THE ENVIRONMENTAL TECHNOLOGY VERIFICATION PROGRAM

U.S. Environmental Protection Agency

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ETV Joint Verification Statement

TECHNOLOGY TYPE:	**Continuous Ambient Fine Particle Monitor**
APPLICATION:	**MEASURING FINE PARTICULATE MASS IN AMBIENT AIR**
TECHNOLOGY NAME:	**PAS 2000 Particulate PAH 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 EcoChem Analytics Photoelectric Aerosol Sensor (PAS) 2000 particulate polycyclic aromatic hydrocarbon (PAH) monitor.

VERIFICATION TEST DESCRIPTION

The objective of this verification test was to provide quantitative performance data on a variety of 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. For verification of the PAS 2000 monitors, 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 May 10 to 23, 2001. Specific performance characteristics to be verified in this test included inter-unit precision, agreement with and correlation to time-integrated reference methods, effect of meteorological conditions, and influence of precursor gases. The PAS 2000 measures electron current associated with ionization of particulate-bound PAH species, and, therefore, was compared to a reference procedure for determining ambient concentrations of particulate-bound PAHs. Additionally, comparisons with a variety of supplemental measurements were made to establish specific performance characteristics. Unfortunately, in both phases of testing, both reference and PAS 2000 data indicated that the ambient PAH levels were often near or below the nominal 3 ng/m^3 detection limit of the monitors. As a result, the quantitative evaluation of PAS 2000 performance was limited.

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 performance evaluation audits were conducted on the FRM samplers used in the verification test. Battelle QA staff conducted 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 PAS 2000 works on the principle of photoionization of particle-bound PAH. Using a 220-nm excimer lamp, the aerosol flow is exposed to high-intensity, narrow band ultraviolet radiation. The narrowly restricted wavelength of the light allows only particulate PAH having ionization potentials of 5.6 eV or less to be ionized, while gas molecules and non-carbon aerosols remain neutral. The aerosol particles that have PAH molecules adsorbed on their surfaces emit electrons as a result of the photoionization process that are removed when an electric field is applied. The remaining positively charged particles are then collected on a filter inside an electrometer, where the charge is measured. The resulting electric current establishes a signal that is proportional to the concentration of total particle-bound PAH. Source-specific calibration curves are available, or can be generated by comparing the monitor output to an analytically determined PAH concentration, based on sampling the source emissions. A source-specific calibration curve can provide greater accuracy for the particle size, charge, and PAH distribution specific to the source. In addition to the source-specific curves, an approximate universal calibration curve can be used for screening and real-time trending applications. That universal calibration curve was used in all PAS 2000 monitoring in this verification test. A specially designed sample conditioning system for monitoring PAH in source emissions consists of a heated probe and a dilution system. These features permit the PAS 2000 to handle emission streams with high particle loading from stacks. The PAS 2000 also can be connected to a rotating disk dilution system. As used in this study for monitoring particle-bound PAH in ambient air, the PAS 2000 had a nominal detection limit of 3 ng/m^3 The PAS 2000 incorporates no internal particle size selection. In this verification, no external particle size selection was used either, because of the predominant occurrence of ambient atmospheric particle-bound PAH in the fine particle size range (i.e., $PM_{2.5}$).

VERIFICATION OF PERFORMANCE

Inter-Unit Precision: During Phase I , the duplicate PAS 2000 monitors showed the same temporal pattern of ambient PAH levels for both the 15-minute data and 24-hour averages. Regression analysis showed $r^2 = 0.989$ for the 15-minute data and $r^2 = 0.979$ for the 24-hour averages. The slopes of the regression lines were 0.779 (0.002) and 0.782 (0.023), respectively, for the 15-minute data and 24-hour averages, indicating a significant bias of

about 22% between the two monitors. The intercept of the regression line was -0.66 (0.01) ng/m^3 for the 15-minute data, and was -0.68 (0.10) ng/m^3 for the 24-hour data. The calculated coefficient of variation (CV) for the 15-minute data was 60.4%; and, for the 24-hour averages, the CV was 40.8%. Much of these CV values may be attributed to the bias between the monitors and to the fact that the ambient PAH concentrations were comparable to the 3 ng/m^3 nominal detection limit of the monitors, making even small inter-unit differences relatively large contributors to the CV.

During Phase II, the duplicate PAS 2000 monitors again showed the same temporal trends when 15-minute average data were considered. Regression analysis showed an r^2 of 0.812, a slope of 0.875 (0.010) and an intercept of -1.98 (0.04) ng/m^3. The calculated CV for these data was 101%, much of which is attributed to an offset (~2 ng/m^3) between the two monitors. No conclusive statistical measure of precision was available for the 24-hour averages, as all the results from one monitor were below the nominal detection limit. However, a linear regression analysis of these data show an r^2 of 0.406, a slope of 0.475 (0.382), and an intercept of -0.65 (1.46) ng/m^3. The calculated CV for these data was 84.3%. In light of the low ambient PAH levels present (comparable to the 3 ng/m^3 nominal detection limit of the monitors), the substantial offset between the two monitors undoubtedly was a major contributor to these CV values.

Comparability/Predictability: In both phases of the verification test, both the reference method and the PAS 2000 data indicated that ambient particulate PAH levels were usually near or below the nominal 3 ng/m^3 detection limit of the PAS 2000 monitors. Consequently, quantitative comparisons to the reference data were not conducted, although the ranges of the reference and PAS 2000 data were similar, and some agreement in temporal trends was observed.

Meteorological Effects: Because the ambient PAH levels were comparable to the nominal detection limit of the monitors, no conclusions could be made from multivariable analysis concerning the influence of meteorological conditions on PAS 2000 readings.

Influence of Precursor Gases: Because the ambient PAH levels were comparable to the nominal detection limit of the monitors, no conclusions could be made from multivariable analysis concerning the influence of precursor gases on PAS 2000 readings.

Other Parameters: The two monitors required no maintenance during either phase of testing. Some periods of data were lost because of recurrent difficulties with the data collection system in the form of failure to restart data collection after power outages. Overall data recovery was approximately 90%.

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