THE ENVIRONMENTAL TECHNOLOGY VERIFICATION PROGRAM

U.S. Environmental Protection Agency

ETV Joint Verification Statement

TECHNOLOGY TYPE:	**PORTABLE CYANIDE ANALYZER**		
APPLICATION:	**DETECTING CYANIDE IN WATER**		
TECHNOLOGY NAME:	**Model 9606 Cyanide Electrode with Model 290 A+ Ion Selective Electrode Meter**		
COMPANY:	**Thermo Orion**		
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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 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 cyanide analyzers used to detect cyanide in water. This verification statement provides a summary of the test results for the Thermo Orion Model 9606 Cyanide Electrode with the Model 290A+ Ion Selective Electrode Meter, which is referred to as the Thermo Orion ion selective electrode (ISE in this verification statement).

VERIFICATION TEST DESCRIPTION

The verification was based on comparing the cyanide concentrations of water samples determined by the Thermo Orion ISE with cyanide concentrations determined by a laboratory-based reference method (EPA Method 335.1, *Cyanides Amenable to Chlorination*). Two Thermo Orion ISEs were tested independently between January 13 and February 4, 2003; and the results were compared to assess inter-unit reproducibility. Some PT samples were reanalyzed on February 24, 2003, due to a laboratory error. Operator bias was not evaluated for the ISE units, so all the results in this report were generated by a technical operator. 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 ISE 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 the Thermo Orion ISE 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). Sample throughput was estimated based on the time required to analyze a sample. Ease of use was based on documented observations by the operator and the Battelle Verification Test Coordinator. The Thermo Orion ISE 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 ISE was provided by the vendor and does not represent verified information.

The Thermo Orion ISE consists of a solid sensing element containing a mixture of inorganic silver compounds bonded into the tip of an epoxy electrode body. When the sensing element is in contact with a cyanide solution, silver ions dissolve from the membrane surface. Silver ions within the sensing element move to the surface to replace the dissolved ions, establishing a potential difference that is dependent on the cyanide concentration in the solution. Upon calibration with solutions of known cyanide concentrations, these potential differences are converted to concentrations and displayed on the digital readout at mg/L when the Thermo Orion ISE is inserted into an unknown solution. The Thermo Orion ISE incorporates the reference and working electrodes into a single electrode shell. The Thermo Orion ISE is accessorized with a hard carrying case, an electrode stand that clips to the carrying case, a one-meter cable, an alkaline reagent for pH adjustment, and an electrode filling solution. The list price for the provided items is $742 for the Thermo Orion Model 290A+ ISE meter, $596 for the Thermo Orion Model 9606 Cyanide Electrode, and $172 for the plastic carrying case. The Thermo Orion ISE operates on a 9-volt battery and has dimensions of 8.08 x 3.26 x 1.9 inches.

VERIFICATION OF PERFORMANCE

Calibration: A three-point calibration using solutions of 0.030, 0.100, and 0.300 mg/L cyanide typically was used. The manufacturer suggested that the slope of the calibration linear regression be within the range of -54 to -60 millivolt per tenfold increase in cyanide concentration. Seventeen of 22 slopes attained were not within this range. However, analyzing samples using a calibration that produced a regression slope outside the acceptable range did not seem to negatively affect the accuracy of the results. Some of the most accurate results produced by the Thermo Orion ISE were produced on a day when the calibration regression slope was farthest from the acceptable range.

Accuracy: Biases for the Thermo Orion ISE ranged from 5 to 66% for the PT samples with concentrations ranging from 0.030 to 25.0 mg/L; 41 to 123% for the surface water samples; 14 to 100% for the drinking water

samples from around the country; and 4 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 ISE in water matrices.

Precision: Relative standard deviation (RSD) ranged from 1 to 18% for the PT samples, 5 to 16% for the surface water samples, 0 to 2% for the drinking water samples from around the country, and 2 to 10% for the Columbus, OH, drinking water samples.

Linearity: The results from the Thermo Orion ISE for the PT samples (0.030 to 25.0 mg/L) plotted against the concentrations of the same samples as determined by the reference method gives the following regression equation:

y (Thermo Orion ISE results in mg/L)=1.00 (± 0.055) x (reference result in mg/L)
+ 0.506 (± 0.530) mg/L with r^2=0.955 and N=65.

where the values in parentheses represent the 95% confidence interval of the slope and intercept. The slope is not significantly different from unity, the intercept is not significantly different from zero, and the r^2 value is above 0.950. From these regression parameters, the Thermo Orion ISE data indicate linearity; but the data are more accurately described with two linear regressions, one for the high-concentration range (5.00 to 25.0 mg/L) and one for the lower concentration range (0.030 to 0.800 mg/L). This underscores the need to encompass the likely concentration of the water samples with calibration standards slightly higher and lower in concentration to avoid systematic error due to calibration over a non-linear concentration range.

Method Detection Limit: The MDLs for the Thermo Orion ISE were determined to be 0.040 and 0.023 mg/L.

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

y (Technology #1 result in mg/L)=0.853 (± 0.019) x (Technology #2 result in mg/L)
+ 0.040 (± 0.127) mg/L with r^2=0.991 and N=80.

where the values in parentheses represent the 95% confidence interval of the slope and intercept. The slope is significantly different from unity, while the intercept is not significantly different from zero. These data indicate that the two Thermo Orion ISEs functioned somewhat differently from one another. This could be because each electrode was polished and calibrated individually before each analysis set.

Lethal/Near-Lethal Dose Response: The bias values ranged from 105 to 375% for analysis of samples with concentrations of 50.0 to 250 mg/L. Precision (in terms of %RSD) for the Thermo Orion ISE analysis of lethal/near-lethal concentrations ranged from 5 to 38%.

Field Portability: From an operational standpoint, the Thermo Orion ISE was easily transported to the field setting, and the samples were analyzed in the same fashion as they were in the laboratory. While no functional aspects of the Thermo Orion ISE were compromised by performing the analyses in the field setting, close attention had to be paid to bringing the calibration solutions to a temperature similar to the samples.

Ease of Use: The instruction manual for the Thermo Orion ISE was clear and concise. Although the Thermo Orion ISE required calibration and electrode polishing before every sample set, it was convenient that calibration could be done with any concentration of cyanide. The pH was easily adjusted before analysis by the Thermo Orion ISE by adding 0.500 mL of Thermo Orion alkaline reagent to 50.0 mL of sample. One drawback of the Thermo Orion ISE was that the battery-powered stirrer would not operate at the slow speeds recommended for making ISE measurements.

Sample Throughput: Sample preparation, including accurately measuring volume and adding the alkaline reagents, took one to two minutes per sample. Calibration took between 15 and 30 minutes. Each sample took approximately five minutes to attain a stable reading. A typical sample set of 12 analyses plus calibration took approximately an hour and a half.

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