

US EPA ARCHIVE DOCUMENT

Environmental Technology Verification Report

RUPPRECHT & PATASHNICK, CO.
SERIES 8400S AMBIENT PARTICULATE
SULFATE MONITOR

Prepared by



Battelle

Under a cooperative agreement with



ETV ✓ ETV ✓ ETV ✓

VERIFICATION TEST DESCRIPTION

The objective of this verification test is to provide quantitative performance data on continuous fine particle monitors under a range of realistic operating conditions. To meet this objective, field testing was conducted in two phases in geographically distinct regions of the United States during different seasons of the year. The first phase of field testing was conducted at the ambient air monitoring station on the Department of Energy's National Energy Technology Laboratory campus in Pittsburgh, PA, from August 1 to September 1, 2000. The second phase of testing was performed at the California Air Resources Board's ambient air monitoring station in Fresno, CA, from December 18, 2000, to January 17, 2001. Particulate sulfate levels differed considerably in the two phases, ranging from about 2 to 22 $\mu\text{g}/\text{m}^3$ in Phase I, as 24-hour averages, but ranging only up to 3.8 $\mu\text{g}/\text{m}^3$ in Phase II. Specific performance characteristics verified in this test include inter-unit precision, agreement with and correlation to time-integrated reference methods, effect of meteorological conditions, and influence of precursor gases. The Series 8400S reports measurement results in terms of particulate sulfate concentration and, therefore, was compared with reference sulfate concentrations determined by ion chromatography of particulate matter samples collected on a filter. Additionally, comparisons with a variety of supplemental measurements were made to establish specific performance characteristics.

Quality assurance (QA) oversight of verification testing was provided by Battelle and EPA. Battelle QA staff conducted a data quality audit of 10% of the test data, and an internal technical systems audit for Phase I and Phase II. EPA QA staff conducted an external technical systems audit during Phase II.

TECHNOLOGY DESCRIPTION

The Series 8400S uses a flash volatilization technique to measure the concentration of total particulate sulfur (which is assumed to be sulfate) contained in $\text{PM}_{2.5}$. The Series 8400S consists of a weather-protection inlet and transport tubing, pulse generator, microprocessor-based control system, user interface, sulfur detector, sample pump, and gas cylinder. Built-in software and hardware automatically calibrate and verify zero and span. Bidirectional RS-232 communication provides the capability for remote data interchange and internal data storage. A stream of ambient air containing particulate matter enters the sample inlet line beneath a rain cap mounted above the roof of the air quality monitoring station. A sheath flow surrounds the sample line, and then enters the sample processing section of the pulse generator after being filtered. The sheath air flow is designed to keep the sample stream and inside of the instrument as close as possible to the ambient air temperature. A $\text{PM}_{2.5}$ sharp cut cyclone removes the larger particles from the sample stream. A bypass flow, which shortens the residence time of the sample stream in the sampling section, passes through a critical orifice. An activated charcoal denuder removes acidic gases that would otherwise interfere with the measurement of the ambient particulate sulfate concentration. To achieve high collection efficiencies even for very small secondary aerosols, a humidifier moistens the sample stream and causes the hygroscopic sulfate particles to grow. The remaining part of the sample stream forms a jet as it passes through a critical orifice. Particles collect on an impactor/flashing strip during the sample collection phase (eight minutes by default). The sample and bypass flows then combine and exit from the instrument on their way to an external pump. Flash volatilization of the collected particulate matter in an air atmosphere occurs at over 600°C through the resistive heating of the metal impactor/flashing strip, which creates a pulse of sulfur dioxide that is quantified in the sulfur detector. A constant flow of ambient air keeps the pulse generator at ambient temperature. The Series 8400S computes a new data point every 10 minutes, with a resolution of the reported values of $\pm 0.2 \mu\text{g}/\text{m}^3$. The Series 8400s is a new instrument; pre-production versions were tested in this verification, and commercial production instruments became available in May 2001.

VERIFICATION OF PERFORMANCE

Inter-Unit Precision: The duplicate Series 8400S monitors were operated for only a few days near the end of Phase I of the verification test as a result of unexpected delays in the manufacturing schedule. Consequently only limited data are available for verification and the results of Phase I may not accurately represent the performance of these monitors. For the hourly data from Phase I, the linear regression analysis showed a slope of 1.09 (0.17),

an intercept of 1.47 (0.71) $\mu\text{g}/\text{m}^3$, and an r^2 value of 0.639, where the values in parentheses are 95% confidence intervals. The regression results of the 24-hour average data (only four data points) show a slope of 0.84 (2.03), an intercept of 2.4 (8.3) $\mu\text{g}/\text{m}^3$, and an r^2 value of 0.614. During Phase II of verification testing, the regression results of the hourly data show a slope of 0.981 (0.60), an intercept of 0.12 (0.08), and an r^2 value of 0.855. For the 24-hour data, the regression results show a slope of 0.969 (0.272), an intercept of 0.20 (0.36) $\mu\text{g}/\text{m}^3$, and an r^2 value of 0.848. For both hourly and 24-hour comparisons in both phases, the slopes are not statistically different from unity.

Comparability/Predictability: For Phase I, the 24-hour average results from the duplicate Series 8400S monitors were compared by linear regression to the sulfate reference results. Again, because of the limited data available from the Series 8400S monitors, these results may not accurately represent the performance of these monitors. The regression results for Monitor 1 show a slope of 0.26 (0.56), an intercept of 2.9 (5.5) $\mu\text{g}/\text{m}^3$, and an r^2 value of 0.288, based on six data points. For Monitor 2, the regression results show a slope of 0.60 (4.58), an intercept of 2.23 (51.7) $\mu\text{g}/\text{m}^3$, and an r^2 value of 0.436, based on three data points. During Phase II, reference sulfate measurements were collected on a 5-per-day schedule. Comparisons of the Series 8400S results to the sulfate reference measurements showed a slope of 1.12 (0.18), an intercept of 0.12 (0.24) $\mu\text{g}/\text{m}^3$, and an r^2 value of 0.681 for Monitor 1. For Monitor 2, the regression results show a slope of 1.18 (0.18), an intercept of 0.18 (0.20) $\mu\text{g}/\text{m}^3$, and an r^2 value of 0.735. No significant bias relative to the reference data is indicated by these results.

Meteorological Effects: No conclusions about meteorological effects during Phase I could be obtained from a multivariable analysis, because of the limited data available from the Series 8400S monitors. The multivariable model ascribed to temperature and barometric pressure an influence on the readings of one monitor relative to the sulfate reference measurements at a 90% confidence level during Phase II. The multivariable results differed by 7% from simple linear regression against the reference data, for average Phase II conditions.

Influence of Precursor Gases: No conclusions about precursor gas influence could be obtained from a multivariable analysis during Phase I because of the limited data available from the Series 8400S monitors. The multivariable model of Phase II data ascribed to nitric oxide and nitrogen oxides an influence on the readings of one monitor, and to ozone an influence on the readings of the other monitor, relative to the sulfate reference measurements at the 90% confidence level. The multivariable results for Monitors 1 and 2 differed by 5.8% and 9.3%, respectively, from the linear regression results.

Other Parameters: Due to the shortened test period, no maintenance of the Series 8400S monitors was required in Phase I other than replacement of gas cylinders. In Phase II, flash strips required frequent (several times per week) replacement, and each monitor also required the replacement of at least one internal electronic circuit board. As a result of the high level of maintenance required, only about 40% data recovery was achieved during Phase II. The vendor indicates that these problems with flash strips and electronics have been addressed in production units of the monitor; the vendor indicates a minimum replacement interval of two weeks for the flash strips.

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August 2001

Environmental Technology Verification Report

ETV Advanced Monitoring Systems Center

Rupprecht & Patashnick, Co.
Series 8400S Ambient Particulate Sulfate
Monitor

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Notice

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Foreword

The U.S. EPA is charged by Congress with protecting the nation's air, water, and land resources. Under a mandate of national environmental laws, the Agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. To meet this mandate, the EPA's Office of Research and Development provides data and science support that can be used to solve environmental problems and to build the scientific knowledge base needed to manage our ecological resources wisely, to understand how pollutants affect our health, and to prevent or reduce environmental risks.

The Environmental Technology Verification (ETV) Program has been established by the EPA to verify the performance characteristics of innovative environmental technology across all media and to report this objective information to permittees, buyers, and users of the technology, thus substantially accelerating the entrance of new environmental technologies into the marketplace. Verification organizations oversee and report verification activities based on testing and quality assurance protocols developed with input from major stakeholders and customer groups associated with the technology area. ETV consists of six technology centers. Information about each of these centers can be found on the Internet at <http://www.epa.gov/etv/>.

Effective verifications of monitoring technologies are needed to assess environmental quality and to supply cost and performance data to select the most appropriate technology for that assessment. In 1997, through a competitive cooperative agreement, Battelle was awarded EPA funding and support to plan, coordinate, and conduct such verification tests for "Advanced Monitoring Systems for Air, Water, and Soil" and report the results to the community at large. Information concerning this specific environmental technology area can be found on the Internet at http://www.epa.gov/etv/07/07_main.htm.

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List of Abbreviations

ADQ	audit of data quality
AMS	Advanced Monitoring Systems
CARB	California Air Resources Board
CI	confidence interval
CO	carbon monoxide
CV	coefficient of variation
DOE	U.S. Department of Energy
DRI	Desert Research Institute
EPA	U.S. Environmental Protection Agency
ETV	Environmental Technology Verification
FRM	federal reference method
H ₂ S	hydrogen sulfide
IC	ion chromatography
IMPROVE	Interagency Monitoring for Protection of Visual Environments
L/min	liters per minute
m	meters
mm	millimeters
NETL	National Energy Technology Laboratory
N ₂	nitrogen
NIST	National Institute of Standards and Technology
NO	nitric oxide
NO ₂	nitrogen dioxide
PVC	polyvinyl chloride
QA/QC	quality assurance/quality control
QMP	quality management plan
R&P	Rupprecht & Patashnick
SFS	sequential filter sampler
TOR	thermal optical reflectance
TSA	technical systems audit
µg	microgram

Chapter 1 Background

The U.S. Environmental Protection Agency (EPA) has created the Environmental Technology Verification (ETV) Program to facilitate the deployment of innovative environmental technologies through performance verification and dissemination of information. The goal of the ETV Program is to further environmental protection by substantially accelerating the acceptance and use of improved and cost-effective technologies. ETV seeks to achieve this goal by providing high-quality, peer-reviewed data on technology performance to those involved in designing, distributing, permitting, purchasing, and using environmental technologies.

ETV works in partnership with recognized testing organizations; with stakeholder groups consisting of regulators, buyers, and vendor organizations; and with the full participation of individual technology developers. The program evaluates the performance of innovative technologies by developing test plans that are responsive to the needs of stakeholders, conducting field or laboratory tests (as appropriate), collecting and analyzing data, and preparing peer-reviewed reports. All evaluations are conducted in accordance with rigorous quality assurance protocols to ensure that data of known and adequate quality are generated and that the results are defensible.

The EPA's National Exposure Research Laboratory and its verification organization partner, Battelle, operate the Advanced Monitoring Systems (AMS) Center under ETV. The AMS Center recently evaluated the performance of fine particle monitors for use in continuous monitoring of fine particulate matter in ambient air. This verification report presents the procedures and results of the verification test for the R&P Series 8400S particulate sulfate monitor.

Chapter 2 Technology Description

The following description of the Series 8400S particulate sulfate monitor is based on information provided by the vendor. The Series 8400S is a new instrument. Pre-production versions were tested in this verification; commercial production units became available in May 2001.

The Series 8400S uses a flash volatilization technique to measure the concentration of particulate sulfur (which is assumed to originate from sulfate) contained in $PM_{2.5}$. The Series 8400S consists of a weather-protection inlet and transport tubing, pulse generator, microprocessor-based control system, user interface, sulfur detector, sample pump, and gas cylinder. Built-in software and hardware automatically calibrate and verify zero and span. Bidirectional RS-232 communication provides the capability for remote data interchange and internal data storage.

A stream of ambient air containing particulate matter enters the sample inlet line beneath a rain cap mounted above the roof of the air quality monitoring station. A sheath flow surrounds the sample line, and then enters the sample processing section of the pulse generator after being filtered. The sheath air flow is designed to keep the sample stream and inside of the instrument as close as possible to the ambient air temperature. A $PM_{2.5}$ sharp cut cyclone removes the larger particles from the sample stream. A bypass flow, which shortens the residence time of the sample stream in the sampling section, passes through a critical orifice. An activated charcoal denuder removes acidic gases that would otherwise interfere with the measurement of the ambient particulate sulfate concentration.



Figure 2-1. Rupprecht & Patashnick, Co. Series 8400S Particulate Sulfate Monitor

To achieve high collection efficiencies even for very small secondary aerosols, a humidifier moistens the sample stream and causes the hygroscopic sulfate particles to grow. The remaining part of the sample stream forms a jet as it passes through a critical orifice. Particles collect on an impactor/flushing strip during the sample collection phase (eight minutes by default). The sample and bypass flows then combine and exit from the instrument on their way to an external pump. Flash volatilization of the collected particulate matter in an air atmosphere occurs at over $600^{\circ}C$ through the resistive heating of the metal

impactor/flushing strip, which creates a pulse of sulfur dioxide that is quantified in the sulfur detector. A constant flow of ambient air keeps the pulse generator at ambient temperature. The Series 8400S computes a new data point every 10 minutes, with a resolution of the reported values of $\pm 0.2 \mu\text{g}/\text{m}^3$.

Chapter 3 Test Design and Procedures

3.1 Introduction

The objective of this verification test is to provide quantitative performance data on continuous fine particle monitors under a range of realistic operating conditions. To meet this objective, field testing was conducted in two phases in geographically distinct regions of the United States during different seasons of the year. Performing the test in different locations and in different seasons allowed sampling of widely different particulate matter concentrations and chemical composition. At each site, testing was conducted for one month during the season in which local PM_{2.5} levels were expected to be highest. The verification test was conducted according to the procedures specified in the *Test/QA Plan for Verification of Ambient Fine Particle Monitors*.⁽¹⁾

The first phase of field testing was conducted at the ambient air monitoring station on the Department of Energy's (DOE's) National Energy Technology Laboratory (NETL) campus in Pittsburgh, PA. Sampling during this phase of testing was conducted from August 1 to September 1, 2000. The second phase of testing was performed at the California Air Resources Board's (CARB's) Air Monitoring Station in Fresno, CA. This site is also host to one of the EPA's PM_{2.5} Supersites being managed by Desert Research Institute (DRI). This phase of testing was conducted from December 18, 2000, to January 17, 2001.

3.2 Test Design

Specific performance characteristics verified in this test include

- Inter-unit precision
- Agreement with and correlation to time-integrated reference methods
- Effect of meteorological conditions
- Influence of precursor gases.

To assess inter-unit precision, duplicate Series 8400S monitors were tested in side-by-side operation during each phase of testing. During Phase I, the Series 8400S monitors tested were Serial Numbers 0007 and 0008. In Phase II, the Series 8400S monitors were Serial Numbers 2014 and 2015. Collocation of the Series 8400S monitors with reference systems for time-integrated sampling of fine particulate mass and chemical speciation provided the basis for assessing the degree of agreement and/or correlation between the continuous and reference methods. Each test site was equipped with continuous monitors to record meteorological

conditions and the concentration of key precursor gases (ozone, nitrogen oxides, sulfur dioxide, etc.). The data from the meteorological and gas monitors were used to assess the influence of these parameters on the performance of the fine particle monitors being tested. Statistical calculations, as described in Chapter 5, were used to establish each of these performance characteristics.

Additionally, other performance characteristics of the technologies being verified, such as reliability, maintenance requirements, and ease of use, were assessed. Instrumental features that may be of interest to potential users (e.g., power and shelter requirements, and overall cost) are also reported.

3.3 Reference Method and Supplemental Measurements

Since no appropriate absolute standards for fine particulate matter exist, the reference methods for this test were well established, time-integrated methods for determining particulate matter mass or chemical composition. It is recognized that comparing real-time measurements with time-integrated measurements does 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-integrated standard methods that are widely accepted was necessary for performance verification purposes. It should be noted that there are necessary differences between continuous and time-integrated, filter-based techniques. For example, in time-integrated sampling, particulate matter collected on a filter may remain there for up to 24 hours, whereas continuous monitors generally retain the particulate sample for one hour or less. Thus, the potential for sampling artifacts differs.

The Series 8400S reports measurement results in terms of particulate sulfate concentration. As such the measurements from the Series 8400S were compared with results of ion chromatography (IC) analysis of collected particulate matter samples. Additionally, comparisons with a variety of supplemental measurements were made to establish specific performance characteristics. Descriptions of the reference method and supplemental measurements used during the verification test are given below.

3.3.1 Sulfate Reference Method

The primary comparisons of the Series 8400S sulfate readings were made relative to IC results for particulate sulfate. This technique involves collection of particulate matter samples and subsequent digestion and analysis of the collected sample.⁽⁴⁾

During Phase I, all sulfate reference samples were collected using an Anderson RAAS PM_{2.5} speciation sampler. Samples were collected daily (i.e., over 24-hour periods) at a normal flow rate of 7.3 L/min on nylon filters downstream of a magnesium oxide-coated compound annular denuder. The samples were collected and analyzed by Consol Energy, of Library, PA, under subcontract with Battelle.

A medium-volume sequential filter sampling system (SFS) sampling at a total flow rate of 113 L/min was used to collect the short-term mass and speciation samples during Phase II. The SFS was configured to take two simultaneous samples (i.e., Teflon-membrane/drain disk/quartz-fiber and quartz-fiber/sodium-chloride-impregnated cellulose-fiber filter packs) at 20 L/min through each sampling port. Anodized aluminum nitric acid denuders were located between the inlets and the filters to remove gaseous nitric acid. The remaining 73 L/min required for the 113 L/min total inlet flow was drawn through a makeup air sampling port inside the plenum. Solenoid valves, controlled by a timer, switched between sets of five filters at midnight each day. A vacuum pump drew air through the paired filter packs when the valves were open. Each set of filters was programmed to carry out sampling in five periods each day (0000-0500, 0500-1000, 1000-1300, 1300-1600, and 1600-2400). The flow rate was controlled by maintaining a constant pressure across a valve with a differential pressure regulator.

The filters were loaded at the DRI's Reno, NV, laboratory into modified Nuclepore filter holders that were plugged into quick-disconnect fittings on the SFS. One filter pack contained a 47-mm-diameter Teflon-membrane filter with quartz-fiber backup filter. A drain disc was placed between the Teflon-membrane and quartz-fiber filters to ensure a homogeneous sample deposit on the front Teflon-membrane filter and to minimize fiber transfer from one filter to the other. The Teflon-membrane filter collected particles for mass and elemental analysis. The other filter pack contained a 47-mm-diameter quartz-fiber filter with a sodium-chloride-impregnated cellulose-fiber backup filter on a separate stage. The deposit on the quartz-fiber filter was analyzed for sulfate, nitrate, and carbon. The sodium-chloride-impregnated cellulose-fiber backup filter was analyzed for nitrate to estimate losses due to volatilization of ammonium nitrate from the front filter during sampling.

Collocated samples were collected during Phase I to establish the precision of the reference method. Precision estimates for Phase II, are based on previously reported results. A discussion of the collocated sampling is presented in Section 4.4 of this report.

3.3.2 Supplemental Measurements

Various supplemental measurements were used to further establish the performance of the continuous monitors being tested. Meteorological conditions were monitored and recorded continuously throughout each phase of the verification test. These measurements included temperature, relative humidity, wind speed, direction, barometric pressure, and solar radiation. These data were provided to Battelle for Phase I by DOE/NETL and for Phase II by DRI. Likewise, the ambient concentrations of various precursor gases including ozone and nitrogen oxides also were measured continuously during the verification test and used to assess the influence of these parameters on the performance of the monitors tested. Continuous measurements of sulfur dioxide, hydrogen sulfide, nitric oxide, nitrogen dioxide, nitrogen oxides, and ozone were provided for Phase I by DOE/NETL; and continuous measurements of carbon monoxide, ozone, nitric oxide, nitrogen dioxide, and nitrogen oxides were provided for Phase II by DRI. These gases were of interest as potential chemical precursors to aerosol components, and as indicators of ambient pollutant levels.

3.4 Data Comparisons

The primary means used to verify the performance of the Series 8400S monitors was comparison with the IC sulfate results of samples from the reference samplers. Additional comparisons were made with the supplemental meteorological conditions and precursor gas concentrations to assess the effects of these parameters on the response of the monitors being tested. The comparisons were based on statistical calculations as described in Section 5 of this report.

Comparisons were made independently for the data from each phase of field testing; and, with the exception of the inter-unit precision calculations, the results from the duplicate monitors were analyzed and reported separately. Inter-unit precision was determined from a statistical inter-comparison of the results from the duplicate monitors.

3.5 Site Layout/Instrument Installation

In each phase of testing, the two Series 8400S monitors were installed and operated in a Battelle instrument trailer. The Series 8400S monitors were placed on a counter top, with each monitor below a port through the roof of the trailer. Separate 3" polyvinyl chloride (PVC) tubes were installed in the sampling ports and extended to approximately 1.5 meters above the roof of the trailer. These PVC tubes were secured to the roof of the trailer using wire guidelines, and a rain cap was positioned on the top of each. Separate flexible sampling lines were run from the monitors to the inside of the rain caps for sampling of the outside air. Particle size selection for the Series 8400S monitors was achieved using internal $PM_{2.5}$ sharp cut cyclones in each of the monitors. Data generated by the Series 8400S monitors were logged internally and downloaded daily onto an on-site PC.

3.5.1 Phase I

Phase I verification testing was conducted at the DOE/NETL facility within the Bruceton Research Center. The facility is located in the South Park area of Pittsburgh, PA, approximately 7 miles from downtown. The air monitoring station where testing was conducted is located on the top of a relatively remote hill within the facility and is impacted little by road traffic. The layout of the testing facility is illustrated schematically in Figure 3-1.

For this test, Battelle provided temporary facilities to augment the permanent facilities in use by the DOE/NETL air monitoring staff. These temporary facilities included a temporary Battelle/ETV platform (16-foot by 14-foot scaffold construction) and a Battelle instrument trailer. The Battelle trailer was positioned parallel with, and approximately 25 feet from, the DOE/NETL instrument trailer. The Battelle/ETV platform was located between the two trailers, with the surface at a height of approximately 2 meters (6 feet).

Most of the DOE/NETL continuous monitoring equipment, including the continuous precursor gas monitors, was located inside the DOE/NETL instrument trailer. A DOE/NETL Andersen RAAS sampler was located outside on a DOE/NETL platform. The Series 8400S monitors were

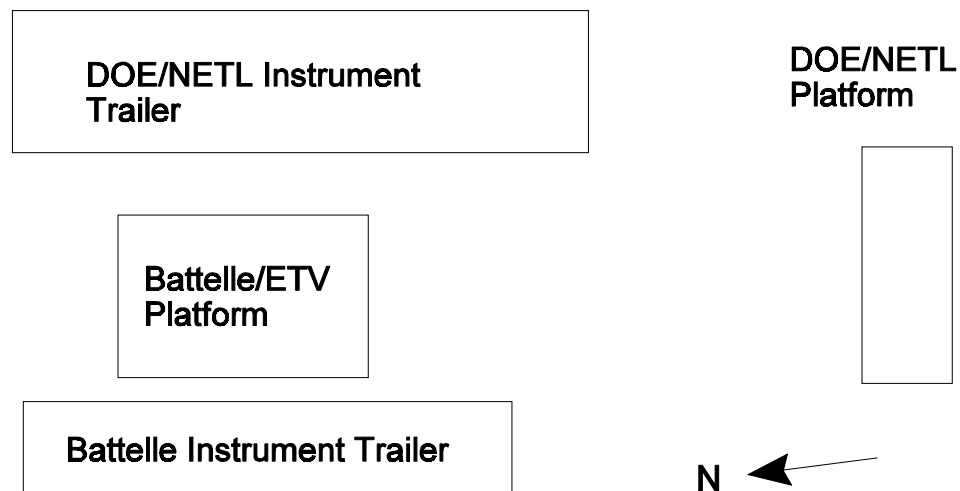


Figure 3-1. Site Layout During Phase I of Verification Testing (not drawn to scale)

installed inside the Battelle trailer, and a Battelle Andersen RAAS sampler was installed on the Battelle/ETV platform. A vertical separation of approximately 2 to 3 meters and a horizontal separation of approximately 3 meters existed between the inlets of the Series 8400S monitors and the BGI FRM sampler. A 10-meter (33-foot) meteorological tower was located approximately 25 meters (80 feet) to the north of the DOE/NETL instrument trailer.

3.5.2 Phase II

Phase II of verification testing was conducted at the CARB site on First Street in Fresno. This site is located in a residential/commercial neighborhood about three miles north of the center of Fresno. The RAAS sequential filter sampler and a 3-meter (10-foot) meteorological tower were located on the roof of the two-story building housing the CARB office. The continuous gas monitors were located inside the CARB office space and sampled through a port in the roof of the building. The RAAS sequential filter sampler was located near the center of the rooftop location. The Battelle trailer used during Phase I of this verification test was also used during Phase II. For Phase II, the Battelle trailer was located in the parking lot adjacent to the building in which the CARB site is located. The trailer was positioned approximately 25 meters (80 feet) to the south of the building, as shown in Figure 3-2. A difference in elevation of approximately 6 meters (20 feet) existed between the top of the trailer and the roof of the building housing the CARB site. The Series 5400 monitors were located inside the Battelle trailer with sampling systems similar to those used in Phase I of the verification test. In this arrangement, the inlets of the Series 5400 monitors were within about 40 m horizontally and 7 to 8 meters vertically of the inlet of the reference sampler.

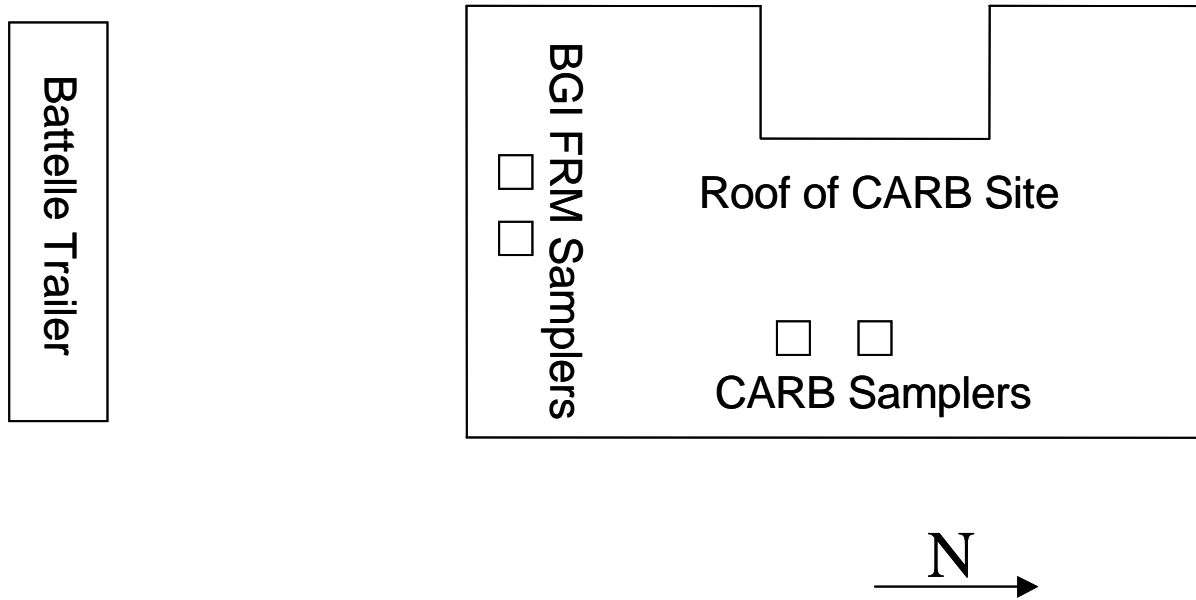


Figure 3-2. Site Layout During Phase II of Verification Testing (not drawn to scale)

Chapter 4 Quality Assurance/Quality Control

4.1 Data Review and Validation

Test data were reviewed and approved according to the AMS Center quality management plan (QMP)⁽³⁾ and the test/QA plan.⁽¹⁾ The Verification Test Coordinator or the Verification Testing Leader reviewed the raw data, laboratory notebook entries, and data sheets that were generated each day and approved them by initialing and dating the records.

Data from the Series 8400S monitors were validated by a representative of R&P and reviewed by the Verification Test Coordinator before being used in statistical calculations. Data were checked for error flags and not used if flagged for power or instrument failure. Obvious outliers in the data were removed and not used in the instrument verification.

4.2 Deviations from the Test/QA Plan

The following deviation from the test/QA plan related to verification of the Series 8400S monitors was documented and approved by the AMS Center Manager. This deviation had no deleterious effect on the verification data.

- The distance between the reference samplers and the monitors being tested was increased to approximately 25 meters to accommodate changes in the overall site layout for Phase II.

4.3 Calibration and Parameter Checks of Reference Sampler

The Andersen RAAS sampler provided by Battelle for Phase I of this verification test was calibrated using National Institute of Standards and Technology (NIST)-traceable flow meters and temperature and pressure sensors.

Prior to shipment to the field for Phase I of the verification test, the Andersen RAAS sampler was calibrated in a laboratory setting at Battelle's facilities in Columbus, Ohio. This procedure included calibration of the flow meters, filter and ambient temperature sensors, and barometric pressure sensor. The calibration and the subsequent verification of these sensors are described below. In Phase II, calibration of the sequential filter sampler was maintained by DRI as part of their ongoing monitoring efforts.

4.3.1 Flow Rate Calibration and Verification

Prior to Phase I of the verification test, a single-point calibration of the flow rate for each channel was performed on July 20, 2000. Flows were measured using a dry gas meter (American Meter Company, Battelle asset number LN 275010, calibrated January 21, 2000).

The on-site operators checked the flow rate of the Andersen RAAS sampler both before and after Phase I of the verification test using an Andersen Instruments Inc. dry gas meter (identification number 103652, calibrated March 30, 2000). The flow rate was checked prior to testing on July 30, 2000 and again after testing on September 11, 2000, using the same Andersen dry gas meter. In both cases, the measured flow rate was verified to be within 4% of the flow rate indicated by the sampler.

Calibration of the flow rate for the SFS sampler used during Phase II was maintained by DRI through daily flow checks with a calibrated rotameter and independent performance evaluation audits conducted by Parson's Engineering. No additional flow verification was performed for this test.

4.3.2 Temperature Sensor Calibration and Verification

The temperature sensors in the Andersen RAAS sampler were checked at the DOE/NETL site both before and after Phase I of the verification test by the on-site operators. Prior to testing, the sensors were checked on July 18, 2000, and July 30, 2000, against the readings from a mercury thermometer (Ever Ready, serial number 6419, calibrated October 29, 1999). For these checks, agreement between the sensors and the thermometer was within $\pm 2^{\circ}\text{C}$.

4.3.3 Pressure Sensor Calibration and Verification

Checks of the pressure sensor in the Andersen RAAS sampler were performed at the DOE/NETL site both before and after Phase I of the verification test. The pressure sensor was checked on July 19, 2000, and July 30, 2000, using an NIST-traceable Taylor Model 2250M barometer (Battelle asset number LN 163609, calibrated January 12, 2000). In both checks the agreement of the sensor and the NIST standard was within 5 mm of mercury.

4.3.4 Leak Checks

Leak checks of the Andersen RAAS sampler were performed every fourth day during Phase I of the verification test. These leak checks were performed according to the procedures in the operator's manual for the Andersen RAAS sampler. All leak checks passed the acceptance criteria provided in the operator's manual.

Leak checks of the SFS sampler were performed daily during Phase II of the verification test. These leak checks were conducted during set-up for each 24-hour sampling period. All leak checks passed before the sampler set-up was completed.

4.4 Collocated Sampling

To establish the precision of the sulfate reference method, the Andersen RAAS sampler was collocated with the DOE/NETL Andersen RAAS sampler for periods prior to and after Phase I of the verification test. During these sampling periods, the Battelle and DOE/NETL Andersen RAAS samplers were located on the same platform and were within four meters of one another. A series of five samples were collected from each of the two samplers during periods before and after Phase I. These collocated samples were analyzed by Consol. The measured sulfate concentration for these samples ranged from 1.4 to 14.4 $\mu\text{g}/\text{m}^3$. On average, these collocated samples showed relative agreement with one another within 6.6%. The observed differences ranged from 0.3% to 18%.

Precision estimates for the SFS sampler used in Phase II are based on previously reported results of a study⁽²⁾ performed in Bakersfield, CA. In that study, collocated SFSs identical to those used in this verification test were used to collect a series of 24 3-hour sulfate samples, at particulate sulfate levels similar to those observed in Phase II. The regression results of these samples showed a slope of 0.85 (0.07), an intercept of 0.10 (0.18) $\mu\text{g}/\text{m}^3$, and an r value of 0.93 ($r^2 = 0.88$), where the values in parentheses are standard errors. The average difference of the sample pairs was 0.26 $\mu\text{g}/\text{m}^3$, with a standard deviation of 0.32 $\mu\text{g}/\text{m}^3$.

4.5 Field Blanks

Ten percent of the samples that were collected throughout Phase I of the verification test were field blanks. These blanks showed sulfate mass per filter ranging from 1.2 to 7.0 μg . Assuming a sample volume of 11 m^3 , these blank values account for 0.11 to 0.64 $\mu\text{g}/\text{m}^3$ of the total observed sulfate concentration. Sulfate reference concentrations for Phase I were not blank corrected. Also, at least 10% of the reference sulfate samples collected during Phase II were field blanks. These samples were analyzed by IC at DRI. Only one of these blank samples showed sulfate mass (1.2 $\mu\text{g}/\text{filter}$) above the method detection limit (0.5 $\mu\text{g}/\text{filter}$). Since the duration of sampling periods varied, the sample volume was not consistent from period to period. However, for the shortest sampling period, the nominal volume sampled was 3.6 m^3 . Assuming this volume, the blank values ranged up to approximately 0.3 $\mu\text{g}/\text{m}^3$ sulfate. These blank values were incorporated into a DRI database of blank results that was used to calculate a running average sulfate blank value. Sulfate reference concentrations for Phase II were then blank corrected by DRI, using that running average.

4.6 Data Collection

4.6.1 Reference Measurements

During Phase I, summary data from the Andersen RAAS sampler were downloaded daily using portable data logging modules. Information recorded on the data sheets included identification of the sampling media (i.e., filter ID numbers) and the start and stop times for the sampling periods.

Summary data from the sampler included the parameters listed above, in addition to the sampling duration, volume sampled, and average temperature and pressure readings.

During Phase II, summary data from the sequential filter sampler were logged daily on sampling sheets by the on-site operators. These data included sample identification, start times for the sampling period, sampling duration, sample flow rate, and average temperature and pressure readings.

4.6.2 Series 8400S Monitors

Data from each of the Series 8400S monitors were recorded in an internal memory buffer every 10 minutes throughout each phase of the verification test. For each day, the data were stored in tabular format with 10-minute values reported along with a variety of instrumental parameters. The recorded data were downloaded directly onto an on-site personal computer and saved as text files. These files were imported into a spreadsheet for analysis, and copies of the data were stored by the Verification Test Coordinator on a floppy disk, as well as on a computer hard drive.

4.7 Assessments and Audits

4.7.1 Technical Systems Audit

Phase I—Pittsburgh

The technical systems audit (TSA) ensures that the verification tests are conducted according to the test/QA plan⁽¹⁾ and that all activities associated with the tests are in compliance with the ETV pilot QMP.⁽³⁾ All findings noted during the TSA on the above dates were documented and submitted to the Verification Test Coordinator for correction. The corrections were documented by the Verification Test Coordinator and reviewed by Battelle's Quality Manager, Verification Testing Leader, and Pilot Manager. None of the findings adversely affected the quality or outcome of this phase of the verification test, and all were resolved to the satisfaction of the Battelle Quality Manager. The records concerning the TSA are permanently stored with the Battelle Quality Manager.

Phase II—Fresno

An internal TSA was conducted by the Battelle Quality Manager on January 9, 2001, at the Fresno test site. An external TSA was also conducted concurrently by EPA quality staff, Ms. Elizabeth Betz and Ms. Elizabeth Hunike. All findings noted during these TSAs were documented and submitted to the Verification Test Coordinator for corrective action. None of the findings adversely affected the quality or outcome of this phase of the verification test for the Series 8400S. All corrective actions were completed to the satisfaction of the Battelle Quality Manager and the EPA.

4.7.2 Performance Evaluation Audit

The reference sampler provided by Battelle for this verification test was audited during Phase I to ensure that it was operating properly. During Phase I of the verification test, the flow rate of the Andersen RAAS sampler was audited on August 28, using a dry gas meter (American Meter Company, Battelle asset number LN 275010, calibrated April 17, 2000). The measured flow rate for the sulfate channel was within the $\pm 4\%$ acceptance criterion with respect to the internal flow meter.

The ambient and filter temperature sensors were checked on August 28, using a Fluke 52 thermocouple (Battelle asset number LN 570068, calibrated October 15, 1999). Agreement between each sensor and the thermocouple was within the $\pm 2^\circ\text{C}$ acceptance criterion.

4.7.3 Audit of Data Quality

Battelle's Quality Manager ensured that an audit of data quality (ADQ) of at least 10% of the verification data acquired during the verification test was completed. The ADQ traced the data from initial acquisition, through reduction and statistical comparisons, to final reporting. Reporting of findings followed the procedures outlined in the Phase I TSA. All findings were minor, and were corrected to the satisfaction of the Battelle Quality Manager.

Chapter 5 Statistical Methods

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

5.1 Inter-Unit Precision

The inter-unit precision of the continuous monitors was 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 the duplicate Series 8400S monitors were paired, and the behavior of their differences was used to assess precision. The following coefficient of variation (CV) was calculated and is reported for the sulfate concentration measurements of the duplicate monitors. 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.

5.2 Comparability/Predictability

The comparability between the continuous monitors and the sulfate reference measurements was assessed for the Series 8400S monitors, since these monitors yield measurements with the same units of measure as the sulfate reference method. The relationship between the two was assessed from a linear regression of the data using the sulfate reference results as the independent variable and the Series 8400S monitor results as the dependent variable as follows:

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

where R_i is the i^{th} sulfate reference measurement; C_i is the average of the Series 8400S measurements over the same 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 the 10-minute data from each Series 8400S monitor is used because this is the quantity that is most comparable to the reference sampler measurements.

Comparability is expressed in terms of bias between the Series 8400S monitor and the sulfate reference method and the degree of correlation (i.e., r^2) between the two. Bias was assessed based

on the slope and intercept of the linear regression of the data from the sulfate reference measurements and the Series 8400S monitor. In the absence of bias, the regression equation would be $C_i = R_i + \varepsilon_i$ (slope = 1, intercept = 0), indicating that the average of Series 8400S sulfate measurements is simply equivalent to the sulfate 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 Series 8400S measurements is almost entirely explained by the variability in the sulfate reference measurements.

Quantities reported include r^2 , intercept, and slope, with estimates of the 95% confidence interval (CI) for the intercept and slope. Comparability to the reference data was determined independently for each of the two duplicate Series 8400S monitors being tested and was assessed separately for each phase of the verification test.

5.3 Meteorological Effects/Precursor Gas Influence

The influence of meteorological conditions on the correlation between the Series 8400S monitors and the sulfate reference measurements was evaluated by using meteorological data such as temperature and humidity as parameters in multivariable analyses of the reference/monitor comparison data. The model used is as follows:

$$C_i = \mu + \beta \times R_i + \sum \gamma_j \times X_{ji} + \varepsilon_i \quad (2)$$

where X_{ji} is the meteorological or precursor gas measurement for the i^{th} reference time period, γ_j is the associated slope parameters, and other notation is as in equation 1. Comparability results are reported again after these variables are adjusted for in the model. Additionally, estimates of γ_j will be provided. Meteorological effects and precursor gas interferences were assessed independently for each of the duplicate Series 8400S monitors tested and were assessed separately for each phase of the verification test. In conducting these multivariable analyses, a significance level of 90% was used in the model selection. This significance level is less stringent than the 95% level used in other aspects of the verification, and was chosen so that even marginally important factors could be identified for consideration.

Note that the multivariable model ascribes variance unaccounted for by linear regression against the reference results to the meteorological or precursor gas parameters. The model treats all candidate parameters equally. The model discards the least significant parameter and is rerun until all remaining variables have the required significance (i.e., predictive power). The results of the model should not be taken to imply a cause-and-effect relationship. It is even possible that the parameters identified as significant for one unit of a monitoring technology may differ from those identified for the duplicate unit of that technology, due to differences in the two data sets.

Chapter 6 Test Results

6.1 Phase I—Pittsburgh (August 1 - September 1, 2000)

Samples were collected daily between August 1 and September 1, 2000, using a PM_{2.5} FRM sampler. During this period, the daily PM_{2.5} concentration as measured by the BGI FRM sampler ranged from 6.1 µg/m³ to 36.2 µg/m³, with an average daily concentration of 18.4 µg/m³.

Typically, the PM_{2.5} composition was dominated by sulfate and carbon species. On average, the measured sulfate concentration, determined by ion chromatography, accounted for approximately 47% of the daily PM_{2.5} mass. Total carbon, as measured by the IMPROVE thermal optical reflectance (TOR) method, accounted for approximately 38% of the PM_{2.5} mass, with elemental carbon contributing approximately 22% and organic carbon contributing approximately 77% of the total carbon. Additionally, nitrate contributed about 8.3% of the daily PM_{2.5} concentration.

Table 6-1 summarizes the meteorological conditions during Phase I, and Table 6-2 summarizes the observed concentrations of the measured precursor gases during this period.

Table 6-1. Summary of Daily Values for the Measured Meteorological Parameters During Phase I of Verification Testing

	Wind Speed (mph)	Vertical Wind Speed (mph)	Wind Direction (degrees)	Air Temp. @ 10 m (C)	Air Temp. @ 2 m (C)	RH (%)	Solar Radiation (W/m ²)	Press. (mbar)	Total Precip. (in.)
Average	3.35	0.09	196	20.0	16.6	89.4	162.8	979.7	0.0014
Max.	6.45	0.29	298	24.1	22.5	95.8	246.1	986.7	0.0297
Min	1.88	-0.03	106	14.6	12.1	80.2	47.9	974.5	0.0000

Table 6-2. Summary of Daily Values for the Measured Precursor Gas Concentrations During Phase I of Verification Testing

	SO ₂ (ppb)	H ₂ S (ppb)	NO (ppb)	NO ₂ (ppb)	NO _x (ppb)	O ₃ (ppb)
Average	6.9	1.5	3.1	10.1	13.0	24
Max	12.8	2.9	10.4	17.4	27.4	51
Min	2.7	-0.6	0.14	5.3	5.3	5

6.1.1 Inter-Unit Precision

As a result of unexpected delays in the manufacturing process, the Series 8400S monitors were not available from the vendor until the last week of testing during Phase I. The ambient particulate sulfate concentrations were measured and recorded every 10 minutes during the last few days of Phase I by the duplicate Series 8400S monitors. These data were averaged to obtain hourly averages for sulfate concentration. Figure 6-1a shows the hourly sulfate averages for the duplicate monitors recorded during Phase I of verification testing. Figure 6-1b is a scatter plot of these same data that illustrates the correlation between the two monitors in measuring particulate sulfate concentration.

For comparison with the 24-hour sulfate reference measurements, the hourly data were averaged from noon to noon for each day to correspond with the 24-hour sampling periods used in Phase I of the verification test. In Figures 6-2a, the noon-to-noon averages for Phase I of the verification test are presented for the two Series 8400S monitors. A correlation plot of these data is shown in Figure 6-2b. Note that 24-hour average data were available from both monitors on only four days in Phase I.

These data were analyzed by linear regression, and the results of this analysis are presented in Table 6-3. The CV for these values was also determined according to Section 5.1, and the calculated CV is shown in Table 6-3.

Table 6-3. Linear Regression and Coefficient of Variation Results for Hourly and 24-Hour Average Sulfate Values from Duplicate Series 8400S Monitors During Phase I

Parameter	Hourly	24-Hour
Slope (95% CI)	1.094 (0.172)	0.841 (2.03)
Intercept ($\mu\text{g}/\text{m}^3$) (95% CI)	1.47 (0.71)	2.4 (8.3)
r^2	0.639	0.614
CV	28.9%	26.6%

The regression results for the hourly average data from the duplicate monitors show a slope of 1.094 (0.172) which is not statistically different from unity at 95% confidence. However, the regression results show a significant intercept [intercept = 1.47 (0.71)], which is apparent in Figure 6-1a as an offset between the two traces (Monitor 2 reading higher than Monitor 1). The CV of the hourly data was 28.9%. Since only four data points are available for the 24-hour average results (Figure 6-2b), the regression results in Table 6-3 show a high degree of uncertainty, and may not accurately represent the performance of the Series 8400S monitors. These results show a slope of 0.841 (2.031), an intercept of 2.4 (8.3), and an r^2 value of 0.614, with a CV of 26.6%.

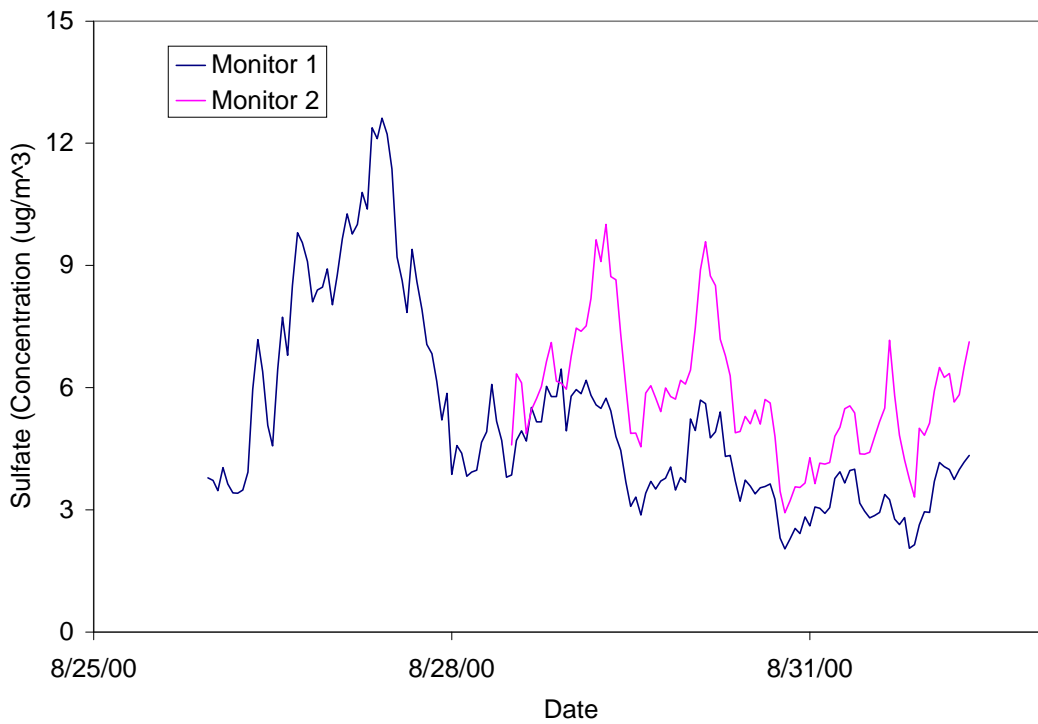


Figure 6-1a. Hourly Average Sulfate Concentrations from Duplicate Series 8400S Monitors During Phase I of Verification Testing

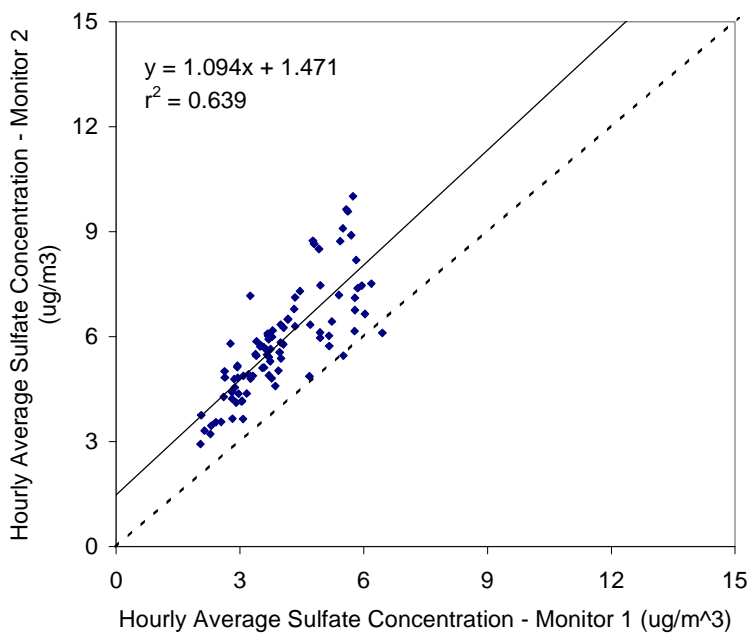


Figure 6-1b. Correlation Plot of Hourly Average Sulfate Concentrations from Duplicate Series 8400S Monitors During Phase 1 of Verification Testing

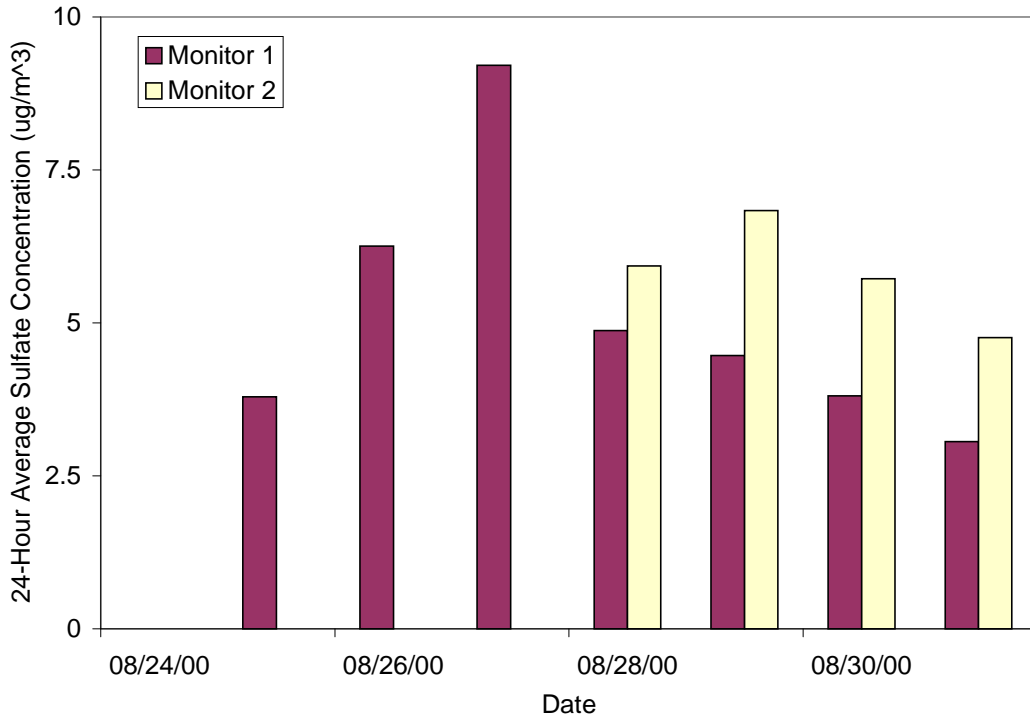


Figure 6-2a. 24-Hour Average Sulfate Concentrations from Duplicate Series 8400S Monitors During Phase I of Verification Testing

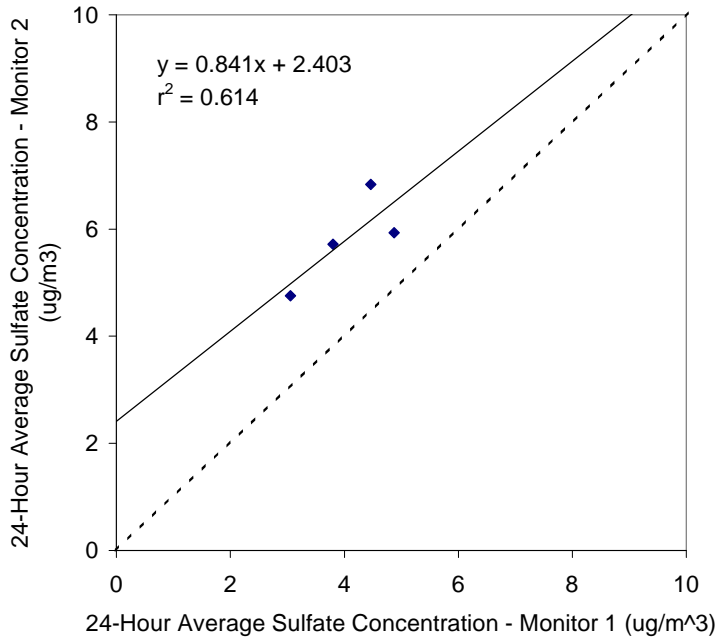


Figure 6-2b. Correlation Plot of 24-Hour Average Sulfate Concentrations from Duplicate Series 8400S Monitors During Phase 1 of Verification Testing

6.1.2 Comparability/Predictability

In Figure 6-3a, the available noon-to-noon averages of the Series 8400S measurements are shown along with the sulfate reference measurements from Phase I. These same data are shown in Figure 6-3b as a scatter plot to illustrate the correlation between the Series 8400S monitors and the reference method. These data were analyzed by linear regression according to Section 5.2 in order to establish the comparability of each of the Series 8400S monitors and the reference measurements. The calculated slope, intercept, and r^2 value of the regression analyses are presented in Table 6-4 for each monitor. For the reasons described in Section 6.1.1, the regression is based on very few data points (i.e., six points for Monitor 1 and three points for Monitor 2).

Table 6-4. Comparability of the Series 8400S Monitors with the Sulfate Reference Method During Phase I

Regression Parameter	Monitor 1	Monitor 2
Slope (95% CI)	0.26 (0.56)	0.60 (4.58)
Intercept ($\mu\text{g}/\text{m}^3$) (95% CI)	2.9 (5.5)	2.23 (51.7)
r^2	0.288	0.436

Table 6-4 shows slopes of 0.26 (0.56) and 0.60 (5.48) for Monitors 1 and 2, respectively, with corresponding r^2 values below 0.3 and below 0.45, respectively. However, since only a very limited amount of data are available for the 24-hour average results for the Series 8400S monitors, the results presented in Table 6-4 show a high degree of uncertainty, and may not accurately represent the performance of these monitors. For example, if just one of the six data points is removed from the analysis for Monitor 1, the regression results show a slope of 1.22, an intercept of $-3.5 \mu\text{g}/\text{m}^3$ and an r^2 value of 0.818, each of which is substantially different from the results presented in Table 6-4.

6.1.3 Meteorological Effects

Multivariable analysis was performed to determine if the meteorological conditions had an influence on the readings of the Series 8400S monitors in Phase I. However, since only limited data were available from the Series 8400S monitors, no conclusive results could be obtained from this analysis.

6.1.4 Influence of Precursor Gases

Multivariable analysis was performed to determine if the presence of precursor gases had an influence on the readings of the Series 8400S monitors in Phase I. However, since only limited data were available from the Series 8400S monitors, no conclusive results could be obtained from this analysis.

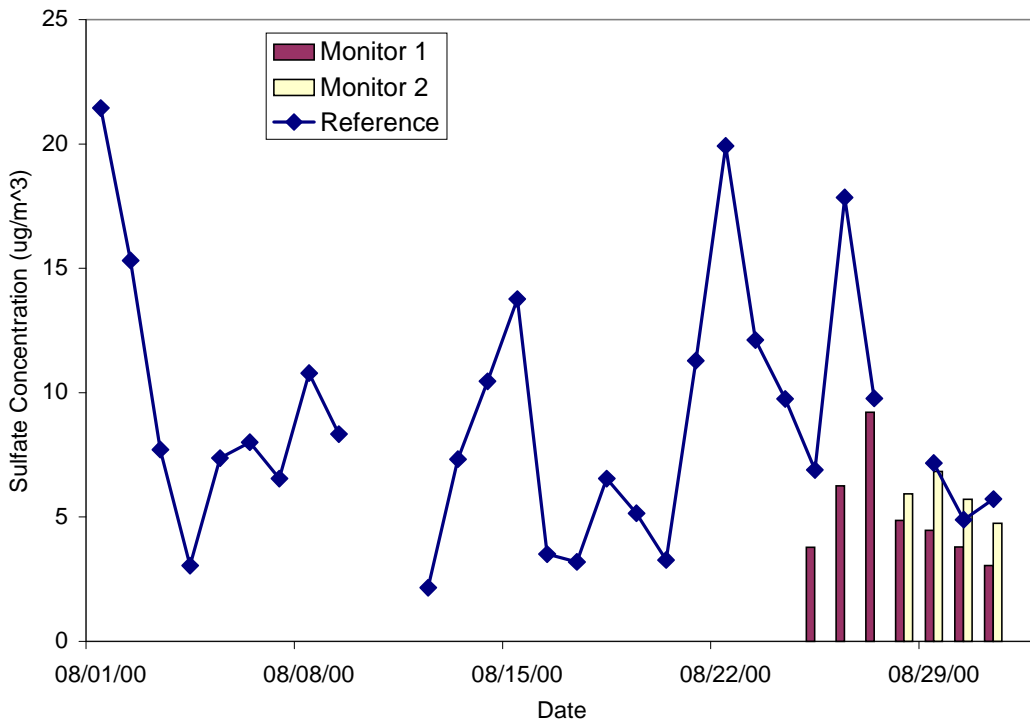


Figure 6-3a. Sulfate Reference Concentrations and 24-Hour Averages from Duplicate Series 8400S Monitors During Phase I of Verification Testing

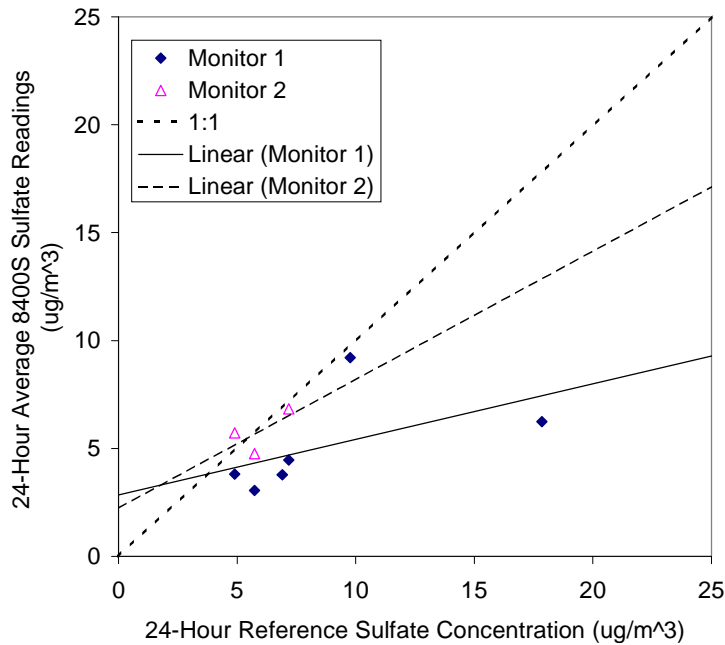


Figure 6-3b. Correlation Plot of the 24-Hour Average Sulfate Concentrations from Duplicate Series 8400S Monitors and Sulfate Reference Concentrations During Phase I of Verification Testing

6.2 Phase II - Fresno (December 18, 2000 - January 17, 2001)

During Phase II, daily 24-hour PM_{2.5} concentrations averaged 74 µg/m³ and ranged from 4.9 µg/m³ to 146 µg/m³. A strong diurnal pattern was observed in the PM_{2.5} concentration, with the peak levels occurring near midnight. Particle composition was dominated by nitrate and carbon. On average, the overall PM_{2.5} concentration comprised 22% nitrate and 40% total carbon. Sulfate accounted for only about 2% of the daily PM_{2.5} mass.

Table 6-5 summarizes the meteorological conditions during Phase II, and Table 6-6 summarizes the observed concentrations of the measured precursor gases during this period.

Table 6-5. Summary of Daily Values for the Measured Meteorological Parameters During Phase II of Verification Testing.

	Wind Speed (mps)	Wind Direction (Degrees)	Air Temp. (C)	RH (%)	Solar Radiation (W/m ²)	Press. (mm Hg)
Average	1.43	186	8.3	75.4	88.2	756.2
Max	4.18	260	12.8	92.0	123.5	761.7
Min	0.91	116	4.6	51.6	17.1	747.3

Table 6-6. Summary of Daily Values for the Measured Precursor Gas Concentrations During Phase II of Verification Testing

	CO (ppm)	O ₃ (ppb)	NO (ppb)	NO ₂ (ppb)	NO _x (ppb)
Average	1.9	13	61.8	32.6	94.4
Max	3.3	28	119.9	50.3	170.2
Min	0.4	6	4.1	14.8	18.9

6.2.1 Inter-Unit Precision

As in Phase I, sulfate concentrations were measured and recorded every 10 minutes throughout Phase II by duplicate Series 8400S monitors. These data were used to calculate hourly averages for Series 8400S sulfate readings. Figure 6-4a shows the hourly sulfate averages for the duplicate monitors recorded during Phase II of verification testing. Breaks in the data indicate periods during which no data are available owing to instrument failure or power outages. Figure 6-4b is a scatter plot of these same data which illustrates the correlation between the two monitors in measuring particulate sulfate concentration.

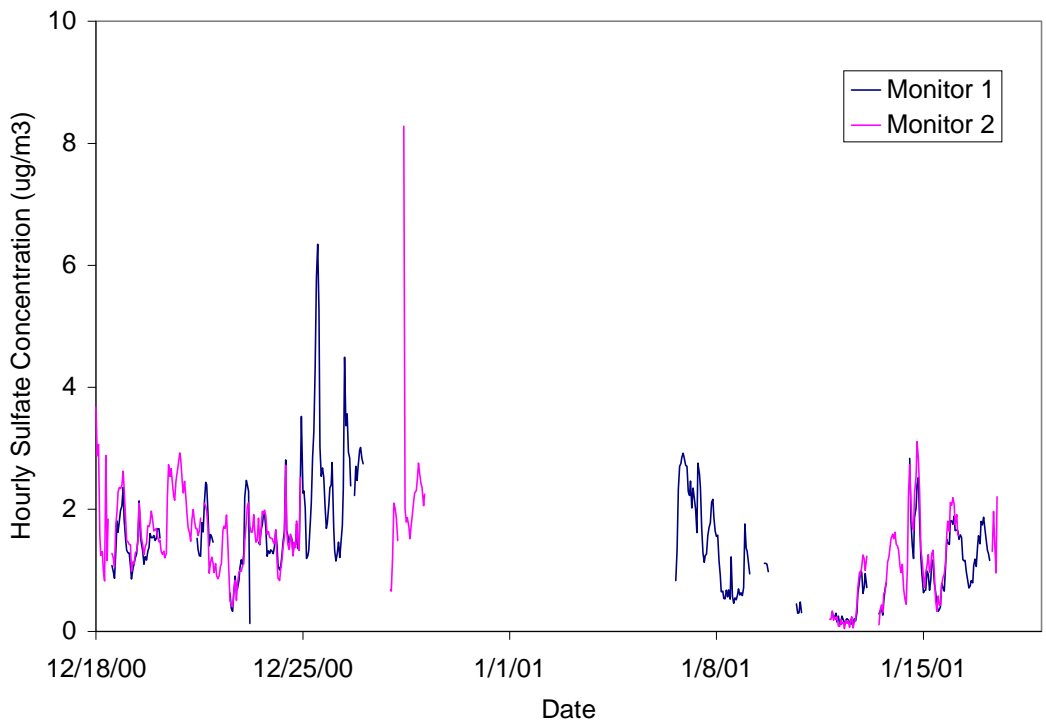


Figure 6-4a. Hourly Average Sulfate Concentrations from Duplicate Series 8400S Monitors During Phase II of Verification Testing

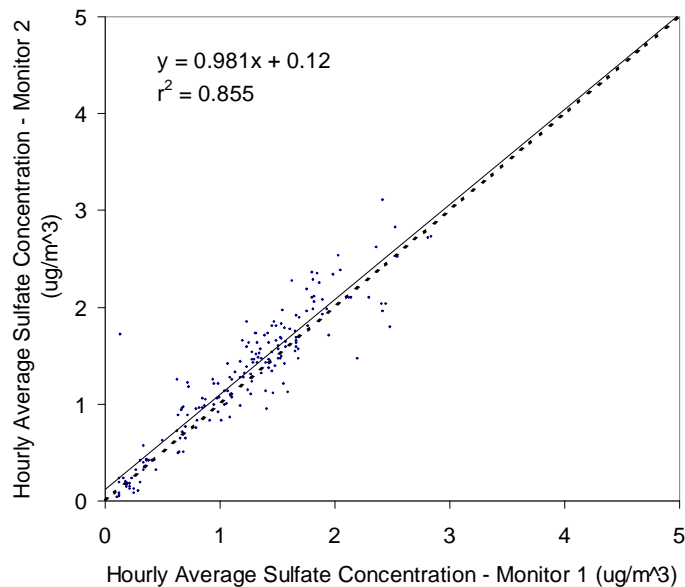


Figure 6-4b. Correlation Plot of Hourly Average Sulfate Concentrations from Duplicate Series 8400S Monitors During Phase II of Verification Testing

The hourly data were also averaged from midnight to midnight to obtain 24-hour averages for the Series 8400S sulfate readings during Phase II of the verification test. In Figure 6-5a, these 24-hour averages for Phase II of the verification test are presented for the two Series 8400S monitors. A correlation plot of these data is shown in Figure 6-5b. In Phase II, 24-hour averages were obtained from both Series 8400S monitors on 13 days.

These data were analyzed by linear regression and the results of this analysis are presented in Table 6-7. The CV for these values was also determined according to Section 5.1, and the calculated CV is shown in Table 6-7.

Table 6-7. Linear Regression and Coefficient of Variation Results for Hourly and 24-Hour Average Sulfate Concentrations from Duplicate Series 8400S Monitors During Phase II

Parameter	Hourly	24-Hour
Slope (95% CI)	0.981 (0.060)	0.969 (0.272)
Intercept ($\mu\text{g}/\text{m}^3$) (95% CI)	0.12 (0.08)	0.20 (0.36)
r^2	0.855	0.848
CV	19.7%	15.7%

The results of the regression analysis for the hourly and 24-hour average data from the duplicate monitors show r^2 values of 0.855 and 0.848, respectively, with a slope of 0.981 (0.060) for the hourly data and 0.969 (0.272) for the 24-hour data. The slope of the regression lines are not statistically different from unity in either case, indicating no bias between the monitors, and the intercepts are both close to zero.

6.2.2 Comparability/Predictability

To compare with the reference measurements, the hourly results from the duplicate Series 8400S monitors were appropriately averaged to correspond to the five daily sampling periods for the reference sequential filter sampler. Table 6-8 summarizes the reference sulfate concentrations during these sampling periods. Figure 6-6a shows the reference measurements and the corresponding averages from the duplicate Series 8400S monitors for Phase II of the verification test. These same data are also shown in Figure 6-6b as a scatter plot to illustrate the correlation between the results of the duplicate Series 8400S monitors and the sulfate reference measurements.

Linear regression analysis of these data was performed independently for each Series 8400S monitor, and the results are presented in Table 6-9. Regression analyses were also performed separately for each of the sampling periods (i.e, 0000-0500, 0500-1000, 1000-1300, 1300-1600, and 100-2400). These regression results are also presented in Table 6-9 for the duplicate Series 8400S monitors.

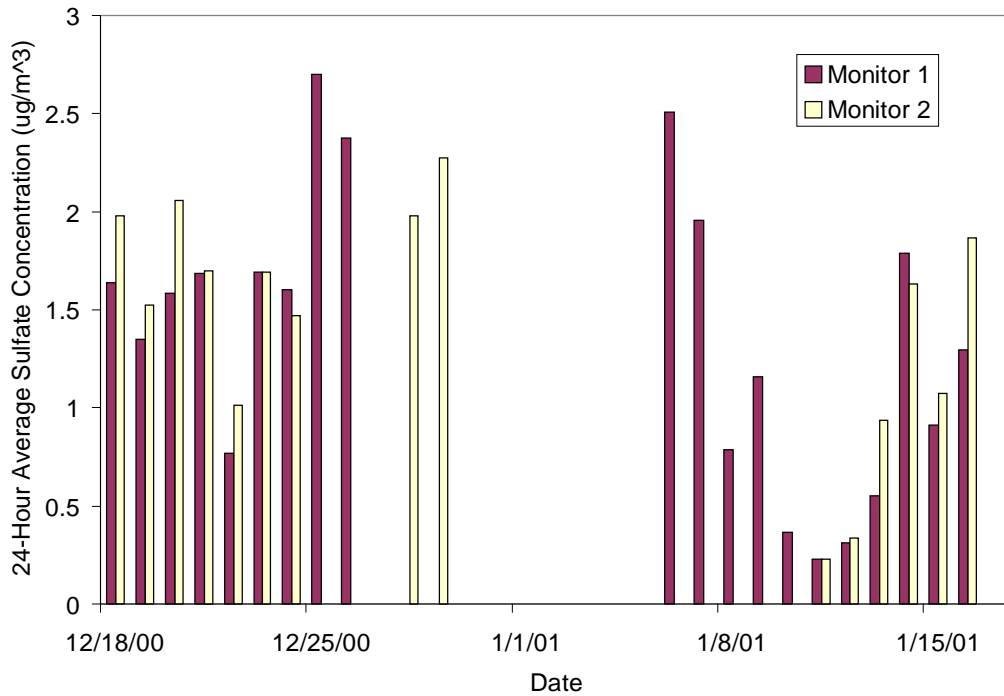


Figure 6-5a. 24-Hour Average Sulfate Concentrations from Duplicate Series 8400S Monitors During Phase II of Verification Testing

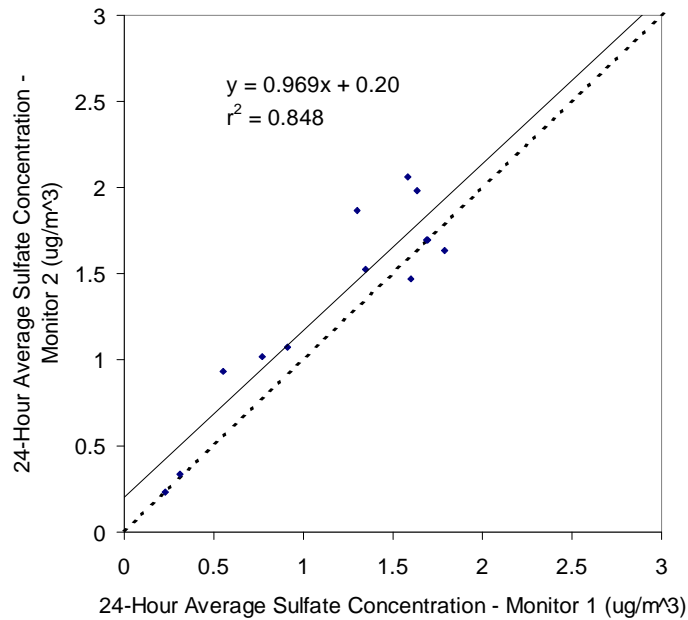


Figure 6-5b. Correlation Plot of 24-Hour Average Sulfate Concentrations from Duplicate Series 8400S Monitors During Phase II of Verification Testing

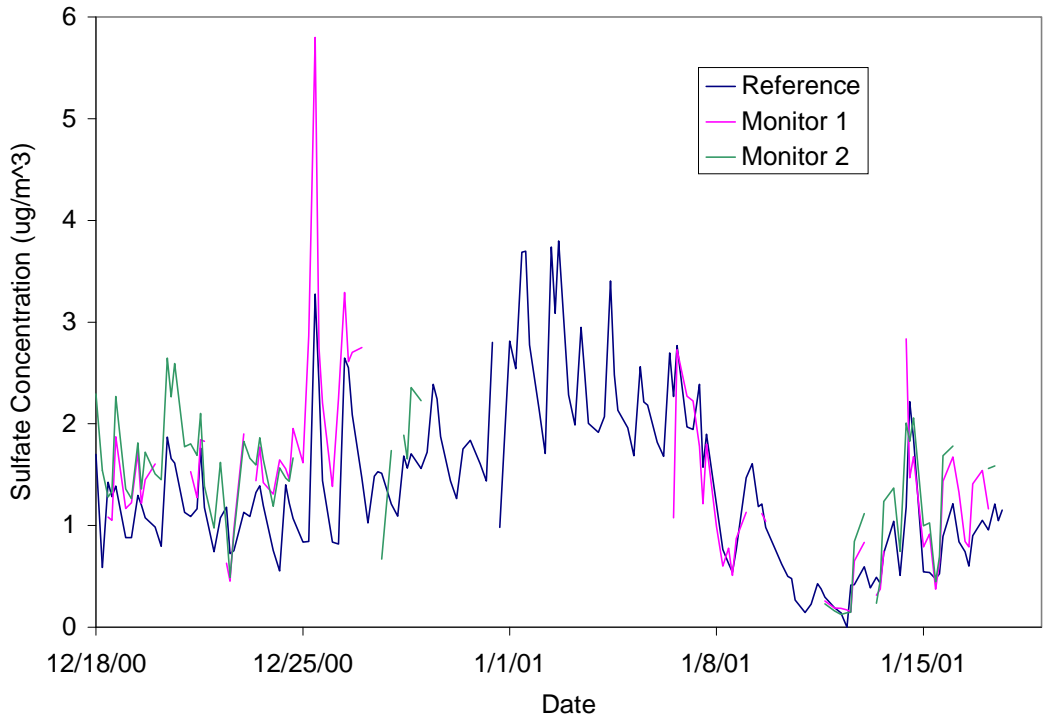


Figure 6-6a. Sulfate Concentrations from Short-Term Reference Samples and Duplicate Series 8400S Monitors During Phase II of Verification Testing

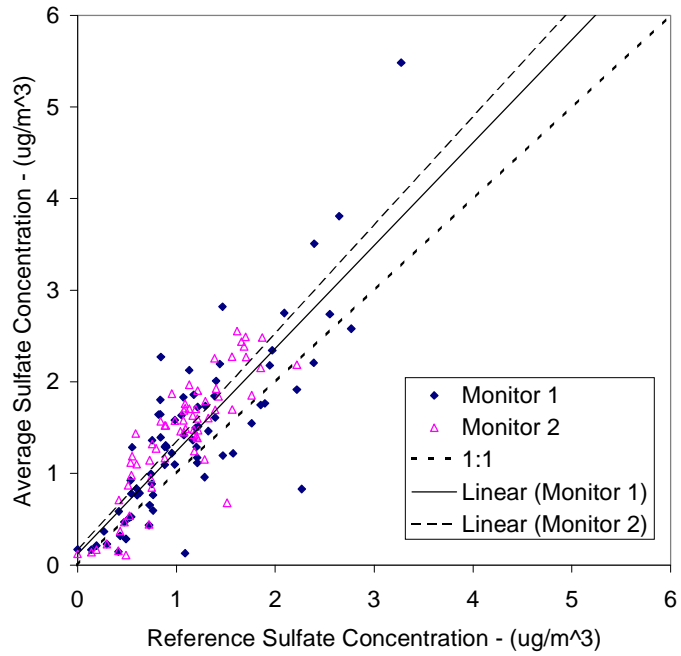


Figure 6-6b. Correlation Plot of Short-Term Reference Samples and Average Sulfate Concentrations from Duplicate Series 8400S Monitors During Phase II of Verification Testing

Table 6-8. Summary of Short-Term Particulate Sulfate Levels During Phase II of Verification Testing

Sulfate Concentration µg/m ³	Sampling Period					
	All ^a	0000-0500	0500-1000	1000-1300	1300-1600	1600-2400
Average	1.43	1.27	1.11	1.74	1.57	1.47
Maximum	3.80	2.81	2.54	3.74	3.70	3.80
Minimum	0.00	0.14	0.14	0.00	0.38	0.27

^aSummary of all individual samples treated equally, i.e., no time-weighting

Table 6-9. Comparability of the Series 8400S Monitors with the Sulfate Reference Method in Phase II

Reference Method Sampling Period	Monitor 1			Monitor 2		
	Slope	Intercept (µg/m ³)	r ²	Slope	Intercept (µg/m ³)	r ²
All	1.12 (0.18)	0.12 (0.24)	0.681	1.18 (0.18)	0.18 (0.20)	0.735
0000 - 0500	1.13 (0.59)	0.36 (0.64)	0.569	1.43 (0.24)	0.11 (0.26)	0.931
0500 - 1000	1.00 (0.81)	0.45 (0.76)	0.504	1.31 (0.52)	0.29 (0.43)	0.736
1000 - 1300	1.50 (0.33)	-0.25 (0.53)	0.913	1.43 (0.25)	-0.20 (0.30)	0.937
1300 - 1600	1.00 (0.38)	-0.08 (0.56)	0.681	1.23 (0.31)	-0.19 (0.41)	0.887
1600 - 2400	1.00 (0.25)	0.25 (0.33)	0.807	1.15 (0.58)	0.20 (0.24)	0.609

Overall, the regression results show a slope of 1.12 (0.18) for Monitor 1 and 1.18 (0.18) for Monitor 2. These slopes are not significantly different from unity at the 95% confidence levels. With all the sampling periods included, the regression analyses show r² values of 0.681 for Monitor 1 and 0.735 for Monitor 2. For the various sampling periods, the slopes of the regression lines vary from 1.00 to 1.50 for Monitor 1, and from 1.15 to 1.43 for Monitor 2. The r² values for the regression analyses of the individual sampling periods vary from 0.504 to 0.913 for Monitor 1 and from 0.609 to 0.937 for Monitor 2. None of the intercepts of the regressions were significantly different from zero, at 95% confidence level.

6.2.3 Meteorological Effects

As with the data from Phase I, a multivariable model analysis was used to determine if the meteorological conditions had an influence on the readings of the Series 8400S monitors. This

analysis involved a backward elimination process to remove from the analysis model those parameters showing no statistically significant influence on the results at a 90% confidence level. This analysis showed no influence of the meteorological variables on Monitor 2, but showed the following relationship for Monitor 1:

$$\text{Monitor 1} = 1.220 \cdot \text{Ref} - 27.6 \mu\text{g}/\text{m}^3 - 0.0801 \cdot \text{T} + 0.0375 \cdot \text{BP}$$

where Ref is the sulfate reference measurement in $\mu\text{g}/\text{m}^3$, T is the ambient air temperature in C, and BP is the barometric pressure in millimeters of mercury.

The magnitude of the implied effects can be examined by comparing the predicted Series 8400S reading from the multivariable model to that based on linear regression against the reference sulfate results. For example, using the average values for these parameters from Phase II (Section 6.2), the multivariable equation would predict an average sulfate concentration of 1.84 $\mu\text{g}/\text{m}^3$ for Monitor 1:

$$\begin{aligned} \text{Monitor 1} &= 1.220 \cdot 1.43 - 27.6 - 0.0801 \cdot 8.3 + 0.0375 \cdot 756.2 \\ &= 1.84 \mu\text{g}/\text{m}^3. \end{aligned}$$

Based on the overall linear regression results presented in Table 6-9 and the average sulfate concentration, Monitor 1 would read,

$$\begin{aligned} \text{Monitor 1} &= 1.12 \cdot 1.43 + 0.12 \\ &= 1.72 \mu\text{g}/\text{m}^3 \end{aligned}$$

thus the multivariable result differs from the linear regression result by 7%.

6.2.4 Influence of Precursor Gases

Multivariable model analysis was also used to establish if the measured precursor gases in Phase II have an effect on the readings of the Series 8400S monitors relative to the sulfate reference measurements. This analysis ascribed to nitric oxide and total nitrogen oxides a significant influence on Monitor 1 during Phase II, and to ozone an influence on Monitor 2, at the 90% confidence level. The analysis shows the following relationships:

$$\text{Monitor 1} = 1.40 \cdot \text{Ref} + 0.191 \mu\text{g}/\text{m}^3 + 0.0345 \cdot \text{NO} - 0.0265 \cdot \text{NO}_x$$

and,

$$\text{Monitor 2} = 0.731 \cdot \text{Ref} + 1.35 \mu\text{g}/\text{m}^3 - 0.0513 \cdot \text{O}_3$$

where Ref is the sulfate reference measurement in $\mu\text{g}/\text{m}^3$, and the concentrations of nitric oxide, nitrogen oxides, and ozone are in ppb.

Substituting the average values for these parameters from Phase II (Section 6.2) into the multivariable equations above, the average sulfate concentrations for the two monitors would be:

$$\begin{aligned}\text{Monitor 1} &= 1.40*1.43 + 0.191 + 0.0345*61.8 - 0.0265*94.4 \\ &= 1.82 \mu\text{g}/\text{m}^3\end{aligned}$$

and,

$$\begin{aligned}\text{Monitor 2} &= 0.731*1.43 + 1.35 - 0.0513*13 \\ &= 1.73 \mu\text{g}/\text{m}^3.\end{aligned}$$

These multivariable results differ from the linear regression estimates of the average sulfate concentrations ($1.72 \mu\text{g}/\text{m}^3$ for Monitor 1, and $1.87 \mu\text{g}/\text{m}^3$ for Monitor 2) by 5.8% and 9.3%, respectively.

6.3 Instrument Reliability/Ease of Use

During Phase I of the verification test, the Series 8400S monitors were only in operation for a few days as a result of delays in manufacturing. No maintenance was required during this period other than the replacement of gas cylinders. However, since the testing period was so short for these monitors, a reasonable estimate of the long-term maintenance requirements cannot be made.

During Phase II, substantial maintenance was required for the two Series 8400S monitors. Each monitor required the replacement of flash strips on a frequent basis. Typically the flash strips lasted only a day or two before burning out. Each monitor also required the replacement of at least one internal electronic component board during Phase II. As a result of these operational problems, during Phase II only approximately 40% data recovery was achieved from the two monitors. Monitor 1 achieved approximately 42% recovery, and Monitor 2 achieved approximately 37% recovery. These maintenance issues are thought to be due to the use of pre-production versions of the Series 8400S monitor in this verification. Commercial production units became available in May 2001. The vendor indicates that in those units the flash strip and electronic problems have been addressed. The vendor indicates a minimum interval of two weeks between replacement of the flash strips; however, these claims were not verified in the test.

6.4 Shelter/Power Requirements

The Series 8400S monitors were installed and operated inside the Battelle instrument trailer during both phases of testing. The monitors and pumps for each were run on a single 15A circuit. During Phase II, the duplicate Series 8400S monitors were installed and operated in the

CARB facility. It is recommended by the vendor that these monitors be operated indoors. Each monitor was run on a single 15A circuit.

6.5 Instrument Cost

The cost of the Series 8400S monitor is subject to change and may be different for domestic and international markets. As such, no pricing data were provided by the vendor for this report.

Chapter 7

Performance Summary

The Series 8400S monitor is designed to provide indications of the ambient particulate sulfate concentration on a 10-minute time scale. Duplicate pre-production versions of the Series 8400S monitors were evaluated under field test conditions in two separate phases of this verification test. The duplicate monitors were operated side by side and were installed with an internal PM_{2.5} cyclone to provide size selection of the aerosol. The results from each phase of this verification test are summarized below.

7.1 Phase I—Pittsburgh (August 1 - September 1, 2000)

The duplicate Series 8400S monitors were operated for only a few days near the end of Phase I of the verification test, as a result of unexpected delays in the manufacturing schedule. Consequently only limited data are available for verification, and the results of Phase I may not accurately represent the performance of these monitors. During Phase I, the linear regression comparison of the hourly data from the duplicate 8400S monitors showed a slope of 1.09 (0.17), an intercept of 1.47 (0.71) $\mu\text{g}/\text{m}^3$, and an r^2 value of 0.639. The regression results of the limited 24-hour average data available (only 4 data points) show a slope of 0.841 (2.03), an intercept of 2.4 (8.3) $\mu\text{g}/\text{m}^3$, and an r^2 value of 0.614. No significant bias between the two monitors is indicated by these results.

The 24-hour Series 8400S results were compared to 24-hour reference sulfate data for Phase I. Again because of the limited amount of available data, the results of this comparison may not accurately represent the performance capabilities of the Series 8400S monitors. The regression results for Monitor 1 show a slope of 0.26 (0.56), an intercept of 2.9 (5.5) $\mu\text{g}/\text{m}^3$, and an r^2 value of 0.288, based on six data points. For Monitor 2, the regression results show a slope of 0.60 (4.58), an intercept of 2.23 (51.7) $\mu\text{g}/\text{m}^3$, and an r^2 value of 0.436, based on three data points.

No conclusions about meteorological and precursor gas effects could be obtained from a multivariable analysis because of the limited data available from the Series 8400S monitors in Phase I.

7.2 Phase II—Fresno (December 18, 2000 - January 17, 2001)

During Phase II of verification testing, the regression comparison of the hourly data from the duplicate Series 8400S monitors shows a slope of 0.981 (0.60), an intercept of 0.12 (0.08), and an r^2 value of 0.855. For the 24-hour data, the regression results show a slope of 0.969 (0.272), an intercept of 0.20 (0.36) $\mu\text{g}/\text{m}^3$, and an r^2 value of 0.848. In both cases, the slope is not statistically different from unity, indicating no bias between the two monitors.

The Series 8400S monitors were averaged for comparison to 3-, 5-, and 8-hour reference sulfate results in Phase II. The regression results for Monitor 1 with all the reference samples showed a slope of 1.12 (0.18), an intercept of 0.12 (0.24) $\mu\text{g}/\text{m}^3$, and an r^2 value of 0.681. For Monitor 2, the regression results show a slope of 1.18 (0.18), an intercept of 0.18 (0.20) $\mu\text{g}/\text{m}^3$, and an r^2 value of 0.735. The intercepts are not significantly different from zero, and the slopes are not significantly different from unity, indicating no bias relative to the reference results.

Multivariable model analysis ascribed to temperature and barometric pressure an influence on the readings of one monitor relative to the sulfate reference measurements at a 90% confidence level. The multivariable model results differed by 7% from the simple linear regression against reference data, under average conditions in Phase II.

Multivariable model analysis also ascribed to nitric oxide and nitrogen oxides an influence on the readings of one monitor, and to ozone an influence on the readings of the other monitor, relative to the sulfate reference measurements at the 90% confidence level. The multivariable model results differed by 5.8% and 9.3% for Monitor 1 and Monitor 2, respectively, from the linear regression results.

Data recovery from the Series 8400S monitors in Phase II was about 40%, primarily because of the need for frequent replacement of flash strips and the failure of at least one electronic circuit board in each monitor. The vendor indicates that these maintenance issues have been addressed in the production units of the monitor. The vendor indicates that the flash strip replacement interval will be at least two weeks; however, this was not verified during testing.

Chapter 8 References

1. *Test/QA Plan for the Verification of Ambient Fine Particle Monitors*, Battelle, Columbus, Ohio, June 2000.
2. *Project Overview: 1995 Integrated Monitoring Study Design, Operations, Measurements, and Post-Field Activities*, Report No.: 026.22-98.2., California Air Resources Board, July 1999.
3. *Quality Management Plan (QMP) for the Advanced Monitoring Systems Pilot*, Version 2.0, Battelle, Columbus, Ohio, October 2000.
4. *Particulate Matter (PM_{2.5}) Speciation Guidance*, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, October 7, 1999.