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THE ENVIRONMENTAL TECHNOLOGY VERIFICATION
PROGRAM



U.S. Environmental Protection Agency

Battelle

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:	TNPC-4110(C)	
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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 permittees), 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 Shimadzu Scientific Instruments, Inc., TNPC-4110(C) on-line water quality analyzer.

VERIFICATION TEST DESCRIPTION

The objective of this verification test was to evaluate the TNPC-4110(C)'s performance in quantifying total nitrogen (TN) and total phosphorus (TP) 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, 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 TNPC-4110(C) was challenged with multi-level nutrient standards and deionized (DI) water for TN and TP to determine its accuracy, bias, linearity, and LOD. The TNPC-4110(C) was challenged with additional nutrient standards for the determination of accuracy for several forms of nitrogen and phosphorus. Reproducibility was evaluated during off-line Phase I by repeatedly challenging the TNPC-4110(C) 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 TNPC-4110(C) for a total of five zero/span checks. During off-line Phase I and Phase II testing, the TNPC-4110(C) was challenged with a series of samples containing altered matrices to determine matrix effects. In the on-line effluent monitoring phase, TNPC-4110(C) 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 TNPC-4110(C) was provided by the vendor and does not represent verified information.

The TNPC-4110(C) is capable of analyzing or monitoring TN, TP, and total organic carbon (TOC). (TOC monitoring was not verified in this test, although measurements were conducted during on-line monitoring of effluent wastewater.) It can be used for nutrient monitoring and process control and automatically performs sampling, pretreatment (physical and chemical), digestion, and analysis. Calibration is required before starting measurements, and both off-line and automatic calibrations can be conducted. For automatic calibrations, an initial calibration is performed followed by additional calibrations during on-line measurement at specified intervals. For this verification test, automatic calibrations were performed every seven days.

Total phosphorus is measured using ozone as the oxidizer, with advanced photochemical oxidation, heat, sulfuric acid, and ultraviolet irradiation, leading to complete oxidation of the phosphorus in the sample. To ensure complete oxidation of the dissolved and particulate phosphates, the oxidation is performed at near boiling-water temperature. Sulfuric acid ammonium molybdate reacts with the phosphate ions, converting them to phosphomolybdate complex. The phosphomolybdate is then reduced, using ascorbic acid, to molybdenum blue. The intensity of the blue color is proportional to the phosphate concentration present in the sample. The minimum measurement cycle for TP is 43 minutes. Total nitrogen is measured using a catalytic combustion method, which involves the decomposition of nitrite, nitrate, ammonia, and organic nitrogen compounds into nitrogen monoxide at 720°C. The carrier gas containing the nitrogen monoxide is cooled and dehumidified using an electronic dehumidifier and passed to a chemiluminescence detector. Within the chemiluminescence detector, ozone is generated, which interacts with the nitrogen monoxide, producing excited nitrogen dioxide. A silicon diode is used to detect the light emitted from the excited molecules, which results in a signal that is proportional to the concentration of TN. The TN minimum measurement cycle is 4 minutes. Measurements can be conducted continuously (i.e., approximately every 4 minutes for TN only, every 43 minutes for TP only, or every 43 minutes for TN, TP, and TOC) or every 1, 2, 3, 4, 6, 12, or 24 hours. The TNPC-4110(C) can be configured to begin on-line measurements immediately or at a specified time.

During this verification test, on-line measurements were conducted at 1-hour intervals, and the nutrient measurement concentrations were output using the internal thermal printer. The TNPC-4110(C) consists of an automated pretreatment filtration system (optional), a multifunction injection system, an oxidation reactor vessel, and an absorbance detector, all in one unit for indoor installation. The dimensions of the TNPC-4110(C) are 980 millimeters (mm, 38.6 inches) in width, 1,560 mm (61.4 inches) in height, and 490 mm in depth (19.3 inches), excluding the pretreatment filtration system. It weighs approximately 100 kilograms (220 pounds) and costs \$34,000. For this verification test, the TNPC-4110(C) was equipped with a backwash strainer sample pretreatment unit, intended to prevent adhesion of contaminants, slime, and/or algae; backwashing the strainer prevents the strainer from clogging.

VERIFICATION OF PERFORMANCE

Accuracy: The accuracy of the TNPC-4110(C) was assessed over the range of 0.5 to 20 milligrams per liter (mg/L) for TN and 0.5 to 5 mg/L for TP in terms of percent recovery (%R) relative to reference method measurements. TN (in the form of nitrate) %R values ranged from 109% to 140%, with an average of 131%. The TNPC-4110(C) %R values for TP (in the form of ortho-phosphate) ranged from 111% to 133%, with an average of 118%. TN accuracy for non-nitrate forms of nitrogen ranged from 31% to 129%. Organic and inorganic phosphorus resulted in %R values of 103% and 113%, respectively; the mixed phosphorus standard %R value was 110%. The TNPC-4110(C) %R values (TN and TP) for a certified simple nutrient standard ranged from 95% to 153% relative to the nominal concentration and from 110% to 178% relative to the reference method results.

Bias: Bias of +31% was observed for the TNPC-4110(C) TN measurements for standards containing nitrogen in the form of nitrate. For TP, the TNPC-4110(C) showed a bias of +18% for standards containing phosphorus in the form of dissolved, inorganic ortho-phosphate.

Linearity: Linearity was evaluated in terms of slope, intercept, and r^2 over the range from 0 to 20 mg nitrogen per liter (N/L) for TN and 0 to 5 mg phosphorus per liter (P/L) for TP. The 95% confidence intervals for the slope and intercept of each regression were also calculated (and are shown in the following text in parenthesis). For TN, the slope of the regression line was 1.34 (± 0.02), with an intercept of 0.03 (± 0.22) and an r^2 value of 0.9998. For TP, the linear regression showed a slope of 1.10 (± 0.02), an intercept of 0.08 (± 0.06), and an r^2 of 0.9996. Over the range of concentrations tested, the TNPC-4110(C) demonstrated a high degree of linearity.

Limit of Detection: The TNPC-4110(C) LOD for TN and TP were determined from 15 blank measurements conducted over the duration of the verification test. All of the TNPC-4110(C) TN measurements for DI water were 0.000 mg N/L. Thus, the average and standard deviation were also equal to zero, giving a detection limit of 0 mg N/L. Based on the consistent reporting of non-detects in the response to DI water blanks, it is suggested that a method detection limit be determined by the user for each sample matrix. The average TNPC-4110(C) TP measurement for DI water blanks was 0.044 mg P/L, with a standard deviation of 0.032 mg P/L, resulting in a TP LOD of 0.141 mg P/L for the range setting of 0 to 5 mg P/L, which uses a five-fold sample dilution. The vendor-reported LOD for TNPC-4110(C) measurements using the lowest measurement range (0 to 0.5 mg P/L) is 0.01 mg P/L. Reference measurement results of the DI water used to challenge the TNPC-4110(C) were below the 0.05 mg P/L quantitation limit, with one exception.

Reproducibility: The reproducibility of the TNPC-4110(C) was evaluated as the % relative standard deviation from six replicate challenges of a mixed nutrient standard (~5 mg N/L nitrate and ~3 mg P/L ortho-phosphate). The reproducibility for TNPC-4110(C) TN and TP measurements was 2% and 1%, respectively.

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 standard deviations (SD)], was calculated for the TNPC-4110(C) span (~5 mg N/L for TN and ~3 mg P/L for TP) response and zero response (to DI water). Drift did not occur in the TN and TP TNPC-4110(C) zero response to DI water blanks. Drift in the TN span response was not observed for the TNPC-4110(C); although four of five span drift check results were outside the warning limit, and the last span drift check result was 1.143 mg N/L greater than the average baseline response. The last three TP drift checks fell above the warning limit, indicating that drift occurred in the TNPC-4110(C) span response. The final TP drift check value was 0.073 mg P/L greater than the average baseline response.

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*. TN %R values ranged from 132% to 136% over pH 5 to 9 and TP %R values ranged from 112% to 114%. The TNPC-4110(C) TN and TP measurements at pH 5 and 9 were within 3% (by %D) of measurements at pH 7. The TN measurement in the presence of chlorophyll *a* (99%R) was 27% (%D) lower than the measurement at the same nitrate concentration in the absence of chlorophyll *a* (130%R). The TP measurements of phosphate in the presence and absence of chlorophyll *a* were within 1% (%D) of each other (%R of 115% and 119%). Percent recovery values for off-line measurements of effluent, process, and influent wastewater samples ranged from 31% to 143% for TN and 72% to 240% for TP. The %R values for the on-line TN measurements of effluent wastewater ranged from 57% to 86%, with an average of 72%. The average TP %R was 128%, and individual values ranged from 55% to 353%. A paired *t*-test applied to the on-line effluent monitoring results indicated that differences in the mean TN concentration measured by the TNPC-4110(C) and the reference method can be considered to be significant at the 95% confidence level. However, the two methods did not give significantly different values for the mean TP concentration. It should be noted that differences between TNPC-4110(C) and reference method measurements cannot be attributed specifically to matrix effects and could have been caused by a number of factors (e.g., differences in calibration standards). Because of the small sample size and high variance in the TN and TP measurements, the probability of detecting a true difference in the mean concentrations measured by the TNPC-4110(C) and reference method is relatively low (less than 17%).

Data Completeness: During on-line monitoring, the TNPC-4110(C) experienced 34 hours of down time following a failed automatic calibration; the nutrient calibration standard level fell below the sample tube inlet. For TN and TP, respectively, 94% and 93% of the possible number of measurements were conducted. Calibrations during the verification test consumed the time equivalent to 37 measurements, and data for a few measurements were lost when tape was inadvertently applied over the text on the thermal print-outs. Upon contact with the tape, the text disappeared completely and could not be recovered. Over the duration of the verification test, the TNPC-4110(C) conducted 766 TN and 755 TP measurements (including both on-line and off-line measurements).

Operational Factors: A user with minimal experience with access to the TNPC-4110(C) instruction manual could install and operate the TNPC-4110(C). Maintenance required during the verification test included replenishing of reagents and DI water, adjusting the calibration span solution after one of the automated calibrations failed, and back-flushing the backwash strainer sample pretreatment unit once during the verification test. One of the air compressors used by the TNPC-4110(C) was damaged during a power loss at the wastewater treatment plant and needed to be replaced. Daily checks of the TNPC-4110(C) were simple and quick, requiring less than five minutes per day.

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