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Environmental Technology Verification Program

Advanced Monitoring Systems Pilot

Generic Verification Protocol for Ambient Fine Particle Monitors

GENERIC VERIFICATION PROTOCOL

FOR

AMBIENT FINE PARTICLE MONITORS

August 2002

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ACRONYMS

AMS	Advanced Monitoring Systems
APS	Aerodynamic particle sizer
BAM	Beta attenuation monitor
CARB	California Air Resources Board
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
OC	Organic carbon
PAH	Polychlorinated aromatic hydrocarbon
PM	Particulate matter
$PM_{2.5}$	Particulate matter with an aerodynamic diameter less than 2.5 μm
PM_{10}	Particulate matter with an aerodynamic diameter less than 10 μm
QA	Quality assurance
QC	Quality control
QMP	Quality management plan
TEOM™	Tapered Element Oscillating Microbalance
TOR	Thermal optical reflectance
WINS	Well-Impactor Ninety Six

1 INTRODUCTION

1.1 Background

1.1.1 Environmental Technology Verification

This protocol provides generic procedures for implementing a verification test of monitors that continuously indicate the mass or chemical composition of fine particulate matter in ambient air. The verification test is conducted under the auspices of the U.S. Environmental Protection Agency (EPA) through its Environmental Technology Verification (ETV) program. The purpose of the ETV program 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 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.

Verification tests are coordinated by Battelle, of Columbus, Ohio, which is managing the ETV Advanced Monitoring Systems (AMS) Center. The scope of the AMS Center covers verification of monitoring technologies for contaminants and natural species in air, water, and soil. In performing any verification, Battelle follows the procedures specified in the test protocol and complies with the data quality requirements in the "Quality Management Plan (QMP) for the ETV Advanced Monitoring Systems Center".[1]

1.1.2 Fine Particulate Monitoring

The EPA promulgated changes to the National Ambient Air Quality Standard for particulate matter (PM) in 1997.[2] Those changes call for revising the existing PM_{10} standard and adding a new standard for $PM_{2.5}$. The revised standard also calls for using "correlated acceptable continuous" monitors to supplement $PM_{2.5}$ sampling at community oriented 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 to develop 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 PM_{10} 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 relatively 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 introducing error, by improper handling, or losing volatile PM components.

In contrast, the primary advantage of continuous or automated monitors is their ability to continuously and rapidly assess particulate matter levels or composition with relatively little operator effort. Collecting 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 PM_{10} 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 purpose of verification tests of ambient fine particle monitors 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 the verification test is to evaluate the performance of ambient fine particle monitors[(a)] under realistic operating conditions. The performance of these monitors shall be evaluated primarily by comparisons with specific reference methods to determine their ability to predict the results of those reference methods.

Specific objectives of verification tests for these monitors are 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
- Determine the intra-method precision of these continuous monitors by comparing simultaneous results from duplicate monitors
- Evaluate the effects of meteorological conditions on the performance of the continuous monitors
- Determine the influence of ambient precursor gases on the instrumental response of the monitors being verified
- 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
- 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 shall 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, is established based on statistical comparisons of the results from each phase. Similarly, statistical comparisons of the results from duplicate monitors is used to assess the intra-method precision for these continuous methods. The two separate phases are conducted in different geographic locations,

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[a] For 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 protocol.

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, the verification test shall report on other operational characteristics including the reliability, necessary maintenance, and ease of operation of these monitors. Verification results shall summarize additional information that may be relevant to potential users, including power and shelter requirements, data output, and the overall cost of these monitors.

The results from performance evaluations shall be made publically available with the goal of providing credible information to potential purchasers, regulators, and permitters of these technologies.

1.3 Test Applicability

This generic protocol is applicable to verification testing of ambient fine particulate matter monitors that 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 shall be commercially available and not developmental products or prototypes.

2 TECHNOLOGY DESCRIPTION

Monitors to be tested are continuous particulate matter monitoring instruments whose designs and principles of operation cover a wide range of analytical capabilities. Nonetheless, they exhibit a rapid, quantitative response to ambient particulate matter and, therefore, may be

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[b] For this generic protocol, fine particulate matter is defined as that fraction of particles with aerodynamic diameters below 2.5 μm ($PM_{2.5}$). 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.

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 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 that can be verified under this protocol. 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 (CO_2), of these two classes of carbon particulate, occurs at very different temperatures. Consequently, by heating particulate samples and monitoring the CO_2 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 that 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 ultraviolet 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 also has 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 (Rupprecht & Patashnick, Co., Inc.) and the Series 8400S Ambient Particulate Sulfate Monitor (Rupprecht & Patashnick, Co., Inc.).

2.2 Mass or Surrogate Mass

A variety of particle properties can be related to, and ultimately 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 (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 that 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 (Dekati, Ltd.) operates on the basis of charging, inertial classification, and electrical detection of aerosol particles. Sampled air is drawn through a corona discharge that 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 that 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 objective of the verification test derived from this generic protocol is to provide quantitative performance data on fine particle monitors under realistic operating conditions. To meet this objective, testing shall 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 shall 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 shall 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 shall 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 shall provide the basis for assessing the degree of agreement and/or correlation between the

[c] Throughout this document the term "reference method" will refer to methods that are used as a basis of comparison for the purposes of technology verification. These reference methods may be, but are not necessarily, FRMs or FEMs.

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 shall be equipped with continuous monitors to record meteorological conditions and the concentration of key precursor gases (O_3, NO_x, SO_2, etc.). Additionally, other performance characteristics of the technologies being verified, such as reliability, maintenance requirements, and ease of operation shall be assessed by field operators and reported. Instrumental features that may be of interest to potential users (e.g., power and shelter requirements, data output, and overall cost) shall 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 the verification test to generate aerosols in the laboratory that are representative of the wide range of aerosol composition typically found in ambient air. This verification test shall be limited to comparisons of data collected in the field under realistic operating conditions. Consequently no laboratory evaluations shall be performed as part of this test.

3.2 Site Selection

Two one-month tests at two distinct geographical regions during different seasons shall be conducted. The testing sites shall be selected based on a number of criteria, including some common characteristics between the sites, as well as some key differences. Common to these sites shall be

- A wide variety of ongoing 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
- Established QA/QC protocols and procedures.

The key difference between the selected sites should be that they are 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, should be among the primary considerations for the selection of sites.

It is recognized that verifying 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. Consequently, the verification reports that result from such tests 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 the verification tests to evaluate the performance of monitors under all conditions in which they are likely to be used. Instead, two test sites will provide a demonstration of instrumental performance under a set (albeit limited) of realistic operational conditions.

3.3 Experimental Design

The design of a fine particle monitor verification test shall be similar to that of the PM instrument intercomparison study performed for CARB.[8] In that study, a variety of continuous and manual methods were intercompared to assess operational relationships among the different methods. Verification tests will be similar to that study in that similar comparisons will be made between the continuous and manual methods. Verification tests will be different in that they 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.

Verification tests involve collocating duplicate commercial monitors at test sites that have established reference methods already in place, including both FRM and speciation samplers. Duplicate monitors are 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 are 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 are used to assess intra-method precision for each type of monitor. Continuous measurements of meteorological conditions and the concentrations of precursor gases are used to support these assessments. In this way, the accuracy and variability of the continuous monitors are assessed under various conditions after adjusting for the influence of those conditions. Additional observations are made by on-site operators and documented to describe the general operational characteristics of the monitors, including general performance, reliability, maintenance, and ease of use.

The primary comparison for each monitor is with daily 24-hour, time-integrated samples collected by the respective reference methods (see Section 3.4). As a result, the primary comparison includes approximately 30 samples from each month-long phase. The actual number of data points available for use in these comparisons may be somewhat smaller than 30. In addition to the 24-hour samples used for the primary comparisons, a number of shorter term samples (3, 5, 8-hour) are 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 also are used to support the primary comparisons. The variability in ambient air parameter levels over the course of a month of data collection is expected to be much larger than the size of the error in measurement, allowing for accurate estimation of the relationship between the reference methods and the monitors tested.

In some cases, the monitors to be verified may be already in use at one or both of the sites. If so, 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 the 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 are to 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 shall 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 the verification tests 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 that 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 tests is given below.

3.4.1 $PM_{2.5}$ Mass

Comparisons to $PM_{2.5}$ mass shall 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 μm 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 shall be collected daily during each phase of the testing using a BGI PQ200 (RFPS-0498-116) or comparable sampler, and $PM_{2.5}$ shall 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 also shall 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,"[9] 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 determining 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 shall be employed as part of the studies performed at those sites. Collected samples from those speciation samplers may 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 may 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."[9] EC/OC fractions will be collected on quartz fiber filters and analyzed by both the IMPROVE thermal optical reflectance and the NIOSH 5040 thermal optical transmission techniques.

For particle-bound PAH measurements, sample collection and analysis procedures based on ASTM Method D 6209-98[10] shall be used. Battelle shall 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 is collected on a quartz fiber filter followed by an XAD-2 resin bed. Particulate matter collected on the combined filter/XAD trains is analyzed for PAH content by solvent extraction and subsequent gas chromatography/mass spectrometry (GC/MS) procedures. Particulate matter samples for PAH determination shall 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 shall be recorded and used to further establish the performance of the continuous monitors being tested. Meteorological conditions shall be

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

To supplement the 24-hour samples, additional samples may be collected 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 shall 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 1 provides a summary of typical primary and supplemental comparisons to be made in evaluating technology performance. These comparisons are intended to evaluate the continuous monitors being verified by comparison to the reference method that most closely matches the quantity measured by the technology. The primary comparisons shall be made with the reference methods described above. Additional comparisons shall 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 shall be based on statistical calculations as described in Section 7.3.

Comparisons shall 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 shall be determined from a statistical intercomparison of the results from the duplicate monitors.

Table 1. Summary of Data Comparisons to be Made in Verification of Continuous Monitors

Parameter Measured	Primary Data	Supplemental Data
Mass	Daily 24-hour FRM samples	3-, 5-, or 8-hour $PM_{2.5}$ mass samples; continuous meteorological data
Light scattering intensity	Daily 24-hour FRM samples	3-, 5-, or 8-hour $PM_{2.5}$ mass samples; continuous meteorological data
Black Carbon	Daily 24-hour EC/OC samples	3-, 5-, or 8-hour EC/OC samples; continuous meteorological data
EC/OC	Daily 24-hour EC/OC samples	3-, 5-, or 8-hour EC/OC samples; continuous meteorological data
NO_3^-	Daily 24-hour NO_3^- samples	3-, 5-, or 8-hour NO_3^- samples; continuous NO_x, O_3 measurements; continuous meteorological data
PAH and EC	Daily 24-hour PAH and EC samples	3-, 5-, or 8-hour EC samples; continuous meteorological data
SO_4^{2-}	Daily 24-hour SO_4^{2-} samples	3-, 5-, or 8-hour SO_4^{2-} samples; continuous SO_2, O_3 measurements; continuous meteorological data

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 $\mu g/m^3$, $R^2 = 0.989$) between the $PM_{2.5}$ FRM and a beta attenuation monitor with a well-impactor ninety-six $PM_{2.5}$ inlet (BAM-WINS).[8] Therefore, in addition to the comparisons outlined in Table 1, 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 $PM_{2.5}$ 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 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 shall be assessed.

If a monitor being verified meets these criteria, it may be used for comparison with other monitors being verified. If an additional method in use at a 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 shall be made. However, the temporal features that 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 that can be used to show temporal features will illustrate the utility of the tested methods.

3.6 Roles and Responsibilities

Verification tests shall be performed by Battelle with the participation of EPA, the vendors who will be having their monitors verified, and the test sites. The chart in Figure 1 shows the organization of responsibilities for Battelle, the vendor companies, EPA, and the test sites. Specific responsibilities are detailed below.

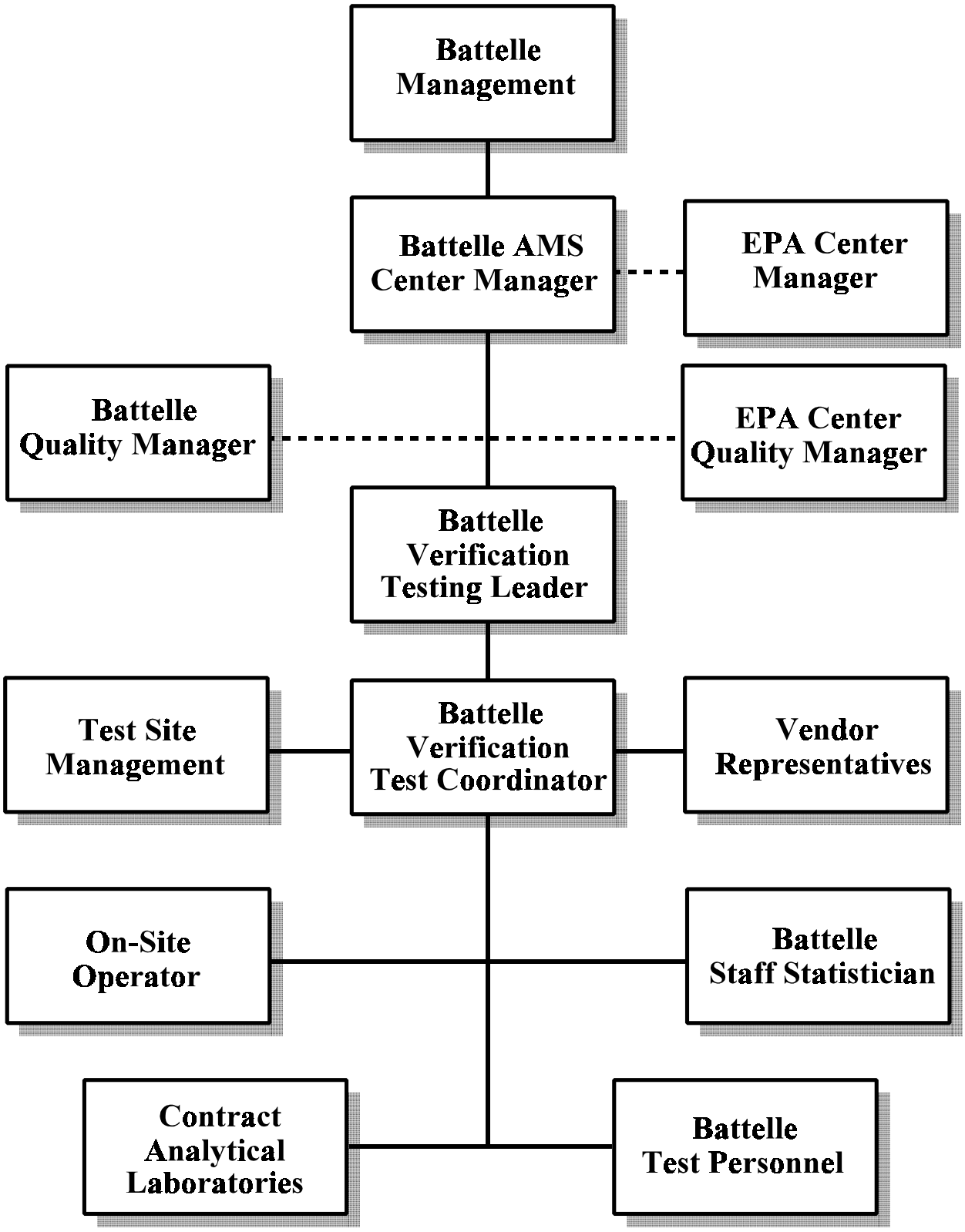

Figure 1. Organization Chart for Ambient Fine Particle Monitor Verification Test

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 shall

- Prepare a 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 distribution of the final test/QA plan, verification reports, and verification statements
- 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 Center shall provide technical guidance and oversee the various stages of verification testing and shall

- 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 Center Manager shall

- Review the draft test/QA plan
- Review the draft 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 AMS Center and ETV Quality Manager.

Battelle shall provide test personnel who assist as necessary during the verification test. The test personnel shall

- Assist in setting up and removing the monitors and testing equipment as needed
- Train on-site operators in operating procedures for Battelle-supplied equipment
- Ensure that confidentiality of vendor information is maintained.

Battelle shall provide a Staff Statistician who supports statistical and data analysis activities for this verification test. Specifically the Staff Statistician shall

- Assist in converting verification data from electronic spreadsheet format to appropriate file format for statistical evaluation
- Support the Verification Test Coordinator in performing statistical calculations specified in the test/QA plan on the verification data
- Provide results of statistical calculations and associated discussion for the verification reports
- 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 shall

- Review the draft test/QA plan
- Conduct a technical systems audit (TSA) 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 Center 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 and QMP are followed

- Ensure that Battelle management is informed if persistent quality problems are not corrected
- Interface with EPA's ETV Quality Manager.

3.6.2 Vendors

Vendor representatives shall

- 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 that adequate facilities are available
- Provide duplicate commercial-ready monitors for testing
- Install the monitors to be verified at each site and ensure proper operation before testing (vendors shall have access to the test sites at least one week in advance of testing during each phase)
- Provide a detailed checklist to on-site operators of items that should be checked to verify proper operation of monitors
- Provide an on-site operator or on-site technical support as needed
- Review and comment upon their respective draft verification reports and statements.

3.6.3 EPA

EPA's responsibilities in the AMS Center are based on the requirements stated in the "Environmental Technology Verification Program Quality and Management Plan for the Pilot Period (1995-2000)" (QMP)[11] or the most current update of this document. The roles of the specific EPA staff are as follows:

EPA's ETV Quality Manager shall

- Review the draft test/QA plan
- Perform, at his/her option, one external TSA during the verification test
- Notify the AMS Center Manager to facilitate a stop work order if an external audit indicates that data quality is being compromised
- Prepare and distribute an assessment report summarizing results of an external audit, if performed
- Review draft verification reports and statements.

EPA's AMS Center Manager shall

- 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 responsibilities of the test sites are to

- Assist in developing the test/QA plan for the verification test
- 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 test 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 the 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 test site's QA/QC procedures
- Review portions of the verification report to assure accurate descriptions of the test 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 shall hire on-site operators to assist, as necessary, in activities associated with verification tests that are not already performed by the test sites. The responsibilities of these on-site operators are to

- 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 the test/QA plan, to document 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

Verification tests rely on the results of various analytical measurements. Battelle shall secure the services of contract analytical laboratories to conduct these measurements. The responsibilities of these laboratories are to

- 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 TSA of laboratory facility, personnel, and procedures by Battelle and/or EPA staff.

4 TEST PROCEDURES

4.1 Field Testing

Field testing shall be conducted in two phases. At each site, data from the monitors being tested, the meteorological monitors, and the precursor gas monitors shall be collected continuously over the course of the verification test. Samples are 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 are 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 protocol, the test/QA plan, or the quality assurance plans in place at the respective sites and the analytical laboratories.

If the monitors being verified are already in operation at the field sites, the vendors shall perform appropriate calibration and maintenance on the monitors before testing begins. For those that are not, the vendor shall install and ensure the proper calibration and operation of the monitors to be verified at each site. Routine operation during the verification test shall be

observed by on-site operators after appropriate training by vendor staff. Instrument 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 shall 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 shall 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.

4.2 PAH Sampling

Particulate PAH data shall be obtained to verify commercial PAH monitors by means of a denuder/filter/sorbent train that separates vapor- and particle-phase PAHs. The method used for PAH determination is based on ASTM Method D 6209-98.[10] 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 determining 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.

4.2.1 Denuders

The denuders to be used for the verification test are based on those developed by Gundel and co-workers,[12] 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 determining the collected vapor-phase PAH.

The denuders used in the verification test may be commercial units such as those by URG Inc. and coated by Restek Corporation. The denuders to be used shall be appropriate for use with the sampler being used to collect the PAH samples. Preliminary chamber and field studies shall be performed to characterize the performance of the denuders before the verification test.

4.2.2 Other Sampling Components

Cleaned quartz fiber filters and XAD-2 resin traps shall be prepared by Battelle. Commercial quartz fiber filters shall be cleaned by heating in a muffle furnace in high-purity air and shall 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 is analyzed as a laboratory blank. A blank is 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).

4.2.3 Shipment of Sampling Components

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

4.2.4 PAH Sampling

Sampling for particle-phase PAH takes place at the test sites on each day of both test phases. At least 10% of the PAH samples collected and analyzed are field blanks. Field blanks are collected by inserting the filter/sorbent assembly into the sampler and removing the assembly without sampling.

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

4.2.5 PAH Analysis

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

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

5 MATERIALS AND EQUIPMENT

In general, verification tests rely 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 is operated and maintained by the personnel at the respective sites. In addition to the on-site equipment operated by the test site, Battelle shall provide the following equipment as needed.

5.1 FRM Sampler

A single-filter BGI PQ200 FRM sampler shall be provided, as needed, at the test sites for use during the verification test. Filter transport cases and extra filter cassettes shall 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, shall be provided, as needed, to the test sites for use during the verification test. Filter transport cases and extra filter cassettes also shall be provided.

5.3 PAH Sampler

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

- Commercial annular denuder coated with XAD-4 resin
- Quartz fiber filter
- Glass backup trap containing XAD-2 resin.

These components shall 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 shall 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 shall be shipped to the respective site before each phase of testing for installation on the sampling platform. These components shall be provided as either a stand-alone unit or as a train in a commercial speciation sampler (e.g., Andersen RAAS2.5-400).

5.4 Sampling Media

All materials necessary for sampling specifically associated with the verification test, including filters, denuders, and sorbent traps, shall be supplied by Battelle. Arrangements for delivery dates and locations shall be made with the respective test site management or on-site operators by the Verification Test Coordinator.

6 QUALITY ASSURANCE/QUALITY CONTROL

The verification effort relies in part on the QA/QC programs in place at the host sites. That is, the QA/QC procedures for the studies ongoing at each site will be adopted as part of the

verification test. These procedures should cover daily operation of the site equipment, calibration, sample collection and handling, laboratory analysis, and data collection and handling, as well as scheduled auditing. These procedures shall be followed by site staff throughout the duration of testing. Adherence to the data quality procedures that relate to the 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 shall be collected by the on-site operators daily during each phase of the test according to the procedures described in this protocol. After receipt by the on-site operators, filters and other necessary materials (i.e., denuders, polyurethane foam cartridges) used to collect samples, as well as 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 shall be transported to the site by the on-site operators to avoid contamination. Filters and other sampling materials 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 is accompanied by a chain-of-custody form during each step of its transport. Information on these forms is completed by the sample sender and recipient as needed. Sample run data forms documenting the sampling parameters are completed by the on-site operators for each sample. On-site operators shall forward these sample run data forms to the Verification Test Coordinator for approval within one week of the sampling date. The contract analytical laboratory shall forward the chain-of-custody forms to the Verification Test Coordinator for approval within one week of completing the sample analysis. Approval of these records shall 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, are recorded according to the site test plans and operating procedures. These data are 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 shall be kept confidential while under the control of Battelle.

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

6.3 Field QA/QC Activities

A variety of QA/QC activities shall 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 and 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 are conducted according to the procedures in place at the respective sites, and the results are 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 is verified through single point checks to ensure the proper operation of the samplers. These flow rate checks are conducted based on the procedures described in the respective manuals and are conducted at least once within one week of the beginning and once within one week of the end of each phase of the verification test. The flow rates are 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 ±4%. If ±5% agreement between the sampler flow rate and the nominal operating flow rate is not achieved, the sampler flow rate is manually adjusted to meet this performance criterion. If agreement between the sampler and audit flow meters does not meet the ±4% acceptance criterion, recalibration of the sampler flow meter is performed according to the procedures in the operator's manual.

6.3.2 Leak Checks

Internal and external leak checks of the reference samplers provided by Battelle shall be performed to ensure the integrity of the sampling system. These leak checks are performed based on the procedures described in the respective sampler manuals and are conducted at least weekly during each phase of the verification test. Leak checks of the FRM sampler are conducted after each cleaning of the WINS impactor in the FRM sampler. The WINS impactor shall be cleaned at least once every five 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 shall be conducted based on the procedures described in the respective manuals. These checks are 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 shall 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 are collected by placing the sampling media in the sampler and removing without sampling. At least 10% of the collected samples shall be field blanks. The acceptance criteria and corrective actions for the field blanks are established based on procedures in place at the respective contract analytical laboratories (based on historical averages if available).

At least one field blank for the PAH sampler will be collected within the first three 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 are 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 is investigated, and the sample is flagged as of questionable validity.

6.3.5 Collocated Samplers

The precision of the reference methods provided by Battelle shall be established by collocating each reference sampler with an identical or a similar sampler. The collocated samplers are placed within four meters of each other and collect at least five 24-hour samples to establish precision. This collocated sampling shall 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 is investigated, additional samples are collected, and the analyses are repeated.

For the chemical speciation (nitrate, sulfate, carbon, and PAH) reference methods, the duplicate samples are 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 is investigated; and, if possible, additional samples are collected, and the analyses are 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, should be 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 shall conduct the PAH analysis according to procedures based on ASTM Method D-6209-98.[10] 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 sorbent/filter assembly from each batch of prepared assemblies shall be analyzed as a laboratory blank. These blanks undergo the same preparation and handling procedures as those traps that are shipped to the test sites for sampling, but will not be shipped or exposed to sampling. The laboratory blanks shall be analyzed at the same time as the PAH samples. Acceptance criteria and corrective actions for these laboratory blanks are the same as those for the PAH field blanks.

6.4.2 Analytical Duplicates

For the PAH analyses, an analytical duplicate of one sample shall 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 shall be investigated and the analyses repeated, if possible.

6.4.3 Analytical Spikes

Analytical spikes shall be used to assess the accuracy of the PAH analytical method. Each sample is 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 the range of 70 to 130% to be acceptable. If this agreement criterion is not met, the source of the discrepancy shall be investigated and appropriate corrective action taken.

6.5 Assessments and Audits

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

6.5.1 Performance Evaluation Audits

6.5.1.1 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, shall 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 QA activities are provided in the test plans or in the standard operating procedures for the respective site or analytical laboratory. When possible Battelle QA staff shall be present during the performance of these audits.

6.5.1.2 Reference Methods Supplied by Battelle

Performance evaluation audits of the reference method equipment supplied by Battelle shall 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 in Section 6.3 with the same acceptance criteria and corrective actions. These audits are conducted using sensors with National Institute of Standards and Technology-traceable calibrations that are not those used for the usual checks described in Section 6.3, but may be traceable to the same primary standards. The audits shall be observed by Battelle staff when possible and, when possible, shall be performed by someone other than the usual on-site operator. These performance evaluation audits shall be conducted at least once during each phase of the verification test, within one month of the beginning of each phase.

6.5.2 Technical Systems Audits

Battelle's Quality Manager shall perform a TSA at least once during each phase of the verification test. The purpose of this audit is to ensure that the verification test is being performed in accordance with AMS Center QMP[1] and this test protocol and that all QA/QC procedures are being implemented. During this audit, the Quality Manager reviews the reference methods used, compares actual test procedures to those specified or referenced in this protocol, and reviews data

acquisition and handling procedures. This effort includes reviewing the procedures used at the test site for compliance with this protocol and with the SOPs for the respective site. When possible, a TSA of the contract analytical laboratories shall be conducted to ensure that analyses are being performed in accordance with the requirements of this protocol and the SOPs of the laboratory. A TSA report shall be prepared, including a statement of findings and the actions taken to address any adverse findings.

At EPA's discretion, the EPA ETV Quality Manager also may conduct an independent TSA of the verification testing procedures. In any case, the EPA ETV Quality Manager shall review Battelle's TSA report and provide comments on the findings and actions presented in that report.

6.5.3 Audits of Data Quality

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

6.6 Reporting

Each audit shall be documented in accordance with the AMS Center QMP.[1] Audit reports include the following:

- Identification of any adverse findings or potential problems
- Corrective actions that address adverse findings or potential problems
- Confirmation by Battelle's Quality Manager that the corrective actions 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 ETV Quality Managers, during the course of any audit, shall 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 audit report has been prepared, the Verification Test Coordinator ensures that a response is provided for each adverse finding or potential problem, and implements any necessary follow-up corrective action. The Battelle Quality Manager shall ensure that follow-up corrective action has been taken.

7 DATA HANDLING AND REPORTING

7.1 Data Acquisition

A variety of data shall 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, are transferred to Battelle either electronically or in hard copy for subsequent reduction and analysis. Other data, namely PAH concentrations, are generated by Battelle. These data are compiled in electronic format and shared with the host sites. In all cases, strict confidentiality of the verification data is maintained for each participating vendor. This is accomplished in part by storing electronic data under separate and clearly identifiable computer file names. All hard copy information similarly is maintained in separate files. At no time during verification testing shall 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 is 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 shall 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. The review is 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 is 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 is 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 protocol.

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 shall be assessed only for monitors that yield measurements with the same units of measure as the reference method with which it is being compared. The relationship between the two is 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:

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

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 β are the intercept and slope parameters, respectively, and ϵ_i is error unexplained by the model. The average of continuous measurements is used because it is the quantity that is most comparable to the reference sampler measurements.

Comparability is 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 is 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 $C_i = R_i + \epsilon_i$ (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 is determined independently for each of the two duplicate monitors being tested and assessed separately for each phase of the verification test.

7.3.2 Predictability

Predictability shall be assessed for continuous monitors that report results in units that are different than those of the reference method with which it is being compared. In these cases the reported predictability is 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 shall 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 is 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 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% prediction interval is calculated for conversion from monitor measurement units to lower and upper bounds on reference method measurement units.

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

7.3.3 Precision

The intra-method precision of the continuous monitors shall 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 are paired and the behavior of their differences used to assess precision. The following statistics shall 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 shall 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 is 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 shall be evaluated by using meteorological data such as temperature and humidity as parameters in multi-variable analyses of the reference/monitor comparison data. The model to be used is as follows:

$$C_i = \mu + \beta \times R_i + \Sigma \gamma_j \times X_{ji} + \epsilon_i \qquad (2)$$

where the X_{ji}'s are meteorological and/or precursor gas measurements for the i^{th} 24-hour time period, the γ_j's are the associated slope parameters, and other notation is as before. Comparability and predictability results are reported again after these variables are adjusted for in the model. Additionally, estimates and standard errors of the γ_j's shall be provided. Meteorological effects and precursor gas interferences are assessed independently for each of the two monitors being tested and assessed separately for each phase of the verification test.

7.3.5 Short-Term Monitoring Capabilities

The capabilities of these monitors also shall be assessed by comparison to reference samples collected over short sampling periods (i.e., three to eight hours). This assessment is based on linear regression analysis of the averaged short-term sampling results from the continuous monitors against the reference results. The analysis shall be conducted and the results reported in a fashion identical to that for the comparability and predictability assessments described in Sections 7.3.1 and 7.3.2 that are based on 24-hour samples.

Short-term comparisons are made only after establishing the relationship between the short-term reference sampling results and the corresponding 24-hour reference results. The relationship between the two sets of reference measurements is established by linear regression using the weighted 24-hour 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 is assessed using equation (1), replacing the average of continuous measures with the weighted average of short-term sampler measurements. The short-term sampling results also shall be used to assess the effects of meteorological conditions and precursor gas concentrations on the response of the monitors. These short-term results are used in place of the 24-hour measurements in the analysis described in Section 7.3.4. Independent assessments are made for the duplicate monitors, and the data from each phase of testing are 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 that other monitors are in use on site that are adequately comparable to the $PM_{2.5}$ FRM. A continuous monitor shall 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 shall consist of overlaid time-series plots of measurements. Such plots allow visual inspection of similarities and dissimilarities in measurements and temporal patterns over the entire period of data collection. Similar overlaid time-series plots shall be made with the results from the continuous meteorological and precursor gas monitors when appropriate. Qualitative comparisons are made separately for each of the two monitors being tested and for each phase of the verification test.

7.4 Reporting

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

The verification report shall briefly describe the ETV program, the AMS Center, and the procedures used in verification testing. The parties involved in the verification test shall be identified and the roles of each described. These sections will be common to each verification report resulting from this verification test. The results of the verification test shall 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 shall be descriptions of the following parameters:

- Operating conditions during testing
- Instrument settings used during testing
- 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, the final approval, and the distribution of the reports will be conducted as stated in the "Generic Verification Protocol for the Advanced Monitoring Systems Pilot."[13] Preparation, approval, and use of verification statements summarizing the results of this test also are subject to the requirements of that same protocol.

After approval, the final verification reports and verification statements shall be made available to the respective vendors as hard copy and will be posted on the ETV Web site (www.epa.gov/etv/centers/center1.html). The reports also may be presented or made available at various technical conferences and trade shows.

8 HEALTH AND SAFETY

Before each phase of testing begins, site management shall 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 shall operate under these established requirements and guidelines. It is expected that, while on-site, EPA and vendor staff shall also operate according to these requirements.

9 REFERENCES

1. "Quality Management Plan (QMP) for the ETV Advanced Monitoring Systems Center," Version 3.0, U.S. EPA Environmental Technology Verification Program, Battelle, Columbus, OH, December 2001.

2. "National Primary and Secondary Ambient Air Quality Standards," 40 CFR Part 50, Federal Register, 62 (138):38651-38760, July 18, 1997.

3. "Research Priorities for Airborne Particulate Matter," National Academy Press, National Research Council, Washington, DC, 1998.

4. "Ambient Air Quality Surveillance," 40 CFR Part 58, Federal Register, 62 (138):38830-38854, July 18 (1997).

5. "Measurement Methods to Determine Compliance with Ambient Air Quality Standards for Suspended Particles," J. C. Chow, *J. Air & Waste Manage. Assoc.*, **48**, 320-382, (1995).

6. A complete list of designated methods can be downloaded from: http://www.epa.gov/ttnamti1/files/ambient/criteria/699pm.pdf

7. "Guidance for Using Continuous Monitors in $PM_{2.5}$ Monitoring Networks," U.S. EPA, Office of Air Quality Planning and Standards, Research Triangle Park, NC, 1998.

8. "Instrument Intercomparison Study - Bakersfield, CA 1998-1999," California Air Resources Board, Sacramento, CA, 1999.

9. "Guideline on Speciated Particulate Monitoring," U.S. EPA, Office of Air Quality Planning and Standards, Research Triangle Park, NC, 1999.

10. "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)," American Society for Testing and Materials, Method D 6209-98, in *Annual Book of Standards, Vol. 11.03*, West Conshohoken, PA, 1998.

11. "Environmental Technology Verification Program Quality and Management Plan for the Pilot Period (1995-2000)," U.S. EPA, EPA-600/R-98/064, Cincinnati, OH, May 1998.

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

13. “Generic Verification Protocol for the Advanced Monitoring Systems Pilot,” U.S. EPA, Environmental Technology Verification Program, Battelle, Columbus, Ohio, October 1998.

APPENDIX A

Example QA/QC Report Forms

SAMPLE RECEIPT

STUDY #: _____ **SPONSOR:** _____

RESPONSIBLE PERSON: _____ **COURIER:** _____

RECEIVED FROM: _____ **TEST MATERIAL:** _____

TRACKING #: _____ **SHIPPING DATE:** _____

RECEIVED BY/DATE: _____ **RECEIPT TIME:** _____

SAMPLE ID	SAMPLE DESCRIPTION	COMMENTS

SAMPLE RECEIPT CONDITION: **FROZEN** **COLD** **RT** **OTHER**

STORAGE LOCATION: **TIME:** _____

WALK-IN FREEZER:	**ROOM** _____, **X48684, ≤-15°C**
SAMPLE REFRIGERATOR:	**ROOM** _____, **X34511, 1-9°C**
SAMPLE REFRIGERATOR:	**ROOM** _____, **X36012, 1-9°C**
SAMPLE REFRIGERATOR:	**ROOM** _____, **S/N 842, 1-9°C**
ROOM TEMPERATURE STORAGE:	**ROOM** _____

ADDITIONAL COMMENTS: _____

_____

_____

DISTRIBUTION: ORIGINAL - STUDY FILE

Single-Filter $PM_{2.5}$ Sampler Run Data Sheet

Set-Up Date and Time:_____ Retrieval Date and Time:_____

Site Name:_____ Sampler ID:_____

Sampler Model:_____ Well number:_____ Installation Date: _____

Start Date _____ Stop Date _____ Retrieval Date _____

Start Time_____ Stop Time _____ Elapsed Time _____

Field

Set-up Date and time:_____

	Sampler	**Check Data**	**Check Device**
Ta	_____	_____	_____
Pa	_____	_____	_____
Q	_____	_____	_____

Initial and final conditions (as retrieved from sampler screen or data storage if available):

	Run Start	**Run End**
Date	_____	_____
Time	_____	_____
Indicated P_a (mm Hg)	_____	_____
Indicated Q (L/min)	_____	_____
Indicated T_a (°C)	_____	_____
Indicated Q_{avg} (L/min)	_____	_____
Indicated Q_{cv}	_____	_____
Volume sampled (m^3)	_____	_____

Sample retrieval date and time:_____ Sample ship date:_____

	Yes	No		Yes	No
Was sample shipped cold?	☐	☐	Questionable sample?	☐	☐

Laboratory

Filter Information: Sample receipt date and time:_____

	Max.	Min.	Upon opening
Interior temp of filter transit container (°C):	____	____	_____

Filter ID:_____ Initial weight:_____mg Final weight:_____mg

Calculated concentration:_____$\mu g/m^3$

Notes:_____

Setup Operator:_____ End Operator:_____

Reviewed by:_____ Date:_____

BAR CODE GOES HERE	$PM_{2.5}$ STN CUSTODY AND FIELD DATA FORM	White – return to lab Yellow – site retains Pink – lab retains
Custody/Data Form No.		

A. CUSTODY RECORD (Name, Date)

1. Laboratory, Out _____ 3. Site, Out _____
2. Site, In _____ 4. Lab, In _____

B. SITE AND SAMPLER INFORMATION

1. Site AIRS Code _____ 5. Site Name _____
2. Sampler S/N _____ 6. Intended date of use _____
3. Sampler Type _____ 7. Date of sampler set-up _____
4. Sampler POC _____ 8. Operator's name _____

C. SAMPLER CHANNEL COMPONENTS

Channel Number	Component ID No.	Component Description
1	I1234567	RAAS cassette (Teflon filter) (GREEN)
2	Kept at Site	RASS denuder assembly (MgO) (RED)
2	I1234569	RAAS cassette (nylon filter) (RED)
5	I1234570	RAAS cassette (quartz filter) (ORANGE)
4	Kept at Site	RAAS cassette (Teflon or other type filter) (BLUE)

D. START, END, AND RETRIEVAL TIMES

Channel No.	Start date	Start time	End date	End time	Retrieval date	Retrieval time
1						
2						
5						
4						

E. SAMPLER CHANNEL INFORMATION (Post-Sampling)

Channel No.	Elapsed sample time	E. S. time Flag	Sample Volume (m3)	Avg. flow (L/min)	Avg. ambient T (°C)	Max. ambient T (°C)	Min. ambient T (°C)
1							
2							
5							
4							

Channel No.	Avg. BP (mm Hg)	Max. BP (mm Hg)	Min. BP (mm Hg)	▲T Flag	▲Flow Flag	Pump P (mm Hg)	Manifold T (°C)
1							
2							
5							
4							

F. Comments _____

(Revised 9/27/99: 5200)