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:	**VVR V-1000 Multi-Analyte Photometer with the V-3803 Cyanide Module**
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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 CHEMetrics VVR V-1000 multi-analyte photometer with the V-3803 cyanide module (which is referred to as the CHEMetrics VVR in this verification statement).

VERIFICATION TEST DESCRIPTION

The verification was based on comparing the cyanide concentrations of water samples determined by the CHEMetrics VVR with cyanide concentrations determined by a laboratory-based reference method (EPA Method 335.1, *Cyanides Amenable to Chlorination*). The CHEMetrics VVR V-1000 photometer was always used in conjunction with the V-3803 cyanide module. Two CHEMetrics VVRs 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 CHEMetrics VVR 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 CHEMetrics VVR and the reference method. To determine the detection limit, a solution with a concentration of 0.200 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 CHEMetrics VVR 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 CHEMetrics VVR 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 CHEMetrics VVR was provided by the vendor and does not represent verified information.

The CHEMetrics VVR is a portable multi-analyte direct reading photometer. It uses CHEMetrics self-filling reagent Vacu-vial® ampoules. The cyanide Vacu-vial® test method employs the isonicotinic-barbituric acid colorimetric chemistry. The CHEMetrics VVR uses optical interference filters and a photodiode detector. Test results are displayed in concentration units of mg/L. Vacu-vials® are packaged in individual V-3803 analyte modules, which contain 30 ampoules, two accessory reagent solutions, a 25.0-milliliter (mL) sample cup and instructions. A storage case, dedicated filter, and a coded sealed water blank ampoule are included. Additionally, a test tube is provided for photometer zeroing in situations where samples have background color. To measure cyanide with the CHEMetrics VVR, a 10.0-mL sample is measured in the sample cup, two reagent solutions are added to the sample, the sample is stirred with the tip of the ampoule, and then the tip of the Vacu-vial® is snapped, allowing the sample to be drawn into the ampoule. If any cyanide is present in the water sample, it will react with the chlorine reagent solution to form cyanogen chloride, which in turn reacts with the reagent in the ampoule to form a blue complex in direct proportion to the cyanide concentration. The ampoules are read in the CHEMetrics VVR after a 15-minute color development time. Results are displayed in concentration units of mg/L. The CHEMetrics VVR operates on four AA batteries, has dimensions of 10 inches by 2 inches by 3 inches, and weighs 16 ounces. The list prices are $612.90 for the photometer, $54.10 for the cyanide module, and $20.10 for the Vacu-vial® refill (which contains 30 ampoules). Accessory solution replenishment packs are available (six bottles/pack).

VERIFICATION OF PERFORMANCE

Accuracy: Biases for the CHEMetrics VVR ranged from 3 to 24% for the PT samples with concentrations ranging from 0.030 to 0.800 mg/L; 4 to 17% for the surface water samples; 7 to 63% for the drinking water samples from around the country; and 42 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 CHEMetrics VVR in water matrices.

Precision: The relative standard deviation ranged from 0 to 13% for the PT samples; 2 to 5% for the surface water samples; 0 to 27% for the drinking water samples from around the country; and 5 to 13% for the Columbus, OH, drinking water samples analyzed at the indoor field site and at the laboratory. The calculation of precision for all the drinking water samples analyzed outdoors and the Columbus, OH, well water samples analyzed at the laboratory was not appropriate because the results were below the MDL of the analyzer.

Linearity: The non-technical operator's results from the CHEMetrics VVR 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)=0.823 (± 0.030) x (reference result in mg/L)
> + 0.005 (± 0.007) mg/L with r^2=0.991 and N=33.

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

> y (technical operator results in mg/L)=0.863 (± 0.023) x (reference result in mg/L)
> + 0.007 (± 0.005) mg/L with r^2=0.995 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 0.990. The linearity of the CHEMetrics VVR 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 CHEMetrics VVR compared with the results produced by the reference method.

Method Detection Limit: The MDL was determined to be 0.034 and 0.031 mg/L for the CHEMetrics VVR when used by the non-technical operator and approximately 0.017 and 0.011 mg/L for the CHEMetrics VVR when used by the technical operator.

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

> y (Unit #1 result in mg/L)=0.998 (± 0.015) x (Unit #2 result in mg/L)
> + 0.0001 (± 0.002) mg/L with r^2=0.991 and N=128.

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

Lethal/Near-Lethal Dose Response: When 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 CHEMetrics VVR, the color of the sample changed within five seconds to 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 produce a small change in the color of the sample and took the full 15-minute reaction time to reach its analysis color of clear, light purple. When these samples with lethal/near-lethal concentrations were inserted into the CHEMetrics VVR after the full reaction time, the digital readout read "over range." Even without using the CHEMetrics VVR, the reagents and Vacu-vials® 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 operator bias gives the following regression equation:

y (non-tech result in mg/L)=0.911 (± 0.053) x (tech result in mg/L) + 0.016 (± 0.007) mg/L with r^2=0.902 and N=128.

where the values in parentheses represent the 95% confidence interval of the slope and intercept. The slope of this regression is less than 10% different from unity, indicating a slight difference in the results produced by the operators.

Field Portability: From an operational standpoint, the CHEMetrics VVR 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 CHEMetrics VVR 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 CHEMetrics V-3803 cyanide reagents.

Ease of Use: The CHEMetrics VVR and associated cyanide test reagents and Vacu-vials® were easy to operate. The instructions were clear, and the sample and reagents were easily measured using a graduated sample cup, syringe, and a dropper bottle. The CHEMetrics VVR recognized the Vacu-vials® when they were inserted and automatically produced the result on the digital output. 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. Instructions for pH adjustment were not included in the manufacturer's instructions. Because the color change took place within the Vacu-vials® and they were disposable, cleanup was simple and free of mess. Only the graduated sample cup used for measuring the sample and adding reagents needed to be rinsed between samples.

Sample Throughput: Since the CHEMetrics VVR and V-3803 cyanide module did not require strict mixing/reaction time periods after adding each reagent, and the Vacu-vials® 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. Since the color development reaction takes place in reusable reaction vials, additional vials would have to be purchased to conveniently analyze large sample sets.

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