment are very limited. In the petroleum industry, combustion devices are found in both “upstream” and “downstream operations. Upstream operations include oil and gas exploration as well as production activities (steam generators, heater treaters, reciprocating engines, etc.). Downstream operations include refining, marketing and transportation operations (boilers, process heaters, gas turbines, thermal oxidizers, etc.). In the natural gas transmission industry, reciprocating and gas turbine internal combustion engines are used in pipeline applications. In the power generation industry, boilers and gas turbines are used for the vast majority of the nation’s generating capacity. 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 refinery 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. 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 focused on a small subset of the total spectrum of organic compound emissions, they provide an incomplete picture of organic emissions.

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 such emissions. Dilution methods have long been employed as the standard 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 both for developing 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 design of dilution sampling system should consider the following criteria.

- Dilution ratio, and residence time: There are numerous on-going research efforts to investigate how to simulate plume conditions by dilution systems. Particle formation is a complex process of condensation growth, coagulation, concentration of pre-existing particles (soot), enrichment and saturation vapor pressure. Chang *et al* (2003) identified a minimum dilution ratio of 20 and residence time of 10 seconds needed for a cross-jet flow dilution sampler, which will lead to a more compact, portable dilution systems. Also, particle losses in the dilution sampler can affect the sampling accuracy. This is especially critical at low PM emission sources such as natural gas combustion, where particle concentration in diluted natural gas exhausts is in the same order of magnitude to either the uncertainty of mechanically recovering particle losses and/or contamination during sample recovery. Operating at the lower dilution air ratio of 20 times can maximize particle concentration in the diluted exhaust, thus increases the confidence of the measurement.

- Mixing rate: Very little information was found concerning how different ways of mixing the dilution air and the raw flue gas sample impact formation of particles in the diluted sample. Different mixing approaches used in various research and commercial dilution samplers include 1-step and 2 (or more)-step dilution, ejectors and turbulent jet mixing systems that mix rapidly, cross-jet systems that mix slowly, and others. This becomes an important design consideration when attempting to design a compact, lightweight, field-portable system. One journal publication indicated that the mixing rate was probably only a second order effect (Lyyränen *et al.*, 2004). At the same time, inter-comparison of co-located dilution systems as well as comparison of the field measurement (plume) and dilution samplers by real-time aerosol instruments will provide a better understanding of how aerosol physical properties are affected by the dilution process.

- Temperature and relative humidity of dilution air: As water vapor is the most abundant vapor species in the ambient air, the meteorological condition, i.e., temperature and relative humidity, can affect particle physicochemical characteristics. The potential effects of water condensation at high relative humidity include growth of pre-existing particles (alter particle sizes), the chemistry taking place in existing particles, and/or contribute to the nucleation of new particles in conjunction with SO_2. It is recommended not to control the temperature and relative humidity of dilution air for better simulation of actual plume.

- Particle losses: Significant losses of charged particles to the electrically non-conducting surface (e.g., polyvinyl chloride [PVC] and Teflon®) of dilution samplers can be significant. Use of conducting surfaces wherever possible and installing charge neutralizers to avoid fine particle losses is recommended. Losses of particles in dilution sampler can affect the sampling accuracy. This can be especially significant at low PM emission source such as natural gas combustion, while particle concentration after dilution is in the same order of magnitude to either the uncertainty of mechanically recovering particle losses and/or contamination during sample recovery. To minimize sample line losses, sampler designs should incorporate heated, temperature controlled probes and hoses to prevent condensation prior to mixing with dilution air. The sample line should avoid sharp change of direction (bending) to reduce potential losses due to impaction. The sample line should be heated 5-6°C higher than exhaust to reduce particle thermophoretic losses. Particle diffusive losses can be reduced by decrease the distances between exhaust and where exhaust is diluted.

- 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. 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

Recent epidemiological studies have shown that while fine (less than 2.5 µm) and/or coarse (2.5-10 µm) particle mass concentration may be an appropriate indicator for adverse public health effects in many areas, it is not likely that it is sufficient to explain the different effects observed in different areas. Other physical properties of aerosols, such as size, number concentration, as well as chemical speciation, could be important.No single instrument can measure all of these particle physicochemical properties and combination of two or more instruments may be necessary to satisfy the objectives of a specific study.

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

- Develop emission factors and speciation profiles for emissions of organic aerosols,
- Identify and characterize PM2.5 precursor compound emissions,
- 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 and natural gas industries 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:

- Characterize primary aerosol emissions after dilution and aging of stack emissions, including size segregated mass, organic carbon, elemental carbon, and metals.
- Characterize major gaseous PM2.5 precursors, specifically organic compounds (especially compounds of carbon [C_7] and above), oxides of nitrogen (NO_x), sulfur dioxide (SO_2), and ammonia.
- Develop organic speciation profiles from particulate matter collected on the filter media after dilution.
- Provide data that can be related to existing ambient particulate data (i.e., of similar quality and completeness).
- Characterize fine particle size distribution using a semi-continuous particle spectrometer(s) at different sources.

- Characterize minor gaseous PM2.5 precursors, specifically sulfur trioxide (SO_3), sulfuric acid (H_2SO_4) and nitric acid (HNO_3).
- Characterize in-stack total particulate mass and particle size distribution, including PM2.5.
- Compare total PM2.5 mass (filterable and condensable) using EPA reference methods and dilution sampling.
- Analyze the in-stack total particulate matter for composition (including elemental carbon, nitrates, sulfate, and ammonium).

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.

Section 1
INTRODUCTION

The Environmental Protection Agency (EPA) has decided to revise the National Ambient Air Quality Standards (NAAQS) for particulate matter with emphasis on particles smaller than 2.5 µm in diameter. Since air emissions from combustion devices are important sources of organic aerosols, particulate matter and fine particulate precursors, changes in NAAQS regulations may have significant impacts on the oil and gas industries (including exploration, production and refining) as well as power generation industries. Within these industries, major impacts are anticipated for processes utilizing different types of stationary combustion devices including gas-fired process heaters, gas-fired utility boilers, gas-fired steam generators, oil-fired commercial boilers, fluid catalytic cracking unit (FCCU) regenerators, catalytic reforming unit (CRU) regenerators, sulfur recovery units, steam generators, heater treaters, coke calciners, thermal oxidizers, stationary internal combustion engines such as gas turbines, and other devices. Most of these combustion devices are gas fired, using process gases (refinery gas, casing gas, etc.) or natural gas. Although gas is a relatively clean fuel, due to the new standards, the variety of gas-fired combustion devices, and the range of process gas compositions, even particle emission from gas combustion may contribute significantly to fine particulate concentrations in ambient air.

In urban non-attainment areas such as Los Angeles emission sources are almost exclusively gas-fired. 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.

Epidemiological and animal studies have found correlations between health and exposure to fine particulate matter. Current hypothesis regarding what agents are causing health effects suggest key roles for particles smaller than 0.1µm (ultrafine particles), specific chemical compounds (e.g., nitro-PAHs), and particles with specific chemical characteristics (e.g., acidity). Particulate matter with these characteristics is believed to be produced and/or released from combustion processes. However, detailed information regarding the emission rates and chemical characteristics of fine aerosols and organic compounds from power industry sources is sparse and limited, especially for particles less than 2.5μm in aerodynamic diameter. Accordingly, a collaborative effort has been initiated by API-CEC-DOE-GRI-NYSERDA (note, agencies listed in alphabetical sequence) to develop and expand the database on emission profiles for fine particulates and particle precursors emitted from stationary power industrial combustion devices. This study is a continuation of a program initiated by API in 1997.

The new API-CEC-DOE-GRI-NYSERDA program proceeds on two parallel tracks: (1) source characterization, and (2) development and evaluation of test methods. It is hoped that these efforts will provide scientifically sound emission inventory data that will be useful in development of future regulations. The objectives of the source characterization efforts are to develop realistic emission factors and speciation profiles for fine particulate emissions from oil and gas-fired combustion systems. The existing PM mass and composition database, developed using existing regulatory stationary combustion test methods is believed to have wide uncertainty and may potentially be inaccurate in critical areas. The second portion of the program focuses on development of more accurate and precise test methods for measuring PM emissions from stationary combustion. Both the existing and new PM stationary source test methods will be validated experimentally.

Design of the API-CEC-DOE-GRI-NYSERDA program requires a thorough understanding of combustion device operating and emission characteristics, available measurement methodology, experimental design approaches, as well as an appreciation of both regulatory agency and industry objectives. It should be noted that measurement of aerosols and aerosol precursor emissions from stationary sources is not common practice; in fact, such measurements are presently at the forefront of science and are thus subject to considerable uncertainty. Because of the overall complexity, caution must be exercised in selecting a particular measurement or experimental approach to ensure that it is capable of achieving specific project goals. Differing measurement approaches have been taken by various researchers to address differing research objectives. Ambient aerosols, especially fine aerosols, are dominated by particles formed after the exhaust gases leave the source stack. Since the mechanisms of aerosol formation are not yet completely known, interpretation of source measurement results is subject to considerable uncertainty. The current report is intended to update a previous API critical review of sampling and analysis methods, and to retain important background information developed following that review (England, *et al*, 1997).

REPORT ORGANIZATION

This report is divided into seven sections as follows:

- Section 1 - Introduction. General overview of current program.
- Section 2 - Background. Provides an overview of proposed fine particle regulations, aerosol formation mechanisms, emissions data for industrial stationary combustion sources, and the important health-related PM characteristics to measure based on recent epidemiological and toxicological studies.
- Section 3 - Ambient Air Sampling and Analysis Methods. Overview of methods that can be applied and modified for dilution sampling.
- Section 4 - Traditional Stationary Source Emissions Measurement Methods. Overview of conventional stationary source testing methods and sampling artifacts relevant to this program.
- Section 5 - Aerosol Source Emissions Measurements. Review of dilution sampler designs in stationary and mobile source testing and previous experience.
- Section 6 - Recommendations. Summary of recommendations for future test programs.
- Section 7 - References. List of literature reviewed to develop this report.

Section 2
BACKGROUND

This Background section provides as a brief review of recent changes to the NAAQS concerning PM2.5 as well as a review of ambient aerosol formation processes. These issues are critical to the debate over the contribution of stationary combustion sources to ambient fine particulate concentrations.

NATIONAL AMBIENT PM2.5 STANDARDS

On July 18, 1997, EPA published revisions to the NAAQS for particulate matter (40 CFR, Parts 50, 53 and 58). These revisions include adding a new annual standard (15 $\mu g/m^3$) and a new 24-hour standard (65 $\mu g/m^3$) for particles smaller than 2.5 µm in aerodynamic diameter. These are collective referred to as the PM2.5 Standard. The 1997 actions retained the annual PM10 standard (50 $\mu g/m^3$), but revised the form of the 24-hour PM10 standard (150 $\mu g/m^3$). The previous form, allowing one exceedance per 24-hour period, was replaced with a form based on the 99th percentile of 24-hour PM10 concentrations in a year, averaged over 3 years. The required sampling frequency for PM10 monitoring was also extended to once in 3 days. As part of the new standard EPA has developed revised PM monitoring requirements, including a reference test method for monitoring ambient PM2.5. This method is reviewed in Section 3 of the current report.

PARTICULATE MATTER IN THE ATMOSPHERE

Particles or particulate matter may be either directly emitted into the atmosphere (primary particles) or formed in the atmosphere by chemical reactions (secondary particles.) The relative importance of primary and secondary particles depends mainly on the geographical location, with its particular mix of emissions, and on the prevailing atmospheric chemistry. For example, in areas where wood is burned as heating fuel during the wintertime, most of the atmospheric particles are primary in nature. However, during summertime photochemical episodes, a substantial fraction of ambient particulate matter can be attributed to secondary reactions in the atmosphere (Grosjean and Friedlander, 1975). As shown in Figure 2-1, secondary particles are formed through several pathways which are discussed in the sections below.

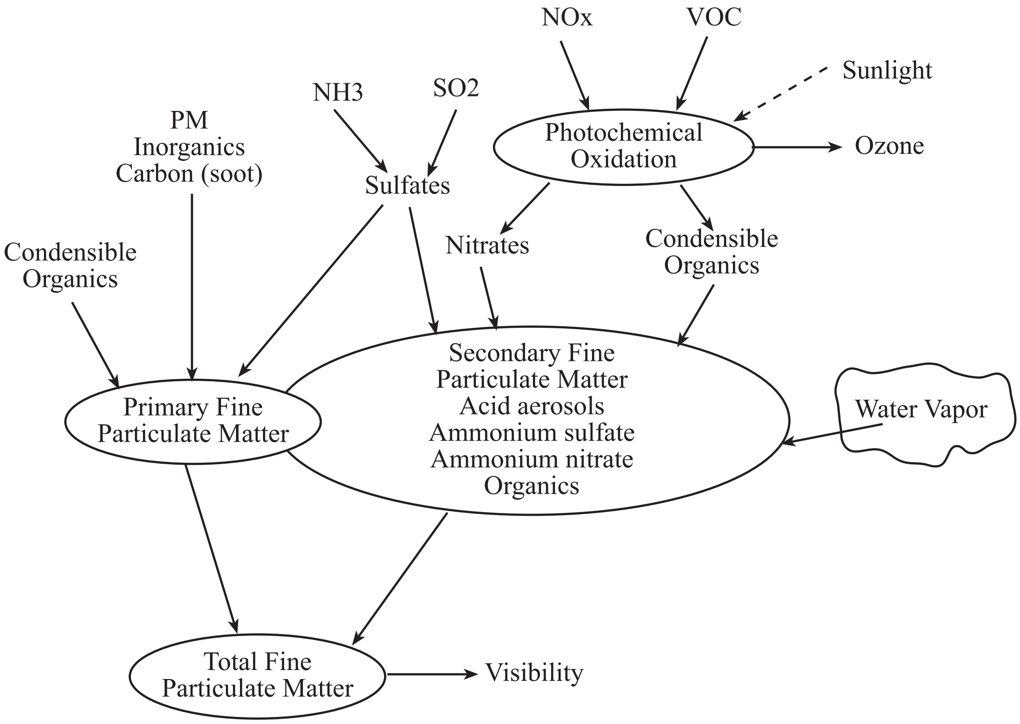


Figure 2-1. Fine particulate formation pathways.

Particle Size

Atmospheric particles may be either solid or liquid and have aerodynamic diameters between approximately 0.002 and 100 µm (Finlayson-Pitts and Pitts, 1986). The lower size limit of approximately 0.002 µm represents the smallest size detectable by condensation nuclei counters. The upper end of this range corresponds to fine drizzle or very fine sand particles that are so large they do not remain suspended for significant times and quickly fall out of the atmosphere. The most important particles with respect to atmospheric chemistry, physics, and health effects related issues are smaller than10-µm diameter.

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. Particle size is usually expressed as 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).

Particle size fractions commonly measured by air quality monitors are illustrated in Figure 2-2 (from Chow, 1995) showing the relative concentration of particles as a function of particle diameter. The mass collected is proportional to the area under the distribution within each size range. The total suspended particulate (TSP) represents all particles in size fractions from 0 to approximately 40 µm, the PM10 fraction ranges from 0 to 10 µm, and the PM2.5 size fraction ranges from 0 to 2.5 µm in aerodynamic diameter. It is important to note that data, such as that presented in Figure 2-2, are generated by air quality monitors that separate particles according to aerodynamic diameter. However, 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.

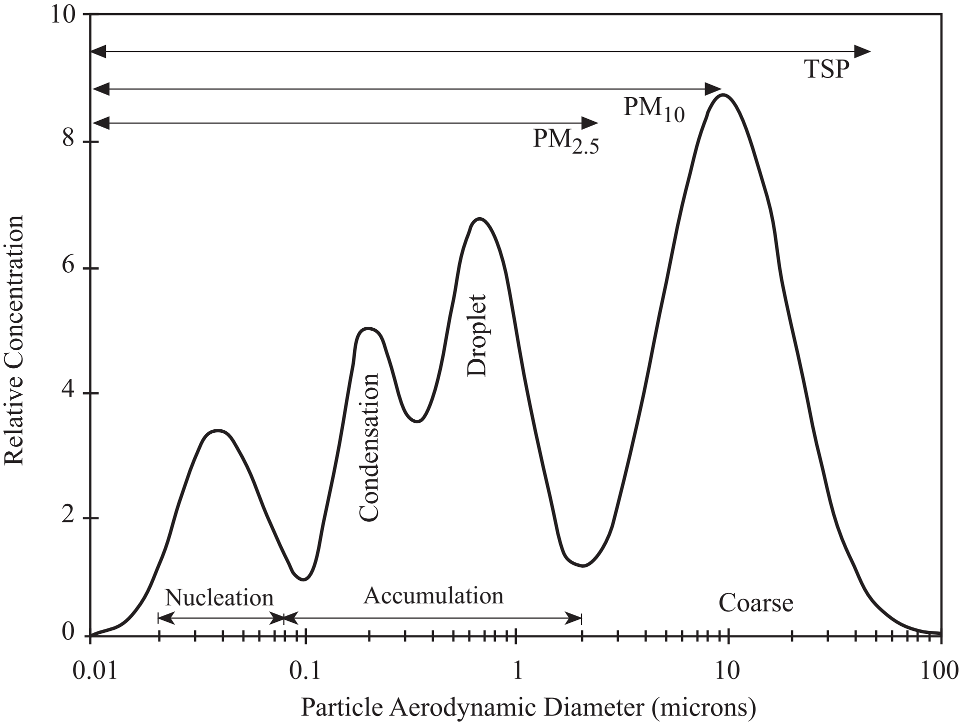


Figure 2-2. Idealized size distribution of particles in ambient air (from Chow, 1995).

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 μm. In this regard, fine particles behave more like gases than coarse particles.

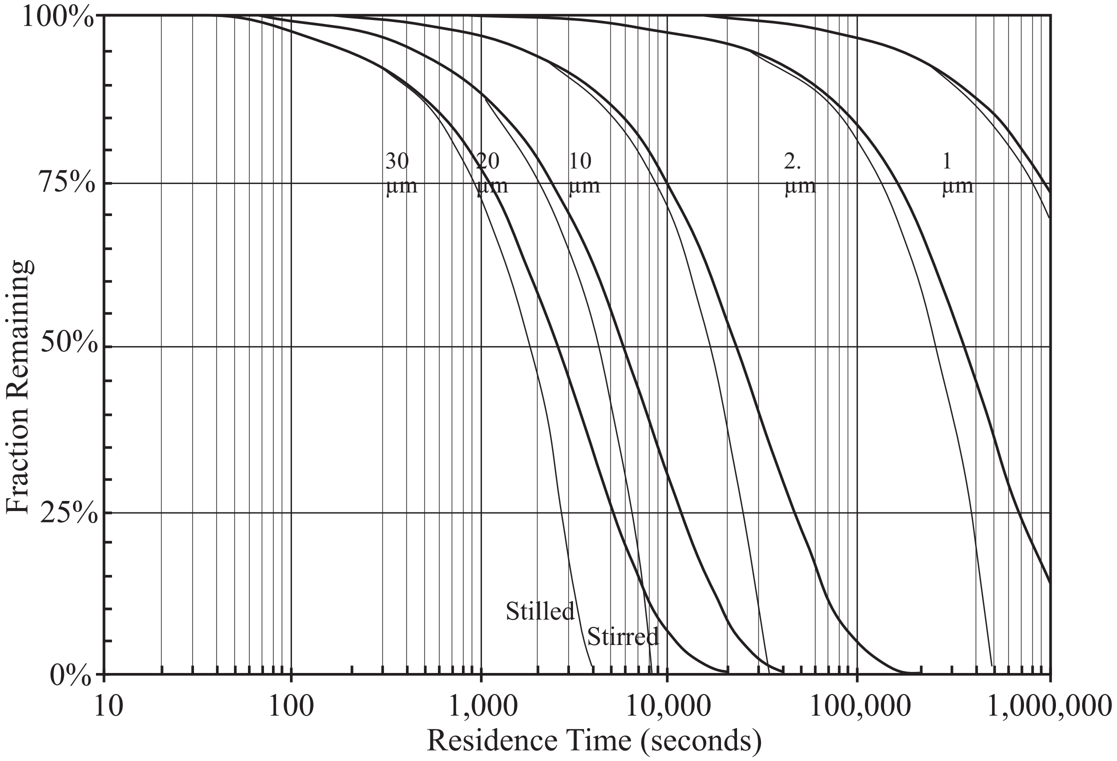


Figure 2-3. Aging time for homogeneously distributed particles of different aerodynamic diameters in a 100 m deep mixed layer. Gravitational settling is assumed for both still and stirred chamber models (Hinds, 1982).

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 indicates 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 release to the atmosphere. Typical lifetime of particles in the nucleation range is 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 formed in the atmosphere (Chow, 1995, and references therein).

The "accumulation" range consists of particles with diameters between approximately 0.08 and 2 µm. 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." Particles in this size range account for the majority of sulfuric acid, ammonium bisulfate, ammonium sulfate, ammonium nitrate, and organic and elemental carbon. Particles larger than approximately 2 or 3 µm 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).

Figure 2-2 indicates that the accumulation range consists of at least two sub-modes. Existence of sub-modes is based on measurements of chemically specific size distributions in several different urban areas. This is contrary to many other presentations that show only a single peak in this region. John *et al.* (1991) interpreted the peak centered at approximately 0.2 µm as a "condensation" mode, containing gas-phase reaction products, and the approximately 0.7 µm peak as a "droplet" mode, resulting from particle nucleation growth and by reactions taking place in water droplets. When these modes contain soluble particles, their peaks shift toward larger diameters as humidity increases (Chow, 1995, and references therein) which can be especially important when relative humidity exceeds 70 %. The peak of the coarse mode may shift between approximately 6 and 25 µm. 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 µm. On the other hand, a similar shift in cut-point near 2.5 µm has a small effect on the mass collected owing to the low quantities of particles in the 1 to 3 µm 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 the six chemical components listed above. Approximately half of PM10 is composed of geological material. However, geological material often constitutes less than 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 provides illustrative data on the chemical composition of particles directly emitted from several representative emission sources. The data for Table 2-1 was gathered from 1993 tests conducted in California (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. As shown, organic carbon (OC) and elemental carbon (EC) are important constituents of most of these emission sources.

Data presented in Figure 2-4 presents compositional information on fine particulate matter collected from sampling sites in western and eastern Los Angeles (Rubidoux). 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

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

Source Type	Dominant Particle Size	< 0.1μm	0.1 to 1 μm	1 to 10 μm	> 10 μm
Paved 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^-, NH_4^+, 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	$SO_4^=$, K^+, S, Ti	OC, Al, K, Ca, Fe	Si
Agricultural Soil	Coarse	NO_3, NH_4^+, Cr, Zn, Sr	$SO_4^=$, NA^+, K^+, S, Cl, Mn, Ba, Ti	OC, Al, K, Ca, Fe	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	Coarse	Mn, Sr, Ba	K^+, Ti	SO_4^+, Na^+, OC, Al, S, Cl, K, Ca, Fe	Si
Motor Vehicle	Fine	Cr, Ni, Y	NH_4^+, 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	NH_4^+, Na^+, Zn, Fe, Si	V, OC, EC, Ni	S, $SO_4^=$
Incinerator	Fine	V, Mn, Cu, Ag, Sn	K^+, Al, Ti, Zn, Hg	NO_3^-, 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	NH_4^+, 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, $SO_4^=$
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	$SO_4^=$, 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

EC = Elemental Carbon
OC = Organic Carbon

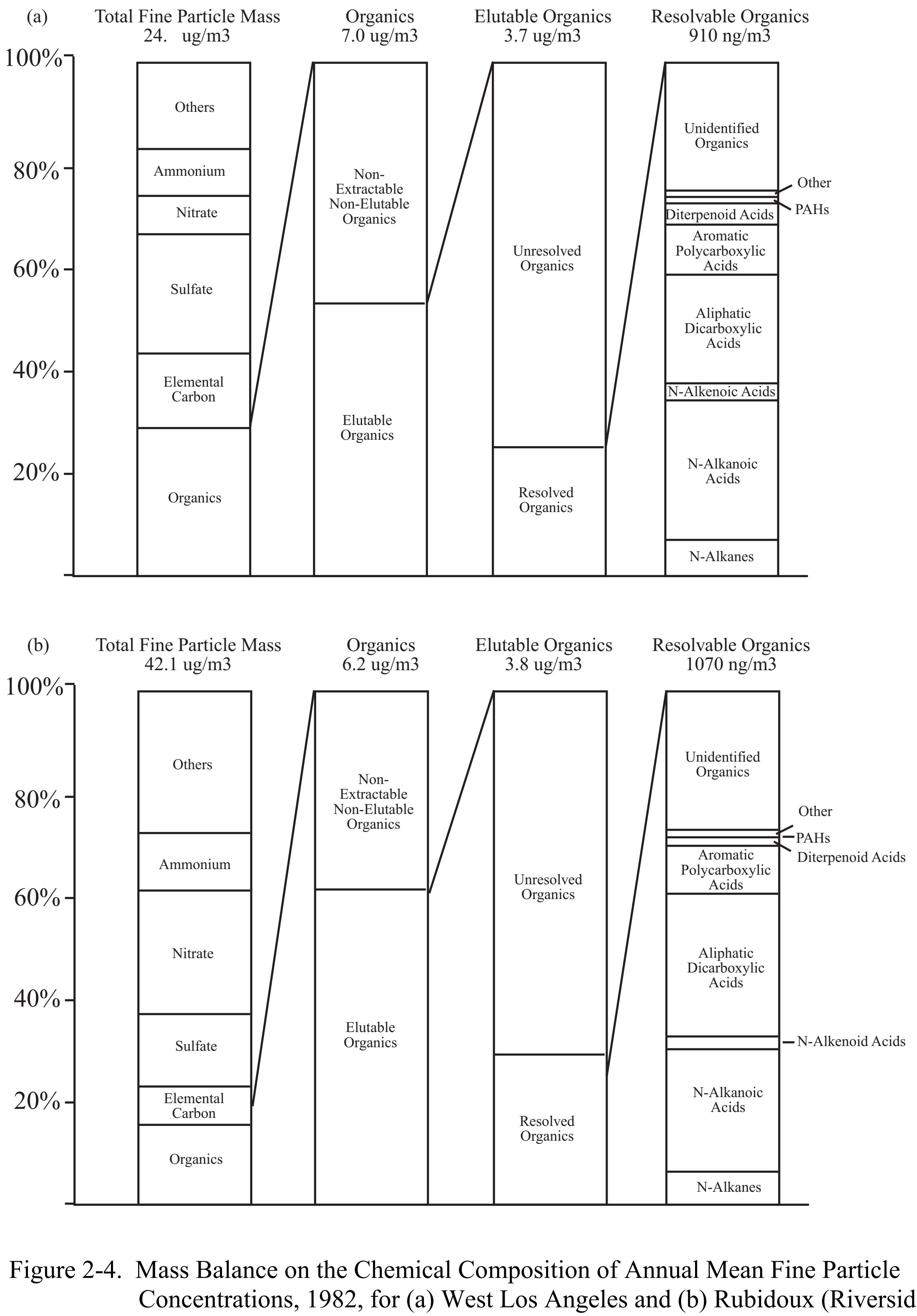


Figure 2-4. Mass Balance on the Chemical Composition of Annual Mean Fine Particle Concentrations, 1982, for (a) West Los Angeles and (b) Rubidoux (Riverside), California (Rogge *et a*l., 1993a).

than in West Los Angeles. Analysis of the fine particle fraction samples identified and quantified more than 80 individual organic compounds [Rogge *et al*. (1993a)]. These compounds included n-alkanes, n-alkanoic acid, one n-alkenoic acid, one n-alkanal, 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 from the sources. Primary particles are emitted in several size ranges, the most common being less than 1 µm in aerodynamic diameter from gas fired combustion sources and larger than 1 µm in aerodynamic diameter from dust sources. Particles larger than 10 µm in aerodynamic diameter usually deposit to 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.

The key emission source categories for primary particles 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).

Gas fired combustion processes (e.g., power plants, incinerators, diesel engines) may produce particles not only in the nucleation range (less than approximately 0.08 µm) but also in the accumulation range. The relative numbers of particles produced in the nucleation range compared to the accumulation range will 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.

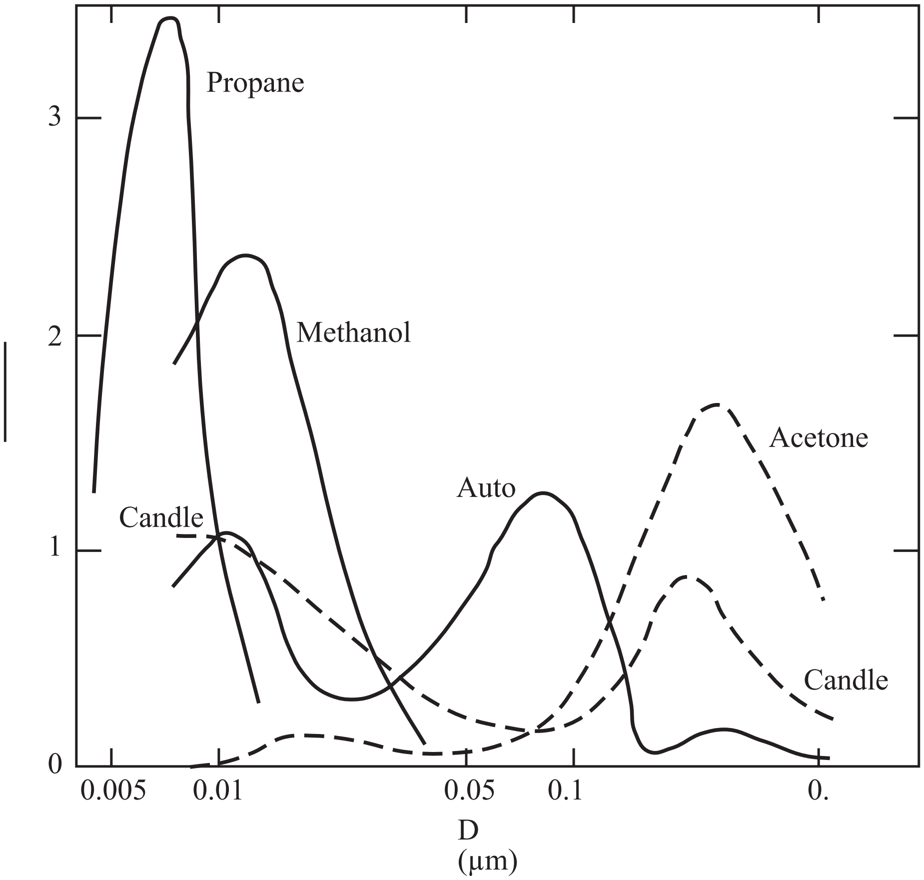


Figure 2-5. Surface Area Distribution of Particles from the Combustion of Several Organics and from Automobiles and a Candle (from National Research Council, 1979).

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 be formed via atmospheric reactions involving volatile organic compounds (VOC).

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, and certain organic gases. Many hydrocarbons are emitted at conditions above their dew point and can rapidly condense 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.

In general 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 source emission rates 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 sulfuric acid (H_2SO_4), ammonium bisulfate (NH_4HSO_4), and ammonium sulfate ($(NH_4)_2SO_4$). The majority of secondary nitrates in PM10 and PM2.5 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 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 usually taken as the most dominant. Calvert and Stockwell (1983) show a wide range of gas-phase transformation rates ranging from less than 0.01 percent/hr to about 5 percent/hr. Observed transformation rates appear to be controlled more by the ambient concentration of the hydroxyl radical (and competing reactions of other gases) than by the sulfur dioxide concentration. Hydroxyl radical concentrations are related closely to photochemistry. Accordingly, 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 will be quickly oxidized to sulfuric acid. If ammonia is also dissolved in the droplet, the sulfuric acid will be 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. 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 (NO_2), 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 participate 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 hydroxyl radicals. 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.

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. 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 where the availability of ammonia is limited, reducing sulfur dioxide emissions might actually result in ammonium nitrate increases which exceed the reductions in ammonium sulfate.

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). It becomes especially important when relative humidity exceeds 70 percent.

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, NO_3 radicals, or O_3. Table 2-2 gives the calculated atmospheric lifetimes (i.e., the time to decay to 1/e of its original concentration), from measured reaction rate constant and average ambient concentration, for some selected compounds present in direct gas-phase emissions. 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.

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

Compound	Atmospheric Lifetime Due to Reaction with:				
	OH[a]	O_3[b]	NO_3[c]	HO_2[d]	hν
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	>4x10^4 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[f]	6 hr	-	64 days	-	-
Pyrene[f]	6 hr	-	20 days	-	-

[a] For 12-hr average concentration of OH radical of 1 x 10^6 molecule/cm^3.

[b] For 24-hr average O_3 concentration of 7 x 10^{11} molecule/cm^3.

[c] For 12-hr average NO_3 concentration of 2 x 10^8 molecule/cm^3.

[d] For 12-hr average HO_2 concentration of 10^8 molecule/cm^3.

[e] For solar zenith angle of 0°.

[g] Lifetimes calculated from kinetic data given in Atkinson *et al*., 1990.

The direct measurements by a ^{14}C-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, $2.4x10^6$ and $9.5x10^6$ radicals cm^{-3}. Nighttime -OH concentrations of less than $2x10^5$ radicals cm^{-3} were measured.

Winter mid-latitude noontime maximum values on the order of approximately $2x10^6$ 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. The calculated lifetimes listed in Table 2-2 are approximate only and are valid for those reactive species concentrations listed in the footnotes. However, these data permit estimates of 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 NO_3 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 $1x10^6$ 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 few data exist concerning the products of these reactions and 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 chemical reaction products achieve concentrations that 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. 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.

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 that 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 that might achieve saturation in the atmosphere. Pandis *et al*. (1992) divided these groups into sub-groups that are more conducive to aerosol formation and 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.

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 NO_2 addition in the C-2 position. Subsequent elimination of water results in the formation of 2-nitrofluoranthene from fluoranthene and 2-nitropyrene from pyrene. Nighttime reactions with the NO_3 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 NO_3 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 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 NO_3 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

[a] From Zielinska *et al*., 1989b.
[b] Daytime sample collected from 1200 to 1800 hr and nighttime sample from 1800 to 2400 hr on 9/13/85.
[c] From Atkinson *et al*., 1988.
[d] Daytime sample collected from 0800 to 2000 hr on 8/20/86 and nighttime sample from 2000 to 0800 hr on 8/20-21/86.
[e] Daytime sample collected from 0500 to 1700 hr on 1/28/86 and nighttime sample from 1700 to 0500 hr on 1/27-28/86.
[f] ND: 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

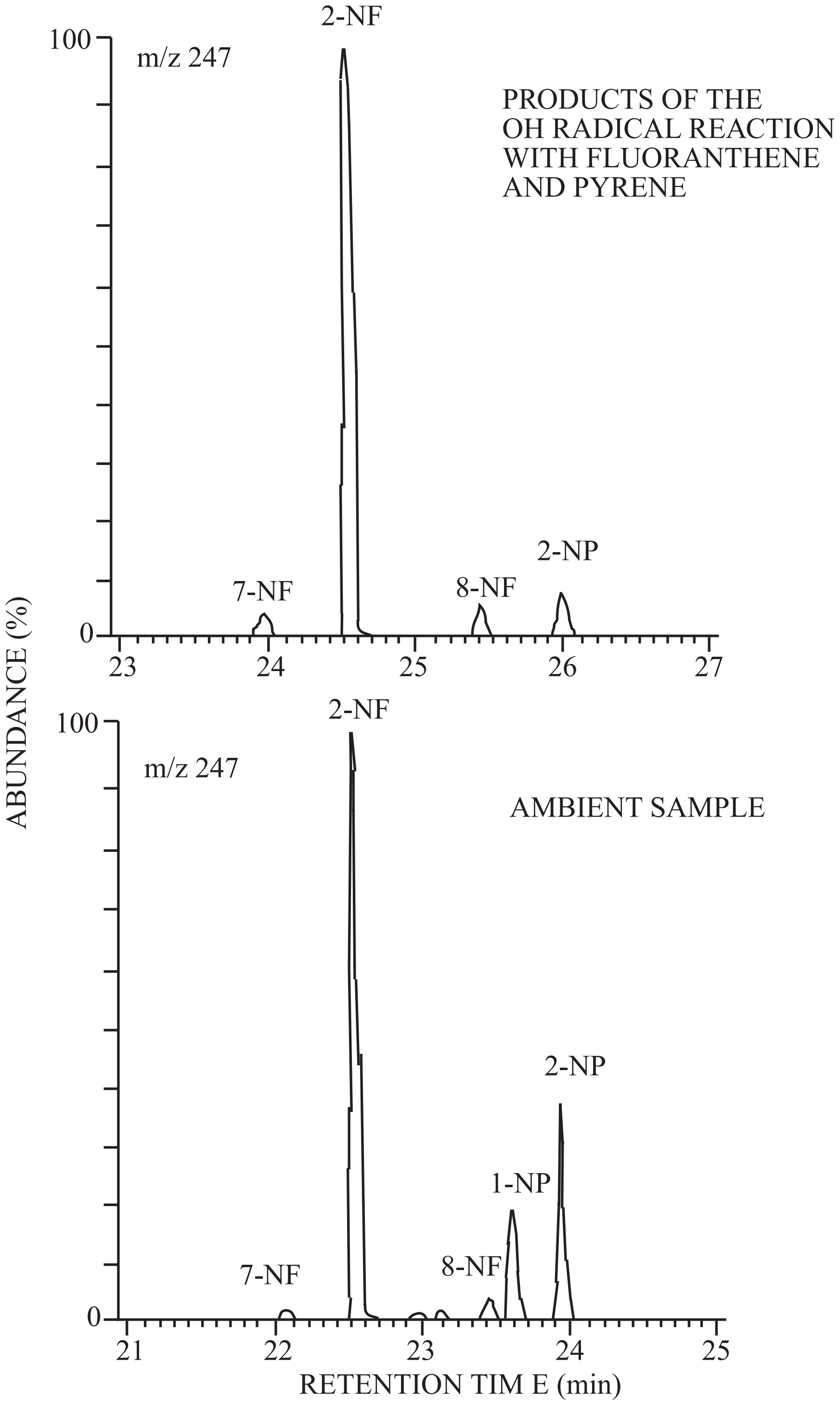


Figure 2-6. Mass Chromatograms of the Molecular Ion of the Nitrofluorantheses (NF) and Nitropyrenes (NP) Formed from the Gas-Phase Reaction of Fluoranthene and Pyrene with the OH Radicals (Top) and Present in Ambient Particulate Sample Collected at Torrance, California (Bottom).

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, 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.

HEALTH EFFECTS

A review of epidemiological studies from 1953-1996 estimated that a 10-µg/m3 increase in PM_{10} resulted in a 1.5-4.0% increase in respiratory mortality, a 0.5-2.0% increase in cardiovascular mortality, a 0.5-4.0% increase in respiratory hospital admissions, and 1.0-4.0% increase in grade-school absences (Pope 1998; Dockery and Pope, 1997). An epidemiological study of daily mortality in six U.S. cities found a strong association with short-terms increases in $PM_{2.5}$ concentration, but a weak association with coarse particles (Schwartz, et al, 1996). In Utah, an elevated PM_{10} concentration, generated from a steel mill operation, was associated with increased hospital admissions for pneumonia, pleurisy, bronchitis, and asthma (Pope, 1991, Ransom & Pope, 1992). However, the mass concentrations of particulate air pollution observed during these epidemiological studies are orders of magnitude below the inhalable particle concentrations often encountered in occupational settings (Lighty *et al* 2000, Watts, 1995; ACGIH, 2000). Studies conducted in Spokane, Washington and Utah suggested no association of observed health effects and coarse, wind-blown particles. A study conducted in Anchorage, AK, argued that observed upper respiratory illness and asthma could be associated with crustal coarse particles, an average of 80% of which were in the PM_{10} size range (Gordian, *et al*, 1996). A 2001 study of adult asthmatic subjects in Helsinki, Finland found that Spirometric lung function [peak expiratory flow rate (PEFR)] was inversely related to the observed number concentration of accumulation mode particles. However, no significant association was noted for either ultrafine particles or PM_{10} (Penttinen *et al*, 2001). Experimental animal exposure studies found that the ultrafine particle fraction is the most pathogenic and suggests that these particles are largely responsible for observed PM associated health effects (Oberdörster *et al*, 2002). However, a study by Churg & Stevens (1996) found that the presence of ultrafine particles in autopsied human lungs represented only a small portion of the total exposure. In general, no particulate pollution threshold was observed.

Measurement Needs in Particulate Characterisation

Currently air quality standards for particulate matter are based on measurements of ambient mass concentrations. Previous epidemiological studies focused on concentrations of PM_{10}, which were typically not measured but estimated by multiplying an empirical factor times the measured concentrations of PM_{13}, British Smoke (BS), TSP, Coefficient of Haze (CoH), or SO_4. More recent studies have focused on the characteristics of fine particulate, which are listed in Table 2-4 (Lighty *et al*, 2000). Most of the epidemiological studies have not been able to evaluate health effects of fine and coarse particles in parallel.

The epidemiological health effect outcomes of particulate air pollution have been controversial. In addition to challenges in analysis, such as inadequate analytic methods, misclassification of the exposure, or the inadequate control for confounding factors, specific characteristics of

Table 2-4. Characteristics of PM to Public Health (from Lighty, *et al.*, 2001)

Characteristic	**Relation to Combustion**	**Epidemiology Studies**	**Toxicology Studies**
Mass	Filterable combustion aerosols are a minor component of urban aerosol, which is dominated by organic, secondary, and geological PM.	Health outcomes have been associated with ambient PM mass	Exposure of young, healthy adults to concentrated ambient particle does not cause acute effects.
Particle Size	Combustion is the major source of submicron and ultrafine PM.	Coarse particles are not associated with mortality, but health outcomes are associated with fine PM.	Iron mobilization from coal fly ash in cell culture increases with decreasing particle size. Mutagenic activity is associated with fine PM.
Ultrafine and Nanoparticles	Inorganic ultrafines are formed by mineral vaporization during combustion followed by nucleation and condensation.	Respiratory effects associated with ultrafine PM number.	Differences between fine and ultrafine particles of the same material.
Transition Metals	Submicron particles from combustion are enriched in transition metals. Fe is more bioavailable from coal fly ash than from geological dust with similar size and total Fe	Associations of health outcomes and transition metals were found in some studies, but not in others.	Transition metals catalyze formation of reactive oxygen species. Metals from ambient PM and coal fly ash induce synthesis of proinflammatory cytokines in cells and lung inflammation in rats.
EC (Soot)	Combustion produces 10- to 50-mm diameter carbon-rich primary particles Diesel exhaust is the major source of urban soot	Weak association between diesel exhaust and cancer risk, but uncertain dose-response relationship	Carbon black and whole diesel exhaust produced similar lung lesions in rats. Ultrafine carbon causes lung inflammation.
OC	Incomplete combustion produces a wide range of organic species	Exposure studies to whole diesel exhaust include the soluble organic fraction.	PAH compounds include known and suspected carcinogens and mutagens.
Secondary SO_4^{2-} and NO_3^-	Most of the urban ambient PM2.5 is secondary aerosol formed from combustion-generated SO_2 and NOx.	SO_4^{2-} and NO_3^- are implicated by studies that correlated risk with PM mass.	NO_3^- not toxic at 1 mg/m^3 agricultural worker exposure. High levels of SO_4^{2-} associated with increased airway resistance.
Acidity	Cl and S in fuels produce HCl and SO_2 in the combustion products.	Some evidence for a correlation of health outcomes with H^+.	Various responses reported to laboratory inhalation of acid aerosols.
Synergistic Effects	Combustion emissions contain EC, OC, metal-rich particles, CO, and acid gases.	Epidemiologic studies are confounded by the complex mixture of pollutants in ambient air.	Exposure to pairs of pollutants can produce greater effect than either one alone: ultrafine PM and O_3, coal fly ash and H_2SO_4, benzo[a]pyrene and carbon black.

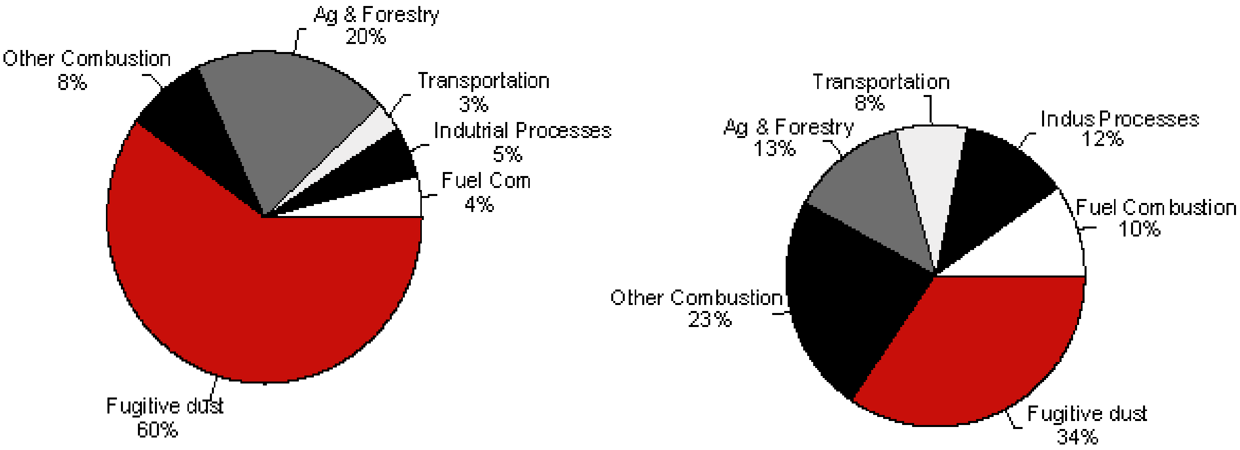
particles can interact with nerve system and amplify biological response. These particle properties include particle size, available surface for deposition, morphology, acidity, the soluble and insoluble fraction, bonding, PH, transit metals from coal fly ash (Miller *et al*, 2001), soot, gas phase toxics. Furthermore, particles can transform physically and chemically, due to the environment, i.e., relative humidity, temperature, in either animal or human subjects. Other issues regarding particulate health effects are: the representative ness of the stationary monitoring data used in epidemiological studies of individual exposures and differences in health response in different geographical regions (e.g., eastern versus western U.S. versus Europe) (see appendix A). However, available data provides little support for the idea that any single, major or trace component of PM is responsible for adverse health effects. The sum of the effects of each individual substance has less toxic effects than combination of these toxic substances.

There is evidence that particle size rather than mass may be the appropriate measure to correlate with health effects (Harrison and Yin, 2000) and there is a need for monitoring particle number and size distribution in addition to particle mass concentration (Penttinen, *et al*, 2001). The generally prevailing focus on fine fraction, which is originated from combustion sources and more pathogenic, rather than coarse particle is oversimplified (Watson *et al*, 1997; Smith *et al,* 2000; RIVM Report 650010 033, 2002). Recent reports have shown that available free radicals, and reduction-oxidation ability in particulate may explain the observed adverse health endpoints.

INDUSTRIAL COMBUSTION SOURCES

The US EPA has studied the relative contribution of different emission sources to the ambient PM10 and PM2.5 loading in 2000 (EPA, 2003). Results, presented in Figure 2-7 indicate that industrial processes and fuel combustion accounts for 5% and 4% of PM10, respectively. However, for PM2.5 these two source categories contribute 12% and 10% of the total.

Related information has been gathered on the major sources of fine carbonaceous aerosol emissions within a heavily urbanized area surrounding Los Angeles (Hildemann *et al*., 1994b).



PM$_{10}$ Emissions by Source Category, 2000`

PM$_{2.5}$ Emissions by Source Category, 2000

Figure 2-7. Inventory of PM$_{10}$ and PM$_{2.5}$ Emissions by Source Category (EPA, 2003)

Results, based on 1982 data and presented in Table 2-5, indicate that emissions from natural and refinery gas combustion, petroleum industrial processes, and coke calciners comprise a minor but significant fraction of total organic aerosol emissions.

Combustion equipment used within the petroleum industry includes a variety of designs that vary widely depending upon the intended application. Hansell (1997) developed an emissions database for petroleum industrial combustion devices. Table 2-6 provides a partial list of stationary equipment included in the database. The study does not encompass all possible air pollution control equipment combinations for each type of combustion device, but the data in Table 2-6 does serve to illustrate the variety of equipment and configurations employed within the industry. Only a small fraction of the fired equipment within 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.

Table 2-5. Apportionment of Carbonaceous Aerosols in South Coast Air Basin.

Source Type	Fine aerosol carbon emitted (kg/day)[a]	% of total emissions	Contemporary % of C used in model[b]	Notes[c]
Meat cooking operations		17.3	99.5	*d*
charbroiling	4938			*e,f*
frying	1576			*e,f,g*
Diesel vehicles		14.4	2.6	
heavy-duty trucks	2800			*e,f*
other vehicles	2635			
Paved road dust	5113	13.6	49.2	*e*
Fireplaces		12.2		
softwood	3690		100.5	*e,f*
hardwood	891		84.2	*e,f*
Noncatalyst gasoline vehicles		10.9	0.5	
automobiles	2343			*e,f*
other vehicles	1744			
Surface coating operations	1433	3.8		*h*
Catalyst-equipped gasoline vehicles		3.4	5.7	
automobiles	1132			*e,f*
other vehicles	143			
Forest fires	933	2.5		*i*
Railroad (diesel oil)	900	2.4	2.6	*j*
Brake lining	857	2.3	51.2	*e*
Cigarettes	808	2.1	100.2	*e,f*
Organic chemical processes	736	2.0		*h*
Tire wear	590	1.6	14.5	*e*
Roofing tar pots	556	1.5	1.7	*e*
Misc. Industrial point sources	424	1.1		*h*
Jet aircraft	394	1.0	1.9	*k*
Natural gas combustion				*e,f*
residential/commercial sources	32			
other sources	262			
Misc. petroleum industrial processes	278	0.7		*h*
Residual oil stationary sources	257	0.7	1.9	*k*
Coke calciners	239	0.6		*h*
Primary metallurgical processes	228	0.6		*h*
Mineral industrial processes	212	0.6		*h*
Refinery gas combustion	195	0.5		*h*
Diesel oil-fired ships	180	0.5	2.6	*j*
Secondary metallurigcal processes	167	0.4		*h*
Distillate oil stationary sources		0.4	1.9	
industrial	89			*e,f*
other	55			
Other sources	825	2.2		*h*
Total	37654			

[a] Annual average emissions stated at a daily rate; includes both elemental and organic carbon. [b] To allow comparison with ambient measurements, contemporary carbon fractions used in model assume that all contemporary carbon was accumulated in 1982; hence, the woodsmoke values differe from those in Table 1. [c] Except where otherwise noted, values are based on literature survey (6,43). [d] While original inventory only considered commercial charbroiling, revised mass emission rates include domestic and commercial frying and charbroiling. [e] Fraction of total carbon in fine emissions revised based on the source tests of Hildemann *et al.* (7). [f] Fine mass emission rate revised based on the source tests of Hildemann *et al.* (7). [g] New emission source not included in original inventory. [h] Carbon isotope composition is uncertain. [i] Intermittant source not included in model due to lack of contributions during the ambient periods sampled in 1982. [j] Assumed to have a carbon isotope composition like that of the heavy-duty diesel truck emissions sample. [k] Assumed to have a carbon isotope composition like that of the distillate oil-fired boiler emissions sample.

Table 2-6. Stationary Combustion Devices.

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 gas	SCR
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 Regenerator	Petroleum Coke	
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 gas	None
Thermal Oxidizer	Refinery gas/water treatment vent gas	None
Thermal Oxidizer	Fuel/gasoline vapors	None
Glycol Dehydrator - vent	Ethylene glycol	None
Glycol Dehydrator - vent	Triethylene glycol	None

Available data from direct measurements of organic aerosol emissions from petroleum industry combustion devices are limited. Table 2-7 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 2-8 are rough estimates of 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.

The Western States Petroleum Association (WSPA) summarized total particulate and PM10 emissions from several fluidized catalytic cracking units (FCCUs) of differing capacity (Wilkness, 1997). Units addressed in this study are all located 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. Results are summarized in Table 2-9. In examining the data it is important to note that the measurements provide information only for particulate matter that is filterable at stack (hot) conditions. It is believed that particulate emissions from FCCUs stem primarily from catalyst fines entrained in the exhaust gas from the catalyst regenerator, plus condensable particles arising from NH_3 and SO_3 and organics. As indicated in the table, PM10 comprises the major fraction of total filterable (at stack conditions) particulate emissions from FCCUs - 67 to 88 percent. The data also vary substantially from refinery to refinery on a mass basis. Also, since primary particles that form in the plume after emission are excluded, primary PM10 is probably greater than these data suggest.

Table 2-7. Example Data of Particulate Emissions from Oil-Fired Boilers.

Boiler Function	Fuel Type	Burn Conditions	PM2.5[a] (lb/MMBtu)	PM10[a] (lb/MMBtu)	Total Filterable Particulate (lb/MMBtu)
Industrial	No. 2 Oil	Baseline	0.034 (40%)	0.034 (40%)	0.084
		Low NOx	0.0234 (35%)	0.0268 (40%)	0.0670
Industrial	No. 6 Oil	Baseline	0.0282 (50%)	0.0197 (35%)	0.0564
		Low NOx	0.0039 (40%)	0.0039 (40%)	0.0097

(Derived from Carter *et al*., 1978)

[a] PM2.5 and PM10 percentages estimated from reported particle size distributions.

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

(Derived from Miller, 1985)

[b] All data are approximate.

Table 2-8. Particulate Emissions and Particle Size Data for Selected Non-Fired Refinery Air Emission Sources.[a]

Device	Particulate Emissions		PM10	PM2.5
	Range (lb/1000 bbl feed)	Mean (lb/1000 bbl feed)		
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 catalyst	--	43.7	--	--
Thermofor CCU with no controls	--	17	--	--
Thermofor CCU with cyclones	--	18.3	--	--
Thermofor CCU with CO boiler	--	15	--	--
Moving bed CCU	--	17	--	--
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	--	6.85	6.0	3.1

[a] Derived from Harris *et al*., 1982.

[b] -- Indicates no data available.

Table 2-9. Total Filterable Particulate and PM10 Emissions from FCCUs in Southern California.

Refinery	Total Filterable Particulate		Filterable PM10[b]	
	lb/hr[a]	Lb/hr[b]	lb/hr	%
A	5.54	6.73	4.59	68
B	6.61	7.11	6.2	87
C	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.

[a] South Coast Air Quality Management District Method 5.2, including probe and filter catch only. Similar to EPA Method 5.

[b] EPA 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 2-10 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, 2000). Method 201A employs an in-stack 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.

Table 2-10. EPA Methods 201/201A and 202 Results for Coal-, Oil- and Gas-Burning Boilers and Turbines.

Source	Unit Type	Fuel	PM10 Emissions			
			Filterable PM		Condensible PM	
			lb/MMBtu	% Total PM 10	lb/MMBtu	% Total PM10
Lakewood Cogeneration, L.P. Cogen. Facility - Unit #1	Turbine	Natural Gas	0.00021	14	0.0012	86
Lakewood Cogeneration, L.P. Cogen. Facility - Unit #2	Turbine	Natural Gas	0.00052	33	0.0011	67
Lakewood Cogeneration, L.P. Cogen. Facility - Unit #1	Turbine	Natural Gas	0.0055	43	0.0073	57
Lakewood Cogeneration, L.P. Cogen. Facility - Unit #2	Turbine	No. 2 Oil	0.0061	37	0.0102	63
Kamine Milford, L.P. Cogen. Facility[a]	Turbine	Natural Gas	0.0132	56	0.0105	44
Kamine Milford, L.P. Cogen. Facility[b]	Turbine	Natural Gas	0.0015	12	0.0112	88
Kamine Milford, L.P. Cogen. Facility[c]	Turbine	Natural Gas	0.0012	10	0.0107	90
Kamine Milford, L.P. Cogen. Facility[d]	Turbine	Natural Gas	0.0014	12	0.01	88
Bristol-Myers Squibb Cogen. Facility (Lawrenceville)[e]	Turbine	Natural Gas	0.0018	25	0.0054	75
Bristol-Myers Squibb Cogen. Facility (Lawrenceville)[f]	Turbine	Kerosene	0.0173	73	0.0063	27
Trigen-Trenton Energy Cogen. Facility - Unit #1	Engine	Dual Fuel[g]	0.0012	20	0.0048	80
Trigen-Trenton Energy Cogen. Facility - Unit #2	Engine	Dual Fuel[g]	0.0027	29	0.0066	71

[a]Steam injection (SI) on, waste heat recovery boiler (WHRB) off; [b]SI off, WHRB off; [c]SI on, WHRB on; [d]SI off, WHRB on; [e]Heat recovery steam generator (HRSG) on; fHRSG off; [g]Dual fuel refers to No. 2 oil and natural gas.

(Corio and Sherwell, 2000)

Semivolatile organic compounds (SVOCs) 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 2-8 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 data 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.

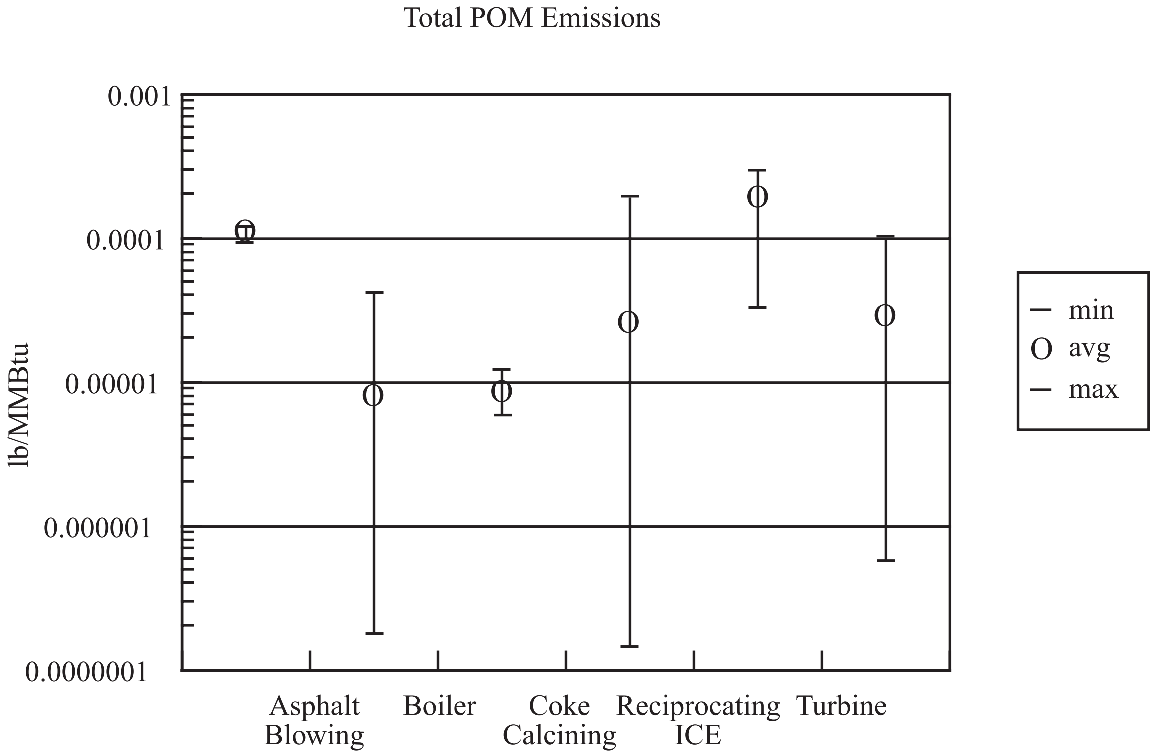


Figure 2-8. Emissions of POM from Selected Petroleum Industry Combustion Devices (Hansell,1997).

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), McMurry (2000) and references therein.

Aerosol measurement instruments can be classified according to their capacity to resolve size, time and compositions. The classifications are illustrated in Figure 3-1 (McMurry, 2000). A perfect aerosol-sampling instrument can provide (1) continuous measurement of particle physical properties with wide range size distribution, (2) complete particle chemical properties (size-resolved composition), and (3) real time measurement. However, no single instrument can measure particle size, mass, and chemical compositions in real time. For example, CNC measures total particle number concentration in real time, but can't provide particle speciation profiles, nor size distribution. While time-integrated sampling can provide chemical speciation, resolution of particle size distribution is either not available (filter) or low (cascade impactor), and it is not a real time measurement. Therefore, it is common to have two or more types of PM measurement instruments co-located at a sampling site. Selection of appropriate instruments for accurate PM measurements greatly depends on the physicochemical characteristics of particles, including particle size distribution and chemical compositions, meteorological conditions, such as relative humidity, and the particle size range of interest.

TIME INTEGRATED AMBIENT PARTICULATE SAMPLING METHODS

Time-integrated aerosol samples are most often acquired by drawing ambient air through aerosol instruments or filter material using a pump. Particle mass and its chemical components are subsequently quantified 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.

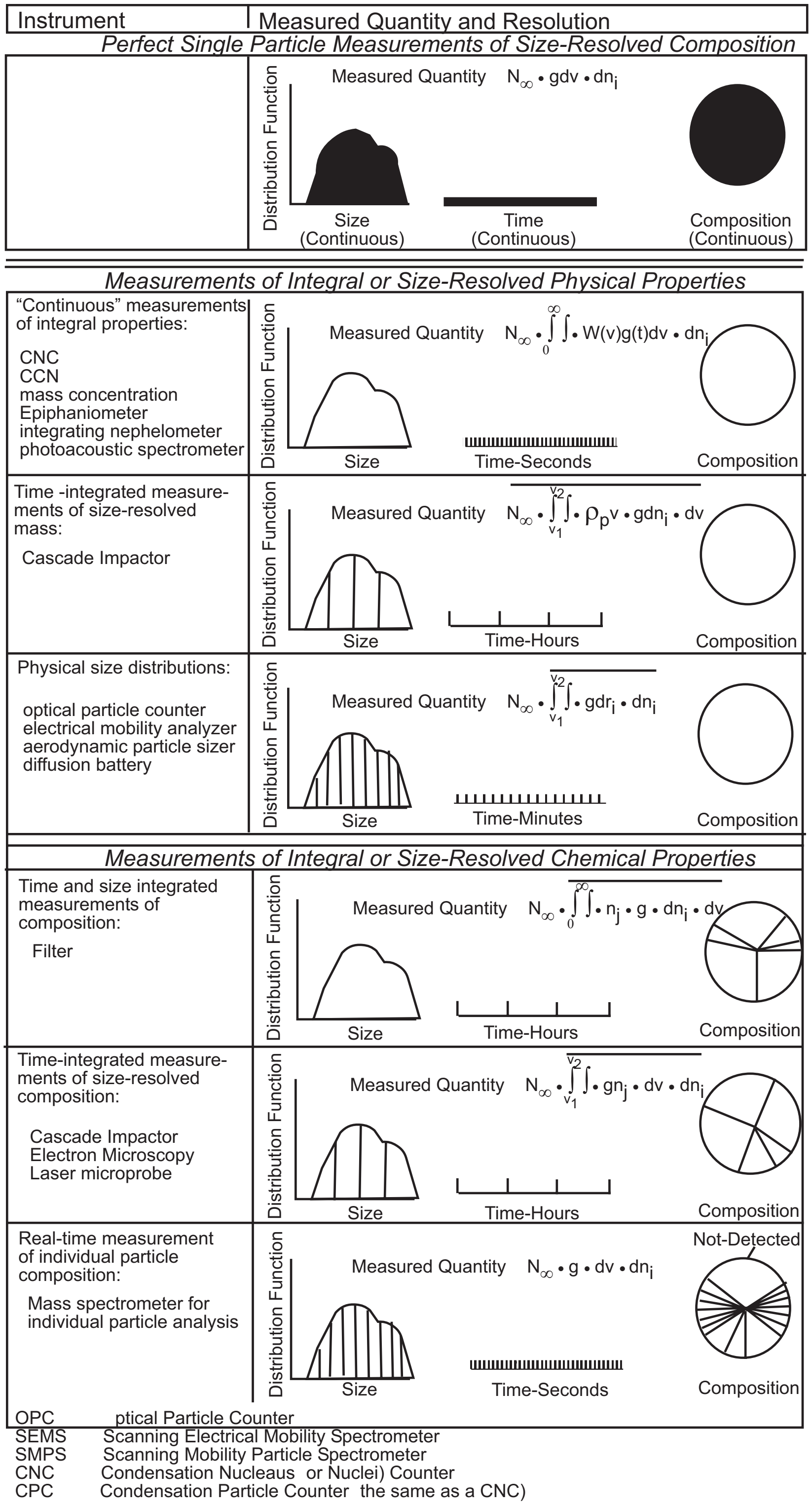


Figure 3-1. Classification of aerosol instrument according to their capacity to resolve size, time, and composition (adapted from McMurry 2000).

The particle sampling systems that have achieved U.S. EPA reference or equivalence status for PM_{10} compliance monitoring involve sampling onto filter media (PM_{10} and $PM_{2.5}$, 40 CFR Part 50 Appendix 1, 1997). 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 cut-points (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 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.

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

Some filters require pre-treatment before sampling for intended chemical characterization. For example, quartz-fiber filters can be baked at high temperatures (greater than 500 °C) 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.

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

Mass

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 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 (>1,000 LPM), special electro-balances with sensitivities as low as ±1 µg are needed for medium- and low-volume samples (<100 LPM). 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 PM_{10} 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).

Ions

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 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 (CO_2) 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 TOT 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 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. Compounds having a saturated vapor pressure at 25 °C of greater than 10^{-1} mm Hg, between 10^{-1} and 10^{-7} mm Hg, and less than 10^{-7} mm Hg, are generally classified as VOC, SVOC, and nonvolatile, respectively (U.S. EPA, 1988) and different sampling techniques are required for the quantitative collection.

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 compounds. However, the 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 under a vacuum can be used as sample containment vessels and 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. A grab sample can be obtained by manually opening the canister valve On a mass flow controller a critical orifice is placed in-line to regulate the flow rate caused by the pressure differences between ambient air and canister vacuum for integrated samples over a given period of time.

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 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 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 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.

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 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 10^7 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 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.

DENUDER SAMPLINGS

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). Denuders are used as part of, or immediately behind, size selective inlets to remove gases that might interfere with aerosol measurements, or to quantify the concentration of gases that are precursors to secondary aerosols (Chow, 1995, and references therein). Geometries of the denuders can be rectangular, cylindrical, annual, or honeycomb; where as honeycomb design provides the highest gas collection surface area and minimum lengths (Koutrakis, P. *et al*, 1993). The denuder technique has been applied not only to measure nitric acid, sulfur dioxide, ammonia gases, semi volatile particulates, such as ammonium nitrate, but also semi-volatile organic compounds. The denuder internal surface is inert (such as glass) and coated with substances that absorb the gases of interest via diffusion, followed by solvent extraction for chemical analyses of gases. Particles are collected by filter packs consisted of a PTFE filter followed by a solvent impregnated filter downstream of the denuder. The PTFE filter collects particulate for mass measurement, and the solvent impregnated filters collect gases volatized from particle collected on PTFE filter.

However, the reliability of presently existing denuders for investigating 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). An 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. 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 adsorbent, and subsequent GC/MS analysis, is on the order of 0.1 ng/m^3 for approximately 100 m^3 of air sampled.

The accuracy with the denuder-based systems depends on the denuder collection efficiencies of the gases. While the denuder removes the gas of interest, the equilibrium between gas and particle phases is disturbed. Materials in the particle phase will evaporate to compensate the amount of gases been removed. The denuder collection efficiencies of gases depend on the denuder surface area, temperature and relative humidity of the airflow, diffusivity and vapor pressure of the interest species, as well as presence of potential competing species. It is generally found that the gas collection efficiency increases with larger surface area, longer residence time, and high gas diffusivity (Turpin et al. 2000 and references within). The gas collection efficiency decreases when the air temperature, relative humidity, flowrate, and gas vapor pressure are high. It is important to evaluate the denuder collection efficiency for compounds of interest over the range of conditions, which could be encountered during sampling. If the collection efficiencies of gases in denuders are low, the "escaped" gases will be collected on the adsorbent-coated media (filter) downstream, which results in overestimation of compounds of interest in particle phase. The known denuder collection efficiency can be used to correct the gas absorbed to the filter and absorbent bed downstream for compounds in particle phase. The residence time in denuder is designed as short (a few seconds) so that only the gases (not contribution from particle phase to keep gas-particle equilibrium) are collected on denuder-coated surface (Forrest, *et al*, 1982; Zhang & McMurry 1987, 1992, Kamens and Coe, 1997).

MEASUREMENT OF ULTRAFINE PARTICLES

Ultrafine particle size distributions can be measured by Scanning Mobility Particle Sizer (SMPS), which combines the use of a Differential Mobility Analyzer (DMA) and a Condensation Particle (or nuclei) Counter (CPC, or CNC). An impactor is placed before the DMA to remove particles larger than the size of measurement. Particles are then drawn through a DMA to classify particles in different size ranges, followed by CPC to count particle number concentrations.

In DMA, particles are neutralized and charged by passing through a bipolar charger such as Kr-85. These bipolar charged particles are then passed through an electric field, which affects the flow trajectory of the particles. The charge element in DMA is form by an inner cylinder that is connected to a negative power supply, and can be precisely controlled. Negative charged particles are repelled and deposit on the outside wall, and positive charged particles are removed by the negatively charged element. Only particles within a very narrow range of electrical mobility exit the DMA and enter the particle counter (CPC). In the particle counter, particles are drawn through a heat saturator, which vaporizes the high molecular weight working fluid; then sufficiently cooled in a condensor, where vapor heterogeneously condenses on particles. Therefore, particles grow 100-1000 time larger, and can be detected and counted optically. By alternating the voltage of the charging element in the DMA, particles in different size range are separated and the entire particle size distribution can be measured. The particle mass concentration can then be calculated by integrating particle number concentration and the assumed density. The performance of SMPS for particles larger than 200nm depends on particle concentrations and size distributions. For example, if particle number concentration in the sample is higher than 9,999,999 particles/cc, particles cannot be counted efficiently and the sample should be diluted. If the particles of interest are too large, particles cannot be charged sufficiently and cannot be classified in DMA correctly. Nevertheless, SMPS is no doubt the best instrument for measuring particle size distribution between 10-200nm.

As aforementioned, particle counters like SMPS cannot provide chemical speciation profiles for particles. When used in conjunction with a cascade impactor, it is possible to fill in the absent chemical properties of particles. Most cascade impactors can only separate particles larger than 56 nm. However, the recent development of low-pressure Nano-MOUDI (MSP Corp, MN) enables collection of particles in the size range of less than 10, 10-18, 18-32, and 32-56nm at a flow rate of 10 lpm. When nano-MOUDI is used in a stand-alone mode, a longer sampling time is required to collect sufficient material for chemical analysis (due to low flow rate). Also, particle volatilization losses can be significant while operating at low pressure and particle bounce at high loading can be more pronounced due to high jet acceleration velocity.

DIRECT READING INSTRUMENT OF AIRBORNE PARTICLES

Choices of direct-reading aerosol sampling instruments used for various measuring objectives are illustrated in Figure 3-2. In general, particles pass through the instrumental sensing zone and result in changes of properties in the zone. Therefore, a relationship between the detected changes and a property of particles can be established. These direct-reading instruments can measure (1) particle mass concentration, (2) particle size concentration, and (3) concentrations of chemical speciation. Different properties of particles are measured by different instrument. For example, measurement of particle size from different instrument can be derived from many of particles properties, such as its optical, aerodynamic, mechanical, forced field mobility, or gravimetric behavior. Thus, data measured from different instruments should be compared with some correction to account for these differences.

The comparisons of these direct-reading aerosol instruments, such as sampling principle, parameters resulting in bias, effective particle size range, output data, advantages, disadvantages and model examples, are shown in Table 3-1. As aforementioned, combinations of two or more aerosol sampling instruments are often used to measure parameters of specific interest. For example, measurement of particles sizes less than 2.5μm requires deployment of condense nuclei particle counter and DMA which measures particle less than 5nm ~ 400nm. In addition, a single particle laser counter can be used for particles larger than 0.3μm. However, corrections for the particles measured at the overlapped size range (0.3 ~ 0.5 μm) are needed to rectify data measured by instruments based on different particle characteristics (electrical mobility diameter and aerodynamic diameter).

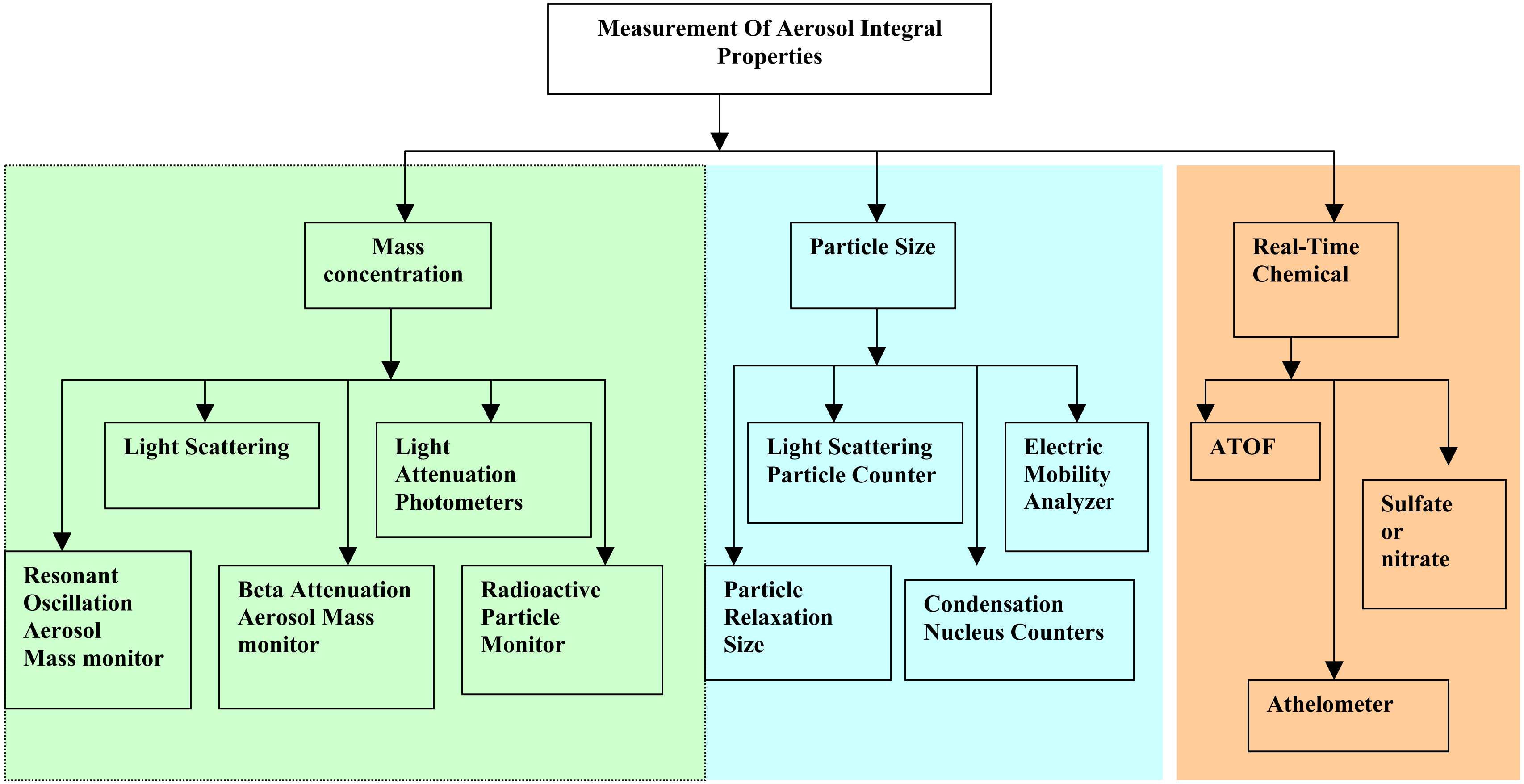


Figure 3-2. Drill down of real time PM measurement.

Table 3-1. Comparison of Real Time PM Instruments

Monitor Principle	Principle	Parameters Affect Measurement	Effect Size Range	Measurement	Advantages	Disadvantages	Model Example
Light Scattering Photometers	The scattered light reaches sensing zone as function of particle counts.	1. Particle diameter 2. Refractive index 3. Wavelength of light sources.	0.1-20	Mass concentration	1. Qualitative mass concentration per second 2. Relative low cost	1. No resolution in particle size distribution 2. Reading and actual concentration	Data RAM (MIE)
Light Scatting, Single Particle	Same as light scattering	1. Particle diameter 2. Refractive index 3. Wavelength of light sources.	0.5-10	Number concentration in specific size range	2. Provide PM mass concentration at specific particle size range	1. Unsuitable when samping under high fluctuation source. 2. High number concentration entering the sensing zone leads to miscount	Airborne Particle counter (CLIMET)
Light-Attenuating Photometers	Light extinction	1. Must contain high PM mass concentration	>0.5	Mass concentration	Good for in-stack	1. Calibration of the transmissionmeters are empirical 2. Not considered as a scientifically established analytical techniques	900RM (DAT) RM-7A (LER)
Condensational Nucleus Counters	Grow particles in a vapor staurated chamber till light scattering detectable size	1. Vapor species used for saturation. 2. Flow stability and laser	0.002-0.450	Size segregated number concentration	Measurement of ultrafine particles	1. Not a field instrument 2. Particle diffusive losses 3. Additional flow needed to fight for flow.	Condensational Particle Counter (TSI)
Particle Relaxation Size Analyzer	Velocity of given particle size creates different lagging time.	1. Coincidence of high particle number concentration 2. Actual particle density	0.3-20	Size segregated number concentration	1. High resolution of particle size distribution 2. Semi-continuous monitor (5 minute)	1. High capital cost 2. Particle number concentration in sample flow less than 100p/cc.	Aero-dynamic Particle Sizer (APS)
Resonant Oscillation Aerosol Mass Monitors	Resonant frequency is leaner to particulate mass collected on media	1. Low sensitivity for particles larger than 10μm. 2. Loss of sensitivity crystal loading	TSP or selective size with pre-impactor	Mass concentration	Real Time	1. Artifacts due to volatile species 2. Require minimum mass deposit on filter media to determine mass	TEOM (R&P) CAMM (R&P)
Electric Mobility Analyzers	Charged particles are classified by a series of stepwise changes in the electric field	1. Efficiency of charging particles 2. Probability of particle charges 3. Resistibility of particles	0.005-1.0	Number concentration	Measurement of ultrafine particles	1. Need to combine with CPC/CNC 2. High capital cost	Dynamic Mobility Analyzer (TSI)
Beta Attenuation Aerosol Mass Monitors	Attenuation of beta radiation	1. Humidity 2. Gas adsorption 3. Particle collection efficiency	TSP or selective size with pre-impactor	Mass concentration	Real time mass concentraiton for ambient PM or higher mass concentration	1. Inappropriate if ultrafine particle fraction is significant (such as diesel emission)	BAM-101 (MDA Scientific, Inc.)

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) that are present at much higher concentrations than in ambient air samples.

Source level sampling (undiluted) for substances such as particulate and SVOCs are often included in test programs 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

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

Measurement Group	Sampling Principle	Reference	Analytical Principle	Reference
Particulate matter (filterable)	Heated out-of-stack filter	EPA Method 5[b]	Gravimetric	Ibid.
Particulate matter (filterable non-sulfuric acid)	Heated out-of-stack filter	EPA Method 5B[b]	Gravimetric	Ibid.
Particulate matter (filterable non-sulfate)	Heated out-of-stack filter/impingers	EPA Method 5F[b]	Gravimetric/IC	Ibid.
Particulate Matter (Filterable)	In-Stack Filter	EPA Method 17[b]	Gravimetric	Ibid.
Particulate matter (condensable)	Heated filter with ice bath impinger collection	EPA Method 202[c]	Methylene chloride extraction with gravimetric analysis	Ibid.
Formaldehyde, acetaldehyde	DNPH impingers (derivitization)	EPA Method 0011[a]	HPLCUV	Ibid.
NH_3	Heated in-stack filter with H_2SO_4 impingers	EPA Method 206	IC	Ibid.
Volatile organic compounds	Preconcentration (Tenax®)	EPA Method 0031[a]	Purge-And-Trap HRGC/LRMS	EPA Methods 5041[a] and 8260[a]
	Tedlar® Bag	EPA Method 0040[a]	GC/MS	EPA Method 8240[a]
			GC/FID (On-Site)	EPA Method 18[b]
Semivolatile organic compounds	Preconcentration (XAD-2) and H_2O Impingers	EPA Method 0010[a]	Solvent Extraction/ HRGC/LRMS	EPA Method 8270[a]
Trace metals	Heated out-of-stack filter with HNO_3/H_2O_2 and $KMnO_4$ impingers	EPA Method 29[b]	ICAP	EPA Method 6010[a]
			CVAAS	EPA Method 7470 and 7471[a]
			GFAAS	EPA Method 7000 Series[a]
Particle size distribution (PM10 and PM2.5)	Cascade impactor	EPA Method 201A[c]	Gravimetric	Ibid.
O_2	Continuous emissions monitors	EPA Method 3A[b]	Paramagnetic	Ibid.
CO		EPA Method 10[b]	NDIR	
CO_2		EPA Method 3A[b]	NDIR	
NO		EPA Method 7E[b]	Chemiluminescence	
SO_2		EPA Method 6C[b]	NDUV	
THC		EPA Method 25A[b]	FID	
Gas Flow Rate	S-Type Pitot Tube	EPA Method 1-3[b]	Manometer	Ibid.
Moisture	Condensation	EPA Method 4[b]	Gravimetric	Ibid.

[a] *Test 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).

[b] Appendix A, Part 60, *Code of Federal Regulations*, Title 40.

[c] Appendix M, Part 51, *Code of Federal Regulations*, Title 40.

Table 4-1. State and Local Flue Gas Source Sampling and Analytical Methods. (continued)

Measurement Group	Sampling Principle	Reference	Analytical Principle	Reference
(Total) Particulate Matter (filterable & condensable including extractable organic matter & sulfuric acid (1))	Ice bath impingers with a back up filter	SCAQMD Method 5.1	Gravimetric/ Dichloromethane Extraction/Sodium Hydroxide Titration & BaSO4 Precipitation	Ibid.
(Solid) Particulate Matter (filterable & condensable minus extractable organic matter & sulfuric acid)	Ice bath impingers with a back up filter	SCAQMD Method 5.1	Gravimetric/ Dichloromethane Extraction/Sodium Hydroxide Titration & BaSO4 Precipitation	Ibid.
(Total) Particulate Matter (filterable & condensable including extractable organic matter & sulfuric acid (1))	Heated out-of-stack filter/iced impingers	SCAQMD Method 5.2 (2)	Gravimetric/ Dichloromethane Extraction/Sodium Hydroxide Titration & BaSO4 Precipitation	Ibid.
(Solid) Particulate Matter (filterable & condensable minus extractable organic matter & sulfuric acid)	Heated out-of-stack filter/iced impingers	SCAQMD Method 5.2 (2)	Gravimetric/ Dichloromethane Extraction/Sodium Hydroxide Titration & BaSO4 Precipitation	Ibid.
(Total) Particulate Matter (filterable & condensable including extractable organic matter & sulfuric acid (1))	In-stack filter/iced impingers	SCAQMD Method 5.3 (2)	Gravimetric/ Dichloromethane Extraction/Sodium Hydroxide Titration & BaSO4 Precipitation	Ibid.
(Solid) Particulate Matter (filterable & condensable minus extractable organic matter & sulfuric acid)	In-stack filter/iced impingers	SCAQMD Method 5.3 (2)	Gravimetric/ Dichloromethane Extraction/Sodium Hydroxide Titration & BaSO4 Precipitation	Ibid.
Particulate Matter (filterable & condensable including extractable organic matter)	Heated out-of-stack filter/iced impingers	CARB Method 5	Gravimetric/ Methylene Chloride Extraction	Ibid.
Particulate Matter (Filterable)	In-Stack Filter	CARB Method 17	Gravimetric	Ibid.
Formaldehyde, acetaldehyde	DNPH impingers (derivitization)	CARB Method 430[d]	HPLCUV	Ibid.
NH_3	H_2SO_4 impingers	SCAQMD Method 207.1	Colorimetry	Ibid.
Volatile organic compounds	Tedlar Bag	CARB Method 422	GC	Ibid.
PAH	Preconcentration (XAD-2) and H_2O Impingers	CARB Method 429	Solvent Extraction/ HRGC/MS	Ibid.
Trace metals	Heated out-of-stack filter with HNO_3/H_2O_2 and $KMnO_4$ impingers	CARB Method 436	ICPAES ICPMS GFAAS CVAAS DAAAS	EPA SW-846 Methods[d] EPA Method 6010 EPA Method 7470 EPA Method 7000 Series
Particle size distribution	Cascade impactor	CARB Method 501	Gravimetric	Ibid.
O_2 CO CO_2 NO SO_2	Continuous emissions monitors	SCAQMD Method 100.1 SCAQMD Method 100.1 SCAQMD Method 100.1 SCAQMD Method 100.1 SCAQMD Method 100.1	Paramagnetic NDIR NDIR Chemiluminescence NDUV	Ibid.
Gas Flow Rate	S-Type Pitot Tube	CARB Method 1-3	Manometer	Ibid.
Moisture	Condensation	CARB Method 4	Gravimetric	Ibid.

[d] *Test 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).

1. An allowance to the total PM is allowed for sulfuric acid formed from reactions between SO_2 and SO3 with sample train components. When ammonia is injected to enhance the efficincy of a control device a second adjustment to total sulfate is allowed.

2. If the probe and filter termperature are kept above 200F and sulfuric acid is present in the sampled gas in quantities greater than 10 percent of the standard for applicable rule, a separate and concurrent measurement of sulfuric acid is required using SCAQMD Method 6.1.

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, labeled as continuous emissions monitors under the sampling principle heading, are continuous sampling methods. All other tests listed in Table 4-1 involve manual sampling.

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 that 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 SO_3, NH_3, HCl and Cl_2, 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

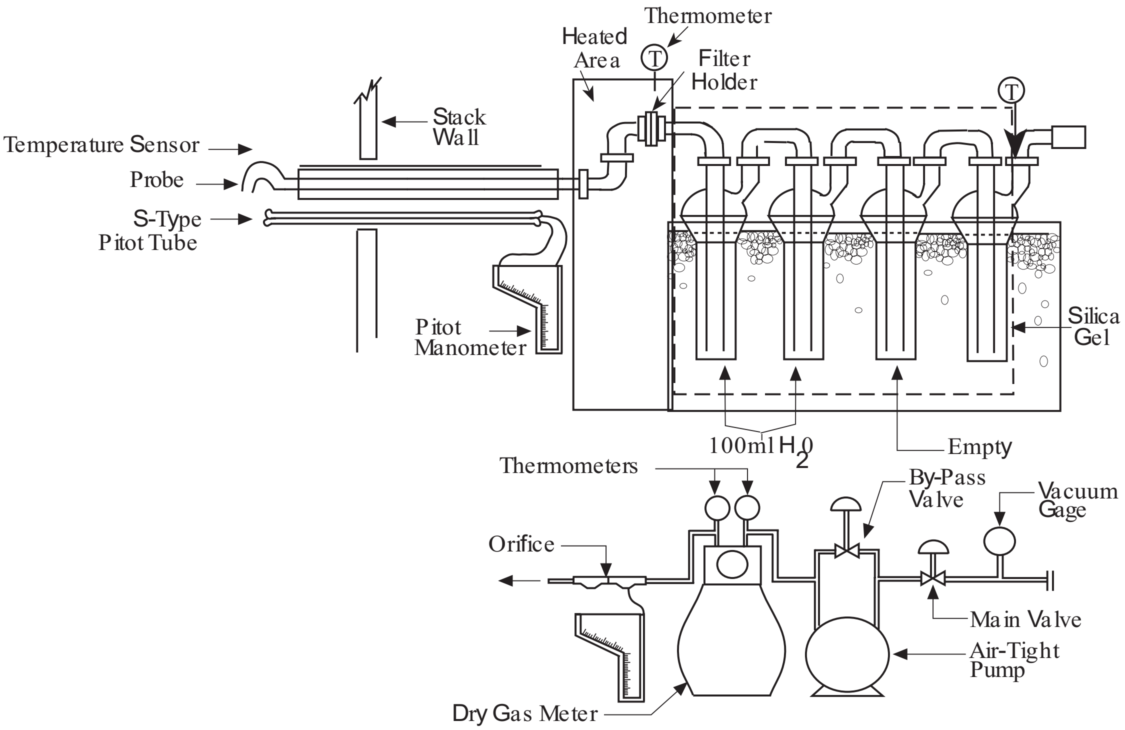


Figure 4-1. EPA Method 5 – Particulate Matter Sampling Train.

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 that pass through the filter and gases that condense at the ice bath temperature. The simplest analytical procedure involves evaporating the impinger liquid after sampling and determining the mass of residue gravimetrically and may be subject to substantial artifacts that do not occurs in the atmospheric processes. Some methods incorporate procedures that 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. The effectiveness of purging to eliminate artifacts has been assessed in an experimental study, in which pure compressed gases were blended to simulate combustion products with varying low concentrations of SO_2 and passed through an EPA Method 5-type impinger train (England, *et al*, 2000). Figure 4-2 shows that for 6-hour sampling runs a significant amount of SO_2 (at levels simulating gaseous fuels) was retained as sulfate in the impingers. A post test purge reduced but did not eliminate the bias. Comparing these results to field results, these tests showed that the SO_2 artifact could account for 50-100% of the measured sulfate reported by the method. In addition, ammonia can reduce the effectiveness of the purge because the purge only removes uncombined SO_2 and ammonia reacts with SO_2 in solution to ammonium sulfate.

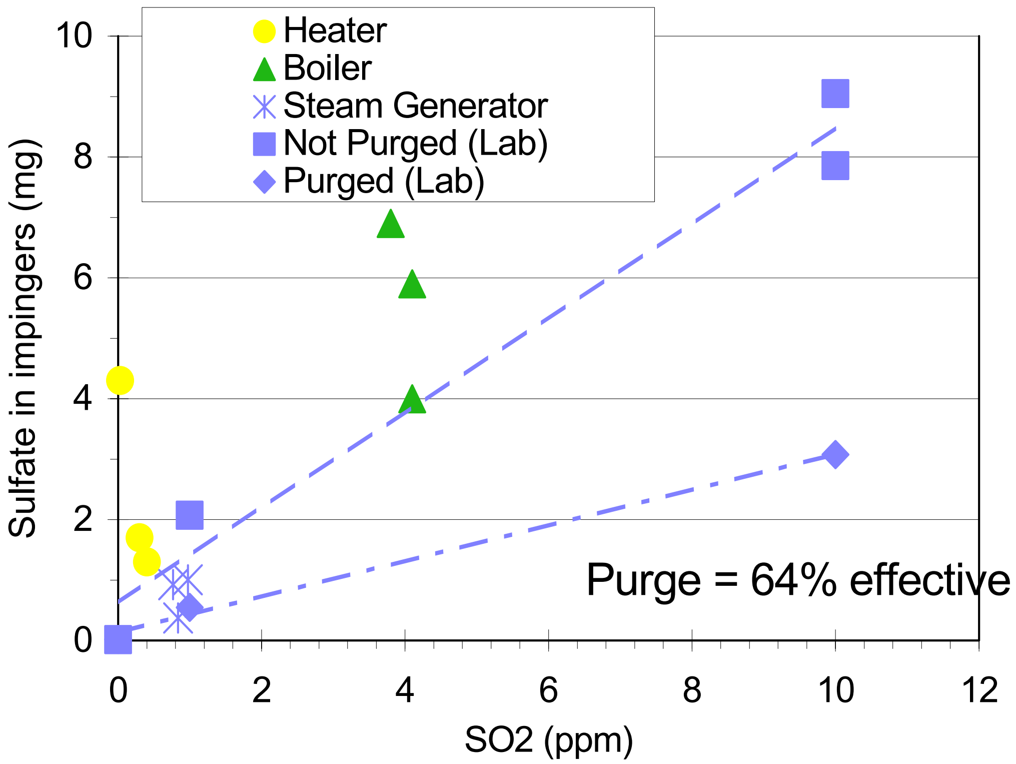


Figure 4-2. Comparison of sulfate artifact with and without purging in impinger methods.

Impinger condensation methods neither completely eliminate 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 (Hildemann *et al*, 1989, England *et al*, 1998). 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 are separated, dried and weighed. Distilled water is then added to the aqueous fraction followed by barium chloride to precipitate sulfate out of solution as barium sulfate. The precipitate is filtered from the aqueous fraction, which is then dried and weighed. Total particulate matter is defined by the method as the solid particulate plus the extracted organics plus the sulfate. Solid particulate matter is defined as the total particulate matter minus the extracted organics and the sulfate. 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, PM_{10} AND $PM_{2.5}$

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 micro orifice uniform deposit impactor (MOUDI) design are generally not used for this reason. The MOUDI is an eight-stage cascade impactor that collects ultrafine particles as small as 0.056 µm 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.

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 the 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. Method Pre 4, illustrated in Figure 4-3 is a modification of EPA Method 201A that enables measurement of PM2.5 by adding a second cyclone in series between the PM10 cyclone and the filter. Any 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 usually 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 over sampling bias in the smaller particle

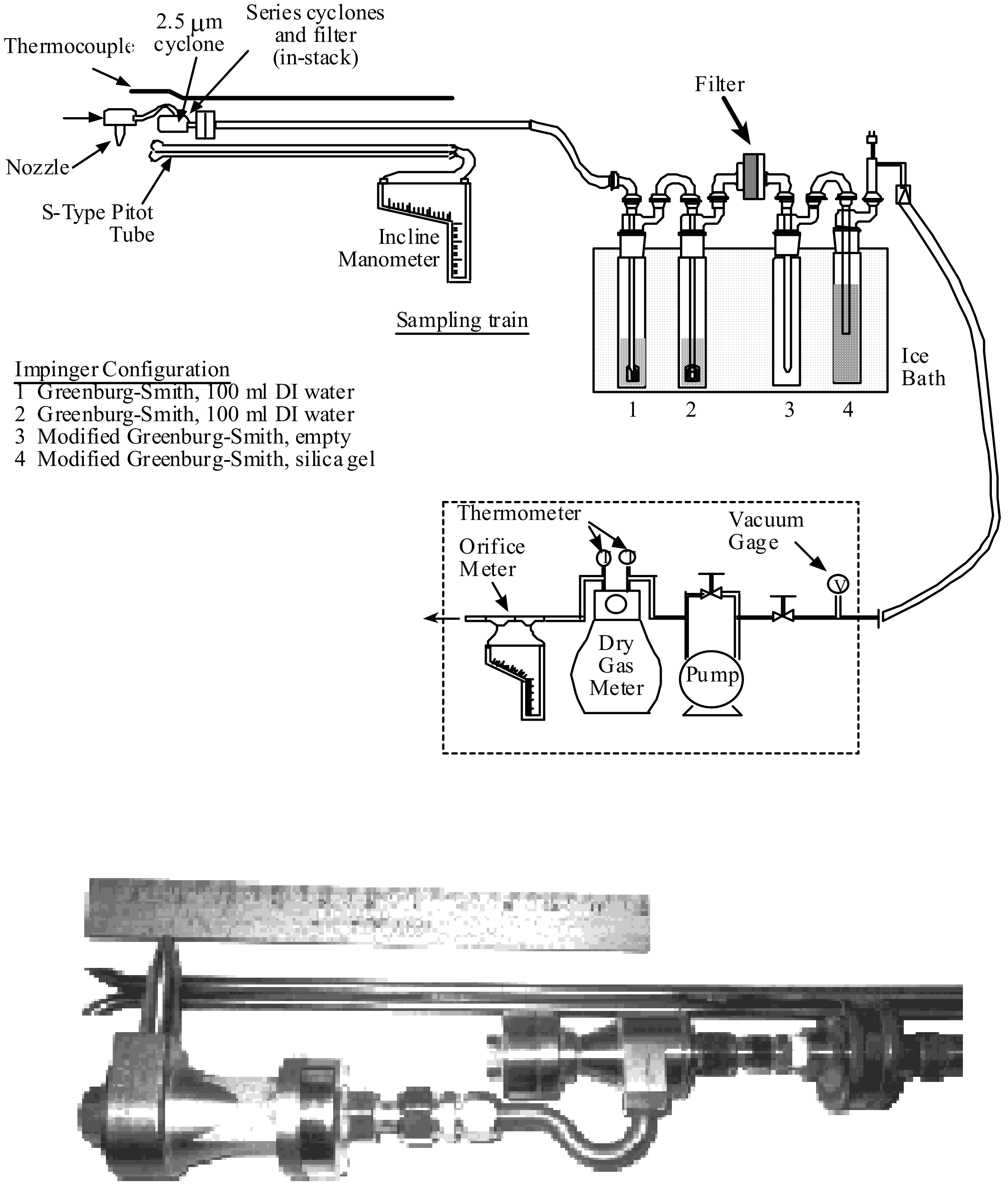


Figure 4-3. Method Pre-4 combining prefiltration with EPA Method 201A for determination of PM2.5.

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 sub-micron light absorbing particles (Garvey and Pinnick, 1983; Clark *et al.,* 1986). While potentially useful diagnostic techniques, 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 that 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 PM_{10} have been used for measuring $PM_{2.5}$ 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 contemplating minor modifications to the methods for $PM_{2.5}$ emission measurements (Logan, 1997). However, only a small fraction of ambient $PM_{2.5}$ 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 semi volatile 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 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 4-4 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 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 gas-phase 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).

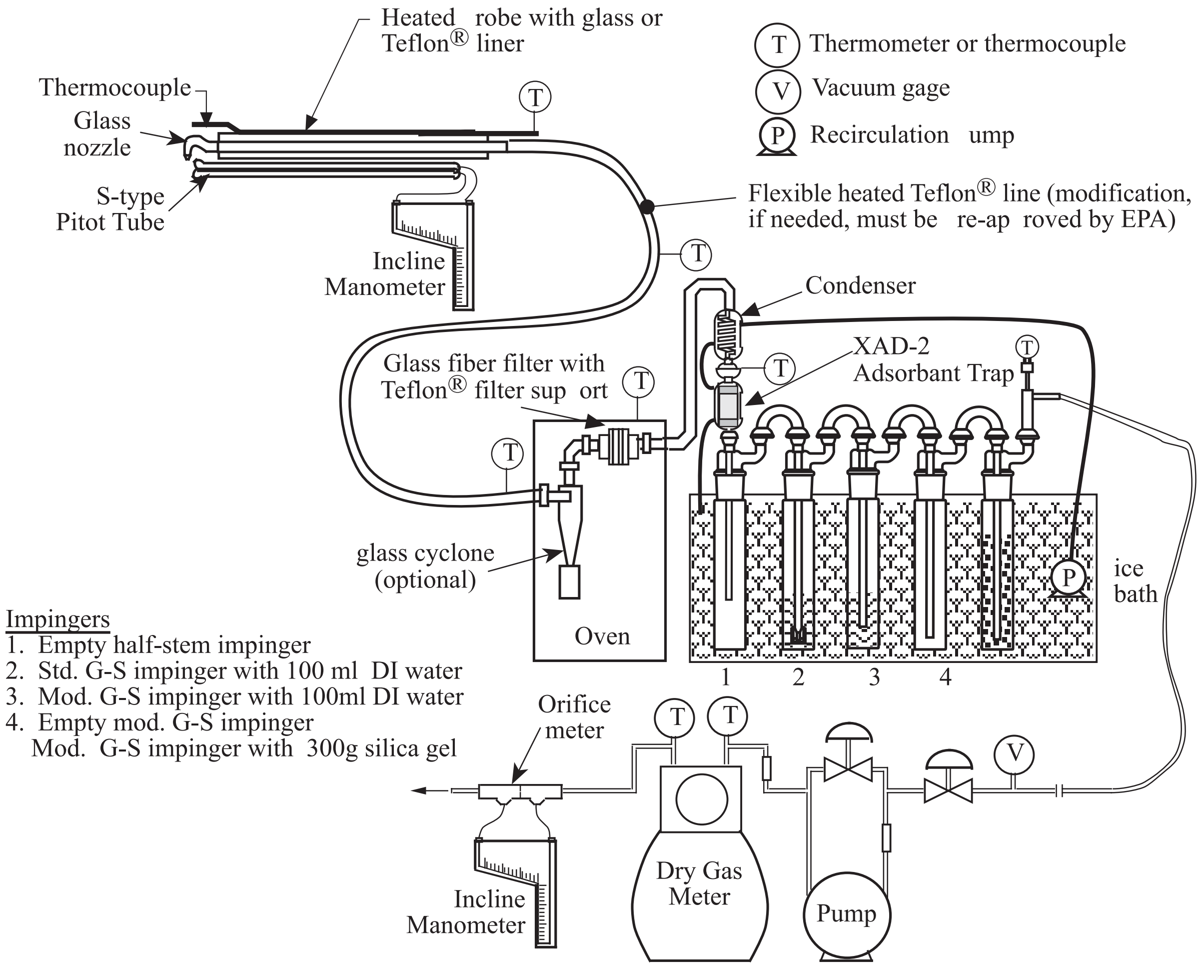


Figure 4-4. EPA Method 0010 Sampling Train for SVOCs.

Table 4-2 lists individual SVOCs that 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. SO_2, HCl and Cl_2 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.

Table 4-2. Method 301 Validation Results for Source Vost Train.

Semivolaile Organic Compound	Mean Recovery	Meets Method 301 Acceptance Criteria?[3]	Meets EPA QA/QC Handbook Acceptance Criteria?[4]	Semivolaile Organic Compound	Mean Recovery	Meets Method 301 Acceptance Criteria?[3]	Meets EPA QA/QC Handbook Acceptance Criteria?[4]
Acids[1]				**Neutrals[2]**			
Di-n-butyl phthalate	46 ± 54%	No	No	styrene oxide	0.5 ± 1481%	No	No
bis(2-ethylhexyl) phthalate	48 ± 23%	No	No	phthalic anhydride	5.3 ± 144%	No	No
m-/p-cresol[7]	69 ± 14%	No	Yes	methoxychlor	73 ± 19%	No[7]	Yes
dimethyl phthalate	82 ± 17%	No	Yes	toluene	76 ± 11%	No[7]	Yes
phenol	89 ± 9%	Yes	Yes	m-/p-xylene[6]	79 ± 12%	Yes	Yes
o-cresol	90 ± 15%	Yes	Yes	quinoline[5]	80 ± 19%	Yes	Yes
2,4-dinitrophenol	111 ± 31%	Yes	Yes	sytrene	84 ± 10%	Yes	Yes
4-nitrophenol	114 ± 31%	Yes	Yes	o-xylene	85 ± 11%	Yes	Yes
4,6-dinitro-o-cresol	122 ± 14%	Yes	Yes	1,4-dioxane	87±11%	Yes	Yes
Bases[1]				cumene	88 ± 11%	Yes	Yes
quinone[6]	2 ± 438%	No	No	ethylbenzene	89 ± 12%	Yes	Yes
hexamethylposphoramide	14 ± 118%	No	No	parathion	89 ± 28%	Yes	Yes
trifluralin	27 ± 41%	No	No	isophorone	93 ± 12%	Yes	Yes
dimethylaminoazo-benzene	31 ± 51%	No	No	acetophenone	96 ± 12%	Yes	Yes
3,3'-dimethoxybenzidine	37 ± 38%	No	No	napthalene	96 ± 11%	Yes	Yes
o-anisidine	39 ± 39%	No	No	dibenzofuran	100 ± 12%	Yes	Yes
o-toluidine	56 ± 30%	No	Yes	dichlorvos	101 ± 18%	Yes	Yes
benzidine	65 ± 119%	No	No	DDE	102 ± 15%	Yes	Yes
N,N,-dimethylaniline	67 ± 24%	No	Yes	4-nitrobiphenyl	102 ± 14%	Yes	Yes
aniline	70 ± 24%	No	Yes	heptachlor	103 ± 12%	Yes	Yes
4,4'-methylene bis(2-chloroaniline)	89 ± 36%	Yes	Yes	biphenyl	103 ± 12%	Yes	Yes
				lindane	104 ± 12%	Yes	Yes
3,3'-dimethylbenzidine	92 ± 44%	Yes	Yes	nitrobenzene	109 ± 12%	Yes	Yes
N,N,diethylaniline	95 ± 19%	Yes	Yes	2,4-dinitrotoluene	109 ± 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[7]	Yes
caprolactam	114 ± 12%	Yes	Yes				
N-nitrosomorpholine	116 ± 12%	Yes	Yes				
N-nitrosodimethyl-amine	117 ± 13%	Yes	Yes				
propoxur	123 ± 12%	Yes	Yes				
2-actylaminofluorene	147 ± 23%	No	Yes				

[1] Values represent the mean from ten complete quad sampling runs with dynamic spiking, two spiked trains and two unspiked trains. [2] Values represent the mean from twenty complete quad sampling runs with dynamic spiking, two spiked trains and two unspiked trains. Neutral compounds were spiked with both the Acid and the Bases, and all neutral data are included in the composite values. [3] EPA Method 301 acceptance criteria include recovery of 70-130%, with a precision ≤50% 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 ≤50% relative standard deviation. [5] Quinoline was placed in Neutral solution rather than Basic solution because of confusion of name with quinone. [6] 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.

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 Conditional Test Method 027 using the sampling equipment illustrated in Figure 4-5. This method 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 iced impingers containing dilute sulfuric acid solution. The samples are analyzed using ion chromatography with a conductivity detector. Bay Area Air Quality Management District Source Test Procedure ST-1B-1 “Ammonia Integrated Sampling” draws sample gas through a series of three impingers immersed in an ice bath containing a solution of hydrochloric acid (HCl) that absorbs the ammonia. This method uses a glass wool filter in the probe nozzle. Samples are analyzed using a specific ion electrode after addition of a pH adjusting solution to the sample. Ammonia from stationary sources can also be measured using South Coast Air Quality Management District Method 207.1 “Analytical Method for Ammonia and Ammonium Compounds from Stationary Sources.” Ammonia in sample gas is collected in the probe and in iced impingers containing sulfuric acid solution. The method has an option to place a filter upstream of the sample train impingers. Sample recovery includes a probe rinse. The rinses and impinger solution are analyzed for ammonia by colorimetry after reaction with Nessler solution.

NO_x and SO_2

NO_x and SO_2 emissions are precursors to nitrate and sulfate in aerosols. Emissions of NO_x 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.

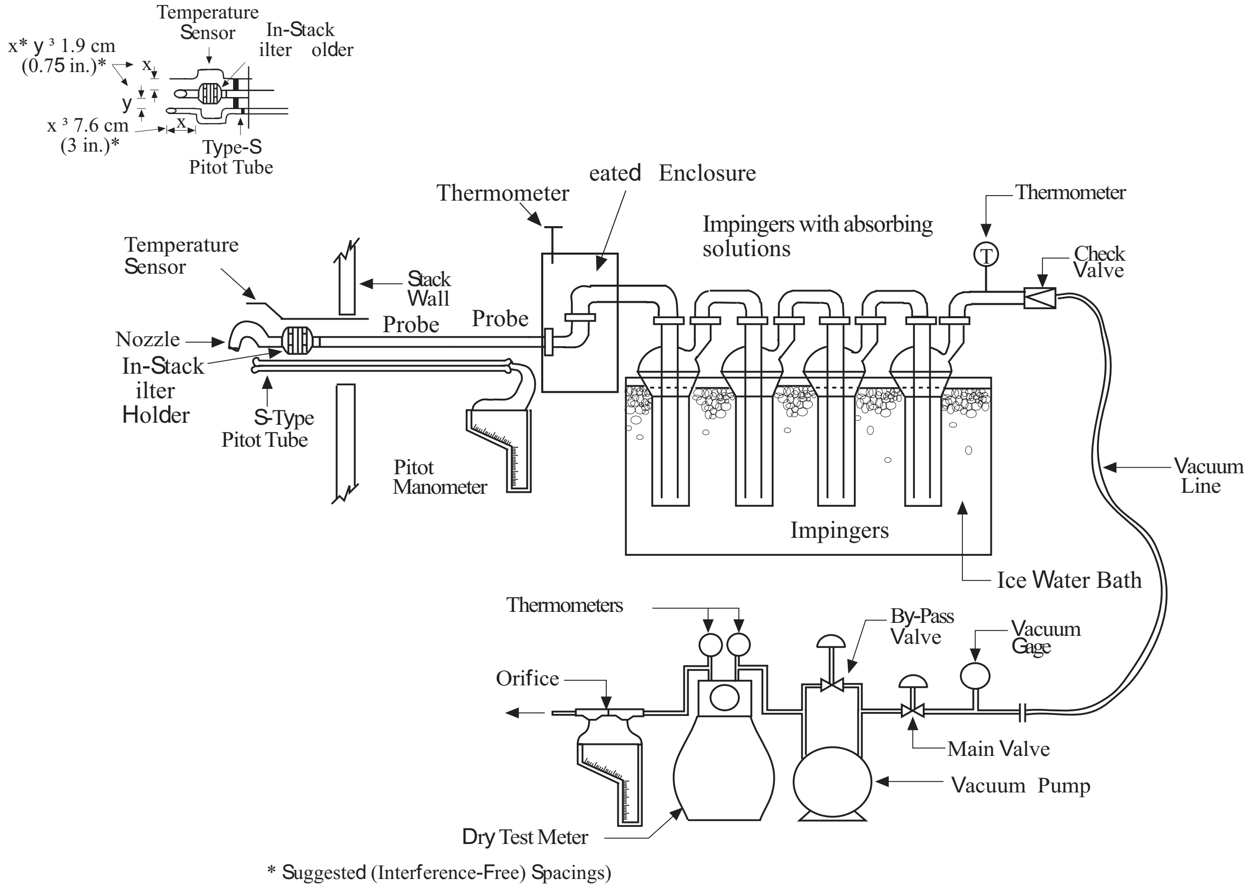


Figure 4-5. Illustration of EPA Conditional Test Method 027 Sampling Train Assembly.

Figure 4-6 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 NO_x and SO_2 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_3</u>

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 two 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 by EPA Method 8 because the method is explicitly for SO_3. EPA Method 8 extracts

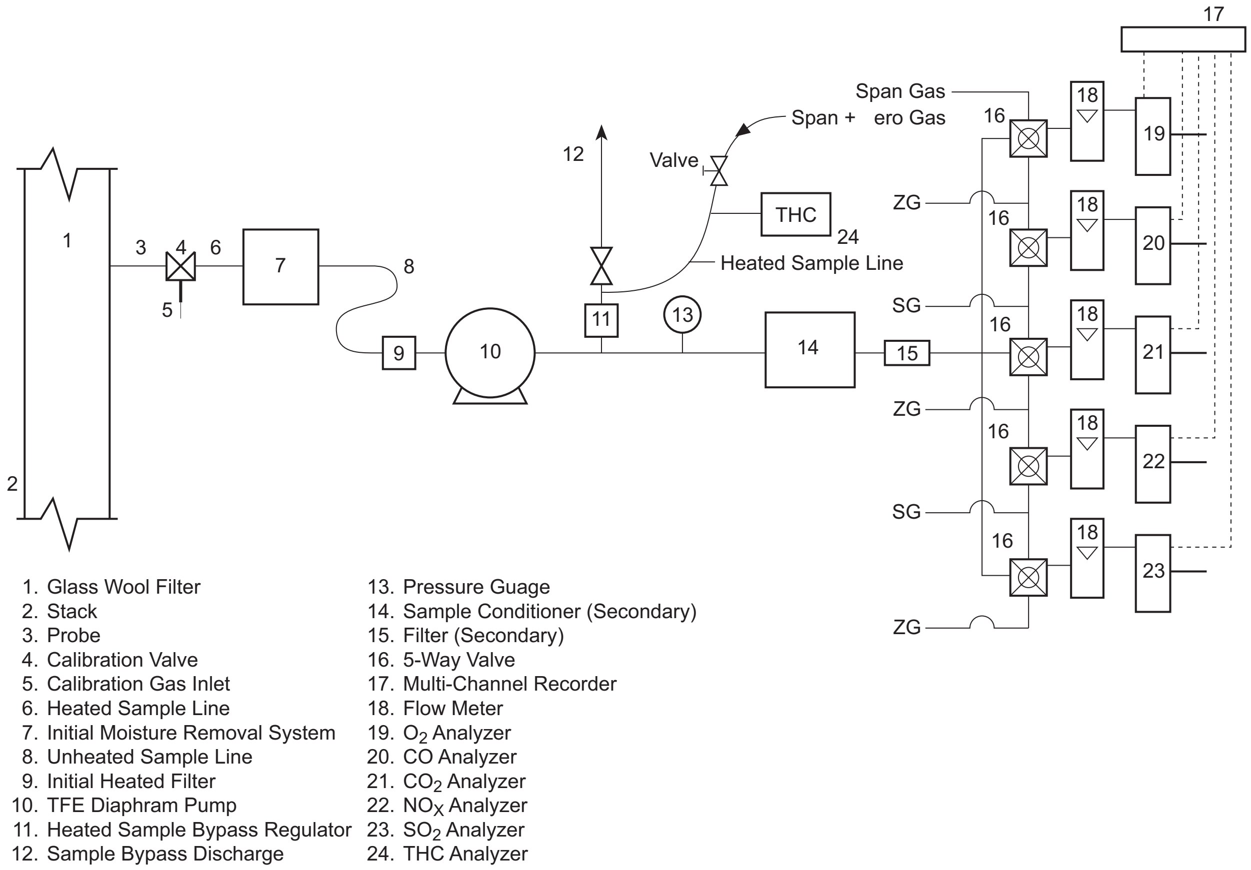


Figure 4-6. Continuous Emissions Monitoring System.

sample gas isokinetically from a stack. The sampling train consists of a heated glass or quartz probe, an isopropanol impinger (to trap sulfuric acid mist and SO_3) in an ice bath followed by an unheated particulate filter, and two impingers with 3% hydrogen peroxide (to trap SO_2) in the ice bath. The sample train is purged post-sampling with clean ambient air for 15 minutes to remove any SO_2 from the isopropanol. Sulfuric acid mist (including sulfur trioxide) and the sulfur dioxide are separated and analyzed by the barium-thorin titration method. Possible interfering agents are fluorides, free ammonia, and dimethyl aniline. SCAQMD Method 6.1 “Determination of Sulfuric Acid and Sulfur Oxides From Stationary Sources” can also be used to measure SOx.

A gas sample is extracted isokinetically and sulfuric acid mist is collected on a Whatman thimble maintained above the dew point of moisture but below 200F. SO_3 is collected in an iced impinger containing 2-propanol downstream of the thimble and SO_2 is then collected in two iced impingers containing hydrogen peroxide. The sample train is purged post-sampling with clean ambient air for 15 minutes. Sodium hydroxide titration is used to measure sulfuric acid and other strong acids. Barium perchlorate titration and barium precipitation are used to measure total sulfates. Possible interfering agents are water-soluble cations, fluorides, phosphates, free ammonia and dimethyl aniline.

Controlled condensation techniques are generally used for SO_3 measurements. This method, illustrated in Figure 4-7 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. The sample is then rinsed from the sampling apparatus and analyzed by conventional titrimetric or ion chromatographic techniques.

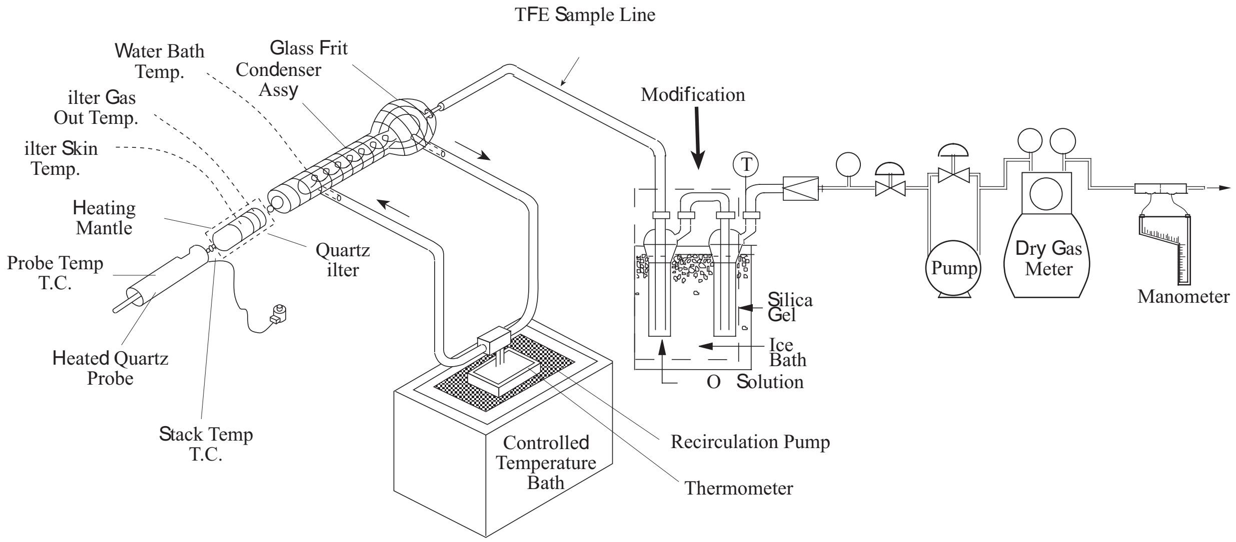


Figure 4-7. Controlled Condensation Sampling Train for SO_3 (with Modification for SO_2 Collection in H_2O_2 Impingers).

Elemental Analysis

Elements that may be characterized in the API-CEC-DOE-GRI-NYSERDA 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.

Section 5

AEROSOL SOURCE EMISSIONS MEASUREMENTS

Traditional stationary source air emission sampling methods tend to either underestimate or overestimate the contribution of the source to ambient aerosols because they do not account for aerosol formation occurring 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 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.

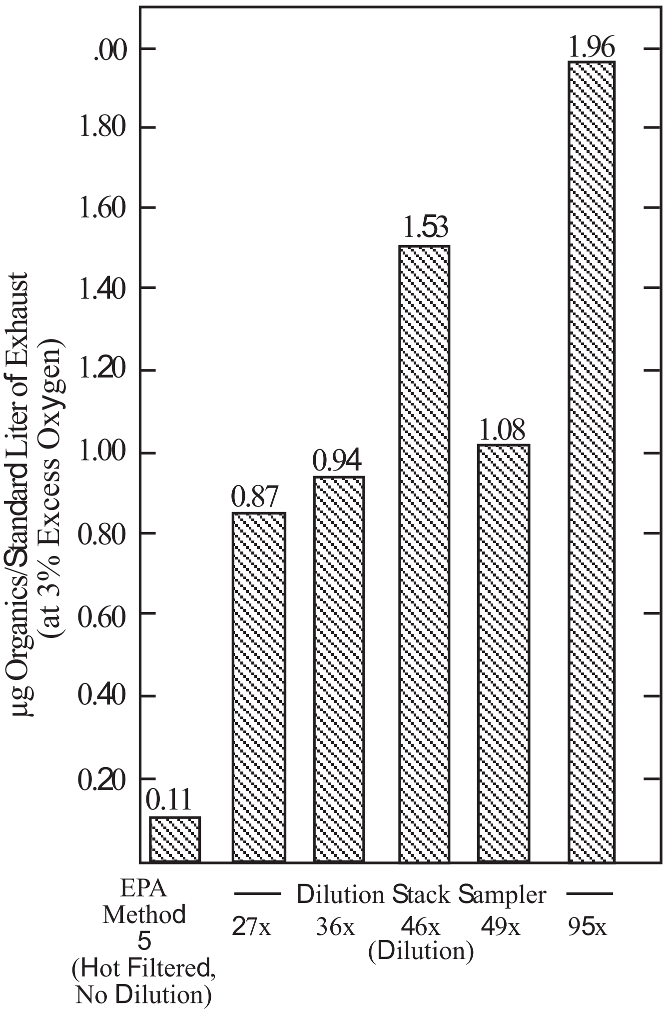
Table 5-1. Comparison of Total Particulate Concentration Using Dilution Sampling Versus EPA Method 5.

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

(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 very dramatically different. As seen in Figure 5-1, a comparison of fine organic carbon emissions from an oil-fired industrial boiler shows that 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



(from Hildemann *et al.*, 1989)

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

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 coal-fired boilers mean particle size decreased from approximately 5 µm, measured at the stack using in- stack cascade impactors, to less than 1 µm, measured in diluted samples (U.S. Department of Energy, 1996; Heinsohn et al., 1980).

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

PAH	ng/dscm		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
3 Rings			
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
Pyrene	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]perylene	7756	2408	3.2

Based on these 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 8178-1, 8178-2, 1996). Static dilution chambers also have been applied to characterize stationary source emissions. For example, atmospheric effects including clouds, rain, and UV-induced photochemical reaction were simulated in a transportable chamber and sampling apparatus during tests to characterize mercury species transformations and fate in coal-fired 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 µm) 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

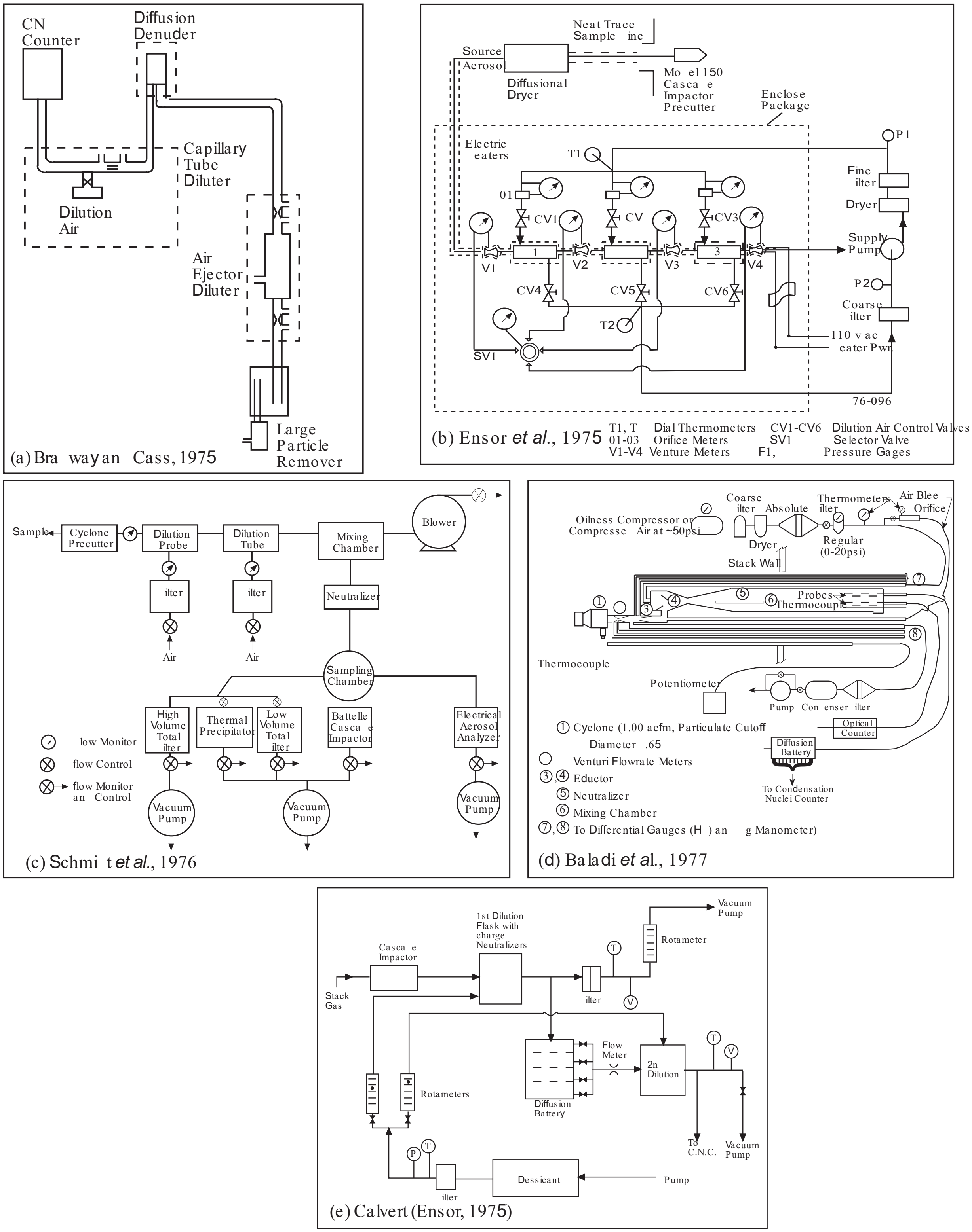


Figure 5-2. Early Dilution Sampling Methods.

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.

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 μm. 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 in-stack, 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 that 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 flows through a large particle precutter that was drawn through an eductor by a vacuum. The vacuum was 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 out-of-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 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 μm and an upper size limit of 2.0 μm; particles smaller than 0.01 μm were lost by diffusion and electrostatic attraction and those larger than 2.0 μm were lost by impaction and settling. Particle losses were determined by passing three sizes (0.822 μm, 1.091 μm, and 2.02 μm) 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 μm particles. At 14:1 dilution 25 percent of the 1.091 and 2.02 μm particles were lost to surfaces. No results were given for the smallest (0.822 μm) 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 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 and updated from Hildemann *et al*., 1989). Only the CMU design, with an average resident time of up to 12 minutes, has a longer residence time than the CIT/Dri systems whose residence time is on the order of 1 minute. URG system can achieve longer residence time by adding more sections to the existing system, but was not designed with residence time in mind. However, The other systems are not designed with sufficient residence time to allow condensational growth of organic species. These designs are discussed in more detail below.

California Institute of Technology 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. Sample then 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 arresting (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 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

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

	Carpenter	NEA	SRI	CalTech	URG	California ARB	DRI	CMU	CETC Design-1	CETC Design-2	CETC Desing-3	EPA	Paprican
Tunnel Diameter (cm)	30	10	21	15	8	15	15	14			5	10	Patterned After DRI Design
Diameter of Effective Mixing Length	12-15D	29D	6D	10D	80D	12D	18D	15D			40D	4D	
Residence Time (s)	1.3	3	6.2	2-180	40	5	80 (typ)	0-720	15-25	40-80	Oct-40	<1	
Dilution Ratio	8-25 (Typ) up to 100	>20	25	40 (Typ) 25 - 100	20 - 40	10 - 50	40 (Typ) 25 - 50	20 - 200	40	up to 100	25 - 80	40	30
Reynolds No.	47,000	11,000 - 23,000	2,800	10,000		10,000	9,000 @ 40:1 dilution	3,000 - 13,000			13,000	?	
Tunnel Material	Stainless Steel	PVC	Plexiglass and Teflon	Stainless Steel and Teflon	Teflon coated glass and aluminum	Teflon coated Stainless Steel	Stainless Steel and Teflon	Stainless Steel	Aluminum with PTFE coating	Aluminum with PTFE coating	Coated Stainless Steel	Coated Stainless Steel	Stainless Steel and Teflon
Portability ?	no	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
References	Carpenter (1978)	Houch *et al* (1982)	Smith *et al.* (1982)	Hildemann *et al.* (1989)	URG (1996)	Linder and Wall (1996)	Watson *et al.* (1996)	Lipsky *et al.* (2002)	Lee *et al.* (2000)	Lee *et al.* (2002)	Lee *et al.* (2003)	Myers and Logan (2002)	O'Connor (2003)

Nuclear Environmenatal Analysis, Inc.
Southern Research Institute
California Institute of Technology
University Research Glassware, Inc.
California Air Research Board
Desert Research Institute
Carnigie-Mellon University
CANMET Energy Technology Center

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 deposited particles from the surfaces using ammonium hydroxide. Recovered samples were analyzed using absorption spectrometry; 93 percent of particles 1 µm in diameter and 85 percent of 2 µm diameter were captured on the filters. Losses of 20 to 30 percent were observed for 2.5 to 5 µm 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.

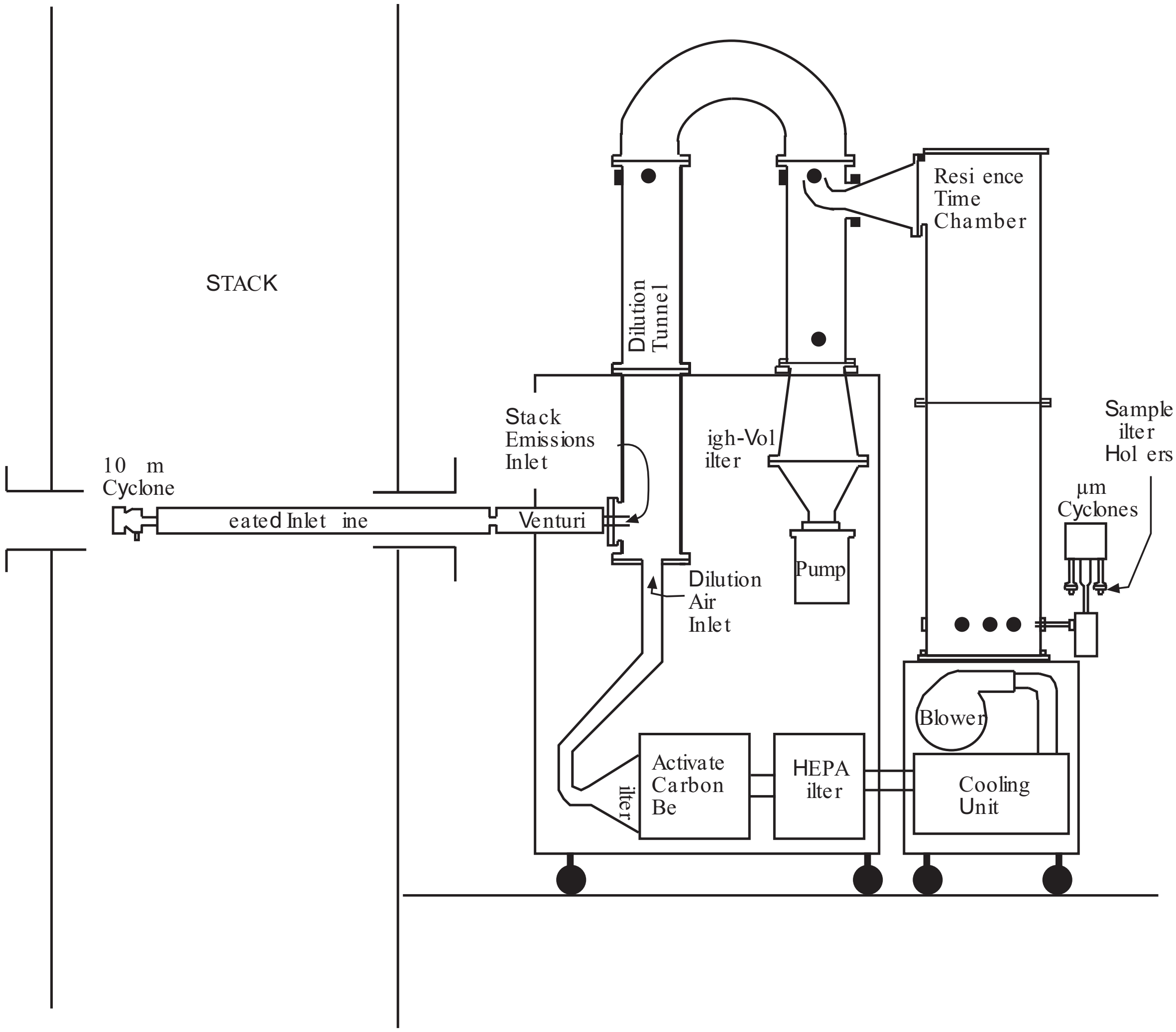


Figure 5-3. CIT Dilution Sampling System Design (Hildemann *et al*., 1989).

Desert Research Institute System

The 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

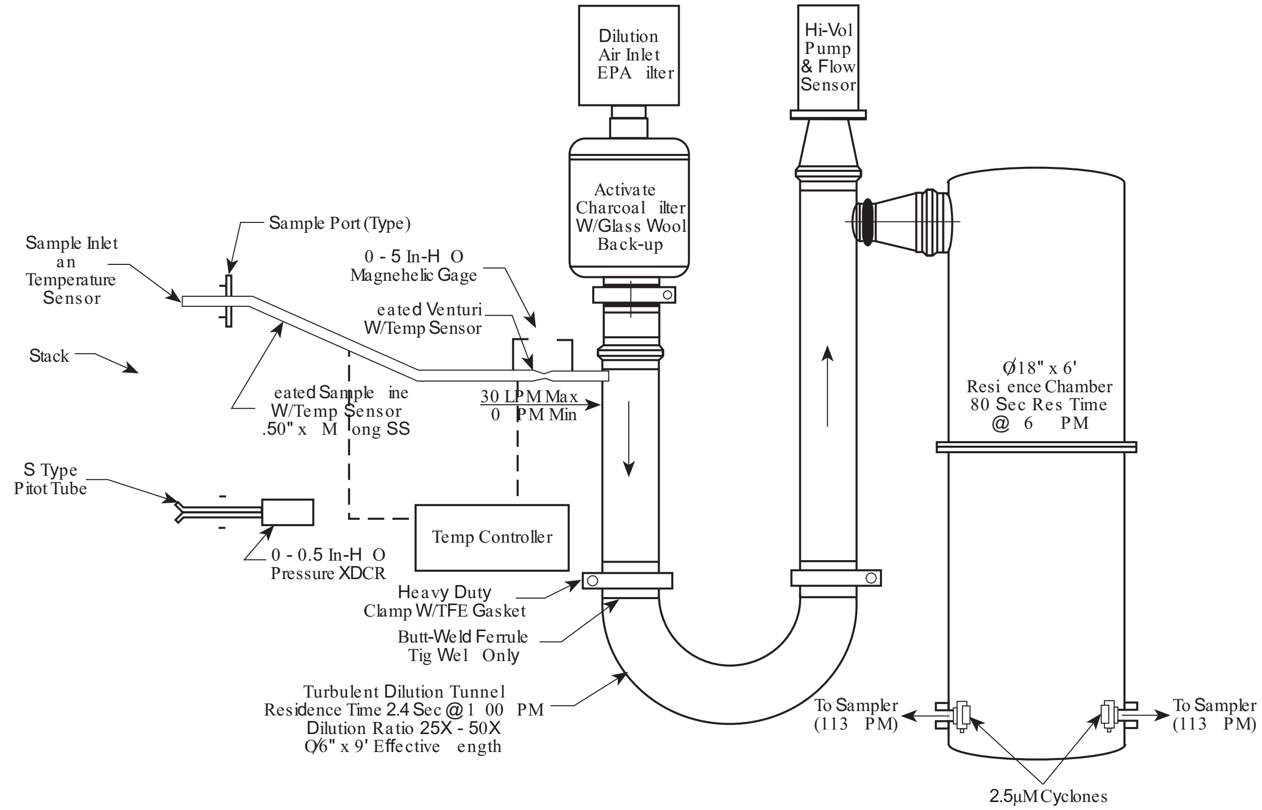


Figure 5-4. Schematic Diagram of the DRI Dilution System.

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 µm, 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.

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.

Paprican

The dilution tunnel sampling system developed by Paprican, Inc is patterned after the DRI system discussed above. It provides for single point iso-kinetic sampling and uses Teflon® coating on both the U-shaped dilution tunnel and residence time chamber. The system, illustrated in Figure 5-6, is approximately 4-ft wide x 6.5 ft high. The dilution ration is typically operated at about 30:1. O'Connor (2003) reports that initial testing verified the dilution ratio using a methyl mercaptant and that undiluted and diluted sample were in excellent agreement. Initial evaluations also included system leak tests and determination that blanks (both laboratory and field) were approximately 0.2 – 0.9µg/hr. Subsequent applications of the Paprican system have included wet stack systems such as Smelt dissolving tanks and Lime kilns; dry sources such as power boilers and recovery furnaces. Data collected to date indicates that the system results are reproducible and that for dry stack systems, results are comparable to EPA Method 201a.

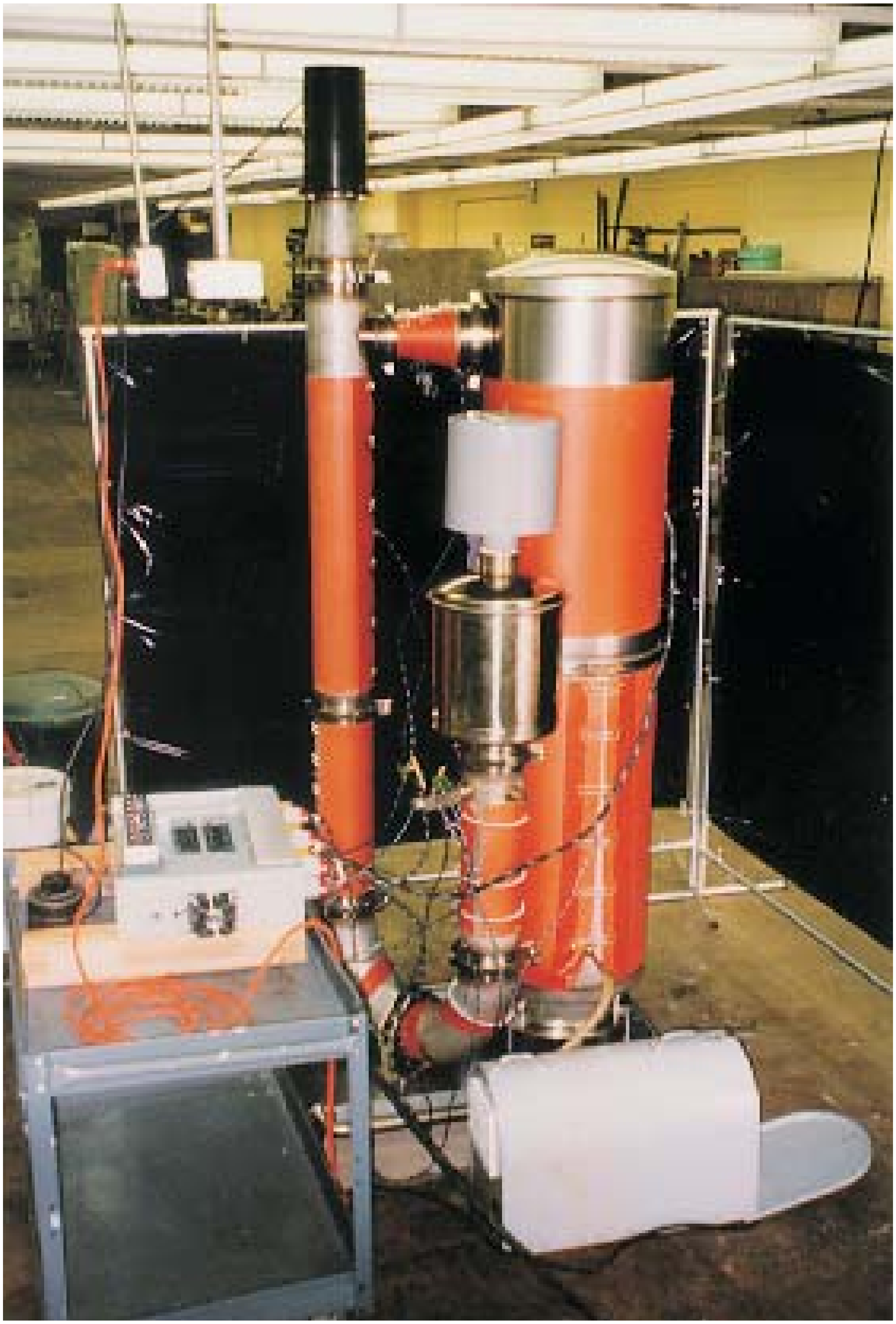


Figure 5-5. Dilution Tunnel Sampler on Top of Test Shed.

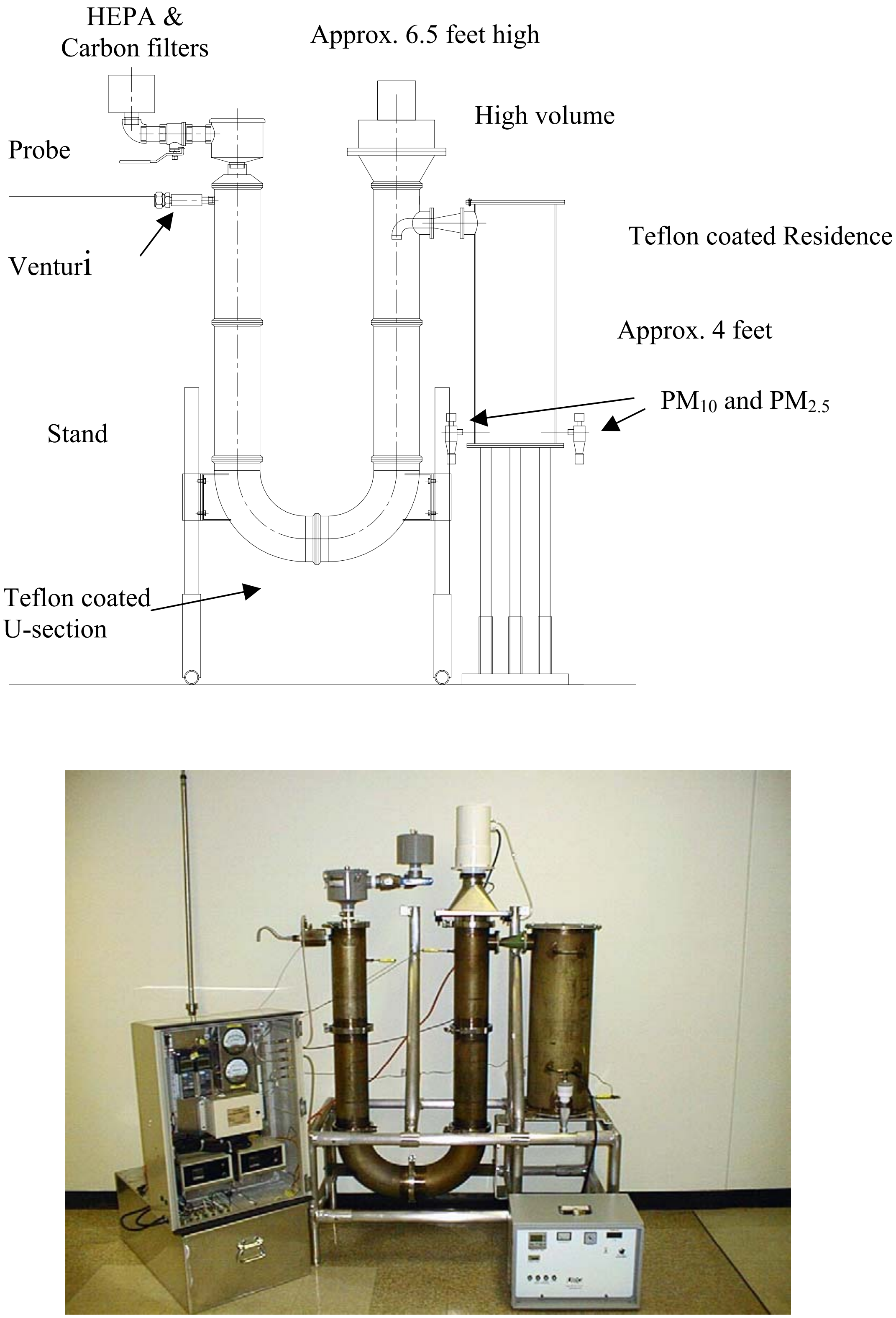


Figure 5-6. Paprican System.

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 T, 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 deposited particles from the entire sampler using 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 5-7 was applied to a field testing program at a coal- fired 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 N_2-21 percent O_2 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 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.

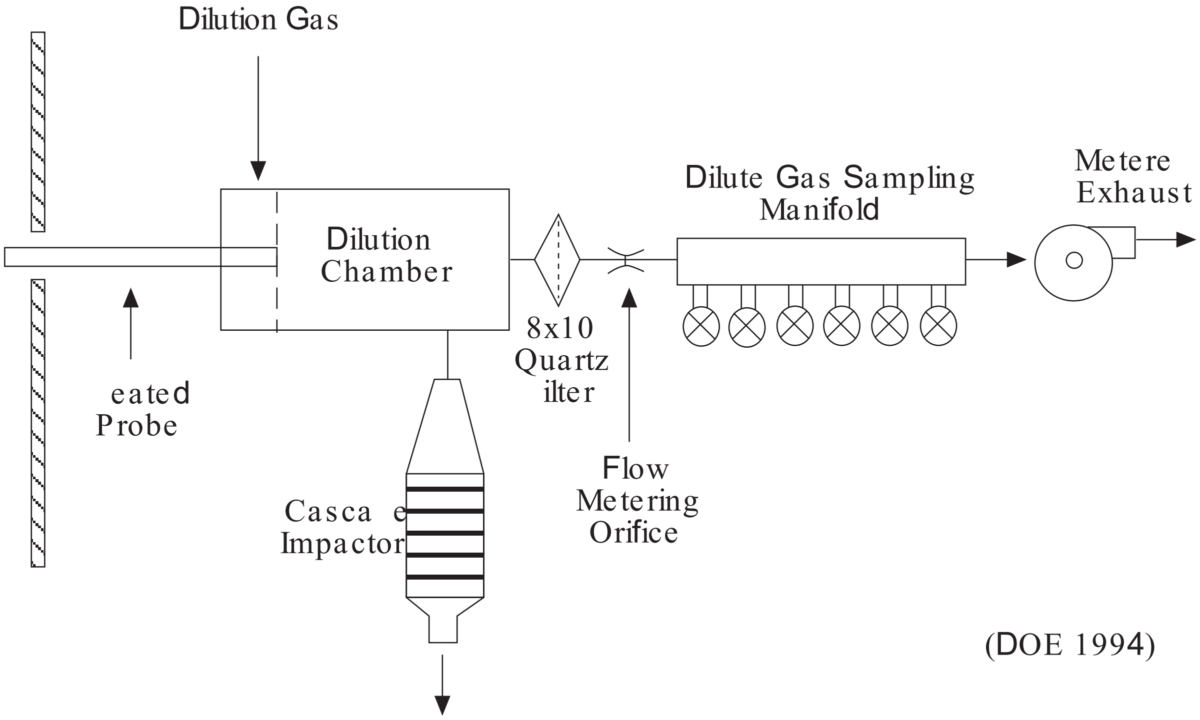


Figure 5-7. NEA (Keystone) Dilution Sampling System Design (U.S. Department of Energy, 1994b).

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. Throttling the positive pressure dilution air source makes adjustments to the dilution chamber pressure, and subsequently the sample flow, dilution ratio and residence time. 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 and electricity generation industries 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).

URG System

The dilution sampler illustrated in Figure 5-8 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 venturi-type 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.

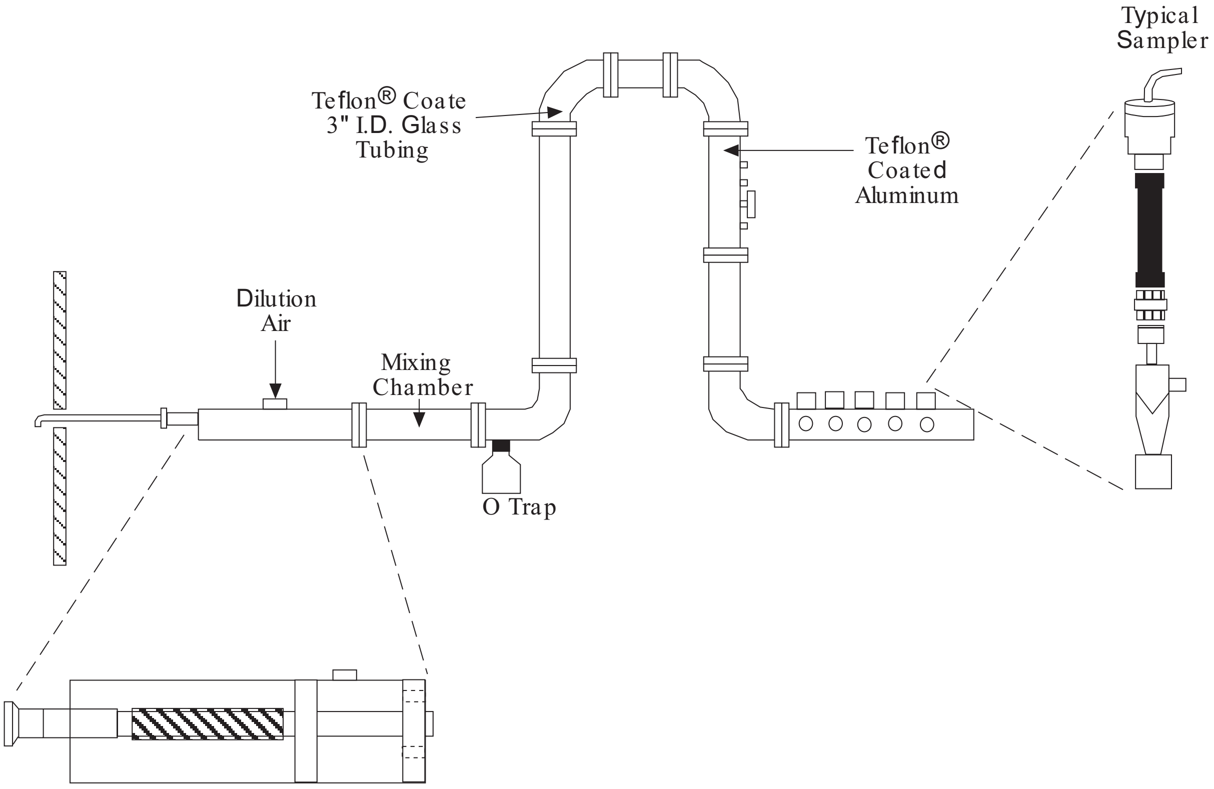


Figure 5-8. URG Dilution Sampling System Design (URG, 1996).

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 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 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.

Southern Research Institute (SRI) System

The SRI system (Figure 5-9) was designed for EPA to quantify aerosols resulting from homogeneous condensation of acid vapors, metal vapors and organics in combustion plumes. This system was 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 is introduced through 82 perforations in a cone, creating mixing between the stack gas and 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 airflows for sufficient sample mass collection, with enough dilution to cool to ambient temperature and prevent condensation of moisture droplets in the sampler.

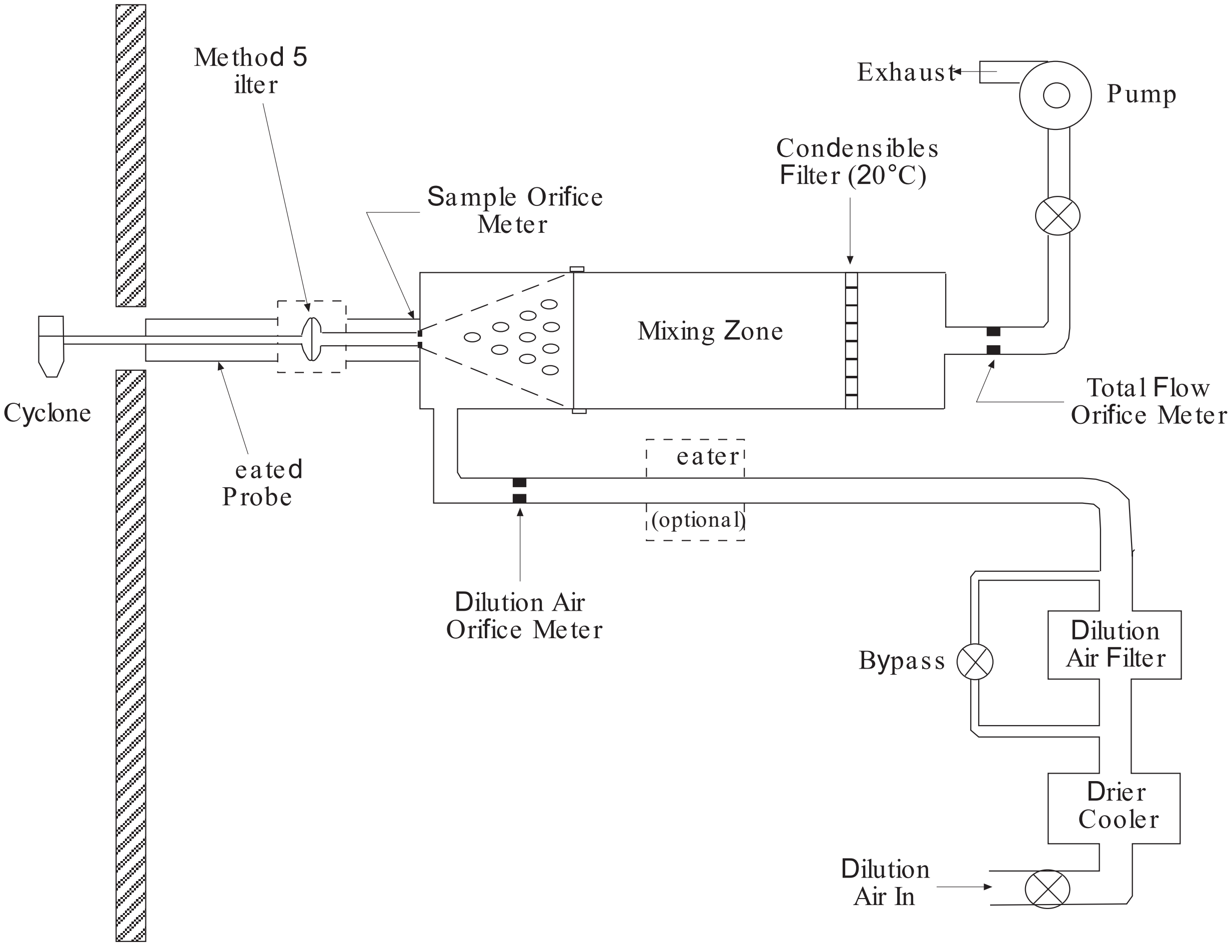


Figure 5-9. SRI Dilution Sampling System Design (U.S. Department of Energy, 1994a).

A condensables filter spanning the dilution chamber is used to capture condensed particulate matter at ambient temperature. In 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 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 the petroleum and electricity generation industries combustion source testing 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 provides 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 5-10, 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.

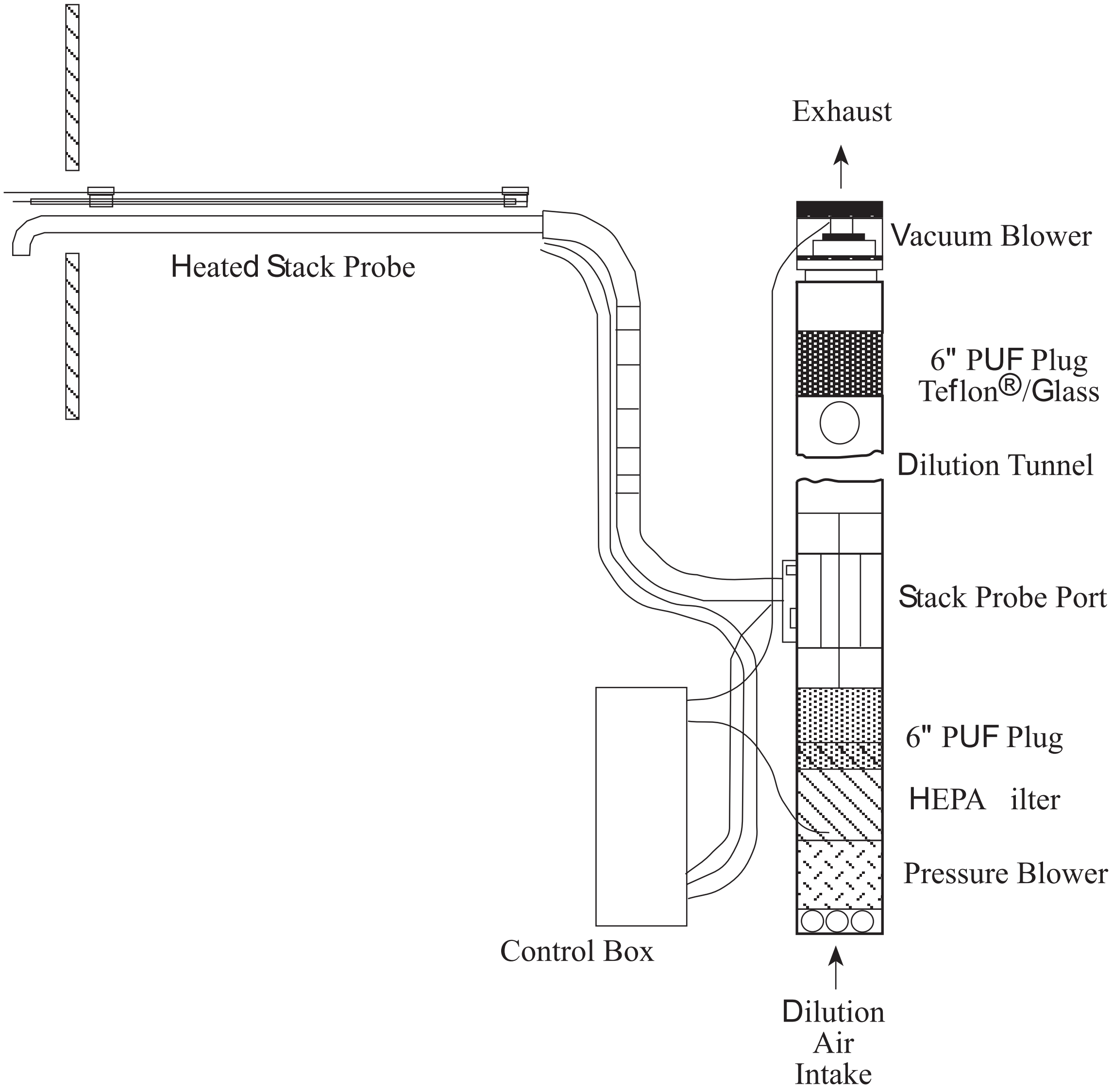


Figure 5-10. California ARB Dilution Sampling System (Wall, 1996).

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.

Carnegie-Mellon University (CMU) Dilution Sampling System

The CMU system developed by Lipsky *et al.* (2002) was based on the CIT dilution sampler and is schematically shown in Figure 5-11. The CMU system was designed to investigate how the dilution processes, i.e., dilution air ratio and residence time, affect the size distribution of PM emitted from pilot-scale coal-fired boilers. There are three major components in the CMU dilution system, including: sampling inlet line, the dilution tunnel, and the residence time tank. Flue gas was sampled isokinetically at flow rate 10-30 Lpm and coarse particles are removed by an in-line PM2.5 cyclone.

The flow through the sample inlet line is measured directly using a venturi flow meter and the flow rate of the dilution air into the tunnel is monitored using an orifice plate. A pre-diluter was added before the inline PM2.5 cyclone when high dilution ratio experiments were conducted. The whole sample line is heated until the point where flue gas is mixed with cool clean ambient air in the dilution tunnel, a 15 cm inside diameter and 2.3 m long stainless steel tube. The dilution air ratio operates in the range of 15-150 times the exhaust. At the lowest dilution air flow rate of 350Lpm, the sample is well mixed at a point 2.2 m downstream of the dilution tunnel inlet. This is approximate 9 sec after entering the tunnel and the flow Reynolds number is ~3200. At the highest dilution air flow rate of 1,400 Lpm, complete mixing can be achieved 0.75 m downstream of the dilution tunnel inlet, with Re ~13,000, 0.33 sec after entering the tunnel. A slipstream of the diluted flue gas is drawn through a stainless steel cylindrical residence time tank (76 cm diameter x 91 cm tall). The diluted sample remained in the residence time tank with a specified residence time from 0.5 to 12 minutes.

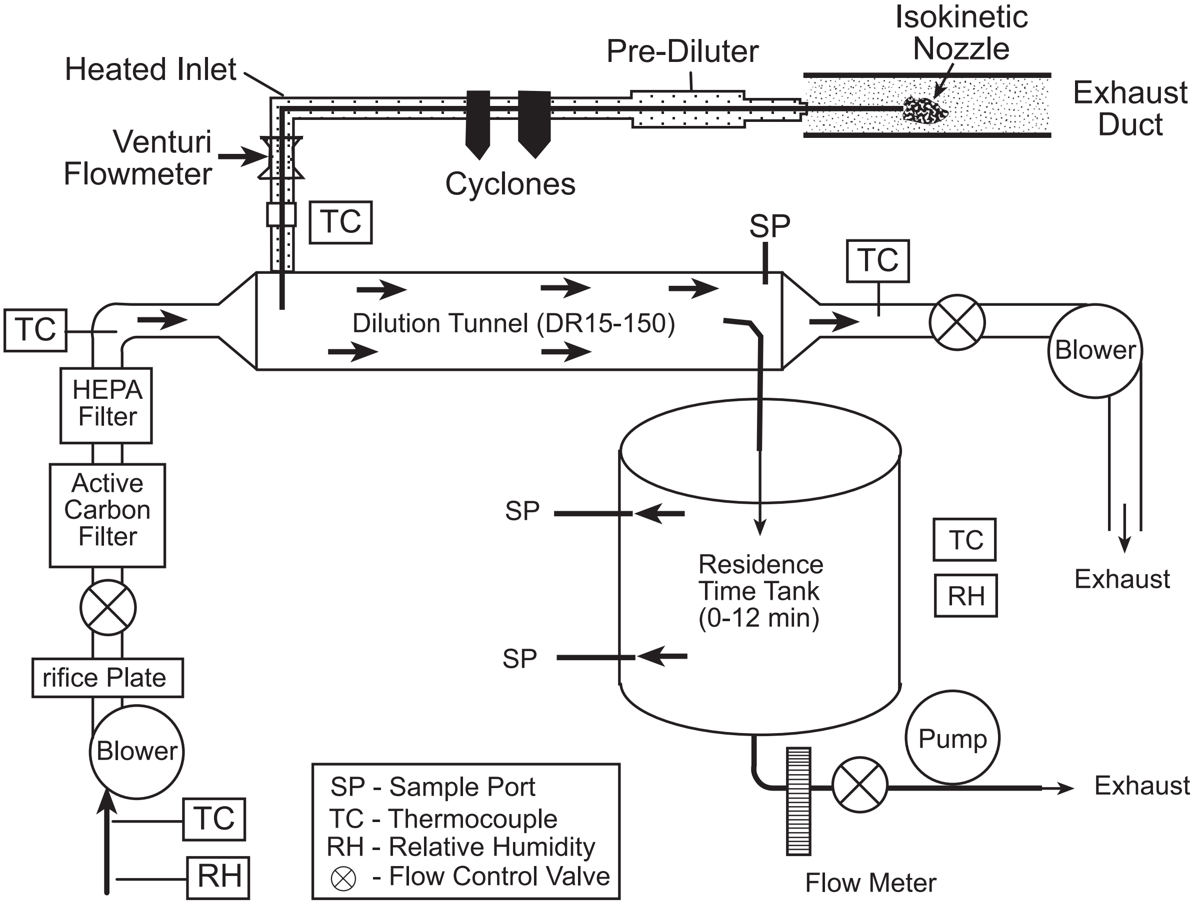


Figure 5-11. Schematic of the CMU Dilution Sampler (Lipsky, *et al.*, 2002)

The larger residence time tank needed to achieve larger residence time and dilution air ratios made the system less portable for use in the sampling stack.

A computer-based data acquisition system continuously monitors the flow rate through the sample inlet line; the temperature and relative humidity of the dilution air entering the tunnel; the temperature of the combustion products entering the tunnel; the temperature of the mixture leaving the tunnel; and the temperature, relative humidity, and pressure of the mixture inside the residence time tank.

CANMET Energy Technology Centre (CETC) Systems

The Source Dilution System 1 and 2, shown in Figure 5-12a and 5-12b respectively, were developed in CETC, Ottawa, Canada. (Lee, S.W. *et al.*, 2000 and Lee, S.W., *et al.*, 2002). The design of CETC dilution system 1 is similar to the URG system described previously. Combustion gases were withdrawn isokinetically and heated till the point of mixing with clean dilution air ratio of 20-40 times and a residence times of 30~35 s was provided for the whole diluted flue gas. The internal surface of the dilution chamber is Teflon coated glass and aluminum.

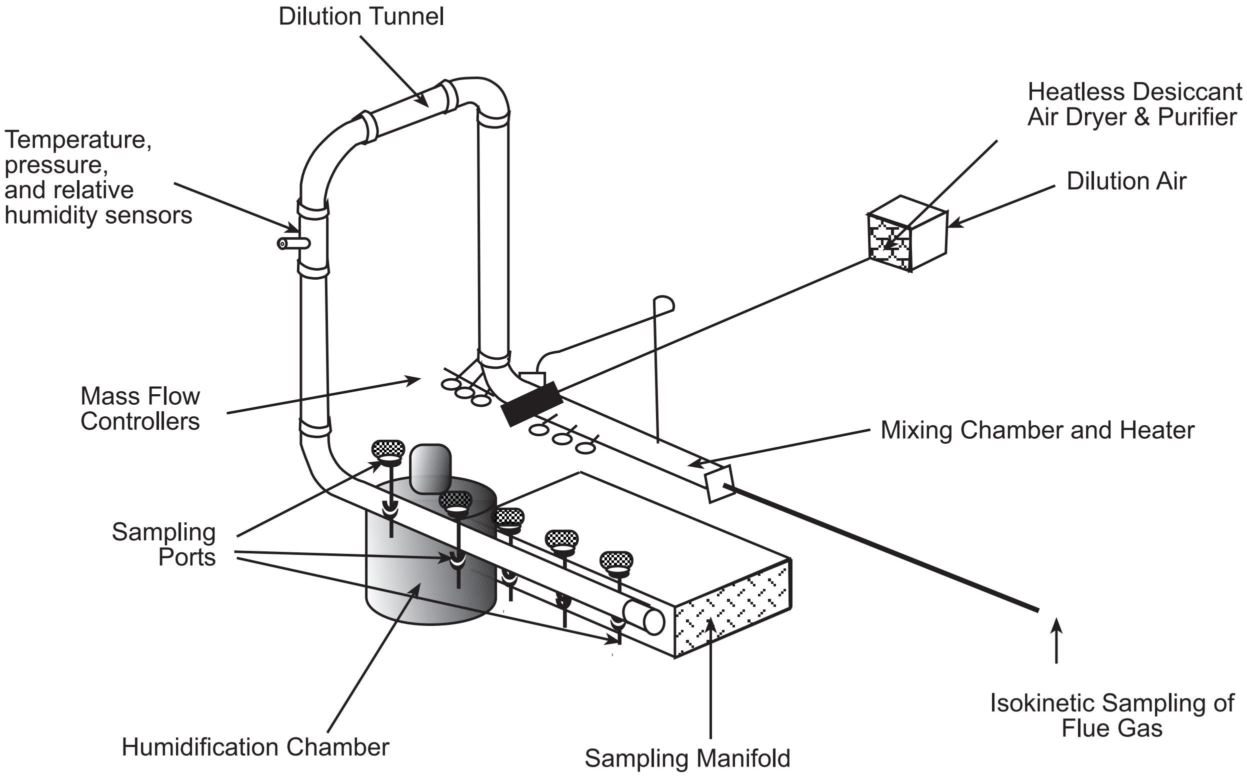


Figure 5-12a. CETC Source Dilution Sampling System 1 (Lee, S.W., *et al.*, 2000)

Portions of the diluted gas samples are withdrawn through size-selective inlet and annular denuder so that only desired particle size fraction will be collected in filter packs. Different PM size fractions collected on suitable filter media are analyzed for particle size and morphological characteristics and chemical constituents including sulfates, nitrates, organic and elemental carbons and trace elements. The CETC dilution system 1 was employed to determine emissions from oil-fired boilers and furnaces with No. 2 type distillate oils (Lee, *et al*, 2002; Lee, *et al*, 2002) , blends of biofuel and distillate oils (Lee *et al*, 2003), No. 4 type residual oils containing different sulfur levels (Lee, *et al*, 2002) and a number of North American coal blends (Lee et al,). The systems are able to demonstrate the impact of fuel sulfur on PM2.5 emissions and their sulfate content for fuel oils and the effect of coal quality on fly ash fine PM composition. The results showed good reproducibility of the fine and coarse PM concentrations as well as mass balance of PM chemical constituents. The reproducibility of mass emission

Figure 5-12b. CETC Source Dilution System 2. (Lee, S.W., *et al.,* 2002)

results for fuel oil PM is found to be better than those of coal. The study, again, indicated insufficient dilution air ratio at 18-fold and sufficient time in the dilution chamber is necessary for particle condensational growth. Although the CETC 1 system incorporates moisture injection and dilution air temperature adjustment inside the dilution chamber to simulate various ambient conditions, the impact of meteorological conditions on particle formation was not studied.

The CETC dilution system 2 was designed to improve the system inadequacies that were identified in the system 1. The new system is very different in design and is made of eight modular pieces made of Teflon coated aluminum specifically for field portability and ruggedness. The horizontal arrangement of sampling ports on system 1 was changed to a vertical arrangement to prevent particle settling. In the new system, the stack gas sample is well mixed in a coaxial flow with the dilution air and the diluted gas is transferred to an aging chamber or residence time chamber before PM sample withdrawal. The improved performance of CETC system 2 has increased the ability to sample at stack velocity from 3 m/s up to 10 m/s, provides dilution air ratios from 25 times to 100 times, and provides residence time from 20 s to 80 s. A flue gas splitter is currently under evaluation to enable handling flue gas velocity up to 35 m/s. To date, system 2 has been used in the fine PM sampling of various No. 4 and No. 6 types residual oils and pulverized coal blends fired in pilot-scale research boilers.

CETC has integrated two unique features on both sampling systems. First, a moisture injection unit was introduced to control relative humidity inside the dilution chamber. The diluted gases can be controlled to RH between 20% and 80% to simulate various ambient meteorological conditions. Second, an online CO_2 tracer technique was incorporated to allow for accurate control of dilution ratio. This is accomplished by incorporating a three-level CO_2 analyzer to simultaneously monitor and control concentrations of stack gas, dilution air and diluted gas stream. This protocol provides accurate online control of gas and sample flows inside the system, resulting in reproducible PM mass concentrations. Customized computer software was developed to operate the combustion system, monitor emissions and sensors and most importantly control all process parameters including dilution air, sample gas flows and humidity level at a preset level, in order to accurately control sample flows and improve reproducibility of the sample collected.

U.S. EPA System

The EPA system developed by Myers and Logan, shown in Figure 5-13, was deployed at a pulverized coal fired electric generating unit (Myer and Logan, 2003). A Method 201A PM_{10}

cyclone followed by a PM2.5 cyclone were placed at the sampling probe to remove particles larger than 2.5 µm in aerodynamic diameter with a sampling flow maintained at 0.14 cubic feet per minute. The isokinetic sampling was maintained by choosing a nozzle with a diameter that results in a sampling velocity that most closely matches the average velocity in the duct. The sample gas flows through the venturi that is maintained 5.6°C hotter than flue gas prior to mixing with clean air. A static mixer is added to enhance turbulent mixing and to reduce the mixing distance. The volume of dilution air is 10 times to 50 times the sample gas and the temperature of the resulting combined gas is less than 6°C hotter than the dilution air prior to mixing.

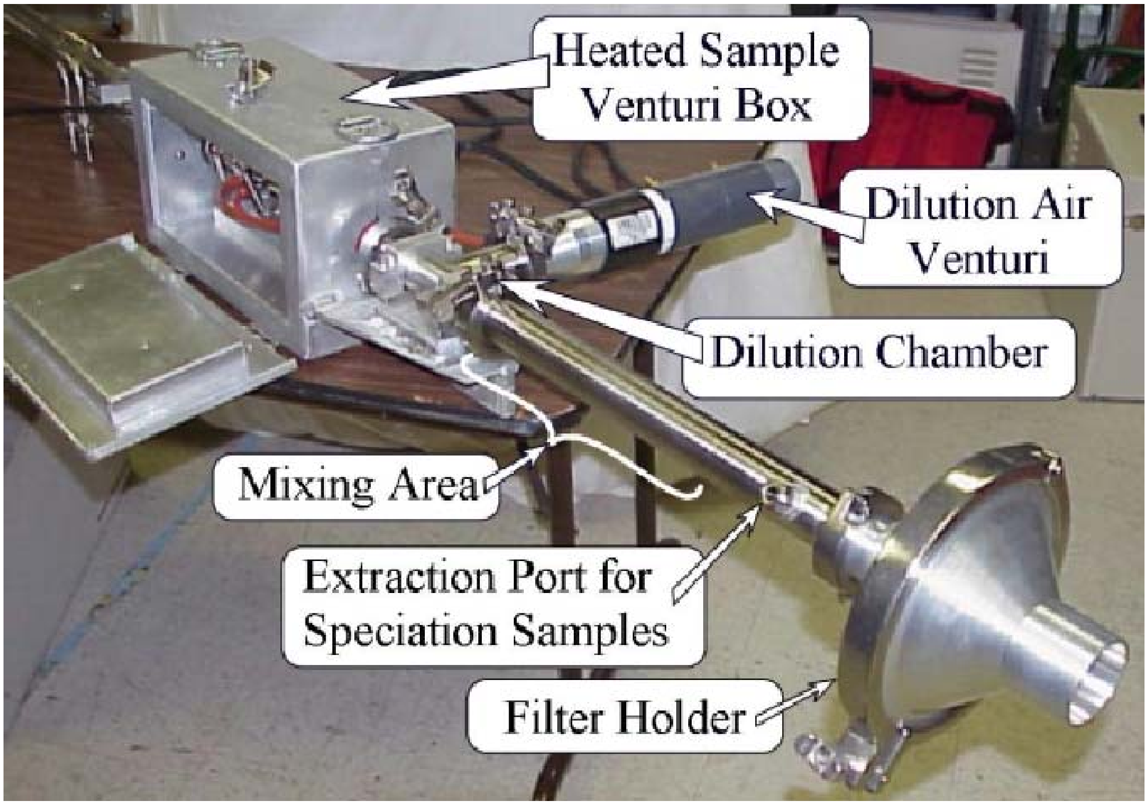


Figure 5-13. EPA Myers and Logan system.

A 142mm PTFE coated quartz filter for gravimetric analysis is placed in the end of the dilution sampler. A portion of diluted flue gas can be extracted from ports prior to the final filter for speciation sampling. A computer Data Acquisition System (DAS) is used to automatically control gas flow rates, monitor and record temperature, relative humidity, pressure, velocities and isokinetic variations. Particle losses in the dilution system range 30-50 percent of total PM and were found mostly in the static mixer. However, the transfer function between particle size and losses is not evaluated. Currently, EPA is designing a new system to reduce particle losses (Logan, 2003).

DILUTION METHOD IN MOBILE SOURCE TESTING

The measurement and evaluation method for particulate exhaust emission from reciprocating internal combustion engines, i.e., mobile source, is specified in ISO 8178 (1996) and 40 CFR Part 86, subpart N (1998). ISO 8178-1 defines emissions under steady-state conditions on a test bed, ISO 8178-2 for at site, and ISO 8178-4 for various combinations of engines load and speed reflecting different engine applications. 40 CFR Part 86, subpart N, specifies gas and particulate exhaust test procedures for Otto-cycle and diesel heavy-duty engines.

In mobile source, particulates are defined as any material collected on a specified filter medium after diluting exhaust gases with clean, filtered air at a temperature of less than or equal to 325 K (52°C), which is measured at a point immediately upstream of the primary filter. The flow capacity of dilution system must be large enough to completely eliminate water condensation in the dilution and sampling system, and maintain the temperature of the diluted exhaust gas at or below 325K (52°C) immediate upstream of the filter holders. Dehumidifying the dilute air before entering the dilution system is permitted. Dilution air temperature may not exceed 325K prior to the introduction of the exhaust in the dilution tunnel. However, if the ambient temperature in the vicinity of the dilution tunnel (DT) is below 293 K (30°C), the tunnel may be insulated or heated (recommended) above 303K (30°C) but no greater than 325 K (52°C) wall temperature. The temperature of diluted gas sample can be heated either directly by the dilution sampler wall, or by pre-heating dilution air.

Fluorocarbon coated glass fiber filters or fluorocarbon based membrane filters are required for certification. Collection efficiency for 0.3μm Dioctylphthalate (DOP) particles must be at least 95% for all filter types. Gas face velocity should be between 35cm and 80cm/sec. Minimum filter size is 47mm (37mm stain diameter) in diameter and backup filters are no more than 100mm downstream of primary filter. Pressure drop increases between the beginning and the end of test can be no more than 25 kPa. The minimum loading of collected sample on filters is 465μg/1,000mm^2 stain area. Gravimetric measurement is conducted in a weighing chamber with the room at a temperature of 295 K ± 3 K and at a RH of 45%±8% (dew point of 282.5 K ± 3 K). Average changes between paired reference filters obtained within 4 hours are ±7.5%, or the paired sample filters are ±5% of the minimum loading. (i.e., 25μg for 37mm stain area). Precision (Std) of 2 μg and resolution of 1μg are for filters less than 70mm in diameter.

Dilution may be accomplished by various dilution flow systems. For partial flow dilution systems, the isokinetic sampling probe with minimum inside diameter of 12 mm should be installed facing upstream on the exhaust pipe centerline. The sample gas is drawn through a transfer tube no more than 5 m in length and is kept at a minimum wall temperature of 523 K (250°C) before the dilution tunnel. The full flow dilution system is based upon the dilution of the total exhaust using the constant volume sampling (CVS) concept. If the diluted gas sample is passed to the particulate sampling system directly, it is referred to as single dilution. If the sample from the dilution tunnel is diluted once more in the secondary dilution tunnel, it is referred to as double dilution, which is useful if the filter face temperature requirement cannot be met with single dilution. The dilution tunnel shall be of a sufficient length to cause complete mixing of the exhaust and dilution air under turbulent flow conditions. Also, the tunnel shall be constructed of stainless steel with thickness/diameter ratio of 0.025 or less with inside diameter greater than 75 mm, or, a nominal thickness of no less than 1.5 mm with inside diameter of equal to or less than 75 mm.

The leakage check of the dilution system is conducted by first plugging the end of sampling system, and after a set of time, all flow meters should read zero. Maximum allowable leakage rate on the vacuum side is 0.5% of in-use flow rate of the system being checked (not total). Measurement accuracy includes: engine speed, torque, power, fuel consumption, specific fuel consumption, air consumption, exhaust gas flow. Permissible deviations of instruments for other essential parameters include coolant temperature, lubricating oil temperature, exhaust gas pressure, inlet manifold depressions, exhaust gas temperature, air inlet temperature (combustion air), atmospheric pressure, intake air humidity (relative), fuel temperature, dilution tunnel temperature, dilution air humidity (relative), diluted exhaust gas flow. The measured dilution ratio should be ±10% of the dilution ratio calculated from CO_2 or NO_x concentration measurements, and the total dilution ratio shall not be less than 4. Filters should be weighed 1-80 hours after samples are collected. A few commercially available dilution systems for mobile source PM testing are randomly selected and illustrated.

EcoChem Matter Dilution System

The EcoChem Matter Diluter (model MD19-2E) is a dilution method developed by Hüglin *et al* (1997) at ETH Zurich, Switzerland, for exhaust sampling from flue gas from wood, oil and coal fired combustors as well as diesel- and spark ignition engines. The performance of MD19-2E is the best for particles in the size range of 10-1000nm. The system is built with stainless steel, non-corroding Erta Peek plastic material, brass fittings and PVC gas tubes and is schematicly shown in Figure 5-14. Sample gas is withdrawn at a rate of 1 Lpm through a 8mm ID x 500 mm long stainless steal tube connected to the dilution system. There are two separate gas channels: a raw gas channel and a diluted measurement channel. A small volume of the sample gas is transported from the raw gas to the measurement channel by cavities in a rotation disk. The ratio of dilution of the raw gas is a linear function of the cavity volume, the number of cavities on the disk, the frequency of rotation and the flow in the diluted gas channel. Different dilution ranges of 30 - 3000 can be selected with 2 standard rotation disks, one with 2 and one with 10 cavities, and the setting of the rotation speed by potentiometer or analog input with an accuracy of ±10% specified by manufacture. Due to the low sample flowrate compared to stationary exhaust and applicable particle size range, the concept has been used only in some diesel engine tests (Matter, *et al*, 1999, Sarofim, *et al*, 2001).

The undiluted gas parts, the dilution unit, and the dilution air may be heated up to a selectable temperature of 80, 120, and 150°C to avoid condensation of raw gas components sampled from stacks and exhaust pipes. Sampling and dilution at different temperatures allows one to distinguish between solid particles and volatile droplets which can be formed in exhaust after-treatment-devices such as particle traps or oxidation catalysts. Applicable temperature of raw gas is in the range of 0-200°C.

A Raw gas channel
ody
3 Disk cavity

Measurement channel
2 Rotating disk
4 Axis of rotation

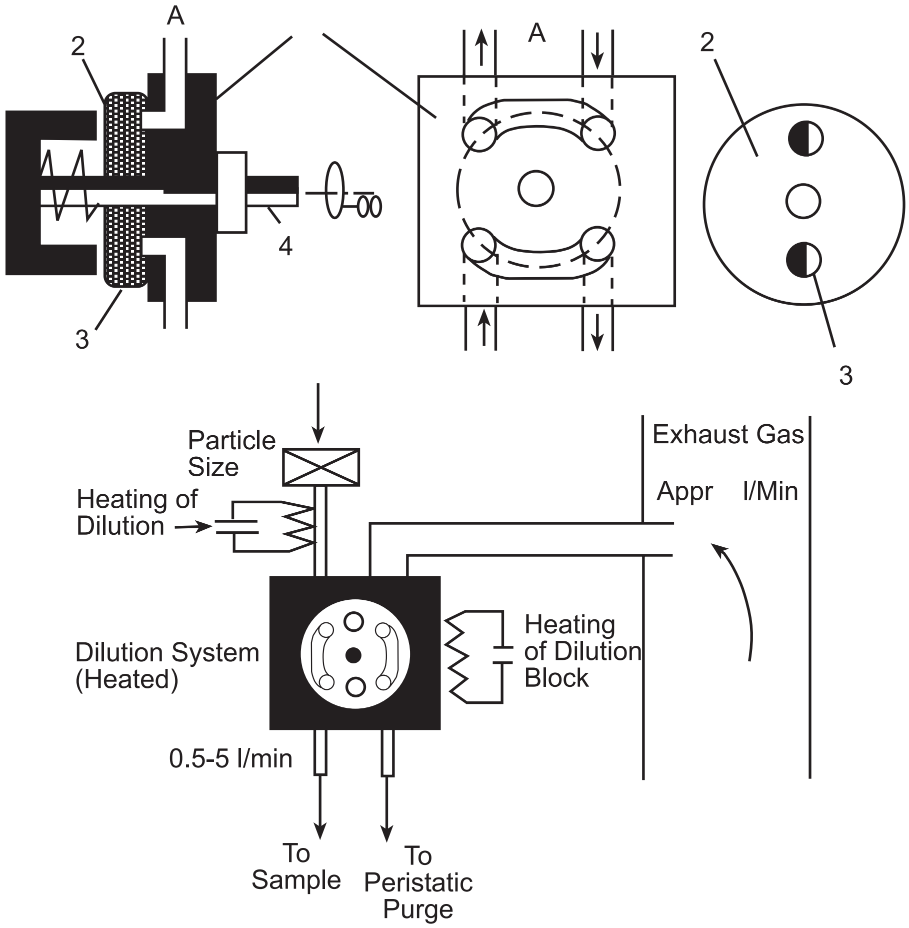


Figure 5-14. Schematic of Echochem Matter Diluter (model MD19-2E).

<u>Horiba Instruments, Inc. MDLT-1300T Micro Dilution Tunnel System</u>

The Micro-Dilution Tunnel (MDLT-1300) manufactured by Horiba Instruments is a partial flow dilution tunnel designed for measuring diesel particulate emissions in transient testing of heavy duty diesel engines and general purpose steady state testing of both large and small engines. The tunnel can simulate both double dilution and single dilution operation when used with a CVS and a small portion of the total exhaust is diluted with air to obtain a constant flow rate. The instrument uses venturi flow meters to enable proportional control: the exhaust volume that enters the tunnel is proportional to the total engine exhaust flow rate.

The MDLT-1300 has tunnel dimensions of 1.26-in OD, 23.6-in straight pipe length, and a filter diameter of 70 mm. Diluted gas flow rates range from 65-130 Lpm, raw gas flow rates from 0-40 Lpm, and PM sampling filter flow rates from 65-130 Lpm (equal to the diluted gas flow). Dilution ratio accuracy is guaranteed to be within ±4% for dilution ratios from 4-20. Response to dilution ratio change is reported to be within 0.5 sec. The tunnel can also operate at a programmable constant dilution ratio or a fixed flow rate. Fast-acting control of the dilution airflow is used for transient test conditions with frequent changes in the exhaust flow rate.

Pierburg Instruments, Inc. PS 2000 Particle Sampling System with Dilution Tunnel

The PS 2000 collects particles present in the exhaust gases of diesel engines, measures the standard flow through the system, and determines the mass of the particles. A proportional part of the flow is filtered, and the system samples the exhaust in a dilution tunnel where turbulent flow exists. The dilution tunnel can be mounted on the wall or placed on a mobile rack. The primary dilution tunnel can have a diameter of approximately 270-mm and a length of 3370-mm or a diameter of 460-mm and a length of 5750-mm. Systems with secondary dilution can also be used in primary dilution mode, with a diameter of approximately 80-mm and a length of approximately 300-mm. The PS 2000 system components are the particle sampling system (control, sensors, sample pump and probe, power supply and filters), and the weighing equipment. Mass flow controllers are used to achieve the proportional flow.

Sierra Instruments, Inc. Model BG-3/TDAC (Transient Dilution Airflow Control)

The Model BG-3/TDAC (Transient Dilution Airflow Control) system uses a partial flow sampling system (PFSS) for transient testing of any-sized diesel engine, regardless of RPM, power output, or stack size. The system is designed for both steady state and transient applications. The micro-dilution chamber draws exhaust directly from the stack and dilutes the entire sample fraction. Dry, hydrocarbon-free air is metered into the chamber under pressure, permeating a porous stainless steel tube.

The system can maintain transient cycle PM correlation to within ±5% of full dilution tunnel (CVS). Digital mass flow controllers allow user-specified flow rates and dilution ratios. Dilution air supply is required at 90 psi and 8.5 scfm. Measurement repeatability is typically better than

±3% with dilution rations of 10:1 or less. Correlation with full dilution is typically ±5% or less of full dilution weighted results.

AVL SPC 472 Smart Sampler

The SPC 472 Smart Sampler is a partial-flow dilution tunnel. The exhaust is sampled into a mini-dilution tunnel and diluted with air which the system conditions internally. Testing has shown that performance can be correlated to that of a full-flow CVS tunnel. The instrument can be used for measurements on engines of all sizes in any location, from passenger cars to ship engines. It can accommodate steady state and transient testing applications.

Dilution air supply is required at 6-10 bar and 200 nano-liter per minute (nLpm). The dilution ratio is adjusted and the partial flow rate set by the mass low controllers for the dilution air and the total tunnel flow, which allows for constant dilution ratios at constant total tunnel flow. The unit has fast flow control and temperature conditioning to enable accurate measurements with high repeatability. It also has automatic calibration with an inbuilt laminar flow element.

COMPARISON OF DILUTION METHOD IN MOBILE AND STATIONARY SOURCES:

Comparison of key features in dilution methods used for stationary and mobile combustion sources is provided in Table 5-4. Similarities and differences can be classified in three aspects: operating conditions, sample collection, and general feature. In general, the conditions of diluted flue gas in mobile source sampling is controlled before samples are collected. For example, ISO8178-1 specified the operating condition at a dilution air ratio of no less than 4, but large enough to eliminate water condensation on filters. Therefore, the temperature of diluted exhaust is controlled between 30-52°C and dehumidification of clean dilution air is optional. In contrast, a minimum dilution air ratio of 20 times is applied in stationary dilution method to obtain the same particle physicochemical characteristics (size distribution and bulk analysis). Also, neither the temperature nor the relative humidity of the clean dilution air is specified in stationary dilution methods. Therefore, the relative humidity and temperature of the diluted exhaust in stationary dilution samplers greatly depend on the ambient meteorological condition. Various studies have reported that high relative humidity in diluted exhaust tends to favor formation of nanoparticles (Abdul-Khalek and Kittelson, 1999; Shi and Harrison, 1999). The dilution methods used in stationary combustion sources simulate real world plume better than in mobile sources.

Most particles emitted from mobile sources are smaller than 2.5 μm. Most of the particle number are less than 50 nm while most of the mass is in the range from 50 nm to 1000 nm. Therefore, pre-selective size inlets are not used and particle losses are not quantified in mobile source dilution system. However, the use of a PM2.5 in-stack cyclone is recommended for stationary source measurements since the primary particle size distribution from stationary combustion sources are generally wider and larger. Also, a minimum mass loading of 465μg/mm^2 (20-60 seconds sampling time, depend on emission rate) on sample collection media is specified in the mobile source dilution testing. However, the collection of enough material to overcome analytical detection limit is still challenging for low emission sources, such as natural gas, while a sampling period of 4-6 hour is used. A shorter sample collection time can be achieved for combustion fuel types with high PM emission. Particle aging time from a few seconds up to 12 minutes are generally used for particle condensational growth in stationary dilution samplers, but not considered in mobile dilution systems.

SAMPLE COLLECTION, MEDIA, AND HANDLING

Generally the ambient air sampling and analysis techniques described in Section 3 are used in stationary dilution methods to (1) allow the comparability of data to ambient aerosol data, and (2) broader media for sample analysis. Each of the dilution samplers illustrated in this review 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.

Figure 5-15 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 aerosol mass and trace metals determinations. Nuclepore or Teflon® filters are used for ionic species.

Table 5-4. Comparison of Dilution Methods in Mobile and Stationary Sources.

Parameters	**ISO 8178-1**	**40 CFR Subpart N**	**General Practice in Stationary Dilution Sampler**
Operating Condition			
Sample Flow	Full or partial	Full or partial	Partial flow
Step of Dilution	Single or double	Single or Double	Mostly single, double only specified
Tube for Transferring Partial Flow	Between dewpoint of the mixture and 121°C		Heated, usually slightly higher than exhaust temperature.
Dilution air Temperature	30-52°C	20 - 30°C	Uncontrolled
Dilution air humidity	Optional dehumidification	Optional Dehumidification	Uncontrolled
Diluted sample temperature	<325 K (52°C)	<325 K (52°C)	Uncontrolled
Target dilution air ratio	No less than 4 and large enough to complete eliminate H2O condensation	Sufficiently high to prevent condensation in bag samples as they cool to room temperature	20-40X
Size selective inlet	None	None	PM2.5 Cyclone
Tube Length from Probe to Filter		< 91 cm	N.S.
Mixing	10 x diameter	10 x diameter	10 x diameter or rapid mixing
Residence Time	N.S.	> 0.25 s	Varies, 0 – 12 minutes
Evaluation of system particle losses	None	None	Recovery of total PM from venture and sampling probe
Sample Collection			
Filter arrangement	Two filters in series less than 10 cm apart and not in contact with each other	Two filter in series less than 10 cm apart and not in contact with each other	Filter packs and aerosol instruments were collocated in parallel from a flow diffuser
Filter face velocity	35-80 cm/s	N.S.	N.S. general practice In the range of 30-116 cm/s
Filter collection efficiency	95% or greater for 0.3μm dioctylpthalate gas face velocity of 35-80 cm/s	N.S.	Ambient filter sampling
Filter type	Fluorocarbon fibre or fluorocarbon based membrane filters	N.S.	Depending on interest of analyte, quartz filter for EC/OC, PTFE for mass, XRF
Filter Size	> 70 mm (60 mm stain)	> 70 mm (60 mm stain)	47 mm (40 mm stain)
Minimum filter loading	465 $\mu g/mm^2$	**353** $\mu g/mm^2$	N.S., minimum 6 hours
Material and method of construction	Electrically conductive, unreactive material, Minimize deposition of PM	Electrically conductive, unreactive material, Minimize deposition of PM	Electrically conductive, unreactive material, Minimize deposition of PM
General Feature			
Material of sampler	Stainless steel	Stainless steel	Stainless steel and/or PTFE coating
Portability of sampler	No	No	Relatively portable
Isokinetic sampling	Optional- only to match flow conditions, not for matching size distribution, requires exhaust gas velocity of 10m/s or more		Pseudo-iso; flows matched as close as possible
Pretest cleaning procedures			Wash and rinse with acetone all components, wiped down large surfaces
Between Sample Run Cleaning Procedures (Same test/ operating condition)			None
Between Test/ Operating Conditions cleaning procedures			Wash and rinse with acetone all components, wide down large surface
Pre-test tunnel blank			Yes, one sample
Post-test condition tunnel blank			Yes, One sample
Field Blank			Yes, One sample

Blank as Not Specified

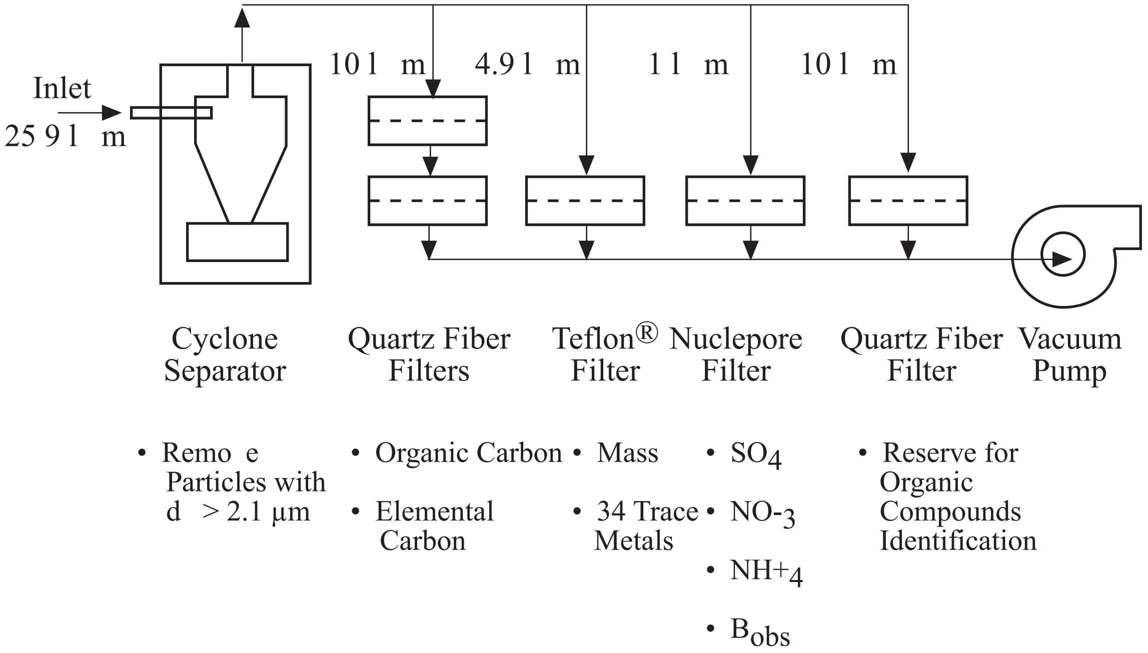


Figure 5-15. Typical Sample Collection Scheme (Gray *et al*., 1986)

Filtering and sorbent media are 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 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 PM_{10} mass, $PM_{2.5}$ 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 followed downstream by a NaCl impregnated cellulose fiber filter. The deposit on the 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.

Section 6

RECOMMENDATIONS

The API-CEC-DOE-GTI-NYSERDA program has two primary objectives: (1) source characterization, and (2) development and evaluation of test methods for use in generating scientifically sound fine particulate emission inventories. The current literature review serves as a background document facilitating efforts to develop an appropriate aerosol source emissions measurement methodology (hardware and procedures) that can be applied for expanding key areas of the fine particulate emissions database.

Numerous groups have developed and applied dilution sampling hardware for sampling fine particulate matter from emissions sources. Those methodologies and some of their key applications were reviewed in section 5. In moving forward, it is appropriate to make use of others' successes and to make adjustments as necessary to enhance future testing activities. All but one of the recent successful source-testing hardware systems are adaptations of the Caltech dilution stack sampler developed by Cass and Hildemann (1989). Those sampling systems and methodologies have been used to develop the majority of the current fine particulate emissions database. The only major drawback to the Hildemann design and the later systems developed by DRI and others is that the equipment is too large and cumbersome to apply in many stack applications. Clearly, the Caltech and DRI systems have been successfully used in numerous field applications but making more compact hardware will enhance future testing efforts. It is critical to note, however, that any design revision must be subjected to extensive evaluation to verify performance and to assure that results are consistent with the existing database.

Based on the available literature, there are several key elements in successful dilution stack sampler designs. These include:

- Sample extraction uses a heated line that has provisions to monitor and control the sample flow rate. The extracted sample then flows to a dilution chamber or tunnel.
- Sample dilution is accomplished using an air stream that has been cleaned of particulate matter with a HEPA filter and scrubbed of organics with an activated carbon system.

- The dilution tunnel must provide for complete mixing of the sample and dilution air streams. It is unclear how rapidly the two streams must be mixed but the mixing must be complete prior to transfer of diluted gases from the tunnel to a residence time chamber. The dilution ratio is another key design issue that directly impacts the physical size of the hardware.

- A portion of the diluted flow is extracted and passes to a large chamber providing time for condensation processes to occur prior to final sample extraction for analysis. The residence time provided by this chamber directly impacts the physical size of resulting hardware. The time must be long enough to accommodate critical physical and chemical processes but no longer than absolutely necessary.

- Finally, the residence time chamber must be equipped with ports for gathering size-segregated samples for appropriate analysis.

To construct a dilution sampling system that is more compact than either the Caltech or DRI designs, it is recommended that development address three key design features:

- Dilution ratio. The Hildemann design provides for a variable dilution ratio, but the system is typically operated at a dilution ratio of at least 40:1. This was based on Hildemann's earlier work indicating that PM concentration decreased at lower dilution ratios. However, some those results suggest that 40:1 dilution ratio may be overly conservative.

- Mixing rate. In Hildermann's earlier work, operation of the system at a dilution ratio of 20:1 indicated incomplete mixing at the end of the dilution tunnel. If the sample/dilution-air mixing rate can be accelerated, it is possible that the dilution ratio can be reduced without adversely impacting data quality. This design change not only allows for a physically smaller dilution tunnel but would also allow use of a smaller dilution air blower, cooler, HEPA filter, and activated carbon scrubber.

- Residence time. The residence time chamber in the Hildemann design provided a residence time of about 40 to 180 seconds while the DRI design provided about 80 seconds. The residence time of this chamber is directly proportional to its volume – a key design consideration for a dilution sampler that is to be used on a stack with a small platform, high above the ground. The overriding factor in selecting the residence time chamber volume in a new design should be data comparability. If residence time can be shortened to about 10 seconds while maintaining data comparability with results gathered with the Caltech or DRI designs, then the shorter time design should be implemented.

Based on the available literature there appears to be several avenues for improving on practical aspects of dilution sampler design. It is recommended that a more compact system be designed, constructed and then thoroughly evaluated for data comparability. After successful validation, the new hardware and associated measurement protocols can be used to fill critical gaps in the existing PM2.5 database.

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Appendix A

Fundamentals of Air Pollution and Public Health

EPIDEMIOLOGY

Epidemiology, the medical science which investigates the quantitative factors controlling the frequency and distribution of disease, has long recognized, if not at least suspected, the association between particulate matter and adverse health effects. The extreme air pollution episodes in the 1930s-1950s associated with dramatically elevated cardiopulmonary morbidity and mortality led to a series of efforts to control air pollution from the 1950s to the 1970s. An extensively researched review (Holland *et al*, 1979) concluded that significant human health effects occurred from high levels of particulates, but others (Shy 1979, Bates 1980, Ware *et al*, 1981) suggested a more likely importance at the low to moderate concentrations that existed in the U.S. and the British by 1970s. Later, health effect associations at unexpectedly low particulate levels were observed in the results from a few studies from 1989-1992. Although some of these studies were controversial, these results motivated more than 150 published epidemiological studies and numerous reviews focused on the contribution of particulate air pollution to human health effects (Pope 2000, and references therein). This appendix only intends to introduce the readers to some fundamental background for PM related public health effects.

Susceptibility

The question of who is susceptible in epidemiological studies is not simple but is dependent on the health effects, level, and length of studies evaluated. Different concepts of susceptibility may lead to different risk-assessment processes. The consensus definition of susceptibility can be scientifically approached by identifying the intrinsic and extrinsic factors, selection of health endpoints, individual and group perspectives (Parkin and Balbus, 2000). The most common subgroups of concern include children, the elderly, pregnant women, and people with chronic cardiopulmonary disease, influenza, and asthma. Table A-1 (adapted from Pope III, 2000) summarized the subgroups who are susceptible to adverse health effects from PM exposure and overall health relevance

Table A-1. Summary of Who's Susceptible to Adverse Health Effects from PM Exposure an Overall Health Relevance (Pope III, 2000)

Health effects	Who's Susceptible?	Overall Health Relevance
Acute exposure		
Mortality	Elderly, infants, persons with chronic cardiopulmonary disease, influenza, or asthtma	Obviously relevant. How much life shortening is involved and how much is due to short-term mortality displacement (harvesting) is uncertain.
Hospitalization/other health care visits	Elderly, infants, persons with chronic cardiopulmonary disease, influenza, or asthma	Reflects substantive health impacts in terms of illness, discomfort, treatment costs, work or school time lost, etc.
Increased respiratory symptoms	Most consistently observed in people with asthma and children	Mostly transient effects with minimal overall health consequence, althoug for a few there may be short-term absence from work or school due to illness.
Decreased lung function	Observed in both children and adults	For most, effects seem to be small and transient, for a few, lung function losses may be clinically relevant.
Plasma viscosity, heart rate, heart rate variability, pulmonary inflammation	Observed in both healthy and unhealthy adults. No studies of children	Effects seem to be small and transient. Overall health relevance is unclear, but may be part of pathophysiologic pathway linking PM with cardiopulmonary mortality.
Chronic exposure		
Increased mortality rates, reduced survival times, chronic cardio-pulmonary disease, reduced lung function	Observed in broad-based cohorts or samples of adults and children (including infants). All chronically exposed potentially are attected	Long-term, repeated exposure appears to increase the risk of cardio-pulmonary disease and mortality. May result in lower lung function. Population average loss of life expectancy in highly polluted cities may be as much as a few years.

Epidemiological Study Designs in Air Pollution Research

Epidemiological studies include *observational study*, in which the investigator does not control assignment of the exposure and is preferred over the *experimental study,* in which the investigator decides how exposure is distributed among study subjects. However, the correlation or estimate of particulate air pollution adverse health effects can result from confounding factors. Randomization of exposure is common in an epidemiological study to prevent the biases caused by confounders, which the investigators do or do not know.

Observational study designs used in past include both longitudinal designs (time series and cohort studies) and cross-sectional designs. The longitudinal design observes the health outcome and the exposure over time. For example, a time series study evaluates the association between the particle series and the mortality series, and a cohort study identifies a sample population then measures and estimates the exposure of an identified population over a period of time. A cross-sectional study assesses the sample population at one point in time when the symptom of interest, such as measurement of level of lung function, is observed. Most of the observational studies on particle pollution health effects are time series studies. The cross-sectional study is not commonly used in the study of particle effects because of the limited ability, and the cost to control the confounding factors.

Validity and Causality

The validity of association between particulate air pollution and various outcomes is judged upon if the relationship observed between exposure to particles and health effects really exists. If the relationship exists it is then justifiable to determine if the relationship is causal. The criteria of causality include the *strength, consistency, specificity, plausibility* and *analogy* of the association (Bates, 2000). Fifteen reviews of studies concluded that the observed association between health effect and particulate air pollution is valid and causal (Dab *et al*, 2001). However, some argued that the conclusion of existing cause-effect relationship does not have substantive basis (Gamble and Lewis, 1996; Gamble, 1998), of which epidemiological studies cannot provide biological mechanisms.

Health Endpoints of Acute and Chronic Exposures

Exposure to particulate air pollution can be either acute or chronic . The health effect indicators include

Health Effects of acute exposures

- Mortality counts: respiratory, cardiovascular
- Hospitalizations: Chronic Obstructive Pulmonary Disease (COPD), Pneumonia, Asthma, Cardiovascular
- Symptoms: upper respiratory, lower respiratory, asthma, cough
- Lung function: Forced Expiratory Volume (FEV), Peak Expiratory Flowrate (PEF)

Health effects of chronic exposure

- Mortality rates
- Survival/Life Expectancy: cardiorespiratory, lung cancer, postneonatal infant
- Disease: bronchitis
- Lung Function
    - Children: Forced Vital Capacity (FVC), FEV, PEF
    - Adults: FVC, FEV

which can be stylized and summarized in Figure A-1 (adapted from Pope III, 2000).

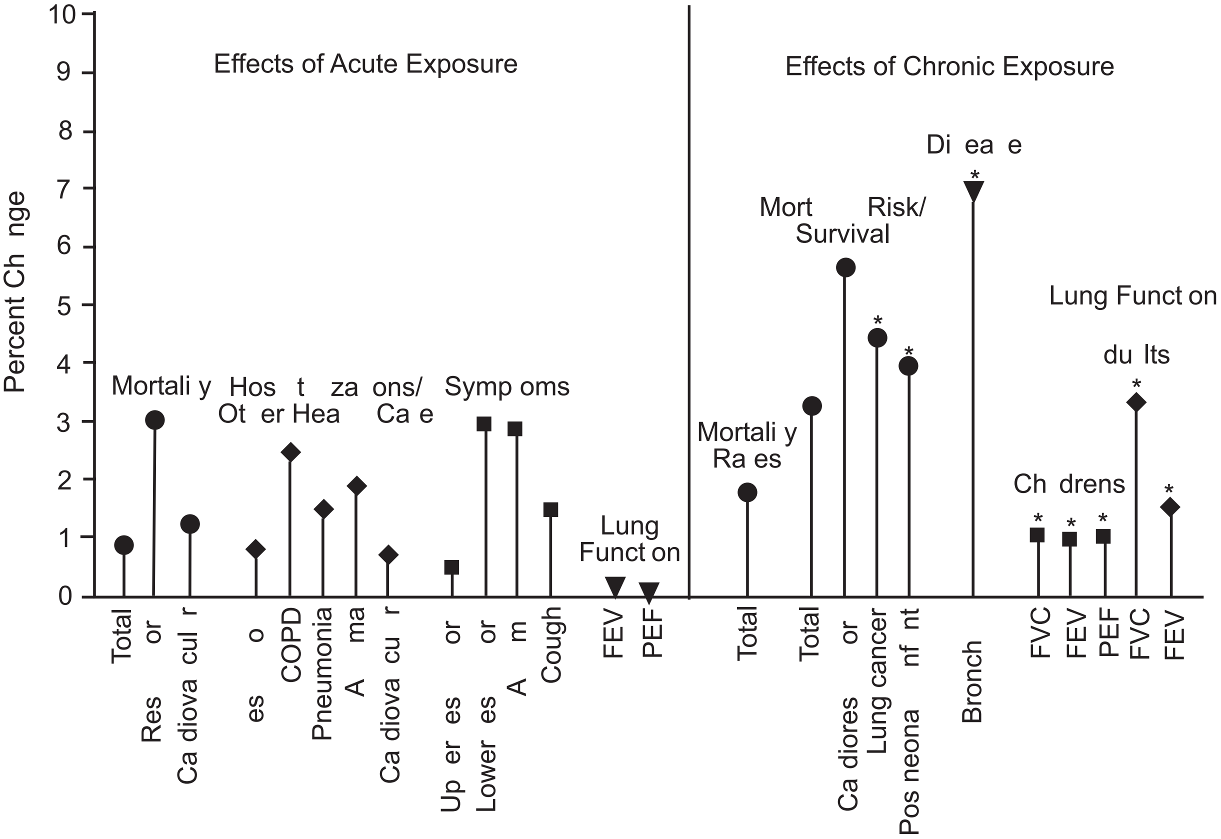

Figure A-1. Stylized summary of observed health effects, presented as approximate percent changes in health end points per 5 μg/m^3 increase in PM2.5. Abbreviations: COPD, chronic obstructive pulmonary disease; FVC, forced vital capacity; PEF, peak expiratory flow. Asterisk (*) indicates estimate based on very limited or inconsistent evidence (Pope III, 2000).

Most of the recent daily time-series mortality studies show that, particulate air pollution had the largest effect on respiratory and cardiovascular disease mortality. The acute effects are typically observed either concurrent or 1 to 5 days after an increase of PM concentration (Pope 1998). Some observations have indicated potential misleading conclusions due to the selection of the modeling techniques and confounding factors such as long-term time trends, season, weather variables, other pollutants, or some other unknown factors. (Moolgavkar and Luebeck, 1996; Lipfert and Wyzga 1995; Gamble and Lewis 1996).

In contrastto acute exposure, chronic exposure studies provide information about how health effects were effected by a low or moderate particulate exposure levels for a long period of time, as well as the cumulative effects of repeated exposure to elevated level of pollution.

Several population-based, cross-sectional mortality studies as well as a few cohort mortality studies have concluded that mortality rates were most strongly associated with fine or sulfate particulate matter. Several studies also indicated a statistically significant association between air pollution and various respiratory symptoms, such as, chronic cough, bronchitis, and chest illness (Pope and Dockery, 1999). Although most reviews of epidemiological studies indicated the non-spurious association between health effects of long-term exposure and particulate air pollution was reasonable, some have questioned and discounted the conclusion due to the low number of high-quality studies for long-term exposures as well as modeling techniques, or confounding by other air pollutants or unknown factors (Moolgavkar and Luebeck, 1996; Lipfert, 1997; Vedal 1997; Gamble 1998).

Particulate Respiratory Deposition

Respiratory PM deposition is a function of age, health, PM size (impaction or diffusion), nasal versus oral breathing, and volume of air breathed. Respiratory deposition models developed by International Commission on Radiological Protection (ICRP, 1995) are shown in Figure A-2 and A-3 (Hinds 1998). The models predict that, high deposit efficiency of coarse particles on head airway via impaction and interception; ultrafine particles in the alveoli region by diffusion. However, deposition efficiency for accumulation mode particulates, i.e., 0.1-1μm, is very low. Similar particle deposition efficiencies are predicted by models developed by the National Council on Radiation Protection and Measurement (NCRP, 1997) and the American Conference of Governmental Industrial Hygienists (ACGIH). Based on the theoretical calculation and realistic ambient air pollution level, a $10 \mu g/m^3$ increase in $PM_{2.5}$ mass concentration results in an increment of 20-50 μg deposit in the lung per day, and a near-highway particle number concentration of $10^5/cm^3$ results in an alveolar deposition rate of approximate 1 particle per cell per day.

Exposure Studies

Experimental studies include data from toxicological studies control exposure settings , such as cell culture, instillation, or inhalation exposures conducted with either laboratory-generated surrogate particles from well-characterized sources, or enriched

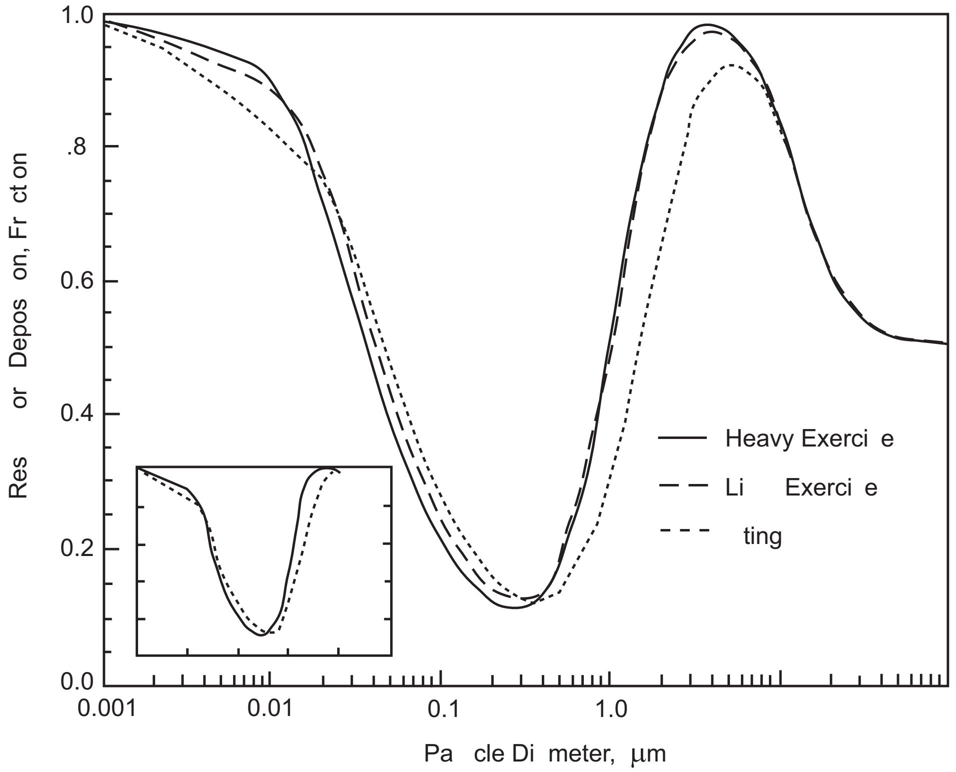

Figure A-2. Predicted total respiratory deposition at three levels of exercise based on ICRP deposition model. Average data for males and females. Inset does not include the effect of inhalability (Hinds, 1998).

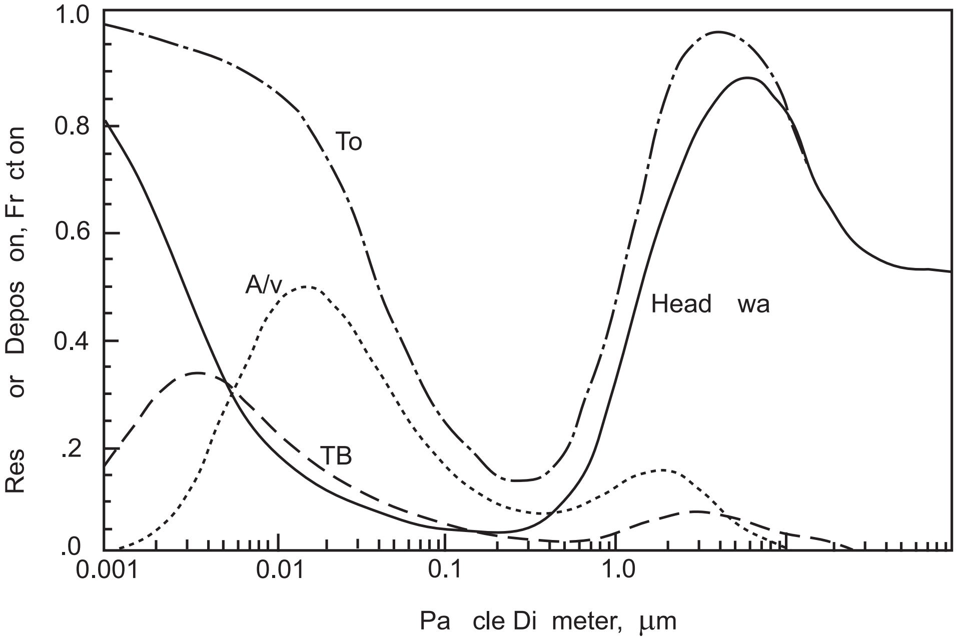

Figure A-3. Predicted total and regional deposition for light exercise (nose breathing) based on ICRP deposition model. Average data for males and females (Hinds, 1998).

ambient particulates to verify exposure hypotheses. The cell culture studies incubate types of target cells , such as macrophages, then exposures the cells to particulates or particulate extracts. However, results from cell culture studies cannot provide the link to exposure results, in which health endpoints were influenced under biological response mechanisms. In the instillation exposure, collected particles are extracted to saline and the solution is instilled to a living organism. However, the results can be biased due to the invasive process, as well as depending on the particle integrity, i.e., shape, redox activities, and insolubility of particles, after extraction.

Animal exposure studies are commonly used in controlled lab settings with artificial particles, such as sulfate coated black carbon, nitrates, or resuspended particles. The exposure with artificial particles may oversimplify the complex mixture in ambient air.The resuspension of collected particles for exposure studies is difficult for small particles due to the surface forces. The recent development of particle concentrator technology (Sioutas, *et al*, 1994; Sioutas, *et al* 1995, Sioutas, *et al,*1999; Gordon, *et al*, 1999; Kim, *et al*, 2000; Chang *et al,* 2002) enables acute exposure studies to be conducted with enriched ambient originated particulates. The ambient particulates were concentrated to 10-50 times the ambient level and then supplied to an inhalation chamber. Such enriched ambient particulate exposure studies have been conducted with both animal (Gldleski, *et al*, 2000; Kadiiska, *et al*, 1997) and human subjects (Gong, *et al* 2000). These exposure study results need to be very careful reviewed, not only because of the complexity of ambient particles, but also because of the exposure design, and formation of particles in the concentration processes. For example, the size distributions of enriched particulates should be the same as in the ambient air, and the enriched concentrations of particulate be comparable to and representative of particulate air pollution episodes.

Biologic Plausibility

Within the substantial limitations and weaknesses of the epidemiology studies of particulate pollution, very little information is known about the relevant biological mechanism. The body can remove inhaled particles by the biological defense system and a number of hypotheses on biological mechanisms were suggested to be responsible for the observed health effects, such as oxidative stress, airway inflammation, oedema formation, impaired gas diffusion resulting in hypoxic stress, increase plasma viscosity and blood coagulation, immunotoxicity, cardiac dysfunction and impaired pulmonary circulation. The relationship can be simplified in Figure A-4 (adapted from RIVM Report 650010033, 2002).

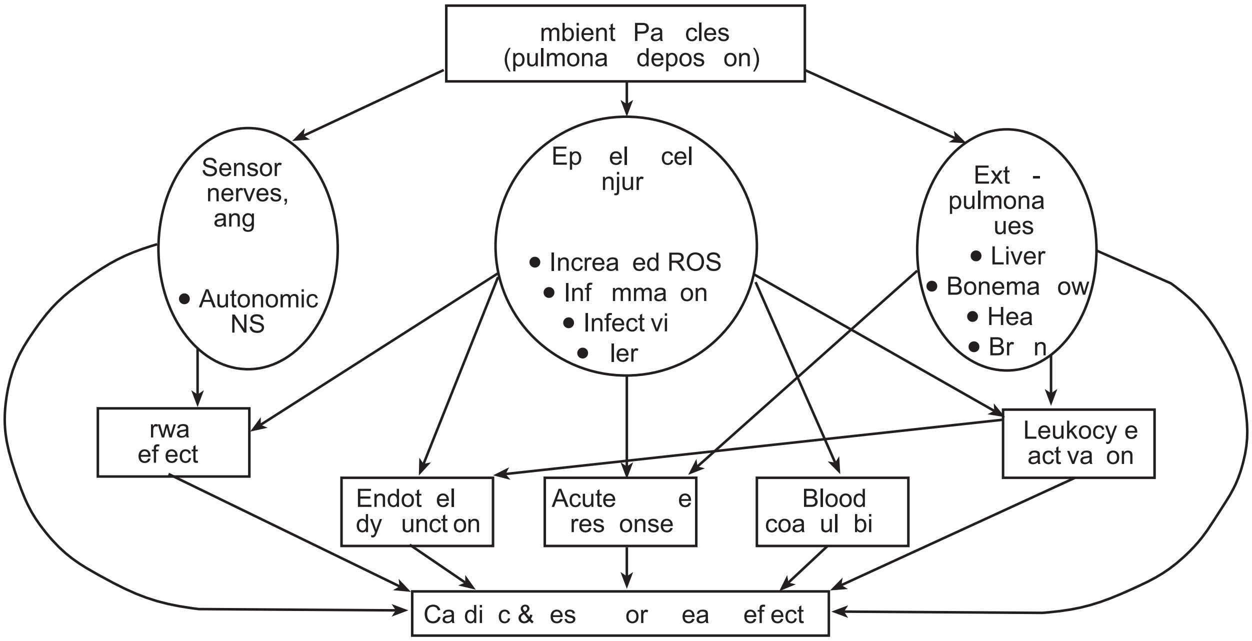

Figure A-4. Possible mechanisms from exposure of PM to effects (RIVM Report 650010033, 2002).

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Appendix B

LIST OF ABBREVIATIONS

µm	micrometer (micron)
2-NF	2-Nitrofluoranthene
AAS	atomic adsorption spectrometry
AC	automated chromatography
API	American Petroleum Institute
ASME	American Society of Mechanical Engineers
b.p.	boiling point
BaP	benzo[a]pyrene
C	centigrade
$C_{15}H_{32}$	n-pentadecane
C_3H_8	propane
CA	California
$CaCO_3$	calcium carbonate
CIT	California Institute of Technology
CARB	California Air Resources Board
CCU	catalytic cracking unit
Cl_2	chlorine (molecular)
cm	centimeter
CO	carbon monoxide
CO_2	carbon dioxide
D_{50}	50 percent cutoff diameter
DHS	Department of Health Services
DNPH	2,4 dinitrophenylhydrazine
DRI	Desert Research Institute
dscm	dry standard cubic meter
EASA	electrical aerosol size analyzer
EC	elemental carbon
ECD	electron capture detector
GE EER	General Electric Energy and Environmental Research Corporation
EPA	Environmental Protection Agency
ESP	electrostatic precipitator
F	Fahrenheit
FCCU	fluidized catalytic cracking unit
FID	flame ionization detector
ft	feet
FTIR	Fourier transform infrared spectroscopy
$g\text{-}cm^{-3}$	grams per cubic centimeter
GC/MS	mass spectrometric detector
GC	gas chromatography
H_2SO_4	sulfuric acid
HEPA	high efficiency particulate air
HEST	high efficiency sampling train

LIST OF ABBREVIATIONS
(Continued)

Hg	mercury
hivol	high volume
HNO_2	nitrous acid
HNO_3	nitric acid
HO_2	hydroperoxyl radical
HPLC	high performance liquid chromatography
HRSG	heat recovery steam generator
IC	ion chromatography
IC engine	internal combustion engine
ICP	inductively coupled plasma
INAA	instrumental neutron activation analysis
K_2CO_3	potassium carbonate
LC	liquid chromatography
lpm	liters per minute
mg	milligram
$MgCO_3$	magnesium carbonate
MOUDI	microorifice uniform deposit impactor
MS	mass spectrometry
Na_2CO_3	sodium carbonate
NAAQS	national ambient air quality standards
NaCl	sodium chloride
$NaNO_3$	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_3	ammonia
$(NH_4)_2SO_4$	ammonium sulfate
NH_4HSO_4	ammonium bisulfate
NH_4NO_3	ammonium nitrate
NMHC	non-methane hydrocarbons
NO	nitric oxide
NO_2	nitrogen dioxide
NO_3	nitrate (ion)
NO_x	oxides of nitrogen
NP	nitropyrene
O_3	ozone
OC	organic carbon
OH	hydroxyl (radical)
PAH	polycyclic aromatic hydrocarbons
PAK	polycyclic aromatic ketones

LIST OF ABBREVIATIONS
(Continued)

PAN	peroxyacetyl nitrate
PAQ	polycyclic aromatic quinones
PCB	polychlorinated biphenyls
PIXE	proton induced X-ray emission
PM	particulate matter
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
SCAQS	Southern California Air Quality Study
SCR	selective catalytic NOx reduction
sec	second
SFS	sequential filter samplers
SO_2	sulfur dioxide
SO_3	sulfur trioxide
SoCAB	South Coast Air Basin
SOx	oxides of sulfur
SRI	Southern Research Institute
T	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

Appendix C

SI CONVERSION FACTORS

	English (US) units	X	Factor	=	SI units
Area:	1 ft^2	x	9.29×10^{-2}	=	m^2
	1 in^2	x	6.45	=	cm^2
Flow Rate:	1 gal/min	x	6.31×10^{-5}	=	m^3/s
	1 gal/min	x	6.31×10^{-2}	=	L/s
Length:	1 ft	x	0.3048	=	m
	1 in	x	2.54	=	cm
	1 yd	x	0.9144	=	m
Mass:	1 lb	x	4.54×10^{2}	=	g
	1 lb	x	0.454	=	kg
	1 gr	x	0.0648	=	g
Volume:	1 ft^3	x	28.3	=	L
	1 ft^3	x	0.0283	=	m^3
	1 gal	x	3.785	=	L
	1 gal	x	3.785×10^{-3}	=	m^3
Temperature	°F-32	x	0.556	=	°C
	°R	x	0.556	=	K
Energy	Btu	x	1055.1	=	Joules
Power	Btu/hr	x	0.29307	=	Watts