THE ENVIRONMENTAL TECHNOLOGY VERIFICATION PROGRAM

U.S. Environmental Protection Agency

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ETV Joint Verification Statement

TECHNOLOGY TYPE:	**Continuous Ambient Particulate Nitrate Monitor**
APPLICATION:	**MEASURING PARTICULATE NITRATE CONCENTRATIONS IN AMBIENT AIR**
TECHNOLOGY NAME:	**Series 8400N Particulate Nitrate Monitor**
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The U.S. Environmental Protection Agency (EPA) has created the Environmental Technology Verification (ETV) Program to facilitate the deployment of innovative or improved 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 the design, distribution, financing, permitting, purchase, and use of environmental technologies.

ETV works in partnership with recognized standards and testing organizations; with stakeholder groups that consist of buyers, vendor organizations, and permitters; 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 Advanced Monitoring Systems (AMS) Center, one of six technology centers under ETV, is operated by Battelle in cooperation with EPA's National Exposure Research Laboratory. The AMS Center has recently evaluated the performance of continuous monitors used to measure fine particulate mass and species in ambient air. This verification statement provides a summary of the test results for the Rupprecht & Patashnick, Co. Series 8400N particulate monitor.

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. 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 8400N reports measurement results in terms of particulate nitrate concentration in $\mu g/m^3$ and, therefore, was compared with ion chromatographic nitrate determinations on collected particulate matter samples. The ambient nitrate concentrations differed markedly in the two phases, ranging from about 0.5 to 3.5 $\mu g/m^3$, averaging 1.2 $\mu g/m^3$ in Phase I, and ranging from about 0.5 to 65 $\mu g/m^3$, averaging 17 $\mu g/m^3$, in Phase II. 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 8400N consists of a weather-protection inlet and transport tubing, pulse generator, microprocessor-based control system, user interface, nitrogen oxides 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 nitrate concentration.The Series 8400N uses a flash volatilization technique to measure the concentration of particulate nitrate contained in $PM_{2.5}$. To achieve high collection efficiencies even for very small secondary aerosols, a humidifier moistens the sample stream and causes the hygroscopic nitrate 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 a nitrogen atmosphere occurs at approx-imately 350°C through the resistive heating of the metal impactor/flashing strip, which creates a pulse of oxides of nitrogen that is quantified by the chemiluminescent reaction with excess ozone. The Series 8400N computes a new data point every 10 minutes, with a resolution of the reported values of ±0.2 $\mu g/m^3$.

VERIFICATION OF PERFORMANCE

Inter-Unit Precision: For the hourly average data from Phase I, the linear regression analysis showed a slope of 0.827 (0.029), an intercept of 0.007 (0.019) $\mu g/m^3$, and an r^2 value of 0.905, where the numbers in parentheses are 95% confidence intervals. The regression results of the 24-hour average data show a slope of 0.802 (0.190), an intercept of 0.008 (0.097) $\mu g/m^3$, and an r^2 value of 0.843. In both cases, a statistically significant bias (95% confidence) between the two monitors was indicated, with Monitor 1 reading higher than Monitor 2. During Phase II, with nitrate concentrations about 10 times higher than in Phase I, the regression results of the hourly average data from the duplicate monitors showed a slope of 1.052 (0.025), an intercept of 0.02 (0.43), and an r^2 value of 0.907. For the 24-hour average data, the regression results showed a slope of 1.089 (0.067), an intercept of -0.42 (1.08) µg/m^3, and an r^2 value of 0.975. In both cases the slope of the regression line is statistically different from unity and the intercept is statistically indistinguishable from zero.

Comparability/Predictability: For Phase I, the 24-hour average results of the duplicate Series 8400N monitors were compared by linear regression to the reference measurements of denuded filter samples analyzed by ion chromatography. The regression results for Monitor 1 during Phase I show a slope of 0.30 (0.20), an intercept of 0.21 (0.25) µg/m^3, and an r^2 value of 0.315, when one apparent outlying reference data point was removed from the analysis. For Monitor 2, the regression results show a slope of 0.37 (0.15), an intercept of 0.02 (0.17) µg/m^3, and an r^2 value of 0.770. During Phase II, with much higher ambient nitrate levels, nitrate reference samples were collected on a 5-per-day schedule. The regression results, including all the reference data, show a slope of 0.600 (0.041), an intercept of 3.18 (0.94) µg/m^3, and an r^2 value of 0.855 for Monitor 1. For Monitor 2, the regression results show a slope of 0.625 (0.054), an intercept of 3.42 (1.22) µg/m^3, and an r^2 value of 0.774. These results indicate a statistical bias relative to the reference measurement for both monitors. For the various sampling periods, the slopes of the regression lines ranged from 0.537 to 0.914 for Monitor 1 and from 0.561 to 1.087 for Monitor 2. The best agreement with the reference measurements was seen during the night time and early morning sampling periods (i.e., 0000-0500, and 0500-1000) and the worst agreement during the mid-day sampling periods (i.e., 1000-1300 and 1300-1600).

Meteorological Effects: The multivariable model of Phase I data provided no conclusive results about the effect of meteorological conditions on the readings of the Series 8400N monitors. Multivariable analysis of Phase II data indicated that, for one monitor, wind speed, relative humidity, and barometric pressure had a significant effect and, for the other monitor, only ambient temperature had a significant effect. However, the effects totaled 5% or less relative to the regression of monitor results against reference data alone.

Influence of Precursor Gases: The multivariable model ascribed to nitric oxide and sulfur dioxide a statistically significant (90% confidence) influence on the readings of the Series 8400N monitors relative to the nitrate reference measurements in Phase I. However, the overall effects of these two gases were small and opposing, amounting to less than 10% difference relative to the regression of monitor results against reference data alone. In Phase II, none of the measured precursor gases had a statistically significant influence on either

Other Parameters: During Phase I, maintenance included replacement of purge and calibration gas cylinders at a greater frequency than expected due to leaks in valves in the Series 8400N monitors. Flash strips were also replaced several times. As a result of the frequent maintenance, data recovery was 80% for one monitor and 44% for the other monitor. In Phase II, less frequent maintenance was required. Data recovery was 91% for one monitor and 100% for the other monitor.

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