

5. Measurement of Particulate Matter

5.1 Introduction

On December 9, 1982, the California Air Resources Board (Board or ARB) replaced the total particulate matter ambient air quality standard with a standard that focused on particles of a smaller diameter. The Board approved amendments to the California Code of Regulations, title 17, section 70200, which modified the definition of suspended particulate matter (PM) to specifically include particulate matter with an aerodynamic diameter of 10 microns or less (PM₁₀), and established PM₁₀ ambient air quality standards. The Board included general reference to a PM₁₀ measurement method in the standard and directed staff to establish more specific criteria for PM₁₀ sampling equipment. Method P, adopted by the Board in 1985, established the State method for ambient PM₁₀ measurement. In 1986, the State identified the size selective inlet (SSI) high volume (hi-vol) PM₁₀ sampler as the PM₁₀ sampler satisfying the requirements of Method P.

In December 2000, the Board determined that the state ambient air quality standards for PM₁₀ and particulate sulfates should be reviewed to ensure they are protective of public health. The Board asked staff to provide this review and any recommendations for changes to the standards by 2002.

This chapter addresses the measurement methods that are required to be used to determine compliance with the newly proposed PM standards. At this time, the ARB proposes to align the state and federal requirements for PM samplers by adopting the Federal Reference Methods (FRMs) for PM₁₀ and PM_{2.5} as the state's method. The FRMs specify performance characteristics and operational requirements applicable to PM₁₀ and PM_{2.5} monitoring methods, and for PM_{2.5}, specify sampler design characteristics. The associated samplers meet the requirements specified in the methods. The method and associated sampler are designated as a reference method. We are not proposing to adopt Federal Equivalent Methods, per se, given their history of poor performance in California. Continuous samplers will be addressed, however, and will be incorporated as California Approved Samplers based on their performance in a recently concluded study in Bakersfield, CA.

The reference methods (FRMs) are traditional, filter-based sampling methods with laboratory weighing of the filters before and after sampling. The sampling and analytical methods are both labor-intensive. Each sample is collected during a 24-hour period, and one sample typically is taken every six days throughout the year at each monitoring station. There is a time-lag of days to weeks from the date of sampling to the time results are available.

Continuous monitoring for either PM₁₀ or PM_{2.5} has many advantages over traditional filter based sampling techniques. A continuous method is an in-situ, automatic measurement method of suspended particle mass with varied averaging time (minutes to hours) that provides an instantaneous result. Their 24/7 sampling schedule will further our understanding of PM emission patterns and exposure, and can be used to enhance public health research into short-term peak exposure. They can provide more data for model validation, to aid in identifying air pollution source(s), and to reflect dispersion patterns. Official approval of continuous instruments/methods will promote further development of continuous samplers and potentially reduce the cost of the air monitoring network.

5.2 Existing Monitoring Requirements

5.2.1 State Method P for PM10

Method P (cited in title 17, California Code of Regulations, sections 70100 and 70200) describes the design and performance requirements for the PM10 sampler to be used to determine compliance with the state ambient air quality standards. Method P is contained in Appendix 5 part A of this document and describes the operating principle and design of the samplers, which are in turn specified in proposed section 70100.1.

An “ideal” sampler should be designed to determine the mass concentration of ambient particulate matter of a mean aerodynamic diameter of 10 micrometer (μm) or less (PM10) to simulate particle penetration of the human respiratory system as described by the Chan-Lippmann model (1980). According to this model, PM10 particles are small enough to enter the thoracic region of the human respiratory tract. An ideal sampler is the one that collects 50 percent (referred as D50) of all particles of $10 \pm 1 \mu\text{m}$ aerodynamic diameter, and which collects a rapidly declining fraction of particles as their diameter increases and rapidly increasing fraction of particles of smaller particle diameters. Aerodynamic diameter is defined as the diameter of a spherical particle of a unit density with settling velocity equal to that of the particle in question. Particles with the same size and shape but with different densities will have different aerodynamic diameters.

Suspended particulate matter refers to atmospheric particles, solids, or liquids, except uncombined water. Dry, free-flowing particles should be sampled with the same efficiency as liquid, sticky particles. The expected mass concentrations of liquid particles should be within the limits of that predicted by the ideal sampler. For solid particles, the expected mass concentration should be no more than 5 percent above that obtained for liquid particles of the same size. The sampler must have less than 15 percent variation in the measurements produced by three collocated samplers.

Meteorology is one of several factors that can effect sampling efficiency. The performance of a PM10 sampler should be independent of wind speed to simulate human respiration. The inlet design and its internal configuration should be such that it shows no dependency on wind direction and wind speed when operated within 2 to 24 kilometers-per-hour wind speeds. To do this, the inlet should be omnidirectional, that is, the inlet should be symmetrical about the vertical axis.

A sampler must possess a sampling medium (filter) upon which the PM is collected without spattering and falling off. The sampler should be designed to hold and seal the filter in a horizontal direction so that the sample air is drawn uniformly downward through the filter to allow a uniform distribution of PM10 collected so as to permit subdivision of the filter for qualitative and quantitative analysis. Filters shall have a collection efficiency of more than 99 percent as measured by the dioctyl phthalate (DOP) test (ASTM-2986), with $0.3 \mu\text{m}$ particles at flow rates equal to the sampler’s operating face velocity. Filters must have mechanical and chemical stability and be stable in a wide temperature range to allow a variety of qualitative and quantitative analyses. Filters must minimize artifacts, that is, should not react with the deposit and must not absorb contaminant gases. They must be non-hygroscopic, and have high chemical purity with alkalinity of <5 microequivalents/gram. The filters must be equilibrated prior to use at constant temperature and humidity conditions.

The sampler must possess an automatic flow control device which maintains a constant flow rate to within ± 10 percent of the recommended range for the sampler inlet over normal variations in line voltage and filter pressure drop during the sampling period. Change in flow velocity will result in change in nominal particle size collected. Therefore, it is important that

the flow rate through the inlet be maintained at a constant value that is as close as possible to the inlet design flow rate.

A timing/control device should be capable of starting and stopping the sampler during a sample collection period of 24 ± 1 hr ($1,440 \pm 60$ min). An elapsed time meter, accurate to within 15 minutes, shall be used to measure sampling time. This meter is optional for samplers with continuous flow recorders if the sampling time measurement obtained by means of the recorder meets the ± 15 minutes accuracy specification. Using the total sampling time, the total volume of air sampled is determined. PM concentration is computed as the total mass of collected particles in PM₁₀ size range divided by the volume of air sampled. The particulate matter concentration is expressed as micrograms per cubic meter ($\mu\text{g}/\text{m}^3$) corrected to standard conditions (760 torr and 25 C).

5.2.2 State Method for Sulfates

State regulations (section 70200 of title 17, California Code of Regulations) contain an independent ambient air quality standard for particulate sulfates. The measurement method for sulfates described in this standard is high-volume TSP sampling, with filter analysis by Turbidimetric Barium Sulfate Spectrometry, AIHL Method 61, or “[a]ny equivalent procedure which can be shown to the satisfaction of the Air Resources Board to give equivalent results at or near the level of the air quality standard.”

The ARB’s current measurement method for sulfates is MLD Method 033, which uses TSP sampling followed by ion chromatography. However, adsorption of SO₂ with subsequent chemical reactions on the filter surface, can, at sufficient concentrations, lead to gas-to-particle conversion, and can create positive artifacts on the filter. These can be minimized with the use of alkalinity-controlled filters which are provided for in the current PM₁₀ network and PM₁₀ Federal Reference Methods.

5.2.3 Federal Methods for PM₁₀

Federal ambient measurement methods must be used to determine the attainment status of air basins nationwide. Federal Reference Methods (FRMs) use the measurement principles and specifications defined in U.S. EPA regulations. Provisions also allow for a Federal Equivalent Method (FEM) to be approved by the U.S. EPA and used for the same purpose. The requirements for an FRM for PM₁₀ are described in Appendix M, Title 40, Code of Federal Regulations Part 50, 1997, and are provided here as Appendix 5 part B to this document. These requirements are, for the most part, the same as the California Method P. This is understandable, as Method P was adopted by the ARB in consultation with the U.S. EPA as that agency was preparing to propose methods for the NAAQS for PM₁₀. A comparison of the two methods, item-by-item, is given in Appendix 5 part C. There are differences in a few specific requirements, which are highlighted in the table. The discussion below focuses only on those differences. The purpose of presenting this information is to highlight the need to update Method P.

- The FRM requires PM₁₀ sampler to simulate particle penetration of the human respiratory system as described by the Chan-Lippmann (1980), penetration model. The D50 cut-point of the sampler is 10 μm with a tolerance of ± 0.5 μm , compared to the tolerance of ± 1.0 μm for Method P.
- The alkalinity of filter medium should be less than 2.5 microequivalents/gram for FRM as opposed to less than 5 microequivalents/gram for Method P. The filters should be equilibrated at constant relative humidity of between 20 percent and 45 percent ± 5 percent for FRM instead of <50 percent relative humidity for Method P before weighing.

- The precision of collocated FRM samplers must be $5\ \mu\text{g}/\text{m}^3$ for PM concentration below $80\ \mu\text{g}/\text{m}^3$ and 7 percent for PM₁₀ concentration above $80\ \mu\text{g}/\text{m}^3$ for FRM, as opposed to 15 percent for all concentrations for Method P.
- The FRM requires the air flow rate through the sampler remain stable over a 24-hour period, regardless of filter loading; the specific requirements are ± 5 percent of the initial reading for the average flow, and ± 10 percent of the initial flow rate for any instantaneous flow measurement. For Method P, the flow rate should be within 10 percent at all times.
- Typically, an analytical balance with a sensitivity of 0.1 mg is required for hi-vol samplers (flow rates $>0.5\ \text{m}^3/\text{min}$, large filters). Lo-vol samplers (flow rates $<0.5\ \text{m}^3/\text{min}$, smaller filters) require a more sensitive balance, which is not indicated in Method P.
- The particulate matter concentration is expressed as micrograms per cubic meter ($\mu\text{g}/\text{m}^3$) at local temperature and pressure (LTP) as opposed to standard temperature and pressure (STP, 760 torr and 25 C) for Method P.

The other major difference between the State and federal method is the designation of FEM test protocols, not included in Method P, although method equivalency is referred to and accepted in general terms in State regulations.

The differences between the FRMs and state-approved samplers can generally be attributed to advancements and improvements in sampler flow control and filter medium technology that occurred since Method P was established. The PM₁₀ air monitoring network in California meets FRM requirements. Consequently, changing Method P to be consistent with the FRM will bring the criteria into line with both equipment and material specifications, and field and laboratory practices.

5.2.4 Federal Methods for PM_{2.5}

The U.S. EPA promulgated rigorous design and performance specifications for its PM_{2.5} FRM samplers (40 CFR part 50, Appendix L; 40 CFR part 53, Subpart E; and 40 CFR part 58, Appendix A, all dated July 18, 1997. These are set forth in Appendix 5, parts D, E and F, respectively, of this document). Only measurements made using U.S. EPA-designated FRM samplers may be used to determine an area's compliance status with the PM_{2.5} NAAQS. The PM_{2.5} sampler is an adaptation of the PM₁₀ lo-vol sampler that initially removes, by impaction, particles larger than PM₁₀. Downstream lies a second impactor (Well Impactor Ninety-Six [WINS]) that reduces the cut point to $2.5\ \mu\text{m}$.

The dimensions and materials of sampler components that come in contact with the sampled air stream (the first stage inlet, the downtube, the second stage separator [WINS], the upper filter holder, the filter cassette, and the filter support screen) are specified by design (40 CFR part 50, Appendix L, July 18, 1997). The design of the other components of the FRM sampler is left to manufacturers, as long as resulting samplers meet all the prescribed performance specifications.

Performance specifications include active monitoring of a number of operational characteristics of the samplers, including sampler volumetric flow, temperature, and pressure. The performance criteria specify strict requirements for controls that must be observed for sampler operations. These include sampling efficiency, accuracy, precision, sampling medium, flow controller, laboratory, calibration, and measurement procedures. The details of the performance criteria are given in Appendix L of 40 CFR part 50 (see Appendix 5 part D to this document).

The current network of PM_{2.5} samplers in California (more than 80) was funded almost entirely by the U.S. EPA following the adoption of the federal PM_{2.5} standard. The U.S. EPA

continues to provide operating funds for the network. The samplers' operation is governed by federal regulation.

The network of PM_{2.5} samplers has been operating in California since 1999. Additional speciation samplers will eventually supplement the FRM samplers and provide information about the composition of the particulate matter in the sample. Staff recommends adopting both the FRM sampler and the performance and operational requirements of the methods for the proposed State PM_{2.5} standard. Staff is not proposing to adopt the U.S. EPA's FEM criteria for PM_{2.5}.

5.3 Available PM Sampling Methods

There are two fundamental methods commonly used to measure atmospheric PM₁₀ and PM_{2.5} that are potentially useable in California. The first is a laboratory-based, gravimetric, or filter method, in which particles segregated by size are collected on a pre-weighed filter medium and weighed after sampling to determine PM mass. PM concentration is calculated by dividing the mass increase of the filter by the 24-hour total volume of air (at ambient conditions) that passed through the filter.

The second fundamental technique employs in-situ field samplers that are based on different operational principles, but that all operate continuously and produce real-time, hourly average concentrations. There are pros and cons to either type of sampler. Over the years, the staff has heard reports of the need for both types of samplers. Consequently, staff is proposing to incorporate the leaders in both types of samplers as part of this regulation as California Approved Samplers for PM.

New technology samplers may be added in future years, and others perhaps deleted, from the list of approved sampler as the situation warrants. The samplers proposed in this action have been demonstrated to have wide applicability, and have good agreement with standard methods. The intent of this rulemaking is to incorporate recent advances in sampler technology, align the state with federal samplers where possible, and incorporate samplers that can be used widely in California in areas with persistent high PM levels. The proposal does not support approving different samplers for every air basin or approving samplers that respond differently based on season of the year unless absolutely necessary.

The staff carefully considered the limitations of a wide variety of samplers in making the method proposals. Filter based methods can result in loss of PM during or after sampling, or formation of PM on the filter medium during sampling. Loss of semi-volatile chemical species such as atmospheric ammonium nitrate and organics may occur during and after sampling as particles move from the particle to the gas phase. The amount of particulate matter lost is dependent on the concentration and composition of the semivolatile components, and the handling and retention time on the sampler at the conclusion of the sample run. Loss of volatile chemical species can underestimate PM mass. PTFE (polytetrafluoroethylene or Teflon[®]) filters can easily lose semi-volatile materials (a so-called negative artifact) (Eatough et al., 1993; Gundel et al., 1995). Therefore, regular sampling procedures now include steps to minimize these losses, including rapid removal of filters from the sampler, prompt storage in Petri dishes, transport in cool environments, expedited transport of filters from the field to the weigh rooms, and prompt extractions once the filters are weighed (Achtelik and Omand, 1998).

Adsorption of gases (such as SO₂) with subsequent chemical reactions with other gases on the filter surface, can, at sufficient concentrations, lead to gas-to-particle conversion, and can create positive artifacts on the filter. These can be reduced with the use of alkalinity-controlled filters and possibly the use of low-volume samplers.

Formation particles from gaseous species can lead to overestimation of PM mass (i.e., a positive artifact). Quartz filters can adsorb some gas-phase organics producing positive artifacts (Gundel et al., 1995; Turpin et al., 1994).

Operation of conventional filter-based samplers with laboratory gravimetric analysis is extremely time-consuming and labor intensive to produce a single mass measurement compared to real time, continuous samplers. Moreover, data are available only on a 24-hour average basis from conventional filter-based techniques. This limits using the data to investigate sub-24-hour health effects. The time lag inherent in data availability in conventional filter-based methods also precludes their use to provide the general public with timely warnings about episodic air pollution hazards. Filter-based systems can also have problems with particle loss during handling and transport, particularly when mass loading on the filter is high. These “sloughing” effects have been minimized by having strict operational protocols.

5.3.1 General Description of Gravimetric Methods

5.3.1.1 High-Volume Size Selective Inlet Sampler

The size selective inlet (SSI) sampler is described in Method P and is recognized by the U.S.EPA as an FRM. California identified the SSI in May 1986 as the PM₁₀ sampler to be used for the State AAQS. The U.S. EPA identified it in 1987 as an FRM (U.S. EPA/ORD, 2000).

The high-volume (hi-vol) SSI sampler used in the State and federal PM₁₀ networks consists basically of a PM₁₀ inlet, an impactor, a flow control system recorder, and a pump. The automatic flow control system consists of either a mass flow controller or a volumetric flow controller, which controls the flow to 40 ft³/min (at standard temperature and pressure). The flow rate through the impactor is used with the elapsed time to determine size of particle collected and the volume of air sampled. According to one manufacturer, its inlet has a cut-point of 9.7 μm in winds up to 22 miles per hour (36 kilometers per hour) (Thermo Andersen, Inc.).

PM₁₀ hi-vol samples are collected on an 8x10 inch (20x25 cm) quartz filter that offers high collection efficiencies and is resistant to absorbing artifacts related to the collection of sulfates and nitrates. However, the quartz filter can under some circumstances adsorb organic vapor more readily than a PTFE filter leading to an overestimation of PM mass (Turpin et al., 1994). Volatile constituent losses during sampling and transport are known to exist; however, prompt sample removal can minimize these losses.

There are three versions of the SSI samplers currently designated as FRMs. The unit widely used in California, the SA-1200 (Sierra-Anderson 1200), is a single-stage fractionator with hinged design to facilitate oiling and cleaning of the impaction shim.

The SSI sampler provides a direct measurement of PM₁₀ mass concentration. The large filter size provides two benefits. First, it increases the precision and accuracy of mass measurement, and second, it provides sufficient PM that can be analyzed for many of the primary constituents of interest.

5.3.1.2 Low-Volume Sampler

5.3.1.2.1 PM₁₀

Low-volume (lo-vol) PM₁₀ FRM samplers collect PM of a specific size range on a filter at a flow rate considerably less than for the hi-vol samplers. A lo-vol sampler consists of a PM₁₀ inlet, an impactor, a pump, a flow rate controller, and a timer. Fundamentally, the operational

principles of the lo-vol and the hi-vol (SSI) samplers are the same. The differences occur with features such as the inlet size, flow rate, and filter size. These differences are discussed below. The flow rate in both cases is a critical feature of the instrument's ability to segregate particle sizes. Lo-vol samplers were not available at the time Method P was promulgated.

Federally approved lo-vol samplers (FRM) are equipped with either a flat or tilted PM10 inlet, as specified in Appendix L of 40 CFR Part 50 (Figures L-2 through L-19). They use small PTFE-coated fiber filters. The filters are chemically stable, and suitable for a wide temperature range. The sampler may have a manual or an automatic filter-changing mechanism. It must be able to measure 24-hour PM10 mass concentrations of at least 300 $\mu\text{g}/\text{m}^3$, while maintaining the operating flow rate within the specified limits.

FRM lo-vol samplers operate at a flow rate of 16.67 lpm. They use gravimetric means to determine ambient PM mass concentrations. The PTFE filters can be analyzed for elements, but are incompatible for analysis of some elements such as carbon, and do not provide a large enough sample to analyze all chemical constituents. The FRM lo-vol samplers have the same labor-intensive limitations of the hi-vol samplers which, in air monitoring networks, allows for only intermittent, 24-hour sampling.

5.3.1.2.2 PM2.5

PM2.5 FRM samplers are updated versions of the PM10 lo-vol FRM samplers. Sampler operation is controlled by a microprocessor. Downstream of the PM10 inlet is a Well Impactor Ninety Six (WINS) impactor, a filter medium, a timer, and a flow controller.

The WINS is a particle separator, where suspended PM2.5 is separated from the PM10. The WINS impactor is a single jet impactor, which impacts into a "well" holding a 37 mm glass fiber substrate impregnated with 1 mL of tetramethyltetraphenyltrisiloxane (silicone oil) single-compound diffusion oil. The WINS impactor inertially separates fine particles of an aerodynamic diameter of 2.5 μm or less from PM10. Larger particles are captured in the oil-impregnated substrate in the wells of the impactor, and the PM2.5 and smaller particles are collected on a 47-mm filter.

The filter is made of PTFE, and has a particle collection efficiency of greater than 99.7 percent. Prior to its use, the filter is equilibrated for 24 hours at a temperature range of 20 to 23 C and at a relative humidity in the range of 20 to 40 percent, and preweighed in a laboratory. The well filter needs to be cleaned regularly or the resulting deposited material can begin to affect the cut point of the inlet.

The sampler flow rate is 16.67 lpm (1.000 m^3/hr), measured by volumetric flow rate at the temperature and pressure of the sample air entering the inlet.

5.3.1.2.3 Dichotomous Sampler

The dichotomous sampler (dichot) is another low-volume sampler (draws air at 16.67 lpm). Ninety percent of the air (15.00 lpm) flows through the fine particulate filter, and the remaining 10 percent (1.67 lpm) flows through the coarse particulate filter.

The dichotomous sampler uses a virtual impactor (region of stagnant air) to segregate the air sample into two fractions. The virtual impactor particle separator accelerates the air sample through a nozzle and then deflects the air at a right angle. Most particles smaller than 2.5 micrometers (fine fraction) will follow the higher air flow path and collect on a fine particulate filter. Particles between 2.5 and 10 micrometers (coarse fraction) have sufficient inertia to impact into the chamber below the nozzle and are collected on a coarse particulate filter. Ten

percent of the sample air flows through the coarse particulate filter and because of this, approximately 1/10 of the fine particulate are collected on the coarse particulate filter.

The coarse and fine particulate filters are 37 mm in diameter and are mounted in plastic rings. The filters are weighed to calculate mass concentrations and, where appropriate, analyzed to determine the concentration of selected chemical elements.

PM_{2.5} measurements made using the dichot with its virtual separation technique do not meet U.S. EPA requirements for PM_{2.5} sampling in terms of the impactor type, filter size, and flow rate. The dichot utilizes a PM₁₀ inlet similar to that in a lo-vol sampler, but the flow rate is only 10 percent of the total flow rate, hence introducing a potential source of difference from the lo-vol PM₁₀ sampler. Therefore, the use of this method for PM_{2.5} produces data that are not usable for compliance designation with the NAAQS for PM_{2.5}. It is a reference sampler, however, for PM₁₀.

5.3.2 General Description of Continuous Methods

Continuous methods produce hourly average PM concentration measurements in real time on a daily basis. In contrast to the intermittent sampling frequency of filter-based methods, continuous monitoring of atmospheric PM concentration has many advantages over periodic sampling; principally, the ability to assess air quality on those days missed by periodic samplers and finer time resolution. Arnold et al., (1992) collected daily 24-hour PM₁₀ samples with an automated monitor and noted that 80 percent of the highest 10 daily concentrations in 1989 and 1990 were not encountered by the commonly used every-sixth-day sampling schedule.

Continuous methods provide data that can be accessed remotely in real time, and fill many needs for information that are very impractical, if not impossible, for typical filter-based methods. These include timely warnings about episodic air pollution hazards, enhanced public health research, air quality indexing, investigating diurnal variation and short term peak exposure, model evaluation, complaint investigation, data analyses, and specifying source impacts.

Several brands of continuous measurement technologies are commercially available. These include the tapered element oscillating microbalance (TEOM) including the SES, FDMS and differential configurations, beta attenuation monitors (BAM), and continuous ambient mass monitors (CAMM).

The CAMM is based on a measure of increasing pressure drop across a membrane filter with increasing particle loading on the filter. The analyzer consists of a diffusion dryer to remove particle-bound water and a filter tape to collect PM. Babich et al. (2000), using a Fluoropore membrane filter, measured PM using the CAMM in seven U.S. cities. Results of comparison to the Harvard Impactor (HI) yielded a good correlation ($r = 0.95$) and the average of CAMM-to-HI of 1.07. When the same sampler was tested by the ARB in 1998/1999 at the Bakersfield monitoring station during the winter months, it yielded a slope of 0.74 and correlation of 0.98 (Chung et al. (2001)). Although well correlated, the sampler showed a bias of 25% compared to the FRM.

The BAM and the TEOM are the two most commonly used, commercially available, continuous PM analyzers in California. Both have been used to measure ambient PM₁₀ and PM_{2.5} mass concentrations. These two technologies are designated FEMs for PM₁₀. Because of their widespread use, a discussion of each is provided below.

5.3.2.1 Beta Attenuation Monitor

Several researchers (Jaklevic et al., 1981 and Kim et al., 1999) have used the measurement principle of absorption of beta radiation by PM on a filter as an indicator of particulate matter mass to provide real-time measurement of atmospheric PM. A Beta Attenuation Monitor (BAM) uses a lo-vol size selective inlet, a filter tape, a beta attenuation source and detector, a lo-vol flow controller, and a timer. The sampler contains a source of beta radiation (^{14}C or ^{85}Kr) and a detector to measure the beta absorption of PM accumulated on a filter. The filter material is a roll or cassette, which advances automatically on a time sequence. When particles are placed between the beta source and the detector, the beta rays are attenuated or absorbed by particles in their path. The difference in attenuation before and after the segment of the tape used to collect PM is attributed to the PM deposited on the filter. The reduction in beta ray intensity passing through the collected PM is assumed to be a function of the mass of material between the source and the detector. The degree of beta radiation attenuation is converted to PM concentration.

5.3.2.1.1 PM_{2.5} Results

Instrument inter-comparison studies of BAM PM_{2.5} units (a Met One model 1020) were conducted at Bakersfield (1998 – 1999) (Chung et al., 2001) and Fresno (1999 – 2000) (Appendix 5 part G). The results at Fresno were good (regression coefficient [R^2] of 0.97, slope of 1.07, intercept of 7.06). At Bakersfield (1998-1999), the PM_{2.5} BAM study compared one BAM equipped with a standard PM_{2.5} WINS inlet and one with sharp cut cyclone with the PM_{2.5} FRM. The comparison showed very good agreement ($R^2 = 0.99$ each, slopes of 0.91 and 0.97, and intercepts of 0.8 and 3.25, respectively). A minimum of 20 data pairs were gathered at each location (Chung et al., 2001). These studies were surveyed and considered in designing the 2001/2002 California Approved Sampler Study in Bakersfield, CA. The sampler comparison study is summarized in Appendix 5 part H. It included collocated Thermo Andersen BAMs (model FH 64 C14, here-after named And-BAM) and Met One BAMs (model 1020, here-after named Met-BAM) were configured to measure PM₁₀ and PM_{2.5}, and were operated in parallel with PM₁₀ (SSI and Partisol) and PM_{2.5} (RAAS) FRMs. Using the results of the collocated samplers, precision was determined. The accuracy was evaluated using the lo-vol FRM as the reference. Two of each of the continuous PM_{2.5} samplers were fitted with sharp-cut cyclones to isolate the PM_{2.5} fraction from PM₁₀.

The accuracy of the PM_{2.5} sampler data was determined by comparing 24-hr average data with the RAAS FRM (Table 4, Appendix 5 part H). There was excellent agreement between the continuous methods and the FRM. Regression analysis of the And-BAM and Met-BAM against the RAAS produced slopes of 1.03 and 1.03, respectively, correlations of 0.98 and 1.0 respectively, and intercepts of -1.32 and -1.58 respectively. A minimum of 102 data pairs was used in the analysis.

5.3.2.1.2 PM₁₀ Results

Data comparing the SSI to the Met One BAM PM₁₀ in Bakersfield in 1998-99 yielded limited but encouraging results ($R^2 = 0.99$ with slope of 1.01 and intercept of $1.90 \mu\text{g}/\text{m}^3$ for eight data pairs (Chung et al., 2001). A study in Fresno in 2000, however, showed a weaker relationship ($R^2 = 0.76$ with slope of 1.11 and intercept of $23.24 \mu\text{g}/\text{m}^3$ for 10 data pairs).

California Approved Sampler Study: In the ARB's 2001/2002 sampler comparison study in Bakersfield, (Appendix 5 part H) the And-BAM and Met-BAM PM₁₀'s compared favorably to the Partisol PM₁₀ yielding slopes of 1.04 and 1.13 respectively, correlation values of 0.99 and 1.0 respectively, and intercepts of -2.50 and -1.65 respectively. Thirty data pairs or more were used for comparison.

The results of comparison of continuous samplers with each other and with PM_{2.5} and PM₁₀ FRMs were compared with U.S. EPA PM₁₀ class II test specifications (slope 1 ± 0.1 , intercept $\pm 5 \mu\text{g}/\text{m}^3$, correlation ≥ 0.97 , and precision of 7%, Table 5, Appendix 5 part H). The rationale for selecting this test is provided in Appendix 5 part H.

Accuracy and precision values of these continuous samplers for both size cuts meet or exceed the proposed test specifications. Consequently, staff recommend that both the Thermo Andersen BAM (FH 64 C14 model), and the Met One BAM (1020 model) be approved for use to determine compliance with the State AAQS for PM_{2.5} and PM₁₀.

5.3.2.1.3 Tapered Element Oscillating Microbalance

The Tapered Element Oscillating Microbalance (TEOM) is a low-volume sampler (16.67 lpm) that uses a mass sensor to measure airborne particle mass in real time. A TEOM consists of a size-selective inlet, flow splitter, sample filter, microbalance, flow controller timer, and software that makes the operation of the instrument fully automatic. In practice, the TEOM collects PM on a filter located on the top of a hollow, oscillating tapered tube. A small portion of the incoming air flow is drawn through the filter and through the tube. The oscillation frequency of the tapered inlet tube is inversely proportional to the mass of the sample that is deposited on the collection filter. The frequency decreases as mass accumulates on the filter, providing a direct measure of inertial mass. The typical measurement is collected over a period of ten minutes. The sample chamber is maintained above ambient temperatures (30-50C) to minimize the effect of temperature changes and thermal expansion of the tapered element that may affect the oscillation frequency, and to reduce particle-bound water (Patashnick et al., 1991).

Several studies (Allen et al. 1997, Chung et al. 2001, Cook et al. 1995) have shown that the concentration of PM₁₀ or PM_{2.5} mass using the TEOM are often lower than PM measurements produced by other methods. Analysis of the constituents typically found in such cases indicates that this is caused by loss in the heated sample chamber of semi-volatile PM, such as ammonium nitrate and/or organic compounds. While most of the volatile components are found in the fine PM fraction (PM_{2.5}), discrepancies between PM₁₀ TEOM and reference samplers have also been observed.

Cook et al. (1995) studied the performance of the PM_{2.5} TEOM with a candidate FRM PM_{2.5} sampler at the Bakersfield monitoring station. The TEOM was operated at two temperatures, 30C and 50C, to determine the effect of temperature on measurement of PM mass. At both temperatures, the TEOM measured lower PM_{2.5} mass than the dichot or a single-stage lo-vol gravimetric sampler. PM concentrations from the TEOM at 50C were much lower (negative bias) compared to those at 30C, confirming the effect of temperature at that location on semi-volatile organics and nitrates from the filter.

In another study in Bakersfield, a PM₁₀ SSI (an FRM) and TEOM sampler operated in parallel from November 1998 to February 1999 (Appendix 5 part G). This is a period when PM concentrations, and in particular volatile components, are high. The samplers correlated well, but again, the TEOM showed a significant negative bias ($R^2 = 0.95$ with slope of 0.37). At the Fresno Supersite, for the 1999 - 2000 sampling period, similar samplers correlated as well, and less bias relative to the FRM was seen ($R^2 = 0.95$ and slope of 0.83).

When PM_{2.5} was evaluated at the Fresno Supersite, the TEOM showed poor correlation and a very large negative bias with respect to the PM_{2.5} ($R^2 = 0.31$ with a slope of 0.42). At both sites, the TEOM underestimated PM mass concentration where semi-volatile components of PM are a significant component in both PM fractions.

In general, EPA-approved TEOMs have not performed well in the two areas of the State with the most persistent PM problem, the San Joaquin Valley Air Basin and the South Coast Air Basin. The TEOM's disadvantage is that the temperature necessary for the proper operation of the microbalance volatilizes a substantial component of the PM as part of the measurement process. This is more pronounced for measurement of fine PM fraction where volatile components make up a large part of the PM. The instrument manufacturer acknowledges this situation, and has developed several enhancements in recent years that address this problem.

A Sampler Equilibration System (SES) conditions the incoming sample air to lower humidity and temperature, to reduce losses of volatile species for the TEOM (Meyer et al., 2000). The SES utilizes a Nafion dryer which fits between the flow splitter that follows the size-selective inlet and the sensor unit. This unit was evaluated by the U.S. EPA as part of the Environmental Technology Verification program. The results were encouraging; however, the negative bias still existed.

Patashnick et al. (2001) subsequently developed a differential TEOM, which is a matched pair of TEOM sensors that operate at ambient temperature. The intent of the design is to measure continuous PM mass including volatile components. Downstream flow from a common size selective inlet is passed through a dryer. At the dryer exit, the flow is split with each branch passing through an electrostatic precipitator (ESP), each of which alternately turns off and on, out of phase with the other. The flow through each ESP is directed to a separate microbalance. The difference in the effective mass measured by the two microbalances is the sum of PM masses due to non-volatile and volatile component, from which filter artifacts and effective mass due to instrument sensitivity due to temperature changes is subtracted. However, this instrument is very expensive and is not applicable for routine field use.

In 2001, Rupprecht & Patashnick developed the commercial version of the differential system, the filter dynamics measurement system (FDMS). The FDMS uses the TEOM-SES system, a dryer, a switch, a purge filter conditioning unit, and a microbalance configured in a way to measure both volatile and non-volatile PM mass.

The sampling process consists of alternate sampling and purge cycles of 5-minutes each. During the first five minutes a PM is collected on the microbalance filter and mass is determined. The next five minutes, the collected PM is purged by air from the purge filter control unit from which PM is removed. Any decrease in filter mass observed during the purging cycle is attributed to the loss of volatile PM. The mass lost is added back to the mass measured during the first cycle (before purging) thus compensating for any loss during sampling. The reported mass concentration approximates the sum of nonvolatile and volatile PM.

California Approved Sampler Study: In the latest Bakersfield sampler study (ARB, 2001 – 2002) (Appendix 5 part H), comparison of the Partisol PM10 and the FDMS produced a slope (1.05), correlation (0.97), and an intercept (1.08) that agree with the proposed test specifications (Table 5, Appendix 5 part H). Thirty data pairs were used in the comparison.

Comparison of PM2.5 FDMS with the RAAS PM2.5 produced a slope (1.03), correlation (0.99), and an intercept (2.92) that are within the acceptable ranges described in the test specifications. At least 100 data pairs were used for the comparison.

Because of its performance, the staff recommends that the FDMS be approved for use to determine compliance with the State AAQS for PM10 and PM2.5.

5.4 Recommendations

The staff recommends the following monitoring methods:

- PM10 Monitoring Method – Adopt the Federal Reference Method (FRM) for PM10 as the method for California.
- PM2.5 Monitoring Method – Adopt the Federal Reference Method (FRM) for PM2.5 as the method for California.
- Continuous PM Samplers – Adopt those continuous PM samplers which have been found to be suitable for determining compliance with the state PM10 and PM2.5 AAQS, and designate them as California approved samplers (CAS).
- Sulfates Monitoring Method – Revise the sulfate monitoring method by deleting the current total suspended particle (TSP) sulfate method, ARB method MLD 033, and replacing it with the existing ARB method for PM10 sulfates, MLD 007.

A summary of measurement methods recommended by staff is provided below.

(a) Measurement of PM10 shall be accomplished by one of the two following techniques:

- (1) A sampler that meets the requirements of the U.S. EPA Federal Reference Method (FRM) sampler for PM10, as specified in 40 CFR Part 50, Appendix M (1997), and which employs an inertial impactor; or,
- (2) A sampler that has been demonstrated to the satisfaction of the Air Resources Board to produce measurements equivalent to the FRM.

At the time of Board consideration of this regulation, the following samplers are deemed to satisfy section (2) above, and staff is recommending their adoption by the Board: A continuous PM10 sampler as specified in Appendix 5 part H, Thermo Andersen BAM (model FH 62 C14), Met One BAM (model 1020), and Rupprecht & Patashnick FDMS (series 8500).

(b) Measurement of PM2.5 shall be accomplished by one of the following two techniques:

- (1) A sampler which meets the requirements of the U.S. EPA Federal Reference Method (FRM) sampler for PM2.5, as specified in the 40 CFR Part 50, Appendix L (1997); with either a WINS impactor or a U.S. EPA approved very sharp cut cyclone (Federal Register, 2002) to isolate PM2.5 from PM10, or
- (2) A sampler which has been demonstrated to the satisfaction of the Air Resources Board to produce measurements equivalent to the FRM.

At the time this regulation is considered by the Board, the following samplers are deemed to satisfy section (2) above, and staff is recommending their adoption by the Board: A continuous PM2.5 sampler as specified in Appendix 5 part H, with either a very sharp cut cyclone or a sharp cut cyclone: Thermo Andersen BAM (model FH 62 C14), Met One BAM (model 1020), and the Rupprecht & Patashnick FDMS (series 8500).

The rationale for these recommendations is given below

5.4.1 PM10

The Board needs to update the State PM10 method to reflect advancements and improvements in sampler technology. The FRM for PM10 is quite similar to Method P and includes requirements that are more up-to-date. The FRM sampler operation requirements

are currently used in the State and local air monitoring network. Incorporating the FRM into the AAQS will simply change legal requirements to reflect practice.

State methods have not been updated since the mid-1980's and need to recognize advances in both hi-vol and lo-vol measurement technology. Expanding the State method for PM monitoring to include all federal high-volume and low-volume samplers will allow the FRM samplers that perform well, but had not been approved for use in California, to be used for both State and federal regulatory activities. This will eliminate confusion of having two methods (State and federal) for the same parameter.

Allowing the use of the lo-vol PM10 method for the State PM10 standard offers the advantage of having one PM10 sampler produce data for both the State PM10 standard and as a possible element for a the potential federal PM coarse standard.

5.4.2 PM2.5

There are more than 80 PM2.5 FRM samplers currently in operation in California. Approval of the staff's proposal by the Board will incorporate these samplers into the State network and enhance their usefulness in the State. Adopting a continuous sampler technology that corresponds to a high degree with the FRM for PM2.5 has many programmatic and public health benefits to the State.

Staff proposes to maintain the provision in regulation for it to evaluate new measurement technologies and approve them pending a determination they are consistent with the applicable FRM.

5.4.3 Sulfates

The current sulfates standard uses MLD Method 033 for the sampling and analysis of sulfate by TSP. The ARB also has MLD Method 007 (latest version dated April 22, 2002) for measuring sulfates on PM10 filters, which uses PM10 sampling with sulfates analysis by ion chromatography. Staff recommends replacing the existing MLD Method 033 with MLD Method 007 as the proposed measurement method. This will provide the capability of using the PM10 sampling network for measuring sulfates, as well as allow for the minimization of any artifact-forming potential through the use of alkalinity-controlled filters.

5.5 Estimated Costs and Impacts

A substantial PM2.5 monitoring network, largely funded by the U.S. EPA, is now in place in California, and the U.S. EPA is in the process of implementing the last stages of the network build-up. A state-funded portion of the PM2.5 network also exists, primarily as continuous samplers. It was funded by the legislature in the late 1990's in response to Health & Safety Code section 39619.5, that requires the Board to conduct "monitoring of airborne fine particles smaller than 2.5 microns in diameter (PM 2.5)." The methods, samplers, and instruments proposed by staff include those used in, and so take full advantage of, these existing networks. Little extra expense is anticipated. However, approval of continuous samplers may result in requests for additional samplers, given their economies of operation.

The Board has had in place an extensive PM10 network for years. This proposal reaffirms the past samplers and incorporates the more recent federal samplers into the list of approved samplers for the State AAQS. The State's PM10 sampling method (Method P) has been the State ambient air monitoring method since 1985. The sampler of choice at that time was the hi-vol SSI. Implementing the proposed changes in Method P to explicitly acknowledge all FRM samplers would not incur any cost to either government entities or private businesses, because it would allow the operators of the PM samplers the option of retaining the current

sampling method. In fact, it would expand the number of acceptable samplers now in use to include heretofore unrecognized methods.

The recommended changes to Method P may result in cost saving to the extent that continuous PM10 monitoring methods are used in place of conventional filter-based methods. Continuous methods are less labor intensive than Method P and generate substantially more data. The staff cannot quantify any cost saving since it is unknown to what extent local agencies would choose to use to continuous samplers, instead of the conventional filter-based samplers used now.

Appendix 5 part I lists PM10 and PM2.5 monitoring sites and includes the various types of samplers that were being used at these sites in June 2001.

5.6 References

- Achtelik, GH and Omand, J. Effects of environmental conditions on particulate nitrate stability during post sampling phase. 1998. MLD, CARB, PO Box 2815, Sacramento, CA 95812.
- Allen G, Sioutas C, Koutrakis P, Reiss R, Lurmann FW, Roberts PT. Evaluation of TEOM method for measurement of ambient particulate mass in urban areas. *J of Air Waste Management Assoc.* 1997; 47:682-689.
- Arnold S, Hague W, Pierce G, Sheetz R. The use of beta gauge monitors for PSI and every day SIP monitoring: an overview of the Denver experience. In: Chow JC; Ono DM. editors. PM10 standards and nontraditional particulate source controls, A&WMA/EPA international specialty conference. V. I; January; Scottsdale, AZ. Pittsburgh, PA, Air Waste Management Assoc.; 1992. p 12-23. (A&WMA transaction series no. 22)
- Babich P, Wang P-Y, Allen G, Sioutas C, Koutrakis P. 2000. Development and evaluation of continuous ambient PM2.5 mass monitor. *Aerosol Science and Technol.* 32:309-324.
- Chan TC and Lippman M. Experimental measurements and empirical modeling of the regional deposition of inhaled particles in humans. *Amer Ind Hyg Assoc. J.* 1980; 41:390-408.
- Chung A, Chang DPY, Kleeman MJ, Perry KD, Cahill TA, Dutcher D, McDougall EM, Stroud K. Comparison of real-time instruments used to monitor airborne particulate matter. *J. Air Waste Management Assoc.*, 2001, 51:109-120.
- Cook JP, Oslund WE, Frank N. Evaluation of fine particulate (PM2.5) in an area of volatile constituents. In: Chow, J, Ono D, editor. *Particulate matter: health and regulatory issues: proceedings of an international specialty conference*; April; Pittsburgh, PA. Pittsburgh, PA: Air & Waste Management Assoc., 1995; 277- 296. (A&WMA publication VIP-49).
- Eatough DJ, Wadsworth, A, Eatough DA, Crawford JW, Hansen LD, Lewis EA. 1993. A multi-system multi-channel diffusion denuder sampler for the determination of fine-particulate organic material in the atmosphere. *Atmos. Environ. Part A* 27:1213-1219.
- Federal Register, Vol 67, No. 63, April 2, 2002, Page 15566.
- Gundel LA, Lee VC, Mahanama KRR, Stevens RK, Daisey JM. 1995. Direct determination of the phase distribution of semivolatile polycyclic aromatic hydrocarbons using annular denuders. *Atmos. Environ.* 29:1719-1733.
- Jaklevic JM, Gatti RC, Goulding FS, Loo BW. A beta gauge method applied to aerosol samples. *Environ Sci Technology* 1981; 15:680-684.

- Kim YJ, Park SS, Lee KW, Chun KJ, Lee JY, Lim YS, Han JS. Development and testing of an automated beta gauge particulate sampler with filter cassette mechanism Air & Waste Management Assoc. 92nd Annual meeting. June 1999; 20-24. St Louis, Missouri.
- Meyer MB, Patashnick H, Ambs JL, Rupprecht EG. Development of a sample equilibration system for the TEOM continuous PM monitor. J. Air Waste Management Assoc. 2000; 50:1345-1349.
- Patashnick H, Rupprecht EG. 1991. Continuous PM10 measurements using the tapered element oscillating microbalance. J. Air Waste Management Assoc. 41(8):1079-1083.
- Patashnick, H, Rupprecht, G, Ambs, JL, Meyer, MB. Development of reference standard for particulate matter in ambient air. . Aerosol Sci. and Technology. 2001; 34:42-45.
- Thermo Andersen, Inc. Reference method PM10 size selective hi-vol air sampler; 500 Technology Court, Smyrna, GA 30082-9211.
- Turpin BJ, Huntzicker JJ, Hering SV. 1994. Investigation of organic aerosol sampling artifacts in the Los Angeles Basin. Atmo. Environ. 28:3061-3071.
- U.S. EPA/ORD. List of designated reference and equivalent methods; May 9, 2000.