Environmental Technology Verification Report

LaMotte
1919 SMART 2 Colorimeter
with 3660-SC Reagent System

Prepared by
Battelle

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Environmental Technology Verification Report

ETV Advanced Monitoring Systems Center

LaMotte
1919 SMART 2 Colorimeter
with 3660-SC Reagent System

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Notice

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Foreword

The U.S. Environmental Protection Agency (EPA) is charged by Congress with protecting the nation's air, water, and land resources. Under a mandate of national environmental laws, the Agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. To meet this mandate, the EPA's Office of Research and Development provides data and science support that can be used to solve environmental problems and to build the scientific knowledge base needed to manage our ecological resources wisely, to understand how pollutants affect our health, and to prevent or reduce environmental risks.

The Environmental Technology Verification (ETV) Program has been established by the EPA to verify the performance characteristics of innovative environmental technology across all media and to report this objective information to permitters, buyers, and users of the technology, thus substantially accelerating the entrance of new environmental technologies into the marketplace. Verification organizations oversee and report verification activities based on testing and quality assurance protocols developed with input from major stakeholders and customer groups associated with the technology area. ETV consists of seven environmental technology centers. Information about each of these centers can be found on the Internet at http://www.epa.gov/etv/.

Effective verifications of monitoring technologies are needed to assess environmental quality and to supply cost and performance data to select the most appropriate technology for that assessment. In 1997, through a competitive cooperative agreement, Battelle was awarded EPA funding and support to plan, coordinate, and conduct such verification tests for "Advanced Monitoring Systems for Air, Water, and Soil" and report the results to the community at large. Battelle conducted this verification under a follow-on to the original cooperative agreement. Information concerning this specific environmental technology area can be found on the Internet at http://www.epa.gov/etv/centers/center1.html.

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List of Abbreviations

AMS	Advanced Monitoring Systems
ASTM	American Society of Testing and Materials
ATEL	Aqua Tech Environmental Laboratories
DPD	n,n-diethyl-p-phenylenediamine
EPA	U.S. Environmental Protection Agency
ETV	Environmental Technology Verification
HCl	hydrochloric acid
ID	identification
KCN	potassium cyanide
L	liter
LFM	laboratory-fortified matrix
MDL	method detection limit
mg	milligram
mL	milliliter
NaOH	sodium hydroxide
PE	performance evaluation
PT	performance test
QA	quality assurance
QA/QC	quality assurance/quality control
QC	quality control
QCS	quality control standard
QMP	Quality Management Plan
RB	reagent blank
RPD	relative percent difference
RSD	relative standard deviation
TSA	technical systems audit

Chapter 1
Background

The U.S. Environmental Protection Agency (EPA) supports the Environmental Technology Verification (ETV) Program to facilitate the deployment of innovative 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 testing organizations; with stakeholder groups consisting of buyers, vendor organizations, and permitters; and with the full participation of 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 EPA's National Exposure Research Laboratory and its verification organization partner, Battelle, operate the Advanced Monitoring Systems (AMS) Center under ETV. The AMS Center recently evaluated the performance of the LaMotte 1919 SMART 2 colorimeter with the 3660-SC Reagent System in detecting the presence of cyanide in water. Portable cyanide analyzers were identified as a priority technology verification category through the AMS Center stakeholder process.

Chapter 2
Technology Description

The objective of the ETV AMS Center is to verify the performance characteristics of environmental monitoring technologies for air, water, and soil. This verification report provides results for the verification testing of the 1919 SMART 2 colorimeter by LaMotte with the 3660-SC reagent system. Following is a description of the SMART 2, based on information provided by the vendor. The information provided below was not verified in this test.

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 analyze cyanide with the LaMotte SMART 2, a 10.0-mL sample is measured into a sample vial, and 1.0 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 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/50Hz. The list price for this unit is $725.00 for the colorimeter and $64.00 for reagents adequate for 50 water samples.

Figure 2-1. LaMotte SMART 2 Colorimeter

Chapter 3
Test Design and Procedures

3.1 Introduction

Cyanide can be present in various forms in water. This verification test focuses on the detection of the free cyanide ion prepared using potassium cyanide (KCN), and referred to as simply "cyanide" in this report. At high doses, this form of cyanide inhibits cellular respiration and, in some cases, can result in death. Because of the toxicity of cyanide to humans, the EPA has set 0.200 mg/L as the maximum concentration of cyanide that can be present in drinking water. In drinking and surface water under ambient conditions, cyanide evolves from aqueous hydrogen cyanide, sodium cyanide, potassium cyanide, and other metal or ionic salts where cyanide is released when dissolved in water. Heavier cyanide complexes (e.g., iron) are bound tightly, requiring an acid distillation to liberate the toxic free cyanide ion, a step not verified as part of this test since field portability would have been eliminated. Because disassociation of the free cyanide ion is unlikely under ambient conditions, the heavier complexes are considered much less toxic than simple cyanide salts such as potassium and sodium cyanide.

This verification test was conducted according to procedures specified in the *Test/QA Plan for Verification of Portable Analyzers for Detection of Cyanide in Water*.[1] The verification was based on comparing the cyanide concentrations of water samples analyzed using the LaMotte SMART 2 with cyanide concentrations analyzed using a laboratory-based reference method. The reference method used during this verification test was EPA Method 335.1, *Cyanides Amenable to Chlorination*.[2] This method was selected because it measures the concentration of the cyanide ion in water samples under ambient conditions, which is the same form of cyanide that the participating technologies are designed to measure. The LaMotte 1919 SMART 2 with the 3660-SC reagent system was verified by analyzing performance test (PT), surface, and drinking water samples. A statistical comparison of the analytical results from the LaMotte SMART 2 and the reference method provided the basis for the quantitative performance evaluations.

The LaMotte SMART 2's performance was evaluated in terms of

- Accuracy
- Precision
- Linearity
- Method detection limit
- Inter-unit reproducibility
- Lethal or near-lethal dose response

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- Operator bias
- Field portability
- Ease of use
- Sample throughput.

3.2 Reference Method

Aqua Tech Environmental Laboratories (ATEL) in Marion, OH, performed the reference analyses of all test samples. ATEL received the samples from Battelle labeled with an identification number meaningful only to Battelle, performed the analyses, and submitted to Battelle the results of the analyses without knowledge of the prepared or fortified concentration of the samples.

The analytical results for the LaMotte SMART 2 were compared with the results obtained from analysis using semi-automated colorimetry according to EPA Method 335.1.[2] For the reference method analyses, the concentration of free cyanide was determined by the difference of two measurements of total cyanide. One colorimetric determination was made after the free cyanide in the sample had been chlorinated to cyanogen chloride, which degrades quickly, and a second was made without chlorination. Typically, samples were sent to the reference laboratory for analysis each testing day. The reference analysis was performed within 14 days of sample collection.

3.3 Test Design

Two LaMotte SMART 2s were tested independently between January 13 and February 4, 2003. All preparation and analyses were performed according to the manufacturer's recommended procedures for the 1919 SMART 2 colorimeter and the 3660-SC reagent system. The verification test involved challenging the LaMotte SMART 2 with a variety of test samples, including sets of drinking and surface water samples representative of those likely to be analyzed by the LaMotte SMART 2. 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 the LaMotte SMART 2 and the reference method.

The LaMotte SMART 2 was tested by a technical and a non-technical operator to assess operator bias. The non-technical operator had no previous laboratory experience. Both operators received a brief orientation with a vendor representative to become acquainted with the basic operation of the instrument. Both operators analyzed all of the test samples. Each operator manipulated the water samples and reagents to generate a solution that could be probed photometrically. Then, each operator analyzed that solution using both LaMotte SMART 2s.

Sample throughput was estimated based on the time required to prepare and analyze a sample. Ease of use was based on documented observations by the operators and 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.

3.4 Test Samples

Test samples used in the verification test included quality control (QC) samples, PT samples, lethal/near-lethal concentration samples, drinking water samples, and surface water samples (Table 3-1). The QC, PT, and lethal/near-lethal concentration samples were prepared from purchased standards. The PT and QC sample concentrations were targeted to the EPA maximum contaminant level in drinking water, which for cyanide is 0.200 mg/L.[3] The PT samples ranged from 0.030 mg/L to 0.800 mg/L. The performance of the LaMotte SMART 2 also was qualitatively evaluated with samples prepared in American Society of Testing and Materials (ASTM) Type II deionized water with cyanide concentrations up to 250 mg/L that could be lethal if ingested. Two surface water sources (Olentangy River and Alum Creek Reservoir) were sampled and analyzed. In addition, five sources of drinking water from around the United States and two sources of Columbus, OH, drinking water were evaluated (Table 3-1).

3.4.1 Quality Control Samples

Prepared QC samples included both laboratory reagent blanks (RBs) and laboratory-fortified matrix (LFM) samples (Table 3-1). The RB samples were prepared from ASTM Type II deionized water and were exposed to handling and analysis procedures identical to other prepared samples, including the addition of all reagents. These samples were used to help ensure that no sources of contamination were introduced in the sample handling and analysis procedures. One reagent blank sample was analyzed for every batch of about 12 water samples. The LFM samples were prepared as aliquots of drinking and surface water samples spiked with KCN as free cyanide to increase the cyanide concentration by 0.200 mg/L. In the case of the drinking water samples, the spike solution used to prepare the LFM was prepared in the laboratory and taken to the field site. Four LFM samples were analyzed for each source of water. These samples were used to monitor the general performance of the reference method to help determine whether matrix effects had an influence on the analytical results.

Quality control standards (QCSs) were used to ensure the proper calibration of the reference instrument. The reference laboratory prepared the QCSs for its use from a stock solution independent from the one used to prepare the QCS analyzed using the LaMotte SMART 2. The QCSs for the LaMotte SMART 2 were purchased by Battelle from a commercial supplier and subject only to dilution as appropriate. An additional independent QCS was used in a performance evaluation (PE) audit of the reference method.

The reference method required that the concentration of each QCS be within 25% of the known concentration. If the difference was larger that 25%, the data collected since the most recent QCS were flagged; and proper maintenance was performed to regain accurate cyanide measurement, according to ATEL protocols. Section 4.1 describes these samples in more detail.

Table 3-1. Test Samples

Type of Sample	Sample Characteristics	Concentration	No. of Samples
Quality Control	RB	~ 0	10% of all
	LFM	0.200 mg/L	4 per water source (also listed below)
	QCS	0.200 mg/L	10% of all
Performance Test	For the determination of method detection limit	0.050 mg/L	7
	Cyanide	0.030 mg/L	4
	Cyanide	0.100 mg/L	4
	Cyanide	0.200 mg/L	4
	Cyanide	0.400 mg/L	4
	Cyanide	0.800 mg/L	4
Lethal / Near-Lethal	Cyanide	50.0 mg/L	4
	Cyanide	100 mg/L	4
	Cyanide	250 mg/L	4
Surface water	Alum Creek Reservoir	Background	4
		0.200 mg/L LFM	4
	Olentangy River	Background	4
		0.200 mg/L LFM	4
Drinking water from around the U.S.	Northwestern U.S.	Background	4[a]
		0.200 mg/L LFM	4
	Southwestern U.S.	Background	1
		0.200 mg/L LFM	4
	Midwestern U.S.	Background	1
		0.200 mg/L LFM	4
	Southeastern U.S.	Background	1
		0.200 mg/L LFM	4
	Northeastern U.S.	Background	4[a]
		0.200 mg/L LFM	4
Columbus, OH, area drinking water	Residence with city water	Background	6
		0.200 mg/L LFM	12
	Residence with well water	Background	6
		0.200 mg/L LFM	12

[a]   Because the initial aliquot analyzed by the technical operator resulted in non-detectable concentrations of cyanide, the technical operator did not analyze additional aliquots. However, the results for the initial aliquots analyzed by the non-technical operator were other than a non-detectable concentration, so three additional aliquots were analyzed.

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The LaMotte SMART 2 was factory calibrated, so no additional calibration was performed by the operators. However, QCSs were analyzed (without defined performance expectations) by the LaMotte SMART 2 to demonstrate their proper functioning to the operator. A QCS was analyzed before and after each sample batch (typically consisting of 12 samples).

3.4.2 Performance Test Samples

The PT samples (Table 3-1) were prepared in the laboratory using ASTM Type II deionized water. The samples were used to determine the LaMotte SMART 2's accuracy, linearity, and detection limit. Seven non-consecutive replicate analyses of a 0.050-mg/L solution were made to obtain precision data with which to determine the method detection limit (MDL).[4] Five other solutions were prepared to assess the linearity over a 0.030- to 0.800-mg/L range of cyanide concentrations. Four aliquots of each of these solutions were analyzed separately to assess the precision of the LaMotte SMART 2. The concentrations of the PT samples are listed in Table 3-1. The operators analyzed the PT samples blindly and in random order to minimize bias.

3.4.3 Lethal/Near-Lethal Concentrations of Cyanide in Water

To assess the response of the LaMotte SMART 2 when cyanide is present in drinking water at lethal and near-lethal concentrations (>50.0 mg/L), samples were prepared in ASTM Type II deionized water at concentrations of 50.0, 100, and 250 mg/L. Qualitative observations were made of the LaMotte SMART 2 while analyzing such samples. Observations of unusual operational characteristics (rate of color change, unusually intense color, unique digital readout, etc.) were documented.

3.4.4 Surface Water; Drinking Water from Around the U.S.; and Columbus, OH, Area Drinking Water

Water samples, including fresh surface water and tap water (well and local distribution sources), were collected from a variety of sources and used to evaluate technology performance. Surface water samples were collected from

- Alum Creek Reservoir (OH)

- Olentangy River (OH).

Drinking water samples were collected from

- Local distribution source water (post-treatment) from five cities (Montpelier, VT; Des Moines, IA; Seattle, WA; Tallahassee, FL; and Flagstaff, AZ)

- Columbus, OH, city water

- Columbus, OH, well water.
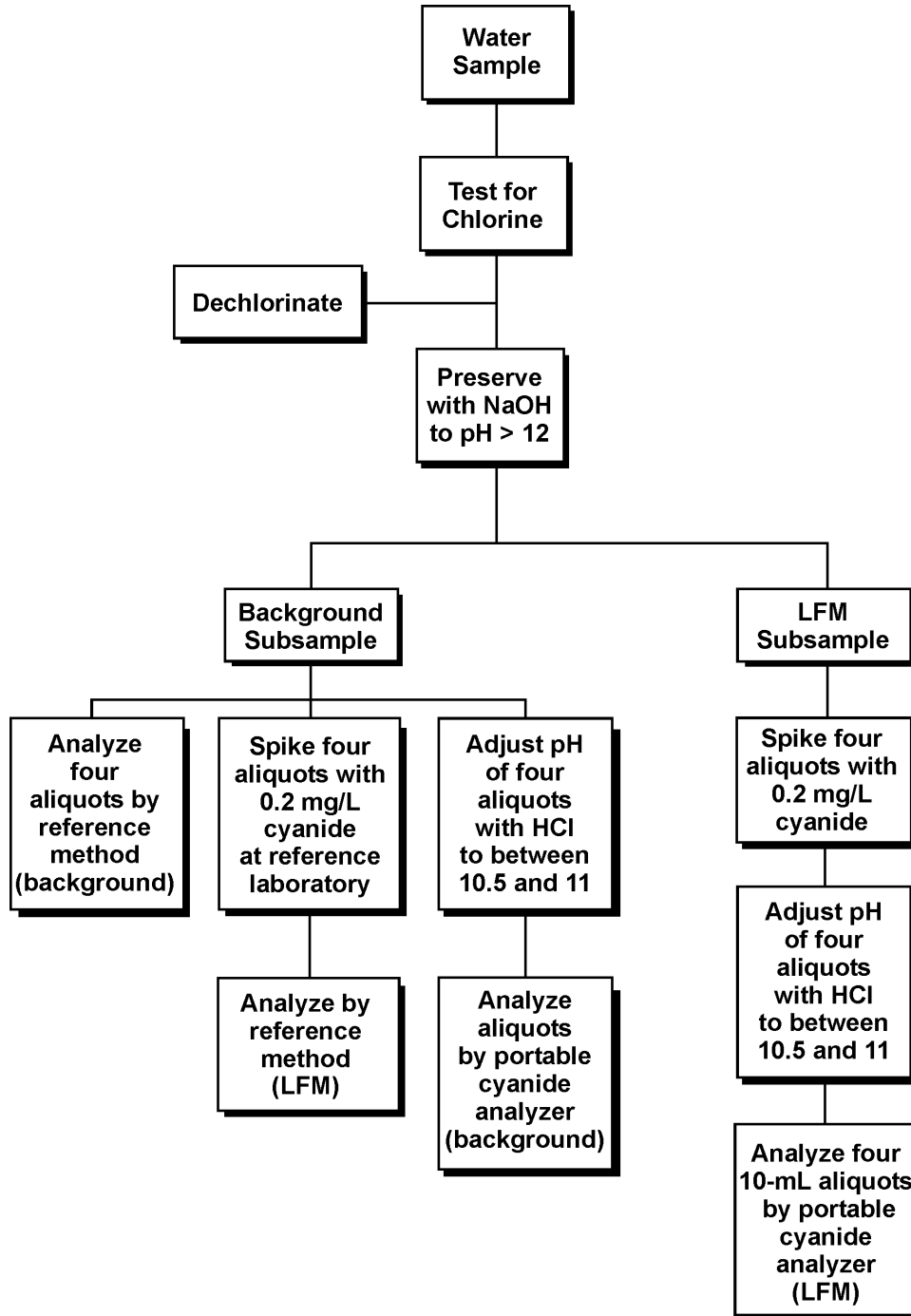
Figure 3-1. Sampling through Analysis Process

The water samples collected as part of this verification test were not characterized in any way (i.e., hardness, alkalinity, etc.) other than for cyanide concentration. Each sample was tested for the presence of chlorine, dechlorinated if necessary, preserved with sodium hydroxide (NaOH) to a pH greater than 12, and split into two subsamples. Figure 3-1 is a diagram of the process leading from sampling to aliquot analysis. One subsample was spiked with 0.200 mg/L of

cyanide to provide LFM aliquots, and the other subsample remained unspiked (background). Four 10.0-mL aliquots were taken from each subsample and analyzed for cyanide by the LaMotte SMART 2. Also taken from the background subsample were eight aliquots used for analysis by the reference method. Four of the aliquots were left unspiked and analyzed by the reference method, and four of the aliquots were fortified with 0.200 mg/L of KCN as free cyanide at the reference laboratory just before the reference analyses took place. This was done to closely mimic the time elapsed between when the LFM samples were fortified with 0.200 mg/L KCN as free cyanide and when they were analyzed during the testing of the participating technologies.

To assess the reproducibility of background water samples, all four replicates of Columbus, OH, city and well water samples were analyzed at the laboratory analysis site regardless of the response of the first aliquot. Four LFM aliquots were prepared and analyzed for every drinking and surface water source, regardless of the concentration of the initial aliquot. To avoid replicating samples with non-detectable concentrations of cyanide, only one background aliquot of each source of drinking water was analyzed if cyanide was not detectable in the first aliquot analyzed by the LaMotte SMART 2. If cyanide was detectable in that initial aliquot, three additional aliquots of that sample were analyzed in addition to four LFM aliquots.

Surface water from the Olentangy River and Alum Creek Reservoir and drinking water samples collected at the five U.S. cities were shipped to Battelle for use in verification testing. Surface water was collected near the shoreline by submerging containers no more than one inch below the surface of the water. Representatives of each city's water treatment facility provided Battelle a sample of water that had completed the water treatment process, but had not yet entered the water distribution system. When the samples arrived at Battelle, they were dechlorinated, preserved, and split into background and LFM subsamples, as described above for the rest of the water samples.

Columbus, OH, city and well water samples were used to verify the field portability of the LaMotte SMART 2. Approximately 20 liters of water were collected from an outside spigot at two participating residences, one with well water and one with Columbus, OH, city water, and split into three samples. One sample was analyzed outdoors at the residence under the current weather conditions. The weather conditions on the two days of outdoor testing happened to be extremely cold (air temperature ~0°C, sample temperature ~4 to 6°C). A second sample was equilibrated to room temperature inside the residence (~17°C) and analyzed inside the residence. These two samples were preserved, split into background and LFM samples, and analyzed at the field location as described for the other water samples (see Figure 3-1). For the third sample, the background and LFM samples were prepared at the field location and transported to Battelle for analysis in the laboratory two to three days later. Because these analyses were done using the same bulk water sample, a single set of four background replicates was analyzed using the reference method. The LFM sample fortified at the field location and the LFM sample fortified at the reference laboratory were analyzed by the reference method (see Table 4-2). These back-ground and LFM reference concentrations were compared to the results produced by the LaMotte SMART 2 at the indoor and outdoor field locations and the laboratory location.

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3.5 Test Procedure

3.5.1 Sample Preparation

QC and PT samples were prepared from a commercially available National Institute of Standards and Technology-traceable standard. The standard was dissolved and diluted to appropriate concentrations using ASTM Type II deionized water in Class A volumetric glassware. The QC and PT samples were prepared at the start of testing, preserved with NaOH, and stored at 4°C for the duration of the test.

Surface and drinking water samples were collected from the sources indicated in Section 3.4.4 and were stored in high-density polyethylene containers. Because free chlorine degrades cyanide during storage, at the time of sample receipt, before NaOH preservation, all of the samples were tested for free chlorine with potassium iodide starch paper. When the samples collected as part of this verification test were tested in this manner, none of them changed the color of the paper, indicating that free chlorine was not present. However, when the LFM samples were analyzed with the colorimetric technologies being verified, non-detectable results were observed. To further investigate the possibility of a chlorine interference, approximately 500 mL of each water sample were added to separate beakers and one n,n-diethyl-p-phenylenediamine (DPD) chlorine indicator tablet (Orbeco Analytical Systems, Inc.) was added and crushed with a glass stirring rod. If the water turned pink, the presence of chlorine was indicated, and ascorbic acid was added a few crystals at a time until the color disappeared. All the drinking water samples were tested in this manner; and, if the presence of chlorine was indicated, approximately 60 mg of ascorbic acid were added per liter of bulk sample to dechlorinate the sample. A separate DPD indicator test (as described above) was done to confirm adequate dechlorination of the sample (indicated by no color change). After dechlorination, all samples to be analyzed by the LaMotte SMART 2 were adjusted to a pH between 10.5 and 11.0, according to the manufacturer's specifications (see Figure 3-1). All the samples to be analyzed by the reference method were stored at 4°C and preserved with NaOH at a pH of greater than 12.0.

3.5.2 Sample Identification

Aliquots to be analyzed were drawn from the prepared standard solutions or from source and drinking water samples and placed in uniquely identified sample containers for subsequent analysis. The sample containers were identified by a unique identification (ID) number. A master log of the samples and sample ID numbers for each technology being verified was kept by Battelle. The ID number, date, person collecting, sample location, and time of collection were recorded on a chain-of-custody form for all field samples.

3.5.3 Sample Analysis

The two LaMotte SMART 2s were tested independently. Each LaMotte SMART 2 analyzed the full set of samples, and verification results were compared to assess inter-unit reproducibility. As shown in Table 3-1, the samples included replicates of each of the PT, QC, surface water, and drinking water samples. The complete set of samples was analyzed twice for each of the units

being verified, once by a non-technical operator and once by a technical operator. The analyses were performed according to the manufacturer's recommended procedures.

Results were recorded manually on appropriate data sheets. In addition to the analytical results, the data sheets included records of the time required for sample analysis and operator observations concerning the use of the LaMotte SMART 2 (i.e., ease of use, maintenance, etc.).

While the participating technologies were being tested, a replicate sample set was being analyzed by the reference laboratory. The reference instrument was operated according to the recommended procedures in the instruction manual, and samples were analyzed according to EPA Method 335.1[2] and ATEL standard operating procedures. Results from the reference analyses were recorded electronically and compiled by ATEL into a report, including the sample ID and the analyte concentration for each sample.

Chapter 4
Quality Assurance/Quality Control

Quality assurance/quality control (QA/QC) procedures were performed in accordance with the quality management plan (QMP) for the AMS Center[5] and the test/QA plan for this verification test.[1]

4.1 Reference Method QC Results

Analyses of QC samples were used to document the performance of the reference method. To ensure that no sources of contamination were present, RB samples were analyzed. The test/QA plan stated that, if the analysis of an RB sample indicated a concentration above the MDL for the reference method, any contamination source was to be corrected and a proper blank reading achieved before proceeding with the verification test. Six reagent blank samples were analyzed, and all of them were reported as below the 0.005 mg/L reporting limit for the reference method.

The reference instrument was calibrated initially according to the procedures specified in the reference method. The accuracy of the reference method was verified with QCS samples analyzed with the sample sets. One of two QCS samples, one with a concentration of 0.150 mg/L and the other with a concentration of 0.200 mg/L, were analyzed with each analytical batch (approximately every 10 water samples). As required by the test/QA plan,[1] if the QCS analysis differed by more than 25% from the true value of the standard, corrective action would be taken before the analysis of more samples. As shown in Table 4-1, the QCS results were always within the acceptable percent recovery range of 75 to 125% and, in fact, were always between 90 and 110%.

Reference LFM samples were analyzed to confirm the proper functioning of the reference method and to assess whether matrix effects influenced the results of the reference method. The LFM recovery (R) of the spiked solution was calculated from the following equation:

$$R = \frac{C_s - C}{s} \times 100 \qquad (1)$$

where C_s is the reference concentration of the spiked sample, C is the reference concentration of the background sample which, in this case, was always zero (results were below the MDL for the reference method), and s is the fortified concentration of the cyanide spike. If the percent recovery of an LFM fell outside the range of 75 to 125%, a matrix effect or some other analytical

Table 4-1. Reference Method QCS Results

Date	Analysis Result	Known QCS Concentration (mg/L)	% Recovery
1/13/2003	0.157	0.150	105
1/13/2003	0.203	0.200	102
1/15/2003	0.142	0.150	95
1/15/2003	0.180	0.200	90
1/16/2003	0.151	0.150	101
1/16/2003	0.194	0.200	97
1/17/2003	0.154	0.150	103
1/17/2003	0.190	0.200	95
1/20/2003	0.190	0.200	95
1/20/2003	0.158	0.150	105
1/21/2003	0.153	0.150	102
1/21/2003	0.205	0.200	103
1/27/2003	0.143	0.150	95
1/27/2003	0.187	0.200	94
1/28/2003	0.146	0.150	97
1/28/2003	0.186	0.200	93
1/29/2003	0.149	0.150	99
1/29/2003	0.189	0.200	95
1/30/2003	0.139	0.150	93
1/30/2003	0.187	0.200	94
1/30/2003	0.139	0.150	93
1/30/2003	0.188	0.200	94
1/31/2003	0.146	0.150	97
1/31/2003	0.150	0.150	100
1/31/2003	0.196	0.200	98
2/3/2003	0.152	0.150	101
2/3/2003	0.189	0.200	95
2/5/2003	0.147	0.150	98
2/5/2003	0.149	0.150	99
2/5/2003	0.194	0.200	97
2/6/2003	0.151	0.150	101
2/6/2003	0.198	0.200	99
2/7/2003	0.154	0.150	103
2/7/2003	0.199	0.200	100
2/10/2003	0.148	0.150	99
2/10/2003	0.181	0.200	90
2/11/2003	0.141	0.150	94
2/11/2003	0.180	0.200	90
2/11/2003	0.136	0.150	91
2/11/2003	0.191	0.200	96
2/12/2003	0.159	0.150	106
2/12/2003	0.211	0.200	106
2/12/2003	0.153	0.150	102
2/12/2003	0.206	0.200	103
2/13/2003	0.158	0.150	105

problem was suspected. As shown in Table 4-2, only the percent recovery for the LFM from the Columbus, OH, well water was outside the acceptable range, indicating a potential matrix effect.

Table 4-2. Reference Method LFM Analysis Results

Sample Description	Fortified Concentration (mg/L)	Average Reference Concentration (mg/L)	% LFM Recovery	Reference RSD
Alum Creek LFM	0.200	0.168	84%	8%
Olentangy River LFM	0.200	0.175	87%	2%
Des Moines, IA, LFM	0.200	0.178	89%	3%
Flagstaff, AZ, LFM	0.200	0.153	76%	12%
Montpelier, VT, LFM	0.200	0.170	85%	2%
Seattle, WA, LFM	0.200	0.173	87%	2%
Tallahassee, FL, LFM	0.200	0.161	80%	2%
Columbus, OH, City Water LFM[a]	0.200	0.172	86%	4%
Columbus, OH, City Water LFM[b]	0.200	0.152	76%	1%
Columbus, OH, Well Water LFM[a]	0.200	0.107	53%	13%
Columbus, OH, Well Water LFM[b]	0.200	<0.005	0%	NA[c]

[a] Reference LFM sample spiked minutes before analysis by the reference method.
[b] Reference LFM sample spiked 8 to 10 days before analysis by the reference method.
[c] Calculation of relative standard deviation (RSD) not appropriate for non-detectable results.

To mimic the elapsed time between fortification and analysis by the technologies being verified, the reference LFM samples were spiked just minutes prior to analysis using the reference method. However, because the well water LFM samples exhibited decreased cyanide concentrations when analyzed by the vendor technologies one or two days after fortification, the LFM samples for the Columbus, OH, city and well water spiked in the field location were also submitted to the reference laboratory for analysis. These samples were analyzed eight to 10 days after initial fortification. The Columbus, OH, city reference LFM result after the eight- to 10-day delay was within 15% of the result obtained from the LFM sample spiked just minutes before reference analysis. However, the well water reference LFM result fortified eight to 10 days prior to analysis was less than the MDL for the reference method. The combination of the poor recovery (53%) of cyanide obtained immediately upon spiking and the complete loss of the reference method's ability to detect the cyanide fortified eight to 10 days before strongly suggests the presence of a time-dependent matrix interference in the well water. In response to this finding, the biases for the well water samples were calculated using the fortified concentration of cyanide (0.200 mg/L) rather than the reference LFM result.

4.2 Audits

4.2.1 Performance Evaluation Audit

A PE audit was conducted once to assess the quality of the reference measurements made in this verification test. For the PE audit, an independent standard was obtained from a different vendor than the one that supplied the QCSs. The relative percent difference (RPD) of the measured concentration and the known concentration was calculated using the following equation:

$$RPD = \frac{M}{A} \times 100 \qquad (2)$$

where M is the absolute difference between the measured and known concentrations, and A is the mean of the same two concentrations. An RPD of less than 25% was required for the reference measurements to be considered acceptable. Failure to achieve this agreement would have triggered a repeat of the PE comparison. As shown in Table 4-3, all the PE sample results were well within this required range.

Table 4-3. Summary of Performance Evaluation Audit

Sample	Date of Analysis	Measured Concentration (mg/L)	Known Concentration (mg/L)	RPD (%)
PE-A	2-12-2003	0.216	0.200	8
PE-B	2-12-2003	0.213	0.200	6
PE-C	2-12-2003	0.218	0.200	9
PE-D	2-12-2003	0.203	0.200	1

4.2.2 Technical Systems Audit

The Battelle Quality Manager performed a pre-verification test audit of the reference laboratory (ATEL) to ensure that the selected laboratory was proficient in the reference analyses. This entailed a review of the appropriate training records, state certification data, and the laboratory QMP. The Battelle Quality Manager also conducted a technical systems audit (TSA) to ensure that the verification test was performed in accordance with the test/QA plan[1] and the AMS Center QMP.[5] As part of the audit, the Battelle Quality Manager reviewed the reference method used, compared actual test procedures to those specified in the test/QA plan, and reviewed data acquisition and handling procedures. Observations and findings from this audit were documented and submitted to the Battelle Verification Test Coordinator for response. No findings were documented that required any corrective action. The records concerning the TSA are permanently stored with the Battelle Quality Manager.

4.2.3 Audit of Data Quality

At least 10% of the data acquired during the verification test were audited. Battelle's Quality Manager traced the data from the initial acquisition, through reduction and statistical analysis, to final reporting, to ensure the integrity of the reported results. All calculations performed on the data undergoing the audit were checked.

4.3 QA/QC Reporting

Each assessment and audit was documented in accordance with Sections 3.3.4 and 3.3.5 of the QMP for the ETV AMS Center.[5] Once the assessment report was prepared, the Battelle Verification Test Coordinator ensured that a response was provided for each adverse finding or potential problem and implemented any necessary follow-up corrective action. The Battelle Quality Manager ensured that follow-up corrective action was taken. The results of the TSA were sent to the EPA.

4.4 Data Review

Records generated in the verification test were reviewed before these records were used to calculate, evaluate, or report verification results. Table 4-4 summarizes the types of data recorded. The review was performed by a technical staff member involved in the verification test, but not the staff member who originally generated the record. The person performing the review added his/her initials and the date to a hard copy of the record being reviewed.

Table 4-4. Summary of Data Recording Process

Data to be Recorded	Responsible Party	Where Recorded	How Often Recorded	Disposition of Data[a]
Dates, times of test events	Battelle	Laboratory record books	Start/end of test; at each change of a test parameter	Used to organize/ check test results; manually incorporated data into spreadsheets as necessary
Test parameters (meteorological conditions, analyte concentrations, location, etc.)	Battelle	Laboratory record books	When set or changed, or as needed to document stability	Used to organize/ check test results; manually incorporated data into spreadsheets as necessary
Water sampling data	Battelle	Laboratory record books	At least at the time of sampling	Used to organize/ check test results; manually incorporated data into spreadsheets as necessary
Reference method sample analysis, chain of custody, results	ATEL	Laboratory record book/data sheets or data acquisition system, as appropriate	Throughout sample handling and analysis process	Excel spreadsheets

[a] All activities subsequent to data recording were carried out by Battelle.

Chapter 5
Statistical Methods and Reported Parameters

The statistical methods presented in this chapter were used to verify the performance parameters listed in Section 3.1.

5.1 Accuracy

Accuracy was assessed relative to the results obtained from the reference analyses. Samples were analyzed by both the reference method and the LaMotte SMART 2. The results for each set of analyses were averaged, and the accuracy was expressed in terms of a relative average bias (B) as calculated from the following equation:

$$B = \frac{\overline{d}}{\overline{C_R}} \times 100 \qquad (3)$$

where $\overline{d}$ is the average difference between the readings from the LaMotte SMART 2 and those from the reference method, and $\overline{C_R}$ is the average of the reference measurements. Accuracy was assessed independently for each LaMotte SMART 2 to determine inter-unit reproducibility. Additionally, the results were analyzed independently for the readings obtained from the two operators to determine whether significant operator bias existed.

5.2 Precision

The standard deviation (S) of the results for the replicate samples was calculated and used as a measure of LaMotte SMART 2 precision at each concentration.

$$S = \left[\frac{1}{n-1} \sum_{k=1}^{n} \left(C_k - \overline{C} \right)^2 \right]^{1/2} \qquad (4)$$

where n is the number of replicate samples, C_k is the concentration measured for the kth sample, and $\overline{C}$ is the average concentration of the replicate samples. The analyzer precision at each concentration was reported in terms of the RSD, e.g.,

$$RSD = \left| \frac{S}{\overline{C}} \right| \times 100 \qquad (5)$$

5.3 Linearity

Linearity was assessed by linear regression, with the analyte concentration measured by the reference method as independent variable and the reading from the LaMotte SMART 2 as dependent variable. Linearity is expressed in terms of the slope, intercept, and the coefficient of determination (r^2).

5.4 Method Detection Limit

The MDL[4] for each LaMotte SMART 2 was assessed from the seven replicate analyses of a fortified sample with a cyanide concentration of approximately five times the vendor's estimated detection limit (see Table 3-1). The MDL[4] was calculated from the following equation:

$$MDL = t \times S \qquad (6)$$

where t is the Student's value for a 99% confidence level, and S is the standard deviation of the replicate samples. The MDL for each LaMotte SMART 2 was reported separately.

5.5 Inter-Unit Reproducibility

The results obtained from two identical LaMotte SMART 2s were compiled independently for each LaMotte SMART 2 and compared to assess inter-unit reproducibility. The results were interpreted using a linear regression of one LaMotte SMART 2's results plotted against the results produced by the other LaMotte SMART 2. If the LaMotte SMART 2s function alike, the slope of such a regression should not differ significantly from unity.

5.6 Lethal or Near-Lethal Dose Response

The LaMotte SMART 2 is not designed to quantitatively measure near-lethal or lethal concentrations of cyanide in water. Therefore, the operators and Battelle Verification Test Coordinator made qualitative observations of its operation while analyzing such samples. Observations of unusual operational characteristics (rate of color change, unusually intense color, unique digital readout, etc.) were documented and reported.

5.7 Operator Bias

To assess operator bias for each technology, the results obtained from each operator were compiled independently and subsequently compared. The results were interpreted using a linear regression of the non-technical operator's results plotted against the results produced by the other technical operator. If the operators obtain identical results, the slope of such a regression should not differ significantly from unity.

5.8 Field Portability

The results obtained from the measurements made on drinking water samples in the laboratory and field settings were compiled independently for each LaMotte SMART 2 and for each operator and compared to assess the accuracy of the measurements under the different analysis conditions. The results were interpreted qualitatively since factors such as temperature and matrix effects largely influenced the results.

5.9 Ease of Use

Ease of use was a qualitative measure of the user friendliness of the instrument, including how easy or hard the instruction manual was to use.

5.10 Sample Throughput

Sample throughput indicated the amount of time required to analyze a sample, including both sample preparation and analysis.

Chapter 6
Test Results

6.1 Accuracy

Tables 6-1a-d present the measured cyanide results from analysis of the PT samples; surface water; drinking water from various regions of the United States; and drinking water from Columbus, OH, respectively, for both the reference analyses and the LaMotte SMART 2. Results are shown for the technical and non-technical operators and for both LaMotte SMART 2s that were tested (labeled as Unit #1 and #2). The 0.800-mg/L PT sample was outside the detectable range of the LaMotte SMART 2. When these samples were inserted into the LaMotte SMART 2, the result was reported as "over range."

All of the background drinking water samples and Alum Creek reservoir surface water samples resulted in concentrations that were near or less than the LaMotte SMART 2's stated detection limit of 0.010 mg/L. When analyzing the Olentangy River background water samples, the technical operator's result on both LaMotte SMART 2 instruments was "BLANK?" for all eight replicates (Table 6-1b). The non-technical operator's results on the same samples were reported as below the detection limit of the LaMotte SMART 2. Both operators were analyzing surface water aliquots from the same sample and using identical analysis techniques. There was no visible color change in these samples, and they were not unusually turbid. The manufacturer stated that the "BLANK?" display occurs when the detector recognizes that a sample contains less color than the blank and is warning the user of such if the sample is a blank. When analyzing an actual sample, a "BLANK?" result is the same as a result below the detection limit of the LaMotte SMART 2 and is reported as such in Table 6-1b.

Tables 6-2a-d present the percent accuracy of the LaMotte SMART 2 results. The bias values were determined according to Equation (3), Section 5.1. Bias was not calculated for background samples with non-detectable concentrations of cyanide. However, in instances when the LFM samples resulted in a non-detect reading from the LaMotte SMART 2, the bias was reported as 100%. The bias values shown in Tables 6-2a-d can be summarized by the range of bias observed with different sample sets. For example, the biases ranged from 2 to 31% for the PT samples; 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. Because of the low well water reference LFM sample recovery (see Section 4.1 and Table 4-2), the well water biases were calculated using the fortified concentration of 0.200 mg/L as the reference concentration.

Table 6-1a. Cyanide Results from Performance Test Samples

Prepared Concentration (mg/L)	Ref. Conc. (mg/L)	Non-Technical Operator		Technical Operator	
		Unit #1 (mg/L)	Unit #2 (mg/L)	Unit #1 (mg/L)	Unit #2 (mg/L)
0.030	0.027	0.03	0.03	0.03	0.03
0.030	0.023	0.03	0.03	0.03	0.03
0.030	0.026	0.03	0.03	0.03	0.03
0.030	0.023	0.04	0.03	0.03	0.03
0.100	0.102	0.11	0.11	0.10	0.10
0.100	0.089	0.12	0.11	0.10	0.10
0.100	0.097	0.13	0.13	0.10	0.10
0.100	0.103	0.08	0.08	0.11	0.11
0.200	0.173	0.22	0.21	0.16	0.17
0.200	0.179	0.22	0.22	0.14	0.14
0.200	0.173	0.20	0.20	0.18	0.18
0.200	0.174	0.24	0.24	0.15	0.15
0.400	0.381	0.39	0.39	0.40	0.41
0.400	0.392	0.40	0.39	0.38	0.39
0.400	0.392	0.38	0.38	0.33	0.33
0.400	0.395	0.43	0.41	0.30	0.30
0.800	0.736	OR[a]	OR	OR	OR
0.800	0.724	OR	OR	OR	OR
0.800	0.720	OR	OR	OR	OR
0.800	0.740	OR	OR	OR	OR

[a] OR = over detectable range of LaMotte SMART 2.

Table 6-1b. Cyanide Results from Surface Water

Sample Description	Ref. Conc. (mg/L)	Non-Technical Operator		Technical Operator	
		Unit #1 (mg/L)	Unit #2 (mg/L)	Unit #1 (mg/L)	Unit #2 (mg/L)
Alum Creek Background	<0.005	<0.01	<0.01	<0.01	<0.01
Alum Creek Background	<0.005	0.01	<0.01	<0.01	<0.01
Alum Creek Background	<0.005	<0.01	<0.01	<0.01	<0.01
Alum Creek Background	<0.005	<0.01	<0.01	<0.01	<0.01
Alum Creek LFM	0.166	0.21	0.21	0.17	0.17
Alum Creek LFM	0.183	0.13	0.13	0.16	0.16
Alum Creek LFM	0.173	0.22	0.21	0.14	0.14
Alum Creek LFM	0.151	0.09	0.09	0.14	0.14
Olentangy River Background	<0.005	<0.01	<0.01	<0.01[a]	<0.01[a]
Olentangy River Background	<0.005	<0.01	<0.01	<0.01[a]	<0.01[a]
Olentangy River Background	<0.005	<0.01	<0.01	<0.01[a]	<0.01[a]
Olentangy River Background	<0.005	<0.01	<0.01	<0.01[a]	<0.01[a]
Olentangy River LFM	0.174	0.19	0.20	0.13	0.13
Olentangy River LFM	0.178	0.21	0.22	0.16	0.17
Olentangy River LFM	0.171	0.23	0.24	0.15	0.15
Olentangy River LFM	0.176	0.17	0.18	0.09	0.09

[a] Result on the LaMotte SMART 2 digital display was "BLANK?."

Table 6-1c. Cyanide Results from U.S. Drinking Water

Sample Description	Ref. Conc. (mg/L)	Non-Technical Operator		Technical Operator	
		Unit #1 (mg/L)	Unit #2 (mg/L)	Unit #1 (mg/L)	Unit #2 (mg/L)
Des Moines, IA, Background	<0.005	0.01	0.01	<0.01	<0.01
Des Moines, IA, LFM	0.173	0.10	0.10	0.17	0.18
Des Moines, IA, LFM	0.173	0.23	0.23	0.17	0.17
Des Moines, IA, LFM	0.183	0.11	0.12	0.17	0.17
Des Moines, IA, LFM	0.181	0.13	0.13	0.16	0.17
Flagstaff, AZ, Background	<0.005	<0.01	<0.01	0.01	<0.01
Flagstaff, AZ, LFM	0.157	0.10	0.10	0.14	0.15
Flagstaff, AZ, LFM	0.132	0.14	0.14	0.20	0.20
Flagstaff, AZ, LFM	SL[a]	0.15	0.15	0.16	0.16
Flagstaff, AZ, LFM	0.169	0.16	0.15	0.16	0.14
Montpelier, VT, Background	<0.005	0.03	0.01	<0.01	<0.01
Montpelier, VT, Background	NR[b]	0.02	<0.01	NR	NR
Montpelier, VT, Background	NR	<0.01	<0.01	NR	NR
Montpelier, VT, Background	NR	0.01	0.01	NR	NR
Montpelier, VT, LFM	0.167	0.14	0.14	0.14	0.14
Montpelier, VT, LFM	0.176	0.14	0.14	0.14	0.14
Montpelier, VT, LFM	0.168	0.15	0.15	0.13	0.13
Montpelier, VT, LFM	0.168	0.15	0.15	0.16	0.16

Table 6-1c. Cyanide Results from U.S. Drinking Water (continued)

		Non-Technical Operator		Technical Operator	
Sample Description	Ref. Conc. (mg/L)	Unit #1 (mg/L)	Unit #2 (mg/L)	Unit #1 (mg/L)	Unit #2 (mg/L)
Seattle, WA, Background	<0.005	0.01	0.01	<0.01	<0.01
Seattle, WA, Background	NR	<0.01	<0.01	NR	NR
Seattle, WA, Background	NR	0.01	<0.01	NR	NR
Seattle, WA, Background	NR	0.03	0.01	NR	NR
Seattle, WA, LFM	0.177	0.13	0.13	0.14	0.14
Seattle, WA, LFM	0.174	0.14	0.14	0.20	0.21
Seattle, WA, LFM	0.170	0.18	0.17	0.16	0.17
Seattle, WA, LFM	0.172	0.03	0.03	0.18	0.18
Tallahassee, FL, Background	<0.005	<0.01	<0.01	<0.01	<0.01
Tallahassee, FL, LFM	0.157	0.11	0.11	0.08	0.08
Tallahassee, FL, LFM	0.161	0.13	0.13	0.11	0.11
Tallahassee, FL, LFM	0.165	0.13	0.14	0.11	0.11
Tallahassee, FL, LFM	0.159	0.09	0.09	0.08	0.08

[a] SL = reference sample lost due to a laboratory error.
[b] NR = sample not analyzed because initial aliquot analyzed by the technical operator resulted in a cyanide concentration below 0.01 mg/L. The non-technical operator analyzed four background samples because of the detectable concentration of cyanide in the initial aliquot.

Table 6-1d. Cyanide Results from Columbus, OH, Drinking Water

Sample Description	Ref. Conc.[a] (mg/L)	Non-Technical Operator		Technical Operator	
		Unit #1 (mg/L)	Unit #2 (mg/L)	Unit #1 (mg/L)	Unit #2 (mg/L)
City Water Background - Outdoor Field Site	<0.005	<0.01	<0.01	<0.01	<0.01
City Water Background - Indoor Field Site	<0.005	<0.01	<0.01	<0.01	<0.01
City Water Background - Lab	<0.005	<0.01	<0.01	<0.01	<0.01
City Water Background - Lab	<0.005	<0.01	<0.01	<0.01	<0.01
City Water Background - Lab	<0.005	<0.01	<0.01	<0.01	<0.01
City Water Background - Lab	<0.005	<0.01	0.01	<0.01	<0.01
City Water LFM - Outdoor Field Site	0.176	0.02	0.02	0.03[b]	0.03[b]
City Water LFM - Outdoor Field Site	0.167	0.02	0.02	0.03[b]	0.03[b]
City Water LFM - Outdoor Field Site	0.165	0.02	0.02	0.02[b]	0.02[b]
City Water LFM - Outdoor Field Site	0.178	0.01	0.01	0.03[b]	0.02[b]
City Water LFM - Indoor Field Site	0.176	0.09	0.09	0.13	0.13
City Water LFM - Indoor Field Site	0.167	0.06	0.06	0.11	0.11
City Water LFM - Indoor Field Site	0.165	0.11	0.11	0.12	0.13
City Water LFM - Indoor Field Site	0.178	0.10	0.11	0.13	0.13
City Water LFM - Lab	0.176	0.13	0.13	0.11	0.11
City Water LFM - Lab	0.167	0.15	0.15	0.13	0.13
City Water LFM - Lab	0.165	0.17	0.17	0.12	0.12
City Water LFM - Lab	0.178	0.14	0.14	0.16	0.16

Table 6-1d. Cyanide Results from Columbus, OH, Drinking Water (continued)

Sample Description	Ref. Conc. (mg/L)	Non-Technical Operator		Technical Operator	
		Unit #1 (mg/L)	Unit #2 (mg/L)	Unit #1 (mg/L)	Unit #2 (mg/L)
Well Water Background - Outdoor Field Site	<0.005	<0.01	<0.01	<0.01	<0.01
Well Water Background - Indoor Field Site	<0.005	<0.01	<0.01	<0.01	<0.01
Well Water Background - Lab	<0.005	<0.01	<0.01	<0.01	<0.01
Well Water Background - Lab	<0.005	<0.01	<0.01	<0.01	<0.01
Well Water Background - Lab	<0.005	<0.01	<0.01	<0.01	<0.01
Well Water Background - Lab	<0.005	<0.01	<0.01	<0.01	<0.01
Well Water LFM - Outdoor Field Site	0.100	<0.01	<0.01	0.02	0.02
Well Water LFM - Outdoor Field Site	0.121	<0.01	<0.01	<0.01	<0.01
Well Water LFM - Outdoor Field Site	0.114	0.01	0.01	0.02	0.02
Well Water LFM - Outdoor Field Site	0.091	<0.01	<0.01	0.01	0.01
Well Water LFM - Indoor Field Site	0.100	0.14	0.14	0.13	0.13
Well Water LFM - Indoor Field Site	0.121	0.16	0.16	0.13	0.14
Well Water LFM - Indoor Field Site	0.114	0.15	0.13	0.13	0.15
Well Water LFM - Indoor Field Site	0.091	0.11	0.11	0.14	0.15
Well Water LFM - Lab	0.100	<0.01	<0.01	<0.01	<0.01
Well Water LFM - Lab	0.121	<0.01	<0.01	<0.01	<0.01
Well Water LFM - Lab	0.114	0.01	0.01	<0.01	<0.01
Well Water LFM - Lab	0.091	<0.01	<0.01	<0.01	<0.01

[a] The same reference LFM samples are used for the outdoor, indoor, and laboratory analysis locations.
[b] Samples analyzed in pH range of 6.0 to 7.0.

Table 6-2a. Percent Accuracy of Performance Test Sample Measurements

Sample Concentration (mg/L)	Non-Technical Operator		Technical Operator	
	Unit #1 (bias)	Unit #2 (bias)	Unit #1 (bias)	Unit #2 (bias)
0.030	31%	21%	21%	21%
0.100	24%	22%	6%	6%
0.200	26%	24%	12%	10%
0.400	4%	2%	12%	12%
0.800	NA[a]	NA	NA	NA

[a] NA = Calculation of bias not appropriate when result was outside the detectable range of the LaMotte SMART 2.

Table 6-2b. Percent Accuracy of Surface Water Test Measurements

Sample Description	Non-Technical Operator		Technical Operator	
	Unit #1 (bias)	Unit #2 (bias)	Unit #1 (bias)	Unit #2 (bias)
Alum Creek LFM	30%	29%	11%	11%
Olentangy River LFM	16%	20%	24%	23%

Table 6-2c. Percent Accuracy of U.S. Drinking Water Measurements

Sample Description	Non-Technical Operator		Technical Operator	
	Unit #1 (bias)	Unit #2 (bias)	Unit #1 (bias)	Unit #2 (bias)
Des Moines, IA, LFM	35%	34%	6%	5%
Flagstaff, AZ, LFM	13%	14%	17%	18%
Montpelier, VT, LFM	15%	15%	16%	16%
Seattle, WA, LFM	34%	32%	12%	12%
Tallahassee FL, LFM	28%	27%	41%	41%

Table 6-2d. Percent Accuracy of Columbus, OH, Drinking Water Measurements

Sample Description	Non-Technical Operator		Technical Operator	
	Unit #1 (bias)	Unit #2 (bias)	Unit #1 (bias)	Unit #2 (bias)
City Water LFM - Outdoor Field Site	90%	90%	84%	85%
City Water LFM - Indoor Field Site	48%	46%	29%	27%
City Water LFM - Lab	15%	15%	24%	24%
Well Water LFM - Outdoor Field Site[a]	99%	99%	94%	94%
Well Water LFM - Indoor Field Site[a]	30%	33%	34%	29%
Well Water LFM - Lab[a]	99%	99%	100%[b]	100%[b]

[a] Due to an approximately 50% reference LFM recovery in the well water sample (see Table 4-2), these biases were calculated using the fortified concentration of 0.200 mg/L as the reference concentration.

[b] 100% bias due to non-detect reading from LaMotte SMART 2.

6.2 Precision

Tables 6-3a-d show the RSDs of the cyanide analysis results for PT samples; surface water; drinking water from around the U.S.; and drinking water from Columbus, OH, respectively, from the LaMotte SMART 2 and the reference method. Results are shown for the technical and non-technical operators and for both units that were tested. RSDs were not calculated for results reported as less than the MDL of the LaMotte SMART 2. The RSD values shown in Tables 6-3a-d can be summarized by the range of RSDs observed with different sample sets. For example, the RSDs 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; and 4 to 77% for the Columbus, OH, drinking water samples.

Table 6-3a. Relative Standard Deviation of Performance Test Sample Measurements

Sample Concentration (mg/L)	Reference Method (RSD)	Non-Technical Operator		Technical Operator	
		Unit #1 (RSD)	Unit #2 (RSD)	Unit #1 (RSD)	Unit #2 (RSD)
0.030	8%	15%	0%	0%	0%
0.100	7%	20%	19%	5%	5%
0.200	2%	7%	8%	11%	11%
0.400	2%	5%	3%	13%	14%
0.800	1%	NA[a]	NA[a]	NA[a]	NA[a]

[a] Results were outside the detectable range of the LaMotte SMART 2 so calculation of precision was not appropriate.

Table 6-3b. Relative Standard Deviation of Surface Water Measurements

Sample Description	Reference Method (RSD)	Non-Technical Operator		Technical Operator	
		Unit #1 (RSD)	Unit #2 (RSD)	Unit #1 (RSD)	Unit #2 (RSD)
Alum Creek LFM	8%	39%	38%	10%	10%
Olentangy River LFM	2%	13%	12%	23%	25%

Table 6-3c. Relative Standard Deviation of U.S. Drinking Water Measurements

Sample Description	Reference Method (RSD)	Non-Technical Operator		Technical Operator	
		Unit #1 (RSD)	Unit #2 (RSD)	Unit #1 (RSD)	Unit #2 (RSD)
Des Moines, IA, LFM	3%	42%	40%	3%	3%
Flagstaff, AZ, LFM	12%	19%	18%	15%	16%
Montpelier, VT, LFM	2%	4%	4%	9%	9%
Seattle, WA, LFM	2%	53%	52%	15%	16%
Tallahassee FL, LFM	2%	17%	19%	18%	18%

Table 6-3d. Relative Standard Deviation of Columbus, OH, Drinking Water Measurements

Sample Description	Reference Method (RSD)	Non-Technical Operator		Technical Operator	
		Unit #1 (RSD)	Unit #2 (RSD)	Unit #1 (RSD)	Unit #2 (RSD)
City Water LFM - Outdoor Field Site	4%	29%	29%	18%	23%
City Water LFM - Indoor Field Site	4%	24%	26%	8%	8%
City Water LFM - Lab	4%	12%	12%	17%	17%
Well Water LFM - Outdoor Field Site	13%	NA	NA	77%	77%
Well Water LFM - Indoor Field Site	13%	15%	15%	4%	7%
Well Water LFM - Lab	13%	NA[a]	NA	NA	NA

[a] NA = calculation of precision was not appropriate when results were outside the detection range of the LaMotte SMART 2.

6.3 Linearity

The linearity of the LaMotte SMART 2 was assessed by using a linear regression of the PT results against the reference method results (Table 6-1a). Figures 6-1 and 6-2 show scatter plots of the results from the non-technical and technical operator, respectively, versus the reference results. A dotted regression line with a slope of unity and an intercept of zero also is shown in Figures 6-1 and 6-2.
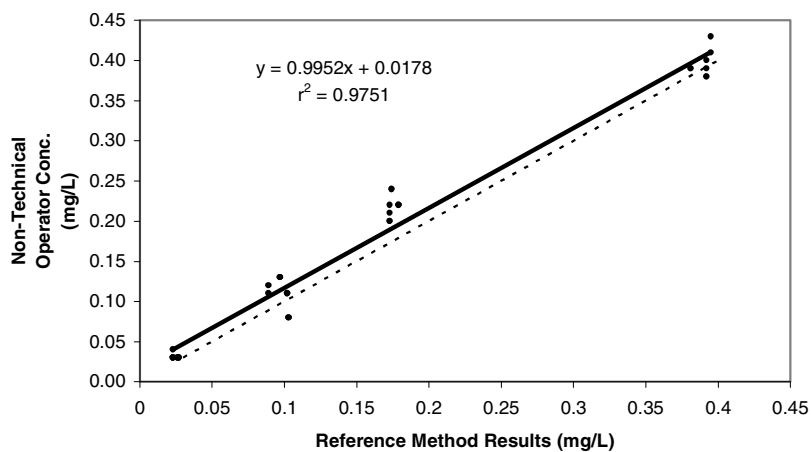

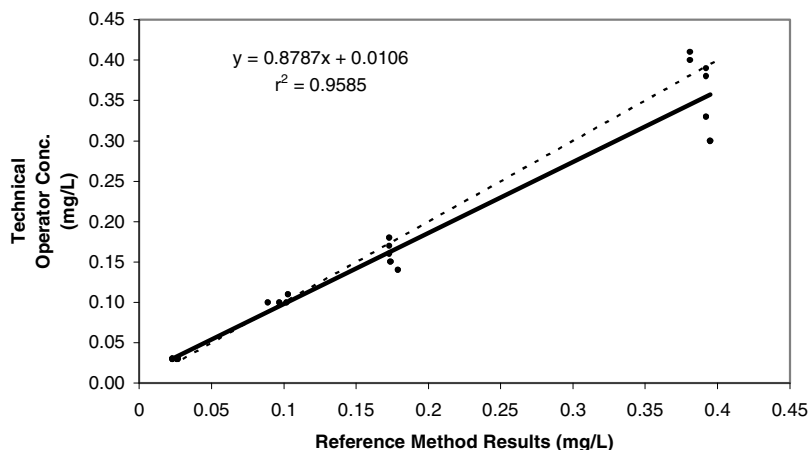**Figure 6-1. Non-Technical Operator Linearity Results**

Figure 6-2. Technical Operator Linearity Results

A linear regression of the data in Figure 6-1 for the non-technical operator 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.

A linear regression of the data in Figure 6-2 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.

6.4 Method Detection Limit

The manufacturer's estimated detection limit for the LaMotte SMART 2 is 0.01 mg/L cyanide. The MDL[4] was determined by analyzing seven replicate samples at a concentration of 0.050 mg/L. Table 6-4 shows the results of the MDL assessment. The MDL determined as described in Equation (6) of Section 5.4 was 0.02 mg/L for the LaMotte SMART 2 when used by either operator.

Table 6-4. Results of Method Detection Limit Assessment

MDL Conc. (mg/L)	Non-Technical Operator		Technical Operator	
	Unit #1 (mg/L)	Unit #2 (mg/L)	Unit #1 (mg/L)	Unit #2 (mg/L)
0.05	0.07	0.05	0.03	0.03
0.05	0.06	0.06	0.04	0.04
0.05	0.06	0.06	0.04	0.04
0.05	0.06	0.06	0.05	0.05
0.05	0.06	0.05	0.05	0.05
0.05	0.05	0.05	0.04	0.04
0.05	0.06	0.06	0.04	0.04
Std Dev	0.006	0.005	0.007	0.007
t (n=7)	3.140	3.140	3.140	3.140
MDL (mg/L)	0.02	0.02	0.02	0.02

6.5 Inter-Unit Reproducibility

The inter-unit reproducibility of the LaMotte SMART 2 was assessed by using a linear regression of the results produced by one LaMotte SMART 2 plotted against the results produced by the other LaMotte SMART 2. The results from all of the samples that had detectable amounts of cyanide (including the PT, surface, and drinking water samples) produced by both operators were included in this regression. Figure 6-3 shows a scatter plot of the results from both LaMotte SMART 2s.
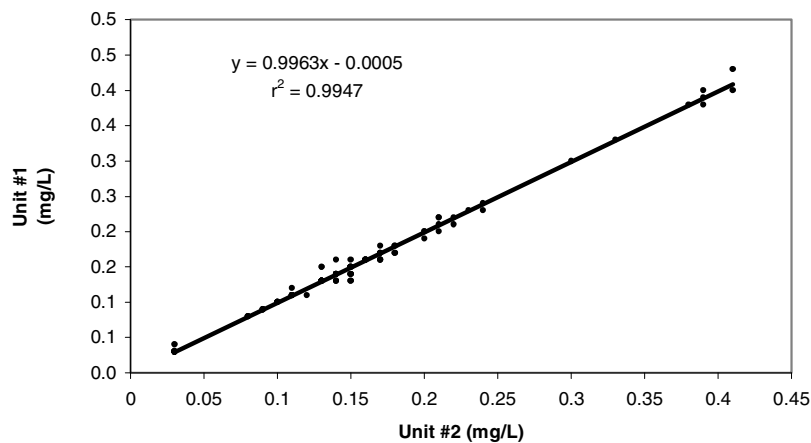

$$y = 0.9963x - 0.0005$$
$$r^2 = 0.9947$$

Figure 6-3. Inter-Unit Reproducibility Results

A linear regression of the data in Figure 6-3 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 (± 0.002) 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.

6.6 Lethal or 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 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."

6.7 Operator Bias

The possible difference in results produced by the non-technical and technical operators was assessed by using a linear regression of the results produced by the non-technical operator plotted against the results produced by the technical operator. The results from all of the samples that had detectable amounts of cyanide (including the PT, surface, and drinking water samples) from both technologies were included in this regression. Figure 6-4 shows a scatter plot of the results from both technologies.

A linear regression of the data in Figure 6-4 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 between 0.100 and 0.200 mg/L, which represent data mostly from the surface and drinking water samples,
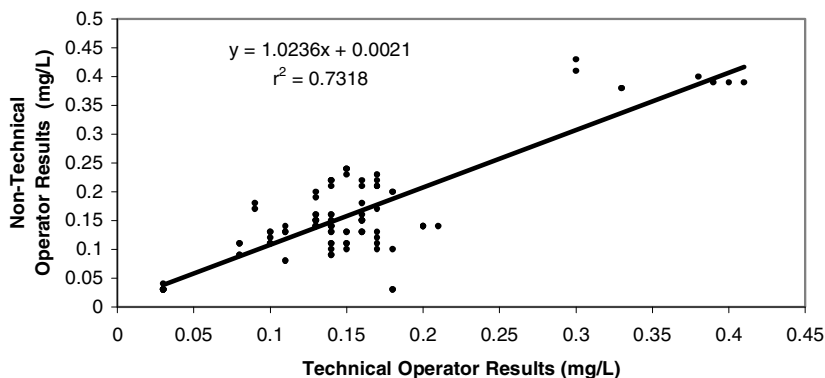
Figure 6-4. Non-Technical vs. Technical Operator Bias Results

display a large amount of scatter about the regression line. The quantitative result of this scatter was the large uncertainty around the slope (11%) and a low coefficient of variation (r^2=0.732). Due to the scatter over a fairly small concentration range (0.1 mg/L), it is difficult to assess by this plot alone the extensiveness of the differences in performance between the two operators; but this can be further examined by referring to the two plots describing linearity in Section 6.3. The non-technical operator's slope was closer to unity than the technical operator's slope, but Table 6-2a shows that the technical operator produced lower biases for all of the PT samples except for the 0.400 mg/L PT sample. The difference in slope between operators apparently was the result of the high degree of uncertainty in the technical operator's 0.400 mg/L results and general trend of a positive bias by the non-technical operator, which is indicated by the regression line being shifted above the dotted line with a slope of unity and a zero intercept. Based on a full evaluation of the data, it seems that the performance of the LaMotte Smart 2 generally was not dependent on which operator performed the analyses.

6.8 Field Portability

The LaMotte SMART 2 was operated in laboratory and field settings during this verification test. Tables 6-1d, 6-2d, and 6-3d show the results of these measurements. From an operational stand-point, 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.

Table 6-2d shows the bias of the samples analyzed in the field setting (indoors with sample temperatures of approximately 16°C and outdoors with sample temperatures of 4 to 6°C) and of the identical samples analyzed at the laboratory at approximately 20°C. The Columbus, OH, city and well water samples were both dechlorinated as described in Section 3.5.1. In addition, because the well water sample had a pungent odor, lead carbonate was added after NaOH preservation to check for the presence of sulfides. The lead carbonate did not turn to black. Such

a color change would have indicated the presence of sulfides. Nonetheless, there was a 27 to 48% bias in the indoor Columbus, OH, city water measurements and a 29 to 34% bias in the indoor well water measurements. Because there was an apparent matrix interference in the reference measurement (see Table 4-2), the well water biases were calculated using the fortified concentration (0.200 mg/L) as the reference concentration.

The apparent matrix interference in the well water LFM continued to mask the cyanide in the LFM sample after it was spiked and analyzed at the indoor field setting (producing a 29 to 34% bias from initial fortification) because, by the time the well water LFM samples were analyzed by the LaMotte SMART 2 at the laboratory two days after initial fortification, there was no detectable cyanide (100% bias from initial fortification). These same samples were analyzed using the reference method eight days after initial fortification and the result was below the MDL of the reference method (see Table 4-2). Because there was an apparent time-dependent matrix interference, the data generated from the well water samples using the LaMotte SMART 2 in the field setting cannot be meaningfully compared with the result produced from the identical samples analyzed with the LaMotte SMART 2 in the laboratory or using the reference method.

The bias in the Columbus, OH, city water indoor LFM sample performed by the technical operator (27 to 29%) was similar to the bias in the Columbus, OH, city water LFM sample analyzed at the laboratory location (24%). The apparent matrix interference causing the progressively larger (see Table 4-2) biases in the well water did not further mask the cyanide in the city water LFM sample as evidenced by the similar biases at the field location and at the laboratory two days later. Also, the reference LFM recoveries in the city water matrix were similar when spiked just minutes before analysis or days before (see Table 4-2). These data support the qualitative assessment that the LaMotte SMART 2 functions properly when operated in field locations.

6.9 Ease of Use

The LaMotte SMART 2 and associated cyanide test reagents were easy to use. The instruction manual was clear, and the sample and reagents were easily measured using a disposable pipet and two 0.100-g scoops. While the sample handling and analysis were easy, the pH of each sample did have to be adjusted to between 10.5 and 11.0 using NaOH and hydrochloric acid (HCl). LaMotte provided dropper bottles of HCl and NaOH, pH paper, and step-by-step instructions for pH adjustment with each cyanide reagent kit. These provisions made a tedious task more convenient for both operators. The sample jars containing the reacted sample had to be emptied and rinsed between sample analyses.

6.10 Sample Throughput

Sample preparation, including accurate volume measurement and the addition of reagents, took one to two minutes per sample. After performing the sample preparation, a 20-minute period of color development is required before sample analysis. Therefore, if only one sample is analyzed, it 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.

Chapter 7
Performance Summary

Biases for the LaMotte SMART 2 ranged from 2 to 31% for the PT samples; 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.

The RSDs ranged from 0 to 20% for the PT samples, 10 to 39% for the surface water samples, and 3 to 53% for the drinking water samples from around the country. For Columbus, OH, drinking water samples, RSDs were 4 to 77%.

A linear regression of the linearity data for the non-technical operator gives the following regression equation:

y (non-technical operator results in mg/L)=0.995 ($\pm$ 0.059) x (reference result in mg/L) + 0.018 ($\pm$ 0.013) mg/L with r^2=0.975 and N=32.

A linear regression of the data for the technical operator gives the following regression equation:

y (technical operator results in mg/L)=0.879 ($\pm$ 0.068) x (reference result in mg/L) + 0.011 ($\pm$ 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.

 The MDL was determined to be 0.02 mg/L for the LaMotte SMART 2 when used by either operator.

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 ($\pm$ 0.013) x (Unit #2 result in mg/L) - 0.0005 ($\pm$ 0.002) 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.

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 even 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, the reagent and glass vial 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.

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 ($\pm$ 0.113) x (tech result in mg/L) + 0.002
($\pm$ 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 repre-senting 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.

From an operational standpoint, the LaMotte SMART 2 was easily transported to the field setting, and samples were analyzed in the same fashion in the field 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.

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 disposa-ble pipet and two 0.100-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.

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.

Chapter 8
References

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4.   *Code of Federal Regulations,* Title 40, Part 136, Appendix B, Definition and Procedure for the Determination of the Method Detection Limit–Revision 1.11.

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