April 2003

Environmental Technology Verification Report

CHEMETRICS
VVR V-1000 MULTI-ANALYTE PHOTOMETER with V-3803 Cyanide Module

Prepared by
Battelle

Battelle
. . . Putting Technology To Work

Under a cooperative agreement with

EPA U.S. Environmental Protection Agency

ETV ETV ETV

April 2003

Environmental Technology Verification Report

ETV Advanced Monitoring Systems Center

CHEMetrics
VVR V-1000 Multi-Analyte Photometer with V-3803 Cyanide Module

by
Ryan James
Amy Dindal
Zachary Willenberg
Karen Riggs

Battelle
Columbus, Ohio 43201

Notice

The U.S. Environmental Protection Agency (EPA), through its Office of Research and Development, has financially supported and collaborated in the extramural program described here. This document has been peer reviewed by the Agency. Mention of trade names or commercial products does not constitute endorsement or recommendation by the EPA for use.

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 agreement 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.

Acknowledgments

The authors wish to acknowledge the support of all those who helped plan and conduct the verification test, analyze the data, and prepare this report. We would like to thank Billy Potter, U.S. EPA, National Exposure Research Laboratory; Ricardo DeLeon, Metropolitan Water District of Southern California; William Burrows, U.S. Army Center for Environmental Health Research; and Kenneth Wood, Du Pont Corporate Environmental Engineering Group, for their technical review of the test/QA plan and for their careful review of this verification report. We also would like to thank Allan Chouinard, City of Montpelier, VT; Gordon Brand, Des Moines, IA, Water Works; Wylie Harper, City of Seattle, WA; John Morrill, City of Tallahassee, FL; and Tom Scott, City of Flagstaff, AZ, water distribution facilities who provided post-treatment water samples for evaluation.

Contents

Page

Figures

Tables

List of Abbreviations

AMS	Advanced Monitoring Systems
ASTM	American Society of Testing and Materials
ATEL	Aqua Tech Environmental Laboratories
CNCl	cyanogen chloride
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 CHEMetrics VVR V-1000 photometer with the V-3803 cyanide module (referred to as the CHEMetrics VVR throughout this report) 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 VVR photometer by CHEMetrics with the V-3803 cyanide module. Following is a description of the CHEMetrics VVR, based on information provided by the vendor. The information provided below was not verified in this test.

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 milligrams per liter (mg/L).

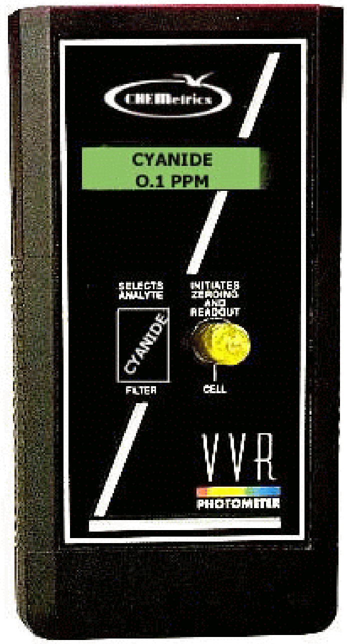

Figure 2-1. CHEMetrics VVR Photometer

Most chemical reaction rates are affected by temperature, so the Vacu-vial® test procedure and VVR photometer factory-set calibration have been established with cyanide standards at room temperature. Consequently, colorimetric analytical methods will be impacted by sample temperature. For this reason, sample temperatures significantly above or below 20°C can be expected to impact the accuracy of test results. The chemical reactions involved in the final color development of the cyanide Vacu-vial® method are also pH dependent. The CHEMetrics VVR factory-set calibration is based on cyanide standards preserved at alkaline pH conditions rather than at neutral/near neutral pH because it is assumed that cyanide testing occurs after samples have been preserved with base to pH values between 10.5 and 11.0.

Vacu-vials® are packaged in individual 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 (CNCl), 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. 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).

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 0.2 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 CHEMetrics VVR 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 CHEMetrics VVR V-1000 photometer with the V-3803 cyanide module was verified by analyzing performance test (PT), surface, and drinking water samples. A statistical comparison of the analytical results from the CHEMetrics VVR and the reference method provided the basis for the quantitative performance evaluations.

The CHEMetrics VVR's performance was evaluated in terms of

- Accuracy
- Precision
- Linearity
- Method detection limit
- Inter-unit reproducibility

- Lethal or near-lethal dose response
- 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 CHEMetrics VVR 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 CHEMetrics VVRs 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 CHEMetrics VVR V-1000 photometer and V-3803 cyanide module. The verification test involved challenging the CHEMetrics VVR with a variety of test samples, including sets of drinking and surface water samples representative of those likely to be analyzed by the CHEMetrics VVR. 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 the CHEMetrics VVR and the reference method.

Each CHEMetrics VVR 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 CHEMetrics VVRs.

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 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.

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 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 CHEMetrics VVR also was qualitatively evaluated with samples prepared in an 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. 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 CHEMetrics VVR. The QCSs for the CHEMetrics VVR 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.

The CHEMetrics VVR was factory calibrated, so no additional calibration was performed by the operators. However, QCSs were analyzed (without defined performance expectations) by the

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
	QCS	0.200 mg/L	10% of all
Performance Test	For the determination of method detection limit	0.200 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	1
		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	1
		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

CHEMetrics VVR to demonstrate their proper functioning to the operator. A QCS was analyzed before and after each sample batch (typically consisting of 12 water 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 CHEMetrics VVR's accuracy, linearity, and detection limit. Seven non-consecutive replicate analyses of an 0.200-mg/L solution were made to obtain precision data with which to determine the method detection limit (MDL).(4) Four 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 CHEMetrics VVR. 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 CHEMetrics VVR 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 CHEMetrics VVR 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.

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-mL aliquots were taken from each subsample and analyzed for cyanide by the CHEMetrics VVR. 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, four replicates of Columbus, OH, city and well water; Alum Creek samples; and Olentangy River samples were analyzed. None of these samples had detectable concentrations of cyanide. Four LFM aliquots were dechlorinated, prepared, and analyzed for every drinking and surface water source. To avoid replicating samples with non-detectable concentrations of cyanide, only one background aliquot of the drinking water samples from around the country was analyzed.

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 CHEMetrics VVR. 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 were 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 background and LFM reference concentrations were compared with the results produced by the CHEMetrics VVR at the indoor and outdoor field locations and the laboratory location.

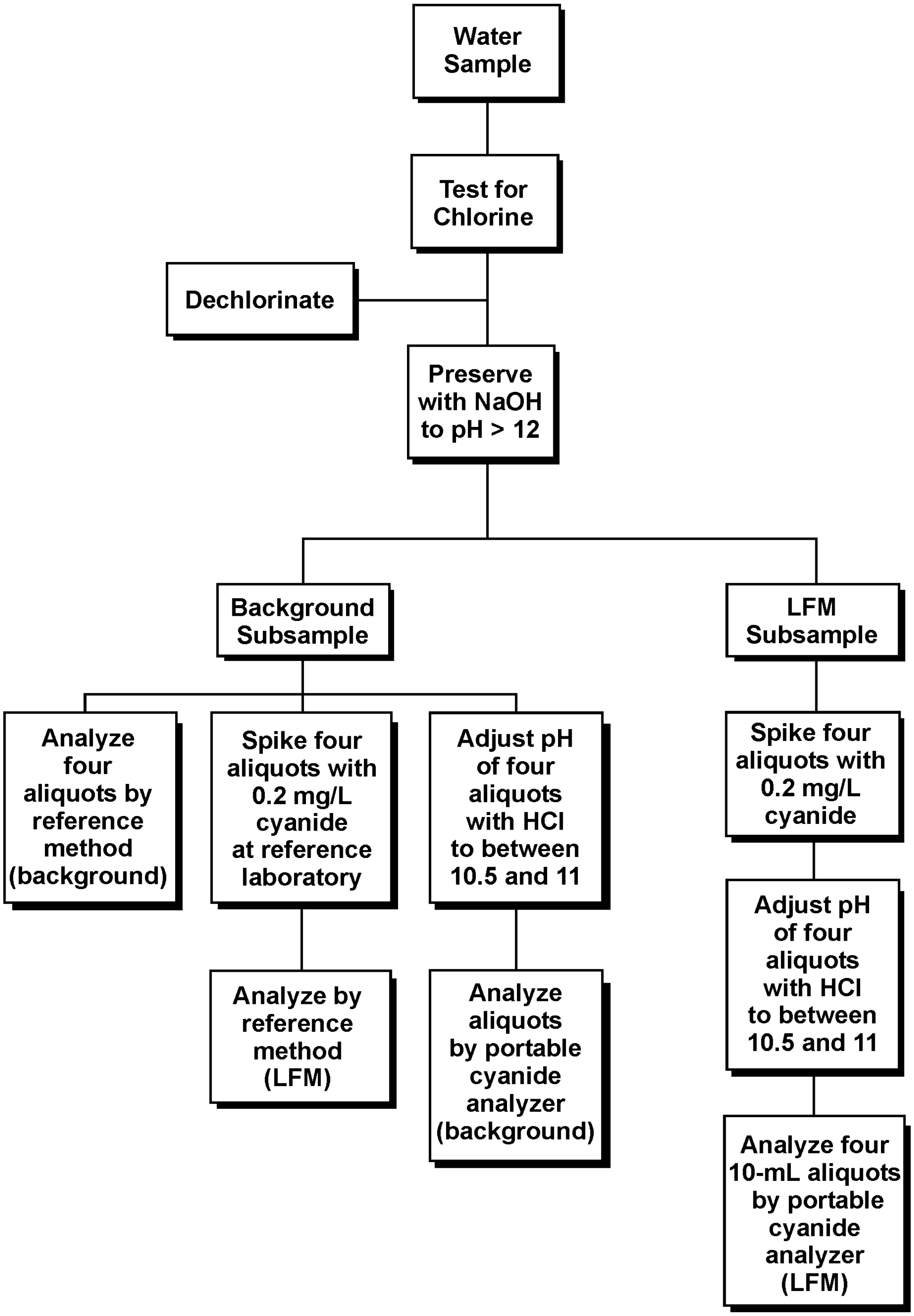

Figure 3-1. Sampling through Analysis Process

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 CHEMetrics VVR 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 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 CHEMetrics VVRs were tested independently. Each CHEMetrics VVR 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 and corresponding laboratory notebooks included records of the time required for sample analysis and operator observations concerning the use of the CHEMetrics VVR (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 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:

$$R = \frac{C_s - C}{s} \times 100 \tag{1}$$

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 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 4-1. 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

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 to 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 sample 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 CHEMetrics VVR. 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 CHEMetrics VVR and those from the reference method, and $\overline{C_R}$ is the average of the reference measurements. Accuracy was assessed independently for each CHEMetrics VVR 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 CHEMetrics VVR 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 CHEMetrics VVR 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 CHEMetrics VVR 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 CHEMetrics VVR was reported separately.

5.5 Inter-Unit Reproducibility

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

5.6 Lethal or Near-Lethal Dose Response

The CHEMetrics VVR 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 their 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 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 CHEMetrics VVR 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

The results of the verification test of the CHEMetrics VVR are presented in this section.

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 CHEMetrics VVR. Results are shown for the technical and non-technical operators and for both CHEMetrics VVRs that were tested (labeled as Unit #1 and #2). The 0.800 mg/L PT samples were outside the detectable range of the CHEMetrics VVR. When these samples were inserted into the CHEMetrics VVR, the result was reported as "over range."

Tables 6-2a-d present the percent accuracy of the CHEMetrics VVR 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 CHEMetrics VVR, 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 3 to 24% for the PT samples; 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. 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.

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 CHEMetrics VVR 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 CHEMetrics VVR. 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 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.

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

		Non-Technical Operator		Technical Operator	
Prepared Concentration (mg/L)	Ref. Conc. (mg/L)	Unit #1 (mg/L)	Unit #2 (mg/L)	Unit #1 (mg/L)	Unit #2 (mg/L)
0.030	0.027	0.020	0.025	0.025	0.020
0.030	0.023	0.020	0.020	0.025	0.025
0.030	0.026	0.020	0.025	0.025	0.025
0.030	0.023	0.015	0.020	0.025	0.025
0.100	0.102	0.085	0.089	0.095	0.090
0.100	0.089	0.085	0.090	0.090	0.085
0.100	0.097	0.075	0.080	0.090	0.085
0.100	0.103	0.075	0.080	0.090	0.090
0.200	0.173	0.160	0.170	0.180	0.165
0.200	0.179	0.155	0.165	0.175	0.170
0.200	0.173	0.155	0.160	0.170	0.165
0.200	0.174	0.160	0.165	0.165	0.160
0.400	0.381	0.310	0.325	0.340	0.330
0.400	0.392	0.325	0.345	0.340	0.325
0.400	0.392	0.300	0.315	0.350	0.335
0.400	0.395	0.320	0.335	0.355	0.345
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 the detectable range of the CHEMetrics VVR.

Table 6-1b. Cyanide Results from Surface Water

Sample Description	Ref. Conc. (mg/L)	Non-Technical Operator Unit #1 (mg/L)	Non-Technical Operator Unit #2 (mg/L)	Technical Operator Unit #1 (mg/L)	Technical Operator Unit #2 (mg/L)
Alum Creek Background	<0.005	<0.03	<0.03	<0.03	<0.03
Alum Creek Background	<0.005	<0.03	<0.03	<0.03	<0.03
Alum Creek Background	<0.005	<0.03	<0.03	<0.03	<0.03
Alum Creek Background	<0.005	<0.03	<0.03	<0.03	<0.03
Alum Creek LFM	0.183	0.145	0.135	0.155	0.140
Alum Creek LFM	0.173	0.145	0.140	0.155	0.150
Alum Creek LFM	0.151	0.145	0.140	0.165	0.155
Alum Creek LFM	0.166	0.150	0.145	0.150	0.140
Olentangy River Background	<0.005	<0.03	<0.03	<0.03	<0.03
Olentangy River Background	<0.005	<0.03	<0.03	<0.03	<0.03
Olentangy River Background	<0.005	<0.03	<0.03	<0.03	<0.03
Olentangy River Background	<0.005	<0.03	<0.03	<0.03	<0.03
Olentangy River LFM	0.171	0.160	0.160	0.180	0.170
Olentangy River LFM	0.178	0.170	0.155	0.165	0.160
Olentangy River LFM	0.176	0.175	0.170	0.175	0.160
Olentangy River LFM	0.174	0.180	0.170	0.170	0.165

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

Sample Description	Ref. Conc. (mg/L)	Non-Technical Operator Unit #1 (mg/L)	Non-Technical Operator Unit #2 (mg/L)	Technical Operator Unit #1 (mg/L)	Technical Operator Unit #2 (mg/L)
Des Moines, IA, Background	<0.005	<0.03	<0.03	<0.03	<0.03
Des Moines, IA, LFM	0.181	0.145	0.150	0.085	0.085
Des Moines, IA, LFM	0.183	0.160	0.165	0.100	0.105
Des Moines, IA, LFM	0.173	0.170	0.175	0.120	0.115
Des Moines, IA, LFM	0.173	0.170	0.175	0.115	0.115
Flagstaff, AZ, Background	<0.005	<0.03	<0.03	<0.03	<0.03
Flagstaff, AZ, LFM	SL(a)	0.120	0.130	0.075	0.070
Flagstaff, AZ, LFM	0.132	0.130	0.140	0.090	0.085
Flagstaff, AZ, LFM	0.169	0.135	0.135	0.060	0.055
Flagstaff, AZ, LFM	0.157	0.140	0.145	0.105	0.105
Montpelier, VT, Background	<0.005	<0.03	<0.03	<0.03	<0.03
Montpelier, VT, LFM	0.168	0.100	0.100	0.105	0.105
Montpelier, VT, LFM	0.168	0.110	0.110	0.115	0.120
Montpelier, VT, LFM	0.167	0.115	0.115	0.115	0.120
Montpelier, VT, LFM	0.176	0.120	0.125	0.115	0.120
Seattle, WA, Background	<0.005	<0.03	<0.03	<0.03	<0.03
Seattle, WA, LFM	0.172	0.120	0.120	0.140	0.140
Seattle, WA, LFM	0.174	0.135	0.145	0.140	0.145
Seattle, WA, LFM	0.177	0.140	0.150	0.140	0.140
Seattle, WA, LFM	0.170	0.140	0.150	0.140	0.145
Tallahassee, FL, Background	<0.005	<0.03	<0.03	<0.03	<0.03
Tallahassee, FL, LFM	0.161	0.070	0.075	0.065	0.065
Tallahassee, FL, LFM	0.165	0.075	0.080	0.065	0.060
Tallahassee, FL, LFM	0.159	0.075	0.075	0.055	0.050
Tallahassee, FL, LFM	0.157	0.090	0.090	0.070	0.065

(a) SL = reference sample lost because of laboratory error.

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

		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)
City Water Background - Outdoor Field Site	<0.005	<0.03	<0.03	<0.03	<0.03
City Water Background - Indoor Field Site	<0.005	<0.03	<0.03	<0.03	<0.03
City Water Background - Lab	<0.005	<0.03	<0.03	<0.03	<0.03
City Water Background - Lab	<0.005	<0.03	<0.03	<0.03	<0.03
City Water Background - Lab	<0.005	<0.03	<0.03	<0.03	<0.03
City Water Background - Lab	<0.005	<0.03	<0.03	<0.03	<0.03
City LFM - Outdoor Field Site	0.176	<0.03	<0.03	<0.03	<0.03
City LFM - Outdoor Field Site	0.167	<0.03	<0.03	<0.03	<0.03
City LFM - Outdoor Field Site	0.165	<0.03	<0.03	<0.03	<0.03
City LFM - Outdoor Field Site	0.178	<0.03	<0.03	<0.03	<0.03
City LFM - Indoor Field Site	0.176	0.070	0.075	0.070	0.065
City LFM - Indoor Field Site	0.167	0.065	0.075	0.070	0.060
City LFM - Indoor Field Site	0.165	0.060	0.070	0.080	0.075
City LFM - Indoor Field Site	0.178	0.075	0.080	0.085	0.080
City LFM - Lab	0.176	0.090	0.085	0.060	0.055
City LFM - Lab	0.167	0.095	0.090	0.060	0.060
City LFM - Lab	0.165	0.100	0.095	0.065	0.060
City LFM - Lab	0.178	0.090	0.095	0.050	0.050

Table 6-1d. Cyanide Results from Columbus, OH, 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)**
Well Water Background - Outdoor Field Site	<0.005	<0.03	<0.03	<0.03	<0.03
Well Water Background - Indoor Field Site	<0.005	<0.03	<0.03	<0.03	<0.03
Well Water Background - Lab	<0.005	<0.03	<0.03	<0.03	<0.03
Well Water Background - Lab	<0.005	<0.03	<0.03	<0.03	<0.03
Well Water Background - Lab	<0.005	<0.03	<0.03	<0.03	<0.03
Well Water Background - Lab	<0.005	<0.03	<0.03	<0.03	<0.03
Well Water LFM - Outdoor Field Site	0.100	<0.03	<0.03	<0.03	<0.03
Well Water LFM - Outdoor Field Site	0.121	<0.03	<0.03	<0.03	<0.03
Well Water LFM - Outdoor Field Site	0.114	<0.03	<0.03	<0.03	<0.03
Well Water LFM - Outdoor Field Site	0.091	<0.03	<0.03	<0.03	<0.03
Well Water LFM - Indoor Field Site	0.100	0.120	0.120	0.120	0.125
Well Water LFM - Indoor Field Site	0.121	0.105	0.110	0.105	0.110
Well Water LFM - Indoor Field Site	0.114	0.095	0.095	0.100	0.110
Well Water LFM - Indoor Field Site	0.091	0.105	0.110	0.115	0.120
Well Water LFM - Lab	0.100	<0.03	<0.03	<0.03	<0.03
Well Water LFM - Lab	0.121	<0.03	<0.03	<0.03	<0.03
Well Water LFM - Lab	0.114	<0.03	<0.03	<0.03	<0.03
Well Water LFM - Lab	0.091	<0.03	<0.03	<0.03	<0.03

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

	Non-Technical Operator		Technical Operator	
Sample Concentration (mg/L)	Unit #1 (bias)	Unit #2 (bias)	Unit #1 (bias)	Unit #2 (bias)
0.030	24%	9%	7%	12%
0.100	18%	14%	7%	10%
0.200	10%	6%	3%	6%
0.400	20%	15%	11%	14%
0.800	NA(a)	NA	NA	NA

(a) NA = Calculation of bias not appropriate when over detectable range of the CHEMetrics VVR.

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

	Non-Technical Operator		Technical Operator	
Sample Description	Unit #1 (bias)	Unit #2 (bias)	Unit #1 (bias)	Unit #2 (bias)
Alum Creek LFM	13%	17%	11%	14%
Olentangy River LFM	4%	6%	4%	6%

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

	Non-Technical Operator		Technical Operator	
Sample Description	Unit #1 (bias)	Unit #2 (bias)	Unit #1 (bias)	Unit #2 (bias)
Des Moines, IA, LFM	9%	7%	41%	41%
Flagstaff, AZ, LFM	12%	12%	59%	62%
Seattle, WA, LFM	23%	18%	19%	18%
Montpelier, VT, LFM	34%	34%	34%	32%
Tallahassee, FL, LFM	52%	50%	60%	63%

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

	Non-Technical Operator		Technical Operator	
Sample Description	**Unit #1 (bias)**	**Unit #2 (bias)**	**Unit #1 (bias)**	**Unit #2 (bias)**
City Water LFM - Outdoor Field Site	100%(a)	100%(a)	100%(a)	100%(a)
City Water LFM - Indoor Field Site	61%	56%	56%	59%
City Water LFM - Lab	45%	47%	66%	67%
Well Water LFM - Outdoor Field Site	100%(a)	100%(a)	100%(a)	100%(a)
Well Water LFM - Indoor Field Site	47%(b)	46%(b)	45%(b)	42%(b)
Well Water LFM - Lab	100%(a)	100%(a)	100%(a)	100%(a)

(a) 100% bias due to non-detect reading from CHEMetrics VVR.

(b) 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.

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

		Non-Technical Operator		Technical Operator	
Concentration (mg/L)	**Reference Method (RSD)**	**Unit #1 (RSD)**	**Unit #2 (RSD)**	**Unit #1 (RSD)**	**Unit #2 (RSD)**
0.030	8%	13%	13%	0%	11%
0.100	7%	7%	7%	3%	3%
0.200	2%	2%	2%	4%	2%
0.400	2%	4%	4%	2%	3%
0.800	1%	NA(a)	NA(a)	NA(a)	NA(a)

(a) NA = Calculation of precision not appropriate when result was outside the detectable range of the CHEMetrics VVR.

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

		Non-Technical Operator		Technical Operator	
Sample Description	**Reference Method (RSD)**	**Unit #1 (RSD)**	**Unit #2 (RSD)**	**Unit #1 (RSD)**	**Unit #2 (RSD)**
Alum Creek LFM	8%	2%	3%	4%	5%
Olentangy River LFM	2%	5%	5%	4%	3%

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

		Non-Technical Operator		Technical Operator	
Sample Description	**Reference Method (RSD)**	**Unit #1 (RSD)**	**Unit #2 (RSD)**	**Unit #1 (RSD)**	**Unit #2 (RSD)**
Des Moines, IA LFM-A	3%	7%	7%	15%	13%
Flagstaff, AZ LFM-A	12%	7%	5%	23%	27%
Montpelier, VT LFM-A	2%	8%	9%	4%	6%
Seattle, WA LFM-A	2%	7%	10%	0%	2%
Tallahassee, FL LFM-A	2%	11%	9%	10%	12%

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

		Non-Technical Operator		Technical Operator	
Sample Description	**Reference Method (RSD)**	**Unit #1 (RSD)**	**Unit #2 (RSD)**	**Unit #1 (RSD)**	**Unit #2 (RSD)**
City Water LFM - Outdoor Field Site	NA[a]	NA	NA	NA	NA
City Water LFM - Indoor Field Site	4%	10%	5%	10%	13%
City Water LFM - Lab	4%	5%	5%	11%	9%
Well Water LFM - Outdoor Field Site	NA	NA	NA	NA	NA
Well Water LFM - Indoor Field Site	13%	10%	9%	8%	6%
Well Water LFM - Lab	13%	NA	NA	NA	NA

[a] Calculation of precision not appropriate when results were outside the detection range of the CHEMetrics VVR.

6.3 Linearity

The linearity of the CHEMetrics VVR 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 intercept of zero also is shown in Figures 6-1 and 6-2.

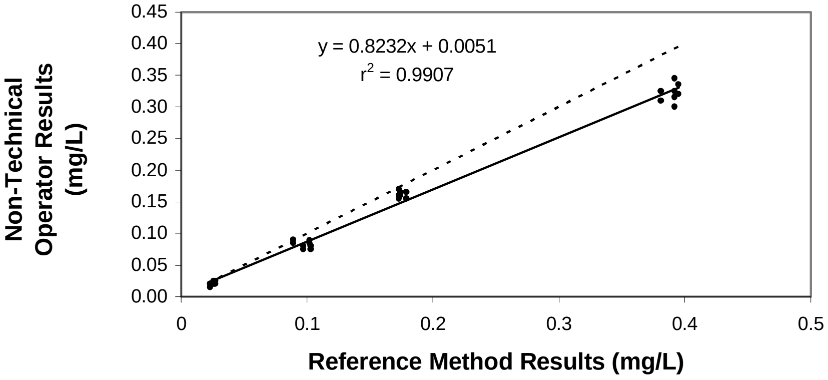

Figure 6-1. Non-Technical Operator Linearity Results

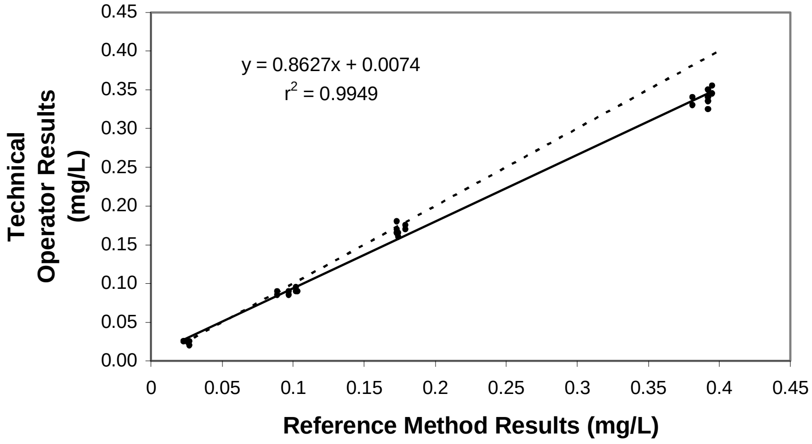

Figure 6-2. Technical Operator Linearity Results

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)=0.823 (± 0.030) x (reference result in mg/L) + 0.005 (± 0.007) mg/L with r^2=0.991 and N=33.

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)=0.863 (± 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. Both slopes are significantly different from unity at the 95% confidence interval, but the slopes from each operator are statistically the same.

6.4 Method Detection Limit

The manufacturer's estimated detection limit for the CHEMetrics VVR is 0.030 mg/L cyanide. The MDL(4) was determined by analyzing seven replicate samples at a concentration of 0.200 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 0.034 and 0.031 mg/L for the CHEMetrics VVR when used by the non-technical operator and 0.017 and 0.011 mg/L for the CHEMetrics VVR when used by the technical operator.

Table 6-4. Results of Method Detection Limit Assessment

	Non-Technical Operator		Technical Operator	
MDL Conc. (mg/L)	**Unit #1 (mg/L)**	**Unit #2 (mg/L)**	**Unit #1 (mg/L)**	**Unit #2 (mg/L)**
0.200	0.160	0.170	0.180	0.165
0.200	0.155	0.165	0.175	0.170
0.200	0.155	0.160	0.170	0.165
0.200	0.160	0.165	0.165	0.160
0.200	0.165	0.170	0.170	0.165
0.200	0.185	0.190	0.170	0.165
0.200	0.155	0.165	0.165	0.160
Std Dev	0.011	0.010	0.005	0.003
t (n=7)	3.140	3.140	3.140	3.140
MDL (mg/L)	0.034	0.031	0.017	0.011

6.5 Inter-Unit Reproducibility

The inter-unit reproducibility of the CHEMetrics VVR was assessed by using a linear regression of the results produced by one CHEMetrics VVR plotted against the results produced by the other CHEMetrics VVR. 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 CHEMetrics VVRs.

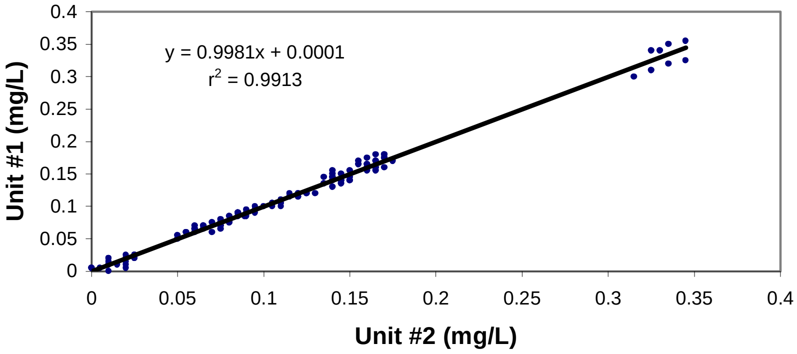

Figure 6-3. Inter-Unit Reproducibility Results

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)=0.998 (± 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.

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 CHEMetrics VVR. Upon breaking the ampoule in the sample, 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 observation of the color development process.

6.7 Operator Bias

The possible difference in results produced by the non-technical and technical operator 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.

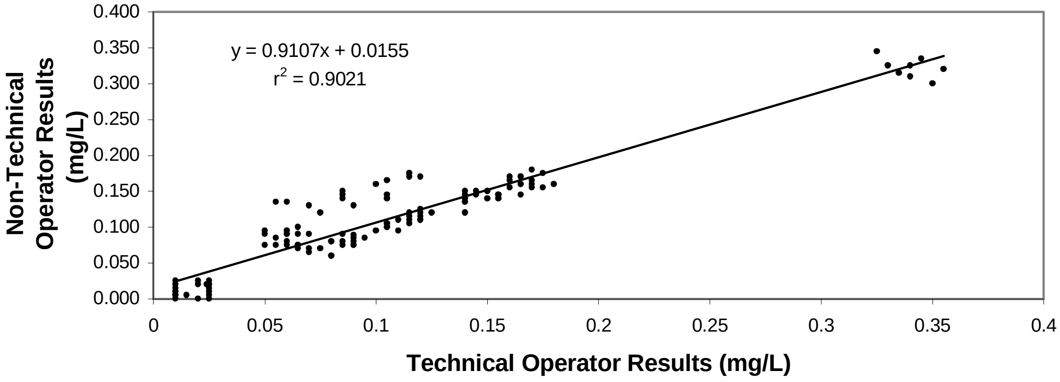

Figure 6-4. Non-Technical vs. Technical Operator Bias Results

A linear regression of the data in Figure 6-4 for the inter-unit comparability assessment 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. The relatively low coefficient of variation is due to the samples from Flagstaff, AZ, and Des Moines, IA. The technical operator's results for these samples were significantly less than the non-technical operator. These samples make up the outlying data points that are above the linear regression line in the 0.050 to 0.125 mg/L range for the technical operator. If these sixteen data points are removed from the data set, the r^2 increases to 0.950. While the difference between the operators (indicated by this slope, which deviates from unity) is not explainable for these samples, these data should not be interpreted to conclude that the effectiveness of the CHEMetrics VVR is dependent on the operator. In the two plots describing linearity in Section 6.3, the slopes for each operator are not significantly different from one another. If one operator was consistently more accurate than the other, the slopes of the linearity plots would be significantly different. Rather than this deviation from unity being a result of the fact that one operator is non-technical and the other technical, it is probably a result of the normal variability of two separate people performing the analyses. Even if both operators had been technically trained, there would probably be a slight difference in performance because of variations in analysis technique.

6.8 Field Portability

The CHEMetrics VVR 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 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 VVR reagents. The low temperatures apparently slowed the chemical reaction rates, which caused the decreased color change in the LFM samples.

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 well and Columbus, OH, city 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 black. Such a color change would have indicated the presence of sulfides. Nonetheless, there was a 56 to 61% bias in the indoor Columbus, OH, city water measurements and a 42 to 47% 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 42 to 47% bias from initial fortification) because, by the time the well water LFM samples were analyzed by the CHEMetrics VVR 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 (Table 4-2). Because there was an apparent time-dependent matrix interference, the data generated from the well water samples using the CHEMetrics VVR in the field setting cannot be meaningfully compared with the result produced from the identical samples analyzed with the CHEMetrics VVR in the laboratory.

The bias in the Columbus, OH, city water indoor LFM sample (56 to 61%) was similar to the bias in the Columbus, OH, city water LFM sample analyzed at the laboratory location (45 to 63%).

The apparent matrix interference causing the large biases did not further mask the cyanide in the LFM sample as evidenced by the similar biases at the field location and at the laboratory two days later. These data support the qualitative assessment that the CHEMetrics VVR functions properly when operated in field locations.

6.9 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. It was convenient that adding reagents did not have strict mixing and reaction time requirements. The operators only had to hold strictly to the 15-minute color development reaction time. Not having to keep track of several short mixing/reaction times after adding each reagent streamlined the analysis and increased sample throughput. 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 very easy, the pH of each sample had to be adjusted to between 10.5 and 11.0 using NaOH and hydrochloric acid (HCl). 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 provided. Because the color change took place within the Vacu-vials® and they were disposable, cleanup was simple and free of mess. Only the sample cup used for measuring the sample and adding reagents had to be rinsed between samples.

6.10 Sample Throughput

Sample preparation, including accurate volume measurement and the addition of reagents, took only one to two minutes per sample. After performing the sample preparation, a 15-minute period of color development is required before sample analysis. Therefore, if only one sample is analyzed, it 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.

Chapter 7
Performance Summary

Biases for the CHEMetrics VVR ranged from 3 to 24% for the PT samples; 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.

The RSD 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 well water samples analyzed at the laboratory was not appropriate because the results were below the MDL of the CHEMetrics VVR.

A linear regression of the linearity data obtained for the non-technical operator 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.

A linear regression of 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. Both operators' intercepts are very close to 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.

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 0.017 and 0.011 mg/L for the CHEMetrics VVR when used by the technical operator.

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 technologies functioned very similarly to one another.

When performing the analysis on samples containing lethal/near-lethal concentrations of cyanide, the difference in the color development was remarkable. Upon snapping the ampoule in the sample, 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. When the samples 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.

A linear regression of the data for the operator bias assessment 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 difference in the results produced by the operators. Rather than this deviation from unity being due to the fact that one operator is non-technical and the other technical, it is probably a result of the normal variability of two separate people performing the analyses. Even if both operators had been technically trained, there would probably be a slight difference in performance due to variations in analysis technique.

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 (4 to 6°C) negatively affected the performance of the CHEMetrics V-3803 reagents. The low temperatures apparently slowed the chemical reaction rates, which caused the decreased color change in the LFM samples.

The CHEMetrics VVR and V-3803 cyanide module 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 using

NaOH and HCl. 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 sample cup used for measuring the sample and adding reagents needed to be rinsed between samples.

Since the CHEMetrics VVR 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 analysis 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.

Chapter 8
References

1. *Test/QA Plan for Verification of Portable Analyzers for Detection of Cyanide in Water,* Battelle, Columbus, Ohio, January 2003.

2. U.S. EPA Method 335.1, *Cyanides Amenable to Chlorination,* 1974, in “Methods for Chemical Analysis of Water and Wastes,” EPA/600/4-79/020, March 1983.

3. United States Environmental Protection Agency, *National Primary Drinking Water Standards,* EPA/816-F-02-013, July 2002.

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.

5. *Quality Management Plan (QMP) for the ETV Advanced Monitoring Systems Center,* Version 4.0, U.S. EPA Environmental Technology Verification Program, Battelle, Columbus, Ohio, December 2002.