

**Compendium of Methods
for the Determination of
Inorganic Compounds
in Ambient Air**

Chapter 10-2

**INTEGRATED SAMPLING OF
SUSPENDED PARTICULATE MATTER
(SPM) IN AMBIENT AIR**

OVERVIEW

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Chapter IO-2

Integrated Sampling of Suspended Particulate Matter (SPM) in Ambient Air

Overview

Under authority granted in Section 109 of the Clean Air Act (the Act) and its amendments, the U. S. Environmental Protection Agency (EPA) has promulgated primary and secondary national ambient air quality standards (NAAQS) for six criteria pollutants: SO₂, NO_x, CO, O₃, PM₁₀, and Pb. These primary (health-related) and secondary (welfare-related) pollutants standards are contained in Title 40, Part 50 of the Code of Federal Regulations(40 CFR 50). The reference methods for monitoring ambient atmospheres for these criteria pollutants are in the Appendices of 40 CFR 50, A through G.

Section 109 of the Act requires EPA to evaluate, at 5-yr intervals, the criteria for which standards have been promulgated and to issue any new standards as may be appropriate.

The issuance of reference methods designed to monitor these criteria pollutants has a legal basis in Section 301 of the Act, which states that the regulations necessary to carry out the provisions of the Act may be promulgated by the Administrator. To evaluate and ascertain the status of air quality with regard to the criteria pollutants, uniform analytical methods are used to ensure consistency and accuracy in the data generated.

Suspended particulate matter (SPM) in air generally is considered to be all airborne solid and low vapor pressure liquid particles, involving a complex, multi-phase system consisting of a spectrum of aerodynamic particle sizes ranging from below 0.01 μm to 100 μm and larger. Historically, particulate matter (PM) measurement has concentrated on total suspended particulates (TSP), with no preference to size selection. The EPA's approach toward regulating and monitoring TSP matter has evolved over time. When EPA first regulated TSP, the NAAQS was stated in terms of particulate matter captured on a filter with an aerodynamic particle size of < 100 μm as defined by the TSP sampler. Recently, the primary standard for TSP was replaced with a PM₁₀ standard, which includes only particles with an aerodynamic diameter of 10 μm or less.

Researchers generally recognize that these particles (< 10 μm) may cause significant, adverse health effects. Recent studies involving particle transport and transformation strongly suggest that atmospheric particles commonly occur in two distinct modes: the fine (< 2.5 μm) mode and the coarse (2.5-10.0 μm) mode. The fine or accumulation mode (also termed the respirable particulate matter) is attributed to growth of particles from the gas phase and subsequent agglomeration, while the coarse mode is made of mechanically abraded or ground particles. Particles that have grown from the gas phase (either because of condensation, transformation, or combustion) occur initially as very fine nuclei--0.05 μm. These particles tend to grow rapidly to accumulation mode particles around 0.5 μm, which are relatively stable in the air. Because of their initially gaseous origin, particle sizes in this range include inorganic ions such as sulfate, nitrate, ammonia, combustion-form carbon, organic aerosols, metals, and other combustion products. Coarse particles, on the other hand, are produced mainly by mechanical forces such as crushing and abrasion. Pollen and spores also inhabit the coarse particle range, thus providing dominance by materials of geological origin. Coarse particles, therefore, normally consist of finely divided minerals such as oxides of aluminum, silicon, iron, calcium, and potassium. Coarse particles of soil or dust mostly result from entrainment by the motion of air or from other mechanical action within their area. Since the size of these particles is normally > 2.5 μm their retention time in the air parcel is shorter than the fine particle fraction.

Overview

The EPA is considering further narrowing the primary NAAQS to even smaller particles ($\leq 2.5 \mu\text{m}$). As shown in Figure 1, these smaller particles penetrate deeply into the lung, where the potential for health effects is greatest. Current knowledge indicates that this size fraction ($< 2.5 \mu\text{m}$) is composed of varying amounts of sulfate, ammonium, and nitrate ions, elemental carbons, organic carbon compounds, water, and small amounts of soil dust, lead compounds, and trace species. This size fraction is generally man made.

Consequently, a wide variety of PM is found in a typical atmosphere which is constantly changing. Such factors as size, chemical composition, affinity for water and chemical reactivity, to name a few, determine the lifetime for the PM in the atmosphere. Generally, the lifetime of coarse particles in the atmosphere are measured in day, whereas fine particles tend to be transported over large areas. As illustrated in Figure 2, the atmosphere is characterized by a typical bimodal distribution of PM.

The sampling methods for characterizing PM in ambient air are divided into two categories: "reference" methods and "equivalent" methods. Equivalent methods were presented in Chapter IO-1. This chapter will present the reference methods and a discussion of filter media and filter holders. The reference methods are manual methods established by EPA for determining TSP and PM_{10} concentrations in ambient air. In these methods, a known volume of air is drawn through the sampler and the particulate fraction of interest (TSP or PM_{10}) is collected. The mass of particulate matter subsequently is determined gravimetrically, and the average ambient concentration over the sampling period is calculated.

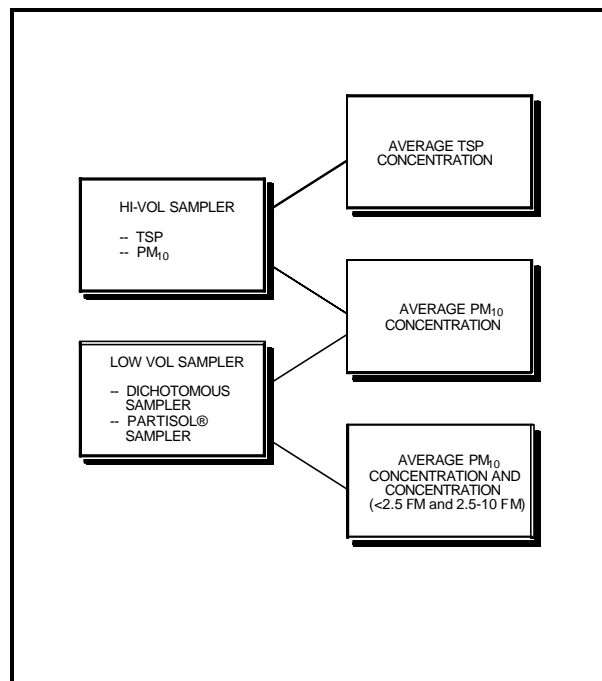
The reference method for TSP is codified at 40 CFR 50, Appendix B. This method uses a high-volume sampler to collect particles with aerodynamic diameters of approximately $100 \mu\text{m}$ or less. The high-volume samples 40-60 cubic feet per minute (ft^3/min) of air with the sampling rate held constant over the sampling period. The high-volume's design causes the TSP to be deposited uniformly across the surface of the filter. The TSP high-volume can be used to determine the average ambient TSP concentration over the sampling period, and the collected material can be analyzed subsequently to determine the identity and quantity of inorganic metals present in the TSP.

The federal reference method for PM_{10} measurements is based on particulate selection by inertial separation followed by filtration and gravimetric determination of the PM_{10} mass on the filter substrate. The reference method for PM_{10} is codified in 40 CFR 50, Appendix J. The standard for this method specifies the features for a reference PM_{10} measurement method. These features are summarized as follows:

- The sampling inlet has a cut-point of $10 \pm 0.5 \mu\text{m}$ aerodynamic diameter, as determined in a wind tunnel using liquid particles of specified diameter at specific wind speeds.
- Flow-rate remains stable over a 24-h period, independent of filter loading, within $\pm 5\%$ of the initial average flow reading and within $\pm 10\%$ of the initial flow rate for instantaneous flow measurements.
- Measurement precision for a 24-h period should be within $\pm 5 \mu\text{g}/\text{m}^3$ for concentrations less than $80 \mu\text{g}/\text{m}^3$ or $\pm 7 \mu\text{g}/\text{m}^3$ of measured PM_{10} for concentrations greater than $80 \mu\text{g}/\text{m}^3$.
- For a nominal air volume sampled over a 24-h period, the filter media should collect more than 99% of a $0.3 \mu\text{m}$ particles and have an alkalinity of < 25 microequivalents per gram and a net equivalent weight gain or loss of not more than $5 \mu\text{g}/\text{m}^3$.
- Prior to weighing, the filter should be equilibrated at a constant temperature ($\pm 3\%$) between 15E and 30EC and constant relative humidity ($\pm 5\%$) between 20 and 45%.

Two technologies have qualified as meeting the sampling requirements of the reference method: a high-volume with a PM₁₀ inlet and a dichotomous sampler. The PM₁₀ high-volume is identical to the TSP high-volume except that it is equipped with an inlet that directs only PM₁₀ to the filter. Dichotomous samplers also collect only PM₁₀, which is split into fractions above and below 2.5 μm. Both samplers collect the particulate matter uniformly across the surface of the filters. Both can be used to determine average ambient PM₁₀ concentration over the sampling period, and the collected material from both can subsequently be analyzed for inorganic metals and other materials present in the collected sample. The dichotomous sampler has the advantage of collecting two fractions so that information can be obtained about total PM₁₀ and/or both of the two fractions. This property may take on added importance if EPA decides to revise the primary NAAQS to address smaller particles. In addition, the dichotomous sampler operates at a low flow rate (about 0.6 ft³/min), which allows the use of filter media that would otherwise quickly clog at high-volume flow rates. However, because of its higher flow rates, the PM₁₀ high-volume collects more material so lower ambient concentrations of inorganic materials can be detected (assuming identical filter medium and analysis technique).

The relationship between sampler type and the type of particulate matter sampled is as follows:



Overview

The major prerequisite in selecting a sampling system is to determine what size range of particles are to be monitored and the method of analysis (if applicable). The analytical method selection is very important, because test will dictate the type of filter media compatible with the sampling system. Several air sampling filter types are available, and the specific filter used depends upon the desired physical and chemical characteristics of the filter and the analytical methods used. No single filter medium is appropriate for all desired analyses. Particle sampling filters consist of a tightly woven fiber mat or plastic membrane penetrated by microscopic pores. Several characteristics are important in selecting a filter media; these characteristics include:

- Particle sampling efficiency;
- Mechanical stability;
- Chemical stability;
- Temperature stability;
- Blank concentrations;
- Flow resistance and loading capacity; and
- Cost and availability.

A comparison of several air sampling filter types with their chemical and physical characteristics and the corresponding chemical analytical methods that can be used for analyzing the sample is presented in Table 1.

Filter holders are also constructed from different types of material, and the material type must be taken into account if reactive components of suspended particles are collected. Filter holders are constructed in either an in-line or open-face configuration. In-line holders have a small diameter opening into a small chamber that contains the filter media. This holder type may concentrate the particles in the center of the filter media, which could lead to a bias in the results if the analyses are not performed on the entire filter. Open-face holders have exposed filters with no constrictions upstream of the filter media and are a better option for ambient aerosol sampling systems. The exposed filters must be protected from excessive vibration that might dislodge the particles on the filter surface. A brief listing of common filter holders, sizes, and physical characteristics is presented in Table 2. A more detailed discussion of filter media, holders, and the determination of mass concentration is provided in Method IO-2.4.

Unfortunately, no one sampling method or filter media can address all data quality objectives for a particular ambient air monitoring program. Each method and filter type has its own attributes, specificities, advantages, and disadvantages, as previously discussed. However, Compendium Method IO-2 attempts to encompass into one chapter the various options, in a step-by-step methodology, to facilitate accurate and reliable data for sampling SPM in the ambient air.

TABLE 1. EXAMPLE OF REPRESENTATIVE FILTER MEDIA FOR PARTICLE SAMPLING¹

Filter type	Filter sizes, mm	Characteristics		Analysis methods
		Chemical	Physical	
Ringed Teflon® membrane	25 37 47	<ul style="list-style-type: none"> • Low blank levels • Low blank weight • No carbon analysis • Low hygroscopic tendency • Inert to gas adsorption 	<ul style="list-style-type: none"> • Thin membrane • White, nearly transparent surface • High particle collection efficiency • High flow resistance • Melts at -60EC • Cannot be accurately sectioned • Multiple pore sizes available • Minimal diffusion of transmitted light 	<ul style="list-style-type: none"> • GRAV, XRF, OA, PIXE, INAA, AAS, ICP/AES, ICP/MS, IC, AC
Teflon® membrane--polypropylene backed	47	<ul style="list-style-type: none"> • Low blank levels • No carbon analysis • High blank weight • Inert to gas adsorption • High background levels for PIXE and XRF • Low hygroscopic tendency 	<ul style="list-style-type: none"> • Thin membrane • White opaque surface • High particle collection efficiency • Melts at -60EC • High flow resistance • Diffuses transmitted light 	<ul style="list-style-type: none"> • GRAV., PIXE, XRF, INAA, AAS, ICP/AES, ICP/MS, IC, AC
Nylon membrane	25 37 47	<ul style="list-style-type: none"> • Low blank weight • Low hygroscopic tendency • High HNO₃ collection efficiency • Passive adsorption of low levels of NO, NO₂, PAN, and SO₂ 	<ul style="list-style-type: none"> • Thin pure nylon membrane • Diffuses transmitted light • High flow resistance • Melts at -60EC • 1 µm pore size 	<ul style="list-style-type: none"> • IC, AC
Silver membrane	25 37	<ul style="list-style-type: none"> • Resistant to chemical attack • Passive adsorption of organic vapors • High blank weight • Low hygroscopic tendency 	<ul style="list-style-type: none"> • Thin membrane • Gray-white surface • Diffuses transmitted light • High flow resistance • Melts at -350EC 	<ul style="list-style-type: none"> • GRAV., XRD
Cellulose esters membrane (cellulose nitrate mixed esters and cellulose acetate)	37 47	<ul style="list-style-type: none"> • Dissolved by several organic solvents • Negligible ash content • Hygroscopic • Low blank weight 	<ul style="list-style-type: none"> • Thin membrane • White opaque surface • Multiple pore sizes available • Surface diffuses transmitted light • High flow resistance • Melts at -70EC 	<ul style="list-style-type: none"> • GRAV., OM, TEM, SEM, XRD • Biomed. appl.

TABLE 1 (Cont'd)

Filter type	Filter sizes, mm	Characteristics		Analysis methods
		Chemical	Physical	
Polycarbonate membrane	47	<ul style="list-style-type: none"> No carbon analysis Low blank levels Low blank weight Low hygroscopic tendency 	<ul style="list-style-type: none"> Smooth, thin surface with straight capillary holes Light gray, nearly transparent surface Minimal diffusion of transmitted light Multiple pore sizes available Use for particle size classification Low particle collection efficiency for some pore sizes Retains static charge Moderate flow resistance Melts at -60EC 	<ul style="list-style-type: none"> GRAV., OA, OM, SEM, XRF, PIXE
Pure quartz filter	25 37 47 203 x 254	<ul style="list-style-type: none"> Contains large and variable quantities of Al and Si Low blank level for ions Passive adsorption of organic vapors Little adsorption of HNO₃, NO₂, and SO₂ Low hygroscopic tendency 	<ul style="list-style-type: none"> White opaque surface Diffuses transmitted light Edges of filter flake in holders High particle collection efficiency Moderate flow resistance Melts at > 900EC 	<ul style="list-style-type: none"> ICP/AES, ICP/MS, IC, AC, OA, T, TOR, TMO, TOT
Mixed quartz fiber (quartz filters with ~5% borosilicate content)	203 x 254	<ul style="list-style-type: none"> Contains large and variable quantities of Na, Al, and Si plus variable levels of other metals Passive adsorption of organic vapors Little adsorption of HNO₃, NO₂, and SO₂ High blank weight Low hygroscopic tendency 	<ul style="list-style-type: none"> White opaque surface Diffuses transmitted light High particle collection efficiency Low flow resistance Becomes brittle on heating Can melt at -500EC 	<ul style="list-style-type: none"> GRAV., XRF, PIXE, AA, ICP/AES, ICP/MS, IC, AC, T, TOR, TMO, TOT
Teflon®-coated glass fiber (borosilicate glass fiber mat with surface layer of Teflon®)	37 47	<ul style="list-style-type: none"> Inert to adsorption of HNO₃, NO₂, and SO₂ Low blank level for ions High blank weight Low hygroscopic tendency 	<ul style="list-style-type: none"> Low flow resistance High particle collection efficiency Melts at -60EC; glass at -500EC 	<ul style="list-style-type: none"> GRAV., IC, AC

TABLE 1 (Cont'd)

Filter type	Filter sizes, mm	Characteristics		Analysis methods
		Chemical	Physical	
Glass fiber (borosilicate glass fiber)	203 x 254	<ul style="list-style-type: none"> • Adsorbs HNO₃, NO₂, SO₂, and organic vapors • High blank levels • High blank weight • Low hygroscopic tendency 	<ul style="list-style-type: none"> • White opaque surface • Diffuses transmitted light • Low flow resistance • High particle collection efficiency • Melts at -500EC 	<ul style="list-style-type: none"> • GRAV., OA, XRF, PIXE, INAA, AAS, ICP/AES, IC, AC
Cellulose fiber ("paper" filter)	25 37 47	<ul style="list-style-type: none"> • No carbon analysis • Low blank levels; high purity • Most useful for adsorption of gases, e.g., HNO₃, SO₂, NH₃, and NO₂ after impregnated with reactive chemicals • High blank weight • Hygroscopic • Adsorbs gases, particularly water vapor 	<ul style="list-style-type: none"> • White opaque surface • Diffuses transmitted light • High mechanical strength • Low particle collection efficiency possible • Variable flow resistance • Burns at -150EC 	<ul style="list-style-type: none"> • GRAV., XRF, PIXE, INAA, AAS, ICP/AES, ICP/MS, IC, AC

Analysis Methods Abbreviations (alphabetical order)

- | | |
|---|--|
| AAS = Atomic absorption spectrophotometry | PIXE = Proton-induced X-Ray emissions |
| AC = Automated colorimetry | SEM = Scanning electron microscopy |
| GRAV = Gravimetry | T = Thermal carbon analysis |
| IC = Ion chromatography | TEM = Transmission electron microscopy |
| ICP/AES = Inductively-coupled plasma with atomic emission spectrophotometry | TMO = Thermal manganese oxidation carbon analysis |
| ICP/MS = Inductively-coupled plasma with mass spectrophotometry | TOR = Thermal/optical reflectance carbon analysis |
| INAA = Instrumental neutron activation analysis | TOT = Thermal/optical transmission carbon analysis |
| OA = Optical absorption or light transmission (b _{abs}) | XRD = X-Ray diffraction |
| OM = Optical microscopy | XRF = X-ray fluorescence |

¹Chow, J. C., "Measurement Methods to Determine Compliance with Ambient Air Quality Standards for Suspended Particles," *J. Air and Waste Manage. Assoc.*, Vol. 45:320-382, 1995.

TABLE 2. REPRESENTATIVE FILTER HOLDERS¹

Holder type	Filter size, mm	Physical characteristics
Polycarbonate	25 47	<ul style="list-style-type: none"> • In-line or open-face configuration • Base has flow resistant outlet • Support grid has polyethylene O-ring • Extender section for multi-stage filter pack sampling
Polypropylene	13 25 37 47	<ul style="list-style-type: none"> • In-line or open-face (37-mm only) configuration • Polypropylene or glass-filled polystyrene base • Support grid has silicon O-ring • 37-mm filter has polypropylene base
Aluminum or stainless steel	25 47	<ul style="list-style-type: none"> • In-line or open-face • Stainless steel screen with Viton O-ring • Has nylon or polyethylene adapters
Stainless steel	25 47 203 x 254	<ul style="list-style-type: none"> • In-line or open-face • Stainless steel base • Stainless steel or nickel-plated screen • Screens use Teflon® or Viton O-rings
Perfluoroalkoxy (PFA) Teflon®	47	<ul style="list-style-type: none"> • In-line or open-face • Base, support grid, and adapter are PFA Teflon® • Support grid has Viton O-ring
Teflon®	47	<ul style="list-style-type: none"> • In-line • Teflon® base

¹Chow, J. C., "Measurement Methods to Determine Compliance with Ambient Air Quality Standards for Suspended Particles," *J. Air and Waste Manage. Assoc.*, Vol. 45:320-382, 1995.

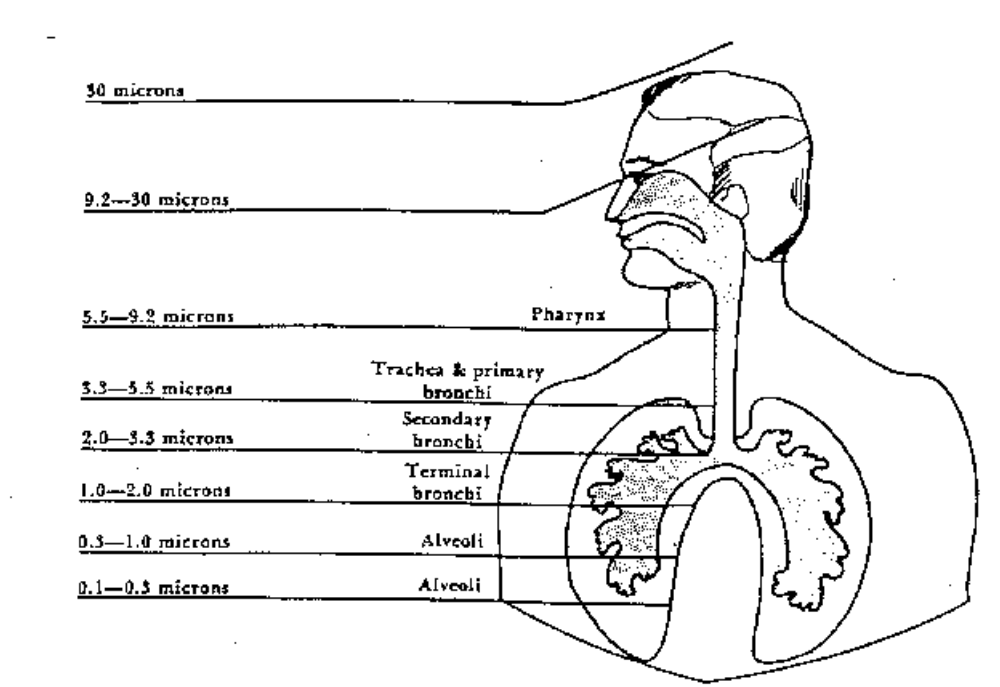


Figure 1. Depth of respiratory system penetration based on particle size.

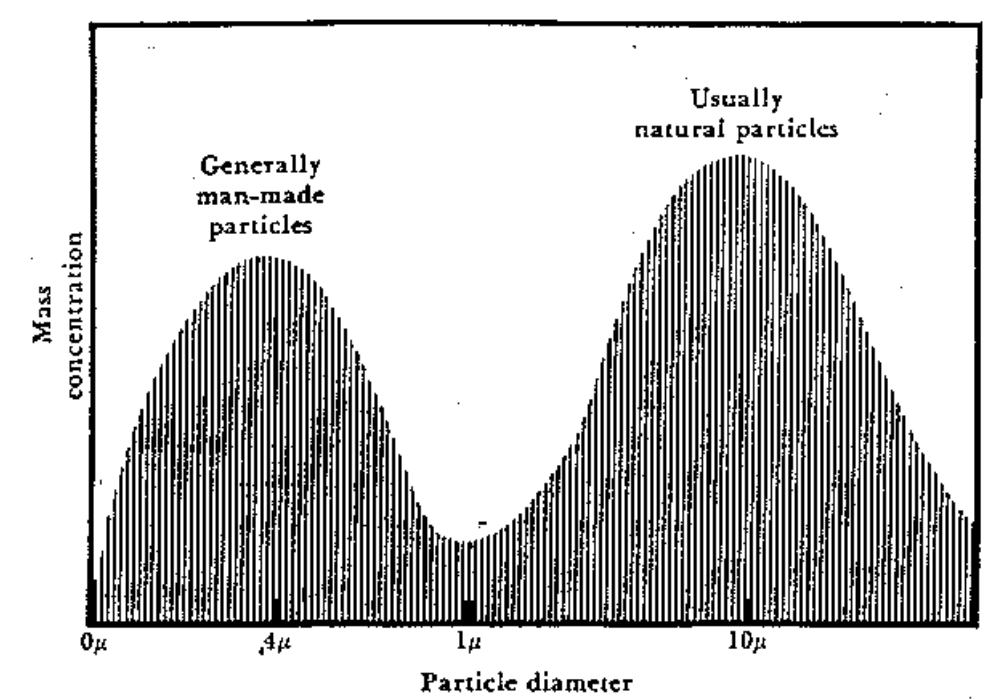


Figure 2. Bimodal distribution of particles in the atmosphere.

