THE ENVIRONMENTAL TECHNOLOGY VERIFICATION PROGRAM

U.S. Environmental Protection Agency

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ETV Joint Verification Statement

TECHNOLOGY TYPE:	**PORTABLE CYANIDE ANALYZER**		
APPLICATION:	**DETECTING CYANIDE IN WATER**		
TECHNOLOGY NAME:	**AQUAfast® IV AQ4000 with AQ4006 Cyanide Reagents**		
COMPANY:	**Thermo Orion**		
ADDRESS:	**500 Cummings Ctr.**	**PHONE:**	**1-800-225-1480**
	Beverly, MA 01915	**FAX:**	**1-978-232-6038**
WEB SITE:	**http://www.thermo.com**		
E-MAIL:	**xiaowen.wen@thermo.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 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 (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 seven technology areas under ETV, is operated by Battelle in cooperation with EPA's National Exposure Research Laboratory. The AMS Center has recently evaluated the performance of portable cyanide analyzers used to detect cyanide in water. This verification statement provides a summary of the test results for the Thermo Orion AQUAfast® IV AQ4000 colorimeter with AQ4006 cyanide reagents.

VERIFICATION TEST DESCRIPTION

The verification was based on comparing the cyanide concentrations of water samples determined by the Thermo Orion AQ4000 with cyanide concentrations determined by a laboratory-based reference method (EPA Method 335.1, *Cyanides Amenable to Chlorination*). The Thermo Orion AQ4000 colorimeter was always used in conjunction with the Thermo Orion AQ4006 cyanide reagents. Two Thermo Orion AQ4000s were tested independently between January 13 and February 4, 2003; and the results were compared to assess inter-unit reproducibility. Samples used in the verification test included quality control samples, performance test (PT) samples, lethal/near-lethal concentration samples, drinking water samples, and surface water samples. The results from the Thermo Orion AQ4000 were compared with the reference method to quantitatively assess accuracy and linearity. Multiple aliquots of each test sample were analyzed separately to assess the precision of both the Thermo Orion AQ4000 and the reference method. To determine the detection limit, a solution with a concentration of 0.100 milligram per liter (mg/L) was used. Seven non-consecutive replicate analyses of this solution were made to obtain precision data with which to determine the method detection limit (MDL). The Thermo Orion AQ4000 was tested by a technical and a non-technical operator to assess operator bias. Sample throughput was estimated based on the time required to analyze a sample. Ease of use was based on documented observations by the operators and the Battelle Verification Test Coordinator. The Thermo Orion AQ4000 was used in a field environment as well as in a laboratory setting to assess the impact of field conditions on performance.

QA oversight of verification testing was provided by Battelle. Battelle QA staff conducted a technical systems audit, a performance evaluation audit, and a data quality audit of 10% of the test data.

TECHNOLOGY DESCRIPTION

The following description of the Thermo Orion AQ4000 was provided by the vendor and does not represent verified information.

The Thermo Orion AQ4000 is a portable colorimeter in which a water sample and Thermo Orion AQ4006 cyanide reagents are mixed and analyzed photometrically to provide a quantitative determination of cyanide in the sample. The Thermo Orion AQ4006 cyanide reagents include Auto-Test™ cuvettes packaged in individual analyte modules that contain 30 ampoules, a 25-milliliter (mL) graduated cylinder, and instructions. A coded blank cuvette and an empty vial for background sample blanks are also included. The Thermo Orion AQ4000 automatically identifies the species to be measured and selects the method, wavelength, and reaction time. The Thermo Orion AQ4000's Auto-ID ensures that the pre-measured reagent is matched to the method. The Auto-Test™ cuvettes containing the pre-measured reagent are broken open as the final step in sample preparation, assuring reagent quality.

To measure cyanide with the Thermo Orion AQ4000, a prepared (dechlorinated and pH adjusted) 10-mL sample is measured into the graduated cylinder, five drops of one reagent and 1.5 mL of another reagent are added to the sample, the sample is stirred with the tip of an Auto-Test™ cuvette, and then the tip of an Auto-Test™ cuvette is broken, allowing the sample to rush up into the vial. If any cyanide is present in the water sample, a reaction between cyanide and the reagents added to the sample and those originally present in the Auto-Test™ cuvette produces a color change. After a reaction time of 15 minutes, the Auto-Test™ cuvette is inserted into the Thermo Orion AQ4000, and the cyanide concentration (in mg/L) is reported on the digital display. The Thermo Orion AQ4000 is waterproof, operates on four AA batteries, has dimensions of 8 inches by 3 inches by 2 inches, and weighs 16 ounces. The list prices are $989 for the colorimeter and $32 for AQ4006 refills. Display units include concentration, absorbance, or percent transmittance. A time and date tag can be added to 100 data points in the field and downloaded to a printer or computer in the laboratory.

VERIFICATION OF PERFORMANCE

Accuracy: Biases for the Thermo Orion AQ4000 ranged from 4 to 23% for the PT samples with concentrations ranging from 0.030 to 0.800 mg/L; 10 to 26% for the surface water samples; 6 to 51% for the drinking water samples from around the country; and 27 to 100% for the Columbus, OH, drinking water samples. Since the latter three types of water samples contained no detectable cyanide, they were fortified with 0.200 mg/L of cyanide to test the performance of the Thermo Orion AQ4000 in water matrices.

Precision: The relative standard deviation ranged from 0 to 22% for the PT samples; 0 to 20% for the surface water samples; 1 to 18% for the drinking water samples from around the country; 3 to 20% for the Columbus, OH, drinking water samples analyzed at the indoor field site.

Linearity: The non-technical operator's results from the Thermo Orion AQ4000 for the PT samples (0.030 to 0.400 mg/L) plotted against the concentrations of the same samples as determined by the reference method gives the following regression equation:

> y (non-technical operator results in mg/L)=0.871 (± 0.020) x (reference result in mg/L) + 0.003 (± 0.004) mg/L with r^2=0.996 and N=33.

The data for the technical operator gives the following regression equation:

> y (technical operator results in mg/L)=0.829 (± 0.038) x (reference result in mg/L) + 0.012 (± 0.008) mg/L with r^2=0.985 and N=33.

where the values in parentheses represent the 95% confidence interval of the slope and intercept. Only the technical operator's intercept is significantly different from zero, and the r^2 values are both above 0.980. The linearity of the Thermo Orion AQ4000 was not dependent on which operator was performing the analyses. The slope of the linear regression was significantly less than unity in both instances. This deviation from unity indicates a low bias in the results generated by the Thermo Orion AQ4000 compared with the results produced by the reference method.

Method Detection Limit: The MDL was determined to be approximately 0.01 mg/L for the Thermo Orion AQ4000 when used by the non-technical operator and approximately 0.02 mg/L for the Thermo Orion AQ4000 when used by the technical operator.

Inter-Unit Reproducibility: A linear regression of the data for the inter-unit reproducibility assessment gives the following regression equation:

> y (Unit #1 result in mg/L)=0.999 (± 0.015) x (Unit #2 result in mg/L) + 0.004 (± 0.002) mg/L with r^2=0.994 and N=112.

where the values in parentheses represent the 95% confidence interval of the slope and intercept. The slope is not significantly different from unity, while the intercept is significantly different from zero. These data indicate that the two Thermo Orion AQ4000s functioned very similarly to one another.

Lethal/Near-Lethal Dose Response: Samples at 50.0-, 100-, and 250-mg/L concentrations (close to what may be lethal if a volume the size of a typical glass of water was ingested) were prepared and analyzed by the Thermo Orion AQ4000. Upon breaking the Auto-Test™ cuvette in the lethal/near-lethal samples, the color of the sample changed within five seconds to a brilliant purple and, after approximately 35 more seconds, to blood red. The change was much more rapid than for any of the PT samples. The PT samples took about 30 seconds to even produce a small change in the color of the sample and took the full 15-minute reaction time to reach its analysis color of a clear, light purple. When these samples with lethal/near-lethal concentrations were inserted into the

Thermo Orion AQ4000 after the full reaction time, the digital readout read "over range." Even without using the AQ4000 colorimeter, the reagents and Auto-Test™ cuvettes would be useful for a first responder seeking to find out whether a toxic level of cyanide is present in a drinking water sample. The presence of such concentrations could be confirmed within minutes by visual observation of the color development process.

Operator Bias: A linear regression of the data for the operator bias assessment gives the following regression equation:

> y (non-tech result in mg/L)=1.000 (± 0.061) x (tech result in mg/L) - 0.013 (± 0.009) mg/L with r^2=0.905 and N=112.

where the values in parentheses represent the 95% confidence interval of the slope and intercept. The slope is not significantly different from unity, while the intercept is significantly different from zero. These data indicate that there was very little difference in results generated by the non-technical operator compared with those of the technical operator.

Field Portability: From an operational standpoint, the Thermo Orion AQ4000 was easily transported to the field setting, and the samples were analyzed in the same fashion as they were in the laboratory. No functional aspects of the Thermo Orion AQ4000 were compromised by performing the analyses in the field setting. However, performing analyses under extremely cold conditions (sample water temperatures between 4 and 6°C) negatively affected the performance of the Thermo Orion AQ4006 cyanide reagents.

Ease of Use: The Thermo Orion AQ4000 and AQ4006 cyanide reagents and Auto-Test™ cuvettes were easy to operate. The instructions were clear, and the sample and reagents were easily measured using a graduated cylinder, syringe, and a dropper bottle. The Thermo Orion AQ4000 recognized the Auto-Test™ cuvettes when they were inserted, and a 15-minute timer appeared on the digital readout. When analyzing large sample sets, this timer had to be overridden before every sample analysis. While the sample handling and analysis were easy, the pH of each sample had to be adjusted to between 10.5 and 11.0 using sodium hydroxide and hydrochloric acid. This step required the availability of acid and base, pH paper or meter, and some knowledge of pH adjustment. The Auto-Test™ cuvettes made waste disposal simple and mess free. Only the graduated cylinder used for measuring the sample and adding reagents needed to be rinsed between samples.

Sample Throughput: Since the Thermo Orion AQ4000 did not require strict mixing/reaction time periods after adding each reagent, and the Auto-Test™ cuvettes automatically measured the volume of sample added to the final reaction vessel, the analysis process was conducive to analyzing large numbers of samples consecutively. Each sample was entirely prepared within one or two minutes, and then the 15-minute color development period started. If only one sample is analyzed, sample throughput would take approximately 17 minutes. However, both operators were able to stagger the start of the color development period every two minutes for subsequent samples, so a typical sample set of 12 analyses took 30 to 40 minutes.

original signed by Gabor J. Kovacs 4/17/03
Gabor J. Kovacs Date
Vice President
Environmental Sector
Battelle

original signed by Timothy E. Oppelt 4/29/03
Timothy E. Oppelt Date
Director
National Homeland Security Research Center
U.S. Environmental Protection Agency

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