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:	**1919 SMART 2 Colorimeter with the 3660-SC Reagent System**
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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 portable cyanide analyzers used to detect cyanide in water. This verification statement provides a summary of the test results for the 1919 LaMotte SMART 2 colorimeter with the 3660-SC Reagent System.

VERIFICATION TEST DESCRIPTION

The verification was based on comparing the cyanide concentrations of water samples determined by the LaMotte SMART 2 with cyanide concentrations determined by a laboratory-based reference method (EPA Method 335.1, *Cyanides Amenable to Chlorination*). The LaMotte SMART 2 colorimeter was always used in conjunction with the 3660-SC reagent system. Two LaMotte SMART 2s 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 LaMotte SMART 2 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 LaMotte SMART 2s and the reference method. To determine the detection limit, a solution with a concentration of 0.05 milligrams 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 LaMotte SMART 2 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 LaMotte SMART 2 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 LaMotte SMART 2 was provided by the vendor and does not represent verified information.

The LaMotte SMART 2 is a portable colorimeter in which a sample and a reagent are reacted. The reaction produces a color whose intensity is proportional to the concentration of the analyte. The color is measured photometrically to provide a quantitative determination of the analyte in the sample. The LaMotte SMART 2 uses LED light sources and filtered photodiode detectors. To measure cyanide with the LaMotte SMART 2, a 10-milliliter (mL) sample is measured into a sample vial, and 1 mL of reagent is added to the sample with the disposable pipet. The sample is shaken, two other granular reagents are added using the provided scoops, and the sample is shaken again. If any cyanide is present in the water sample, a reaction between cyanide and the reagents added to the sample produces a color change. After a 20-minute color development period, the sample vial is inserted into the LaMotte SMART 2; and the cyanide concentration (in parts per million) is reported on the digital display. For consistency with the results reported by the reference laboratory, the data produced by the LaMotte SMART 2 are reported in the equivalent units of milligrams per liter (mg/L). The range of the LaMotte SMART 2 cyanide test is 0 to 0.50 parts per million. It has automatic wavelength selection and is supplied with four sample tubes, an AC adapter, and an instruction manual including test procedures. The dimensions of the LaMotte SMART 2 are 15 x 8 x 5.5 centimeters (6 x 3.25 x 2.5 inches), and it weighs 312 grams (11 ounces). The LaMotte SMART 2 operates at 120V/60Hz or 220V/50Hs. The list price for this unit is $725.00 for the colorimeter and $64.00 for reagents adequate for 50 water samples.

VERIFICATION OF PERFORMANCE

Accuracy: Biases for the LaMotte SMART 2 ranged from 2 to 31% for the PT samples with concentrations ranging from 0.030 to 0.800 mg/L; 11 to 30% for the surface water samples; 5 to 41% for the drinking water samples from around the country; and 15 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 LaMotte SMART 2 in water matrices.

Precision: Relative standard deviation ranged from 0 to 20% for the PT samples; 10 to 39% for the surface water samples; 3 to 53% for the drinking water samples from around the country; 4 to 77% for the Columbus, OH, drinking water samples.

Linearity: The non-technical operator's results from the LaMotte SMART 2 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)=0.995 (± 0.059) x (reference result in mg/L) + 0.018 (± 0.013) mg/L with r^2=0.975 and N=32.

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

y (technical operator results in mg/L)=0.879 (± 0.068) x (reference result in mg/L) + 0.011 (± 0.015) mg/L with r^2=0.959 and N=32.

where the values in parentheses represent the 95% confidence interval of the slope and intercept. Only the non-technical operator's intercept is significantly different from zero, and the r^2 values are both above 0.950. The non-technical operator's slope is not significantly different from unity; whereas, the technical operator's slope is significantly different from unity. However, at the 95% confidence level, the uncertainty around both slopes is such that they are not significantly different from one another.

Method Detection Limit: The MDL was determined to be 0.02 mg/L for the LaMotte SMART 2 when used by either 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)=0.996 (± 0.013) x (Unit #2 result in mg/L) - 0.0005 (± 0.003) mg/L with r^2=0.995 and N=120.

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 LaMotte SMART 2s 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 LaMotte SMART 2. Upon the addition of the reagents to the water sample, the color of the sample changed within five seconds to orange and, after approximately 35 more seconds, to dark 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 20-minute reaction time to reach its analysis color of a clear lavender. When the samples with lethal/near-lethal concentrations were inserted into the LaMotte SMART 2 after the full reaction time, the digital readout read "over range." Even without using the LaMotte SMART 2 colorimeter, the reagents and glass 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 the operator bias assessment gives the following regression equation:

y (non-tech result in mg/L)=1.024 (± 0.113) x (tech result in mg/L) + 0.002 (± 0.018) mg/L with r^2=0.732 and N=120.

where the values in parentheses represent the 95% confidence interval of the slope and intercept. The slope of this regression is not significantly different from unity. However, the data representing mostly the surface and drinking water samples display a large amount of scatter about the regression line. This scatter resulted in a 11% uncertainty around the slope and a relatively low coefficient of variation (r^2=0.732). However, after further analysis of the operator-specific linearity data in Section 6.3, it seems that the performance of the LaMotte SMART 2 generally was not dependent on which operator performed the analyses.

Field Portability: From an operational standpoint, the LaMotte SMART 2 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 LaMotte SMART 2 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 LaMotte SMART 2 reagents.

Ease of Use: The operators found the LaMotte SMART 2 and associated cyanide test reagents easy to use. The instruction manual was clear, and the sample and reagents were easily measured using a disposable pipet and two 0.1-g scoops. LaMotte provided dropper bottles of HCl and NaOH, pH paper, and step-by-step instructions for adjusting the pH of the water sample to between 10.5 and 11.0. The inclusion of these items made it convenient for both the non-technical and technical operators to complete the pH adjustment step. The sample jars containing the reacted sample had to be emptied and rinsed between sample analyses.

Sample Throughput: Within one to two minutes, the sample volume could be accurately measured and the reagents added to the sample, which after 20 minutes would produce a color change in the presence of cyanide. If only one sample was analyzed, sample analysis would take approximately 22 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 40 to 45 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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