

US EPA ARCHIVE DOCUMENT

Environmental Technology Verification Program Advanced Monitoring Systems Pilot

Test/QA Plan for
Verification of Ambient
Fine Particle Monitors

US EPA ARCHIVE DOCUMENT

ETV ✓ ETV ✓ ETV ✓

TEST/QA PLAN

FOR

**VERIFICATION OF
AMBIENT FINE PARTICLE MONITORS**

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ACRONYMS

AMS - Advanced Monitoring Systems

APNM - Ambient Particulate Nitrate Monitor

APSM - Ambient Particulate Sulfate Monitor

ARB - Air Resources Board (same as CARB)

BAM - Beta attenuation monitor

CAC - Correlated acceptable continuous

CAMM - Continuous Ambient Mass Monitor

CARB - California Air Resources Board (same as ARB)

CRPAQS - California Regional Particulate Air Quality Study

DOE - United States Department of Energy

DRI - Desert Research Institute

EC - Elemental carbon

ELPI - Electrical low pressure impactor

EPA - United States Environmental Protection Agency

ETV - Environmental Technology Verification

FEM - Federal equivalent method

FRM - Federal reference method

NAAQS - National Ambient Air Quality Standard

NAMS - National Air Monitoring Station

NETL - National Energy Technology Laboratory

OC - Organic carbon

PAMS - Photochemical Assessment Measurements Station

PM - Particulate matter

PM_{2.5} - Particulate matter with an aerodynamic diameter less than 2.5 μm

PM₁₀ - Particulate matter with an aerodynamic diameter less than 10 μm

QA - Quality assurance

QC - Quality control

QMP - Quality management plan

SJVUAPCD - San Joaquin Valley Unified Air Pollution Control District

SOP - Standard operating procedure

TEOM™ - Tapered Element Oscillating Microbalance

TOR - Thermal optical reflectance

UORVP - Upper Ohio River Valley Project

WINS - Well-Impactor Ninety Six

1. INTRODUCTION

1.1. Background

1.1.1 ETV

This test/QA plan provides detailed procedures for a verification test of monitors that continuously indicate the mass or chemical composition of fine particulate matter in ambient air. The verification test will be conducted under the auspices of the U.S. Environmental Protection Agency (EPA) through the Environmental Technology Verification (ETV) program. The purpose of ETV is to provide objective and quality assured performance data on environmental technologies, so that users, developers, regulators, and consultants can make informed decisions about these technologies. ETV verification does not imply approval, certification, or designation by EPA, but rather provides a quantitative assessment of the performance of a technology under the specified test conditions.

The verification test will be coordinated by Battelle, of Columbus, Ohio, which is managing the ETV Advanced Monitoring Systems (AMS) pilot through a cooperative agreement with EPA (CR 826215-01-1). The scope of the AMS pilot covers verification of monitoring technologies for contaminants and natural species in air, water, and soil. In performing the verification test, Battelle will follow the procedures specified in this test/QA plan, and will comply with the data quality requirements in the “Quality Management Plan for the ETV Advanced Monitoring Systems Pilot” (QMP).¹

1.1.2 Fine Particulate Monitoring

The EPA promulgated changes to the National Ambient Air Quality Standard (NAAQS) for particulate matter (PM) in 1997.² Those changes call for revision of the existing PM₁₀ standard and the addition of a new standard for PM_{2.5}. The revised standard also calls for the use of “correlated acceptable continuous” (CAC) monitors to supplement PM_{2.5} sampling at community oriented (CORE) monitoring sites in large metropolitan areas. Additionally, a need to determine the chemical components of particulate matter has been identified,³ and consequently, a network of speciation monitoring sites has been initiated.⁴ As a result of these needs there has been substantial effort in the development of methods for PM monitoring.

Methods used for measurement of PM mass and chemical composition include both manual, filter-based methods, requiring sampling and subsequent laboratory analysis, and continuous or automated methods which provide results in real time or nearly real time.⁵ Manual sampling methods are well established, and several commercial devices for such sampling have received Federal Reference Method (FRM) or Federal Equivalent Method (FEM) designation,⁶ and are currently in widespread use for PM₁₀ and PM_{2.5} monitoring. However, these filter-based methods suffer from a number of limitations including relatively poor time resolution (i.e., typically 24 hour), and the fact that they are rather labor intensive and typically require a number of activities to obtain a single result. As a result of these limitations, data from time-integrated filter-based methods are not suitable for some valuable non-compliance purposes, such as assessing short-term variability in PM, tracking source contributions, and monitoring human exposures. Furthermore, an additional limitation of these methods is the potential for the introduction of error, by improper handling, or the loss of volatile PM components.

In contrast, the primary advantages of continuous or automated monitors lie in their ability to continuously and rapidly assess particulate matter levels or composition with relatively little operator effort. The collection of real-time data of this type without the labor constraints imposed by the manual methods makes continuous monitors invaluable tools for some particulate matter monitoring applications. Indeed, many of these monitors have already been used for

research purposes when rapid time response is needed in PM monitoring. However, only a few continuous monitors have received FEM designation status for PM₁₀ monitoring, and none has received that status for PM_{2.5} monitoring. This, along with a lack of independent verification data for these monitors, has limited their credibility and acceptance. Consequently, they are not yet widely used, despite considerable interest within the air monitoring and research communities. The aim of this verification test is to provide potential purchasers, users, and regulators of these monitors with quality assured performance data, with which informed decisions can be made about these monitors.

1.2. Test Objective

The purpose of this verification test is to evaluate the performance of a number of commercially available continuous, or semi-continuous monitors^a of ambient fine particulate matter under realistic operating conditions. The performance of these monitors will be evaluated primarily by comparisons with specific reference methods to determine their ability to predict the results of those reference methods.

Specific objectives of the verification test for these monitors include:

- To assess the degree of agreement between these continuous technologies and time-integrated reference methods when possible, or the degree to which the technologies being verified can predict the results of the reference methods,
- To determine the intra-method precision of these continuous monitors by comparing simultaneous results from duplicate monitors,
- To evaluate the effects of meteorological conditions on the performance of the continuous monitors,

^aFor the purpose of clarity, technologies capable of monitoring ambient levels or composition of particulate matter either continuously or semi-continuously will be referred to as “continuous” monitors throughout this test/QA plan.

- To determine the influence of ambient precursor gases on the instrumental response of the monitors being verified,
- To investigate the capabilities of these technologies to monitor short term changes in ambient particulate matter, through comparisons to reference method samples collected over various sampling durations,
- To evaluate the reliability and general ease-of-use of these technologies over the course of the testing period.

To address these objectives, verification of these monitors will involve field testing in two separate phases. The degree to which the results from these monitors agree with those of the reference methods, or can be used to predict the results of the reference methods, will be established based on statistical comparisons of the results from each phase. Similarly, statistical comparisons of the results from duplicate monitors will be used to assess the intra-method precision for these continuous methods. The two separate phases will be conducted in different geographic locations, and during different seasons to assess the effects of temperature, humidity, particulate matter concentration, and chemical composition on the performance of the monitors being verified. In addition, this verification test will report on other operational characteristics including the reliability, necessary maintenance, and ease of operation of these monitors. Verification results from this test will also summarize additional information which may be relevant to potential users, including power and shelter requirements, data output, and the overall cost of these monitors.

The results from these performance evaluations will be made publically available with the goal of providing credible information to potential purchasers, regulators, and permittees of these technologies. **Note:** Verification of these technologies under ETV is a quantitative evaluation of the performance of the monitors based on the techniques and procedures described in this test/QA plan. This test is not meant to be, and should not be construed as, an alternate for any form of the Federal Reference or Equivalency designation which is required for PM_{2.5} or PM₁₀

compliance reporting purposes. Verification does not imply acceptance, certification, or endorsement, by EPA.

1.3. Test Applicability

This test/QA plan is applicable to the verification testing of ambient fine particulate matter monitors. The devices to be tested under this plan are capable of providing real-time, or nearly real-time, indications of the ambient level of fine particulate matter,^b and do not require discrete manual steps for sample collection, preparation, and laboratory analysis. Although not necessarily designed to monitor the same physical quantity or property of ambient particulate matter, each of these devices can be useful for PM monitoring by providing rapid assessment of various properties of ambient fine particulate matter. In accordance with the intent of the ETV program, the monitors to be tested are commercially available, and not developmental products or prototypes.

2. TECHNOLOGY DESCRIPTION

The monitors to be tested under this test/QA plan are all continuous particulate matter monitoring instruments, however their designs and principles of operation cover a wide range of analytical capabilities. Nonetheless, they each exhibit a rapid, quantitative response to ambient particulate matter, and therefore, may be useful in ambient PM monitoring research applications. Based on the principle of operation of these monitors, each can be grouped into categories for measuring either (1) chemical composition, or (2) mass or “surrogate mass.” The technologies

^b For this test, fine particulate matter is defined as that fraction of particles with aerodynamic diameters below 2.5 μm ($\text{PM}_{2.5}$). This is a general definition and will be adopted for all monitors to be tested unless otherwise noted. Individual vendors may wish to adopt a different definition for their monitor, however, in all cases, the definition of fine particulate matter will be clearly indicated in each verification report resulting from this test.

that fall within the former category provide nearly continuous indication of some aspect of the chemical composition of ambient particulate matter. The technologies within the latter category are used to monitor mass, or what may be called “surrogate mass,” in that they measure a physical property that should correlate with the mass of fine particulate matter present. That is to say, particle mass itself is not necessarily measured by these techniques, but they may provide valuable indicators of particle mass. A brief summary of some of the monitors in these general measurement categories is provided below. This list is not meant to be exhaustive and is representative of the monitors which can be verified under this test/QA plan. Descriptions of additional monitors may be added as needed and these monitors may also be verified under this test/QA plan. More complete descriptions of these technologies can be found in the EPA “Guidance for Using Continuous Monitors in PM_{2.5} Monitoring Networks.”⁷

2.1. Chemical Composition

Chemical composition monitors perform automated and repetitive procedures to determine some portion of the chemical composition of fine particles in nearly real time. The classes of particulate compounds for which there are continuous analyzers include carbonaceous material, both elemental and organic, and ionic species such as nitrate and sulfate.

Analysis of carbon-containing particulate matter can be used to quantify both the elemental carbon (EC) and organic carbon (OC) ambient concentrations. The thermal volatilization or conversion to carbon dioxide (CO₂), of these two classes of carbon particulate occurs at very different temperatures. Consequently, by heating particulate samples and monitoring the CO₂ generated at different temperatures, the EC and OC concentrations can be determined. Some carbon analyzing technologies, such as the Series 5400 Automated Carbon Particulate Monitor (ACPM, Rupprecht & Patashnick, Co., Inc.) include two sample collectors which can be used alternately for collection and analysis steps, thereby allowing continuous monitoring.

In addition to total EC and OC concentrations, specific chemical classes of organic particulate can be measured in-situ. One such class of compounds is particulate-bound polycyclic aromatic hydrocarbons (PAHs). Measurement of PAHs is based on UV photoionization of the particulate PAH and subsequent measurement of the ionization current formed by the emitted electrons. Monitors of this type respond to the sum of all PAH compounds in the particle phase, and do not respond to vapor-phase PAH. EcoChem Analytics provides a commercial version of the PAH monitor, in the form of the PAS 2000 instrument. This monitor has also been used to monitor overall EC levels.

The concentration of ambient “elemental carbon” or “black carbon” particulate can be measured by light absorption using an aethalometer (Andersen Instruments). In these devices, light is passed through a filter, or a sample spot on a continuous tape, and detected. Particulate deposition on this filter results in the attenuation of the light in proportion to the loading of light absorbing particulate on the filter. Using appropriate conversion factors, the degree of light attenuation is converted to “black carbon” concentration.

Automated monitors have been developed to measure particulate nitrate or sulfate concentrations. These monitors use flash volatilization of a filter sample, entrainment of the evolved oxides in an inert carrier stream, and chemiluminescent or gas-phase fluorescent detection to determine particulate nitrate or sulfate concentrations, respectively. Examples of these monitors are the Series 8400N Ambient Particulate Nitrate Monitor (APNM, Rupprecht & Patashnick, Co., Inc.), and the Series 8400S Ambient Particulate Sulfate Monitor (APSM, Rupprecht & Patashnick, Co., Inc.).

2.2. Mass or Surrogate Mass

There are a variety of particle properties which can be related to, and ultimately can be used to predict, particle mass. A number of techniques have been developed to probe these physical properties.

The Tapered Element Oscillating Microbalance (TEOM[®], Rupprecht & Patashnick, Co., Inc.), directly measures particulate matter mass in real time by drawing air through a hollow tapered element on which an exchangeable filter is mounted. The tapered element is mechanically oscillated and as particulate matter deposits on the filter, the frequency at which the tapered element oscillates changes. This change in the frequency of oscillation has a direct relationship to the mass of the deposited particulate matter. By “continuously” monitoring (once every two seconds) the oscillation frequency, the TEOM is able to obtain near real-time measurements of the deposited mass. These measurements can then be used to calculate an average mass over time periods ranging from 10 minutes to 24 hours. Mass flow controllers are used to maintain a constant air mass flow rate which, when adjusted for ambient temperature and pressure, remains within the appropriate specifications for volumetric flow rate. From the data for both mass and flow, the TEOM calculates an ambient concentration for PM_{2.5}.

Beta Attenuation Monitors (BAMs) provide an indication of particulate matter mass by measuring the attenuation of beta radiation through a filter on which particulate matter is deposited. As the fine particles deposit, fewer of the beta particles penetrate the filter and reach the detector. By measuring the intensity of beta particle penetration before and after, or during a period of air sampling, a measure of the mass deposited on the filter can be obtained. The degree to which the beta radiation is attenuated is approximately proportional to particle mass based upon the Beer-Lambert law, but is also dependent upon the chemical composition of the particulate matter. Commercial versions of beta attenuation monitors are available from Andersen Instruments, Met One Instruments, and Opsis AB.

The Continuous Ambient Mass Monitor (CAMM, Andersen Instruments) measures the drop in pressure across a porous membrane filter to monitor particle mass. As air is drawn through the filter, particulate matter is deposited on the filter and obstructs the air flow through the filter. This flow obstruction results in an increasing pressure differential across the filter which can be measured and correlated to the mass of the deposited material.

Several techniques involve the use of light scattering to quantify the concentration and size of ambient particulate matter. Among the more common of the instruments exploiting light scattering for particulate matter monitoring are nephelometers. In these devices, a fixed volume of aerosol sample is illuminated by an incident beam of light, and the total intensity over a range of scattering directions is detected. The scattering intensity can be used to estimate particle mass concentration.

Some continuous particle sizing instruments can also be used to provide an indication of particulate mass. Light scattering monitors such as the Aerodynamic Particle Sizer (APS, TSI Inc.) provide real time size distributions which can be related to mass concentrations. In the APS, sampled air is drawn into a flight tube where the transit time of particles through overlapping light beams is measured. Size classification is based on the relationship between this transit time and the aerodynamic size of the particles being interrogated.

The Electrical Low Pressure Impactor (ELPI, Dekati, Ltd.) operates on the basis of charging, inertial classification, and electrical detection of aerosol particles. Sampled air is drawn through a corona discharge which imparts an electrical charge to the particles. The particles are then separated based on their aerodynamic size in an inertial impactor. The individual stages of the impactor are electrically isolated from one another and individually monitored by an electrometer which monitors the charge collected on each stage. Real-time size distributions are determined from the current produced on each stage.

3. VERIFICATION APPROACH

3.1. Scope of Testing

The overall objective of the verification test is to provide quantitative performance data on fine particle monitors under realistic operational conditions. To meet this objective, testing

will occur in two phases, at established sites with ongoing particulate matter monitoring programs conducted with appropriate quality assurance/quality control (QA/QC) efforts. The field sites will be located in two geographically distinct regions of the United States to allow exposure to different particulate matter concentration levels and chemical composition. At each site, the technologies will undergo intensive testing for a period of at least one month focusing on the season in which local PM_{2.5} levels are likely to be highest.

Performance verification will be based, in part, on comparisons to the established reference methods^c already in place as part of the monitoring programs at the field sites, or provided by Battelle specifically for this test. Collocation of the technologies being verified with systems for time-integrated monitoring of fine particulate mass and chemical speciation will provide the basis for assessing the degree of agreement and/or correlation between the continuous and time-integrated methods. Other parameters to be assessed during the verification test include the effects of meteorological conditions and the influence of interfering gases on technology performance. Consequently, each test site will be equipped with continuous monitors to record meteorological conditions and the concentration of key precursor gases (O₃, NO_x, SO₂, etc.). Additionally, other performance characteristics of the technologies being verified, such as reliability, maintenance requirements, and ease of operation will be assessed by field operators and reported. Instrumental features which may be of interest to potential users (e.g., power and shelter requirements, data output, and overall cost) will also be reported.

Although aerosols of known composition and size distribution can be created in a laboratory, such aerosols are limited in their representativeness of actual ambient fine particulate matter. It is beyond the scope of this verification test to generate aerosols in the laboratory which are representative of the wide range of aerosol composition typically found in ambient air. This

^c Throughout this document the term “reference method” will refer to methods which are used as a basis of comparison for the purposes of technology verification. These reference methods may be, but are not necessarily, Federal Reference Methods (FRM), or Federal Equivalent Methods (FEM)

verification test will be limited to comparisons of data collected in the field under realistic operating conditions. Consequently no laboratory evaluations will be performed as part of this test.

3.2. Site Selection

The first phase of this verification test will be performed at the DOE/National Energy Technology Laboratory (NETL) site near Pittsburgh, PA. This phase will be conducted for a one month period late in the summer of 2000. The second phase of the test will take place at the California Air Resources Board (CARB) First Street site in Fresno, CA. This second phase of the test will be conducted over a period of one month in the winter of 2000/2001. General descriptions of each site are provided below.

These sites were selected based on a number of criteria including some common characteristics between the sites as well as some key differences. Common to these sites are:

- a wide variety of on-going ambient monitoring activities, including appropriate reference methods,
- sufficient space and facilities for verification testing of participating technologies,
- trained site personnel or subcontractors,
- appropriate site security, and
- established QA/QC protocols and procedures.^{8, 9, 10}

The key difference between these sites is the location of these sites in distinctly different regions of the country, which results in exposure to different climates and meteorological conditions, as well as different levels and chemical composition of particulate matter. These factors, along with the willingness of the site management to collaborate with this verification test, were among the primary considerations for the selection of these sites.

It is recognized that verification of these monitors at only two sites for one season each represents only a small portion of the potential conditions under which these monitors are likely to be used. As such, the verification reports which result from this test will clearly indicate the conditions of the verification test and will not make generalizations about the performance of these monitors under different conditions. It is beyond the scope of this verification test to evaluate the performance of these monitors under all conditions in which these monitors are likely to be used. Instead, these two test sites will provide a demonstration of instrumental performance under a set (albeit limited) of realistic operational conditions.

3.2.1 Phase I

Phase I of testing will be conducted at the DOE/NETL research site located in South Park, PA, approximately eight miles south of Pittsburgh. This site is operated by NETL as part of the Department of Energy - Office of Fossil Energy's Ambient Fine Particulate (PM_{2.5}) Research Program,¹¹ which has three primary objectives:

- Monitor and analyze ambient fine particulate matter
- Characterize the emissions from fossil fuel based power systems
- Develop and evaluate effective control technologies.

The largest component of this research effort is the Upper Ohio River Valley Project (UORVP). The UORVP is focused on ambient monitoring along the upper Ohio River corridor in eastern Ohio, northwestern West Virginia, and western Pennsylvania, including the South Park site. This region is characterized by a relatively high concentration of both urban and industrial activities. Approximately 2 million residents live within the metropolitan Pittsburgh area, and heavy industries such as steel and coke making are important components of the local economy. Additionally, the UORVP region has a relatively high number of coal-fired power plants.

Consequently, this area is an excellent candidate for ambient air quality studies owing to the wide variety of potential emission sources.

Within the UORVP there are a number of ambient fine particulate monitoring sites, of which the South Park site is one. Monitoring objectives at this site include a general assessment of the relative contributions to ambient air quality from both anthropogenic and biogenic sources, as well as specific goals in the areas of:

- Emission trend analysis
- Equipment development and performance evaluation
- Source apportionment
- Management strategy development
- Health study correlations.

To address the monitoring and analysis efforts of the UORVP program, the DOE/NETL site at South Park is equipped with a variety of PM samplers, including FRM and speciation, as well as continuous particulate monitors, for the collection and characterization of ambient $PM_{2.5}$. To support these measurements, a variety of continuous meteorological and gas monitors are on-site to characterize the ambient conditions during sample collection. A partial list of the ambient air parameters to be monitored at this site is provided in Table 1.

The verification test objectives will be addressed at this site primarily through comparisons of the technologies being verified to samples collected daily by the various reference methods. The sampling duration for the FRMs, speciation sampler, and PAH sampler will each be 24 hours. The collected samples will be analyzed and used as the basis for comparison for mass measurements, chemical speciation, and particulate PAH concentration, respectively, as measured by the continuous monitors.

Testing at the DOE/NETL site will be conducted in the summer, when data show that the composition of fine particulate matter will be dominated by secondary aerosol components

(sulfate, nitrate, and ammonium), with a significant amount of both organic and elemental carbon content as well.

Table 1. Parameters Being Monitored by DOE/NETL at Pittsburgh Site

Monitored Parameter	Monitoring Equipment	Avg Time	Frequency
Filter-Based Mass and Chemical Composition			
PM _{2.5} mass	R&P 2025 sequential FRM sampler	24-hr	daily
PM ₁₀ mass	Andersen high volume sampler	24-hr	daily
PM _{2.5} mass, elements, ions, carbon	Andersen RAAS2.5-400 PM _{2.5} speciation sampler	24-hr	daily
Continuous Monitors			
PM _{2.5} mass	R&P 1400a TEOM™ PM _{2.5} sampler equipped with an AccuSampler	1-hour	daily
Polycyclic aromatic hydrocarbons	EcoChem PAS 2000 continuous PAH monitor	10-min	daily
PM _{2.5} organic and elemental carbon	R&P 5400 continuous carbon analyzer	3-hour	daily
Precursor Gases			
O ₃ , SO ₂ , NH ₃ , NO _y , NO _x , CO, H ₂ S	API continuous gas monitors	5-min	daily
Meteorology			
Wind speed/direction	High accuracy sensor	5-min	daily
Temperature	High accuracy sensor	5-min	daily
Relative humidity	High accuracy sensor	5-min	daily
Solar Radiation	High accuracy sensor	5-min	daily
Barometric pressure	High accuracy sensor	5-min	daily
Rain fall	High accuracy sensor	5-min	daily

3.2.2 Phase II

The second phase of the verification test will be conducted in Fresno, California. The Fresno site, which is operated by the California Air Resources Board (CARB),¹⁰ is part of both the California Regional PM₁₀/PM_{2.5} Air Quality Study (CRPAQS), and the National Air Monitoring Stations (NAMS) network. Additionally, under the direction of the Desert Research Institute (DRI), it is one of the host sites for the EPA Supersites program.¹²

The different programs which are being operated at the Fresno site are each designed around a unique set of program objectives. For example, NAMS sites are focused on long-term monitoring to assess trends in air quality and community exposure as well as determining compliance with air quality standards. The monitoring efforts in place throughout the NAMS network will be useful in assessing national trends and in supporting decisions based on those trends. The CRPAQS program is designed with a number of specific objectives described in the study program plan.⁹ These objectives focus on collecting air quality data in central California which can be used, in part, to characterize the nature and the causes of particulate matter to determine the spatial distribution and temporal variation of PM, and to quantify source contributions in the region. Additional objectives relating to determining specific population exposures, characterizing zones of influence, and understanding transport and diffusion phenomena are also addressed in the program plan. The EPA Supersites program is designed to establish PM_{2.5} monitoring sites to: (1) characterize PM in terms of regional concentrations, chemical composition, and transport phenomena in order to understand source-receptor relationships; (2) obtain air quality data to support health effects and human exposure research; and (3) provide sites which can be used for methods development and advanced monitoring efforts. Owing to the diverse set of objectives encompassed in these programs, the Fresno site houses a wide variety of equipment for routine air quality monitoring, as well as for research purposes, and is an ideal candidate site for verification testing. A list of the ambient air parameters to be monitored at this site, and the planned sampling schedules in the programs listed above, are provided in Table 2.

Table 2. Parameters Being Monitored by CARB/DRI at Fresno Supersite

Monitored Parameter	Monitoring Equipment	Avg Time	Frequency
Filter-Based Mass and Chemical Composition			
TSP Mass	Hivol w/ quartz filter	24-hr	12th day
PM ₁₀ mass, sulfate, nitrate, chloride, ammonium, carbon	Hivol SSI w/ quartz filter	24-hr	6th day
PM ₁₀ and PM _{2.5} mass, elements	Collocated dichotomous sampler with Teflon filter	24-hr	6th day
PM _{2.5} mass	Collocated sequential FRM w/ Teflon filter)	24-hr	daily for primary sampler and 3rd day for collocated sampler
Toxic (metals, chromium VI, aldehydes)	Xontec 920 Sampler	24-hr	12th day
PM _{2.5} mass, light absorption, elements, and ions	Sequential FRM w/ Teflon filters	24-hr	6th day
PM _{2.5} mass, elements, ions, carbon, nitric acid, ammonia	Five channel speciation sampler w/ denuders and backup filters)	24-hr	6th day
PM ₁₀ single particles, elements	MiniVol w/ Nuclepore filter for microscopic analysis	24-hr	6th day
PM _{2.5} mass, elements, ions, carbon	Two channel sequential filter sampler w/ denuders and backup filters	24-hr	daily
Continuous Surrogate Mass			
Light scattering	Heated nephelometer	5-min	daily
Light scattering	Ambient temperature nephelometer	5-min	daily
Light scattering	Photometer	5-min	daily
Light scattering	Heated nephelometer	5-min	daily

Table 2 (continued)

Monitored Parameter	Monitoring Equipment	Avg Time	Frequency
Continuous Surrogate Mass			
0.003-0.2 μm size distribution	Ultrafine Condensation Particle Counter ^a	5-min	daily
0.3-30 μm size distribution	Optical Particle Counter	5-min	daily
Light absorption	Coefficient of Haze	2-hr	daily
Light absorption	Aethalometer	5-min	daily
Light absorption	7-wavelength aethalometer	30-min	daily
PM _{2.5} mass	BAM	1-hr	daily
PM ₁₀ mass	BAM	1-hr	daily
Continuous Particle Mass and Chemistry			
PM _{2.5} mass	TEOM™ monitor	1-hr	daily
PM ₁₀ mass	TEOM™ monitor	1-hr	daily
PM _{2.5} nitrate, sulfate, and carbon	ADI flash volatilization with TEI NO _x , SO ₂ , and NDIR detectors	10-min	daily
PM _{2.5} organic and elemental carbon	In-situ analyzer	1-hour	daily
Precursor Gases			
NO/NO _x	Continuous chemiluminescence monitor	1-hr	daily
Ozone	UV absorption monitor	1-hr	daily
Carbon Monoxide	Infrared absorption monitor	1-hr	daily
Non-Methane Hydrocarbons	FID	1-hr	daily
NO _y /HNO ₃	High sensitivity chemiluminescent monitor with external converters, denuders, and sequencers	5-min	daily
Ammonia	High sensitivity monitor with NO _x scrubbers and oxidizers	5-min	daily

Table 2 (continued)

Monitored Parameter	Monitoring Equipment	Avg Time	Frequency
Organic Gases and Particles			
Toxic hydrocarbons	Xontec 910 canister sampler	24-hr	12th day
Carbonyls	Xontec 925 DNPH sampler	24-hr summer 4 per day	12th day 3rd day
Meteorology			
Temperature	High accuracy sensor	5-min	daily
Wind speed/direction	High sensitivity wind vane and anemometer	5-min	daily
Relative humidity	High accuracy sensor	5-min	daily
Solar radiation	Radiometer	5-min	daily

a May be integrated with scanning mobility particle sizer (0.005 to 1.0 µm).

Located in central California, Fresno is included in the San Joaquin Valley Unified Air Pollution Control District (SJVUAPCD) and is impacted by a wide variety of both primary and secondary air quality influences. The region is relatively densely populated, with approximately 3 million people living within the 64,000 km² which comprise the SJVUAPCD. The primary industry in the region is agriculture, however, other local industries include oil and gas production, refining, waste incineration, transportation, and light manufacturing.

The Fresno site is expected to experience high concentrations of ambient ammonium, nitrate, geological, and carbonaceous material during the winter.⁹ During winter, the high local concentration of gaseous ammonia combined with the low temperatures and high humidity conditions in central California favor the equilibrium formation of particulate ammonium nitrate from the available nitrate. Though less than in other seasons, geological material from agricultural activities, construction, road dust, and wind erosion contributes significantly to the PM_{2.5} concentrations during winter. Carbon-containing PM (both organic and elemental) levels

are also high in the winter as a result of various activities including fuel combustion, vehicle exhaust, meat cooking, and agricultural burning.

3.3. Experimental Design

The design of this verification test is similar to that of a recent instrument intercomparison study performed for CARB.¹³ In that study, a variety of continuous and manual methods were intercompared to assess operational relationships among the different methods. This verification test will be similar to that study in that similar comparisons will be made between the continuous and manual methods. This verification test will be different in that it will expand on some of the comparisons, and will be performed at two different sites and in different seasons. However, in contrast to the CARB study, no intercomparison of the monitors being verified will be made in this verification test.

This verification test will involve collocation of duplicate commercial monitors to be verified at the test sites, which have established reference methods already in place, including both FRM and speciation samplers. The duplicate monitors will be placed in close proximity to each other (< 5 meters) and to reference samplers (<10 meters) to eliminate spatial variability as a source of error in statistical comparisons. Comparisons between the continuous monitors and the reference methods will be made to assess the comparability of the monitors being tested and the reference methods, or the capabilities of the continuous monitors in predicting the results from the reference methods. Comparisons of the results from duplicate monitors will be used to assess intra-method precision for each type of monitor. Continuous measurement of meteorological conditions and the concentration of precursor gases will be used to support these assessments. In this way, the accuracy and variability of the continuous monitors may be assessed under various conditions after adjusting for the influence of those conditions. Additional observations will be made by On-Site Operators and documented to describe general

operational characteristics of these monitors, including general performance, reliability, maintenance, and ease of use.

The primary comparison for each monitor will be with the 24-hour time-integrated samples collected by the respective reference methods (see Section 3.4). As a result, the primary comparison will include approximately 25 samples from each month-long phase. In likelihood, the actual number of data points available for use in these comparisons will be somewhat smaller than 25. In addition to the 24-hour samples used for the primary comparisons, a number of shorter term samples (3, 5, 8-hour) will be collected and used for supplemental comparisons. The data sets available for the supplemental comparisons may be larger based on the frequency of data collection (up to 5 samples per day). Continuous meteorological and precursor gas concentration data will also be used to support the primary comparisons. The variability in ambient air parameter levels over the course of the month of data collection is expected to be much larger than the size of error in measurement, allowing for accurate estimation of the relationship between the reference methods and the monitors tested.

In some cases, monitors to be verified in this test are already in use at one or both of the sites. As such, the vendor of a monitor already on site will provide a single additional monitor for verification. The test for that type of monitor will thus include a monitor that has been operating in the field, and one newly installed in the field. In these cases, the history of these monitors may provide useful information about performance issues, and records of performance (including monitoring results and maintenance activities) at the site may be used to support the observations made during the intensive portion of the verification test. When available, monitoring results from these continuous monitors and the reference methods may provide an indication of performance of these monitors during multiple seasons at a given site, and maintenance records may provide an indication of the long-term reliability of these monitors.

When possible, the same monitors will be verified in the two phases of this test. However, when a monitor being tested is part of the site monitoring equipment, a different monitor will necessarily be tested at the other site. The additional monitor provided by the

vendor will be used at both sites. In all cases, the verification report will clearly indicate which monitors (by serial number) were tested at the respective sites. Furthermore, as a result of the time difference between the two phases of the verification test, there is a potential that design modifications may be made to one or more of the monitors being tested. If changes of this type are made, the updated version may be used in the second phase. Again, the verification report will clearly indicate what design changes were made. As the statistical analyses will be performed separately for the individual monitors at each site, the potential use of different monitors at different sites will not affect the validity of statistical comparisons made in the verification process. Records indicating which monitors were verified in each phase may be used to explain potential differences in verification results between monitors at a site.

3.4. Reference Methods and Supplemental Measurements

Verification of the performance of continuous ambient fine particle monitors will be based in part on comparisons to appropriate reference methods or procedures. Since no appropriate absolute standards for fine particulate matter exist, the reference methods for this test were selected to provide comparisons of the results from the continuous monitors to those of currently accepted methods for the determination of particulate matter mass or chemical concentration. It is recognized that comparisons of real-time measurements to time-averaged measurements may not fully explore the capabilities of the real-time monitors. However, in the absence of accepted standards for real-time fine particulate matter measurements, the use of time-averaged standard methods which are currently widely accepted is necessary. The limitations associated with the use of these methods (including measurement uncertainties) will be discussed in the verification reports. A summary of each reference method to be used during the verification test is given below.

3.4.1 $PM_{2.5}$ Mass

Comparisons to $PM_{2.5}$ mass will be made relative to the FRM for $PM_{2.5}$ mass determination, i.e., the 24 hour time-averaged procedure detailed in 40 CFR Part 50.² This method involves manual sampling using any of a number of designated commercially available filter samplers, followed by gravimetric analysis of the collected sample. In this method a size selective inlet is used to sample only that fraction of aerosol of interest (i.e., $<2.5 \mu\text{m}$ diameter). The air sample is drawn into the sampler at a fixed rate and the aerosol is collected on an appropriate filter for gravimetric analysis. After equilibration of the sample and filter in a temperature and humidity controlled environment, the sample is weighed on an appropriate microbalance. The particulate sample weight is determined by subtracting the weight of the filter alone, determined prior to sampling after similar equilibration. Protocols for sample collection, handling, and analysis are described by EPA and will be followed for this verification test.

FRM samples will be collected daily during each phase of the testing using a BGI PQ200 Sampler (RFPS-0498-116), or comparable sampler, and $PM_{2.5}$ will be determined according to the FRM procedures mentioned above. Results from other single filter or sequential FRM samplers may be used after the comparability of these other samplers and the BGI sampler is established (see Section 3.5.2 and Section 7.3). Time periods shorter than the FRM-prescribed 24-hour sampling will also be used in some cases to assess the short-term capabilities of the continuous monitoring technologies. This short-term $PM_{2.5}$ sampling will augment, rather than replace, the 24-hour FRM sampling.

3.4.2 Speciation

The reference methods to be used for chemical speciation of ambient $PM_{2.5}$ are described in the EPA guidance document "Guideline on Speciated Particulate Monitoring",¹⁴ with the exception of the method for particle-bound PAH analysis. As with the gravimetric mass determination, these reference methods involve time-integrated sample collection and subsequent

laboratory analysis, although the collection media and the methods of analysis vary for the different species.

In general, the speciation samplers have individual trains for the determination of specific components of the ambient aerosol. The aerosol is drawn into the sampler through a size selective inlet, and divided into separate streams for collection and subsequent chemical-specific analysis. Alternatively, separate size-selective inlets may be used for each stream. After sampling, the collected fractions are sent for preparation and laboratory analysis. At each field site, one or more approved speciation samplers will be employed as part of the studies performed at those sites. Collected samples from those speciation samplers will be analyzed by contract laboratories selected by Battelle, and the results of those analyses will be used for the data comparisons. Particulate nitrate, particulate sulfate, and elemental/organic carbon are the chemical species for which samples from the speciation samplers will be analyzed. At each site, particulate nitrate and particulate sulfate fractions will be collected on nylon filters downstream from a MgO denuder used to remove gaseous nitric acid. These fractions will subsequently be analyzed by ion chromatography as suggested in the EPA's "Guideline on Speciated Particulate Monitoring".¹⁴ EC/OC fractions will be collected on quartz fiber filters and analyzed by both the IMPROVE thermal optical reflectance (TOR) and the NIOSH 5040 thermal optical transmission (TOT) techniques. At the Fresno site, 24-hour chemical speciation sampling will be augmented with 3, 5, and 8-hour sampling, to allow data comparisons over shorter time periods. At the DOE/NETL site, only 24-hour chemical sampling will be conducted.

For particle-bound PAH measurements, sample collection and analysis procedures based on ASTM Method D-6209-98¹⁶ will be used. Battelle will supply filter/XAD resin sampling trains and appropriate denuders to determine the particle-phase PAH species. After removal of the vapor phase material in the denuder, the total particle-phase PAH will be collected on a quartz fiber filter followed by an XAD-2 resin bed. Particulate matter collected on the combined filter/XAD trains will be analyzed for PAH content by solvent extraction and subsequent gas chromatography/mass spectrometry (GC/MS) procedures. Particulate matter samples for PAH

determination will be collected daily over 24-hour periods at each test site, and used to verify the performance of the commercial particulate PAH monitor.

3.4.3 Supplemental Measurements

Various supplemental measurements will be recorded and used to further establish the performance of the continuous monitors being tested. Meteorological conditions will be monitored and recorded continuously throughout each phase of the verification test. These measurements will include at least temperature, relative humidity, wind speed, and direction. Likewise, the ambient concentrations of various precursor gases including ozone and NO_x will also be measured continuously during the verification test, and will be used to assess the influence of these parameters on the performance of the monitors being tested.

To supplement the 24-hour samples, additional samples will be collected at the Fresno site over shorter sampling periods (i.e., 3, 5, 8-hour) to help assess the capabilities of the monitors being tested, in indicating short term PM levels. These short-term samples will be collected and analyzed for PM_{2.5} mass, nitrate, sulfate, and carbon fractions. Before use in evaluating the performance of the continuous monitors, these short term sampling measurements will be compared with the corresponding 24-hour results of the reference methods. These comparisons will be used to establish the relationship between the two sets of measurements.

3.5. Data Comparisons

3.5.1 Quantitative Comparisons

Table 3 provides a summary of the primary and supplemental comparisons to be made in evaluating technology performance. These comparisons are intended to evaluate the continuous

**Table 3. Summary of Data Comparisons to be Made
 in Verification of Continuous Monitors**

Technology to be Verified	Parameter Measured by Technology to be Verified	Primary Data to be Used for Comparison	Supplemental Data to be Used for Comparisons
Aethalometer	Black Carbon	Daily 24-hour EC/OC samples	3, 5, or 8 hour EC/OC samples; ^a continuous meteorological data
ACPM	EC/OC	Daily 24-hour EC/OC samples	3, 5, or 8 hour EC/OC samples; ^a continuous meteorological data
APNM	NO ₃ ⁻	Daily 24-hour NO ₃ ⁻ samples	3, 5, or 8 hour NO ₃ ⁻ samples; ^a continuous NO _x , O ₃ measurements; continuous meteorological data
APS	Mass	Daily 24-hour FRM samples	3, 5, or 8 hour PM _{2.5} mass samples; ^a continuous meteorological data
BAM	Mass	Daily 24-hour FRM samples	3, 5, or 8 hour PM _{2.5} mass samples; ^a continuous meteorological data
CAMM	Mass	Daily 24-hour FRM samples	3, 5, or 8 hour PM _{2.5} mass samples; ^a continuous meteorological data
ELPI	Mass	Daily 24-hour FRM samples	3, 5, or 8 hour PM _{2.5} mass samples; ^a continuous meteorological data
Nephelometer	Light scattering intensity	Daily 24-hour FRM samples	3, 5, or 8 hour PM _{2.5} mass samples; ^a continuous meteorological data
PAS	PAH and EC	Daily 24-hour PAH and EC samples	3, 5, or 8 hour EC samples; ^a continuous meteorological data
Sulfate Monitor	SO ₄ ²⁻	Daily 24-hour SO ₄ ²⁻ samples	3, 5, or 8 hour SO ₄ ²⁻ samples; ^a continuous SO ₂ , O ₃ measurements; continuous meteorological data
TEOM	Mass	Daily 24-hour FRM samples	3, 5, or 8 hour PM _{2.5} mass samples; ^a continuous meteorological data

^a Short-term samples collected at Fresno only.

monitors being verified by comparison to the reference method which most closely matches the quantity measured by the technology. The primary comparisons will be made with the reference methods described above. Additional comparisons will be made with the supplemental measurements to assess (1) the effects of meteorological conditions and precursor gas concentrations on the response of the monitors being tested, and (2) the capabilities of these monitors to indicate short-term levels of ambient PM. The comparisons will be based on statistical calculations as described in Section 7.3 of this test/QA plan.

Comparisons will be made independently for the data from each site, and, with the exception of the intra-method precision calculations, the results from the duplicate monitors will be analyzed and reported separately. Intra-method precision will be determined from a statistical intercomparison of the results from the duplicate monitors.

3.5.2 Qualitative Comparisons

There is evidence that some continuous monitors may be considered comparable with the FRM. For example, a recent study commissioned by the California Air Resources Board to intercompare a variety of PM measuring equipment, has shown high a degree of comparability (slope = 0.91, intercept = $0.80 \mu\text{g}/\text{m}^3$, $R^2 = 0.989$) between the $\text{PM}_{2.5}$ FRM and a Beta Attenuation Monitor with a Well-Impactor Ninety-Six $\text{PM}_{2.5}$ inlet (BAM-WINS).¹³ Therefore, in addition to the comparisons outlined in Table 3, additional comparisons may be made with other available methods if appropriate methods are in place at the test site and can be shown to be adequately comparable to the $\text{PM}_{2.5}$ FRM. Although less stringent than the criteria for FEM equivalence, the criteria used in this test for a continuous monitor to be considered adequately comparable with the FRM are based on those presented in the EPA guidance document for the use of continuous monitors.⁷ These criteria require that the results of the continuous monitor be compared with the reference method and analyzed by linear regression. The results of that statistical analysis must have a slope within three standard deviations of unity, an intercept within three standard deviations of zero, and have a squared correlation coefficient of greater than 0.9,

for that monitor to be accepted as a comparable method. The degree to which each monitor being verified meets these comparability criteria will be assessed.

If a monitor being verified in this test meets these criteria, it may be used for comparison with other monitors being verified. If an additional method in use at either test site shows comparability with the FRM, it may be used as a secondary means of comparison for illustration of the temporal response of the monitors being tested. The use of these data will be limited to qualitative comparisons, and no quantitative conclusions about the performance of the monitors tested will be made. However, the temporal features which appear in real-time measurements of PM_{2.5} mass (for example) may correlate with features in the PM mass or composition measurements of the other continuous monitors being verified. Comparisons of this type which can be used to show temporal features will illustrate the utility of the tested methods.

3.6. Roles and Responsibilities

The verification test will be performed by Battelle with the participation of EPA, the vendors who will be having their monitors verified, and the test sites. The organizational chart below shows the individuals from Battelle, the vendor companies, EPA, and the test sites who will have responsibilities in the verification test. The specific responsibilities of these individuals are detailed below.

3.6.1 Battelle

The Verification Test Coordinator will have the overall responsibility for ensuring that the technical, scheduling, and cost goals established for the verification test are met. The Verification Test Coordinator will:

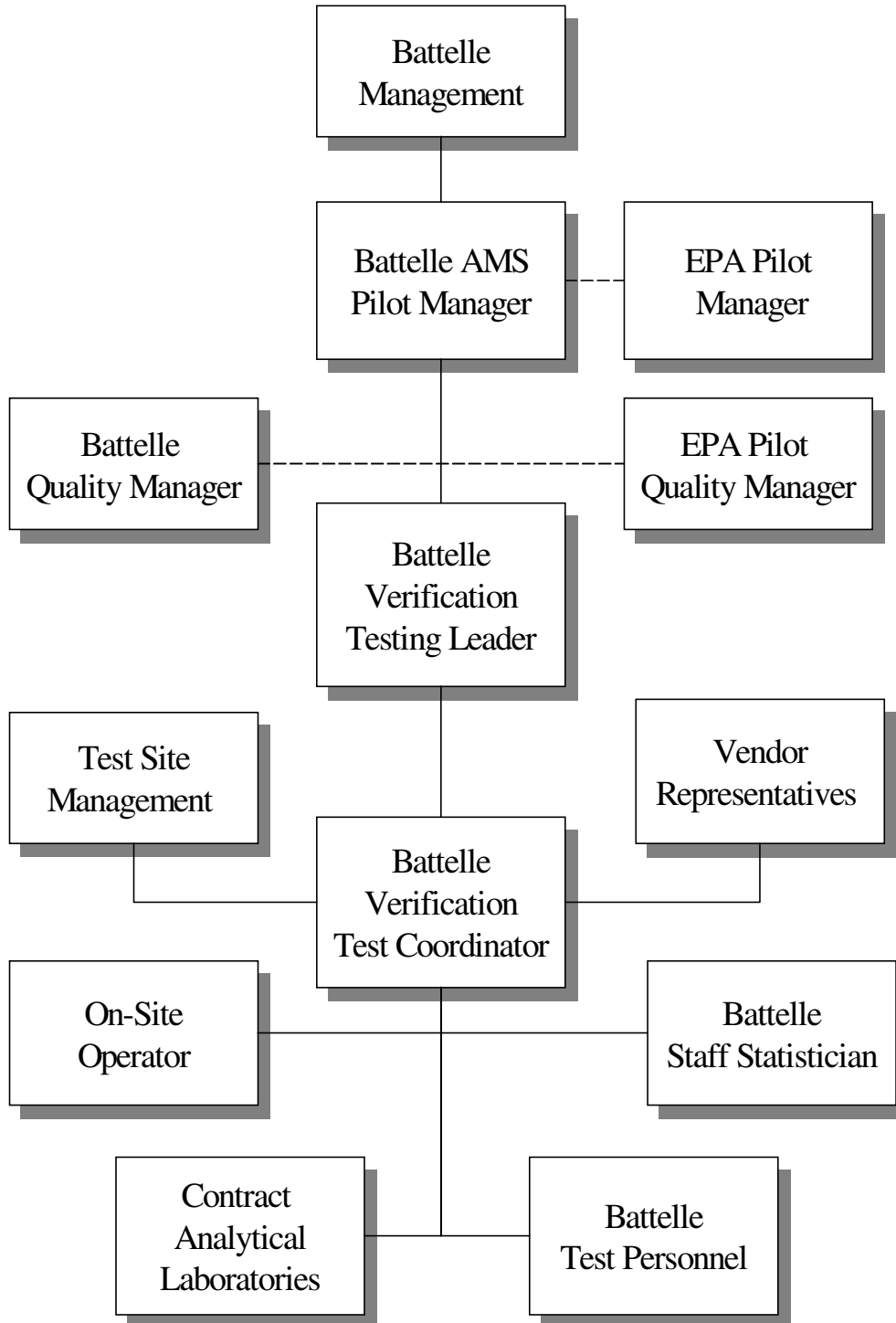


Figure 1. Organizational Chart for Ambient Fine Particle

Monitor Verification Test

- Prepare the draft test/QA plan, verification reports, and verification statements
- Revise the draft test/QA plan, verification reports, and verification statements in response to the reviewers' comments
- Coordinate testing parameters and test schedule with management and technical staff at each testing site
- Arrange for necessary Battelle materials to be available at the test sites when needed
- Ensure that all quality procedures specified in the test/QA plan and in the QMP are followed
- Respond to any issues raised in assessment reports and audits, including instituting corrective action as necessary
- Serve as the primary point of contact for vendor and site representatives
- Establish a budget for the verification test and monitor staff effort to ensure that the budget is not exceeded
- Ensure that confidentiality of vendor information is maintained.

The Verification Testing Leader for the AMS pilot will provide technical guidance and oversee the various stages of verification testing, and will:

- Support the Verification Test Coordinator in preparing the test/QA plan and organizing the testing
- Review the draft test/QA plan
- Review the draft verification reports and statements
- Ensure that confidentiality of vendor information is maintained.

Battelle's AMS Pilot Manager will:

- Review the draft test/QA plan
- Review the draft verification reports and statements
- Coordinate distribution of the final test/QA plan, verification reports and statements
- Ensure that necessary Battelle resources, including staff and facilities, are committed to the verification test
- Ensure that vendor confidentiality is maintained
- Support the Verification Test Coordinator in responding to any issues raised in assessment reports and audits
- Maintain communication with EPA's pilot and quality manager.

Battelle will provide test personnel who will assist as necessary during the verification test. The responsibilities of these test personnel include:

- Assist in the set-up and removal of the monitors and testing equipment as needed
- Train On-Site Operators in operating procedures of Battelle-supplied equipment
- Ensure that confidentiality of vendor information is maintained.

Battelle will provide a Staff Statistician who will support statistical and data analysis activities for this verification test. Specifically the Staff Statistician will:

- Assist in the conversion of verification data from electronic spreadsheet format to appropriate file format for statistical evaluation

- Support the Verification Test Coordinator in performing statistical calculations specified in this test/QA plan on the verification data
- Provide results of statistical calculations and associated discussion for the verification reports as needed
- Support the Verification Test Coordinator in responding to any issues raised in assessment reports and audits related to statistics and data reduction.

Battelle's Quality Manager for this verification test will:

- Review the draft test/QA plan
- Conduct a technical systems audit once during each phase of the verification test
- Review results of performance evaluation audits specified in this test/QA plan
- Audit at least 10% of the verification data
- Prepare and distribute an assessment report for each audit
- Verify implementation of any necessary corrective action
- Issue a stop work order if self audits indicate that data quality is being compromised; notify Battelle AMS Pilot Manager if stop work order is issued
- Provide a summary of the QA/QC activities and results for the verification reports
- Review the draft verification reports and statements
- Have overall responsibility for ensuring that the test/QA plan is followed
- Ensure that Battelle management is informed if persistent quality problems are not corrected
- Interface with EPA's Pilot Quality Manager
- Have overall responsibility for ensuring that the QMP is followed.

3.6.2 Vendors

Vendor representatives will:

- Review the draft test/QA plan and provide comments and recommendations
- Approve the revised test/QA plan
- Provide Battelle with detailed description of installation requirements prior to testing to ensure adequate facilities are available
- Provide duplicate commercial ready monitors for testing for the duration of each phase of the verification test at each site
- Install the monitors to be verified at each site and ensure proper operation before testing (vendors will have access to the test site at least one week in advance of testing during each phase)
- Provide detailed checklist to On-Site Operators of items which should be checked to verify proper operation of monitors
- Provide on-site operator or on-site technical support as needed
- Review and comment upon their respective draft verification report and statement.

3.6.3 EPA

EPA's responsibilities in the AMS pilot and this verification test are based on the requirements stated in the "Environmental Technology Verification Program Quality and Management Plan for the Pilot Period (1995-2000)" (QMP)¹⁵. The roles of the specific EPA staff are as follows:

EPA's Pilot Quality Manager will:

- Review the draft test/QA plan
- Perform, at her option, one external technical system audit during the verification test

- Notify the Battelle Pilot Manager to facilitate a stop work order if external audit indicates that data quality is being compromised
- Prepare and distribute an assessment report summarizing results of external audit, if performed
- Review draft verification reports and statements.

EPA's Pilot Manager will:

- Review the draft test/QA plan
- Approve the final test/QA plan
- Approve the final verification reports
- Review the draft verification statements.

3.6.4 Test Sites

The verification testing will be conducted in two phases. The first phase will be conducted at the DOE/NETL site in Pittsburgh, PA. The second phase will be conducted at the CARB/EPA supersite in Fresno, CA. The responsibilities of the host sites are:

- Assist in developing a plan to conduct verification tests at the site in collaboration with ongoing measurements
- Allow facility access to vendor, Battelle, and EPA representatives during the scheduled verification testing including set-up and tear-down operations
- Provide adequate working space at the testing site for the duration of verification testing
- Provide sufficient power for the simultaneous operation of all test equipment and technologies being verified

- Provide access to data from equipment collocated at test site, including available reference methods, continuous gas monitors, and meteorological monitors.
- Assist Battelle in arranging for augmented sampling schedules or additional sample analysis
- Cooperate with Battelle's documentation of the host site's QA/QC procedures
- Review portions of the verification report to assure accurate descriptions of the host site operations, and to provide technical insight on verification results
- Provide safety instructions to test and QA personnel for operations at the test site.

3.6.5 On-Site Operators

Battelle will hire On-Site Operators to assist, as necessary, in activities associated with this test that are not already performed by the test sites. The responsibilities of these on-site operators are:

- Observe the operation of the monitors being test and complete checklists for each monitor, as well as make general observations about the performance and maintenance of the monitors being tested
- Perform sampling activities according to this test/QA plan, documented procedures, and as instructed by the Verification Test Coordinator
- Arrange for and ship samples to the respective Contract Analytical Laboratories
- As necessary, inform respective vendors and Battelle of problems associated with the monitors being tested
- Ensure that confidentiality of vendor information is maintained.

3.6.6 Contract Analytical Laboratories

This verification test relies on the results of various analytical measurements. Battelle will secure the services of Contract Analytical Laboratories to conduct these measurements. The responsibilities of these laboratories are:

- Conduct quality assured analytical measurements of collected samples
- Provide Battelle with results of analytical measurements in mutually agreed upon format
- Provide Battelle and EPA, as necessary, with appropriate QA records and documents, including standard operating procedures, calibration records, training records, etc.
- As necessary, allow an external technical systems audit of laboratory facility, personnel, and procedures by Battelle and/or EPA staff.

4. TEST PROCEDURES

Field testing will be conducted in two separate phases. Phase I will be conducted at the DOE/NETL site for an approximately one month period of intensive sampling from Monday, July 31 to Friday, August 25, 2000. Phase II of the verification test is to be conducted at the EPA supersite in Fresno, between December 11, 2000 and January 12, 2001. At each site data from the monitors being tested, the meteorological monitors, and the precursor gas monitors will be collected continuously over the course of the verification test. Samples will be collected by the reference methods (i.e., FRM, speciation, and PAH samplers) according to the schedules in place at the sampling sites. In all cases, the monitoring and sampling equipment will be operated according to the recommendations provided in the respective operator's manual or standard operating procedures for the samplers, and within the procedures and protocols set forth in this

test/QA plan or the quality assurance plans^{8, 9, 10} in place at the respective sites and the analytical laboratories.

In some cases, monitors being verified are already in operation at the field sites. In these cases, the vendors will be allowed to perform appropriate calibration and maintenance on their respective monitors before testing begins. For those that are not, the vendor will install and ensure the proper calibration and operation of the monitors to be verified at each site. Routine operation during the verification test will be observed by On-Site Operators after appropriate training by vendor staff. Instrumental status will be documented by the On-Site Operators by completing checklists provided by the respective vendors. In the case of instrument failure, the vendor will be notified by the on-site operators and allowed to perform on-site repair if necessary. Since testing at each site will be conducted over a limited time period, it is expected that the vendor will arrange for adequate time for installation and training at each site before testing begins. Testing will not be delayed if installation of the monitors is not complete, and will not be extended to make up for downtime if a monitor being verified fails during the test.

At each site, On-Site Operators will be asked to make observations about the operational performance, maintenance, ease of use and reliability of each technology, as well as provide additional insight concerning general technology performance, and sampling conditions on the respective checklists provided by the vendors. If existing records pertaining to the past performance of one or more of the monitors are available, they may be used in the respective verification report to support discussions of operational performance. Information concerning maintenance and daily operation of these monitors, including data output requirements, will be recorded by site operators and summarized in the verification reports.

4.1. Phase I - Pittsburgh

Table 1 lists the equipment that is scheduled to be operated by DOE/NETL at the Pittsburgh site. The entries in this table are grouped according to the parameter to be measured, and include the monitoring equipment to be used, the averaging time, and the frequency of measurement for each of these instruments. Procedures for the operation of this monitoring equipment are provided in the respective instrument manuals or in the SOPs for the DOE/NETL study.

To augment the measurements made by NETL, Battelle will provide an FRM sampler, and a speciation sampler, with which to collect the reference samples. The speciation sampler provided will be equipped to collect samples for carbon, nitrate, sulfate, and PAH analyses. The procedures to be followed for the daily operation and routine maintenance of the Battelle-supplied FRM and speciation sampler are described in the respective instrument manuals provided by the manufacturers. Procedures for the daily sampling for PAHs are provided below. On-Site Operators responsible for the operation of these samplers will be trained in the procedures for daily operation of this equipment before verification testing begins and will follow these procedures during testing. Gravimetric and chemical analysis of the samples will be performed by Contract Analytical Laboratories according to their respective SOPs. Preparation of the denuders and analysis of the PAH samples will be performed at Battelle according to the procedures described in Section 4.3.

4.2. Phase II - Fresno

A list of the equipment to be operated by CARB/DRI as part of the various studies performed at the Fresno Supersite is provided in Table 2. This table also identifies the parameter to be measured, the average time for measurement, as well as the frequency of measurement. Procedures for the operation of these monitoring and sampling technologies are provided in the respective operator's manuals, or in the site planning documents.^{9, 10}

In addition to the instruments listed in Table 2, Battelle will provide a PAH sampler for particulate-bound PAH monitoring. Procedures for the denuder preparation, operation of the PAH sampler, and the analysis of the PAH samples are provided in Sections 4.3. On-Site Operators will be trained by Battelle in the procedures for the daily operation of the PAH sampler.

4.3. PAH Sampler

Particulate PAH data will be obtained for verification of the commercial PAH monitor by means of a denuder/filter/sorbent train that separates vapor- and particle-phase PAHs. The method to be used for PAH determination is based on ASTM Method D-6209-98.¹⁶ The principle of this method is that, as sample air is drawn through the train, vapor-phase PAHs diffuse rapidly to the walls of an annular denuder tube and are captured. Particles pass through the denuder in the sample air stream because of their much slower rate of diffusion, and are collected on a quartz fiber filter backed up by a sorbent trap. The sorbent trap serves to collect any PAH that volatilizes from the filter after particle collection. The particle-phase PAH concentration is determined by extracting and analyzing the filter/sorbent combination together. In addition, if needed the denuder can be extracted for determination of the vapor-phase PAHs.

The procedures for the daily operation of the PAH sampler are summarized below, including the origin, handling, shipping, and installation of the denuders, handling and installation of the sample filters, field sampling, and laboratory analysis.

4.3.1 Denuders

The denuders to be used are based on those developed by Gundel and co-workers,¹⁷ and consist of a glass annular denuder with a sandblasted inner surface coated with finely ground XAD-4 resin. The resin particles collect vapor-phase PAH from the air stream, but are resistant to removal from the glass surface during air sampling, solvent extraction, and handling of the denuder. The primary purpose of the denuder is to provide an air stream free of vapor-phase PAH, so that particle-phase PAH may be collected without artifact from the vapor phase. However, the denuders can also be extracted with solvent for determination of the collected vapor-phase PAH.

The denuders used in this verification test will be commercial units supplied by URG and coated by Restek Corporation. The denuders to be used will be appropriate for use with the sampler being used to collect the PAH samples. Preliminary chamber and field studies will be performed to characterize the performance of these denuders before the verification test.

4.3.2 Other Sampling Components

Cleaned quartz fiber filters and XAD-2 resin traps will be prepared by Battelle. Commercial quartz fiber filters will be cleaned by heating in a muffle furnace in high purity air, and will be stored wrapped in similarly muffled aluminum foil. XAD-2 resin is cleaned by Soxhlet extraction with multiple solvents, and stored in sealed, pre-cleaned glass sampling cartridges. At least one sampling assembly from each batch will be analyzed as a laboratory blank. A blank will be considered acceptable if the mass of each individual PAH species does

not exceed 10 ng, and if the blank PAH concentration is less than 10% of the expected ambient concentration (based on historical averages if available).

4.3.3 Shipment of Sampling Components

Sets of denuders, filters, and XAD-2 traps will be shipped to the test site at weekly to twice-weekly intervals in protective shipping containers by overnight delivery service. These materials will be stored at room temperature and kept sealed until the time of use. After sample collection, the sampling components will be resealed in their original containers and kept refrigerated (below 4°C) until enough samples are collected for a return shipment to Battelle. Refrigerated samples will then be returned to Battelle in the same containers used for shipment to the site. Field blank sampling materials will undergo the same handling and shipment procedures as actual samples. Temperature records of the shipped samples will accompany the samples.

4.3.4 Field Sampling for PAH

Sampling for particle-phase PAH is scheduled to take place at the respective test site on each day of both test phases. At least 10 % of the PAH samples collected and analyzed will be field blanks. Field blanks will be collected by inserting the filter/sorbant assembly into the sampler and removing the assembly without sampling.

The air flow rate of the PAH sampler will also be checked as part of the field performance audit schedule at each site as a quality control procedure. The procedures sampler operation and for flow rate checks are provided by the manufacturer in the operator manual.

4.3.5 PAH Analysis

Upon return to Battelle, each quartz fiber filter and its corresponding XAD-2 resin trap will be extracted in methylene chloride using Soxhlet apparatus, and the extracts will be concentrated to less than 1 mL volume. Analysis will be by GC/MS using the electron impact mode of ionization. All samples and blanks will be spiked prior to extraction with perdeuterated PAH as internal standards in the analysis. The particle-phase PAH data obtained from the filter/XAD combinations will be the primary basis for comparison with the continuous PAH monitor.

Performance verification of the continuous PAH monitor will be based on the response of the monitor to only those particle-bound PAH species which are expected to be ionized by the light source employed in the monitor (i.e., the ionization potential is below the photon energy).

5. MATERIALS AND EQUIPMENT

In general, this verification test relies on the materials and equipment in use as part of routine monitoring efforts at each of the two field sites. The equipment in use as part of those studies will be operated and maintained by the personnel at the respective sites. In addition to the on-site equipment operated by the test site, Battelle will provide the following equipment as needed.

5.1. FRM Sampler

A single filter BGI PQ200 FRM sampler will be provided, as needed, to the test sites for use during the verification test. Filter transport cases and extra filter cassettes will be provided, as will a BGI DataTrans module for retrieval of stored sampling information.

5.2. Speciation Sampler

An Andersen RAAS2.5-400 Chemical Speciation sampler, or similar sampler, will be provided, as needed, to the test sites for use during verification. Filter transport cases and extra filter cassettes will be provided.

5.3. PAH Sampler

The sampler to be used for the PAH sampling will be provided by Battelle for each phase of the verification test. The sampler will be equipped with the following components for the separation and collection of particle-phase PAH:

- commercial annular denuder coated with XAD-4 resin
- quartz fiber filter
- glass backup trap containing XAD-2 resin.

These components will be prepared and shipped to the respective sites by Battelle weekly to twice weekly during the individual verification test phases. After sample collection, these assemblies will be properly stored and shipped back to Battelle by site staff for analysis.

The other components of the sampler include the inlet, vacuum system, and pump. These components will be shipped to the respective site before each phase of testing for installation on the sampling platform. These components will be provided as either a stand-alone unit or as a train in a commercial speciation sampler (i.e., Andersen RAAS2.5-400, etc.).

5.4. Sampling Media

All materials necessary for sampling specifically associated with this verification test, including filters, denuders, and sorbent traps, will be supplied by Battelle. Arrangements for delivery dates and locations will be made with the respective Test Site Management or On-Site Operators by the Verification Test Coordinator.

6. QUALITY ASSURANCE/QUALITY CONTROL

This verification effort relies in part on the existing QA/QC programs in place at the DOE/NETL and Fresno sites. That is, the QA/QC procedures for the studies ongoing at each site will be adopted as part of this verification test. Each site has established QA/QC activities in accordance with appropriate guidelines from various sources including NARSTO, EPA, and DOE. These procedures cover daily operation of the site equipment, calibration, sample collection and handling, laboratory analysis, data collection and handling, as well as scheduled auditing. These procedures will be followed by site staff throughout the duration of testing at these sites, including the period during which the verification test is conducted. Adherence to those existing data quality procedures that relate to this test will be assessed by Battelle QA personnel, through review of procedures during the field verification periods. Additional QA/QC procedures specific to this verification test are described below.

6.1. Sample Collection/Transfer

Samples collected using Battelle-supplied equipment will be collected by On-Site Operators daily during each phase of the test according to the procedures described in this test/QA plan. After receipt by the On-Site Operators, filters and other necessary sampling

materials (i.e., denuders, PUF cartridges) for collection of these samples, as well as for the collection of field blanks, will be kept in a clean, temperature and humidity controlled environment until transported to the test site for sampling. If kept off-site these sampling materials will be transported to the site by the On-Site Operators so as to avoid contamination. Filters and other sampling materials will receive unique codes for identification according to the procedures of the On-Site Operators or Contract Analytical Laboratory depending on which party prepares the materials for sampling. Each sample will be accompanied by a chain-of-custody form during each step of its transport. Information on these forms will be completed by the sample sender and recipient as needed. Chain-of-custody forms will accompany samples which will be transported to or from the Contract Analytic Laboratories which are independent of the On-Site Operators. Sample run data forms documenting the sampling parameters will be completed by the On-Site Operators for each sample. On-Site Operators will forward these sample run data forms to the Verification Test Coordinator for approval within one week of the sampling date. The Contract Analytical Laboratories will forward the chain-of-custody forms to the Verification Test Coordinator for approval within one week of completion of the sample analysis. Approval of these records will be indicated by the signature of the Verification Test Coordinator on each form. Example forms are shown in Appendix A.

6.2. Data Collection/Transfer

Data from the time integrated and continuous monitors operated at each site and the results of laboratory analyses will be recorded according to the procedures described in the respective test plans for the sites or standard operating procedures, and will be transferred to Battelle after validation procedures are performed. The data received by Battelle from each site will be maintained by Battelle's Verification Test Coordinator, and information regarding specific technologies being tested will be kept confidential while under the control of Battelle.

Data generated by Battelle or on behalf of Battelle for this verification test, and that is

not already covered by procedures at the test site will be recorded either electronically, on data sheets, or in laboratory notebooks. These data include those associated with particulate PAH measurements, and will include observations on the operation of the monitors being tested, weather observations, and other information. These data will be compiled in electronic format and, excluding confidential information about specific technologies being verified, will be made available to each site upon request.

6.3. Field QA/QC Activities

A variety of QA/QC activities will be performed by the On-Site Operators at the test sites to ensure that the samplers provided by Battelle are operating properly. These activities include flow rate checks, internal and external leak checks, as well as checks of the temperature and pressure sensors in the samplers. QA/QC activities associated with the reference methods supplied by the test sites will be conducted according to the procedures in place at the respective sites and the results will be provided to Battelle. For the reference methods supplied by Battelle, the QA/QC activities to be performed are based on those described in the manuals for the respective samplers and are summarized below.

6.3.1 Flow Rate Check

The flow rate of the reference samplers provided by Battelle will be verified through single point checks to ensure the proper operation of the samplers. These flow rate checks will be conducted based on the procedures described in the respective manuals, and will be conducted at least once before (within one week of the start) and again once after (within one week of the end) each phase of the verification test. The flow rates will be checked using a calibrated flow meter to verify that the sampler is operated at a flow rate within +/- 5 % of the nominal operating flow rate of the sampler. Also, if the sampler includes an internal flow meter, agreement

between the audit flow meter and the sampler flow meter must be within $\pm 4\%$. If $\pm 5\%$ agreement between the sampler flow rate and the nominal operating flow rate is not achieved, the sampler flow rate will be manually adjusted to meet this performance criterion. If agreement between the sampler and audit flow meters does not meet the $\pm 4\%$ acceptance criterion, recalibration of the sampler flow meter will be performed per the procedures in the operators manual.

6.3.2 Leak Checks

Internal and external leak checks of the reference samplers provided by Battelle will be performed to ensure the integrity of the sampling system. These leak checks will be performed based on the procedures described in the respective sampler manuals and will be conducted at least weekly during each phase of the verification test. Leak checks of the FRM sampler will be conducted after each cleaning of the Well-Impactor Ninety Six (WINS) impactor in the FRM sampler. The WINS impactor will be cleaned at least once every 5 sampling days. Acceptance criteria and corrective actions for these activities are described in the respective manuals for the reference samplers.

6.3.3 Temperature and Pressure Checks

Single point calibration checks of the temperature and pressure sensors in the reference samplers provided by Battelle will be conducted based on the procedures described in the respective manuals. These checks will be performed at least twice during each phase of the verification test, once within one week of the beginning and once within one week of the end of each phase. Acceptance criteria and corrective actions for these activities are described in the respective manuals for the reference samplers.

6.3.4 Field Blanks

Field blanks will be collected and analyzed for all the reference methods supplied by Battelle to assess the contamination levels associated with activities other than sampling. The field blanks will be collected by placing the sampling media in the sampler and removal without sampling. At least 10% of the collected samples will be field blanks. The acceptance criteria and corrective actions for the field blanks will be established based on procedures in place at the respective Contract Analytical Laboratories (based on historical averages if available).

For the field blanks for the PAH sampler, at least one will be collected within the first 3 days of sampling, and again within the last week of sampling of each test phase, with at least one additional blank collected during each phase. Blank levels for the PAH sampler will be considered acceptable if the mass of each individual PAH species, excluding naphthalene, does not exceed 20 ng on the filter/sorbent assembly, and if the blank PAH concentration is less than 10 % of the average ambient concentration. For naphthalene, the acceptance level for the blank sample is 200 ng. If this acceptance criterion is not met, the source of the contamination will be investigated, and the sample will be flagged as of questionable validity.

6.3.5 Collocated Samplers

The precision of the reference methods provided by Battelle will be established by collocation of each reference sampler with an identical or a similar sampler. The collocated samplers will be placed within four meters of each other and will collect at least five 24-hour samples to establish precision. This collocated sampling will be completed at the verification test site, before the start of the verification test sampling.

For the FRM reference method, agreement between the duplicate samples must be within 10% to be considered acceptable. If this agreement criterion is not met, the source of the discrepancy will be investigated, additional samples will be collected, and the analyses will be repeated.

For the chemical speciation (nitrate, sulfate, carbon, and PAH) reference methods, the duplicate samples will be analyzed concurrently, and agreement between the observed concentration of each analyte must be within +/- 35% to be acceptable. If this agreement criterion is not met, the source of the discrepancy will be investigated, and if possible additional samples will be collected, and the analyses will be repeated.

6.4. Laboratory QA/QC Activities

QA/QC practices performed by the laboratories used to conduct all the chemical and gravimetric analyses for this verification test, except for the PAH analysis, are described in their respective standard operation procedures or laboratory quality manuals. These activities include instrument calibration and verification, as well as analysis of laboratory and lot blanks. The acceptance criteria and corrective actions for these activities are described in the respective procedures.

Battelle will conduct the PAH analysis according to procedures based on ASTM Method D-6209-98. QA/QC activities for these analyses include analysis of laboratory blanks, analytical duplicates, and analytical spikes as described below.

6.4.1 Laboratory Blanks

At least one sorbant/filter assembly from each batch of prepared assemblies will be analyzed as a laboratory blank. These blanks will undergo the same preparation and handling procedures as those traps which are shipped to the test sites for sampling, but will not be shipped or exposed to sampling. The laboratory blanks will be analyzed at the same time as the PAH samples. Acceptance criteria and corrective actions for these laboratory blanks will be the same as those for the PAH field blanks.

6.4.2 Analytical Duplicates

For the PAH analyses, an analytical duplicate of one sample will be run for each batch of samples analyzed to assess the precision of the analytical method. Agreement between the results from the duplicate analyses must be within 15% to be acceptable. If this agreement criterion is not met, the source of the discrepancy will be investigated and the analyses will be repeated, if possible.

6.4.3 Analytical Spikes

Analytical spikes will be used to assess the accuracy of the PAH analytical method. Each sample will be spiked prior to extraction with 100 ng each of pyrene- d_{10} and chrysene- d_{12} to serve as surrogate recovery standards. The percent recovery of each standard must be within +/-30% to be acceptable. If this agreement criterion is not met, the source of the discrepancy will be investigated and appropriate corrective action will be taken.

6.5. Assessments and Audits

Independent of site and EPA QA activities, Battelle will be responsible for ensuring that the following audits are conducted as part of this verification test.

6.5.1 Performance Audits

Reference methods supplied by the test sites

Performance evaluation audits of the reference methods supplied and operated by the test sites, and of the laboratory analyses, will be performed according to the procedures and schedules provided in the procedures for the respective sites and Contract Analytical Laboratories, respectively. The audits of the reference samplers may include, among other activities, flow rate checks of the reference method samplers using calibrated flow meters to ensure proper flow during sample collection, and collocation of audit samplers with the reference samplers to assess

the precision of the reference methods. Performance evaluation audits for laboratory analysis include calibration checks of balances and other analytical instrumentation, as well as analysis of blank samples. Acceptance criteria and corrective actions for these quality assurance activities are provided in the test plans or in the standard operating procedures for the respective sites or analytical laboratory. When possible Battelle QA staff will be present during the performance of these audits.

Reference methods supplied by Battelle

Performance evaluation audits of the reference method equipment supplied by Battelle will be performed during the verification test. These audits include verification of the sampler flow rate, as well as verification of the temperature and pressure sensors to ensure proper sampler operation.

Performance evaluation audits of the flow rate, as well as the temperature and pressure sensors for the reference samplers provided by Battelle will be conducted according to the procedures described above in Section 6.2 with the same acceptance criteria and corrective actions. These audits will be conducted using sensors with NIST-traceable calibrations that are not those used for the usual checks described in Section 6.2 but may be traceable to the same primary standards. The audits will be observed by Battelle staff when possible, and when possible, will be performed by someone other than the usual On-Site Operator. These performance evaluation audits will be conducted at least once during each phase of the verification test and may be conducted within one month of the beginning of each phase.

6.5.2 Technical Systems Audits

Battelle's Quality Manager will perform a technical systems audit (TSA) at least once during each phase of this verification test. The purpose of this audit is to ensure that the verification test is being performed in accordance with this test/QA plan and that all QA/QC procedures are being implemented. In this audit, the Quality Manager will review the reference methods used, compare actual test procedures to those specified or referenced in this plan, and review data acquisition and handling procedures. This effort will include reviewing the procedures used at the test site for compliance with this test/QA plan and with the SOPs for the respective site. When possible, a TSA of the Contract Analytical Laboratories will be conducted to ensure that analyses are being performed in accordance with the requirements of this test/QA plan and the SOPs of the laboratory. A TSA report will be prepared, including a statement of findings and the corrective actions taken to address any adverse findings.

At EPA's discretion, EPA QA/QC staff may also conduct an independent TSA of the verification test. In any case, EPA QA/QC staff will review Battelle's TSA report, and provide comments on the findings and actions presented in that report.

6.5.3 Data Audits

Battelle's Quality Manager will audit at least 10 percent of the verification data acquired during the verification test. The Quality Manager will trace the data from initial acquisition, through reduction and statistical comparisons, and to final reporting. All calculations performed on the data undergoing the audit will be checked.

6.6. QA/QC Reporting

Each assessment and audit will be documented in accordance with Section 2.9.7 of the QMP for the AMS pilot.¹ Assessment reports will include the following:

- Identification of any adverse findings or potential problems
- Response to adverse findings or potential problems
- Recommendations for resolving problems
- Confirmation that solutions have been implemented and are effective
- Citation of any noteworthy practices that may be of use to others.

6.7. Corrective Action

The Battelle or EPA Quality Managers during the course of any assessment or audit will identify to the technical staff performing experimental activities any immediate corrective action that should be taken. If serious quality problems exist, the Battelle Quality Manager is authorized to stop work. Once the assessment report has been prepared, the Verification Test Coordinator will ensure that a response is provided for each adverse finding or potential problem, and will implement any necessary follow-up corrective action. The Battelle Quality Manager will ensure that follow-up corrective action has been taken.

7. DATA HANDLING AND REPORTING

7.1. Data Acquisition

A variety of data will be acquired and recorded electronically, or manually, by site or laboratory personnel in each phase of the verification test. After the prescribed validation at the respective test site, these data, including most reference method results, meteorological conditions, precursor gas concentrations, and the data from the technologies being verified, will be transferred to Battelle either electronically or in hard copy for subsequent reduction and analysis. Other data, namely PAH concentrations, will be generated by Battelle. These data will be compiled in electronic format and will be shared with the host sites. In all cases, strict confidentiality of the verification data will be maintained for each participating vendor. This will be accomplished in part by storing electronic data under separate and clearly identifiable computer file names. All hard copy information similarly will be maintained in separate folder files. At no time during verification testing will Battelle engage in any comparison or discussion of test data or intercomparison of different monitors undergoing verification. However, much of the data used in this verification test will be obtained from sources outside of the control of Battelle. Consequently, the same data that are used for technology verification through ETV may be used in intercomparative studies by other organizations.

7.2. Data Review

Records received by or generated by Battelle staff in the verification test will receive a one-over-one review within two weeks after receipt or generation, respectively, before these records are used to calculate, evaluate, or report verification results. These records may include electronic records; laboratory record books; operating data from the test site; or equipment

calibration records. This review will be performed by a Battelle technical staff member involved in the verification test, but not the staff member that originally received or generated the record. The review will be documented by the person performing the review by adding his/her initials and date to a hard copy of the record being reviewed. This hard copy will then be returned to the Battelle staff member who received or generated or who will be storing the record.

In addition, data calculations performed by Battelle will be spot-checked by Battelle technical staff to ensure that calculations are performed correctly. Calculations to be checked include determination of predictability or comparability, intra-method precision, and other statistical calculations to assess meteorological and precursor gas effects, and short term monitoring capabilities as identified in Section 7.3 of this test/QA plan.

7.3. Statistical Calculations

Performance verification is based, in part, on statistical comparisons of continuous monitoring data to results from the reference methods. A summary of the calculations to be made is given below.

7.3.1 Comparability

The comparability between the continuous monitors and reference methods will be assessed only for monitors which yield measurements with the same units of measure as the reference method with which it is being compared. The relationship between the two will be assessed from a linear regression of the data using the reference method results as the independent variable and the continuous monitor results as the dependent variable as follows:

$$C_i = \mu + r \times R_i + \epsilon_i \quad (1)$$

where R_i is the i^{th} reference measurement (for a 24 hour period), C_i is the average of the continuous measurements over the same 24 hour time period as the i^{th} reference measurement, μ and ρ are the intercept and slope parameters, respectively, and ζ_i is error unexplained by the model. The average of continuous measurements is used as this is the quantity that is most comparable to the reference sampler measurements.

Comparability will be expressed in terms of bias between the continuous monitor and the reference method and the degree of correlation (i.e., r^2) between the two. Bias will be assessed based on the slope and intercept of the linear regression analysis of the data from the reference method and the continuous monitor. In the absence of bias, the regression equation would be $C_i = R_i + \zeta_i$ (slope = 1, intercept = 0) indicating that the 24 hour average of continuous measurements is simply the reference measurement plus random error. A value of r^2 close to 1 implies that the amount of random error is small, that is, the variability in the continuous measurements is almost entirely explained by the variability in the reference measurements.

Quantities to be reported include sample size, r^2 , estimates and standard errors of the intercept and slope parameters, and the numbers of standard errors between the slope estimate and unity and between the intercept estimate and zero.

Comparability will be determined independently for each of the two duplicate monitors being tested and will be assessed separately for each phase of the verification test.

7.3.2 Predictability

Predictability will be assessed for continuous monitors which report results in units which are different than those of the reference method with which it is being compared. In these cases the reported predictability will be representative of the usefulness of that monitor as a surrogate of the reference method, i.e., its ability to predict the measurement made by the reference method. The relationship between the two will be assessed from a linear regression of the data using the reference method results as the independent variable and the continuous monitor results

as the dependent variable. The predictability of the continuous monitor will be expressed by the correlation coefficient of a linear regression analysis, and the slope and intercept of the regression analysis can be used to express the relationship between the two. The statistical model to be used is identical to model (1) for comparability. Quantities to be reported include sample size, r^2 , and estimates and standard errors of the intercept and slope parameters. Additionally, by reversing the roles of the independent and dependent variables, a 95% percent prediction interval will be calculated for conversion from monitor measurement units to lower and upper bounds on reference method measurement units.

Predictability will be determined independently for each of the two duplicate monitors being tested and will be assessed separately for each phase of the verification test.

7.3.3 Precision

The intra-method precision of the continuous monitors will be determined based on procedures described in Section 5.5.2 of EPA 40 CFR 58, Appendix A, which contains guidance for precision assessments of collocated non-FRM samplers. Simultaneous measurements from duplicate monitors will be paired and the behavior of their differences used to assess precision. The following statistics will be reported for each parameter measured: sample size, mean difference, standard deviation of the difference, coefficient of variation (CV), and a 90% confidence interval for CV. As suggested by the EPA guidance, only measurements above level of detection will be used in precision calculations. The CV is defined as the standard deviation of the differences divided by the mean of the measurements and expresses the variability in the differences as a percentage of the mean.

Precision will be assessed separately for each phase of the verification test.

7.3.4 Meteorological Effects/Precursor Gas Interferences

The influence of meteorological conditions on the correlation between the continuous monitors and the reference methods will be evaluated by using meteorological data such as temperature, humidity, etc. as parameters in multi-variable analyses of the reference/monitor comparison data. The model to be used is as follows:

$$C_i = \mu + \rho \times R_i + \sum_j \alpha_j \times X_{ji} + \epsilon_i \quad (2)$$

where the X_{ji} 's are meteorological and/or precursor gas measurements for the i^{th} 24 hour time period, the α_j 's are the associated slope parameters, and other notation is as before.

Comparability and predictability results will be reported again after these variables are adjusted for in the model. Additionally, estimates and standard errors of the α_j 's will be provided.

Meteorological effects and precursor gas interferences will be assessed independently for each of the two duplicate monitors being tested and will be assessed separately for each phase of the verification test.

7.3.5 Short-Term Monitoring Capabilities

The capabilities of these monitors will be assessed from comparison to gravimetric samples collected of short sampling periods (3-8 hours) by the reference methods. This assessment will be based on linear regression analysis of the short-term sampling results from the continuous monitors and the reference method to which it is being compared. The analysis will be conducted and the results will be reported in a fashion identical to that for the comparability and predictability results described in Sections 7.3.1 and 7.3.2.

Comparisons of this type will be made only after establishing the relationship between the short-term sampling results and the corresponding 24-hour results. The relationship between the two sets of reference measurements will be made by linear regression using the average of the

results from the short-term sampling as the dependent variable and the 24-hour results as the independent variable in the regression analysis. Comparability will be assessed using equation (1), replacing the average of continuous measures with the average of short-term sampler measurements.

The short term sampling results will also be used to assess the effects of meteorological conditions and precursor gas concentrations on the response of the monitors. These short term results will be used in place of the 24-hour measurements in the analysis described in Section 7.3.4.

Independent assessments will be made for the duplicate monitors and the data from each phase of testing will be analyzed separately.

7.3.6 Qualitative Comparisons

As described in Section 3.5.2, additional qualitative comparisons may be made between the monitors being verified and other monitors provided other monitors are in use on site that are adequately comparable to the $PM_{2.5}$ FRM. A continuous monitor will be considered adequately comparable if, under analysis using equation (1), the squared correlation coefficient (r^2) is at least 0.90 and the slope and intercept estimates are within three standard deviations of unity and zero, respectively.

Given an adequately comparable continuous monitor, qualitative comparisons between this monitor and the tested monitor will consist of overlaid time-series plots of measurements. Such plots allow visual inspection of similarities and dissimilarities in measurements and temporal patterns continuously over the entire month of data collection.

Similar overlaid time-series plots will be made with the results from the continuous meteorological and precursor gas monitors when appropriate.

Qualitative comparisons will be made separately for each of the two duplicate monitors being tested and for each phase of the verification test.

7.4. Reporting

The statistical data comparisons that result from each of the tests described above will be conducted separately for each technology being verified, and information on the additional cost factors (i.e., costs associated with calibration gases, etc.) will be reported. Separate verification reports will then be prepared, each addressing an individual technology provided by one commercial vendor. For each test conducted in this verification, the verification report will present the test data, as well as the results of the statistical evaluation of those data.

The verification report will briefly describe the ETV program and the AMS pilot, and will describe the procedures used in verification testing. The parties involved in the verification test will be identified and the roles of each will be described. These sections will be common to each verification report resulting from this verification test. The results of the verification test will then be stated quantitatively, without comparison to any other technology tested, or comment on the acceptability of the technology's performance. Included in the verification report will be descriptions of the following parameters:

- operating conditions during testing,
- instrument settings used during testing,
- and the inlet used during the test.

The preparation of draft verification reports, the review of reports by vendors and others, the revision of the reports, final approval, and the distribution of the reports, will be conducted as stated in the Generic Verification Protocol for the Advanced Monitoring Systems Pilot.

Preparation, approval, and use of verification statements summarizing the results of this test will also be subject to the requirements of that same Protocol.

After approval, the final verification reports and verification statements will be made available to the respective vendors in hard-copy, and will be posted on the ETV website

(www.epa.gov/etv/). The reports may also be presented or made available at various technical conferences and trade shows.

8. HEALTH AND SAFETY

Before each phase of testing begins, site management will be responsible for reviewing the necessary health and safety requirements and guidance for the respective test sites with Battelle, EPA, and vendor staff. While on site, Battelle staff will operate under these established requirements and guidelines. It is expected that while on site EPA and vendor staff will also operate according to these requirements.

9. REFERENCES

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- ⁸ Federal Energy Technology Center, “Test Plan and Quality Assurance Procedures-OST PM_{2.5} Sampling and Analysis Program”, draft prepared by Brigham Young University, Provo, UT, and Federal Energy Technology Center, Pittsburgh, PA., 1999.
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- ¹⁰ California Air Resources Board, “Aerometric Monitoring Program Plan for the California Regional PM_{2.5}/PM₁₀ Air Quality Study”, draft prepared by Desert Research Institute, Reno, Nevada, December, 1998.

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¹⁶ American Society for Testing and Materials, "Standard Test Method for Determination of Gaseous and Particulate Polycyclic Aromatic Hydrocarbons in Ambient Air (Collection on Sorbent-Backed Filters with Gas Chromatography/Mass Spectrometric Analysis)", ASTM Method D 6209-98, in *Annual Book of Standards, Vol. 11.03*, West Conshohoken, PA, 1998.

¹⁷ L. A. Gundel, V. C. Lee, K. R. R. Mahanama, R. K. Stevens, and J. M. Daisey, *Atmos. Environ.*, **29**, 1719-1733, (1995).

APPENDIX A

Example QA/QC Report Forms