THE ENVIRONMENTAL TECHNOLOGY VERIFICATION PROGRAM

U.S. Environmental Protection Agency

The Business of Innovation

ETV Joint Verification Statement

TECHNOLOGY TYPE:	**ON-LINE NUTRIENT ANALYZER**
APPLICATION:	**NUTRIENT MONITORING AT AN INDUSTRIAL WASTEWATER TREATMENT PLANT**
TECHNOLOGY NAME:	**Multi-Parameter Analyzer (MP-1)**
COMPANY:	**ZAPS Technologies, Inc.**
ADDRESS:	**131 NW 4th Street, PO Box 401 Corvallis, Oregon 97330**
PHONE:	**541-520-2663**
FAX:	**541-753-3467**
WEB SITE:	**www.zapstechnologies.com**
E-MAIL:	**joe@zapstechnologies.com**

The U.S. Environmental Protection Agency (EPA) supports 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 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. Information and ETV documents are available at www.epa.gov/etv.

ETV works in partnership with recognized standards and testing organizations, with stakeholder groups (consisting of buyers, vendor organizations, and permitters), and with 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 (QA) 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 verification centers under ETV, is operated by Battelle in cooperation with EPA's National Exposure Research Laboratory. In collaboration with the DuPont Company, the AMS Center evaluated the performance of nutrient monitors to measure water quality. This verification statement provides a summary of the test results for the ZAPS Technologies, Inc., Multi-Parameter Analyzer (MP-1) for nutrient monitoring.

VERIFICATION TEST DESCRIPTION

The objective of this verification test was to evaluate the MP-1's performance in quantifying nitrate concentrations in wastewater at an industrial wastewater treatment plant. The verification test was conducted between May 5 and June 16, 2005, at the DuPont Company's industrial wastewater treatment facility at the Spruance Plant in Richmond, Virginia. At the Spruance Plant, DuPont manufactures engineering polymers/ plastics and fibers (e.g., NOMEX® flame retardant and KEVLAR®). Operations Management International (OMI), Inc., operates the wastewater treatment plant under contract with DuPont and provided the day-to-day logistical support for this verification test. The wastewater from the Spruance Plant provided a single example of possible matrix effects associated with wastewater monitoring. The verification test was designed to evaluate accuracy, bias, linearity, limit of detection (LOD), reproducibility, span and zero drift, interference effects, matrix effects, data completeness, and operational factors.

The test had two components: off-line testing (two phases) and on-line effluent monitoring. During off-line Phase I testing, the MP-1 was challenged with multi-level nitrate standards and deionized (DI) water to determine its accuracy, bias, linearity, and LOD. The MP-1 was challenged with additional nutrient standards for the determination of interference effects for several forms of nitrogen and phosphorus. Reproducibility was evaluated during off-line Phase I by repeatedly challenging the MP-1 with a mixed standard containing potassium nitrate and potassium dihydrogenphosphate. To determine span and zero drift, once each week, DI water and the mixed nutrient standard were supplied to the MP-1 for a total of five zero/span checks. During off-line Phase I and Phase II testing, the MP-1 was challenged with a series of samples containing altered DI water or wastewater matrices to determine matrix effects. During on-line effluent monitoring, MP-1 matrix effects were evaluated for the final effluent. Data completeness was assessed based on the overall data return, and operational factors were evaluated based on the observations of Battelle and OMI staff.

QA oversight of verification testing was provided by Battelle and EPA. Battelle QA staff conducted a technical systems audit, a performance evaluation audit, and a data quality audit of 10% of the test data. This verification statement, the full report on which it is based, and the test/QA plan for this verification test are all available at www.epa.gov/etv/centers/center1.html.

TECHNOLOGY DESCRIPTION

The following description of the MP-1 was provided by the vendor and does not represent verified information.

The MP-1 was designed to serve as a first-alert system for water treatment plants and can also be used for routine monitoring of source and product waters. The MP-1 provides high-quality, continuous, in-line monitoring of water quality, using a combination of measured and calculated parameters. Data are captured 25 times per second and processed in real time. The MP-1 is a sequential fiber-optic spectrometer that measures nitrate by its absorption at 220 nanometers. In unfiltered natural water, two artifacts affect this absorption band: blocking of light by particles in the water (turbidity) and absorption by natural organic matter. The MP-1 minimizes these artifacts by making corrections using light measurements at other wavelengths.

Since it can operate from 200 to 800 nanometers, the MP-1 can be programmed to measure standard laboratory water-quality parameters, including those in the ultraviolet (UV) range. The MP-1 is capable of providing over 100 channels of optical data by monitoring absorption, fluorescence, and total reflection bands. It can control and acquire data from other sensors such as thermistors and pH probes, as well as for MP-1 satellite units and single element analyzers. The MP-1 used in this verification test was configured to measure corrected nitrate absorption, temperature, and several other channels related to dissolved organic carbon, complex hydrocarbons, bacterial abundance, and chlorophyll *a*. The MP-1 sequentially measured each of nine channels (including nitrate absorbance, UV absorbance, and others) for approximately 13 seconds, for a total loop time of approximately two minutes. The MP-1 measured value displayed on-screen was updated after each channel measurement, and the MP-1 reported a nitrate concentration value in units of milligrams (mg) nitrogen (N) per liter (L) at the end of each loop. Thus, a nitrate measurement was reported every two minutes. The Raman scattering (RS) channel value was used as a diagnostic tool to determine whether or not the MP-1 was working properly. Values for the RS channel less than 20 indicated that residue in the flow cell had accumulated on the internal components and was blocking the UV radiation, while RS values greater than 70 were caused by entrained air bubbles in the flow cell. Data from the MP-1 were written to a computer in real time and stored as a comma separated values file format (*.csv) and a new file was written every 24 hours.

The MP-1 verified in this test utilized the prototype configuration, which consisted of a rack-mounted personal computer and analog board, an instrument enclosure, and a plumbing board, which held the MP-1 flow cell and inlet valve system. Nutrient standards and other test samples were delivered to the MP-1 by gravity-feeding the standard through the flow cell, using the off-line measurement sample bottle. For on-line monitoring, the sample was supplied at positive pressure through the inlet valve, filling the flow cell, and discharging through the overflow outlet. The angle of the flow cell allowed it to be drained (back-flushed) by opening the inlet drain valve. Subsequent to this verification test, the valve system was upgraded to facilitate cleaning the flow cell and its components.

The computer rack was approximately 1.7 meters tall (66 inches) and was positioned within two feet of the instrument enclosure for connecting power and computer cables. The instrument enclosure weighed approximately 14 kilograms (30 pounds) and was 508 millimeters (mm, 20 inches) wide, 610 mm (24 inches) tall, and 229 mm (9 inches) deep. The plumbing board was 737 mm (29 inches) tall. The MP-1 has full network capabilities, allowing results to be forwarded to a remote location. The node MP-1, with the full data acquisition system, costs $54,900. Satellite MP-1 units and single-element analyzers that can be controlled by node MP-1 units cost $45,540 and $33,630, respectively.

VERIFICATION OF PERFORMANCE

Accuracy: The accuracy of the MP-1 nitrate measurements was assessed over the range of 0.1 to 5 mg N/L in terms of percent recovery (%R) relative to reference method measurements. Nitrate %R values ranged from 98% to 251%, with an average of 157%.

Bias: Bias of +57% was observed for the MP-1 nitrate measurements, calculated using data from the multi-level nitrate standards.

Linearity: Linearity was evaluated in terms of slope, intercept, and r^2 over the nitrate range from 0 to 5 mg N/L. The 95% confidence intervals for the slope and intercept of each regression were also calculated (and are shown in the following text in parenthesis). The slope of the regression line was 1.34 (± 0.37), with an intercept of 0.19 (± 0.77) and an r^2 value of 0.9574.

Limit of Detection: The MP-1 LOD for nitrate was determined from 15 DI water blank measurements conducted over the duration of the verification test. The average MP-1 nitrate measurement for DI water blanks was 0.043 mg N/L, with a standard deviation of 0.063 mg N/L, resulting in a nitrate LOD of 0.232 mg N/L. The vendor-reported MP-1 nitrate LOD is 0.05 mg N/L (determined as three times the signal-to-noise ratio). Reference method DI water nitrate measurements ranged from < 0.04 to 0.08 mg N/L. Variability in the nitrate content of the DI water used for testing would be reflected in the calculated MP-1 LOD.

Reproducibility: The reproducibility of the MP-1 was evaluated as the % relative standard deviation from five replicate challenges of a mixed nutrient standard (~5 mg N/L nitrate and ~3 mg P/L ortho-phosphate). The reproducibility for MP-1 nitrate measurements was 14%.

Span and Zero Drift: Drift, defined as three consecutive drift check results that fell either above or below the warning limit (average baseline response ± 2 SD) was calculated for the MP-1 span (~5 mg N/L nitrate) response and zero response (to DI water). Drift in the normalized nitrate span response was not observed for the MP-1 relative to the corrected baseline response, although the last span drift check result was 1.22 mg N/L greater than the target concentration. However, if the uncorrected baseline response data were used to evaluate drift, none of the span check results fell within the warning limit. Drift was not observed in the MP-1 response to DI water blanks. The final drift check result was 0.04 mg N/L less than the average baseline zero response.

Interference Effects: The effect of non-nitrate nutrients on the MP-1 response was assessed by challenging the MP-1 with the series of nitrogen- and phosphorus-containing compounds. All of the non-nitrate nutrients tested produced an interference effect less than or equal to 7% except for nitrite, for which a 97% interference effect was observed. The MP-1 response to nitrite was expected since nitrite absorbs UV radiation from the nitrogen-oxygen bond present in nitrate and nitrite ions.

Matrix Effects: Matrix effects were evaluated by calculating the %R value for several matrices. The percent difference (%D) was calculated for test samples with varied pH and in the presence of chlorophyll *a*. The MP-1 RS values during the pH and chlorophyll *a* matrix effects challenges ranged from 5 to 7, indicating that the measurement accuracy was greatly impacted by residue on the flow cell components and, therefore, the MP-1 was not operating properly. The MP-1 nitrate measurements at pH 5 and 9 were within 1% (by %D) of measurements at pH 7. The nitrate measurement in the presence of chlorophyll *a* was 4% (%D) higher than the measurement at the same nitrate concentration in the absence of chlorophyll *a*. Given the MP-1's reduced sensitivity during the measurement of these samples, it is not known whether a change in the MP-1 response could have been detected. Percent recovery values for off-line measurements of effluent, process, and influent wastewater samples ranged from 33% to 162%. The %R values for the on-line nutrient measurements of effluent wastewater ranged from 38% to 208%, with an average of 143%. A paired *t*-test applied to the on-line effluent monitoring results indicated that differences in the mean nitrate concentration measured by the MP-1 and the reference method were not significant at the 95% confidence level. Because of the small sample size and high variance in the nitrate measurements, the probability of detecting a true difference in the mean concentration measured by the MP-1 and reference method is relatively low (less than 10%).

Data Completeness: The MP-1 was operating during 100% of the verification test with the exception of two power losses at the Plant that occurred for a total of approximately 38 hours. Over the duration of the verification test, the MP-1 conducted 26,057 nitrate measurements (including both on-line and off-line measurements). The RS value was between 20 and 70 for 31% of all measurements recorded during the verification test. Measurements outside of this optimal range were caused by residue or entrained bubbles in the flow cell and include nitrate measurements recorded while the flow cell was being cleaned. Any testing activities for which the RS values were outside of the optimal range (between 20 and 70), and the data used to evaluate the MP-1's performance, are specified in the verification report.

Operational Factors: A user with minimal experience could operate the MP-1. The only maintenance required during the verification test included the daily cleaning of the flow cell, which required approximately 15 minutes to complete. Daily checks of the MP-1 were simple and quick, requiring less than five minutes per day.

Original signed by Gabor J. Kovacs 9/14/05
Gabor J. Kovacs Date
Vice President
Energy and Environment Division
Battelle

Original signed by Lawrence W. Reiter 9/29/05
Lawrence W. Reiter Date
Director
National Exposure Research Laboratory
Office of Research and Development
U.S. Environmental Protection Agency