**THE ENVIRONMENTAL TECHNOLOGY VERIFICATION PROGRAM**

U.S. Environmental Protection Agency

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# ETV Joint Verification Statement

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| **TECHNOLOGY TYPE:** | **PORTABLE CYANIDE ANALYZER** |
| **APPLICATION:** | **DETECTING CYANIDE IN WATER** |
| **TECHNOLOGY NAME:** | **Cyanide Electrode CN 501 with Reference Electrode R503D, and Ion Pocket Meter 340i** |
| **COMPANY:** | **WTW Measurement Systems** |
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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 WTW Measurement Systems Cyanide Electrode CN 501 with the Reference Electrode R503D and Ion Pocket Meter 340i, which is referred to as the WTW 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 WTW ISE with cyanide concentrations determined by a laboratory-based reference method (EPA Method 335.1, *Cyanides Amenable to Chlorination*). Two WTW 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 technologies, 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 WTW 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 WTW ISE and the reference method. To determine the detection limit, a solution with a concentration of 0.800 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 WTW 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 WTW ISE was provided by the vendor and does not represent verified information.

The WTW 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 a digital readout as mg/L when the WTW ISE is inserted into an unknown solution. WTW ISE accessories include a hard carrying case, an electrode stand, a one-meter cable, and a reference electrode filling solution. The list price for the provided items is $985 for the Ion Pocket Meter 340i and carrying case, $596 for the Cyanide Electrode CN501, and $121 for the electrode stand. The WTW ISE operates on four AA batteries and has dimensions of 6.9 x 3.2 x 1.5 inches.

## VERIFICATION OF PERFORMANCE

**Calibration:** A three-point calibration using 0.200, 2.00, and 20.0 mg/L was typically performed as suggested by the manufacturer's instructions. The manufacturer suggested that the slope of the calibration linear regression be within the range of -54 to -60 millivolt (mV) per tenfold increase in cyanide concentration. The slopes attained were usually in this range or within 10% of this range. Regardless of whether the slope was within the suggested range, one calibration was performed and then the samples were analyzed.

**Accuracy:** Biases for the WTW ISE ranged from 2 to 17% for the PT samples with concentrations ranging from 0.030 to 25.0 mg/L; 31 to 128% for the surface water samples; 2 to 39% for the drinking water samples from around the country; and 3 to 44% for the Columbus, OH, drinking water samples. Since the latter three types of water samples contained no detectable cyanide, they were fortified with 2.00 mg/L of cyanide to test the performance of the WTW ISE in water matrices.

**Precision:** Relative standard deviation (RSD) ranged from 1 to 23% for the PT samples, 5 to 10% for the surface water samples, 2 to 13% 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 WTW 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 (WTW ISE results in mg/L)=0.99 (± 0.02) x (reference result in mg/L)
+ 0.075 (± 0.200) mg/L with $r^2$=0.993 and N=64.

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 0.99.

**Method Detection Limit:** The MDLs for the WTW ISE were determined to be 0.221 and 0.271 mg/L.

**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)=1.113 (± 0.017) x (Unit #2 result in mg/L)
+ 0.028 (± 0.095) mg/L with $r^2$=0.995 and N=92.

where the values in parentheses represent the 95% confidence interval of the slope and intercept. While the slope is significantly different from unity, further analysis of the data revealed that the deviation is heavily influenced by the 15- and 25-mg/L concentration levels.

**Lethal/Near-Lethal Dose Response:** The bias values ranged from 3 to 34%, and the RSD ranged from 2 to 19% for analysis of samples with concentrations of 50.0 to 250 mg/L.

**Field Portability:** From an operational standpoint, the WTW 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 WTW 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 WTW ISE was not easy to understand. However, after a one-hour telephone consultation with WTW, the WTW ISE was easy to operate. The WTW ISE required calibration and electrode polishing before every sample set. Calibration concentrations were pre-programmed into the ISE meter, and pH adjustment was not necessary once the sample was preserved at a pH greater than 12.0. One drawback of the WTW ISE was that the battery-powered stirrer would not operate at the slow speeds recommended for making ISE measurements.

**Sample Throughput:** Calibration took between 15 and 30 minutes. Once the WTW ISE was calibrated, 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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