☙ EPA GUIDELINES FOR PM-10 SAMPLING AND ANALYSIS APPLICABLE TO RECEPTOR MODELING

Office of Air Quality

Clean Air

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Planning and Standards

GUIDELINES FOR PM-10 SAMPLING AND ANALYSIS APPLICABLE TO RECEPTOR MODELING

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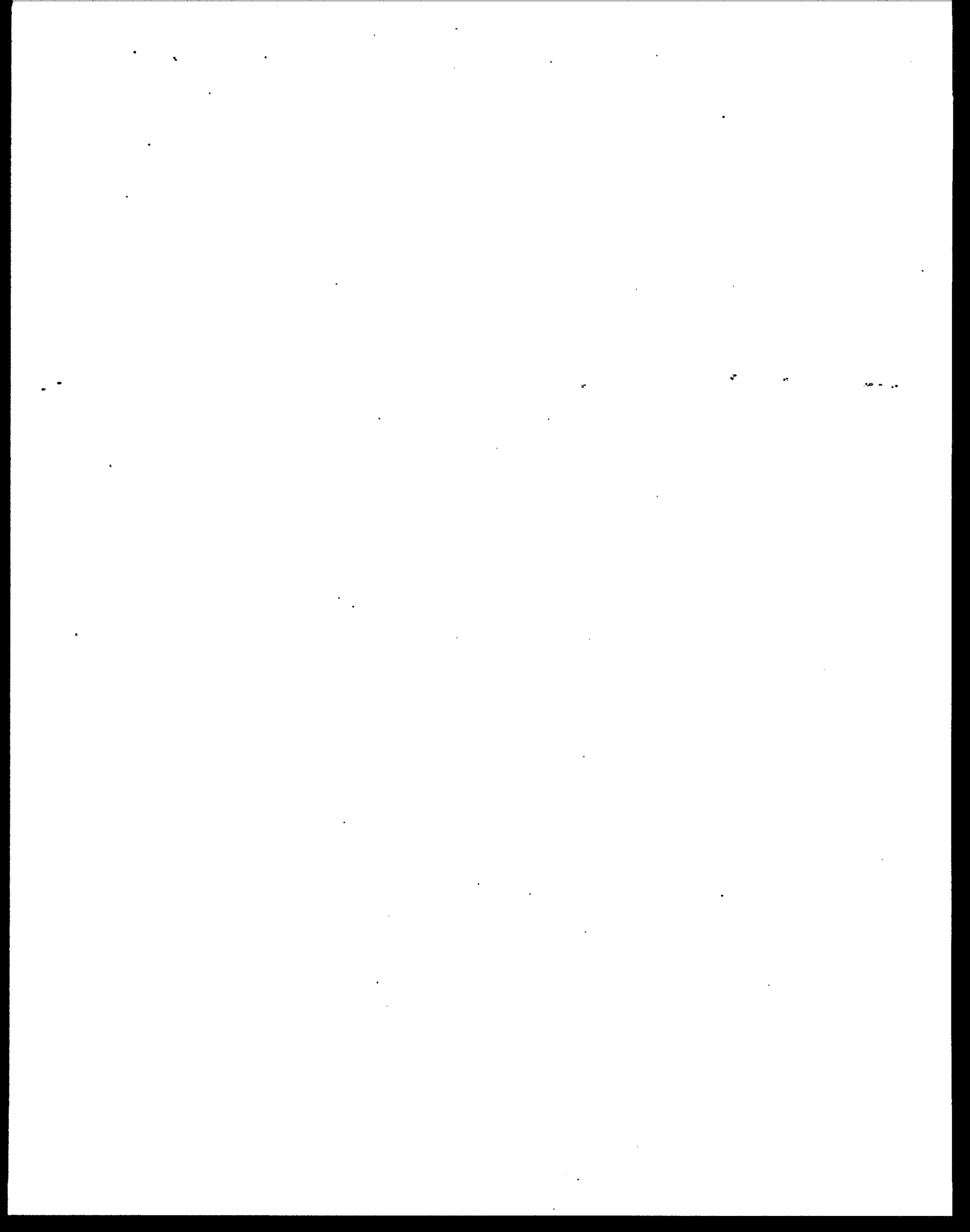Office of Air Quality Planning and Standards
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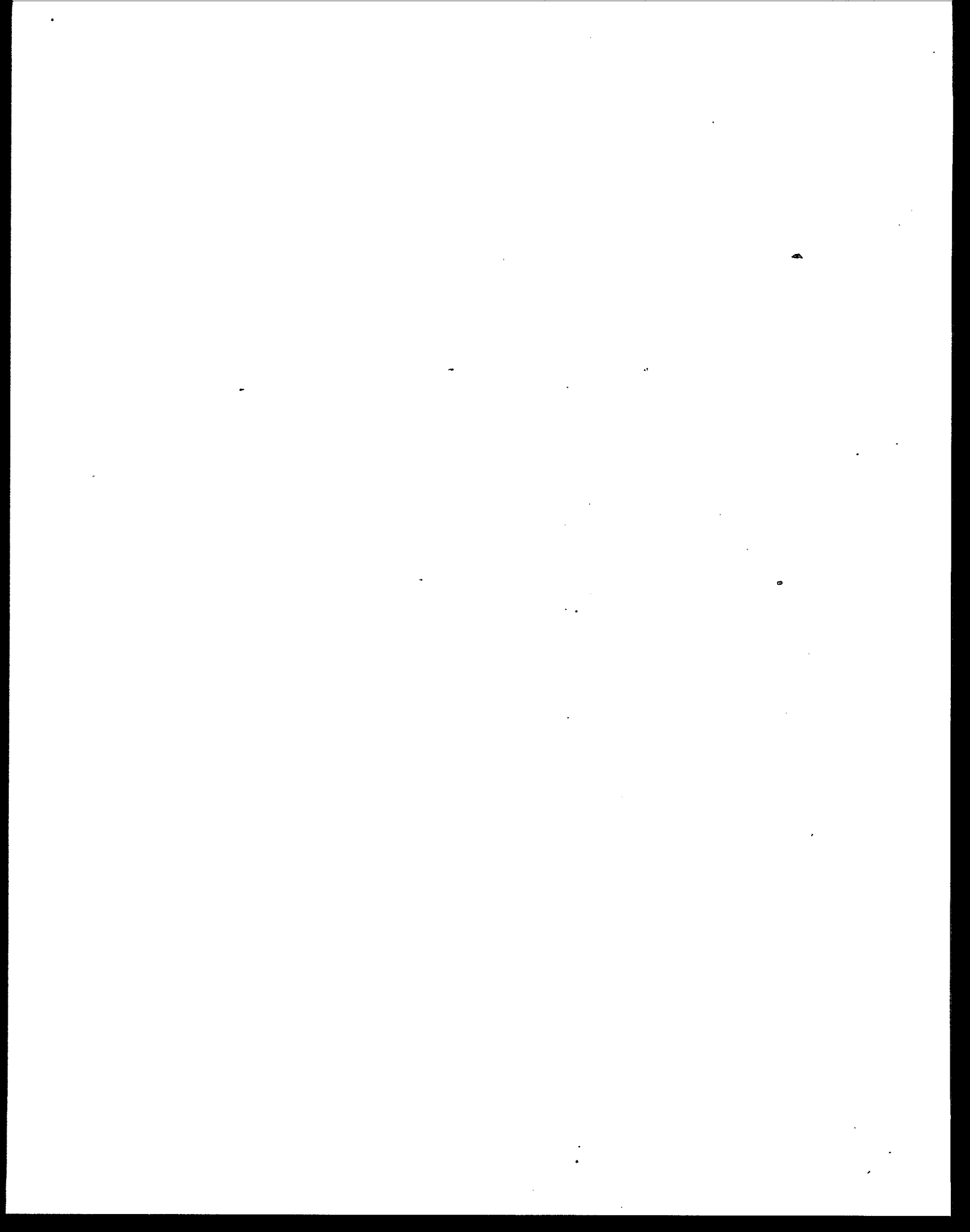
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1.0 INTRODUCTION

Chemical characterization of suspended particles is necessary, along with the application of receptor models, to apportion ambient concentrations to their sources for the development of emissions reduction strategies. This document identifies current technology for the sampling and analysis of PM_{10} and its chemical constituents on filter deposits.

1.1 Background

The national ambient air quality standards (NAAQS) for PM_{10} (particulate matter with a nominal aerodynamic diameter less than or equal to 10 micrometers, [μm]) (Federal Register, 1987a; 1987b; 1987c; 1987d; 1987e; 1987f; 1987g; 1987h; 1987i) allow PM_{10} concentrations in an air quality maintenance area to reach an annual arithmetic average of 50 $\mu g/m^3$ and a maximum 24-hour average of 150 $\mu g/m^3$, not to be exceeded more than three times in three years. Secondary PM_{10} standards were set identical to primary PM_{10} standards for the protection of public welfare.

The 1990 Clean Air Act Amendments (CAAA, the Act) (U.S. Government Printing Office, 1991) and several years of ambient PM_{10} monitoring designated 75 U.S. areas as "moderate" non-attainment for PM_{10} (Federal Register, 1991; 1994), 5 areas as "serious" non-attainment (Federal Register, 1993), and the remaining areas as unclassifiable. Table 1-1 identifies these designated non-attainment areas. The unclassifiable areas may be re-designated as non-attainment areas in the future if ambient PM_{10} concentrations exceed the standards. The 1990 CAAA charge "moderate" non-attainment areas to achieve the PM_{10} NAAQS as expeditiously as practicable but no later than December 31, 1994. For "serious" non-attainment areas, the CAAA require attainment of the PM_{10} NAAQS by December 31, 2001.

Under the amended Act, states must develop and submit State Implementation Plans (SIPs) which specify the emissions reductions which need to be executed in each non-attainment area. SIPs specify the technologies and activities which will be applied, and the regulations which will enforce these technologies or emitters. The SIP must also demonstrate, in a scientifically defensible manner, that these emissions reductions will be successful in attaining PM_{10} standards.

U.S. EPA guidelines for SIPs (U.S. EPA, 1987a) recommend the application of both source and receptor models to quantify the major contributors to excess PM_{10} concentrations, and linear rollback of emissions to estimate the effects of alternative emission controls (Pace and Watson, 1987; U.S. EPA, 1987b). Source models use emissions inventories and meteorological measurements to predict the PM_{10} concentrations measured at receptors. Receptor models use the chemical composition of source emissions and receptor concentrations to infer the source contributions which constitute the measured PM_{10} mass. The Chemical Mass Balance (CMB, Watson et al., 1984; 1990a; 1991a) receptor model uses source profiles (i.e., the fractional amount of each chemical in source emissions) and ambient concentrations of chemicals measured at PM_{10} sampling sites as model inputs. Other receptor models apply single particle analysis and

Table 1-1

Summary of designated moderate and serious PM$_{10}$ non-attainment areas in the U.S. as of 2/1/94

State	Planning Area Name	Counties Fully or Partially Included in Planning Area	Moderate[a,b]	Serious[c]
Alaska	Community of Eagle River	Anchorage	X	
	Juneau: Mendenhall Valley Area	Juneau	X	
Arizona	Paul Spur	Coshise	X	
	Douglas	Coshise	X	
	Nogales	Santa Cruz	X	
	Rillito	Pima	X	
	Ajo	Pima	X	
	Phoenix	Maricopa and Pinal	X	
	Yuma	Yuma	X	
	Payson	Gila	X[b]	
	Bullhead City	Mohave	X[b]	
	Hayden/Miami	Pinal and Gila	X	
California	Owens Valley	Inyo		X
	Searles Valley	San Bernardino, Inyo, and Kern	X	
	Mammoth Lake	Mono	X	
	San Joaquin	Fresno, Kern, Kings, Tulare, San Joaquin, Stanislaus, and Madera		X
	South Coast Air Basin	Riverside, Los Angeles, Orange, and San Bernardino		X
	Coachella Valley	Riverside		X
	Sacramento County	Sacramento County	X[b]	X
	San Bernardino County	San Bernardino County (note: excludes portions located in the Searles Valley Planning Area and South Coast Air Basin)		
	Imperial Valley	Imperial	X[b]	
			X	
Colorado	Pagosa Springs	Archuleta	X	
	Denver Metropolitan Area	Adams, Denver, Arapahoe, Jefferson, Douglas and Boulder	X	

Table 1-1 (continued)

Summary of designated moderate and serious PM₁₀ non-attainment areas in the U.S. as of 2/1/94

State	Planning Area Name	Counties Fully or Partially Included in Planning Area	Moderate[a,b]	Serious[c]
Colorado (cont.)	Telluride	San Miguel	X	
	Lamar	Prowers	X	
	Aspen	Pitkin	X	
	Canon City	Fremont	X	
	Steamboat Springs	Routt	X[b]	
Connecticut	New Haven	New Haven	X	
Idaho	Boise	Ada	X	
	Pinehurst	City of Pinehurst in Shoshone County	X	
	Shoshone County (excluding Pinehurst)	Shoshone	X[b]	
	Pocatello	Bannock and Power	X	
	Sandpoint	Bonner	X	
Illinois	Lyons Township	Cook	X	
	Southeast Chicago	Cook	X	
	Oglesby including some Townships	LaSalle	X	
	Granite City and Nameoki Townships	Madison	X	
Indiana	Cities of East Chicago, Hammond, Whiting, and Gary	Lake	X	
	Clinton Township	Vermillion	X	
Maine	Presque Isle	Aroostook	X	
Michigan	Detriot	Wayne	X	
Minnesota	Rochester	Olmsted	X	
	St. Paul	Ramsey	X	
Missouri	Audrain	Audrain	X	

Table 1-1 (continued)

Summary of designated moderate and serious PM$_{10}$ non-attainment areas in the U.S. as of 2/1/94

State	Planning Area Name	Counties Fully or Partially Included in Planning Area	Moderate[a,b]	Serious[c]
Montana	Columbia Falls	Flathead	X	
	Kalispell	Flathead	X	
	Libby	Lincoln	X	
	Ronan and Polson	Lake	X	
	Missoula Township	Missoula	X	
	Lame Deer	Rosebud	X	
	Butte	Silver Bow	X	
	Thompson Falls and vicinity	Sanders	X[b]	
Nevada	Reno	Washoe	X	
	Las Vegas	Clark		X
New Mexico	Anthony	Dona Ana	X	
New York	New York County	New York County	X[b]	
Ohio	Cuyahoga	Cuyahoga	X	
	Mingo Junction/Steubenville	Jefferson	X	
Oregon	Medford-Ashland (including White City)	Jackson	X	
	Grants Pass	Josephine	X	
	Springfield/Eugene	Lane	X	
	Oakridge	Lane	X[b]	
	Klamath Falls	Klamath	X	
	LaGrande	Union	X	
Pennsylvania	Area including Liberty, Lincoln, Port Vue, and Glassport Boroughs, and the Clairton	Allegheny	X	
Puerto Rico	Municipality of Guaynabo	Guaynabo	X	

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Table 1-1 (continued)

Summary of designated moderate and serious PM_{10} non-attainment areas in the U.S. as of 2/1/94

State	Planning Area Name	Counties Fully or Partially Included in Planning Area	Moderate[a,b]	Serious[c]
Texas	El Paso	El Paso	X	
Utah	Salt Lake	Salt Lake	X	
	Utah	Utah	X	
Washington	Seattle	King	X	
	Kent	King	X	
	Tacoma Metropolitan Area	Pierce	X	
	Spokane	Spokane	X	
	Yakima	Yakima	X	
	Olympia, Tumwater, and Lacey	Thurston	X	
	Wallula	Walla Walla	X	
West Virginia	Follansbee	Brooke	X	
	Weirton	Hancock and Brook Counties	X[b]	
Wyoming	Sheridan	Sheridan	X	

[a] Federal Register (1991).
[b] Federal Register (1994).
[c] Federal Register (1993).

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multivariate decompositions of many measurements taken in space and time (e.g., Henry *et al.*, 1991; Gebhardt *et al.*, 1990; Kim *et al.*, 1992). Chemically-speciated particulate data sets have been acquired in many urban and non-urban areas to determine the sources of PM_{10} and the causes of visibility impairment. Appendix A identifies many of these data sets.

Figure 1-1 shows the locations of current PM_{10} non-attainment areas in the U.S. and classifies them by major source contributors based on emissions inventories. The general source types in these PM_{10} non-attainment areas are combinations of area-wide emitters such as fugitive dust from roads, construction, and agriculture; smoke from residential wood combustion, prescribed burning, and forest fires; directly emitted exhaust from motor vehicle engines; primary industrial emissions from steel mills, power plants, incinerators, smelters, cement plants, oil extraction, and oil refining; and secondary sulfate, nitrate, ammonium, and organic compounds formed from sulfur dioxide, nitrogen oxides, ammonia, and reactive organic gas (ROG) emissions. The distinction between primary and secondary contributors to PM_{10} is important, and obtaining this distinction is a major motivation for determining the chemical composition of PM_{10}.

1.2   Primary and Secondary Aerosol

Both primary and secondary particles contribute to suspended particles in the U.S., and especially to PM_{10} concentrations which exceed standards. Primary particles are those which are directly emitted by sources. These particles undergo few changes between source and receptor, and the atmospheric concentrations are, on average, proportional to the quantities which are emitted. Secondary particles are those which form in the atmosphere from gases which are directly emitted by sources. Sulfates and nitrates are the most common secondary particles, though a fraction of organic carbon can also result from volatile organic compounds (VOCs) via atmospheric reactions.

Suspended particles congregate in different sub-ranges according to the method of formation (Whitby *et al.*, 1972). The "nuclei" range consists of particles < 0.08 μm in aerodynamic diameter which are emitted directly from combustion sources. In polluted areas, the lifetimes of particles in the nuclei range are usually less than one hour because they rapidly coagulate with large particles or serve as nuclei for cloud or fog droplets. This size range is detected only when fresh emissions sources are close to the measurement site.

The "accumulation" range consists of particles of ~0.08 to ~2 μm in aerodynamic diameter. These particles result from the coagulation of smaller primary particles emitted from combustion sources, from condensation of volatile species, from gas-to-particle conversion, and from finely ground dust particles. The nuclei and accumulation ranges constitute most of the $PM_{2.5}$ (particulate matter with a nominal aerodynamic diameter less than or equal to 2.5 μm) size fraction. This size range includes contributions from primary as well as secondary particles. $PM_{2.5}$ contains most of the sulfate, nitrate, ammonium, organic carbon, and elemental carbon found in suspended particles. Hering and Friedlander (1982), John *et al.* (1991), and Sloane *et*
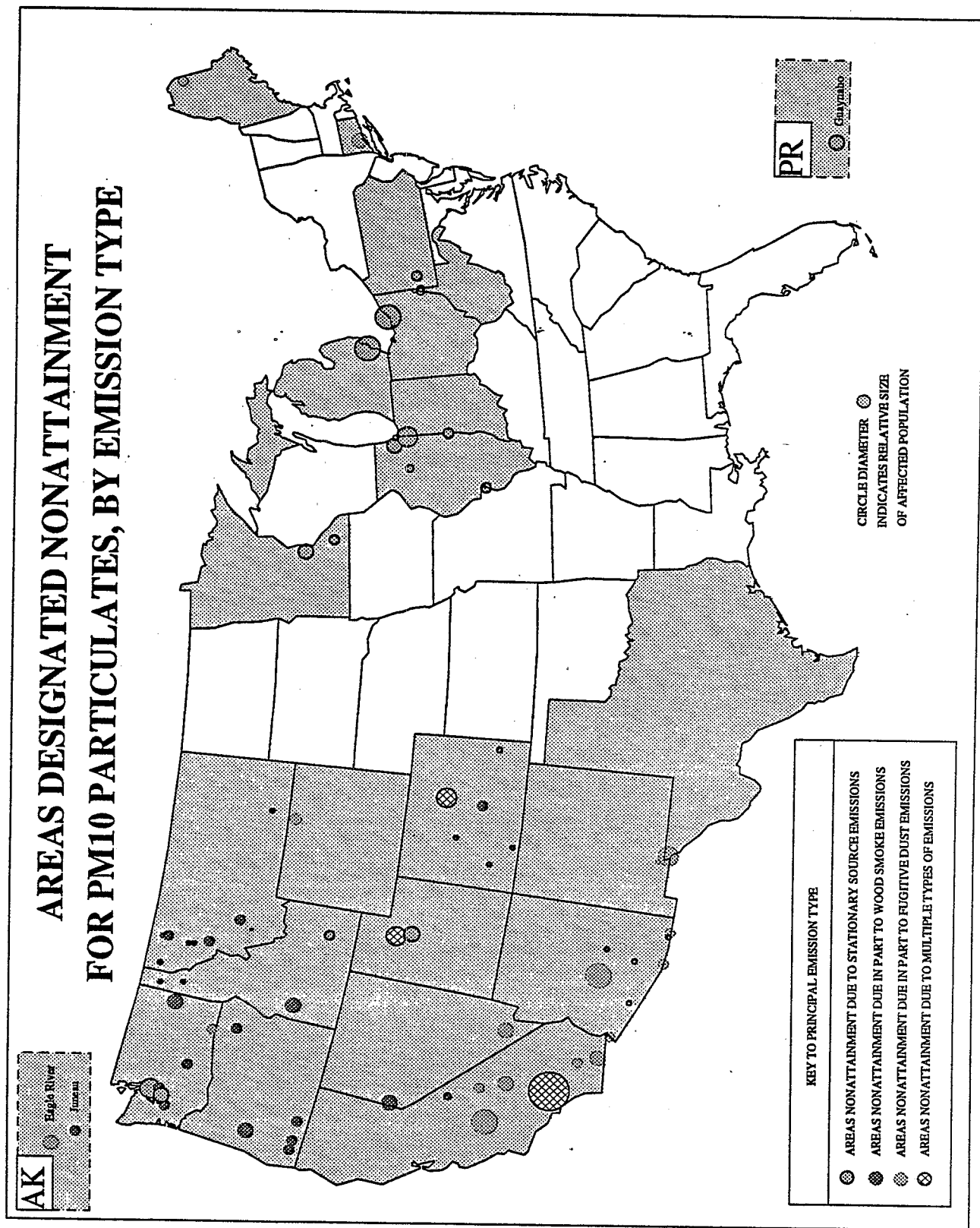
Figure 1-1. Designated PM_{10} non-attainment areas in the United States (accurate as of December 17, 1993, courtesy of T. Rosendahl and T.G. Pace, U.S. EPA/OAQPS).

al. (1991) show that the accumulation range consists of several modes. One of these, which peaks at ~0.2 μm, is interpreted as a "condensation" mode containing gas-phase reaction products. A ~0.7 μm peak is interpreted as a "droplet" mode which forms as the "condensation" mode accumulates water.

The "coarse" particles (PM_{10} minus $PM_{2.5}$) consist of particles between 2.5 μm and 10 μm. Coarse particles result from grinding activities and are dominated by material of geological origin. Pollen and spores are also in this size range, as are ground up trash, leaves, tire wear, other detritus, and sea salt. Coarse particles may also result when clouds and fog droplets form in a polluted environment, then dry out after having scavenged other particles and gases.

The gaseous precursors of most particulate sulfates and nitrates are sulfur dioxide (SO_2) and oxides of nitrogen (NO and NO_2, the sum of which is designated NO_x), respectively. Ambient concentrations of sulfate and nitrate are not necessarily proportional to quantities of emissions since the rates at which they form may be limited by factors other than the concentration of the precursor gas. Secondary sulfates most often occur as a combination of sulfuric acid (H_2SO_4), ammonium bisulfate (NH_4HSO_4), and ammonium sulfate (($NH_4)_2SO_4$). Ammonium nitrate (NH_4NO_3) is a common secondary constituent of $PM_{2.5}$. A portion of PM_{10} nitrate may be found in the coarse particle fraction 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. All of these are soluble in water, and liquid water may be a major component of PM_{10} when relative humidities exceed 70%.

Secondary organic compounds in particulate matter include aliphatic acids, aromatic acids, nitro-aromatics, carbonyls, esters, phenols, and aliphatic nitrates (Grosjean and Seinfeld, 1989; Grosjean, 1992). The exact precursors of these secondary organics are not well understood, but they are believed to consist of heavier hydrocarbons (i.e., molecules which contain more than seven or eight carbon atoms). Many of the suspected precursors of secondary organic particles are not measured by the usual VOC sampling and analysis methods.

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 makes accurate measurements of particulate nitrate and nitric acid exceedingly difficult, since ammonium nitrate particles on a filter may disappear during sampling or between sampling and analysis with changes in temperature and gas concentrations.

The sulfur dioxide to particulate sulfate reaction and the nitrogen oxide to particulate nitrate reaction compete for available hydroxyl radicals and ammonia. Ammonia is preferentially scavenged by sulfate to form ammonium sulfate and ammonium bisulfate, and the amount of ammonium nitrate formed is significant only 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 implies that sulfur dioxide, oxides of nitrogen, and ammonia must be treated as a coupled system and cannot be dealt with separately. Reducing sulfur dioxide emissions might actually result in ammonium nitrate increases which exceed the reductions in ammonium sulfate where the availability of ammonia is limited. In areas where sulfates and nitrates are present, it is necessary to measure the gaseous ammonia and nitric acid precursors to determine whether or not this is a possibility (e.g., Watson *et al.*, 1994a).

1.3   Guideline Objectives

While the NAAQS address only the mass concentrations of PM_{10}, there are ample reasons to understand the chemical constituents of that mass. The first is that such chemical characterization is needed to apportion PM_{10} to its sources using receptor models. The second is to evaluate the effects of emissions reductions on PM_{10} mass. Finally, health effects may be different for different chemical compounds. The PM_{10} mass concentration standard provides an easily measured surrogate for a composite of chemical compositions, but these compositions vary substantially depending on sampling site and time of year for the same mass concentration. It is probable that chemical composition will be carefully studied as part of the re-assessment of the NAAQS standards for suspended particles.

These guidelines describe technologies for the measurement of chemical components of PM_{10} on filter deposits. The objectives of this report are to:

- Describe practical PM_{10} sampling methods which are compatible with chemical analysis methods and compliance assessment.

- Describe accurate, precise, and cost-effective chemical analyses which can be applied to PM_{10} filter deposits.

- Develop practical approaches for PM_{10} sampling and analysis which are tailored to the solution of specific PM_{10} problems.

1.4   Overview and Guide to Report

Section 1 states the background and objectives of these PM_{10} sampling and analysis guidelines. Section 2 summarizes PM_{10} sampling methods. It lists sampling system requirements and filter media, and reviews the reference and equivalent sampling methods for

PM_{10}. Section 3 enumerates the chemical analysis options for chemicals measured on PM_{10} filter, typical detection limits, and sample requirements for each method. PM_{10} sampling and analysis options are offered in Sections 4. Report summary is given in Section 5. A comprehensive bibliography is presented in Section 6. Appendix A contains summaries of existing data sets which can be used to evaluate PM_{10} problems and to assist in the design of future studies.

2.0 PM₁₀ SAMPLING METHODS FOR CHEMICAL ANALYSIS

Chemical analysis of filter deposits **cannot** be separated from the methods used to obtain the sample. Many scientists obtain long records of PM_{10} filter samples following normal U.S. EPA procedures, store them in envelopes or file boxes for many years, then send them to a general chemical laboratory to obtain some numbers for different chemical constituents. These scientists are usually disappointed when they choose to make a regulatory decision and have to defend these numbers as representing what was in the air at the time of sampling. Sampling for chemical analysis requires stringent attention to filter media, sample handling, sample storage, and to the sampler used to obtain the filter deposits. When chemical analysis is intended for source apportionment receptor modeling, sequential sampling systems, denuders, dichotomous samplers, or saturation samplers may be needed. When chemical analysis of PM_{10} samples is anticipated, the first consideration should be how the samples will be obtained.

Ambient aerosol sampling is performed for a variety of purposes, and PM_{10} mass determination for compliance with standards is only one of them. A sampling system designed for one purpose does not necessarily meet the needs for other or additional purposes. The standard sampling methods applied to PM_{10} for mass determination need to be enhanced when chemical analyses are desired. This section describes the sampling options which are available to meet different requirements and the enhancements which are needed when chemical characterization of the samples is intended. Mass, elements, carbon, and soluble ions are the most commonly measured constituents of PM_{10}.

To determine compliance, a reference or equivalent PM_{10} sampling method must be applied. The requirements for reference or equivalence status are outlined in the Federal Register (1987d), and Table 2-1 lists the reference and equivalent methods which have been approved to date.

Watson and Chow (1993) observed that commercial systems are not entirely adequate for many sampling programs, though well-tested and commercially-available size-selective inlets, sampling manifolds, filter holders, flow controllers, and pumps can often be assembled into cost-effective and reliable systems which are tailored to specific measurement objectives. Several of these systems, with references describing them and the projects in which they were applied, are identified in Table 2-2. These samplers have been designed specifically to acquire deposits on filters which can be submitted to chemical analyses. They are sometimes operated alongside reference or equivalent samplers to gain a better understanding of the causes of elevated PM_{10} concentrations. All of these samplers consist of sampling inlets, sampling surfaces, filter holders, and flow movers.

2.1 Sampling Inlets

Sampling inlets are intended to remove particles which exceed a specified aerodynamic particle diameter. Hering (1989) identifies a comprehensive list of commercially-available size-

Table 2-1

PM_{10} reference and equivalent sampling methods

Designation No.	Sampler Description	Reference/ Equivalent Method[a]	Federal Register Citation	Notice Date
RFPS-1087-062	Wedding & Associates' PM_{10} Critical Flow High-Volume Sampler (using Wedding PM_{10} inlets and Wedding & Associates' critical flow device)	Reference Method	Vol. 52, 37366	10/06/87
RFPS-1287-063	Sierra-Andersen (SA) or General Metal Works (GMW) Model 1200 PM_{10} High-Volume Air Sampler System (using SA- or GMW-1200 PM_{10} size-selective inlets and any of the following air samplers: SAUV-10H, SAUV-11H, GMW-IP-10, GMW-IP-10-70, GMW-IP-10-801, GMW-IP-10-8000).	Reference Method	Vol. 52, 45684 Vol. 53, 1062	12/01/87 01/15/88
RFPS-1287-064	Sierra-Andersen or General Metal Works Model 321-B PM_{10} High-Volume Air Sampler System (using SA- or GMW-321-B PM_{10} size-selective inlets and any of the following air samplers: SAUV-10H, SAUV-11H, GMW-IP-10, GMW-IP-10-70, GMW-IP-10-801, GMW-IP-10-8000).	Reference Method	Vol. 52, 45684 Vol. 53, 1062	12/01/87 01/15/88

Table 2-1 (continued)
PM_{10} reference and equivalent sampling methods

Designation No.	Sampler Description	Reference/ Equivalent Method[a]	Federal Register Citation	Notice Date
RFPS-1287-064	Sierra-Andersen or General Metal Works Model 321-C PM_{10} High-Volume Air Sampler System (using SA- or GMW-321-C PM_{10} size-selective inlets and any of the following air samplers: SAUV-10H, SAUV-11H, GMW-IP-10, GMW-IP-10-70, GMW-IP-10-801, GMW-IP-10-8000).	Reference Method	Vol. 52, 45684 Vol. 53, 1062	12/01/87 01/15/88
RFPS-0389-071	Oregon DEQ Medium-Volume PM_{10} Sampler (using SA-254 PM_{10} Inlet, and 47 mm Teflon-membrane and quartz-fiber filters. Samples are collected simultaneously onto two substrates and can be programmed for up to six days of unattended operation and allow automatic filter-sequencing as filter overloading occurs).	Reference Method	Vol. 54, 12273	03/24/89
RFPS-0389-073	Sierra-Andersen Models SA-241 and SA-241M or General Metal Works Models G241 and GA-241M PM_{10} Dichotomous Samplers (using SA-246B or G246 PM_{10} inlet, 2.5 μm virtual impactor assembly, and 37 mm fine and coarse filter holders.)	Reference Method	Vol. 54, 31247	07/27/89

Table 2-1 (continued)
PM$_{10}$ reference and equivalent sampling methods

Designation No.	Sampler Description	Reference/ Equivalent Method[a]	Federal Register Citation	Notice Date
EQPM-0990-076	Andersen Instruments Model FH621-N PM$_{10}$ Beta Attenuation Monitor (using SA-246b PM$_{10}$ inlet, FH101 vacuum pump assembly, FH102 accessory kit, FH107 roof flange kit, and FH125 zero and span PM$_{10}$ mass flow calibration kit.)	Equivalent Method	Vol. 55, 38387	09/18/90
EQPM-1090-079	Rupprecht & Patashnik TEOM Series 1400a PM$_{10}$ Monitor (using SA-246b PM$_{10}$ inlet) and internal tapered element oscillating microbalance.	Equivalent Method	Vol. 55, 43406	10/29/90

[a] Code of Federal Regulations (1988). (40 CFR, Part 50, Appendix J).

Table 2-2

Examples of ambient aerosol sampling systems assembled for major studies[·]

Sampling System	Inlet and Particle Size (μm)	Flow Rate (lpm)	Sampling Surface	Filter Holders	Filter Media	Features	Descriptive Reference
Stacked Filter Unit (SFU)	Large-pore etched polycarbonate filters (2 - 3 μm)	10	Polycarbonate	Nuclepore	47mm etched poly-carbonate membrane; 47mm Teflon membrane	Uses large-pore etched polycarbonate filters as $PM_{2.5}$ inlet	Cahill et al., 1990
Sequential Filter Sampler (SFS)	SA-254 medium-volume inlet (PM_{10})	20 out of 113	Aluminum	Nuclepore polycarbonate open-face	47mm Teflon membrane; 47mm quartz fiber	Option to add nitric acid denuders in the sampling stream. Sequential sampling.	Watson et al., 1991b
	Bendix 240 cyclone ($PM_{2.5}$)	20 out of 113	Teflon-coated aluminum	Nuclepore polycarbonate open-face	47mm Teflon membrane; 47mm quartz fiber; 47mm nylon membrane; 47mm impregnated cellulose fiber		
Western Region Air Quality Study (WRAQS) Sampler	SA-320 high-volume inlet (PM_{15})	113 out of 1,130	Aluminum and copper	Nuclepore polycarbonate in-line	47mm Teflon membrane; 47mm quartz fiber		Tombach et al., 1987
	Bendix 240 cyclone	113	Aluminum and copper	Nuclepore polycarbonate in-line	47mm Teflon membrane; 47mm quartz fiber		
Size Classifying Isokinetic Sequential Aerosol (SCISAS) Sampler	SA-320 high-volume inlet (PM_{15})	113 out of 1,130	Aluminum and polyvinyl chloride	Nuclepore polycarbonate open-face	47mm Teflon membrane; 47mm quartz fiber	Sequential sampling.	Rogers et al., 1989

Table 2-2 (continued)

Examples of ambient aerosol sampling systems assembled for major studies

Sampling System	Inlet and Particle Size (μm)	Flow Rate (lpm)	Sampling Surface	Filter Holders	Filter Media	Features	Descriptive Reference
SCISAS (continued)	Bendix 240 cyclone (PM$_{2.5}$)	113 out of 1,130	Stainless steel and aluminum	Nuclepore polycarbonate open-face	47mm Teflon membrane 47mm quartz fiber		
Interagency Monitoring of Protected Visual Environments (IMPROVE) Sampler	Wedding low-volume inlet (PM$_{10}$)	18	Aluminum	Nuclepore polycarbonate open-face	25mm Teflon membrane 25mm quartz fiber	Nitric acid denuders can be placed in inlet line.	Eldred *et al.*, 1990
	Modified AIHL cyclone (PM$_{2.5}$)	24	Aluminum	Nuclepore polycarbonate open-face	25mm Teflon membrane 25mm quartz fiber 47mm nylon membrane		
California Institute of Technology Sampler	SA-246 low-volume inlet (PM$_{10}$)	16.7	Stainless steel and aluminum	Gelman stainless steel in-line	47mm Teflon membrane 47mm quartz fiber		Solomon *et al.*, 1988; Solomon *et al.*, 1989
	AIHL cyclone	22	Teflon-coated aluminum and glass	Gelman stainless steel in-line	47mm Teflon membrane 47mm quartz fiber 47mm nylon membrane		

Table 2-2 (continued)

Examples of ambient aerosol sampling systems assembled for major studies

Sampling System	Inlet and Particle Size (μm)	Flow Rate (lpm)	Sampling Surface	Filter Holders	Filter Media	Features	Descriptive Reference
Southern California Air Quality Study (SCAQS) Sampler	SA-254 medium-volume inlet (PM$_{10}$)	35 out of 113	Stainless steel and aluminum	Gelman stainless steel in-line	47mm Teflon membrane, 47mm quartz fiber	Option to add 20 cm flow homogenizer.	Fitz et al., 1989
	Bendix 240 cyclone (PM$_{2.5}$)	35 out of 113	Teflon-coated aluminum and Teflon	Gelman Stainless steel and Savillex PFA Teflon in-line	47mm Teflon membrane, 47mm quartz fiber, 47mm impregnated quartz fiber, 47mm nylon membrane, 47mm etched poly-carbonate	Option to add 20 cm flow homogenizer.	
California Acid Deposition Monitoring Program (CADMP) Dry Deposition Sampler	SA-245 medium-volume inlet (PM$_{10}$)	20 out of 113	Aluminum	Savillex open-face	47mm Teflon membrane, 47mm impregnated cellulose fiber	Includes nitric acid denuders. Sequential sampling.	Chow et al., 1991
	Teflon-coated Bendix 240 cyclone (PM$_{2.5}$)	20 out of 113	PFA Teflon-coated aluminum	Savillex PFA Teflon open-face	47mm Teflon membrane, 47mm nylon membrane		
Versatile Ambient Particulate Sampler (VAPS)	Teflon-coated rain cap (PM$_{10}$) and virtual impactor (PM$_{2.5}$)	33	Teflon-coated aluminum	University Research Glassware open-face	47mm Teflon membrane, 47mm etched polycarbonate membrane, 47mm quartz fiber	Includes annular denuders to capture nitric acid, nitrous acid, and sulfur dioxide; and polyurethane foam (PUI) to collect organic compounds.	Stevens et al., 1993

Table 2-2 (continued)

Examples of ambient aerosol sampling systems assembled for major studies

Sampling System	Inlet and Particle Size (μm)	Flow Rate (lpm)	Sampling Surface	Filter Holders	Filter Media	Features	Descriptive Reference
Harvard/EPA Annular Denuder System (HEADS)	Glass impactor (PM$_{2.5}$)	10	Glass	Sierra-Andersen open-face ring	37mm Teflon membrane 37mm impregnated quartz fiber	Includes sodium carbonate coated denuders to collect acidic gases (eg, nitric acid, nitrous acid, sulfur dioxide, organic acids) and citric acid coated denuders to collect ammonia.	Koutrakis et al., 1988; 1991; 1992
New York University Medical Center/ Sequential Acid Aerosol Sampling System (NYUMC/SAASS)	Teflon-coated glass (PM$_{2.5}$)	4	Teflon-coated glass.	Sierra-Andersen open-face rings	37mm Teflon membrane 37mm nylon membrane	Sequential sampling	Thurston et al., 1992
BYU Organic Sampling System (BOSS)	Teflon-coated cyclone (PM$_{2.5}$)	140 lpm through inlet and 35 lpm per channel	Teflon-coated stainless steel	University Research glass filter pack (Model 2000-30F)	47mm Quartz-fiber 47mm activated charcoal impregnated filter (CIF)	A multichannel diffusion denuder sampler to determine semi-volatile organic compounds	Eatough et al., 1993a, 1993b; Eatough, 1993
Big BOSS	Virtual impactor inlets with 2.5 μm, 0.8 μm, and 0.4 μm cutpoint	1,130 lpm through inlet, with 11, 60, 93, and 200 lpm per channel	Teflon-coated stainless steel	University Research Glass filter pack (Model 2000-30F)	47mm Quartz-fiber 47mm activated charcoal impregnated filter (CIF)	A multichannel diffusion denuder sampler to determine semi-volatile organic compounds	Tang et al., 1994

selective inlets and provides photographs of several of them. These inlets are characterized by sampling effectiveness curves which show the fraction of spherical particles of unit density penetrating through the inlet to the filter surface (Watson *et al.*, 1983; Wedding and Carney, 1983). Figure 2-1 shows an example of these curves. These curves are measured by presenting known concentrations of particles of selected aerodynamic diameters to the inlet, often at different wind velocities in a wind tunnel (Federal Register, 1987d), and measuring the fraction of particles which are transmitted through the inlet. This sampling effectiveness is characterized by a 50% cut-point (d_{50}), the diameter at which half of the particles in the ambient air pass through the inlet, and a slope (or geometric standard deviation), which is the square root of the ratio of the diameter of particles excluded by the inlet with an 84% efficiency (d_{84}) to the diameter of particles removed with a 16% efficiency (d_{16}). A slope of unity indicates a step-function, while a slope which exceeds two does not provide a definitive size-cut. Slopes of 1.3 to 1.5 are considered to provide well-defined particle size fractions.

Acceptable size-selective inlets must possess particle transmission characteristics which are independent of wind speed and wind direction. The sampling efficiency of the rectangular peaked-roof inlet of the high-volume (HIVOL) sampler for total suspended particulate matter (TSP, particles with nominal aerodynamic diameters of 30 to 40 μm) was found to have a large variability in sampling effectiveness in response to these environmental variables (Wedding *et al.*, 1977; McFarland *et al.*, 1980). Table 2-3 lists the size-selective inlets which have undergone wind-tunnel testing with the reference or equivalent sampling systems to which they are attached.

The 50% cut-point varies with flow rate through the inlet. These flow rates fall into ranges appropriate for high-volume (~1000 ℓ/min) sampling (Wedding *et al.*, 1977; McFarland *et al.*, 1980; Wedding and Weigand, 1985), medium-volume (~100 ℓ/min) sampling (Olin and Bohn, 1983; Wedding *et al.*, 1983), and low-volume (~10 to 20 ℓ/min) sampling (McFarland *et al.*, 1978; John and Reischl, 1980; John *et al.*, 1983a, 1983b). The medium- and high-volume inlets are especially useful when samples are taken in parallel on several substrates, since flow rates can be kept high enough to obtain an adequate deposit for analysis. Several inlets can be placed in a series, in the form of a "cascade impactor," to obtain more detailed size distributions of chemical concentrations (Berner *et al.*, 1979; Hering *et al.*, 1979a, 1979b; Marple *et al.*, 1981; Raabe *et al.*, 1988).

Ambient sampling inlets operate on the principles of direct impaction, virtual impaction, cyclonic flow, selective filtration, and elutriation. The direct impaction systems consist of a set of circular jets positioned above an impaction plate. The impactor dimensions are selected to allow the particles which exceed the desired cut-point to strike the plate, and those which are less than the cut-point to follow the airstream which passes the plate. John and Wang (1991) proved that re-entrainment and disaggregation of particles occurs on the impaction surface of high-volume impactor inlets, and these surfaces are often oiled or greased to assure specified sampling effectiveness. Woods *et al.* (1986) conducted extensive wind tunnel tests on clean and dirty, greased and ungreased high-volume PM_{10} inlets which showed a positive shift in d_{50} for the impactors and a negative shift for cyclones. These results imply that frequent inlet cleaning

Figure 2-1. Sampling characteristics of the Sierra Andersen Model 321A inlet (A) and the Wedding IP_{10} inlet (B) at a wind speed of 8 km/hr (McFarland and Ortiz, 1984a; 1984b).

Table 2-3
Summary of size-selective inlets for ambient aerosol samplers

Inlet Identifier & Manufacturer	d_{50} (μm); slope	Flow Rate (lpm)	Operating Principle	Sampling Effectiveness Reference	PM_{10} Reference or Equivalence Reference Number	Comments
High-Volume						
SA[a] or GMW[b] Model 320	15; 1.5	1,133	Impactor	McFarland et al., 1980	NA	Single stage, no greased shim
SA or GMW Model 1200	9.7; 1.40	1,133	Impactor	McFarland and Ortiz, 1987	RFPS-1287-063 FR[e] 12/1/87, p.45683	Single-stage with greased shim (body hinged)
SA or GMW Model 321-A	10.2; 1.45	1,133	Impactor	McFarland and Ortiz, 1984a	RFPS-1287-065 FR 12/1/87, p.45683 (named 321-C)	Single-stage with greased shim
SA or GMW Model 321-B	9.7; 1.40	1,133	Impactor	McFarland and Ortiz, 1987; VanOsdell and Chen, 1990; Woods et al., 1986	RFPS-1287-064 FR 12/1/87 p.45683	Two-stage with greased shim
Wedding IP$_{10}$ (PM$_{10}$)	9.6; 1.37	1,130	Cyclonic Flow	Wedding and Weigand, 1985; Woods et al., 1986	RFPS-1087-062 FR 10/6/87 p.3736	

Table 2-3 (continued)
Summary of size-selective inlets for ambient aerosol samplers

Inlet Identifier & Manufacturer	d_{50} (μm); slope	Flow Rate (lpm)	Operating Principle	Sampling Effectiveness Reference	PM$_{10}$ Reference or Equivalence Reference Number	Comments
High-Volume (continued)						
GMW Wedding PM$_{10}$	8.8; 1.7	1,130	Cyclonic Flow	Woods et al., 1986	None	
Medium-Volume						
SA 254 Medium Volume PM$_{10}$ Sampler	10; 1.6[d]	113	Impactor	Olin and Bohn, 1983	RFPS-0389-071 FR 3/24/87, p.12273)	Designated for Oregon only
Wedding Medium Flow	9.5; 1.12	113	Cyclonic Flow	Wedding et al., 1983	None	
Bendix 240 Cyclone	2.5; 0.82	113	Cyclonic Flow	Chan and Lippman, 1977; Mueller et al., 1983	None	

Table 2-3 (continued)
Summary of size-selective inlets for ambient aerosol samplers

Inlet Identifier & Manufacturer	d_{50} (μm); slope	Flow Rate (lpm)	Operating Principle	Sampling Effectiveness Reference	PM_{10} Reference or Equivalence Reference Number	Comments
Low-Volume						
SA246b	10.2; 1.41	16.7	Virtual Impactor	McFarland and Ortiz, 1984c; Van Osdell and Chen, 1990	RFPS-0789-073 FR 7/27/89, p.31247 EQPM-0990-076 FR 9/18/90, p.38387 EQPM-1090-079, FR 10/29/90, p.43406	Used on dichotomous sample, beta attenuation monitor, and tapered element oscillating microbalance
Sierra-Andersen 244 and 245		15	Virtual Impactor	McFarland et al., 1978; Olin, 1978	None	
Wedding TP[10]	9.9; 0.76[d]	16.67	Cyclonic Flow	Wedding et al., 1982	EQPM-0391-081 FR 3/5/91, p.9216	
Bendix Unico 18	2.5; 1.83[d]	18	Cyclonic Flow	Chan and Lippman, 1977	None	
AIHL Cyclone	2.5; 1.38[e] 3.5; 1.40[e]	21.7 15.4	Cyclonic Flow	John and Reischl, 1980	None	

Table 2-3 (continued)
Summary of size-selective inlets for ambient aerosol samplers

Inlet Identifier & Manufacturer	d_{50} (μm); slope	Flow Rate (lpm)	Operating Principle	Sampling Effectiveness Reference	PM_{10} Reference or Equivalence Reference Number	Comments
Low-Volume (continued)						
AIHL Cyclone	2.2; 1.87	26.6		John and Reischl, 1980	None	
Stacked Filter Unit	2 to 3	10	Selective Filtration	John et al., 1983; Cahill et al., 1990	None	

[a] Sierra-Andersen.

[b] General Metal Works.

[c] FR = Federal Register.

[d] slope = $(\sqrt{d_{84}/d_{16}})$, as defined in text.

[e] slope is estimated based on $\sqrt{d_{90}/d_{10}}$.

and re-greasing are essential to maintaining well-defined size fractions using the high volume inlets. Re-entrainment of dust particles from the inlet into the air stream will positively bias the results of mass and chemical analyses on the sampled filters. The Sierra-Andersen SA-1200 inlet has a hinged lid which allows easy access for cleaning and greasing. The SA-246 inlet can be unscrewed for access to the impaction plate. The SA-254 inlet requires the removal and replacement of a dozen small screws for cleaning and is not as convenient to clean as the other inlets. The non-reference impactor inlet used on portable survey samplers can be easily removed for cleaning between each sample. This is absolutely necessary for this unit because the area of the impaction plate is too small to accommodate a large buildup of removed particles.

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 another sampling substrate. This principle is used effectively in the Sierra-Andersen dichotomous sampler, described below, to separate particles into $PM_{2.5}$ and coarse particle (PM_{10} minus $PM_{2.5}$) size fractions.

Cyclonic flow inlets use an impeller to impart a circular motion to air entering the inlet. This air enters a cylindrical tube oriented perpendicular to the impellers and the centripetal force on the particles in the airstream moves them toward the walls of this tube. Those particles reaching the tube wall adhere to it, often with the help of an oil or grease coating. The Wedding cyclonic flow inlets have an oiled inner surface and a collection area at the bottom of the cyclone. Heavy particles which do not adhere to the cyclone wall settle into this collection area. The Wedding IP_{10} inlet has an access port through which a cleaning brush may be inserted.

Selective filtration takes advantage of the uniform pore size and known sampling effectiveness of etched polycarbonate filters manufactured by Nuclepore Corporation. Eight micrometer pore size filters collect particles by interception and impaction in the vicinity of the pores to provide 50% cut-points for particles between 2 and 3 μm at flow rates of ~10 ℓ/min. A ~0.4 μm pore size filter is place behind the 8 μm filter to collect the transmitted particles. Cahill et al. (1990) observed re-entrainment of large, dry particles from the front filter and developed a greasing method to reduce this artifact. The sampling effectiveness curve for this sampler has a broad slope (Buzzard and Bell, 1980), and the method does not provide as distinctive a separation between $PM_{2.5}$ and larger particle size ranges as the direct impaction, virtual impaction, or cyclonic inlets. No selective filtration inlets have achieved reference method status.

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. This type of inlet was originally mated to the virtual impactor dichotomous sampler to provide a 15 μm cut-point. Wind tunnel tests (Wedding et al., 1980) found the cut-point to be highly dependent on wind speed, and this inlet was later replaced by the SA-246 PM_{10} direct impaction inlet. None of the elutriator inlets have reference method status.

2.2   Sampling Surfaces

In some cases, it is desirable to measure the gaseous precursors of secondary aerosols such as ammonium nitrate and ammonium sulfate. This is necessary when sampling is done for input to equilibrium receptor models to determine whether gaseous ammonia or nitric acid limits the formation of ammonium nitrate in the atmosphere (Watson *et al.*, 1994a). Most samplers are manufactured from aluminum (which later oxidizes), plastic (polycarbonate or polyvinylchloride), galvanized steel or stainless steel. These sampling surfaces adsorb or react with gases and particles, thereby preventing their collection on sampling substrates (Hering *et al.*, 1988; John *et al.*, 1986). This is especially the case for nitric acid vapor which sticks to nearly everything. Removal of nitric acid in an inlet or sampling duct can change the gas/particle equilibrium of particulate ammonium nitrate, causing this substance to dissociate into ammonia and nitric acid gases, thereby biasing measurement results. This is also true for some volatile organic species.

In the case of denuder-type sampling systems for nitric acid (Stevens *et al.*, 1990) and organics (Eatough *et al.*, 1990; Fitz *et al.*, 1989), a surface which <u>does</u> adsorb gases but allows particles to pass is desired. Denuders are constructed with dimensions such that over 90% of selected gaseous concentrations will diffuse to the sampler surface while less than 10% of the particles will deposit on the surface. Examples of denuder systems are presented in Figure 2-2. The surface can be coated with an absorbent, which is then extracted and analyzed for the desired gaseous species. In the case of all other sampling components, an inert surface which <u>does not</u> act as a sink for atmospheric constituents is desired.

John *et al.* (1986) have tested different materials with respect to their affinity for nitric acid. These studies indicate that surfaces coated with perfluoroalkoxy (PFA) Teflon can pass nitric acid with 80% to 100% efficiency. John *et al.* (1986) also observed that the aluminum surfaces common to many samplers and inlets have an almost infinite capacity for adsorbing nitric acid vapor while transmitting particles with high efficiency. Prior to use in sampling, PFA Teflon surfaces should be washed with a dilute solution of nitric acid to season them. Little has been published concerning the affinity of other gaseous components to sampler surfaces. Additional tests need to be conducted for volatile organic particles, ammonia, sulfur dioxide, and other gases which are often acquired on impregnated substrates.

Plastic surfaces can acquire an electrical charge which might attract suspended particles to them, though the dimensions of most ambient sampling systems are sufficiently large that this attraction is negligible (Rogers *et al.*, 1989).
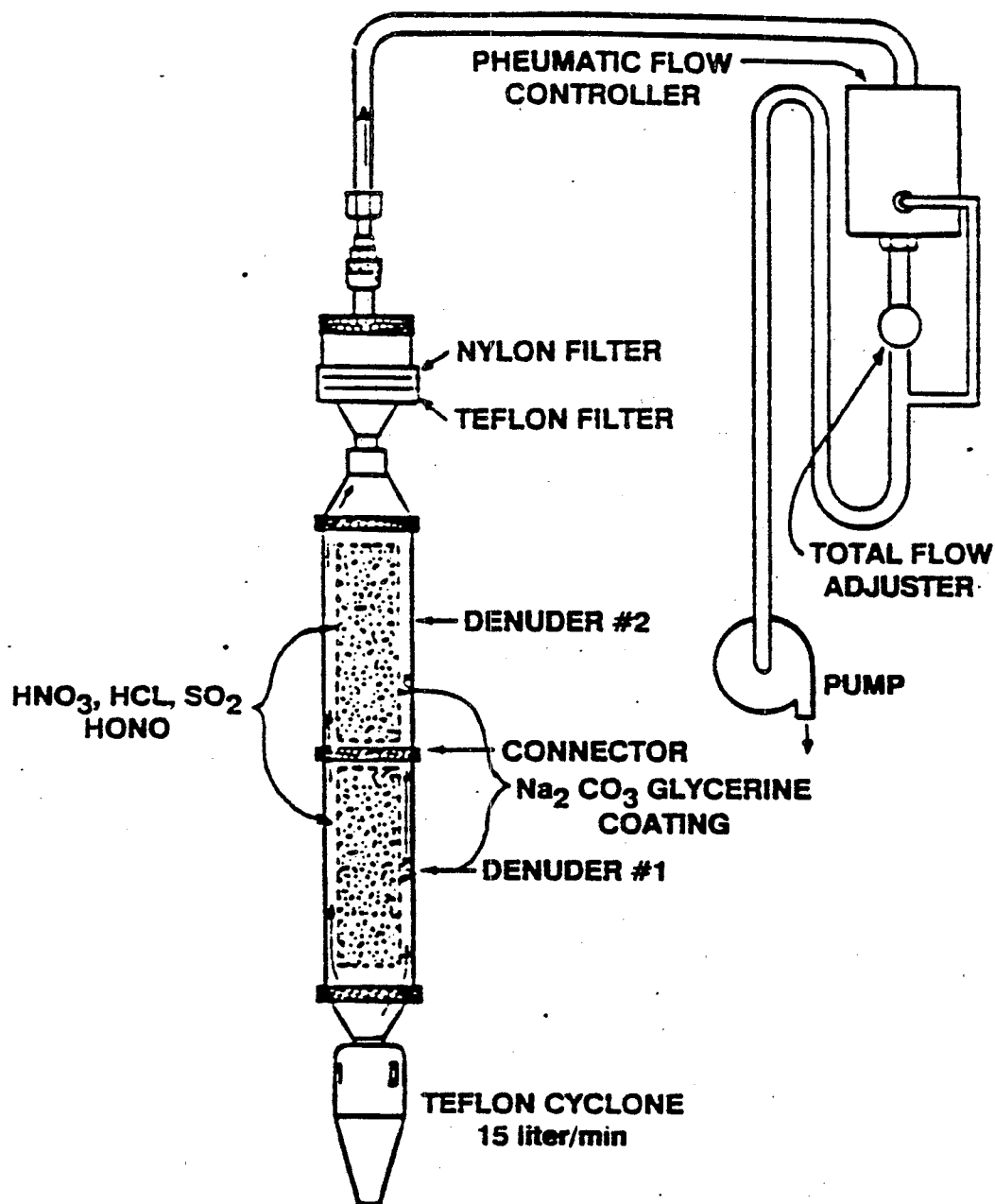
Figure 2-2.   Example of an ambient aerosol sampler with annular denuders (Stevens, 1986).

2.3 Filter Media

The choice of filter media results from a compromise among the following filter attributes:

- **Mechanical Stability:** The filter must remain in one piece, lie flat in the sampler filter holder, and provide a good seal with the sampling system to eliminate leaks. A brittle filter material may flake and negatively bias mass measurements. If the filter is to be divided into more than one portion, the filter must allow precise and accurate sectioning. Pure quartz-fiber filters are very brittle, and portions of their edges often become attached to the filter holder. Quartz-fiber filters must be handled carefully when mass measurements are desires. Ringed Teflon membranes are stretched between a ring, and these curl when they are cut in half or when a punch is removed. Ringed Teflon-membrane filters should not be used when filter sectioning is required.

- **Temperature Stability:** The filter must retain its porosity and structure in the presence of temperatures typical of the sampled airstream and of the analysis methods. Plastic filters, for example, may melt in the presence of hot exhaust from an industrial source. Filters that melt during thermal carbon analysis can encapsulate the deposit, making it unavailable for combustion and detection. All of the membrane filters have a plastic base, and should not be used to sample air streams with temperatures exceeding ~50°C. All but the pure quartz-fiber filters will melt when subjected to the temperatures commonly applied for thermal carbon analysis.

- **Chemical Stability:** The filter should not interact chemically with the deposit, even when submitted to strong extraction solvents. It should not adsorb gases that are not intended to be measured. When gas collection is desired, the filter material should adsorb those gases at near 100% efficiency. Coutant (1977), Spicer and Schumacher (1977), and Meserole et al. (1976; 1979) tested a variety of filter materials for these species and found substantial adsorption for all of these species on glass- fiber filters, with a minor adsorption of nitric acid on quartz-fiber filters. Eatough et al. (1990) and McDow and Huntzicker (1990) demonstrate evidence of organic vapor adsorption on quartz-fiber filters. Demuynck (1975) and Charell and Hawley (1981) show the large effect on mass of water vapor adsorption on cellulose- fiber filters.

- **Particle Sampling Efficiency:** The filter must collect most of the particles in the air being drawn through it, regardless of particle size or flow rate. Some loosely-woven fiber filters or membrane filters with large pores allow an excessive fraction of particles to pass through the filter with the air stream. Lippmann (1989) and Lee and Ramamurthi (1993) tabulate the sampling efficiencies for several filter media with different pore sizes and flow rates. Most filter materials allow less than 1% of the submitted particles to be transmitted, regardless of particle size. The exceptions are cellulose-fiber filters and etched polycarbonate-membrane filters, which have

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efficiencies lower then 50% for some porosities, pore sizes, and particle sizes. Lower porosities and pore sizes generally result in higher sampling efficiencies. These characteristics also increase flow resistance, however.

- **Flow Resistance and Loading Capacity:** Flow resistance refers to the amount of pressure drop across a filter required for a given flow rate. The larger the pressure difference required for a constant flow rate, the greater the flow resistance. As the filter acquires particles, its flow resistance increases because pores and fibers become clogged. Lippmann (1989) and Lee and Ramamurthi (1993) tabulate these resistances for several different filter types. Membrane filters have higher flow resistances and lower loading capacities than fiber filters. Lower resistances and higher capacities can be attained by increasing the filter size, increasing the porosity or pore size, increasing the number of pores (in a membrane filter), and decreasing the filter thickness. Decreased flow resistance is often gained at the expense of decreased sampling efficiency.

- **Blank Concentrations:** The filter material 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. Blank levels will be measured as if they were part of the particulate deposit.

- **Cost and Availability:** Lee and Ramamurthi (1993) provide cost comparisons for different filter material, but these vary substantially with the filter size, the quantity purchased, and the current competition. Ringed Teflon-membrane filters are typically the most costly (~$4.50 for each 47 mm diameter filter), with cellulose-fiber and glass-fiber filters (~$0.25 for each 47 mm diameter filter) being the least expensive. The cost of the filter is a small fraction of the cost of sampling and analysis, and the validity of the measurement should not be compromised because one filter is "cheaper" than another. Filters are not always kept in stock, and even when they are, the lead times for acceptance testing and preparation can require one month or more. Filters should be procured well in advance of a monitoring program and in sufficient quantity to last the duration of the study.

U.S. EPA filter requirements for PM_{10} sampling specify 0.3 μm dioctyl phthalate (DOP) sampling efficiency in excess of 99%, weight losses or gains due to mechanical or chemical instability of less than a 5 μg/m^3 equivalent, and alkalinity of less than 25 microequivalents/gm to minimize absorption of sulfur dioxide and nitrogen oxides (Federal Register, 1987b). These are only the minimal requirements for samples which require chemical analyses. The most commonly used filter media for atmospheric particle and gas sampling are cellulose-fiber, glass-fiber, Teflon-coated glass-fiber, Teflon-membrane, etched polycarbonate-membrane, quartz-fiber, and nylon-membrane. None of these materials is perfect for all purposes. Table 2-4 summarizes different filter substrates and their relevant physical and chemical characteristics.

Table 2-4

Aerosol filter substrates and relevant physical and chemical characteristics

Filter Type, Major Manufacturer, and Example	Compatible Analysis Methods[a]	Physical Characteristics	Chemical Characteristics
Ringed Teflon membrane, Gelman (Ann Arbor, MI), Teflo®, R2PJ047, R2PJ037	Gravimetry, light transmission, XRF, PIXE, INAA, AAS, ICP/AES, IC, AC	• Thin membrane stretched between polymethylpentane ring. • White surface, nearly transparent. • Minimal diffusion of transmitted light. • Cannot be accurately sectioned. • 1.2, 2.0, and 3.0 μm pore sizes. • Melts at ~60°C. • High flow resistance.	• Usually low blank levels, but several contaminated batches have been found. Made of carbon-based material, so inappropriate for carbon analysis. • Inert to adsorption of gases. • Low blank weight.
Pure quartz-fiber, Pallflex (Putnam, CT), 2500 QAT-UP	ICP/AES, IC, AC, T, TOR, TMO, TOT	• Mat of pure quartz fibers. • White opaque surface, diffuses transmitted light. • Edges flake in most filter holders. • Melts at >900°C. • Moderate flow resistance.	• Extensively washed during manufacture—low blank levels for ions. • Contains large and variable quantities of Al and Si. Some batches contain other metals. • Passively adsorbs organic vapors. Adsorbs little HNO_3, NO_2, and SO_2. • High blank weight.
Mixed quartz fiber, Whatman (Hillsboro, OR), QM/A #1861865	Gravimetry, XRF, PIXE, AA, ICP/AES for some metals, IC, AC, T, TOR, TMO, TOT	• Quartz (SiO_2) fibers with ~5% borosilicate content. • White opaque surface, diffuses transmitted light. • Some batches can melt at ~500°C. Effects on thermal carbon analysis are unknown. • Becomes brittle when heated. • Low flow resistance.	• Contains large and variable quantities of Na, Al, and Si in all batches. Variable levels of other metals are found in many batches. • Passively adsorbs organic vapors. Adsorbs little HNO_3, NO_2, and SO_2. • Low hygroscopicity. • High blank weight.

Table 2-4 (continued)
Aerosol filter substrates and relevant physical and chemical characteristics

Filter Type, Major Manufacturer, and Example	Compatible Analysis Methods[a]	Physical Characteristics	Chemical Characteristics
Backed Teflon membrane, Gelman (Ann Arbor, MI), "Zefluor", F2996-25	Gravimetry, XRF, PIXE, INAA, AAS, ICP/AES, IC, AC	• Thin membrane mounted on thick polypropylene backing. • White opaque surface, diffuses transmitted light. • Melts at ~60°C. • High flow resistance.	• Usually low blank levels. Made of carbon-based material, so inappropriate for carbon analysis. • Inert to adsorption of gases. • Higher background levels for XRF and PIXE than Teflo® owing to greater filter thickness. • Low hygroscopicity. • High blank weight.
Cellulose fiber, Whatman (Hillsboro, OR), #1441047	Gravimetry, XRF, PIXE, INAA, AAS, ICP/AES, IC, AC	• Thick mat of cellulose fibers, often called a "paper" filter. • White opaque surface, diffuses transmitted light. • Low sampling efficiencies, <70% for some variations of this filter. • Burns at elevated temperatures (exact temperature depends on nature of particle deposit). • Low flow resistance.	• Low blank levels. Made of carbon-based material, so inappropriate for carbon analysis. • Adsorbs gases, especially water vapor. • Most appropriate for adsorbing gases such as HNO_3, SO_2, NH_3, and NO_2 when impregnated with reactive chemicals. • High blank weight.
Nylon membrane, Gelman (Ann Arbor, MI), #66509	IC, AC	• Thin membrane of pure nylon. • White opaque surface, diffuses transmitted light. • 1 μm pore size. • Melts at ~60°C. • High flow resistance.	• High HNO_3 collection efficiency. • Adsorbs low levels of NO, NO_2, PAN, and SO_2. • Low blank weight.

Table 2-4 (continued)

Aerosol filter substrates and relevant physical and chemical characteristics

Filter Type, Major Manufacturer, and Example	Compatible Analysis Methods[a]	Physical Characteristics	Chemical Characteristics
Polycarbonate capillary pore membrane, Nuclepore (Pleasanton, CA), #111129.	XRF, PIXE, electron-microscopy	• Smooth, thin, polycarbonate surface with straight through capillary holes. • Light green surface, nearly transparent. • Minimal diffusion of transmitted light. • Low sampling efficiencies, <70% for some larger pore sizes. • Retains static charge. • 0.2, 0.3, 0.4, and 8.0 μm uniform pore sizes. • Melts at ~60°C. • Moderate flow resistance.	• Low blank levels. (Made of carbon-based material, so inappropriate for carbon analysis.) • Low hygroscopicity. • Low blank weight.
Teflon-coated glass fiber, Pallflex (Putnam, CT), TX40HI20	• Gravimetry	• Thick mat of borosilicate glass fiber with a layer of Teflon on the surface. • Glass fiber supporting Teflon is shiny. • Melts at ~500°C. • Low flow resistance.	• Low blank levels for ions. (Glass backing and carbon content make it less suitable for elemental and carbon analyses. • Inert to adsorption of HNO_3, NO_2, and SO_2. • Low hygroscopicity. • High blank weight.
Glass fiber, Gelman (Ann Arbor, MI), Type A/E	• Gravimetry, light transmission, XRF, PIXE, INAA, AAS, ICP/AES, IC, AC	• Borosilicate glass fiber. • White opaque surface, diffuses transmitted light. • Melts at ~500°C. • Low flow resistance.	• High blank levels. • Adsorbs HNO_3, NO_2, SO_2, and organic vapors. • Low hygroscopicity. • High blank weight.

[a] Analysis methods are identified in Table 5-1.

Cellulose-fiber filters consist of a tightly-woven paper mat. These filters meet requirements in most categories with the exception of sampling efficiency and water vapor artifacts. Sampling efficiencies below 50% in the sub-micrometer region have been observed, but these are highly dependent on the filter weave. These efficiencies are generally lower than those required for reference sampling. Cellulose-fiber is hygroscopic and requires precise relative humidity control in the filter processing environment to obtain accurate mass measurements. This substrate has low elemental blanks and is commonly used for elemental and ionic analyses of the deposit, but it is not suitable for carbon analysis. Cellulose-fiber filters can be impregnated with gas-adsorbing compounds and located behind more efficient particle-collecting filters. This allows gases such as sulfur dioxide, nitrogen dioxide, and ammonia to be measured with suspended particles. The most commonly used cellulose-fiber filters are Whatman 41 and Whatman 31ET.

Glass-fiber filters consist of a tightly-woven mat of borosilicate glass filaments. These filters meet requirements in most categories with the exception of artifact formation and blank levels. Sampling efficiency is very high for all particle sizes. The high alkalinity of these substrates causes sulfur dioxide, nitrogen oxides, and gaseous nitric acid to be adsorbed (Coutant, 1977; Spicer and Schumacher, 1977), and they do not attain the reference method requirements for alkalinity. Blank levels for most elements of interest are high and variable (Witz et al., 1983). Particulate nitrate and ammonium losses have been observed when these samples are stored at room temperature for long periods, but this is also true of deposits on other filter media (Witz et al., 1990). Glass-fiber filters adsorb organic carbon vapors which are measured as particulate carbon during analysis. The most commonly used glass-fiber filters are Gelman Type A/E and Whatman EP2000.

Teflon-coated glass-fiber filters impregnate a Teflon slurry onto a loosely-woven glass-fiber mat. These filters meet requirements in all categories except blank element and carbon levels. Though a small nitric acid artifact has been observed (Mueller et al., 1983), it is tolerable in most situations. These filters are excellent for ion analyses but not for carbon analyses owing to their Teflon coating. The most commonly used Teflon-coated glass-fiber filters are Pallflex TX40HI20 and T60A20.

Teflon-membrane filters consist of a porous Teflon sheet which is either stretched across a plastic ring or supported by a loosely-woven Teflon mat. These filters meet requirements in all categories except flow resistance and carbon blank levels. Because of their low porosity, it is not usually possible to attain the flow rates needed by the size-selective inlets in high-volume sampling, though it is possible to obtain flow rates required for low-volume and medium-volume inlets. These filters are not analyzed for carbon by thermal methods because of its presence in the filter material, though they have very low blank levels for ions and elements. Most non-destructive multi-elemental analysis methods use Teflon-membrane filters. The deposit of particles on the filter surface makes these substrates especially amenable to x-ray fluorescence (XRF) and proton induced x-ray emission (PIXE) analyses. Gelman 1.0, 2.0, and 3.0 μm pore size Teflon-membrane filters, which are made of polytetrafluoroethylene (PTFE) Teflon stretched across a polymethylpentane ring, are the most commonly used Teflon-membrane filters. Gelman

Zefluor filters consist of PTFE Teflon mounted on a woven PTFE mat. The Zefluor filters are less desirable because their larger mass density decreases XRF and PIXE sensitivity, and because the similar appearance of both sides often results in them being mounted upside down with the particles drawn through the mat rather than onto the surface of the membrane.

Etched polycarbonate-membrane filters are constructed from a thin polycarbonate sheet through which pores of uniform diameter have been produced by radioactive particle penetration and chemical etching. These filters have low sampling efficiencies (<80%), even for small pore sizes (Liu and Lee, 1976; Buzzard and Bell, 1980). This low efficiency is used as an advantage when making size-specific measurements. Polycarbonate-membrane filters have low elemental blank levels, except for bromine, and are appropriate for elemental and ion analysis. They are the best filter media for single particle analysis by electron microscopy, but they cannot be submitted to thermal carbon analysis owing to their composition. The filters hold an electrostatic charge which influences mass measurements unless substantial effort is invested in discharging them with a small radioactive source (Engelbrecht et al., 1980). Electrostatic discharging is good practice for all filter media, even though others do not retain as much charge as the Nuclepore membranes. The Nuclepore 8.0 μm and 0.4 μm filters are most commonly used in ambient aerosol sampling. While the 0.2 μm pore size filter provides a higher sampling effectiveness, its higher flow resistance requires excessive vacuum for a reasonable flow rate.

Quartz-fiber filters consist of a tightly-woven mat of quartz filaments. These filters meet requirements in most categories and have artifact properties which are significantly lower than those for glass-fiber filters, though quartz substrates adsorb hydrocarbon gases during sampling (Eatough et al., 1990; McDow and Huntzicker, 1990). They should be baked at ~900°C prior to sampling to remove adsorbed organic vapors. Blank levels are high and variable for several elements (especially aluminum and silicon), though newer formulations are cleaner than earlier formulations. These filters are widely used for ion and carbon analyses. The greatest drawback of quartz-fiber filters is their fragility; they require extremely careful handling for accurate mass measurements. The Whatman QM/A quartz-fiber filter contains a 5% borosilicate glass binder which minimizes its friability while still attaining the reference method alkalinity standard. This filter is often used in high-volume PM_{10} samplers for mass measurements. Quartz-fiber filters can also be used for sulfate and nitrate analysis, carbon analysis, and limited elemental analysis when lots have been tested for background contaminants prior to sampling. The manufacturer does not test these for blank levels, and many manufacturing lots contain excessive amounts of the materials being sought for analysis. The Pallflex 2500 QAT-UP filter is pure quartz and undergoes a distilled water washing (thus the "UP", or "ultra-pure" designation). These filters have low blank levels, but they are very brittle and flakes are often removed from them when they are placed in a sampler filter holder. This flaking makes these filters unsuitable for mass analysis unless especially gentle handling is implemented to minimize flaking.

Nylon-membrane filters consist of thin sheets of porous nylon. They are used almost exclusively for the collection of nitric acid when secondary particles are large components of PM_{10}. These filters were not originally manufactured for this purpose, however, and there is a substantial difference among the properties of filters from different manufacturers. Nylon-

membrane filters have high flow resistance, which increases rapidly with filter loading. These filters passively adsorb nitric acid, and their blank nitrate levels can be high, depending on how long they have been exposed to an acid-rich environment. They should be washed in a sodium bi-carbonate solution followed by distilled deionized water (Chow *et al.*, 1990a; 1993a; Watson *et al.*, 1990b, 1991d) prior to use in the field. Nylon-membrane filters may also adsorb small quantities of sulfur dioxide (Japar and Brachaczek, 1984) which may interfere with sulfate measurements. Schleicher and Schuell Grade 66 and Gelman Nylasorb are the nylon-membrane filters most commonly used for ambient air sampling.

As noted above, blank levels must be low when filters are to be submitted to chemical analysis. Even batches of ultra-pure filters have been found to be contaminated, and a sample from each batch of filters (1 out of 50 to 100 filters) should be submitted to the intended chemical analyses prior to use in a field study. Though not reported in the literature, recent studies have found elevated levels of lead, calcium, and nitrate in batches of blank Teflon-membrane filters. Filters may also become contaminated in the field or during handling by passive deposition before and after sampling starts. Dynamic field blanks can be placed in the field under situations similar to that of the sampled filter. These are then analyzed so average blank levels can be subtracted from the chemical measurement.

2.4   Filter Holders

Filter are protected from contamination prior to, during, and after sampling by placing the filter in a filter holder. These holders must: 1) mate to the sampler and to the flow system without leaks; 2) be composed of inert materials which do not adsorb acidic gases; 3) allow a uniformly distributed deposit to be collected; 4) have a low pressure drop across the empty holder; 5) accommodate the sizes of commonly available air sampling filters (e.g., 37 or 47 mm); and 6) be durable and reasonably priced.

Most filter holders are configured as in-line or open-faced. In-line holders often concentrate the particles in the center of the substrate, and this will bias the results if analyses are performed on portions of the filter. Tombach *et al.* (1987) and Fujita and Collins (1989) show differences as high as 600% between chemical measurements in the middle and at the edges of filters sampled with in-line filter holders. Open-faced filter holders are a better choice for ambient aerosol sampling systems. All PM_{10} reference samples use open-face filter holders. Lippmann (1989) shows specifications and photographs for a large variety of commercially available filter holders. The holders most commonly used for PM_{10} chemical analysis are: 1) Andersen filter paper cartridge; 2) Gelman stainless steel; 3) Nuclepore polycarbonate plastic; 4) Savillex PFA Teflon; and 5) Sierra-Andersen polyethylene rings.

The Andersen filter paper cartridge is an 20.32 cm × 25.40 cm frame with a mesh support onto which an 20.32 cm × 25.40 cm filter is loaded for high volume sampling. This frame has a cover which protects the filter from contamination during handling and transport. The cover is removed and the frame is mounted into a high volume sampler in back of the size-selective

inlet. This cartridge is optional for mass measurements, where the filter is often changed with bare hands in the field. This cartridge is essential when samples are to be submitted to chemical analyses to prevent contamination by body oils and dirt. The cartridge should be loaded and unloaded in a clean indoor work area using gloved hands.

The Gelman stainless steel filter holder accommodates 28 and 47 mm filters and, though it has an open-faced adapter, it is sometimes used with an in-line coupler. As noted above, this in-line holder results in a spot in the center of the filter. Since these filter holders are expensive, they are often loaded and unloaded in the field which increases the potential for contamination.

The Nuclepore polycarbonate plastic filter holders accommodate 25, 37, and 47 mm diameter filters. Since the cost of these filter holders is modest, it is feasible to have a sufficient number of them such that filters can be loaded in the laboratory for transport to the field. These holders can be modified by widening the outlet hole to reduce flow resistance, using multiple extender sections for filter stacking, and replacing the rubber O-ring with a Viton O-ring to minimize carbon adsorption from the rubber.

The Savillex PFA Teflon 47 mm filter holder is made of injection molded PFA Teflon, which was previously noted as having the least inclination to adsorb nitric acid. These filter holders have a tapered extender section (called a receptacle) which can be mated to a sampler plenum with an O-ring in a retainer ring. Several grids and grid rings can be stacked within the holder to obtain series filtration. The cost of these filter holder combinations is low enough to allow a sufficient quantity to be purchased for laboratory loading.

The Sierra-Andersen polyethylene filter holders are two-piece rings which accommodate 37 mm diameter filters. They are used exclusively with the Sierra-Andersen 240 series of virtual impactor samplers. They are inexpensive and can be loaded in the laboratory and placed in plastic Petri dishes for shipment to field sites.

2.5   Flow Measurement and Control

An accurate measure of the air passing through each filter is needed to obtain accurate chemical concentration measurements for PM_{10}. Though a filter may be very good for chemical analysis, it may provide too much flow resistance to allow a sampler to operate properly. For example, 20.32 cm × 25.40 cm Teflon-membrane filters are available for the high-volume reference PM_{10} samplers, but they provide such a high pressure drop that no more than 20 ℓ/min of air can pass through them using the standard high-volume blower motor. This low flow raises the cut-point of the inlet such that the sample taken is no longer representative of PM_{10}.

Air is passed through the sampling substrates by means of a vacuum created by a pump. Rubow and Furtado (1989) describe commercially available air pumps, their capacities, and operating principles. Rogers et al. (1989) have found that a 3/4 horsepower carbon vane pump

is sufficient to draw in excess of 120 ℓ/min through a 47 mm Teflon-membrane filter. Smaller μg/m³pumps can be used for lower flow rates and filter media with lower resistances.

Regardless of the pump used, the quantity of air per unit time must be precisely measured and controlled to determine particle concentrations and to maintain the size-selective properties of the sampling inlet. Four general methods are used in particle sampling systems: 1) manual volumetric; 2) automatic mass; 3) differential pressure volumetric; and 4) critical orifice volumetric flow controls.

Manual control is accomplished when the operator initializes a setting, such as a valve adjustment, and then relies on the known and constant functioning of sampler components, such as pumps and tubing, to maintain flows within specifications. Flow rates which are set manually change over a sampling period as the collection substrate loads up and presents a higher flow resistance. For most filter loadings (<200 μg/m³), the flow will not change by more than 10% during sampling, and the average of flow rates taken before and after sampling provides an accurate estimate of the actual flow.

Automatic mass flow controllers use thermal anemometers to measure the heat transfer between two points in the gas stream. To a first approximation, the heat transfer is proportional to the flux of gas molecules between the two points, and hence the mass flow controller is able to sense the flux of mass. Mass flow controllers require compensating circuitry to avoid errors due to absolute temperature variations of the gas itself as well as the controller sensing probe. Wedding (1985) estimates potential differences in excess of 10% between mass and volumetric measurements of the same flow rates, depending on temperature and pressure variations.

Differential pressure volumetric flow control maintains constant pressure across an orifice (usually a valve which can be adjusted for a specified flow rate) by a diaphragm-controlled valve located between the filter and the orifice (Chow et al., 1993a). The diaphragm is controlled by the pressure between the orifice and the pump. When this pressure increases (as it does when filters load up), the diaphragm opens the valve and allows more air to pass.

A critical orifice consists of a small circular opening between the filter and the pump. When the pressure at the minimum flow area downstream of the orifice is less than 53% of the upstream pressure, the air velocity attains the speed of sound and it will remain constant, regardless of increased flow resistance. Critical orifices provide very stable flow rates, but they require large pumps and low flow rates (typically less than 20 ℓ/min with commonly available pumps) to maintain the high pressure differences. Wedding et al. (1987) have developed a "critical throat" which uses a diffuser arrangement to allow recovery of over 90% of the energy which is normally expended in back pressure behind a critical orifice. This design allows higher flow rates to be obtained with a given pump than does a simple critical orifice.

2.6 PM$_{10}$ Sampling Systems for Chemical Analysis

Tables 2-1 and 2-2 identify several reference and non-reference sampling systems which can be applied to PM$_{10}$ sampling intended for chemical analysis. Rubow and Furtado (1989), Perry (1989), and Hering (1989) also describe commercially-available systems for ambient aerosol sampling. The most widely used of these are the high-volume PM$_{10}$ samplers manufactured by Graseby-Andersen (formerly Sierra-Andersen) and Wedding & Associates that are designated reference methods for the PM$_{10}$ NAAQS. These samplers use a low-pressure blower to draw air through 20.32 cm × 25.40 cm fiber filters. The peaked roof dust cover which was formerly used to measure TSP is replaced with one of the high volume inlets specified in Table 2-3. Procedures for these samplers are well established (e.g., Watson et al., 1989a) and mass concentration from high-volume sampling with PM$_{10}$ inlets at over 2,000 sites within the U.S. is the most commonly available measurement. As noted above, frequent inlet cleaning is necessary for accurate size sampling by these units, and filters must be carefully handled if chemical analysis is anticipated. Whatman QM/A quartz-fiber filters which have been submitted to acceptance testing can be used in these samplers for most chemical analyses. The materials in these filters contain large amounts of sodium, aluminum, and silicon, so these species cannot be measured with this system. The thickness of the quartz-fiber filter also raises the background in x-ray fluorescence analysis, thereby decreasing the sensitivity of these analyses. Several elements which might be helpful in identifying sources are often below detection limits on these filters, while they can be measured with high sensitivity from a Teflon-membrane filter. High-volume PM$_{10}$ samplers are commercially available in a number of configurations from Graseby-Andersen and Wedding & Associates.

The Graseby-Andersen low-volume dichotomous sampler is also commercially available as a PM$_{10}$ reference sampler, and this unit is often used with appropriate filter media when elemental, ionic, and carbon analyses are desired. This sampler uses a virtual impactor to separate the PM$_{2.5}$ and coarse particle size fractions. Flow rates are controlled by a differential pressure regulator. Ten percent of the PM$_{2.5}$ particles are sampled on the coarse particle filters, and corrections must be made (Evans and Ryan, 1983) to the coarse particle measurements to compensate for the difference. John et al. (1988) describe how dichotomous samplers can be adapted for nitric acid sampling. The inlet and virtual impactor should be disassembled and thoroughly cleaned on a regular schedule. The virtual impactor can be assembled in a reverse orientation, with the impactor jet over the PM$_{2.5}$ filter rather than over the coarse particle filter, and care must be taken to correctly re-assemble this unit. When two or more dichotomous samplers are collocated, different filter materials can be used in each unit to accommodate a larger number of analyses. These samplers have been applied to PM$_{10}$ source apportionment studies (e.g., Chow et al., 1982; Thurston et al., 1984) which required chemical analysis in Houston, TX (Stevens et al., 1979); St Louis, MO and Elkaman, TN (Dzubay, 1980); Charleston, WV (Lewis and Macias, 1980); Denver, CO (Heisler et al., 1980a; 1980b); Buffalo, NY, El Paso, TX, and Philadelphia, PA (Chow et al., 1981; Watson et al., 1981a); East Halena, MT (Houck et al., 1982a); Kellogg, ID (Houck et al., 1982b); Shenandoah Valley, VA (Stevens et al., 1984); Phoenix, AZ (Chow et al., 1991a); Tucson, AZ (Chow et al., 1991b; 1992a); Tacoma, WA (Conner and Stevens, 1991); and Southern Ontario, Canada (Conner et al., 1993). Many of them

are operated with Teflon-membrane filters for mass and elemental analysis to assess concentrations of toxic metals near major industries and remediation sites.

The sequential filter sampler (SFS) equipped with the SA-254 inlet became a reference method under application from the State of Oregon. The SFS was originally designed in the late 1970s for use in the SUlfate Regional Experiment (SURE, Mueller et al., 1983) and the Portland Aerosol Characterization Study (PACS, Watson, 1979) and has been applied in over a dozen subsequent studies related to PM_{10} and visibility impairment. The SFS consists of an aluminum plenum to which the PM_{10} inlet is attached. Up to 12 sampling ports within the plenum are controlled by solenoid valves which divert flow from one channel to the next by means of a programmable timer. These ports accept filters which have been pre-loaded into open-faced 47 mm Nuclepore filter holders. The sample flow can be divided for simultaneous collection on two or more filter media. A differential pressure volumetric flow controller splits the flow between filters and maintains a constant flow rate despite filter loading. The State of Oregon sought and obtained reference status for the SFS because it desired two filter media taken simultaneously for different chemical analysis and because it needed to take multiple sequential samples without having to send someone to the site for frequent sample changing (Federal Register, 1987i). The SFS is especially useful when less than 24-hour average samples are sought. These samples are useful for distinguishing between sources with similar chemical profiles. For example, chemical profiles for residential wood combustion and for agricultural burning may be chemical indistinguishable, but agricultural burning contributions occur during daylight hours while the majority of residential wood combustion contributions occur at night. Four- to six-hour average sampling intervals can be applied using the SFS to provide this differentiation. The SFS has been applied to PM_{10} source apportionment studies which required chemical analysis in Portland, OR (Cooper and Watson, 1979; Cooper et al., 1979; Watson, 1979), Medford, OR (DeCesar and Cooper, 1982a; 1982b), San Jose, CA (Chow et al., 1994a) Santa Barbara County, CA (Countess, 1991), Reno, NV (Chow et al., 1988d; Watson et al., 1988a), Phoenix, AZ (Chow et al., 1991a), Tucson, AZ (Chow et al., 1991b; 1992a), and Denver, CO (Heisler et al., 1980a, 1988b; Watson et al., 1988b, 1988c, 1988d).

Two types of continuous monitors have achieved equivalence for PM_{10} monitoring with hourly averages, the Tapered Element Oscillating Microbalance (TEOM) and the Beta Attenuation Monitor (BAM). These monitors have potential for providing samples which can be chemically analyzed.

The TEOM (Patashnick and Rupprecht, 1991; Rupprecht and Patashnick, 1992) uses a hollow tapered tube. The wider end of the tube is fixed, while the narrow end oscillates in response to an applied electric field. Air is drawn through an inlet, then through the filter and the tapered tube and past a flow controller to the pump. The frequency of oscillation is a function of the restoring force constant of the tapered element, the mass of the tapered element, the mass of the filter, and the mass of the aerosol particle deposit on the filter. The filter loading causes a mass change which is detected as a change in the frequency of oscillation of the tapered element. The filter is only about 0.5 cm in diameter, and while it might be submitted to

chemical analysis, the deposit on it is small and the analytical sensitivity would be low. The filter is usually changed weekly, so analysis for a 24-hour period would not be possible.

The TEOM draws air through this filter at a flow rate of 3 ℓ/min. This flow is extracted from a total flow of 16.7 ℓ/min which is drawn through the SA-246 PM_{10} inlet. The make-up air flow of 13.7 ℓ/min can be diverted through one or more larger filters which can then be submitted to chemical analysis after sampling. A sequential sampling feature, similar to that of the SFS, could be added to allow sequential 24-hour filter samples, or every sixth day samples, to be taken between maintenance visits.

The TEOM tapered element and sensing head are thermostatted at user-programmable values. The default value for these settings is 50°C, and this may cause mass measurements to be lower than those measured with other reference samplers when PM_{10} contains volatile species such as ammonium nitrate and certain organic carbon compounds. There is no inherent reason why the TEOM cannot be thermostatted at an ambient temperature value, but temperatures which change too rapidly set up gradients in the tapered element, in turn changing its resonant frequency.

Several Beta Attenuation Monitors have attained equivalence status for PM_{10} monitoring, as shown in Table 2-1. The attenuation of beta rays (moderately high energy electrons) emitted by a radioactive source when they pass through an aerosol filter deposit indicates the mass of that filter deposit (e.g., Lillienfeld and Dulchinos, 1972; Husar, 1974; Lillienfeld, 1975; Macias and Husar, 1976; Lillienfeld, 1979). The equivalent PM_{10} systems consist of a filter tape which is first drawn across the path between the beta emitter and a detector to measure blank attenuation, then across a sampling area in which ambient air is deposited on the tape, and finally across the detection path to measure the combined attenuation of the filter and the deposit. The beta attenuation is caused by the inelastic collision of the incident electrons with the orbital electrons of the atoms in the samples for energies less than 1 MeV. The filter spots are approximately five centimeters in diameter, and depending on the filter media used, these might be submitted to chemical analysis. This has not yet been attempted, however, and development is required before these filter deposits should be considered for chemical characterization.

PM_{10} reference samplers cannot be adapted to every application which requires chemical analysis of aerosol samples. This is especially the case for source apportionment studies in areas which have many fugitive dust sources and in areas with large contributions from secondary aerosol formation. Non-reference portable PM_{10} survey samplers have been developed to allow spatially-dense PM_{10} sampling networks to be deployed. These battery-powered units can be hung from power poles and building walls and do not require complicated sampler siting efforts (Watson *et al.*, 1991b). They can be placed in and around fugitive dust emissions sources to help locate the most significant contributors to high PM_{10} caused by dust emissions. The portable survey samplers consist of a pump, timer, tubing and fittings, removable filter holder, flow meter, impactor inlet, and battery pack. All of these are packaged in a plastic cylindrical enclosure which is about 10 inches in diameter and 18 inches long. A carrying bale allows the sampler to be hung from a hook or hanging bracket. The sampler weighs about 15 pounds, most of which

is due to the weight of the battery. It can be located and removed from elevated locations with a grappling pole.

Removable 47 mm diameter Nuclepore filter holders used on this sampler are similar to those used on the SFS. These are loaded with Teflon-membrane filters in the laboratory for placement in the survey sampler. Two removable battery packs accompany each sampler so that one may be charging while the other is sampling. Every time a filter is changed, the spent battery is replaced with a recharged battery. At least six hours are needed to assure that batteries are fully charged for the next sample.

PM_{10} is collected through an impactor inlet which contains a small amount of vacuum grease on the impaction plate to trap the larger particles. The 50% size-cut is preserved at 10 μm when the sampler's nominal flow rate is 5 ℓ/min. At this flow rate, the pump can operate for over 24-hours with a fully-charged battery pack. Flow rates are determined with a calibrated orifice or reference rotameter and verified by an in-line rotameter. An internal timer turns the sampler on and off at pre-set times. Portable PM_{10} survey samplers have been used in recent PM_{10} studies where emissions inventories were questionable. These include studies in El Paso, TX (Kemp, 1990), Rubidoux, CA (Zeldin, 1993), Omaha, NB (Kelly, 1991), Tacoma, WA (Schweiss, 1991), and Calexico, CA (Watson et al., 1991b).

The California Institute of Technology (CIT) and Southern California Air Quality Study (SCAQS) samplers are of similar design, though inlets and flow rates differ. These samplers acquired source apportionment data sets in California's South Coast Air Basin (Solomon et al., 1989; Wolff et al., 1991; Chow et al., 1992b; Solomon et al., 1992; Chow et al., 1994a, 1994b; Watson et al., 1994b) and San Joaquin Valley (Chow et al., 1992c; 1993b) which were chemically analyzed and submitted to receptor modeling. Both samplers were intended to measure PM_{10}, $PM_{2.5}$, and gaseous components of the aerosol on substrates for chemical analysis. The SCAQS sampler took samples of 4- to 6-hours duration in Los Angeles and samples of 24-hours duration, with lower flow rates, in the San Joaquin Valley. These systems draw air through several filters in parallel and in series using Gelman in-line filter holders, and use critical orifice flow control.

As noted above, annular denuder systems are designed for the measurement of acidic species. These systems use Teflon-coated inlets, mass flow controllers, and in-line filter holders. Nitric acid, sulfur dioxide, and other gases are adsorbed on the inner surfaces of the denuder inlet and are removed by washing with an extraction solution (Stevens et al., 1990). These systems are still undergoing design changes. The system developed by Koutrakis et al. (1988) has been applied in a nationwide network and has developed a degree of standardization. These systems are useful when an examination of the chemistry of secondary particles and their precursors is desired.

2.7 Summary of Potential Sampling Artifacts

Watson *et al.* (1989b) and Countess *et al.* (1989) identify several sampling artifacts, including those discussed above, which can bias PM_{10} mass and chemical concentrations. These must be evaluated at the time of sampling if the integrity of the data is to be preserved. The potential artifacts and methods to avoid them are as follows:

- **Passive Deposition** of windblown dust on the filter prior to and following sampling can positively bias PM_{10} measurements. For the peaked roof high-volume TSP samplers (Federal Register, 1982; 1983), Rogers and Watson (1984) observed biases of 10% to 15% for samples which were left in the sampler prior to and following the sixth-day sampling schedule. This bias can be minimized by more frequent sample changing and by the use of a "Sample Saver", a device which covers the filter inside the sampler until the pump blower starts.

- **Re-entrainment** of large particles collected in the size-selective inlets can positively bias PM_{10} measurements. As noted above, impaction inlets may become saturated. Frequent cleaning and greasing of inlet impaction surfaces will minimize re-entrainment biases to chemical concentrations.

- **Recirculation** of pump exhaust can positively bias PM_{10} measurements. Every flow mover contains fragments of its brushes and armatures in the exhaust (Countess, 1974). Most high vacuum pumps have outlet filters which should be installed and changed at least quarterly. New pumps should be broken in for at least 48-hours prior to taking the first sample, and the break-in filter should be replaced. A piece of clothes-dryer duct can be attached to the high-volume exhaust plenum to direct pump exhaust away from the sampler inlet.

- **Volumetric Flow Rate** errors may be caused by infrequent performance tests and calibrations of flow controllers. This is especially true of mass flow controllers, for which the set-point is temperature dependent. Wedding (1985) observed that flow rate biases of 10% to 20% will occur when flow rate measurements are taken during the winter using a calibration representative of summertime temperatures. Frequent flow meter calibrations and performance tests are required to assure that the sampled volume is accurate.

- **Artifact Formation**, the adsorption of gases on filter media, was identified in Section 2.3 as a positive bias for certain chemical species, especially for sulfate and nitrate on glass-fiber filters. Use of quartz-fiber and Teflon-membrane filters is the best way to minimize adsorption artifacts.

- **Volatilization** of chemical compounds which are in equilibrium with their environment causes losses of ammonium nitrate and certain organic compounds. The most accurate monitoring of these species involves denuder-type sampling systems.

This bias can be minimized by removing samples soon after sampling, storing them in sealed containers under refrigeration, and keeping them in coolers for transport between the sampling site and laboratory.

- **Particle Loss During Transport** occurs when a large deposit is collected and samples experience rough handling during movement from the field site to the laboratory (Dzubay and Barbour, 1983). Shorter sample durations and lower flow rates may be required in very polluted environments, especially those in which fugitive dust is a large contributor, to prevent overloading. Careful handling during transport will also minimize the loss of particles from the filter surface.

- **Filter Contamination** involves the presence of species to be measured in the filter material, or their inadvertent introduction during filter handling prior to sampling. This can be minimized by acceptance testing of several blank filters from each manufacturing lot to assure that blank levels are low. Subsequent contamination can be reduced by loading and unloading filters in a laboratory setting, keeping them in containers before and after sampling, and eliminating contact of the filters with bare hands.

- **Filter Integrity** is compromised by handling which causes some of the filter to be lost after the pre-exposure weighing. Teflon-membrane filters are the least likely to lose filter mass, and these are best for gravimetric mass measurements. Careful laboratory loading and unloading into filter holders also reduces over compression which sometimes causes portions of the filter to adhere to the holder.

3.0   PM$_{10}$ CHEMICAL ANALYSIS METHODS

Once filter deposits have been obtained by one or more sampling methods, they can be submitted to a variety of chemical analyses. It is important that all the analyses to which the sample might be submitted are identified prior to performing the first one, since some analyses may invalidate the filter for subsequent analyses. Some methods are non-destructive, and these are preferred because they reserve the filter for other uses. Methods which require destruction of the filter are best performed on a section of the filter rather than on the entire filter. This leaves a portion of the filter for other re-analyses or to be used as a quality control check on the same analysis method. As noted in the previous section, filter sectioning requires that the particles are homogeneously deposited across the filter surface so that the concentrations measured on a portion of the filter can be extrapolated to the entire deposit area.

Table 3-1 compares minimum detectable concentrations achievable by different analysis methods for elements, ions, organic carbon, and elemental carbon. The values in Table 3-1 are nominal, and actual detection limits should be supplied by the laboratory performing the analysis prior to sampling, so that sample durations and flow rates can be adjusted to acquire sufficient samples for the intended analyses. The most common aerosol analyses can be divided into the categories of 1) mass, 2) elements, 3) water-soluble ions, and 4) organic and elemental carbon. Less common analytical methods which are applied to a small number of specially-taken samples include Carbon-14 (Currie, 1982); organic compounds (Rogge et al., 1993a; 1993b); and single-particle characterization (Cassuccio et al., 1989). The reader is referred to the cited references for greater detail on sampling and analysis methods for these highly-specialized methods.

3.1   Mass Measurement Methods

Particulate mass concentration is the most commonly made measurement on aerosol samples. It is used to determine compliance with PM$_{10}$ standards and to select certain samples for more detailed, and more expensive, chemical analyses. As noted in Section 2, the beta attenuation and inertial microbalance methods have been incorporated into in situ measurement systems which acquire real-time mass measurements. Gravimetric analysis is used almost exclusively to obtain mass measurements of filters in a laboratory environment. U.S. EPA (1976) and Watson et al. (1989a) have published detailed procedures for mass analyses associated with 20.32 cm × 25.40 cm fiber filters, but the guidance for other types of filters used for chemical analyses is less well documented.

Gravimetry measures the net mass on a filter by weighing the filter before and after sampling with a balance in a temperature- and relative humidity-controlled environment. PM$_{10}$ reference methods require that filters be equilibrated for 24 hours at a constant (within ±5%) relative humidity between 20% and 40% and at a constant (within ±3°C) temperature between 15°C and 30°C. These are intended to minimize the liquid water associated with soluble compounds and to minimize the loss of volatile species. Nominal values of 30% RH and 15°C to 20°C best conserve the particle deposits during sample weighing.

Table 3-1
Analytical measurement specifications for air filter samples

Species	ICP/ AES[b,d]	AA Flame[b,d]	AA Furnace[b]	INAA[b,f]	PIXE[g]	XRF[c]	IC[b]	AC[b]	TOR[b]
						Minimum Detection Limit in ng/m^3 [a]			
Be	0.06	2[d]	0.05	NA[h]	NA	NA	NA	NA	NA
Na	NA	0.2[d]	< 0.05	2	60	NA	NA	NA	NA
Mg	0.02	0.3	0.004	300	20	NA	NA	NA	NA
Al	20	30	0.01	24	12	5	NA	NA	NA
Si	3	85	0.1	NA	9	3	NA	NA	NA
P	50	100,000	40	NA	8	3	NA	NA	NA
S	10	NA	NA	6,000	8	2	NA	NA	NA
Cl	NA	NA	NA	5	8	5	NA	NA	NA
K	NA	2[d]	0.02	24	5	3	NA	NA	NA
Ca	0.04	1[d]	0.05	94	4	2	NA	NA	NA
Sc	0.06	50	NA	0.001	NA	NA	NA	NA	NA
Ti	0.3	95	NA	65	3	2	NA	NA	NA
V	0.7	52	0.2	0.6	3	1	NA	NA	NA
Cr	2	2	0.01	0.2	2	1	NA	NA	NA
Mn	0.1	1	0.01	0.12	2	0.8	NA	NA	NA
Fe	0.5	4	0.02	4	2	0.7	NA	NA	NA
Co	1	6[d]	0.02	0.02	NA	0.4	NA	NA	NA
Ni	2	5	0.1	NA	1	0.4	NA	NA	NA
Cu	0.3	4	0.02	30	1	0.5	NA	NA	NA
Zn	1	1	0.001	3	1	0.5	NA	NA	NA
Ga	42	52	NA	0.5	1	0.9	NA	NA	NA
As	50	100	0.2	0.2	1	0.8	NA	NA	NA
Se	25	100	0.5	0.06	1	0.6	NA	NA	NA
Br	NA	NA	NA	0.4	1	0.6	NA	NA	NA
Rb	NA	NA	NA	6	2	0.5	NA	NA	NA
Sr	0.03	4	0.2	18	2	0.5	NA	NA	NA
Y	0.1	300	NA	NA	NA	0.6	NA	NA	NA
Zr	0.6	1000	NA	NA	3	0.8	NA	NA	NA
Mo	5	31	0.02	NA	5	1	NA	NA	NA
Pd	42	10	NA	NA	NA	5	NA	NA	NA
Ag	1	4	0.005	0.12	NA	6	NA	NA	NA
Cd	0.4	1	0.003	4	NA	6	NA	NA	NA
In	63	31	NA	0.006	NA	6	NA	NA	NA
Sn	21	31	0.2	NA	NA	8	NA	NA	NA
Sb	31	31	0.2	0.06	NA	9	NA	NA	NA

Table 3-1 (continued)
Analytical measurement specifications for air filter samples

	Minimum Detection Limit in ng/m^3 [a]								
Species	ICP/ AES[b,d]	AA Flame[b,d]	AA Furnace[b]	INAA[b,f]	PIXE	XRF[c]	IC[b]	AC[b]	TOR[b]
I	NA	NA	NA	1	NA	NA	NA	NA	NA
Cs	NA	NA	NA	0.03	NA	NA	NA	NA	NA
Ba	0.05	8[d]	0.04	6	NA	25	NA	NA	NA
La	10	2,000	NA	0.05	NA	30	NA	NA	NA
Au	2.1	21	0.1	NA	NA	2	NA	NA	NA
Hg	26	500	21	NA	NA	1	NA	NA	NA
Tl	42	21	0.1	NA	NA	1	NA	NA	NA
Pb	10	10	0.05	NA	3	1	NA	NA	NA
Ce	52	NA	NA	0.06	NA	NA	NA	NA	NA
Sm	52	2,000	NA	0.01	NA	NA	NA	NA	NA
Eu	0.08	21	NA	0.006	NA	NA	NA	NA	NA
Hf	16	2,000	NA	0.01	NA	NA	NA	NA	NA
Ta	26	2,000	NA	0.02	NA	NA	NA	NA	NA
W	31	1,000	NA	0.2	NA	NA	NA	NA	NA
Th	63	NA	NA	0.01	NA	NA	NA	NA	NA
U	21	25,000	NA	NA	NA	1	NA	NA	NA
Cl-	NA	NA	NA	NA	NA	NA	50	NA	NA
NO$_3^-$	NA	NA	NA	NA	NA	NA	50	NA	NA
SO$_4^=$	NA	NA	NA	NA	NA	NA	50	NA	NA
NH$_4^+$	NA	NA	NA	NA	NA	NA	50	NA	NA
OC	NA	NA	NA	NA	NA	NA	NA	50	100
EC	NA	NA	NA	NA	NA	NA	NA	NA	100

[a] Minimum detection limit is three times the standard deviation of the blank for a filter of 1 mg/cm^2 areal density.
ICP/AES = Inductively Coupled Plasma with Atomic Emission Spectroscopy.
AA = Atomic Absorption Spectrophotometry.
PIXE = Proton Induced X-ray Emissions Spectrometry.
XRF = Non-Dispersive X-ray Fluorescence Spectrometry.
INAA = Instrumental Neutron Activation Analysis.
IC = Ion Chromatography.
AC = Automated Colorimetry.
TOR = Thermal Optical Reflectance.
[b] Concentration is based on the extraction of 1/2 of a 47mm filter in 15 mℓ of deionized-distilled water, with a nominal flow rate of 20 ℓ/min for 24-hour samples.
[c] Concentration is based on 13.8 cm^2 deposit area for a 47 mm filter, with a nominal flow rate of 20 L/min for 24-hour samples with 100 sec radiation time.
[d] Harman (1989).
[e] Fernandez (1989).
[f] Olmez (1989).
[g] Eldred (1993).
[h] Not Available.

Balances used to weigh 20.32 cm × 25.40 cm filters from high volume PM_{10} samples must have a sensitivity of at least 100 μg. Balances used for medium volume PM_{10} samples should have a sensitivity of at least 10 μg, and those used for low-volume PM_{10} samples should have a sensitivity of at least 1 μg. Modifications to the balance chamber are sometimes needed to accommodate filters of different sizes. All filters, even those from high-volume PM_{10} samplers, should be handled with gloved hands when subsequent chemical analyses are a possibility.

Balance calibrations should be established before and after each weighing session using Class M and Class S standards, and they should be verified with a standard mass every ten filters. Approximately one out of ten filters should be re-weighed by a different person at a later time. These re-weights should be used to calculate the precision of the measurement as outlined by Watson et al. (1989b).

Feeney et al. (1984) examined the gravimetric measurement of lightly loaded membrane filters and obtained excellent precision and accuracy. The sensitivity of the electrobalance is about ±0.001 mg, though tolerances on re-weights of Teflon-membrane filters are typically ±0.010 mg. The main interference in gravimetric analysis of filters results from electrostatic effects. Engelbrecht et al. (1980) found that residual charge on a filter could produce an electrostatic interaction between the filter on the pan and the metal casing of the electrobalance. This charge can be removed by exposing the filter to a radioactive polonium source before and during sample weighing.

Beta attenuation methods have been applied in the laboratory as well as in the field, and the results are comparable to those of gravimetric measurements. The precision of beta-gauge measurements has been shown to be ±5 μg/m^3 or better for counting intervals of one minute per sample, which translates into ±32 μg/filter for 37 mm diameter substrates. This is substantially higher than the ±6 μg/filter precision determined by gravimetric analysis using an electrobalance (Feeney et al., 1984). Jaklevic et al. (1981) found equivalent accuracy and precision for both techniques as they were used in that study. Courtney et al. (1982) found beta attenuation and gravimetric mass measurements to differ by less than ±5%. Patashnick and Rupprecht (1991) examine results from TEOM samplers operated alongside filter-based PM_{10} samplers and Barnes et al. (1988) and Shimp (1988) report comparisons with beta attenuation field monitors; these comparisons all show good agreement for mass measurements.

3.2   Elemental Analysis Methods

The most common interest in elemental composition derives from concerns about health effects and the utility of these elements to trace the sources of suspended particles. Instrumental neutron activation analysis (INAA), atomic absorption spectrophotometry (AAS), inductively coupled plasma with atomic emission spectroscopy (ICP/AES), photon-induced x-ray fluorescence (XRF), and proton induced x-ray emission (PIXE) have all been applied to elemental measurements of aerosol samples. AAS and ICP/AES are also appropriate for ionic

measurements when the particles are extracted in deionized distilled water (DDW). Since air filters contain very small particle deposits (20 to 100 $\mu g/cm^2$), preference is given to methods which can accommodate small sample sizes. XRF and PIXE leave the sample intact after analysis so that it can be submitted to additional examinations by other methods.

In INAA (Dams *et al.*, 1970; Zoller and Gordon, 1970; Olmez, 1989), a sample is irradiated in the core of a nuclear reactor for periods ranging from a few minutes to several hours. The neutron bombardment chemically transform many elements into radioactive isotopes. The energies of the gamma rays emitted by these isotopes identify them, and therefore their parent elements. The intensity of these gamma rays is proportional to the amount of the parent element present in the sample. Different irradiation times and cooling periods are used before counting with a germanium detector. INAA does not quantify some of the abundant species in ambient particulate matter such as silicon, nickel, tin, and lead. While INAA is technically nondestructive, sample preparation involves folding the sample tightly and sealing it in plastic, and the irradiation process makes the filter membrane brittle and radioactive. These factors limit the use of the sample for subsequent analyses.

In AAS (Ranweiler and Moyers, 1974; Fernandez, 1989), the sample is first extracted in a strong solvent to dissolve the solid material; the filter or a portion of it is also dissolved during this process. A few milliliters of this extract are introduced into a flame where the elements are vaporized. Most elements absorb light at certain wavelengths in the visible spectrum, and a light beam with wavelengths specific to the elements being measured is directed through the flame to be detected by a monochromater. The light absorbed by the flame containing the extract is compared with the absorption from known standards to quantify the elemental concentrations. AAS requires an individual analysis for each element, and a large filter or several filters are needed to obtain concentrations for all of the elements specified in Table 3-1. AAS is a useful complement to other methods, such as XRF and PIXE, for species such as beryllium, sodium, and magnesium which are not well-quantified by these methods. A typical double-beam AAS system is schematically illustrated in Figure 3-1. Airborne particles are chemically complex and do not dissolve easily into complete solution, regardless of the strength of the solvent. There is always a possibility that insoluble residues are left behind and soluble species may co-precipitate on them or on container walls.

In ICP/AES (Fassel and Kniseley, 1974; McQuaker *et al.*, 1979; Lynch *et al.*, 1980; Harman, 1989), the dissolved sample is introduced into an atmosphere of argon gas seeded with free electrons induced by high voltage from a surrounding Tesla coil. The high temperatures in the induced plasma raise valence electrons above their normally stable states. When these electrons return to their stable states, a photon of light is emitted which is unique to the element which was excited. This light is detected at specified wavelengths to identify the elements in the sample. ICP/AES acquires a large number of elemental concentrations using small sample volumes with acceptable detection limits for atmospheric samples. As with AAS, this method requires complete extraction and destruction of the sample.
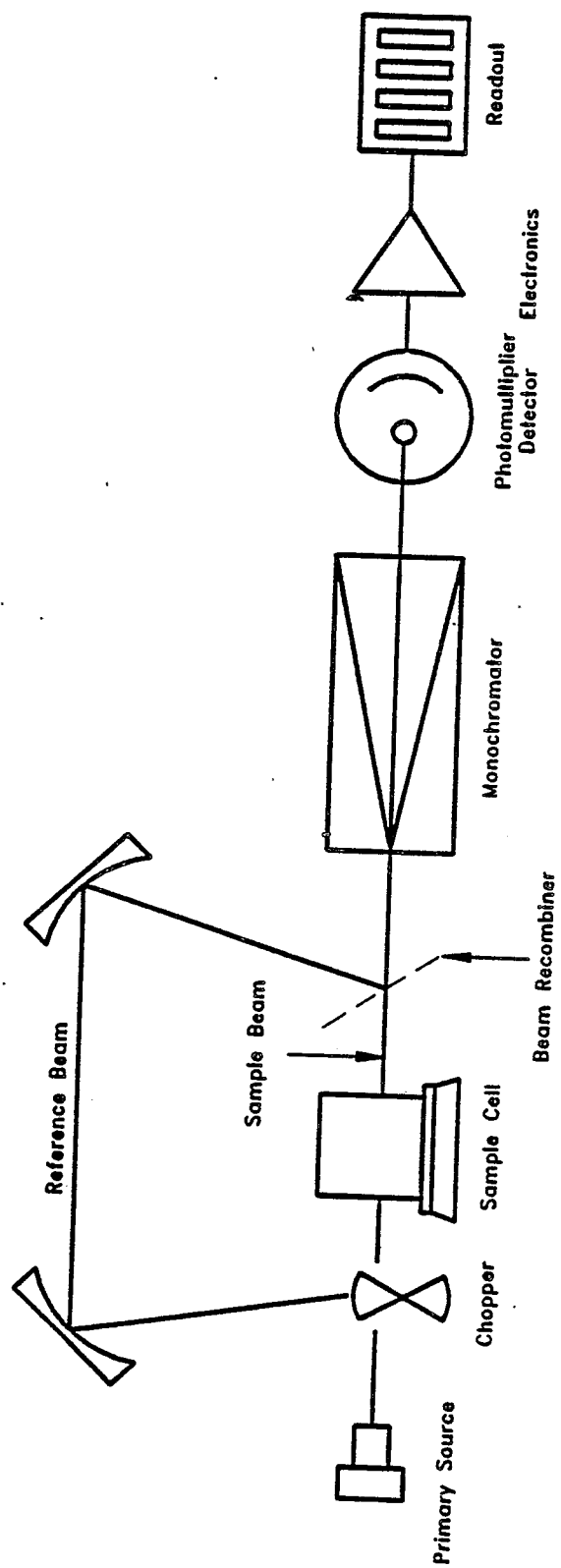
Figure 3-1. Schematic of a typical double-beam AAS system.

In XRF (Dzubay and Stevens, 1975; Jaklevic *et al.*, 1977) and PIXE (Cahill *et al.*, 1990; Eldred, 1993), the filter deposit is irradiated by high energy x-rays (XRF) or protons (PIXE)which eject inner shell electrons from the atoms of each element in the sample. When a higher energy electron drops into the vacant lower energy orbital, a fluorescent x-ray photon is released. The energy of this photon is unique to each element, and the number of photons is proportional to the concentration of the element. Concentrations are quantified by comparing photon counts for a sample with those obtained from thin-film standards of known concentration.

Emitted x-rays with energies less than ~4 kev (affecting the elements sodium, magnesium, aluminum, silicon, phosphorus, sulfur, chlorine, and potassium) can be absorbed in the filter, in a thick particle deposit, or even by large particles in which these elements are contained. Very thick filters also scatter much of the excitation radiation or protons, thereby lowering the signal-to-noise ratio for XRF and PIXE. For this reason, thin membrane filters with deposits in the range of 10 to 50 $\mu g/cm^2$ provide the best accuracy and precision for XRF and PIXE analysis.

XRF methods can be broadly divided into two categories: wavelength dispersive (WDXRF), which utilizes crystal diffraction for observation of fluorescent x-rays, and energy dispersive (EDXRF), which uses a silicon semiconductor detector. The WDXRF method is characterized by high spectral resolution, which minimizes peak overlaps. WDXRF requires high power excitation to overcome low sensitivity which results in excessive sample heating and potential degradation. Conversely, EDXRF features high sensitivity but less spectral resolution, requiring complex spectral deconvolution procedures.

XRF methods can be further categorized as direct/filtered excitation, where the x-ray beam from the tube is optionally filtered and then focused directly on the sample, or secondary target excitation, where the beam is focused on a target of material selected to produce x-rays of the desired energy. The secondary fluorescent radiation is then used to excite the samples. The direct/filtered approach has the advantage of delivering higher incident radiation flux to the sample for a given x-ray tube power, since about 99% of the incident energy is lost in a secondary fluorescer. The secondary fluorescer approach, however, produces a more nearly monochromatic excitation which reduces unwanted scatter from the filter, yielding better detection limits.

XRF and PIXE are usually performed on Teflon-membrane filters for sodium, magnesium, aluminum, silicon, phosphorus, sulfur, chlorine, potassium, calcium, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, gallium, arsenic, selenium, bromine, rubidium, strontium, yttrium, zirconium, molybdenum, palladium, silver, cadmium, indium, tin, antimony, barium, lanthanum, gold, mercury, thallium, lead, and uranium.

A typical XRF system is schematically illustrated in Figure 3-2. The x-ray output stability should be within ±0.25% for any 8-hour period within a 24-hour duration. Analyses are typically controlled, spectra are acquired, and elemental concentrations are calculated by software on a computer which is interfaced to the analyzer.
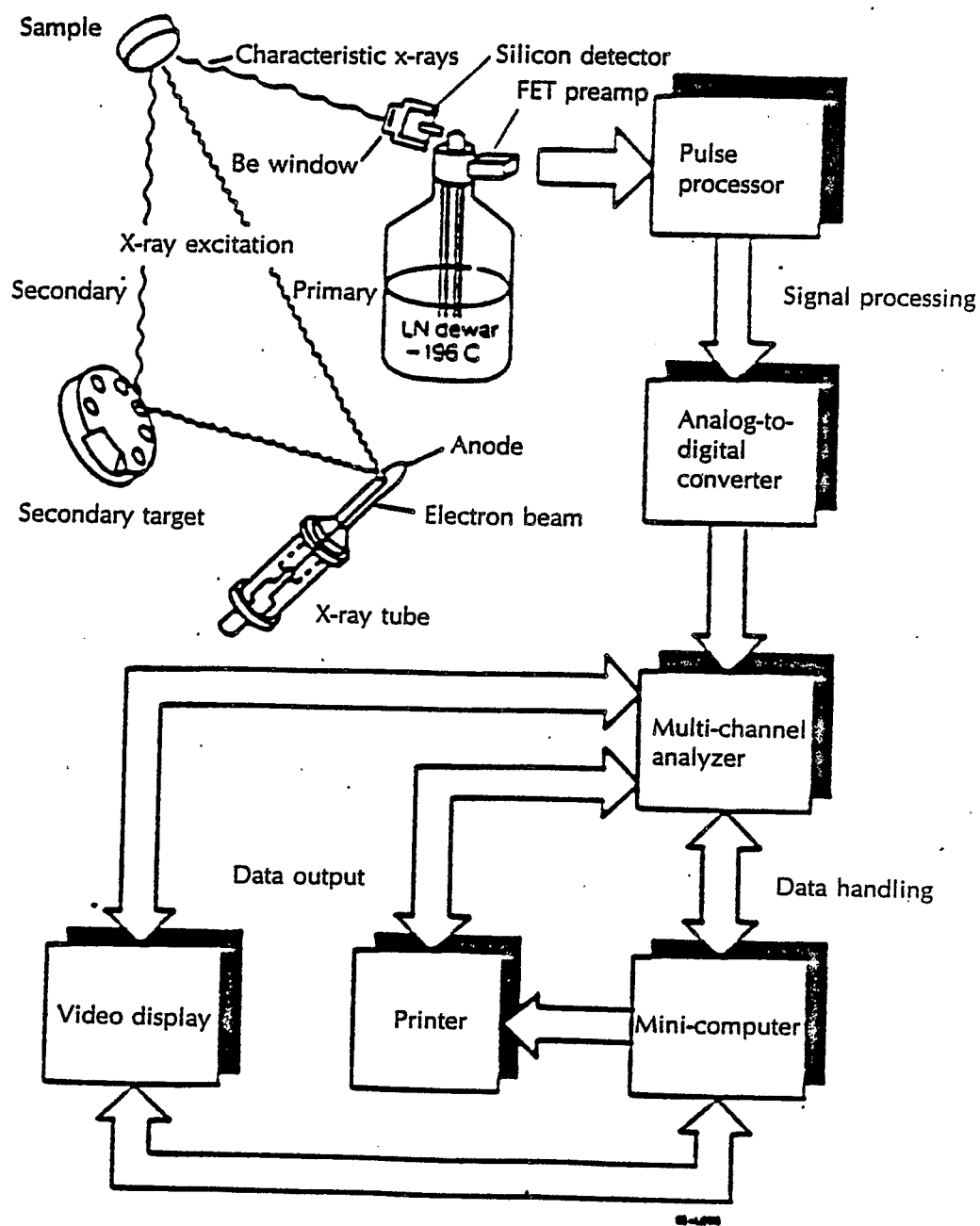
3-7

Figure 3-2. Schematic of a typical x-ray fluorescence (XRF) system (Kevex, 1985).

Separate XRF analyses are conducted on each sample to optimize detection limits for the specified elements. A comparison of the minimum detectable limits of Teflon-membrane and quartz-fiber filters is listed in Table 3-2. Figure 3-3 shows an example of an XRF spectrum.

Three types of XRF standards are used for calibration, performance testing, and auditing: 1) vacuum-deposited thin-film elements and compounds (Micromatter); 2) polymer films (Dzubay et al., 1981); and 3) the National Institute of Science and Technology (NIST; formerly NBS) thin-glass films. The vacuum deposits cover the largest number of elements and are used to establish calibration curves. The polymer film and NIST standards are used as quality control measures. NIST produces the definitive standard reference material, but these are only available for the species aluminum, calcium, cobalt, copper, manganese, and silicon (SRM 1832), and iron, lead, potassium, silicon, titanium, and zinc (SRM 1833). A separate Micromatter thin-film standard is used to calibrate the system for each element.

Sensitivity factors (number of x-ray counts per $\mu g/cm^2$ of the element) are determined for each excitation condition. These factors are then adjusted for absorption of the incident and emitted radiation in the thin film. These sensitivity factors are plotted as a function of atomic number and a smooth curve is fitted to the experimental values. The calibration sensitivities are then read from these curves for the atomic numbers of each element in each excitation condition. Polymer film and NIST standards should be analyzed on a periodic basis using these sensitivity factors to verify both the standards and the stability of the instrument response. When deviations from specified values are greater than $\pm 5\%$, the system should be re-calibrated.

The sensitivity factors are multiplied by the net peak intensities yielded by ambient samples to obtain the $\mu g/cm^2$ deposit for each element. The net peak intensity is obtained by: 1) subtracting background radiation; 2) subtracting spectral interferences; and 3) adjusting for x-ray absorption.

The elemental x-ray peaks reside on a background of radiation scattered from the sampling substrate. A model background is formed by averaging spectra obtained from several blank filters of the same type used in ambient sampling. It is important to retain blank filters for this purpose when XRF or PIXE analyses are anticipated. This model background has the same shape and features of the sample spectra (minus the elemental peaks) if the deposit mass is small relative to the substrate mass (Russ, 1977). This model background is normalized to an excitation radiation scatter peak in each sample spectrum to account for the difference in scatter intensity due to different masses.

The number and spacing of the characteristic x-ray lines relative to detector resolution are such that the peaks from one element can interfere with a peak from another element (Dzubay, 1986). A variety of methods has been used to subtract these peak overlaps (Arinc et al., 1977; Parkes et al., 1979; Drane et al., 1983), including least squares fitting to library spectra, Gaussian and other mathematical functions, and the use of peak overlap coefficients.

Table 3-2
X-ray fluorescence air filter analysis interference-free minimum detectable limits[a] using DRI standard analysis protocols

Element	Condition Number[d]	Quartz-Fiber Filter[b] Protocol QA-A ng/cm^2 [e]	Teflon-Membrane Filter[c] Protocol A ng/cm^2 [d]	Protocol B ng/cm^2	Protocol C ng/cm^2	Protocol D ng/cm^2
Al	5	NA[f]	10	7.2	3.6	2.5
Si	5	NA	6.3	4.4	2.2	1.4
P	5	NA	5.6	4.0	2.0	1.4
S	5	40[g]	5.0	3.5	1.8	1.2
Cl	4	30	10	7.4	3.7	2.6
K	4	40	6.1	4.3	2.2	1.5
Ca	4	100	4.5	3.2	1.6	1.1
Ti	3	50	2.9	2.1	1.0	0.73
V	3	20	2.5	1.7	0.87	0.62
Cr	3	8	1.9	1.4	0.67	0.48
Mn	3	7	1.6	1.1	0.56	0.40
Fe	3	15	1.5	1.1	0.54	0.38
Co	3	5	0.88	0.62	0.31	0.22
Ni	3	4	0.89	0.63	0.31	0.22
Cu	3	4	1.1	0.76	0.38	0.27
Zn	3	6	1.1	0.76	0.38	0.27
Ga	2	8	1.9	1.4	0.68	0.48
As	2	9	1.6	1.1	0.56	0.39
Se	2	5	1.2	0.86	0.43	0.31
Br	2	5	1.0	0.72	0.36	0.25
Rb	2	5	1.0	0.68	0.34	0.24
Sr	2	8	1.1	0.78	0.39	0.28
Y	2	8	1.3	0.92	0.46	0.33
Zr	2	10	1.7	1.2	0.59	0.42
Mo	4	20	2.7	1.9	0.95	0.67
Pd	1	20	11	7.6	3.8	2.7
Ag	1	20	12	8.6	4.3	3.0
Cd	1	25	12	8.6	4.3	3.0
In	1	30	13	9.5	4.8	3.4
Sn	1	40	17	12	6.2	4.4
Sb	1	50	18	13	6.4	4.5
Ba	1	170	52	37	18	13
La	1	190	62	44	22	16
Au	2	NA	3.1	2.2	1.1	0.77
Hg	2	20	2.6	1.8	0.91	0.65

Table 3-2 (continued)
X-ray fluorescence air filter analysis interference-free minimum detectable limits[a] using DRI standard analysis protocols

Element	Condition Number[d]	Quartz-Fiber Filter[b] Protocol QA-A ng/cm² [e]	Teflon-Membrane Filter[c] Protocol A ng/cm² [d]	Protocol B ng/cm²	Protocol C ng/cm²	Protocol D ng/cm²
Tl	2	NA	2.5	1.8	0.88	0.62
Pb	2	14	3.0	2.2	1.1	0.76
U	2	NA	2.3	1.7	0.83	0.59

[a] MDL defined as three times the standard deviation of the blank for a filter of 1 mg/cm² areal density.

[b] Analysis times are 100 sec. for Conditions 1 and 4, and 400 sec. for Conditions 2 and 3. Actual MDL's for quartz filters vary from batch to batch due to elemental contamination variability.

[c] Analysis times are 100 sec. for Conditions 1, 4 and 5, and 400 sec. for Conditions 2 and 3 for Protocol A; 200 sec. for Conditions 1, 4 and 5 and 800 sec. for Conditions 2 and 3 for Protocol B; 800 sec. for Conditions 1,4 and 5 and 3200 sec. for Conditions 2 and 3 for Protocol C; and 1600 sec. for Conditions 1, 4 and 5 and 6400 sec. for Conditions 2 and 3 for Protocol D.

[d] Condition 1 is direct mode excitation with a primary excitation filter of 0.15 mm thick Mo. Tube voltage is 50 KV and tube current is 0.6 mA. Condition 2 is direct mode excitation with a primary excitation filter of 0.13 mm thick Rh. Tube voltage is 35 KV and tube voltage is 2.0 mA. Condition 3 uses Ge secondary target excitation with the secondary excitation filtered by a Whatman 41 filter. Tube voltage is 30 KV and tube current is 3.3 mA. Condition 4 uses Ti secondary target excitation with the secondary excitation filtered by 3.8 μm thick mylar film. Tube voltage is 30 KV and tube current is 3.3 mA. Condition 5 uses direct mode excitation with a primary excitation filter consisting of 3 layers of Whatman 41 filters. Tube voltage is 8 KV and tube current os 0.6 mA. Multi-channel analyzer energy range is 0 - 40 KeV for condition 1, 0 - 20 KeV for condition 2, and 0 - 10 KeV for conditions 3, 4, and 5.

[e] Typical exposed area is 406 cm² for standard high-volume filters; 6.4 cm² for 37 mm ringed Teflon-membrane filters; and 13.8 cm² for 47 mm ringed Teflon-membrane filters.

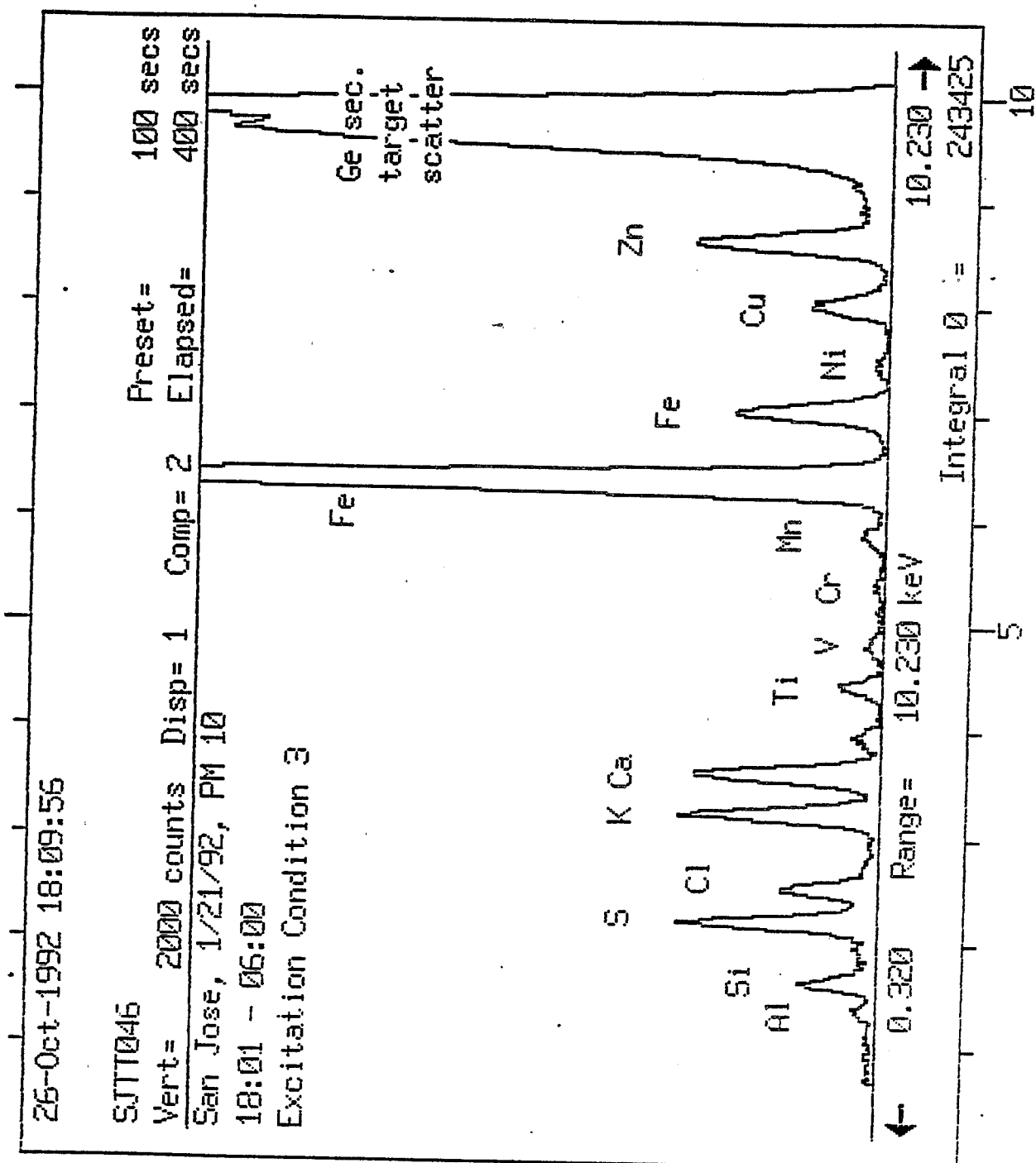[f] Information not available.

[g] For condition 4.

Figure 3-3.   Example of an x-ray fluorescence (XRF) spectrum (Chow *et al.*, 1990d).

Peak overlap coefficients are applied to aerosol deposits. The most important of these overlaps are the K-beta to K-alpha overlaps of elements which increase in atomic number from potassium to zirconium, the lead L-alpha to arsenic K-alpha interference, and the lead M line to sulfur K line interference. The ratios of overlap peaks to the primary peak are determined from the thin film standards for each element for the spectral regions of the remaining elements. These ratios are multiplied by the net peak intensity of the primary peak and subtracted from the spectral regions of other elements. ·

The ability of an x-ray to penetrate matter depends on the energy of the x-ray and the composition and thickness of the material. In general, lower energy x-rays, characteristic of light elements, are absorbed in matter to a much greater degree than higher energy x-rays. XRF analysis of air particulate samples has had widest application to samples collected on membrane-type filters such as Teflon- or polycarbonate-membrane filter substrates. These membrane filters collect the deposit on their surfaces, which eliminates biases due to absorption of x-rays by the filter material. These filters also have a low areal density which minimizes the scatter of incident x-rays, and their inherent trace element content is very low.

Quartz-fiber filters used for high-volume aerosol sampling do not exhibit these features. · As noted earlier, blank elemental concentrations in quartz-fiber filters which have not undergone acceptance testing can be several orders of magnitude higher than the concentrations in the particulate deposits. They vary substantially among the different types of quartz-fiber filters available, and even within the same filter type and manufacturing lot. Blank impurity concentrations and their variabilities decrease the precision of background subtraction from the XRF spectral data, resulting in higher detection limits. Impurities observed in various types of glass- and quartz-fiber filters include aluminum, silicon, sulfur, chlorine, potassium, calcium, iron, nickel, copper, zinc, rubidium, strontium, molybdenum, barium, and lead. Concentrations for aluminum, silicon, and phosphorus cannot be determined for quartz-fiber filters because of the large silicon content of the filters.

Quartz-fiber filters also trap particles within the filter matrix, rather than on its surface. This causes absorption of x-rays within the filter fibers yielding lower concentrations than would otherwise be measured. The magnitude of this absorption increases exponentially as the atomic number of the analyte element decreases and varies from sample to sample. Absorption factors generally are 1.2 or less for iron and heavier elements, but can be from two to five for sulfur.

Quartz-fiber filters are much thicker than membrane filters resulting in the scattering of more x-rays with a consequent increase in background and degradation of detection limits. The increased x-ray scatter also overloads the x-ray detector which requires samples to be analyzed at a lowered x-ray intensity. These effects alone can result in degradation of detection limits by up to a factor of ten with respect to Teflon-membrane substrates.

Larger particles collected during aerosol sampling have sufficient size to cause absorption of x-rays within the particles. Attenuation factors for $PM_{2.5}$ are generally negligible (Criss, 1976), even for the lightest elements, but these attenuations can be significant for coarse fraction

particles (particles with aerodynamic diameters from 2.5 to 10 μm). Correction factors have been derived using the theory of Dzubay and Nelson (1975) and should be applied to the coarse particle measurements for SFS PM_{10} samples.

During XRF or PIXE analysis, filters are removed from their Petri slides and placed with their deposit sides down into filter cassettes. These cassettes are loaded into a mechanism which exposes the filter deposits to protons for PIXE and x-rays for XRF. The sample chamber is evacuated and a computer program controls the positioning of the samples and the excitation conditions. The vacuum in the x-ray chamber and the heat induced by the absorption of x-rays can cause certain materials to volatilize. For this reason, labile species such as nitrate and organic carbon are better measured on a quartz-fiber filter which samples simultaneously with the Teflon-membrane filter.

Quality control standards and replicates from previous batches should be analyzed for every 10 to 20 samples. When quality control results differ from specifications by more than $\pm 5\%$, or if the replicate concentrations differ from the original values (assuming they are at least 10 times detection limits) by more than $\pm 10\%$, the samples should be re-analyzed.

XRF and PIXE are the most commonly used elemental analysis methods owing to their multi-element capabilities, relatively low cost, high detection limits, and preservation of the filter for other analyses. XRF sometimes needs to be supplemented with INAA when extremely low detection limits are needed, but the high cost of INAA prevents this method from being applied to large numbers of samples. Atomic absorption spectroscopy is a good alternative for water-soluble species, but it requires large dilution factors to measure many different elements. ICP is a viable alternative, but it is less desirable because of the expense required to extract the sample and the destruction of the filter sample.

3.3   Water-Soluble Ion Measurement Methods

Aerosol ions refer to chemical compounds which are soluble in water. The water-soluble portion of suspended particles associates itself with liquid water in the atmosphere when relative humidity increases, thereby changing the light scattering properties of these particles. Different emissions sources may also be distinguished by their soluble and non-soluble fractions. Gaseous precursors can also be converted to their ionic counterparts when they interact with chemicals impregnated on the filter material. Samples are generally extracted in DDW which is filtered to remove suspended particulate matter prior to analysis. Several simple ions, such as sodium, magnesium, potassium, and calcium can be quantified by AAS as described above. In practice, AAS has been very useful for measuring water-soluble potassium and sodium, which are important in apportioning sources of vegetative burning and sea salt, respectively. 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, and fluoride may also be measured by these methods along with the polyatomic ions.

All ion analysis methods require a fraction of the filter to be extracted in DDW and then filtered to remove insoluble residues prior to analysis. The extraction volume needs to be as small as possible, lest the solution become too dilute to detect the desired constituents at levels typical of those found in PM_{10}. Each square centimeter of filter should be extracted in no more than 2 ml of solvent for typical sampler flow rates of 20 to 30 ℓ/min and sample durations of 24 hours. This often results in no more than 20 ml of extract which can be submitted to the different analytical methods, thereby giving preference to those methods which require only a small sample. Sufficient sample deposit must be acquired to account for the dilution volume required by each method.

When other analyses are to be performed on the same filter, the filter is first sectioned using a precision positioning jig attached to a paper cutter. For rectangular filters (typically 20.32 cm × 25.40 cm), a 2.54 × 20.32 cm wide strip is cut from the center two-thirds of the filter. High-volume PM_{10} samplers have a 1.27 cm border around them, making the exposed area ~406 cm^2 and the area of the deposit on the filter strip 33.9 cm^2. The analysis results must be multiplied by ~12.0 to estimate the ion deposit on the entire filter. These values should be verified by measurement, since different filter frames may have different dimensions. Circular filters are usually cut in half for these analyses, so the results need to be multiplied by two to obtain the deposit on the entire filter. Filter materials for these analyses must be chosen so that they can be easily sectioned without damage to the filter or the deposit. The cutting blade should be cleaned between each filter cutting. The filter section is placed in an extraction vial which is capable of allowing it to be fully immersed in ~10 ml of solvent (the Falcon #2045 16 × 150 mm polystyrene vials are good choices). Each vial should be properly labeled with the sample ID and capped. Since much of the deposit is inside a fiber filter, agitation is needed to extract the water soluble particles into the solution. Experiments show that sonication for ~1 hour, shaking for ~1 hour, and aging for ~12 hours assures complete extraction of the deposited material in the solvent. The sonicator bath water needs to be periodically replaced or recirculated to prevent temperature increases from the dissipation of ultrasonic energy in the water. After extraction, these solutions should be stored under refrigeration prior to analysis. The unused filter sections should be placed back into their labeled containers and stored under refrigeration. These can be used for other analyses or they can serve as a backup if the original solution becomes contaminated or is insufficient for the planned ionic analyses.

The operating principle for AAS was described above. For potassium, the monochromater is set at 766.5 nm with a 2.0 nm bandpass. For sodium, the monochromater is set at 589.0 nm with a 0.7 nm bandpass. Approximately one to two ml of the extract are aspirated into an air/acetylene flame at approximately 0.5 ml/min. The output of the photomultiplier can be recorded on a data acquisition computer at rates of approximately two readings per second, and an overall 30 second average can be taken to attenuate variability due to flame fluctuation. This averaging should begin only after the sample has been aspirated for at least 30 seconds to assure that the flame has equilibrated. Two ml of DDW should be run between each sample to minimize carryover from the sample line. A blank and a known standard should be analyzed every ten samples to verify the span and baseline. Ten percent of the samples should be run in replicate at a later time, when there is sufficient extract, to evaluate

analysis precision. American Chemical Society (ACS) reagent grade salts are dissolved in carefully measured volumes of DDW to create calibration and performance testing standards. Ionization interference is eliminated by addition of cesium chloride to samples and standard solutions.

IC can be used for both anions (fluoride, phosphate, chloride, nitrate, sulfate) and cations (potassium, ammonium, sodium) with separate columns. Applied to aerosol samples, the anions are most commonly analyzed by IC with the cations being analyzed by a combination of AAS and AC. In IC (Small et al., 1975; Mulik et al., 1976, 1977; Butler et al., 1978; Mueller et al., 1978; Rich et al., 1978; Small, 1978), the sample extract passes through an ion-exchange column which separates the ions in time for individual quantification, usually by a electroconductivity detector. Figure 3-4 shows a schematic representation of the IC system. Prior to detection, the column effluent enters a suppressor column where the chemical composition of one element is altered, resulting in a matrix of low conductivity. The ions are identified by their elution/retention times and are quantified by the conductivity peak area or peak height. IC is especially desirable for particle samples because it provides results for several ions with a single analysis and it uses a small portion of the filter extract with low detection limits. Figure 3-5 shows an example of an IC anion chromatogram. IC analyses can be automated by interfacing to an automatic sampler which can conduct unattended analysis of as many as 400 samples (Tejada et al., 1978).

In IC, approximately 2 ml of the filter extract are injected into IC system. The resulting peak integrals are converted to concentrations using calibration curves derived from solution standards. Standard solutions of sodium chloride, sodium nitrate, and sodium sulfate can be prepared with reagent grade salts which are dehydrated in a desiccator several hours prior to weighing. NIST traceable simulated rain water standards (Standard Reference Materials: SRM 2694-I and SRM 2694-II) and the Environmental Research Associates (ERA) standard solution are available as independent quality control checks for the ions commonly measured by IC. Blanks and standards should be analyzed every ten samples, and one tenth of all PM_{10} extracts should be re-analyzed in the next analysis batch to estimate precision.

Though automated data processing is usually applied to IC output, the chromatograms are too complex for such software to detect deviations from measurement assumptions. Each chromatogram should be examined individually to verify: 1) proper operational settings; 2) correct peak shapes and integration windows; 3) peak separation; 4) correct background substraction; and 5) quality control sample comparisons. When values for replicates differ by more than ±10%, or values for standards differ by more than ±5%, all samples before and after these quality control checks should be re-analyzed. Individual samples with unusual peak shapes, background subtractions, or operating parameters should also be re-analyzed.

AC applies different colorimetric analyses to small samples volumes with automatic sample throughput. The most common ions measured are ammonium, chloride, nitrate, and sulfate (Butler et al., 1978; Mueller et al., 1978; Fung et al., 1979; Pyen and Fishman, 1979).

Delivery Module

Eluent
Reservoir

Pump

Sample
Injector

Chromatography Module

Guard
Column

Separator
Column

Detector Module

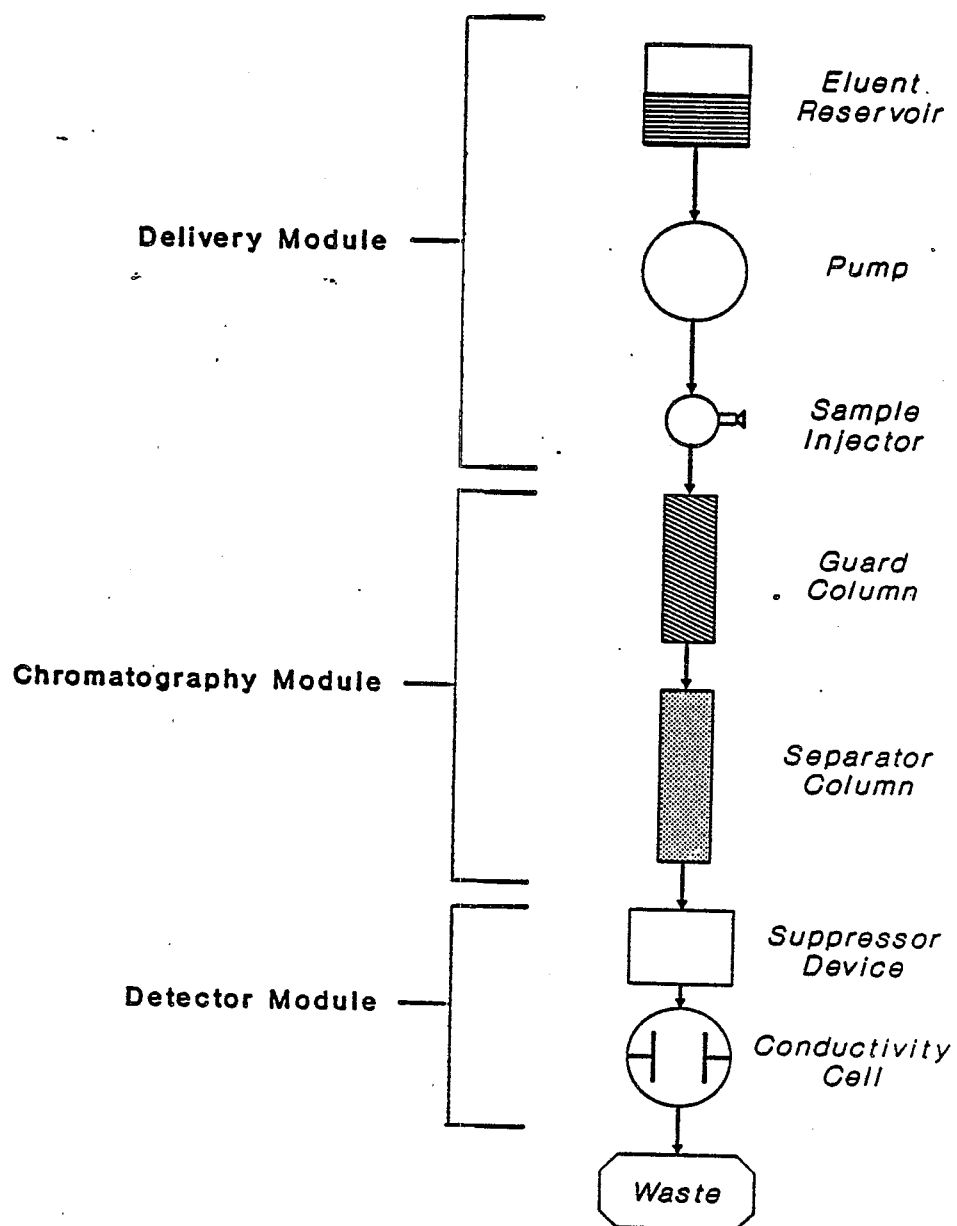Suppressor
Device

Conductivity
Cell

Waste

Figure 3-4.   Schematic representation of an ion chromatography (IC) system (Chow and Richards, 1990).
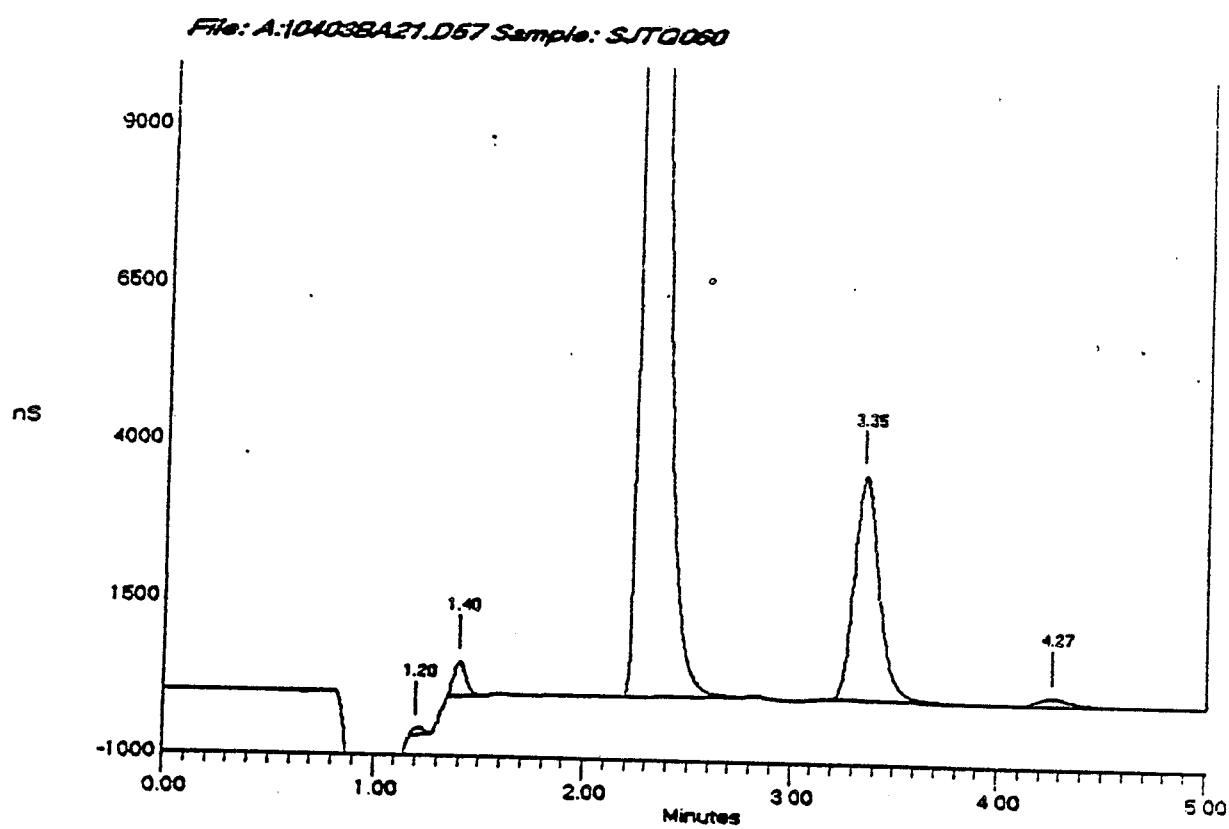
Figure 3-5.   Example of an ion chromatogram (Chow *et al.*, 1993d).

Since IC provides multi-species analysis for the anions, ammonium is most commonly measured by AC.

The AC system is illustrated schematically in Figure 3-6. The heart of the automated colorimetric system is a peristaltic pump, which introduces air bubbles into the sample stream at known intervals. These bubbles separate samples in the continuous stream. Each sample is mixed with reagents and subjected to appropriate reaction periods before submission to a colorimeter. The ion being measured usually reacts to form a colored liquid. The liquid absorbance is related to the amount of the ion in the sample by Beer's Law. This absorbance is measured by a photomultiplier tube through an interference filter which is specific to the species being measured.

The standard AC technique can analyze ~50 samples per hour per channel, with minimal operator attention and relatively low maintenance and material costs. Several channels can be set up to simultaneously analyze several ions. The methylthymol-blue (MTB) method is applied to analyze sulfate. The reaction of sulfate with MTB-barium complex results in free ligand, which is measured colorimetrically at 460 nm. Nitrate is reduced to nitrite which reacts with sulfanilamide to form a diazo compound. This is then reacted to an azo dye for colorimetric determination at 520 nm. Ammonium is measured with the indophenol method. The sample is mixed sequentially with potassium sodium tartrate, sodium phenolate, sodium hypochlorite, sodium hydroxide, and sodium nitroprusside. The reaction results in a blue-colored solution with an absorbance measured at 630 nm.

Formaldehyde has been found to interfere with ammonium measurements when present in an amount which exceeds 20% of the ammonium content, and hydrogen sulfide interferes in concentrations which exceed 1 mg/ml. Nitrate and sulfate are also potential interferents when present at levels which exceed 100 times the ammonium concentration. These levels are rarely exceeded in ambient samples. The precipitation of hydroxides of heavy metals such as magnesium and calcium is prevented by the addition of disodium ethylenediamine-tetracetate (EDTA) to the sample stream (Chow et al., 1980; Chow, 1981). It was learned in the SUlfate Regional Experiment (SURE) (Mueller et al., 1983) that the auto-sampler should be enclosed in an atmosphere which is purged of ammonia by bubbling air through a phosphoric acid solution.

The automated colorimetric system requires a periodic standard calibration with the daily prepared reagents flowing through the system. Lower quantifiable limits of automatic colorimetry for sulfate and nitrate are an order of magnitude higher than those obtained with ion chromatography.

Intercomparison studies between automated colorimetry and ion chromatography have been conducted by Butler et al. (1978); Mueller et al. (1978); Fung et al. (1979); and Pyen and Fishman (1979). Butler et al. (1978) found excellent agreement between sulfate and nitrate measurements by automated colorimetry and ion chromatography. The accuracy of both methods is within the experimental errors, with higher blank values observed from automated
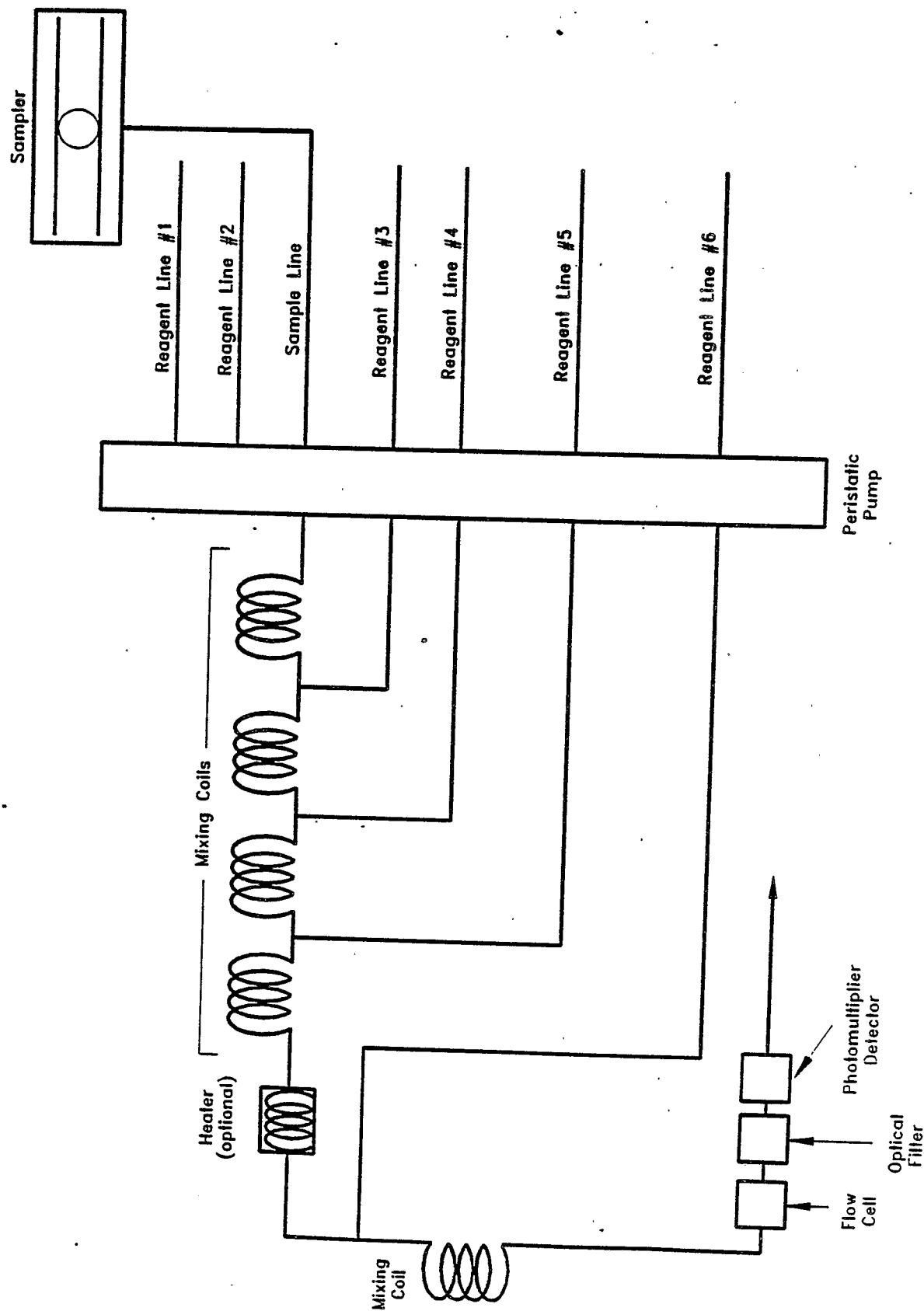
3-19

Figure 3-6. Schematic of a typical automated colorimetric (AC) system (Technicon Instruments Corporation, 1986).

colorimetric techniques. Comparable results were also obtained between the two methods by Fung *et al.* (1979). The choice between the two methods for sample analysis are dictated by sensitivity, scheduling, and cost constraints.

The major sampling requirement for analysis of water-soluble species is that the filter material be hydrophilic, allowing the water to penetrate the filter and fully extract the desired chemical compounds. Small amounts of ethanol or other wetting agents are sometimes added to the filter surface to aid the wetting of hydrophobic filter materials, but this introduces the potential for contamination of the sample.

3.4   Carbon Measurement Method Selection

Three classes of carbon are commonly measured in ambient 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 (i.e., 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 (Johnson *et al.*, 1981). Though progress has been made in the quantification of specific organic chemical compounds in suspended particles (e.g., Rogge *et al.*, 1991), sampling and analysis methods have not yet evolved for use in practical monitoring situations.

Several analytical methods for the separation of organic and elemental carbon in ambient and source particulate samples have been evaluated (Cadle and Groblicki, 1982; Stevens *et al.*, 1982). These methods include:

- Solvent extraction of the organics followed by total carbon analysis (Gordon, 1974; Grosjean, 1975; Appel *et al.*, 1976, 1979; Daisey *et al.*, 1981; Muhlbaier and Williams, 1982; Japar *et al.*, 1984).

- Nitric acid digestion of the organics followed by total carbon analysis (McCarthy and Moore, 1952; Kukreja and Bove, 1976; Pimenta and Wood, 1980).

- Absorption of radiation using an integrating plate to determine elemental carbon. Infrared absorbance (Smith *et al.*, 1975), Raman spectroscopy (Rosen *et al.*, 1978), and visible absorbance (Lin *et al.*, 1973; Weiss *et al.*, 1979; Gerber, 1982; Heintzenberg, 1982) are variations of this method.

- Thermal combustion including both temperature programmed (Muhlbaier and Williams, 1982) and step-wise pyrolysis followed by oxidation using either carbon dioxide or methane detection (Mueller *et al.*, 1971, 1981; Patterson, 1973; Merz, 1978; Johnson and Huntzicker, 1979; Johnson *et al.*, 1980; Malissa, 1979; Cadle *et al.*, 1980a, 1980b; Heisler *et al.*, 1980a, 1980b; Novakov, 1981; Tanner *et al.*, 1982; Wolff *et al.*, 1982).

- A combination of thermal and optical methods (Appel *et al.*, 1976; Dod *et al.*, 1979; Macias *et al.*, 1979; Cadle *et al.*, 1980a, 1980b; Johnson *et al.*, 1981; Novakov, 1982; Huntzicker *et al.*, 1982; Rosen *et al.*, 1982; Chow *et al.*, 1993c).

Table 3-3 summarizes different carbon analysis methods and reports typical carbon concentrations in urban and non-urban areas.

The definitions of organic and elemental carbon are operational (i.e., method dependent) and reflect the method and purpose of measurement (Grosjean, 1980). Elemental carbon is sometimes termed "soot", "graphitic carbon", or "black carbon." For studying visibility reduction, light-absorbing carbon is a more useful concept than elemental carbon. For source apportionment by receptor models, several consistent but distinct fractions of carbon in both source and receptor samples are desired, regardless of their light-absorbing or chemical properties. Differences in ratios of the carbon concentrations in these fractions form part of the source profile which distinguishes the contribution of one source from the contributions of other sources (Watson *et al.*, 1994c).

Light-absorbing carbon is not entirely graphitic carbon, since there are many organic materials which absorb light (e.g., tar, motor oil, asphalt, coffee). Even the "graphitic" black carbon in the atmosphere has only a poorly developed graphitic structure with abundant surface chemical groups. "Elemental carbon" is a poor but common description of what is measured. For example, a substance of three-bond carbon molecules (e.g., pencil lead) is black and completely absorbs light, but four-bond carbon in a diamond is completely transparent and absorbs very little light. Both are pure, elemental carbon.

Chow *et al.* (1993c) document several variations of the thermal (T), thermal/optical reflectance (TOR), thermal/optical transmission (TOT), and thermal manganese oxidation (TMO) methods for organic and elemental carbon. The TOR and TMO methods have been most commonly applied in aerosol studies.

3.4.1 Thermal Manganese Oxidation Method for Carbon

The thermal manganese oxidation (TMO) method (Mueller *et al.*, 1982; Fung, 1990) uses manganese dioxide present and in contact with the sample throughout the analysis, as the oxidizing agent. Temperature is relied upon to distinguish between organic and elemental carbon. Carbon evolving at 525°C is classified as organic carbon, and carbon evolving at 850°C is classified as elemental carbon.

This method has been used for the five year SCENES (the Subregional Cooperative Electric Utility, Department of Defense, National Park Services, and Environmental Protection Agency Study) (i.e., Mueller and McDade, 1986; Sutherland and Bhardwaja, 1986; Mueller *et*

Table 3-3
Carbon analysis method characteristics

Typical Ambient Concentration ($\mu g/m^3$)	Measurement Method	Precision[a]	Accuracy[b]	LQL[c]	Advantages and Disadvantages
Urban sites (0 to 2.5 μm)[d] OC[i] 2.7 to 12.9 EC 0.9 to 7.0 TC 3.6 to 19.0 Non-urban sites (0 to 2.5 μm)[d] OC 1.2 to 4.3 EC 0.5 to 2.2 TC 1.5 to 6.0	Solvent Extraction	5 to 15%[e]	20 to 54%[e]	NA[f]	Only 30 to 50% of volatilizable carbon can be removed The procedure underestimates volatilizable carbon and overestimates elemental carbon by 9 to 20% Pyrolytic conversion of volatilizable to elemental carbon is minimized These methods require significant quantities of sample and are time consuming and expensive
	Nitric Acid Digestion	1.4 to 5.8%[e]	15 to 32%[e]	NA[f]	Some elemental carbon is measured as volatilizable carbon because nitric acid converts elemental carbon to volatilizable carbon
	Integrating Plate Method	NA[f]	NA[f]	NA[f]	Relies on poorly determined absorption coefficients and is subject to interferences Interference by non-absorbing species such as $(NH_4)_2 SO_4$ on elemental carbon measurements
	Thermal Combustion Method	1 to 2%[g]	14-15%[g,h]	0.3$\mu g/cm^2$ for OC 0.5$\mu g/cm^2$ for EC	Different thermal combustion analyzers with different procedures often yield different values for identical samples Overestimates elemental carbon due to the carbonization of volatilizable material Underestimates elemental carbon due to the measurement of volatilizable carbon at high temperatures

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Table 3-3 (continued)
Carbon analysis method characteristics

Typical Ambient Concentration $(\mu g/m^3)$	Measurement Method	Precision[a]	Accuracy[b]	LQL[c]	Advantages and Disadvantages
	Thermal/ Optical Method	2 to 4%[j]	2 to 5%[k]	$0.5\mu g/cm^2$[j] for OC	Separates volatilizable from elemental carbon
				$0.2\mu g/cm^2$ for EC	Corrects for pyrolysis
					Carbonate carbon is measured as volatilizable and elemental carbon if present as more than 5% at total carbon

[a] $\pm$ one standard deviation, per filter, unless otherwise specified

[b] $\pm$ absolute error

[c] LQL = Lower Quantifiable Limit; often determined by variability in blank analysis or minimum detectable limit - whichever is greater

[d] From Shah (1981)

[e] From Cadle and Groblicki (1982)

[f] NA = not available

[g] From Mueller et al. (1983)

[h] From Watson et al. (1981)

[i] From Stevens et al. (1982)

[j] From Johnson (1981)

[k] From Rau (1986) and Chow et al. (1993b)

[l] OC: Organic Carbon
EC: Elemental Carbon
TC: Total Carbon

al., 1986; Watson *et al.*, 1987) visibility network, as well as Southern California Air Quality Study (SCAQS, Chow *et al.*, 1994b, 1994c; Watson *et al.*, 1993, 1994b, 1994d).

3.4.2 Thermal Optical Reflectance/Transmission Method for Carbon

The thermal/optical reflectance (TOR) method of carbon analysis developed by Huntzicker *et al.* (1982) has been adapted by several laboratories for the quantification of organic and elemental carbon on quartz-fiber filter deposits. While the principle used by these laboratories is identical to that of Huntzicker *et al.* (1982), the details differ with respect to calibration standards, analysis time, temperature ramping, and volatilization/combustion temperatures.

In the most commonly applied version of the TOR method (Chow *et al.*, 1993c), a filter is submitted to volatilization at temperatures ranging from ambient to 550°C in a pure helium atmosphere, then to combustion at temperatures between 550°C to 800°C in a 2% oxygen and 98% helium atmosphere with several temperature ramping steps. The carbon which evolves at each temperature is converted to methane and quantified with a flame ionization detector. The reflectance from the deposit side of the filter punch is monitored throughout the analysis. This reflectance usually decreases during volatilization in the helium atmosphere owing to the pyrolysis of organic material. When oxygen is added, the reflectance increases as the light-absorbing carbon is combusted and removed. An example of the TOR thermogram is shown in Figure 3-7.

Organic carbon is defined as that which evolves prior to re-attainment of the original reflectance, and elemental carbon is defined as that which evolves after the original reflectance has been attained. By this definition, "organic carbon" is actually organic carbon that does not absorb light at the wavelength (632.8 nm) used and "elemental carbon" is light-absorbing carbon (Chow *et al.*, 1993c). The thermal/optical transmission (TOT) method applies to the same thermal/optical carbon analysis method except that transmission instead of reflectance of the filter punch is measured.

Chow *et al.* (1993c) document several variations of the thermal (T), thermal/optical reflectance (TOR), thermal/optical transmission (TOT), and thermal manganese oxidation (TMO) methods for organic and elemental carbon. Chow *et al.* (1993c) also examine results from collocated elemental carbon measurements by optical absorption (OA), photoacoustic spectroscopy, and nonextractable mass. TOR was consistently higher than TMO for elemental carbon, especially in woodsmoke-dominated samples, where the disparity was as great as seven fold. For the sum of organic and elemental carbon, these methods reported agreement within 5% to 15% for ambient and source samples (Houck *et al.*, 1989; Kusko *et al.*, 1989; Countess, 1990; Shah and Rau, 1991) and within 3% on carefully prepared standards. Evaluation of these methods then becomes a matter of assessing how they differentiate between organic and elemental carbon. The TMO method attributes more of the total carbon to organic carbon and less to elemental carbon than the TOR and TOT methods.
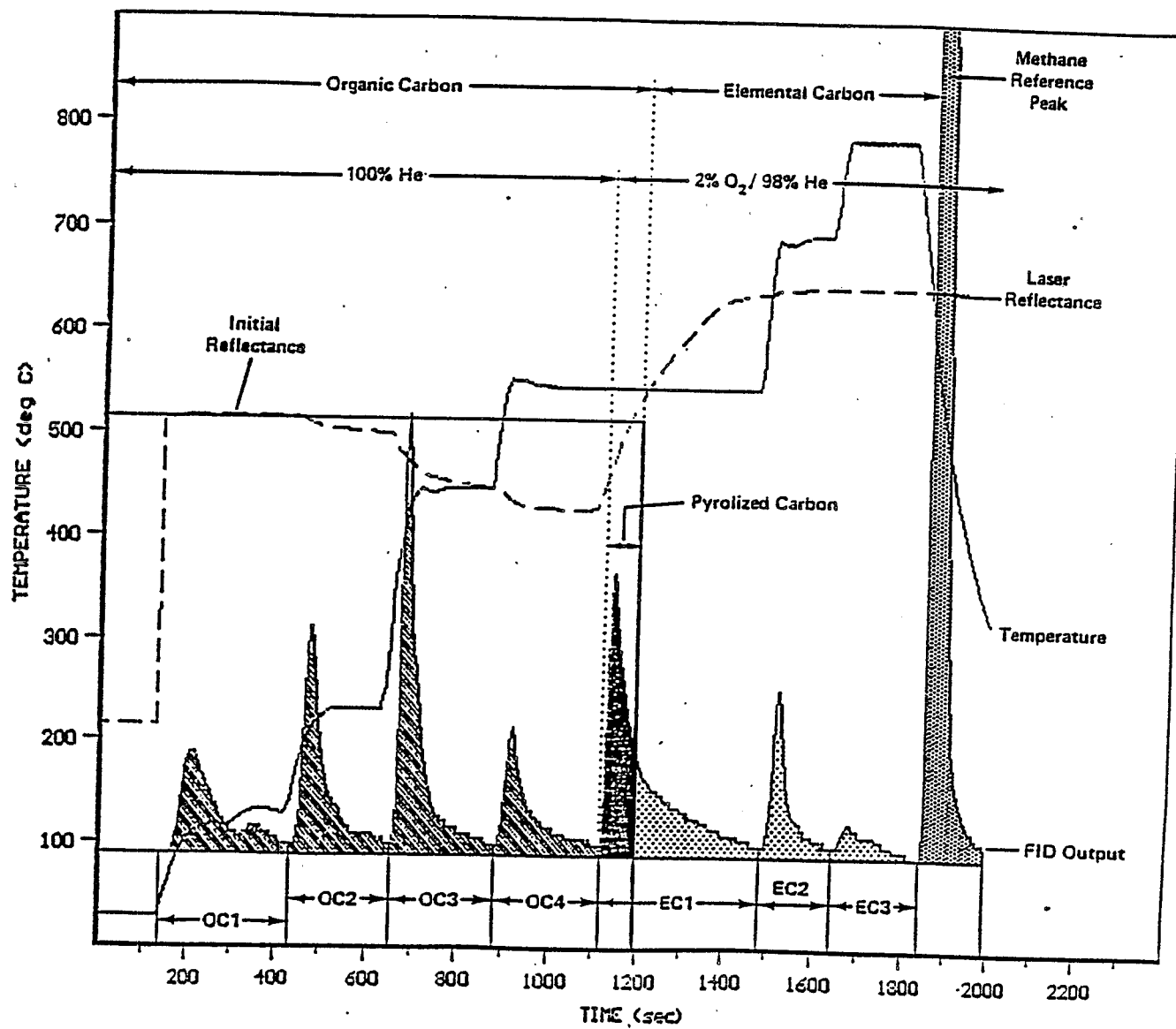
Figure 3-7. Example of a thermal optical reflectance (TOR) thermogram (Chow *et al.*, 1993c).

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 (Countess, 1990; Hering *et al.*, 1990). None of them represents an ideal separation procedure of organic from elemental carbon.

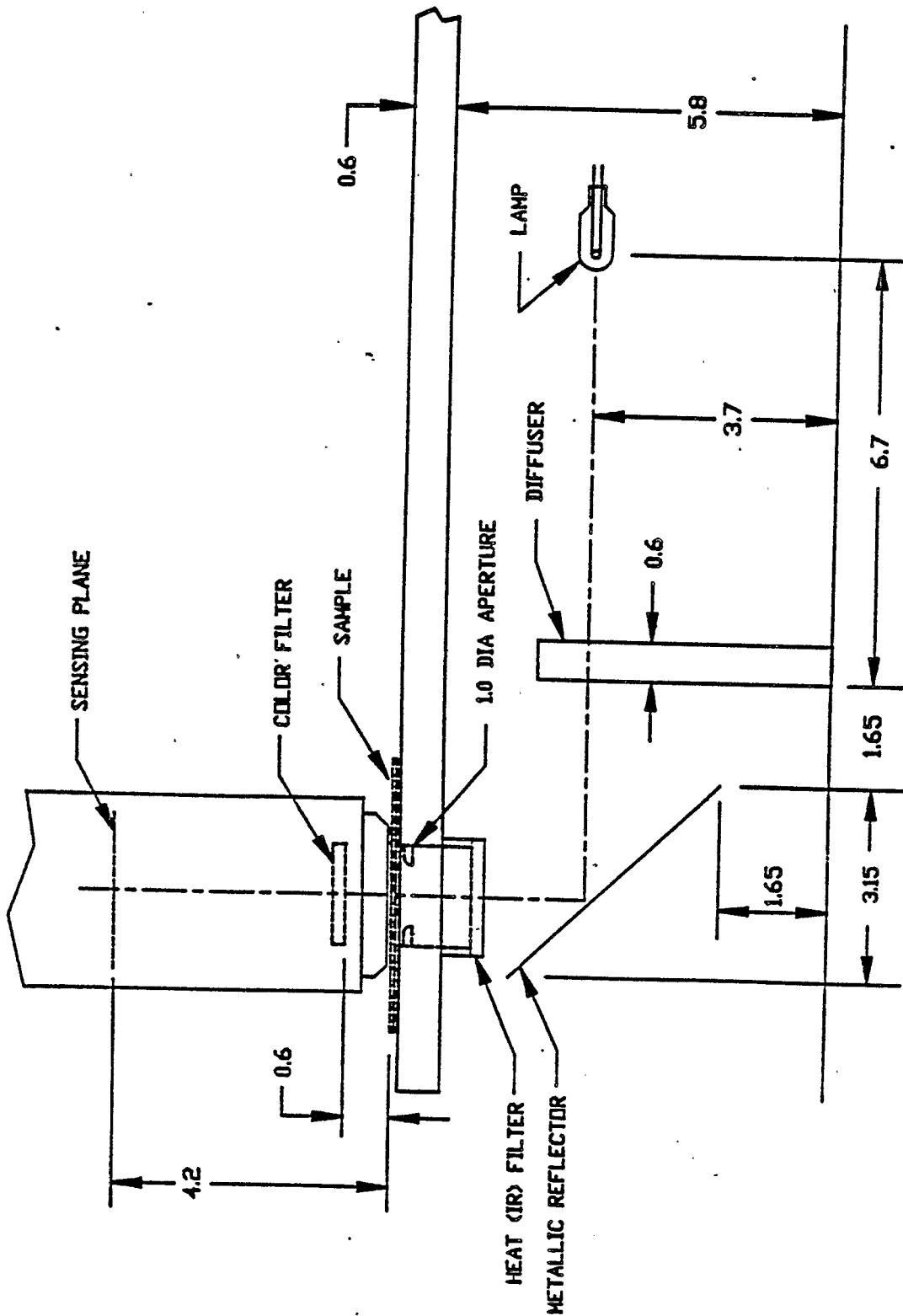### 3.4.3 Filter Transmission for Light Absorbing Carbon

Teflon-membrane and quartz-fiber filters can be submitted to a light transmission measurement before and after sampling on a transmission densitometer. An example of the measurement system is illustrated in Figure 3-8. Each filter is placed in a jig over a diffused vertical light beam. The spectral distribution is approximately Gaussian, peaking near 550 nm with full·width at half maximum of about 150 nm. A detector is brought to a constant height above the filter and is precisely positioned with a shim to prevent contact with the filter itself.· The filter density is displayed by the densitometer and can be later converted to transmittance. The same measurement is repeated on the exposed filter.

The instrument is calibrated with neutral density filters, and one of these standards is analyzed every 10 filters to verify instrument stability. If the response to these standards differs from specifications by more than 0.03 density units, the instrument is re-calibrated and the measurements are repeated on the previous ten samples. Replicate analyses are performed on one out of every ten samples, and when replicates deviate by more than ±0.05 density units from their original levels, samples are re-measured.

Informal intercomparisons among different filter transmission methods have shown high correlations of absorption, but differences of up to a factor of two in absolute values (Watson *et al.*, 1988c). These differences are functions of: 1) the type of filter; 2) filter loading; 3) the chemical and physical nature of the deposit; 4) the wavelengths of light used; 5) calibration standards; and 6) light diffusing methods. At the current time, there is no agreement on which combination most accurately represents light absorption in the atmosphere. This method is applied with the knowledge that absolute differences in absorption may be found between the measurements made on Teflon-membrane and quartz-fiber filters and with respect to absolute absorption measurements made on the same samples in other laboratories.

3.5 Filter Selection, Preparation, Handling, and Storage

No chemical analysis method, no matter how accurate or precise, can provide an accurate representation of atmospheric constituents if the filters to which these methods are applied are improperly selected or handled. The different filter media available for PM_{10} sampling for chemical analysis were described in Section 2. This sub-section describes how these filters should be selected, prepared, handled, and stored from a laboratory standpoint. Mass concentrations associated with PM_{10} are usually measured in micrograms, one millionth of one gram. These are very small quantities, and even the slightest contamination can bias these mass

NOTE: DIMENSIONS IN CENTIMETERS
OK TO SCALE DRAWING

Figure 3-8. Example of a light transmission measurement system (Watson *et al.*, 1988b).

measurements. Most of chemical species which constitute PM_{10} are measured in nanograms, one-billionth of one gram. The potential for contamination from these chemical components is ten to one-thousand times greater than it is for contamination of mass concentrations. Small biases in chemical concentrations can greatly affect the decisions which are made with respect to source apportionment or health effects, so extra precautions are warranted when selecting and using filters.

As pointed out in Section 2, the choice of filter type results from a compromise among the following filter attributes: 1) mechanical stability; 2) chemical stability; 3) particle or gas sampling efficiency; 4) flow resistance; 5) loading capacity; 6) blank values; 7) artifact formation; 8) compatibility with analysis method; and 9) cost and availability. Teflon-membrane and quartz-fiber filters are most commonly used for the PM_{10} chemical analyses described above, though cellulose-fiber filters lend themselves nicely to impregnation for absorbing gaseous precursors, and etched polycarbonate-membrane filters are best suited for microscopic analyses. Specific choices which have been found to be useful in previous receptor modeling source apportionment studies are: 1) Gelman (Ann Arbor, MI) polymethylpentane ringed, 2.0 μm pore size, 47 mm and 37 mm diameter PTFE Teflon-membrane filters (#R2PJ047, #R2PJ037) for mass by gravimetry, elements by XRF or PIXE, and optical absorption measurements by filter transmission; 2) Schleicher and Schuell (Keene, NH) 1.2 μm pore size, grade 66, 47 mm diameter, nylon-membrane filters (#00440) for volatilized particle nitrate as well as total nitrite; 3) Pallflex (Putnam, CT) 47 mm diameter quartz-fiber filters (#2500 QAT-UP) for carbon by combustion methods as well as water-soluble chloride, nitrate, sulfate, ammonium, sodium, and potassium by IC, AC, and AAS measurements; and 4) Whatman 41 (Maldstone, England) 47 mm diameter cellulose-fiber filters (#1441047) impregnated with adsorbing chemicals for sulfur dioxide and ammonia measurements. These filters have been used primarily in the low-volume samplers described in Tables 2-1 and 2-2. High-volume PM_{10} samplers require 20.32 cm $\times$ 25.40 cm rectangular filters, of which the Gelman Zefluor Teflon-membrane, 2 μm pore size filters (#F2996-25) have been most commonly used for elemental analyses and the Gelman quartz-fiber (QM/A) filters have been used for other analyses. The manufacturer's identification numbers are important specifications since only these particular filters have been found to acceptably meet the requirements for chemical characterization in previous studies.

As noted in Section 2, filters require treatment and representative chemical analyses before they can be used (Chow, 1987). At least one filter from each lot purchased from the specified manufacturers should be analyzed for all species to verify that pre-established specifications have been met. Table 3-4 tabulates filter acceptance test results between 1992 and 1993 on over 200 lots for different filters. Lots are rejected for chemical analysis when blank levels for individual species exceed 1 μg/filter. Table 3-4 shows that blank values are verified for various species on different filter types. Each filter should also be individually examined prior to labeling for discoloration, pinholes, creases, or other defects. Testing of sample media should continue throughout the course of a monitoring project. In addition to laboratory blanks, 5% to 10% of all samples are designated as field blanks, and these follow all handling procedures except for actual sampling. Sample pre-treatments may include:

Table 3-4
Summary of filter acceptance test results performed at DRI's Environmental Analysis Facility between 1992 and 1993

Chemical Species	Filter Type	Manufacturer	Standard Avg. ± Deviation[a]	Unit	Filter Lots	Filters Tested
Chloride (Cl⁻)	Teflon-membrane (2.0 μm pore size, 47 mm diameter, #R2PJ047)	Gelman Instrument Co. 600 S. Wagner Rd. Ann Arbor, MI 48106 (313) 665-0651	0.35 ± 0.27	μg/filter	84	112
	Quartz-fiber (#2500 QAT-UP)	Pallflex Production Co. Kennedy Dr. Putnam, CT 06260 (203) 928-7761	0.46 ± 0.19	μg/filter	108	160
Nitrate (NO₃⁻)	Teflon-membrane (2.0 μm pore size, 47 mm diameter, #R2PJ047)	Gelman Instrument Co. 600 S. Wagner Rd. Ann Arbor, MI 48106 (313) 665-0651	0.032 ± 0.097	μg/filter	84	112
	Quartz-fiber (#2500 QAT-UP)	Pallflex Production Co. Kennedy Dr. Putnam, CT 06260 (203) 928-7761	0.18 ± 0.24	μg/filter	108	160

Table 3-4 (continued)

Summary of filter acceptance test results performed at DRI's
Environmental Analysis Facility between 1992 and 1993

Chemical Species	Filter Type	Manufacturer	Standard Avg. ± Deviation[a]	Unit	Filter Lots	Filters Tested
Nitrate (NO₃) (continued)	Nylon-membrane (1.2 μm pore size, grade 66, 47 mm diameter, #00440)	Schleicher & Schuell, Inc. 543 Washington St. Keene, NH 03431 (800) 245-4029	0.21 ± 0.18	μg/filter	30	51
Sulfate (SO₄⁼)	Teflon-membrane (2.0 μm pore size, 47 mm diameter, #R2PJ047)	Gelman Instrument Co. 600 S. Wagner Rd. Ann Arbor, MI 48106 (313) 665-0651	0.034 ± 0.087	μg/filter	84	112
	Quartz-fiber (#2500 QAT-UP)	Pallflex Production Co. Kennedy Dr. Putnam, CT 06260 (203) 928-7761	0.28 ± 0.25	μg/filter	108	160
	Nylon-membrane (1.2 μm pore size, grade 66, 47 mm diameter, #00440)	Schleicher & Schuell, Inc. 543 Washington St. Keene, NH 03431 (800) 245-4029	0.086 ± 0.13	μg/filter	30	51

Table 3-4 (continued)

Summary of filter acceptance test results performed at DRI's
Environmental Analysis Facility between 1992 and 1993

Chemical Species	Filter Type	Manufacturer	Standard Avg. ± Deviation[a]	Unit	Filter Lots	Filters Tested
Sulfate ($SO_4^=$) (continued)	Whatman 41 Cellulose Fiber Impregnated with K_2CO_3 (47 mm diameter, #1441047)	Whatman, Inc. 9 Bridewell Place Clifton, NJ 07014 (201) 773-5800	0 ± 0	μg/filter	3	6
Ammonium (NH_4^+)	Teflon-membrane (2.0 μm pore size, 47 mm diameter, #R2PJ047)	Gelman Instrument Co. 600 S. Wagner Rd. Ann Arbor, MI 48106 (313) 665-0651	0.16 ± 0.18	μg/filter	86	121
	Quartz-fiber (#2500.QAT-UP)	Pallflex Production Co. Kennedy Dr. Putnam, CT 06260 (203) 928-7761	0.14 ± 0.27	μg/filter	102	153
	Whatman 41 Cellulose Fiber Impregnated with Citric Acid (47 mm diameter, #1441047)	Whatman, Inc. 9 Bridewell Place Clifton, NJ 07014 (201) 773-5800	0.17 ± 0.03	μg/filter	4	8
Soluble Sodium (Na^+)	Teflon-membrane (2.0 μm pore size, 47 mm diameter, #R2PJ047)	Gelman Instrument Co. 600 S. Wagner Rd. Ann Arbor, MI 48106 (313) 665-0651	0.19 ± 0.19	μg/filter	86	114

Table 3-4 (continued)
Summary of filter acceptance test results performed at DRI's Environmental Analysis Facility between 1992 and 1993

Chemical Species	Filter Type	Manufacturer	Standard Avg. ± Deviation[a]	Unit	Filter Lots	Filters Tested
Soluble Sodium (Na⁺) (continued)	Quartz-fiber (#2500 QAT-UP)	Pallflex Production Co. Kennedy Dr. Putnam, CT 06260 (203) 928-7761	0.47 ± 0.32	μg/filter	97	140
Soluble Potassium (K⁺)	Teflon-membrane (2.0 μm pore size, 47 mm diameter, #R2PJ047)	Gelman Instrument Co. 600 S. Wagner Rd. Ann Arbor, MI 48106 (313) 665-0651	0.15 ± 0.17	μg/filter	86	114
	Quartz-fiber (#2500 QAT-UP)	Pallflex Production Co. Kennedy Dr. Putnam, CT 06260 (203) 928-7761	0.11 ± 0.13	μg/filter	115	173
Organic Carbon (OC)	Quartz-fiber (#2500 QAT-UP)	Pallflex Production Co. Kennedy Dr. Putnam, CT 06260 (203) 928-7761	0.40 ± 0.31	$\mu g/cm^2$	187	396
Elemental Carbon (EC)	Quartz-fiber (#2500 QAT-UP)	Pallflex Production Co. Kennedy Dr. Putnam, CT 06260 (203) 928-7761	0.029 ± 0.083	$\mu g/cm^2$	187	396

Table 3-4 (continued)

Summary of filter acceptance test results performed at DRI's Environmental Analysis Facility between 1992 and 1993

Chemical Species	Filter Type	Manufacturer	Standard Avg. ± Deviation[a]	Unit	Filter Lots	Filters Tested
Total Carbon (TC)	Quartz-fiber (#2500 QAT-UP)	Pallflex Production Co. Kennedy Dr. Putnam, CT 06260 (203) 928-7761	0.43 ± 0.32	$\mu g/cm^2$	187	396

[a] The acceptance level are: 1.0 μg/37mm- or 47mm-filter for anions and cations, 1.5 $\mu g/cm^2$ for organic carbon, 0.5 $\mu g/cm^2$ for elemental carbon, and 2.0 $\mu g/cm^2$ for total carbon.

- **Pre-firing of quartz-fiber filters.** Quartz-fiber filters adsorb organic vapors over time. Blank quartz-fiber filters should be heated for at least three hours at 900°C. A sample of each batch of 100 pre-fired filters is tested for carbon blank levels prior to sampling, and sets of filters with carbon levels exceeding 1 $\mu g/cm^2$ are re-fired or rejected. All pre-fired filters should be sealed and stored in a freezer prior to preparation for field sampling.

- **Washing nylon-membrane filters.** Nylon-membrane filters absorb nitric acid over time. Blank nylon-membrane filters should be soaked for four hours in 0.015 M sodium carbonate then rinsed in DDW for 10 minutes, soaked overnight in DDW, rinsed three times in DDW, then dried in a vacuum oven at 60°C for 5 to 10 minutes. Extraction efficiency tests have shown that the sodium carbonate IC eluent is needed to remove nitrates from the active sites of the nylon filter. Sets of washed nylon filters with nitrate levels exceeding 1 μg/filter should be rejected. Pre-washed nylon filters should be sealed and refrigerated prior to preparation for field sampling.

- **Equilibrating Teflon-membrane filters.** On several occasions over the past 10 years (e.g., Tombach *et al.*, 1987), batches of Gelman ringed Teflon-membrane filters have yielded variable (by up to 100 μg/filter over a few days) blank masses. As the time between manufacture and use increases, this variability decreases. Since Gelman has minimized its long-term inventory of these filters and is manufacturing them on an as-ordered basis, this variability is being observed with greater frequency. A one-month storage period in a controlled environment, followed by one week of equilibration in the weighing environment, has been applied in several studies, and this appears to have reduced the variability to acceptable (within ±15 μg/filter for re-weights of 47 mm and 37 mm diameter filters) levels. Sets of Teflon-membrane filters which exceed twice XRF detection limits for elements are rejected.

The results of all filter treatments, chemical analyses, and visual inspections should be recorded in a data base with the lot numbers. A set of filter IDs is assigned to each lot so that a record of acceptance testing can be associated with each sample.

In areas with large secondary contributions to PM$_{10}$, Whatman 41 cellulose-fiber filters can be impregnated with gas-adsorbing solutions to collect gaseous ammonia and sulfur dioxide. Several impregnation solutions have been used, and these solutions differ with respect to their reactive components and formulations. The criteria which must be met by the impregnation solution are: 1) availability of pure reagents; 2) stability of the impregnation solution composition before and after impregnation; 3) low degree of hazard or toxicity; 4) lack of interferences with other pollutants being sampled or with analytical methods; and 5) minimal effects of environmental factors such as temperature and water vapor content.

Sulfuric acid (Okita and Kanamori, 1971; Knapp *et al.*, 1986), oxalic acid (Ferm, 1979; Ohira *et al.*, 1976; Shendrikar and Lodge, 1975), phosphoric acid, sodium carbonate (Ferm, 1986), and citric acid (Stevens *et al.*, 1985) have been used as the active agent in the sampling

of ammonia on a variety of substrates. Citric acid impregnating solutions best meet the criteria described above.

Fung (1988) tested the ammonia absorption capacity of Whatman 41 cellulose-fiber filters impregnated with 0.13 µg of citric acid and 0.024 µg of glycerine. These filters adsorbed more than 4,000 µg of ammonia with better than 99% efficiency. Tests at temperatures ranging from -20°C to 25°C and at high and low relative humidities showed sampling efficiencies for ammonia in excess of 99%.

Potassium carbonate or sodium carbonate with glycerine has been used in impregnated filters for sulfur dioxide, nitric acid, or organic acid sampling (Forrest and Newman, 1973; Johnson and Atkins, 1975; Anlauf et al., 1985; Daum and Leahy, 1985; Hering et al., 1993; Tanner et al., 1993). The carbonate in the impregnating solution presents interferences to both the IC and AC analyses of extracts from these filters, however. In IC, the carbonate interferes with the nitrate peak and broadens the sulfate peak. In colorimetric methylthymol-blue analysis, the reaction of the MTB-Ba complex needs to be acidic and the carbonate raises the pH. Steps can be taken to alleviate these in the preparation of the filter extract prior to analysis.

Triethanolamine (TEA) has been used as an absorbent for nitrogen dioxide and to measure aerosol acidity (Dzubay et al., 1979). When used as a solution in a bubbler, TEA is a U.S. EPA equivalent method (No. EQN-1277-028) for monitoring nitrogen dioxide. Alary et al. (1974), Ohtsuka et al. (1978), Gotoh (1980), and Knapp et al. (1986) have applied TEA solutions to filter media such as Whatman 31 chromatographic paper for the collection of nitrogen dioxide. The TEA is usually mixed with glycol or glycerine to improve its absorbing capacity (Doubrava and Blaha, 1980). Peroxyacetyl nitrate (PAN), organic nitrates, and sulfur dioxide are also collected by this substrate, and the nitrogen-containing compounds will appear as nitrate during analysis. TEA oxidizes in air and light, so impregnated filters must be stored in the dark in sealed containers.

Practical impregnation solutions consist of:

- 25% citric acid and 5% glycerol (balance being water) for ammonia sampling.

- 15% potassium carbonate and 5% glycerol solution (balance being water) for sulfur dioxide sampling.

- 25% TEA and 5% ethylene glycol (balance being water) for nitrogen dioxide sampling.

- 5% sodium chloride (balance being water) for nitric acid sampling.

To impregnate filters, cellulose-fiber filter disks are immersed in the impregnating solution for approximately 30 minutes. These disks are then removed and placed in clean Petri slides for drying in a vacuum oven for five to ten minutes. One hundred of the dried

impregnated filters are immediately sealed in polyethylene bags and placed under refrigeration for later loading into filter holders. One sample from each lot of citric acid filters is submitted to ammonium analysis prior to use. One sample from each lot should be extracted and analyzed prior to field sampling to assure that filter batches have not been contaminated. It is also useful to analyze each filter for a component of the impregnating solution (e.g., potassium on potassium carbonate impregnated filters) to verify that filters have acquired a sufficient amount of the adsorbing chemicals.

3.6   Filter Analysis Protocol

The selection of appropriate analysis methods, filter media, and sampling hardware must be complemented with detailed sample handling and analysis procedures. Figure 3-9 shows an example of the flow diagram for a typical PM_{10} sampling system. This diagram also shows the chemical analyses on different sampling channels to which these samples are submitted. Figure 3-10 shows a flow diagram of the different operations which are applied in a typical aerosol characterization monitoring program. Each box represents a set of actions which must be taken as part of the overall measurement process. Flow charts such as these should be prepared prior to aerosol sampling for chemical analyses. They show precisely how samples are to be loaded and which analyses they will receive. This minimizes the possibility of submitting samples to the wrong analyses when filters are returned to the laboratory.
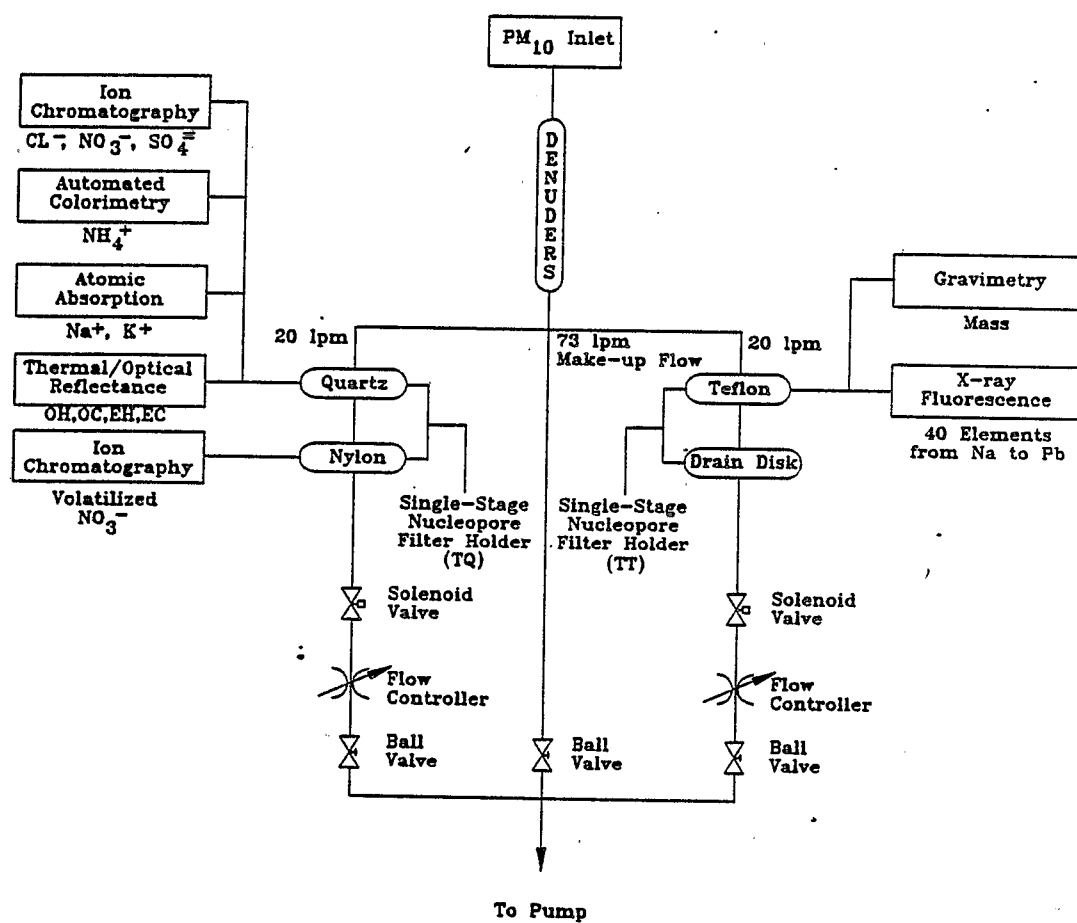
Figure 3-9. Flow diagram of the PM_{10} sequential filter sampler (Chow *et al.*, 1993d).
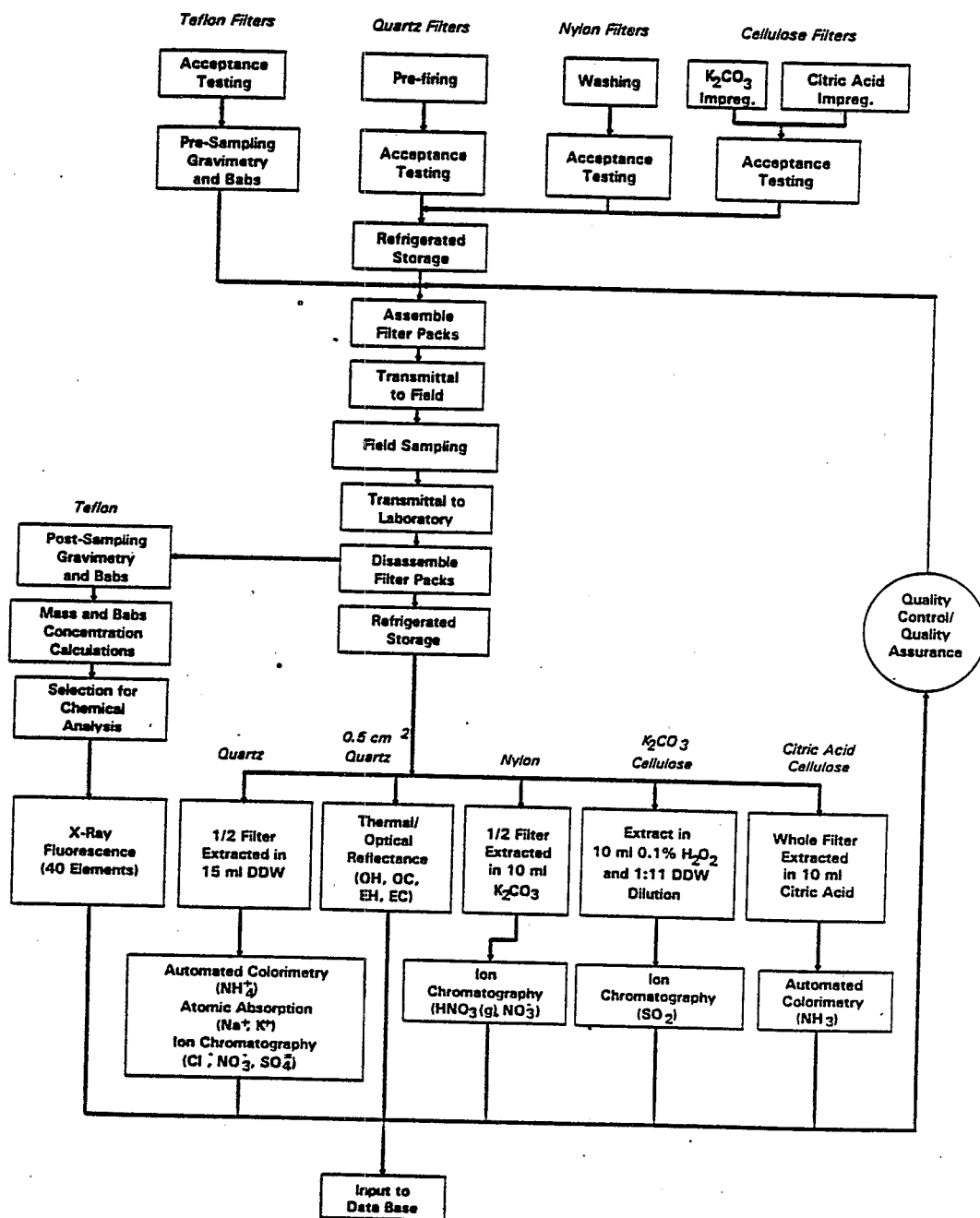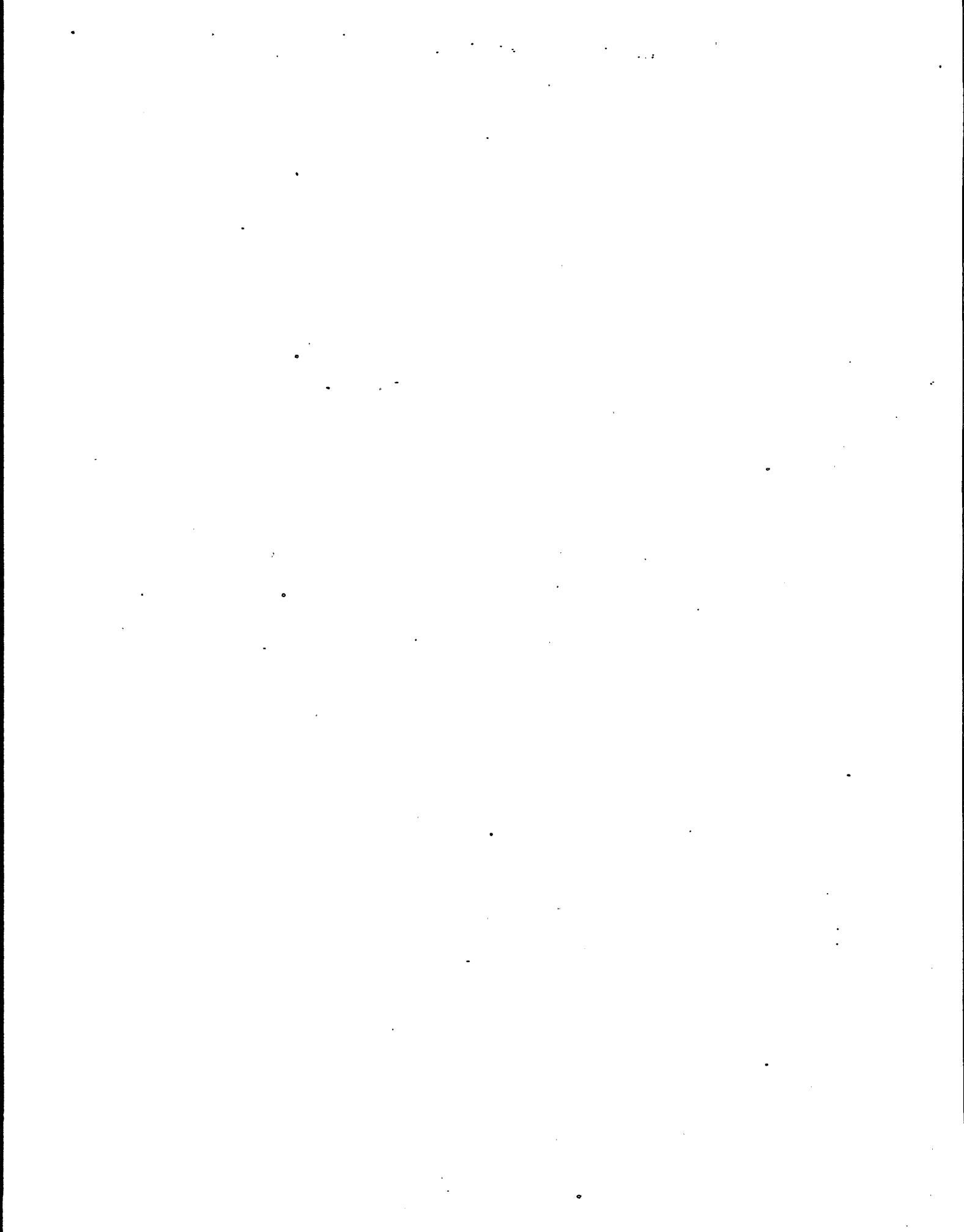
Figure 3-10. Flow diagram of filter processing and chemical analysis activities for an aerosol and gaseous sampling system (Watson *et al.*, 1990b).

4.0 SAMPLING AND ANALYSIS STRATEGIES

4.1 General Approach

The preceding sections have identified different methods for PM_{10} sampling and chemical analysis. These sections have emphasized that chemical analysis of PM_{10} samples must be closely coupled with the appropriate sampling methods and filter handling procedures. This section organizes that general knowledge into specific steps which can be applied when planning a PM_{10} measurement study.

The first step is to determine the specific monitoring objectives. Compliance determination, source apportionment, and control strategy evaluation are the most common objectives for PM_{10} non-attainment areas. Compliance determination requires that PM_{10} mass be measured at least every sixth-day using a U.S. EPA-designated reference or equivalent sampler. As noted in earlier sections, substantial guidance has been given by U.S. EPA for compliance monitoring, and this is not repeated here. The important point to remember is that adherence to these compliance monitoring methods is not sufficient to provide samples amenable to chemical analysis. Source apportionment and control strategy evaluation require chemical speciation, so additional measures must be taken when these objectives are to be addressed.

The second step is to determine which chemicals need to be measured and at what levels they are expected. When source apportionment is an objective, it is desirable to obtain chemicals which are present in the sources which are suspected of contributing to PM_{10}. Table 4-1 identifies several source types which are commonly found in PM_{10} non-attainment areas, along with the types of chemicals which are known to be present in these source emissions. This table can be used in conjunction with Table 4-2 to determine which methods should be applied to obtain the needed measurements.

The potential contributors can often be determined from emissions inventory summaries such as that illustrated in Table 4-3. These inventories should include emissions estimates for suspended particles, carbon monoxide (CO), sulfur dioxide (SO_2), nitrogen oxides (NO_x), volatile organic compounds (VOCs), and ammonia (NH_3), if possible. The gaseous precursors are needed to assess whether or not secondary aerosol might contribute to elevated PM_{10} concentrations. When gridded inventories are available, or the locations of point sources are known, these should be examined to determine the locations of emitters relative to sampling locations. The closer the source, the greater the probability that some of the chemicals it emits will be detected at the receptor. Emissions events should be identified, such as prescribed fires, wildfires, construction and demolition activities, and plant upsets. These may have a different chemical character from the sources which are listed in the inventory. Agricultural extension offices should be contacted to obtain land-use maps and soil conservation surveys. Periods of tilling, fertilizing, and grazing might be indicative of elevated emissions from these activities. Local fire departments, the National Forest Service, the Bureau of Land Management, and other fire management agencies can often supply information on local burning events.

Table 4-1
Typical chemical abundances in source emissions

Source Type	Dominant Particle Size	Chemical Abundances			
		≤0.1%	0.1 to 1%	1 to 10%	>10%
Geological Material	Coarse	Cr Zn Rb Sr Zr	Cl^- NO_3^- $SO_4^=$ NH_4^+ P S Cl Ti Mn Ba La	OC EC Al K Ca K Ca Fe	Si
Motor Vehicle	Fine	Cr Ni Y^+	NH_4^+ Si Cl Al Si P Ca Mn Fe Zn Br Pb	S Cl^- NO_3^- $SO_4^=$ NH_4^+	OC EC
Vegetative Burning	Fine	Ca Mn Fe Zn Br Rb Pb	NO_3^- $SO_4^=$ NH_4^+ Na^+	K^+ K Cl Cl^-	OC EC
Residual Oil Combustion	Fine	K^+ OC Cl Ti Cr Co Ga Se	Na^+ NH_4^+ Zn Fe Si	Ni OC EC V	S $SO_4^=$

Table 4-1 (continued)
Typical chemical abundances in source emissions

Source Type	Dominant Particle Size	Chemical Abundances			
		$\leq 0.1\%$	0.1 to 1%	1 to 10%	$\geq 10\%$
Incinerator		V	K^+	NO_3^-	$SO_4^=$
		Mn	Al	Na^+	NH_4^+
		Cu	Ti	Ec	OC
		Ag	Zn	Si	Cl
		Sn	Hg	S	
				Ca	
				Fe	
				Br	
				La	
				Pb	
Coal Fired Power Plant	Fine	Cl	NH_4^+	$SO_4^=$	Si
		Cr	P	OC	
		Mn	K	EC	
		Ga	Ti	Al	
		As	V	S	
		Se	Ni	Ca	
		Br	Zn	Fe	
		Rb	Sr		
		Zr	Ba		
			Pb		
Marine	Coarse	Ti	K	NO_3^-	Na^+
		V	Ca	$SO_4^=$	Cl^-
		Ni	Fe	OC	Na
		Sr	Cu	EC	Cl
		Zr	Zn		
		Pd	Ba		
		Ag	La		
		Sn	Al		
		Sb	Si		
		Pb			

Table 4-2

Analytical measurement specifications for 4-hour, 6-hour, 8-hour, and 24-hour $PM_{2.5}$ and PM_{10} sequential filter samples

Chemical Species	Analysis Method[a]	MDL[b] μg/m³ (4-hour Sample)[b,c]	MDL[b] μg/m³ (6-hour Sample)[b,d]	MDL[b] μg/m³ (8-hour Sample)[b,e]	MDL[b] μg/m³ (24-hour Sample)[b,f]	Concentration Range (μg/m³)[g]	No. of Samples
Mass	Gravimetry	0.95	0.64	0.48	0.16	8.4 - 135.1	36
Chloride (Cl⁻)	IC	0.31	0.21	0.16	0.05	0.1 - 2.6	36
Nitrate (Quartz) (NO₃⁻)	IC	0.31	0.21	0.16	0.05	0.5 - 28.5	36
Nitrate (Quartz / Nylon) (NO₃⁻)	IC	0.31	0.21	0.16	0.05	0.4 - 7.9	36
Sulfate (SO₄⁼)	IC	0.31	0.21	0.16	0.05	0.2 - 9.9	36
Ammonium (NH₄⁺)	AC	0.31	0.21	0.16	0.05	0.1 - 4.6	36
Sodium (Na⁺)	AA	0.16	0.10	0.78	0.26	0.1 - 1.3	36
Potassium Ion (K⁺)	AA	0.23	0.15	0.11	0.04	0.1 - 4.6	36
High Temperature Organic Carbon (OH)	TOR	0.50	0.34	0.25	0.08		36
Total Organic Carbon (OC)	TOR	0.50	0.34	0.25	0.08	5.3 - 39.3	36
High Temperature Elemental Carbon (EH)	TOR	0.0	0.0	0.0	0.0		36
Total Elemental Carbon (EC)	TOR	0.0	0.0	0.0	0.0	0.9 - 18.1	36
Aluminum (Al)	XRF	0.014	0.018	0.016	0.005	0.1685 - 1.974	36
Silicon (Si)	XRF	0.016	0.011	0.010	0.003	0.5620 - 5.742	36
Phosphorus (P)	XRF	0.0080	0.0053	0.0050	0.0017	0.0032 - 0.059	36
Sulfur (S)	XRF	0.0063	0.0042	0.0038	0.0013	0.2170 - 4.420	36
Chlorine (Cl)	XRF	0.018	0.012	0.011	0.004	0.0160 - 3.399	36
Potassium (K)	XRF	0.0080	0.0053	0.0045	0.0015	0.1958 - 1.696	36
Calcium (Ca)	XRF	0.0080	0.0053	0.0045	0.0010	0.1279 - 1.552	36
Titanium (Ti)	XRF	0.0048	0.0032	0.0029	0.006	0.0114 - 0.121	36
Vanadium (V)	XRF	0.0030	0.0021	0.0019	0.006	0.0012 - 0.013	36
Chromium (Cr)	XRF	0.0030	0.0021	0.0019	0.006	0.0012 - 0.009	36
Manganese (Mn)	XRF	0.0030	0.0021	0.0019	0.006	0.0024 - 0.026	36
Iron (Fe)	XRF	0.0015	0.0011	0.0009	0.0003	0.1585 - 1.498	36
Cobalt (Co)	XRF	0.0015	0.0011	0.0009	0.0003	0.0006 - 0.000	36
Nickel (Ni)	XRF	0.0015	0.0011	0.0009	0.0003	0.0013 - 0.008	36
Copper (Cu)	XRF	0.0015	0.0011	0.0009	0.0003	0.0049 - 0.046	36

Table 4-2 (continued)

Analytical measurement specifications for 4-hour, 6-hour, 8-hour, and 24-hour PM$_{2.5}$ and PM$_{10}$ sequential filter samples

Chemical Species	Analysis Method[a]	MDL[b] μg/m³ (4-hour Sample)[b,c]	MDL[b] μg/m³ (6-hour Sample)[b,d]	MDL[b] μg/m³ (8-hour Sample)[b,e]	MDL[b] μg/m³ (24-hour Sample)[b,f]	Concentration Range (μg/m³)[g]	No. of Samples
Zinc (Zn)	XRF	0.0030	0.0021	0.0019	0.0006	0.0110 - 0.282	36
Gallium (Ga)	XRF	0.0048	0.0032	0.0029	0.0010	0.0019 - 0.001	36
Arsenic (As)	XRF	0.0048	0.0032	0.0029	0.0010	0.0019 - 0.004	36
Selenium (Se)	XRF	0.0030	0.0021	0.0019	0.0006	0.0026 - 0.022	36
Bromine (Br)	XRF	0.0012	0.001	0.0009	0.0003	0.0026 - 0.022	36
Rubidium (Rb)	XRF	0.0015	0.001	0.0009	0.0003	0.0006 - 0.003	36
Strontium (Sr)	XRF	0.0030	0.0021	0.0018	0.0003	0.0042 - 0.112	36
Yttrium (Y)	XRF	0.0030	0.0021	0.0018	0.0006	0.0012 - 0.001	36
Zirconium (Zr)	XRF	0.0048	0.0032	0.0029	0.0006	0.0002 - 0.057	36
Molybdenum (Mo)	XRF	0.0080	0.0053	0.0047	0.0016	0.0032 - 0.008	36
Palladium (Pd)	XRF	0.018	0.012	0.011	0.004	0.007 - 0.009	36
Silver (Ag)	XRF	0.018	0.012	0.011	0.004	0.007 - 0.015	36
Cadmium (Cd)	XRF	0.018	0.012	0.011	0.004	0.007 - 0.018	36
Indium (In)	XRF	0.025	0.016	0.014	0.005	0.010 - 0.016	36
Tin (Sn)	XRF	0.030	0.021	0.018	0.006	0.012 - 0.027	36
Antimony (Sb)	XRF	0.040	0.025	0.023	0.008	0.016 - 0.026	36
Barium (Ba)	XRF	0.14	0.09	0.07	0.02	0.055 - 0.107	36
Lanthanum (La)	XRF	0.15	0.10	0.09	0.03	0.060 - 0.102	36
Gold (Au)	XRF	0.13	0.08	0.06	0.02	0.05 - 0.002	36
Mercury (Hg)	XRF	0.0115	0.0076	0.0056	0.0019	0.0046 - 0.003	36
Thallium (Tl)	XRF	0.0100	0.0066	0.0054	0.0018	0.0040 - 0.001	36
Lead (Pb)	XRF	0.0080	0.0053	0.050	0.017	0.0032 - 0.084	36
Uranium (U)	XRF	0.043	0.029	0.025	0.008	0.017 - 0.002	36

[a] Analysis Method: AC: Automated Colorimetry; IC: Ion Chromatography; AA: Atomic Absorption Spectroscopy; TOR: Thermal/Optical Reflectance; XRF: X-Ray Fluorescence.

[b] Minimum Detectable Limit (MDL) is the concentration at which instrument response equals two times the standard deviation of the response to a known concentration of zero.

[c] Concentration is based on 13.8 cm³ deposit area for a 47 mm filter substrate with a nominal 4.8 m³ sample volume for 4-hour samples.

[d] Concentration is based on 13.8 cm³ deposit area for a 47 mm filter substrate with a nominal 7.2 m³ sample volume for 6-hour samples.

[e] Concentration is based on 13.8 cm³ deposit area for a 47 mm filter substrate with a nominal 9.6 m³ sample volume for 8-hour samples.

[f] Concentration is based on 13.8 cm³ deposit area for a 47 mm filter substrate with a nominal 28.8 m³ sample volume for 24-hour samples.

[g] PM$_{10}$ data are obtained from the Bay Area 1991-1992 Wintertime PM$_{10}$ Pilot Study (Fairley et al., 1992).

4-5

Source	County	Species[b]					
		TOG	ROG	NO$_x$	SO$_x$	CO	PM
Stationary Fuel Combustion (agricultural, oil & gas production, petroleum refining, other manufacturing, industrial, electric util., other services & commerce, residential)	North San Joaquin[c]	2.2	1.2	17.5	3.5	17.6	1
	Fresno	1.0	0.5	18	8.9	5.6	3
	Central San Joaquin[d]	0.9	0.5	5.2	1.5	8.9	0
	Kern	33	10	160	20	37	9
	All	37.1	12.2	200.7	33.9	69.1	14
Stationary Waste Burning (agricultural debris, range and forest management, incineration)	North San Joaquin[c]	16.4	12	--	--	109.3	11
	Fresno	2.5	1.0	0.3	--	5.4	0
	Central San Joaquin[d]	8.4	6.1	--	--	63	6
	Kern	2.3	1.6	--	--	15	1
	All	29.6	20.7	0.3	--	192.7	21
Stationary Solvent Use (dry cleaning, degreasing, architectural coating, asphalt paving, printing, consumer products, industrial solvent use)	North San Joaquin[c]	33.4	31.6	--	--	0.2	--
	Fresno	24	22	--	--	--	--
	Central San Joaquin[d]	12.2	11.4	--	--	--	--
	Kern	15	13	--	--	--	--
	All	84.6	78.0	--	--	0.2	--
Stationary Petroleum Processing, Storage, and Transfer (oil & gas extraction, petroleum refining and marketing)	North San Joaquin[c]	8.8	4.3	--	0.1	--	--
	Fresno	24	12	0.1	0.3	0.3	0.
	Central San Joaquin[d]	3.2	1.9	--	--	--	--
	Kern	430	300	0.8	1.4	0.2	0.
	All	466.0	318.2	0.9	1.8	0.5	0.
Stationary Industrial Processes (chemical, food, agricultural, mineral and metal processing, wood and paper industries)	North San Joaquin[c]	3.6	3.2	3.4	5.3	--	4.9
	Fresno	3.9	3.8	5.5	1.5	--	2.6
	Central San Joaquin[d]	0.8	0.7	--	--	0.9	3.8
	Kern	0.4	0.3	--	--	0.2	3.3
	All	8.7	8.0	8.9	6.8	1.1	14.6
Stationary Miscellaneous Processes (pesticide application, farming, construction and demolition, road dust, unplanned fires, waste disposal, natural sources)	North San Joaquin[c]	74.5	29.4	0.1	--	9.3	235
	Fresno	230	16	0.4	--	28	290
	Central San Joaquin[d]	19.7	17.3	1.1	--	75	180
	Kern	78	33	3.4	--	220	280
	All	402.2	95.7	5.0	--	332.3	985
Mobile On-Road Vehicles (light duty passenger, light and medium duty trucks, heavy duty gas and diesel trucks, motorcycles, and buses)	North San Joaquin[c]	65.1	59.6	99	9.4	460	10.3
	Fresno	35	33	47	4.9	230	5.4
	Central San Joaquin[d]	23.9	22.5	40	4.1	174	4.6
	Kern	29	27	56	6.0	200	6.7
	All	153	142.1	242	24.4	1,064	27.0

Source	County	Species[b]					
		TOG	ROG	NO$_x$	SO$_x$	CO	PM$_{10}$
Other Mobile Sources	North San Joaquin[c]	24.2	22.9	33.2	3.9	137	6.2
(off road vehicles, trains, ships, aircraft,	Fresno	11	11	23	2.3	73	·2.8
mobile and utility equipment)	Central San Joaquin[d]	10.9·	10.2	21.3	2.0	51	2.5
	Kern	10	9.8	21	2.0	55	2.3
	All	56.1	53.9	98.5	10.2	316	13.8
All Sources	North San Joaquin[c]	229	164	153	22.4	734	272
	Fresno	330	99	95	18	340	310
	Central San Joaquin[d]	80	70	67	7.6	369	196
	Kern	600	400	240	30·	530	300
	All	1,239	733	555	78	1,973	1,078

[a] California Air Resources Board, 1991.

[b] Species:

> TOG: Total Organic Gases, compounds reported as equivalent amounts of methane (CH$_4$), containing hydrogen and carbon in combination with one or more other elements. These include methane, aldehydes, ketones, organic acids, esters, and ethers.

> ROG: Reactive Organic Gases, compounds reported as equivalent amounts of methane (CH$_4$) including all organic gases except non-reactive species such as methane and low molecular weight halogenates. ROGs are relatively reactive and are the most likely precursors of photochemical aerosol.

> NO$_x$: Nitrogen Oxides, reported as equivalent amounts of NO$_2$, including nitric oxide (NO) and nitrogen dioxide (NO$_2$) gases.

> SO$_x$: Sulfur Oxides, reported as equivalent amounts of SO$_2$, including sulfur dioxide (SO$_2$) and sulfur trioxide (SO$_3$).

> CO: Carbon Monoxide, a pure species that is reported as equivalent amounts of CO.

> PM$_{10}$: Primary PM$_{10}$, particles in the 0 to 10 μm aerodynamic size range that are emitted in a liquid or solid phase. This includes dust, sand, salt spray, metallic and mineral particles, pollen, smoke, mist, and acid fumes.

[c] San Joaquin, Stanislaus, Merced, and Madera counties.

[d] King and Tulare counties.

Microinventories are also helpful for identifying potential contributors and the chemical species which correspond to these contributions (Pace, 1979). Microinventories include detailed surveys and locations of vacant lots, storage piles, major highways, construction sites, and industrial operations. These are plotted on a map with notes regarding the visual appearance of each potential emitter. For example, if several streets near the sampling site are extremely dirty, this observation is recorded and photographs are taken. Street sweeping locations and schedules are obtained. Roads in the vicinity of sampling sites are classified with respect to the type of traffic on them and whether or not they have sidewalks and paved shoulders.

Expected emissions cycles should be examined to determine sampling periods and durations. For example, residential woodburning will usually show up on samples taken during the night whereas agricultural burning will usually show up during the daytime. While these two source types may be indistinguishable based on their chemical profiles, their diurnal cycles will provide convincing evidence that one or the other is a major contributor when both activities occur simultaneously. As Table 4-1 shows, particle size is of value in separating one source from another. Particle size fractions, chemical analyses, sampling frequencies, and sample durations need to be considered because more frequent samples, or samples taken at remote locations, may require a sequential sampling feature to minimize operator costs. Shorter sample durations may require a larger flow rate to obtain an adequate sample deposit for analysis. The types of analyses and size fractions desired affect the number of sampling ports and different filter media needed.

The third step is to calculate the expected amount of deposit on each filter for each chemical species and compare it to typical detection limits for the analyses being considered. The references in Appendix A provide typical concentrations which can be compared with detection limits for the flow rates and filter sizes of different sampling systems. Urban samples acquire adequate deposits for analysis with flow rates as low as ~ 20 ℓ/min for as short as 4-hour sample durations. Samples at non-urban sites may require > 100 ℓ/min flow rates for 24-hour durations to obtain an adequate deposit. The analytical laboratory should be involved at the sampler design stage to assure compatibility between sampling methods, analysis methods, filter media, and lower quantifiable limits.

The fourth step is to apply, create, adapt, or purchase the sampling system which provides the most cost-effective and reliable means of meeting the monitoring needs. Tables 2-1 and 2-2 identify several sampler designs which have been applied to PM_{10} studies. Some of these are reference methods which can also determine compliance with the PM_{10} standard. In complicated situations, however, especially those with many contributing sources, unknown sources, or secondary contributions, more complex sampling systems are needed which do not have reference status. The reference and research sampling systems have been operated side-by-side in many studies when this is the case.

The final step is to create a written plan which specifies the study objectives, sampling locations, analysis methods, filter media, sampling systems, sampling frequencies and durations, nominal flow rates, methods and schedules for inlet cleaning, calibration and performance tests,

filter transport and handling procedures, database management system, data analysis methods, and record keeping protocols. A representative flow diagram of sampling and analysis strategies is shown in Figure 4-1, while Table 4-4 contains a typical outline for a study plan. Such a plan is essential for assuring that all participants know what roles they are required to carry out as part of a PM_{10} study.

The procedure outlined above describes an ideal program which may require several hundred thousand dollars to complete. Such expenditures are often worthwhile when costly pollution control decisions must be made, since these decisions may result in tens of millions of dollars of expenditures. These expenditures cannot always be justified without some pilot studies using existing equipment and samples to provide screening analysis. Sometimes these initial analyses can provide information which is sufficient to design the desired control strategy, and further measurements are not needed. The following sub-sections provide guidance on what can be done with different sampling and analysis configurations in a step-wise fashion.

4.2   Analysis of Archived PM_{10} Filters from High-Volume Samplers

As noted earlier, filters which are taken without the intent of chemical analysis can rarely be used to provide defensible chemical concentrations for source apportionment. Chemical measurements are still useful in a semi-quantitative or qualitative sense to identify, though not to quantify, the major source types which contribute to high PM_{10} concentrations, and to examine intersite variability. Elemental, ion, and carbon analysis methods can be applied to these filters subject to the limitations stated in Section 3. Archived 20.32 cm × 25.40 cm quartz-fiber filters should be re-weighed prior to sectioning, and the re-weight should be compared with the final weight which was taken immediately following sampling. This will provide an approximation for the particulate matter (typically volatile organics and nitrates) which has been lost during storage.

The archived filters of greatest interest are those which exhibited PM_{10} concentrations in excess of 150 $\mu g/m^3$. Filters from all sites within the air quality management area on an exceedance day should be examined, even though the PM_{10} standard may not be exceeded at every site. Differences in chemical content among sites, coupled with knowledge of emissions source locations, will assist in determining whether or not chemical contributions have a local or a regional effect on PM_{10}. If blank filters from lots corresponding to the samples have been archived, these should be submitted to the same analyses as the exposed filters. The levels of chemical concentrations in these blanks provide information on how the chemical concentrations on the exposed filters should be interpreted. If the blanks concentrations are more than 30% of the concentrations on the exposed filter for a chemical species, then the concentration of that species should not be used for interpretive purposes as it probably does not represent the concentrations in the deposited particles.
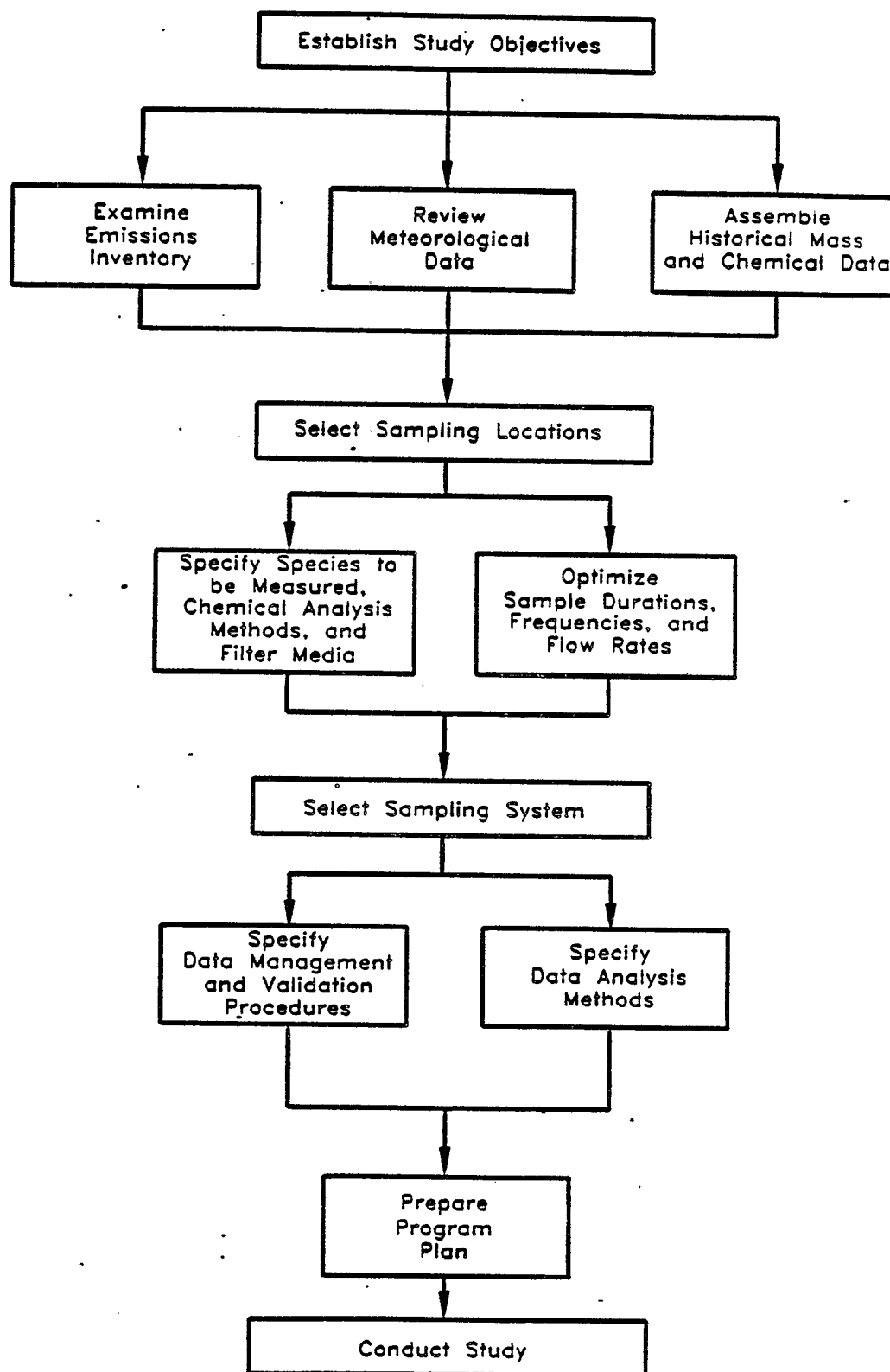
Figure 4-1. Steps in designing a PM_{10} source apportionment study.

Table 4-4
Example of program plan outline for PM_{10} measurement and modeling

1.0 INTRODUCTION

    1.1   Background
    1.2   Objectives
    1.3   Overview

2.0 AIR QUALITY IN THE STUDY AREA

    2.1   Emissions
    2.2   Meteorology
    2.3   Atmospheric Transformations
    2.4   Historical PM_{10} Data
    2.5   Implications for PM_{10} Study Design

3.0 DATA ANALYSIS AND MODELING

    3.1   Data Evaluation
    3.2   Descriptive Air Quality Analysis
    3.3   Descriptive Meteorological Analysis
    3.4   Source Profile Compilation
    3.5   Emissions Inventory
    3.6   Receptor Model Source Apportionments
    3.7   Trajectory Modeling
    3.8   Secondary Aerosol Modeling
    3.9   Case Study Descriptions

4.0 PROPOSED AMBIENT MONITORING NETWORK

    4.1   Sampling Sites
    4.2   Sampling Frequency and Duration
    4.3   Sampling Methods

5.0 EMISSIONS CHARACTERIZATION

    5.1   Emissions Activities and Microinventories
    5.2   Geological Source Profiles
    5.3   Motor Vehicle Exhaust Characterization
    5.4   Residential Wood Combustion Characterization
    5.5   Other Source Characterization

6.0   LABORATORY OPERATIONS

    6.1   Substrate Preparation
    6.2   Gravimetric Analysis
    6.3   Light Absorption
    6.4   Elemental Analysis
    6.5   Carbon Analysis
    6.6   Filter Extraction
    6.7   Ion Analysis
    6.8   Specialized Analysis

7.0   QUALITY ASSURANCE

    7.1   Standard Operating Procedures
    7.2   Performance Tests
    7.3   Quality Audits
    7.4   Standard Traceability

8.0   DATA PROCESSING, MANAGEMENT, AND CHAIN-OF-CUSTODY

    8.1   Data Base Requirements
    8.2   Levels of Data Validation
    8.3   Continuous Data Processing
    8.4   Substrate Data Processing

9.0   MANAGEMENT, REPORTING, AND SCHEDULE

    9.1   Tasks and Responsibilities
    9.2   Resource Requirements
    9.3   Reports
    9.4   Schedule and Milestones

10.0   REFERENCES

A quick examination of particle sizes on the filter under a reflecting microscope can often reveal whether or not the particles are truly PM_{10} or are the result of inlet re-entrainment or large particle contamination. A large proportion of particles exceeding 10 microns indicates that there may have been a problem with the sampling system, and that the elevated concentration may not really represent high PM_{10} levels in the atmosphere at the time of sampling.

4.3 Planned High-Volume PM_{10} Sampling

If it is known that chemical analyses will be applied to some or all of the 20.32 cm × 25.40 cm quartz-fiber filters used in a high-volume PM_{10} sampler, the following precautions should be taken. When procuring filters, minimally acceptable blank concentrations should be stated for each chemical to be quantified. Each box should be labelled when it is received from the vendor and one filter from each box should be submitted to the same chemical analysis methods which might be applied to all filters. If the blank levels exceed one-third of the expected concentrations for any of the chemical concentrations to be analyzed, the box should be returned to the manufacturer. Specifications of maximum tolerable levels in the purchase agreement will offer the opportunity to obtain replacements at no additional cost.

Filter cassettes which can be mated to the high-volume PM_{10} sampler should be obtained, and filters should be loaded and unloaded using gloved hands in a laboratory setting. Each filter should be folded in half with the exposed side inward and stored in a Zip-lock bag. These bags should be placed in hanging folders with their corresponding data sheets and stored in a refrigerator or freezer after weighing.

4.4 High-Volume and Dichotomous PM_{10} Sampling

As noted earlier, the quartz-fiber filters used for high-volume sampling are especially poor for elemental measurements owing to the penetration of particles into the filter and high blank levels for many of the species to be measured. The procedure described in Section 4.3 can be complemented by operating a dichotomous sampler alongside the high-volume PM_{10} sampler. The two 37 mm diameter Teflon-membrane filters (one for $PM_{2.5}$ and one for coarse particles) can be submitted to XRF or PIXE for elemental analysis, while portions of the 20.32 cm × 25.40 cm quartz-fiber filter can be submitted to ion and carbon analyses. This provides accurate measurements for receptor modeling in most cases, plus the additional information from two different particle sizes obtained from the dichotomous sampler. Since there are slight differences between the sampler PM_{10} cut-points, the concentrations are not entirely comparable for these two samples. A more accurate sampling method would be to collocate two dichotomous samples, one with Teflon-membrane filters and one with quartz-fiber filters. When all of the filters are submitted to gravimetric analysis, additional validation information is available when the two PM_{10} concentrations are compared. Since both sampling systems are

reference samplers, compliance can be determined from either sampler. All filter media should undergo the acceptance testing, handling, and storage procedures described earlier.

4.5 High-Volume or Dichotomous PM_{10} and Continuous PM_{10} Sampling

A continuous TEOM or BAM can be operated along with a high-volume or dichotomous PM_{10} sampling system. This configuration is most useful when short-term events, such as fires or windblown dust, are hypothesized to be major contributors to excessive PM_{10} concentrations. The dichotomous sampler using Teflon-membrane filters is preferred, since this allows particle size as well as elements and mass to be measured. When the TEOM is equipped with the bypass channel, a quartz-fiber filter can be taken simultaneously with the hourly measurements to be analyzed for ions and carbon. If a high-volume PM_{10} sampler with a quartz-fiber filter is used, the bypass should use a Teflon-membrane filter for elemental analysis.

4.6 Sequential Filter Sampling

When high PM_{10} levels are suspected to result from multi-day buildup of a variety of sources, it is desirable to have daily samples available which can be submitted to analysis. High-volume and dichotomous PM_{10} sampling can be applied to this task, but this requires someone to change the filters at midnight every night, or several samplers and a timing mechanism to switch between them. Manpower and equipment costs can become prohibitive. Many sampling sites have limited space and cannot accommodate a large number of sampling systems. In this case, Sequential Filter Samplers (SFSs) using Teflon-membrane filters for mass and elemental analysis and quartz-fiber filters for ion and carbon analysis are a good choice. The SFS can also be applied to situations where more than one sample per day is needed to bracket emissions events with samples amenable to chemical analysis. In this case, two to six samples of four- to twelve-hours duration are taken sequentially and analyzed separately for the desired chemical species.
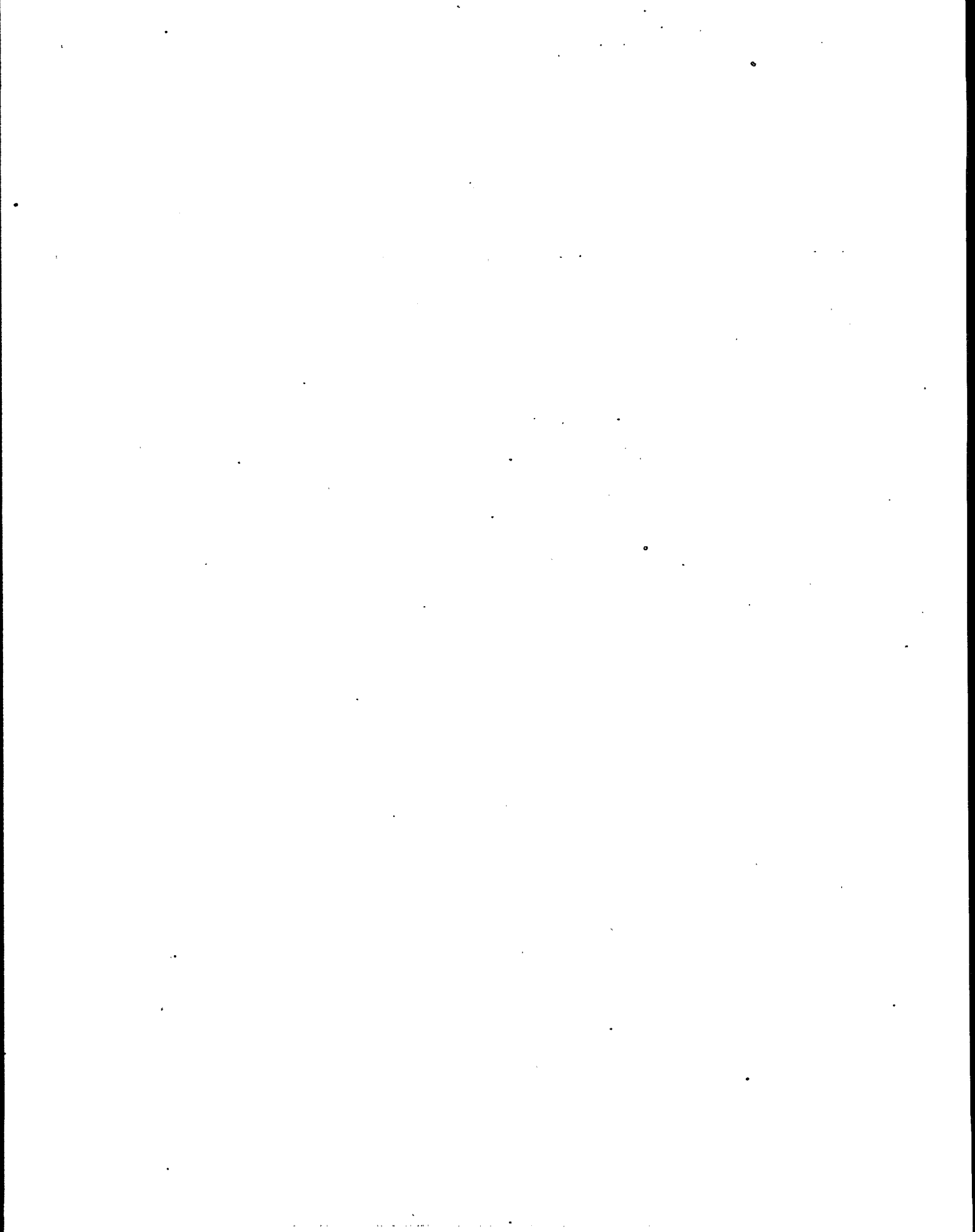
4.7 Saturation Sampling

There may be cases where one or more source categories are identified as major contributors to elevated PM_{10}, but the chemical profiles of specific emitters are too similar to differentiate them from each other. In this case, the portable survey samplers using Teflon-membrane filters can be located within and around the suspected emitters (Watson *et al.*, 1991b). If the objective of the study is to characterize fugitive dust sources, mass and elemental analyses are sufficient to separate this source category from others by receptor modeling. Many past studies have applied the portable survey sampling approach to characterize the impact of residential wood combustion. In this case, collocated samplers with Teflon-membrane and quartz-fiber filters are required for full chemical speciation. The remaining geological source

contributions can be used in spatial receptor models to identify the locations of specific emissions sources.

4.8 Denuder Difference Sampling

In cases where secondary ammonium sulfate and ammonium nitrate are major contributors, one or more sites should be operated to obtain precursor concentrations of nitric acid and ammonia gas (e.g., Chow *et al.*, 1993a). In the eastern United States, sulfuric acid and ammonium bisulfate are also important components. In this situation, denuder methods can be applied to obtain accurate measures of the secondary aerosol and the precursor gases. These precursor gas measurements should be accompanied by collocated temperature and relative humidity measures so that equilibrium receptor models (e.g., Watson *et. al.*, 1994a) can be applied to determine whether the secondary particles are limited by ammonia or oxides of nitrogen emissions.

5.0 SUMMARY

Chemical characterization of suspended particles is necessary, along with the application of receptor models, to apportion ambient concentrations to their sources for the development of emissions reduction strategies. This document identifies current technology for the sampling and analysis of PM_{10} and its chemical constituents on filter deposits.
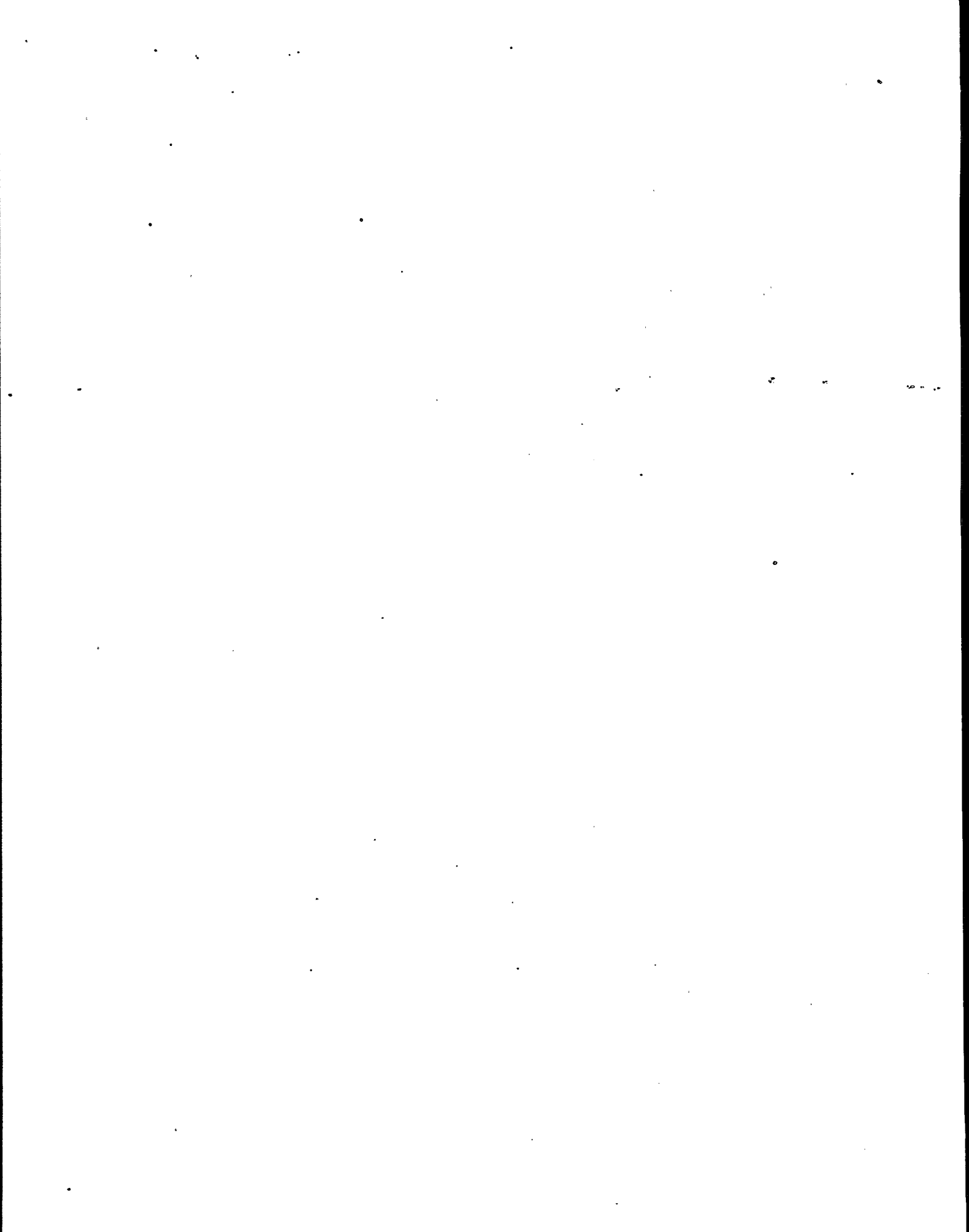
Particle sampling on filters is the most practical method currently available to characterize the sizes and chemical compositions of PM_{10} and its sub-fractions. Ambient aerosol sampling systems consist of a combination of monitoring hardware, filter media, laboratory methods, and operating procedures which are specifically tailored to different monitoring objectives. No single sampling system can meet all needs, and it is often necessary to adapt existing sampling components to the specific situation being studied. Examples of successful sampling systems which can be copied or modified to meet these specific needs have been identified.

Chemical analysis of filter deposits **cannot** be separated from the methods used to obtain the sample. Sampling for chemical analysis requires stringent attention to choice of filter media, sample handling, sample storage, and to the sampler used to obtain the filter deposits. When chemical analysis is intended for source apportionment receptor modeling, sequential sampling systems, particle and gas sampling systems with denuders, portable samplers, dichotomous samplers, or a combination of several samplers may be needed.

An overview of filter-based particle and gas sampling systems has been provided. These systems consist of more than the mechanical device used to acquire the sample. The laboratory analyses to be applied, the type of filters which are amendable to those analyses, the minimum deposits needed on these filters, the sampling hardware which extracts pollutants from the atmosphere onto the filters, and the procedures which assure the accuracy, precision, and validity of the acquired atmospheric concentrations must all be considered.

General steps to formulate the sampling and analysis strategies have been given. A written program plan needs to be assembled which specifies the study objectives, sampling locations, analysis methods, filter media, sampling systems, sampling frequencies and durations, nominal flow rates, methods and schedules for sampler maintenance, calibration and performance tests, filter transport and handling procedures, data base management system, data analysis methods, and record keeping protocols. This plan is an evolving document, and remains in draft form until the majority of the program activities have been executed. The plan needs to be revised and finalized to reflect the actual conduct of the study and to identify improvements which should be incorporated into future plans.

Extensive references and existing data bases have been identified to provide more detail in each subject area.

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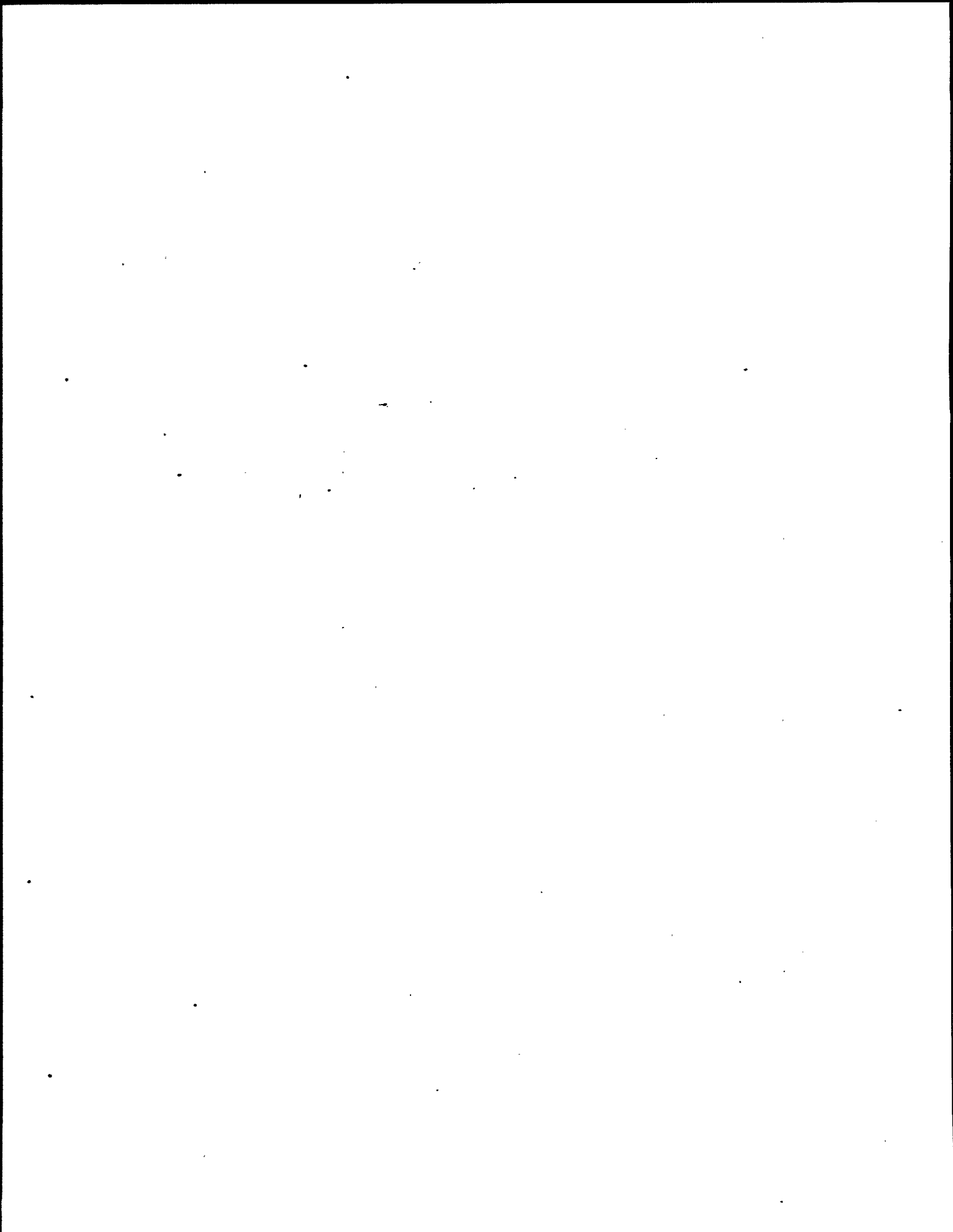
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APPENDIX A

SUMMARY OF PM$_{10}$ STUDIES AND DATA BASES

Table A-1

Summary of PM_{10} studies and data bases

Study and References	Study Objectives	Site Location and Study Period	Chemical Measurements
• State of Nevada Air Pollution Study II (SNAPS-II) Wood Combustion Control Evaluation (Chow et al., 1986a, 1988, 1989a; Watson et al., 1988a; Benedict and Nylor, 1988; Broten, 1992).	To evaluate effectiveness of mandatory curtailment of residential wood burning on wintertime PM_{10} levels.	24-hour samples taken during the winter of 1991-92 in Sparks, NV.	PM_{10} samples were collected on Teflon and quartz substrates for mass, 38 elements (Al to Pb), ions (Cl$^-$, NO$_3^-$, SO$_4^=$, NH$_4^+$, K$^+$), and carbon (OC, EC) analyses.
• State of Nevada Air Pollution Study II (SNAPS-II) Street Sweeping Control Evaluation (Chow et al., 1986b; 1990a).	To evaluate the effectiveness of street sweeping on geological contributions to ambient PM_{10} concentrations.	24-hour samples were collected daily between February and March, 1987 during sweeping and non-sweeping periods in Reno, NV.	$PM_{2.5}$ and PM_{10} samples were collected on Teflon and quartz substrates for mass, 38 elements (Al to Pb), ions (Cl$^-$, NO$_3^-$, SO$_4^=$, NH$_4^+$, K$^+$), and carbon (OC, EC) analyses.
• Neighborhood-Scale Study of PM_{10} Source Contributions in Rubidoux, CA (Chow et al., 1989b; 1989c; 1989d; 1992b).	To estimate the neighborhood-scale versus urban-scale source contributions to PM_{10}.	24-hour samples were collected every sixth day between January, 1988 and January, 1989 at 3 sites in Riverside County, CA.	$PM_{2.5}$ and PM_{10} samples were collected on Teflon and quartz substrates for mass, 38 elements (Al to Pb), ions (NO$_3^-$, SO$_4^=$, NH$_4^+$), and carbon (OC, EC) analyses.
• California Air Resources Board Dichotomous Sampling Network (Davis, 1992).	To establish a size-classified data base.	24-hour particulate samples have been collected every sixth day at 7 sites in California.	$PM_{2.5}$ and coarse (PM_{10} minus $PM_{2.5}$) aerosol samples were collected on Teflon substrate for mass and 38 elements (Al to Pb) analyses.

Table A-1 (continued)

Summary of PM₁₀ studies and data bases

Study and References	Study Objectives	Site Location and Study Period	Chemical Measurements
• Puerto Rico Receptor Modeling Study (Lowenthal et al., 1991).	To identify and quantify source contributions for SIP development.	24-hour samples were collected between August, 1987 and January, 1991 at 2 sites in north and northeast Puerto Rico.	$PM_{2.5}$ and PM_{10} samples were collected on Teflon and quartz substrates for mass, 38 elements (Al to Pb), ions (Cl^-, NO_3^-, SO_4^-, Na^+, K^+), and carbon (OC, EC) analyses.
• Valley Air Quality Study (VAQS) (Chan et al., 1990; Chow et al., 1990c, 1992c, 1993b).	To evaluate contributions from cogeneration sources in the San Joaquin Valley, CA.	24-hour samples were collected every sixth day between June, 1988 and June, 1989 at 6 sites in the San Joaquin Valley, CA.	$PM_{2.5}$ and PM_{10} samples were collected on Teflon and quartz substrates for mass, 38 elements (Al to Pb), ions (Cl^-, NO_3^-, SO_4^-, NH_4^+, Na^+, K^+), and carbon (OC, EC) analyses.
• Santa Barbara PM₁₀ Study (Countess, 1991).	To evaluate PM₁₀ source contributions in Santa Barbara County, CA.	24-hour samples were collected every sixth day between January, 1989 and December, 1989 at 6 sites in Santa Barbara County, CA.	PM_{10} samples were collected on Teflon and quartz substrates for mass, 40 elements (Na to Pb), ions (NO_3^-, SO_4^-, NH_4^+, Na^+), and carbon (OC, EC) analyses.
• Residential Wood Combustion Source Apportionment Study (Larson et al., 1992).	To develop weekly composite samples for source apportionment.	15-minute samples were taken every 2 hours for one week between January and December, 1991 at 3 sites in the Puget Sound area, WA.	$PM_{2.5}$ samples were collected on Teflon substrate for mass, 38 elements (Al to Pb), and ions (NO_3^-, SO_4^-, Na^+, K^+) analyses.
• PM₁₀ SIP Development (Chow, et al., 1990d).	To establish a PM₁₀ data base for SIP development.	24-hour samples were collected every sixth day at sampling sites in AZ, CA, CO, ID, MT, OH, and UT.	$PM_{2.5}$, coarse, and PM_{10} samples were collected on Teflon and/or quartz substrates for mass, 38 elements (Al to Pb), ions (Cl^-, NO_3^-, $SO_4^=$, NH_4^+, K^+), and carbon (OC, EC) analyses.

Table A-1 (continued)

Summary of PM₁₀ studies and data bases

Study and References	Study Objectives	Site Location and Study Period	Chemical Measurements
• 1989-1990 Phoenix PM₁₀ Study (Watson et al., 1990c; Chow et al., 1991a).	To establish quantitative relationships between PM₁₀ concentrations and emissions source contributions during fall and winter months.	24-hour samples were collected every other day between September, 1989 and January, 1990 at 8 sites in and around the metropolitan Phoenix, AZ, area.	PM₂.₅ and coarse samples were collected on Teflon and quartz substrates for mass, 40 elements (Na to Pb), ions (Cl⁻, NO₃⁻, SO₄⁻, NH₄⁺, K⁺), and carbon (OC, EC) analyses.
• PM₁₀ SIP Jefferson County, Ohio, PM₁₀ Air Quality Assessment Study (Lowenthal 1991; Pacific Environmental Services, 1991; Skidmore and Chow, 1992).	To establish a data base and to develop a basis for PM₁₀ SIP development.	24-hour particulate samples have been collected on every-third- and/or every-sixth-day schedule with 6 dichotomous samplers between January and December, 1991 at 5 sites in the Mingo Junction/ Steubenville, OH areas.	PM₂.₅ and coarse samples were collected on Teflon and quartz substrates for mass, 38 elements (Al to Pb), ions (NO₃⁻, SO₄⁻), and carbon (OC, EC) analyses.
• 1989-1990 Pilot Tucson PM₁₀ Study (Watson et al., 1990d; Chow et al., 1991b, 1992a).	To establish quantitative relationships between PM₁₀ concentrations and emissions source contributions.	24-hour samples were collected every other day between September, 1989 and January, 1990 at 4 sites in and around the Tucson, AZ, metropolitan area.	PM₂.₅ and coarse samples were collected on Teflon and quartz substrates for mass, 40 elements (Na to Pb), ions (Cl⁻, NO₃⁻, SO₄⁻, NH₄⁺, K⁺), and carbon (OC, EC) analyses.
• Imperial Valley/Mexicali PM₁₀ Source Apportionment Study (Watson et al., 1991b).	To estimate cross-border transport of PM₁₀ in the Imperial Valley.	24-hour samples are collected every sixth day between February, 1992 and July, 1993 at Calexico, CA and Mexicali, Mexico.	PM₁₀ samples are collected on Teflon and quartz substrates for mass, 38 elements (Al to Pb), ions (Cl⁻, NO₃⁻, SO₄⁻, NH₄⁺, Na⁺, K⁺) and carbon (OC, EC) analyses.

Table A-1 (continued)

Summary of PM$_{10}$ studies and data bases

Study and References	Study Objectives	Site Location and Study Period	Chemical Measurements
● Oregon Air Quality Surveillance Network (Oregon Department of Environmental Quality, 1991).	To attain and maintain air quality standards without inhibiting economic growth.	24-hour particulate samples were collected on a daily, every-third-day, or every-sixth-day schedule with high-volume PM$_{10}$, medium volume PM$_{10}$, and/or dichotomous samplers since 1983, at up to 25 sites in OR.	PM$_{2.5}$, PM$_{10}$, and/or coarse samples were collected on Teflon and/or quartz substrates for mass. Samples from selected days and sites were submitted for 16 elements, ions (NO$_3^-$, SO$_4^-$, NH$_4^+$), and carbon (OC, EC) analyses.
● Illinois Air Monitoring Network (Illinois Environmental Protection Agency, 1991).	To assess the air quality levels and to implement air quality control measures.	24-hour particulate samples have been collected on a daily, alternate day, or every sixth day schedule with high-volume PM$_{10}$ samplers since 1984 at up to 15 NAMS (National Air Monitoring Station) and 22 SLAMS (State/Location Monitoring Stations) sites (Two sites are included as part of the U.S. EPA's Urban Air Toxics Monitoring Program [UATMP]).	TSP samples from certain sites were selected for 9 elements and ions (NO$_2^-$, NO$_3^-$, SO$_4^-$) analyses.

TECHNICAL REPORT DATA
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16. ABSTRACT
Chemical characterization of suspended particles is necessary, along with
the application of receptor models, to apportion ambient concentrations
to their sources for the development of emission reduction strategies.
This document identifies current technology for the sampling and analysis
of PM-10 and its chemical constituents on filter deposits.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
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