

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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