THE ENVIRONMENTAL TECHNOLOGY VERIFICATION PROGRAM

U.S. Environmental Protection Agency

ETV Joint Verification Statement

TECHNOLOGY TYPE:	**Ballast Water Exchange Screening Tool**	
APPLICATION:	**Screening Ballast Water for Fluorescence of Colored Dissolved Organic Matter (CDOM)**	
TECHNOLOGY NAME:	**Ballast Water Exchange Assurance Meter (BEAM) 100**	
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The U.S. Environmental Protection Agency (EPA) has established 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 technology areas under ETV, is operated by Battelle in cooperation with EPA's National Exposure Research Laboratory. The AMS Center evaluated the performance of the Dakota Technologies, Inc. Ballast Water Exchange Assurance Meter (BEAM) 100. This verification statement provides a summary of the test results.

VERIFICATION TEST DESCRIPTION

To support ballast water exchange (BWE) regulations, accurate and portable verification tools are needed to determine that BWE has taken place. One parameter proposed as a means of distinguishing between coastal and open-ocean water content in ballast water is fluorescence due to colored dissolved organic matter (CDOM). CDOM refers to the fraction of dissolved organic matter that absorbs light and fluoresces in the ultraviolet (UV) and visible regions of the spectrum. This verification test evaluated the performance of the BEAM 100 in measuring CDOM relative to a standard CDOM measurement approach using a laboratory bench-scale excitation-emission spectrometer under controlled laboratory conditions. The results from the BEAM instruments and reference method instrument were not expected to be exactly the same because of differences in type and efficiency of gratings, detectors, the light source, and other conditions that vary from instrument to instrument. However, the instrumental differences can be partially compensated for by correlating the BEAM and reference method results based on the relationship between standards analyzed on each instrument. For ETV testing, quinine sulfate standards were used to generate a correlation between the BEAMs and the reference method. Both laboratory-prepared, performance test (PT) samples and real-world open-ocean and coastal environmental samples were used for testing. This test did not verify that the BEAM 100 successfully quantified CDOM concentrations or detected BWE, but rather evaluated how well it measured fluorescence from CDOM compared with a standard technique for measuring fluorescence. This test also did not represent all types of waters that may be encountered in BWE screening, but a range of water (and subsequently the range of fluorescence measurements generated from various types of water) that may be expected in practical application.

The BEAM 100 was evaluated by:

- Accuracy—Comparison of the percent difference (PD) between BEAM 100 CDOM measurement to CDOM measurements generated by a Varian Cary Eclipse Spectrometer with both instruments at ambient laboratory temperature (approximately 24°C).
- Linearity—CDOM measurements from varying concentrations of standard analytes known to fluoresce plotted against the analyte concentration. Linearity was evaluated based on linear regression statistics (i.e., the slope and correlation coefficients [R^2]).
- Precision—The relative standard deviation (RSD) of triplicate measurements of the same sample.
- Method detection limit (MDL)—Analysis of seven replicates of known fluorescing analytes at a concentration five times Dakota Technologies, Inc.'s expected detection limit for the analyte.
- Inter-unit reproducibility—Relative percent difference (RPD) between the average of triplicate CDOM measurements of the same sample taken at the same temperature made using two different BEAM 100 units.
- Temperature effects—Comparison of the BEAM 100 CDOM measurements at approximately 4 degrees Celsius (°C) and 34°C with CDOM measurements at ambient laboratory temperature (approximately 24°C) .
- Matrix effects—Evaluated by comparing the percent difference (PD) of the BEAM 100 measurements with the Varian Cary Eclipse spectrometer measurements for the various types of samples analyzed during verification testing.
- Data completeness—The number of valid measurements out of the total number of measurements taken.
- Operational factors—Observations and records related to maintenance needs, calibration frequency, data output, consumables used, ease of use, repair requirements, waste production, and sample throughput.

The PT samples (quinine sulfate and Suwanee River [SR] fulvic acid solutions) and environmental samples from 12 separate locations in the U.S. and Canada were analyzed in triplicate with the BEAM 100 and compared with triplicate measurements taken with the reference method. These samples were evaluated for accuracy by comparing expected responses based on the reference method CDOM analyses which were correlated to BEAM measurements based on the response to quinine sulfate standards in both instruments, instrument linearity across the range of concentrations tested, and precision among the replicate measurements obtained. Two BEAM 100 units were used to measure the test samples. Measurements of aliquots of the same sample were taken sequentially with the two units and with the reference method within minutes of each other. Inter-unit reproducibility was evaluated based on the measurements taken with the two

BEAM units. All measurements made for direct comparison with the reference method were conducted at ambient room temperature.

Because these technologies will be used in a wide range of temperatures in practical application and because temperature can affect CDOM fluorescence, a subset of test samples was analyzed using only the BEAM 100 units at two additional temperatures (approximately 4°C and 34°C) to evaluate the BEAM 100's variability due to temperature effects. Testing at 4°C took place inside a walk-in refrigerator and testing at 34°C took place inside a heated chamber.

Quality control samples included negative control samples (Burdick and Jackson HPLC grade water), positive control samples (5,000 parts per billion [ppb] SR fulvic acid), and a continuing calibration check (10 ppb quinine sulfate).

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 BEAM 100 is based on information provided by the vendor. This technology description was not verified in this test.

The BEAM 100 is a portable, handheld fluorimeter designed to generate a response relative to the amount of CDOM in ballast water. The CDOM related response is determined by exciting the sample with near UV light and measuring the resulting fluorescence to Raman scatter ratio.

The unit consists of a cuvette well permanently mounted in the BEAM. The BEAM is operated through four user-interface buttons. Acquired data are shown in a display screen and can be transferred to a personal computer for long-term storage. Internally, the BEAM consists of electronics; a light-emitting diode used as an excitation source; and two photodetectors, each with different wavelength filters. All measurements are recorded to the BEAM's internal memory. The BEAM's durable plastic carrying case includes space for cuvette cleaning and sample filtering accessories. The BEAM unit is 10.5 by 4.5 by 3.0 inches and weighs 2.5 pounds (with batteries). The carrying case is 16 by 12 by 7 inches and weighs approximately 10 pounds with the BEAM unit and kit supplies in place. The BEAM 100 costs approximately $6,000 per unit.

VERIFICATION RESULTS

Performance Factor	Sample Information	Result
Accuracy	Five concentrations of quinine sulfate prepared in Burdick and Jackson HPLC grade water per ASTM E579-04 (QS) plus one unspiked blank; five concentrations of Suwannee River fulvic acid (SRFA) plus one unspiked blank; and 12 environmental (natural water) samples. All testing was performed at approximately 24°C.	PD from reference method measurements (using a quinine sulfate[A] correlation between the BEAM and reference method results) was less than 20% for both QS and SRFA samples, except for the unspiked, blank samples. PD was also less than 20% for environmental samples. PD values increased with lower measurements of CDOM.
Linearity	Five concentrations of QS plus one unspiked blank; five concentrations of SRFA plus one unspiked blank. All testing was performed at approximately 24°C.	Individual signals at 460 nanometers (nm) and 430 nm were linear across the concentrations tested and had R^2 values >0.99 for both QS and SRFA test solutions.
Precision	Five concentrations of QS plus one unspiked blank; five concentrations of SRFA plus one unspiked blank; and 12 environmental (natural water) samples. Testing was performed at approximately 24°C, 4°C, and 34°C.	RSD of triplicate measurements of each test sample was <10% except for low CDOM concentration samples such as the unspiked blank samples for which the highest RSD was 22.9%.
MDL	Seven replicates of 1 ppb QS and seven replicates of 100 ppb SRFA analyzed following 40 CFR 136 Appendix B procedures. Concentrations were set at 5 times the vendor-specified detection limit for each compound. All testing was performed at approximately 24°C.	Calculated MDLs were lower than the unspiked blank sample CDOM values (<0.01) and may not represent practical detection limits. The BEAMs detected CDOM values <0.06 to 0.07, which were the CDOM values of the lowest concentration QS and SRFA analyzed.
Inter-unit Reproducibility	All test samples. Testing was performed at approximately 24°C, 4°C, and 34°C.	RPD values between the average of triplicate measurements were mostly <10% at all testing temperatures. RPD increased as CDOM concentration decreased.
Temperature Effects	Five concentrations of QS plus one unspiked blank; five concentrations of SRFA plus one unspiked blank. Testing was performed at temperature extremes of approximately 4°C and 34°C and compared with results obtained at approximately 24°C (ambient conditions).	For the spiked samples, PD values ranged as follows: QS solutions: 0.4 to 6.7% for 4°C vs 24°C 0.9 to 31.9% for 34°C vs 24°C SRFA solutions: 25.9 to 98.3% for 4°C vs 24°C 2.1 to 22.9% for 34°C vs 24°C For the unspiked blanks, the PD values ranged from 13.0 to 95.7%. The results indicate that temperature changes can cause deviations in performance and illustrate the importance of calibrating the BEAM units at the testing temperature.
Matrix Effects	Five concentrations of QS plus one unspiked blank; five concentrations of SRFA plus one unspiked blank; and 12 environmental (natural water) samples. All testing was performed at approximately 24°C. The accuracy PD measurements comparing BEAM CDOM values to reference method values (using a quinine sulfate correlation between the BEAM and reference method results) of the same solution were evaluated for differences between matrix type.	Distinct differences in correlation to reference method values were observed based on matrix type. Environmental samples and fulvic acid samples were between 2 and 20% PD from BEAM equivalent reference method measurements (using a quinine sulfate[A] correlation between the BEAM and reference method results), whereas quinine sulfate samples were all less than 5% PD.
Data Completeness	All test samples.	Data completeness was 100%.
Operational Factors	The BEAM 100 units were portable, convenient, and easy to use. Written instructions were clear. Sample throughput was 20 to 25 samples/hour. Sample and rinse water waste (~32 milliliters) were generated per sample. Factors limiting continuous operation of the BEAM include battery life (six AA batteries were replaced after ~100 measurements), BEAM internal memory size (data are overwritten after 256 measurements), access to distilled water (rinse bottle provided with BEAM holds enough distilled water for ~15 samples), and operator hand strength (each sample must be filtered through a 0.45-micron filter). Technical difficulties with displays and system interlocks resulted in the vendor replacing one BEAM unit during testing. Technical difficulties increased when testing at approximately 4°C, and 34°C. Not enough BEAM units were evaluated to know whether these technical difficulties indicate more than a random instrument failure.	

[A] Quinine sulfate was selected to correlate the BEAM and reference instruments because of its use as a spectroscopic standard. Use of other standards with properties closer to the environmental samples may have improved PD values for the environmental samples; however, this was not verified as part of this test.

Signed by Greg Mack 09/28/07
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