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Environmental Technology Verification Report

THERMO ORION MODEL
9606 CYANIDE ELECTRODE
WITH MODEL 290 A+
ION SELECTIVE ELECTRODE METER

Prepared by
Battelle



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Environmental Technology Verification Report

ETV Advanced Monitoring Systems Center

THERMO ORION MODEL 9606 CYANIDE ELECTRODE WITH MODEL 290 A+ ION SELECTIVE ELECTRODE METER

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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 permittees, 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
ID	identification
ISE	ion selective electrode
KCN	potassium cyanide
L	liter
LFM	laboratory-fortified matrix
MDL	method detection limit
mg	milligram
mL	milliliter
mV	millivolt
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 permittees; 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 Thermo Orion Model 9606 Cyanide Electrode with the Model 290 A+ Ion Selective Electrode (ISE) Meter (referred to as the Thermo Orion ISE in 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 Thermo Orion ISE. Following is a description of the Thermo Orion ISE, based on information provided by the vendor. The information provided below was not verified in this test.

The Thermo Orion ISE consists of a solid sensing element containing a mixture of inorganic silver compounds bonded into the tip of an epoxy electrode body. When the sensing element is in contact with a cyanide solution, silver ions dissolve from the membrane surface. Silver ions within the sensing element move to the surface to replace the dissolved ions, establishing a potential difference that is dependent on the cyanide concentration in the solution. Upon calibration with solutions of known cyanide concentrations, these potential differences are converted to concentrations and displayed on the digital readout when the Thermo Orion ISE is inserted into an unknown solution.

The Thermo Orion ISE is accessorized with a hard carrying case, an electrode stand that clips to the carrying case, a one-meter cable, an alkaline reagent for pH adjustment, and an electrode filling solution. The list price for the provided items is \$742 for the Thermo Orion Model 290Aplus ISE meter, \$596 for the Thermo Orion Model 9606 Cyanide Electrode, and \$172 for the plastic carrying case. The Thermo Orion ISE operates on a 9-volt battery and has dimensions of 8.08 x 3.26 x 1.90 inches.



Figure 2-1. Thermo Orion ISE

To analyze water samples for cyanide with the Thermo Orion ISE, it first has to be calibrated using calibration solutions of known concentrations of cyanide in 0.1 M sodium hydroxide (NaOH). Once calibrated, 0.500 milliliter (mL) of Thermo Orion alkaline reagent is added to 50.0 mL of water sample. The sample is stirred using a magnetic stirrer, and the ISE is lowered into the sample. When a stable reading (indicated by the disappearance of a blinking "AR" in the display) is attained, the concentration is recorded in milligrams per liter (mg/L).

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 salts 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 Thermo Orion ISE 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 Thermo Orion ISE was verified by analyzing performance test (PT), lethal/near-lethal concentration, surface, and drinking water samples. A statistical comparison of the analytical results from the Thermo Orion ISE and the reference method provided the basis for the quantitative performance evaluations.

The Thermo Orion ISE’s performance was evaluated in terms of

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

-
- Lethal or near-lethal dose response
 - 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 Thermo Orion ISE 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 Thermo Orion ISEs were tested independently between January 13 and February 4, 2003. All preparation and analyses were performed according to the manufacturer's recommended procedures. Some PT samples were reanalyzed on February 24, 2003, due to a laboratory error. Because ISE technologies are not likely to be operated by non-technical users, operator bias was not evaluated. All the results in this report were generated by a technical operator. The verification test involved challenging the Thermo Orion ISE with a variety of test samples, including sets of drinking and surface water samples representative of those likely to be analyzed by the Thermo Orion ISE. The results from the Thermo Orion ISE were compared with the reference method to quantitatively assess accuracy and linearity. Multiple aliquots of each test sample were analyzed separately to assess the precision of the Thermo Orion ISE and the reference method.

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 operator and the Battelle Verification Test Coordinator. The Thermo Orion ISE 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 25.0 mg/L. The performance of the Thermo Orion ISE also was quantitatively 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 Thermo Orion ISE. The QCSs for the Thermo Orion ISE 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 than 25%, the data collected since the most recent QCS were flagged; and proper maintenance was performed to regain accurate cyanide measurement, according to ATEL's protocols. Section 4.1 describes these samples in more detail.

QCSs were analyzed (without defined performance expectations) by the Thermo Orion ISE to demonstrate their proper functioning to the operator. A QCS was analyzed before and after each sample batch (typically consisting of 12 samples).

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	0.100 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
	Cyanide	5.00 mg/L	4
	Cyanide	15.0 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	12
		0.200 mg/L LFM	12

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 Thermo Orion ISE's accuracy, linearity, and detection limit. Seven non-consecutive replicate analyses of a 0.100 mg/L solution were made to obtain precision data with which to determine the method detection limit (MDL).⁽⁴⁾ Seven other solutions were prepared to assess the linearity over a 0.030- to 25.0-mg/L range of cyanide concentrations. Four aliquots of each of these solutions were analyzed separately to assess the precision of the analyzers. The concentrations of the PT samples are listed in Table 3-1. The operator 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 Thermo Orion ISE 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. Quantitative comparison of the results generated by the Thermo Orion ISE to results from the reference method while analyzing such samples was done. This is a change from the original test/QA plan.⁽¹⁾ Originally the ISE technologies were not to be tested on the lethal/near-lethal concentration samples, but the ISE vendors recommended that the technologies be tested quantitatively at these concentrations.

3.4.4 Surface Water; Drinking Water from Around the U.S.; and Columbus, OH, 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 NaOH to a pH greater than 12.0, 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

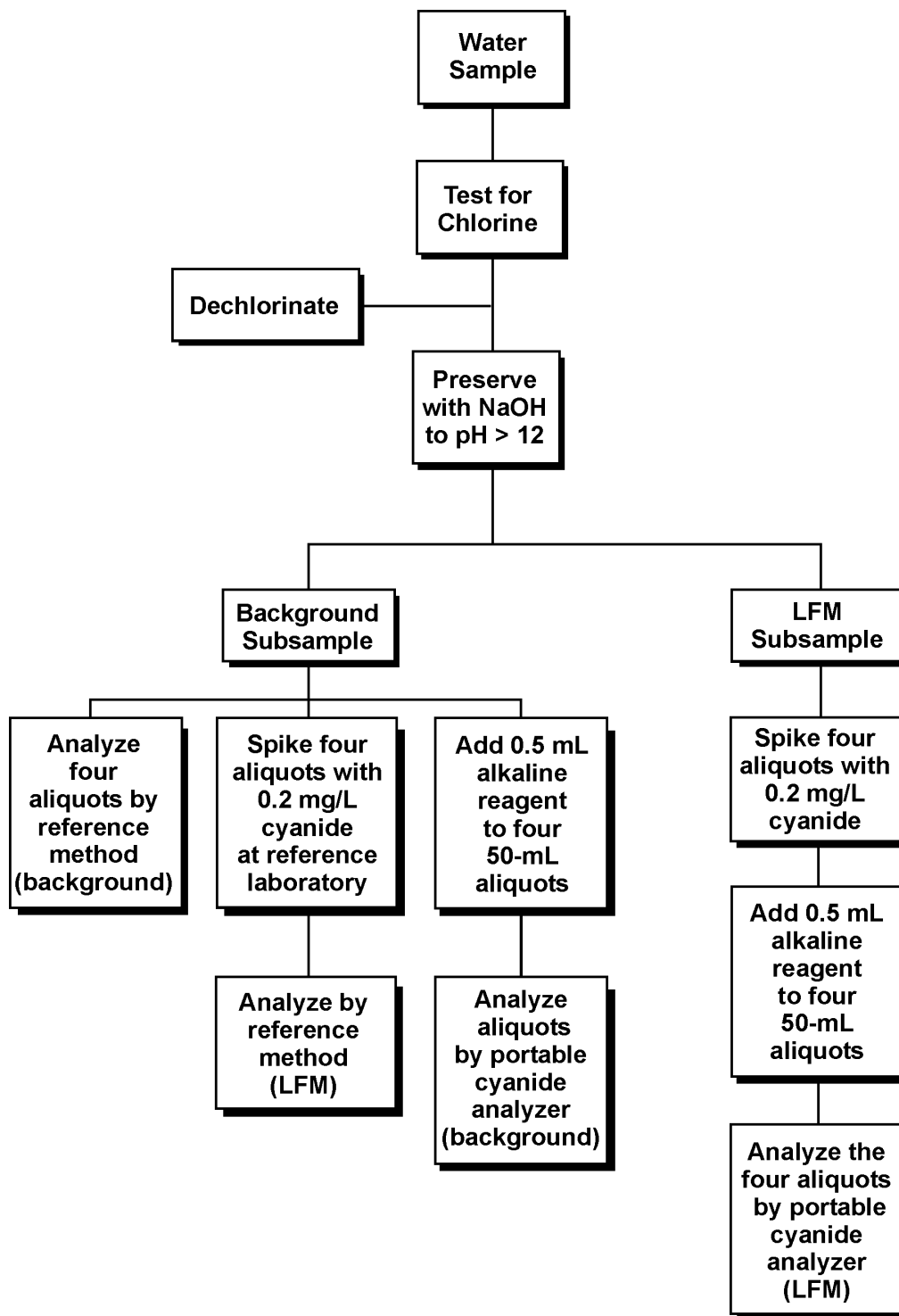


Figure 3-1. Sampling through Analysis Process

aliquots, and the other subsample remained unspiked (background). One 50.0-mL aliquot was taken from each subsample and analyzed for cyanide by the Thermo Orion ISE four separate times. 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 drinking water samples, all four background replicates of Columbus, OH, city and well water 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 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 Thermo Orion ISE. 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 Thermo Orion ISE. 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 $\sim 0^{\circ}\text{C}$, sample temperature 4 to 6°C). A second sample was equilibrated to room temperature inside the residence ($\sim 17^{\circ}\text{C}$) 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 five to six 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 background and LFM reference concentrations were compared to the results produced by the Thermo Orion ISE at the indoor and outdoor field locations and the laboratory location.

3.5 Test Procedure

3.5.1 Calibration and Maintenance

The Thermo Orion ISE required a daily calibration using three calibration solutions. Solutions of 0.030, 0.100, 0.300, 1.00, 2.00, 3.00, 15.0, 25.0, and 200 mg/L were used depending on the expected concentration of the samples to be analyzed. For example, the 0.030, 0.100, and 0.300 mg/L solutions were used most often for calibration because most of the QC, PT, surface, and drinking water samples were within the range of 0.030 to 0.300 mg/L cyanide. However, if the test samples to be analyzed were outside of that range, other calibration solutions were used according to manufacturer recommendations. The operator also polished the Thermo Orion ISE daily before calibration to ensure a clean electrode surface. This was done by wetting a polishing strip (provided by the manufacturer) with ASTM Type II deionized water and gently rubbing the face of the electrode in a single direction for about 30 seconds. The operator attempted to polish each electrode in an identical fashion.

3.5.2 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 water in Class A volumetric glassware. The QC and PT samples were prepared at the start of testing, preserved with NaOH at a pH greater than 12, 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 cyanide 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 per liter of bulk sample 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, 0.500 mL of alkaline reagent provided by Thermo Orion was added to 50.0 mL of each sample to be analyzed by the Thermo Orion ISE, 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.

3.5.3 *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 unit 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.

3.5.4 *Sample Analysis*

The two Thermo Orion ISEs were tested independently. Each Thermo Orion ISE 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 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 Thermo Orion ISE (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 cyanide 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:

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

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 from 75 to 125%, a matrix effect or some other

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	0.200	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	0.201	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	0.201	0.200	106
2/12/2003	0.153	0.150	102
2/12/2003	0.201	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.

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.

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 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:

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

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, cyanide 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 Thermo Orion ISE. 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:

$$B = \frac{\bar{d}}{\bar{C}_R} \times 100 \quad (3)$$

where \bar{d} is the average difference between the readings from the Thermo Orion ISE and those from the reference method, and \bar{C}_R is the average of the reference measurements. Accuracy was assessed independently for each Thermo Orion ISE to determine inter-unit reproducibility.

5.2 Precision

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

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

where n is the number of replicate samples, C_k is the concentration measured for the k^{th} sample, and \bar{c} is the average concentration of the replicate samples. The precision at each concentration was reported in terms of the RSD, e.g.,

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

5.3 Linearity

Linearity was assessed by linear regression, with the cyanide concentration measured by the reference method as independent variable and the reading from the Thermo Orion ISE 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 Thermo Orion ISE 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:

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

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 Thermo Orion ISE was reported separately.

5.5 Inter-Unit Reproducibility

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

5.6 Lethal or Near-Lethal Dose Response

The accuracy of the Thermo Orion ISE for analyzing solutions at lethal/near-lethal concentrations was assessed relative to the results obtained from the reference analyses. Samples were analyzed by both the reference method and the Thermo Orion ISE. The results for each set of analyses were averaged, and the accuracy was expressed in terms of a relative average bias (B) as described in Section 5.1.

5.7 Field Portability

The results obtained from the measurements made on drinking water samples in the laboratory and field settings were compiled independently for each Thermo Orion ISE 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.

5.8 Ease of Use

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

5.9 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 Thermo Orion ISE are presented in this section.

6.1 Calibration Results

Table 6-1 shows the calibration results recorded throughout the verification test, including the calibration solutions used and the actual slopes attained from the calibration linear regressions. Upon calibration with three calibration solutions performed as suggested by the manufacturer's instructions, the Thermo Orion ISE would automatically calculate and report the slope of the calibration linear regression. The manufacturer suggested that this slope should be within the range of -54 to -60 millivolt (mV) per tenfold increase in cyanide concentration. Seventeen of the 22 slopes attained were well outside this range. To simulate the situation that a field technician would be in when using this technology, one calibration was performed; and then the rest of the samples were analyzed. Analyzing the samples using a calibration that produced a regression slope outside the suggested range did not seem to negatively affect the accuracy of the results. The best examples are the samples analyzed following the calibrations performed on January 28, 2003. One calibration was performed at the indoor field location and one at the outdoor field location before analyzing the Columbus, OH, city water. The calibration slope ranged from -72.4 to -79.2, significantly outside the suggested range. As shown in Table 6-3d, biases for these samples ranged from 9 to 24% and were among the smallest attained regardless of the sample type or the slope of the calibration regression line.

6.2 Accuracy

Tables 6-2a-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 Thermo Orion ISE. Results are shown for both Thermo Orion ISEs that were tested (labeled as Unit #1 and #2).

Tables 6-3a-d present the percent accuracy of the Thermo Orion ISE 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. In instances when the LFM samples had a detectable concentration in the reference analysis, but a non-detect reading from the Thermo Orion ISE, the bias was reported as 100%. The bias values shown in Tables 6-3a-d can be summarized by the range of bias observed with different sample sets.

Table 6-1. Calibration Results

Date	Calibration Solutions (mg/L)	Unit #1 ^(a) (Slope)	Unit #2 ^(a) (Slope)
1/15/2003	0.030, 0.100, 0.300	-68.3	-66.8
1/17/2003	3.00, 15.0, 25.0	-53.9	-58.2
1/20/2003	0.030, 0.100, 0.300	-64.0	-66.7
1/21/2003	0.030, 0.100, 0.300	-53.8	-58.8
1/24/2003	0.030, 0.100, 0.300	-67.6	-66.7
1/28/2003 ^(b)	0.030, 0.100, 0.300	-76.5	-72.4
1/28/2003 ^(b)	0.030, 0.100, 0.300	-73.2	-79.2
1/29/2003 ^(b)	0.030, 0.100, 0.300	-59.9	-62.0
1/29/2003 ^(b)	0.030, 0.100, 0.300	-82.0	-71.2
2/3/2003	0.030, 0.300, 1.00	-72.4	-66.0
2/4/2003	2.00, 20.0, 200	-49.3	-49.2

^(a) Slopes are in units of mV per tenfold increase in cyanide concentration.

^(b) ISE was calibrated twice on these two days because a calibration was completed before samples were run both indoors and outdoors.

For example, the biases ranged from 5 to 66% for the PT samples; 41 to 123% for the surface water samples; 14 to 100% for the drinking water samples from around the country; and 4 to 100% for the Columbus, OH, drinking water samples. The biases for the PT samples were highest for the 0.03-mg/L samples (54 and 66%), which is near the MDL for the Thermo Orion ISE, but typically less than 20% for the remaining samples up to 25.0 mg/L, except for the 5.00-mg/L samples where the biases were 41 and 56%. Because of the low well water reference LFM sample recovery (see Table 4-2), the well water biases were calculated using the fortified concentration of 0.200 mg/L as the reference concentration rather than the result produced by the reference method.

6.3 Precision

Tables 6-4a-d show the RSD 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 Thermo Orion ISE and the reference method. Results are shown for both units that were tested. RSD was not calculated for results reported as less than the MDL of the Thermo Orion ISE. The RSD values shown in Tables 6-4a-d can be summarized by the range of RSDs observed with different sample sets. For example, the RSD ranged from 1 to 18% for the PT samples; 5 to 16% for the surface water samples; 0 to 2% for the drinking water samples from around the country; and 2 to 10% for the Columbus, OH, area drinking water samples.

Table 6-2a. Cyanide Results from Performance Test Samples

Prepared Concentration (mg/L)	Ref. Conc. (mg/L)	Unit #1 (mg/L)	Unit #2 (mg/L)
0.030	0.027	0.0449	0.0384
0.030	0.023	0.0395	0.0414
0.030	0.026	0.0415	0.0380
0.030	0.023	0.0383	0.0348
0.100	0.102	0.105	0.0985
0.100	0.089	0.122	0.115
0.100	0.097	0.118	0.122
0.100	0.103	0.126	0.115
0.200	0.173	0.197	0.191
0.200	0.179	0.211	0.207
0.200	0.173	0.212	0.212
0.200	0.174	0.140	0.177
0.400	0.381	0.346	0.413
0.400	0.392	0.386	0.414
0.400	0.392	0.372	0.401
0.400	0.395	0.371	0.407
0.800	0.736	0.624	0.674
0.800	0.724	0.653	0.665
0.800	0.720	0.657	0.710
0.800	0.740	0.644	0.676
5.00	4.60	6.75	7.52
5.00	4.50	6.60	6.95
5.00	4.60	6.38	6.90
5.00	4.58	6.08	7.09
15.0	13.3	14.4	18.8
15.0	13.8	15.0	18.6
15.0	13.5	15.6	18.5
15.0	13.2	14.1	18.3
25.0	22.6	21.4	26.1
25.0	23.5	22.7	22.2
25.0	22.4	19.5	22.7
25.0	22.0	18.8	21.5

Table 6-2b. Cyanide Results from Surface Water

Sample Description	Ref. Conc. (mg/L)	Unit #1 (mg/L)	Unit #2 (mg/L)
Alum Creek Background	<0.005	<0.030	<0.030
Alum Creek Background	<0.005	<0.030	<0.030
Alum Creek Background	<0.005	<0.030	<0.030
Alum Creek Background	<0.005	<0.030	<0.030
Alum Creek LFM	0.166	0.222	0.232
Alum Creek LFM	0.183	0.286	0.224
Alum Creek LFM	0.173	0.302	0.240
Alum Creek LFM	0.151	0.311	0.255
Olentangy River Background	<0.005	<0.030	<0.030
Olentangy River Background	<0.005	<0.030	<0.030
Olentangy River Background	<0.005	<0.030	<0.030
Olentangy River Background	<0.005	<0.030	<0.030
Olentangy River LFM	0.174	0.297	0.290
Olentangy River LFM	0.178	0.430	0.321
Olentangy River LFM	0.171	0.416	0.322
Olentangy River LFM	0.176	0.414	0.305

Table 6-2c. Cyanide Results from U.S. Drinking Water

Sample Description	Ref. Conc. (mg/L)	Unit #1 (mg/L)	Unit #2 (mg/L)
Tallahassee, FL, Background	<0.005	<0.030	<0.030
Tallahassee, FL, LFM	0.157	<0.030	<0.030
Tallahassee, FL, LFM	0.161	<0.030	<0.030
Tallahassee, FL, LFM	0.165	<0.030	<0.030
Tallahassee, FL, LFM	0.159	<0.030	<0.030
Flagstaff, AZ, Background	<0.005	<0.030	<0.030
Flagstaff, AZ, LFM	0.157	0.191	0.195
Flagstaff, AZ, LFM	0.132	0.189	0.193
Flagstaff, AZ, LFM	NA	0.187	0.193
Flagstaff, AZ, LFM	0.169	0.189	0.194
Des Moines, IA, Background	<0.005	<0.030	<0.030
Des Moines, IA, LFM	0.173	0.227	0.236
Des Moines, IA, LFM	0.173	0.218	0.223
Des Moines, IA, LFM	0.183	0.221	0.228
Des Moines, IA, LFM	0.181	0.229	0.228
Montpelier, VT, Background	<0.005	<0.030	<0.030
Montpelier, VT, LFM	0.167	0.192	0.193
Montpelier, VT, LFM	0.176	0.200	0.200
Montpelier, VT, LFM	0.168	0.193	0.191
Montpelier, VT, LFM	0.168	0.196	0.193
Seattle, WA, Background	<0.005	<0.030	<0.030
Seattle, WA, LFM	0.177	0.209	0.208
Seattle, WA, LFM	0.174	0.203	0.214
Seattle, WA, LFM	0.170	0.207	0.214
Seattle, WA, LFM	0.172	0.217	0.216

Table 6-2d. Cyanide Results from Columbus, OH, Drinking Water

Sample Description	Ref. Conc. (mg/L)	Unit #1 (mg/L)	Unit #2 (mg/L)
City Water Background - Outdoor Field Site	<0.005	<0.030	<0.030
City Water Background - Indoor Field Site	<0.005	<0.030	<0.030
City Water Background - Lab	<0.005	<0.030	<0.030
City Water Background - Lab	<0.005	<0.030	<0.030
City Water Background - Lab	<0.005	<0.030	<0.030
City Water Background - Lab	<0.005	<0.030	<0.030
City Water LFM - Outdoor Field Site	0.176	0.196	0.149
City Water LFM - Outdoor Field Site	0.167	0.177	0.154
City Water LFM - Outdoor Field Site	0.165	0.179	0.166
City Water LFM - Outdoor Field Site	0.178	0.194	0.156
City Water LFM - Indoor Field Site	0.176	0.164	0.167
City Water LFM - Indoor Field Site	0.167	0.170	0.169
City Water LFM - Indoor Field Site	0.165	0.175	0.177
City Water LFM - Indoor Field Site	0.178	0.174	0.184
City Water LFM - Lab	0.176	0.134	0.134
City Water LFM - Lab	0.167	0.140	0.133
City Water LFM - Lab	0.165	0.140	0.132
City Water LFM - Lab	0.178	0.143	0.125
Well Water Background - Outdoor Field Site	<0.005	0.0368	0.0340
Well Water Background - Outdoor Field Site	<0.005	0.0362	0.0339
Well Water Background - Outdoor Field Site	<0.005	0.0379	0.0350
Well Water Background - Outdoor Field Site	<0.005	0.0371	0.0346
Well Water Background - Indoor Field Site	<0.005	0.0392	0.0409
Well Water Background - Indoor Field Site	<0.005	0.0406	0.0354
Well Water Background - Indoor Field Site	<0.005	0.0416	0.0365
Well Water Background - Indoor Field Site	<0.005	0.0415	0.0381
Well Water Background - Lab	<0.005	<0.030	<0.030
Well Water Background - Lab	<0.005	<0.030	<0.030
Well Water Background - Lab	<0.005	<0.030	<0.030
Well Water Background - Lab	<0.005	<0.030	<0.030
Well Water LFM - Outdoor Field Site	0.100	0.101	0.0955
Well Water LFM - Outdoor Field Site	0.121	0.115	0.0970
Well Water LFM - Outdoor Field Site	0.114	0.126	0.0990
Well Water LFM - Outdoor Field Site	0.091	0.127	0.100

Table 6-2d. Cyanide Results from Columbus, OH, Drinking Water (continued)

Sample Description	Ref. Conc. (mg/L)	Unit #1 (mg/L)	Unit #2 (mg/L)
Well Water LFM - Indoor Field Site	0.100	0.149	0.144
Well Water LFM - Indoor Field Site	0.121	0.175	0.150
Well Water LFM - Indoor Field Site	0.114	0.142	0.126
Well Water LFM - Indoor Field Site	0.091	0.157	0.129
Well Water LFM - Lab	0.100	<0.030	<0.030
Well Water LFM - Lab	0.121	<0.030	<0.030
Well Water LFM - Lab	0.114	<0.030	<0.030
Well Water LFM - Lab	0.091	<0.030	<0.030

Table 6-3a. Percent Accuracy of Performance Test Sample Measurements

Sample Concentration (mg/L)	Unit #1 (bias)	Unit #2 (bias)
0.030	66%	54%
0.100	20%	17%
0.200	18%	13%
0.400	5%	5%
0.800	12%	7%
5.00	41%	56%
15.0	9%	37%
25.0	11%	8%

Table 6-3b. Percent Accuracy of Surface Water Measurements

Sample Description	Unit #1 (bias)	Unit #2 (bias)
Alum Creek LFM	67%	41%
Olentangy River LFM	123%	77%

Table 6-3c. Percent Accuracy of U.S. Drinking Water Measurements

Sample Description	Unit #1 (bias)	Unit #2 (bias)
Des Moines, IA, LFM	26%	29%
Flagstaff, AZ, LFM	24%	27%
Montpelier, VT, LFM	15%	14%
Seattle, WA, LFM	21%	23%
Tallahassee, FL, LFM	100% ^(a)	100% ^(a)

^(a) 100% bias because measurement was below MDL for Thermo Orion ISE.

Table 6-3d. Percent Accuracy of Columbus, OH, Drinking Water Measurements

Sample Description	Unit #1 (bias)	Unit #2 (bias)
City Water LFM - Outdoor Field Site	9%	9%
City Water LFM - Indoor Field Site	4%	4%
City Water LFM - Lab	19%	24%
Well Water LFM - Indoor Field Site	22% ^(a)	31% ^(a)
Well Water LFM - Outdoor Field Site	41% ^(a)	51% ^(a)
Well Water LFM - Lab	100% ^(a,b)	100% ^(a,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 because measurement was below MDL for Thermo Orion ISE.

Table 6-4a. Relative Standard Deviation of Performance Test Measurements

Sample Concentration (mg/L)	Reference Method (RSD)	Unit #1 (RSD)	Unit #2 (RSD)
0.030	8%	7%	7%
0.100	7%	8%	9%
0.200	2%	18%	8%
0.400	2%	5%	1%
0.800	1%	2%	3%
5.00	1%	5%	4%
15.0	2%	5%	1%
25.0	3%	9%	9%

Table 6-4b. Relative Standard Deviation of Surface Water Measurements

Sample Description	Reference Method (RSD)	Unit #1 (RSD)	Unit #2 (RSD)
Alum Creek LFM	8%	14%	6%
Olentangy River LFM	2%	16%	5%

Table 6-4c. Relative Standard Deviation of U.S. Drinking Water Measurements

Sample Description	Reference Method (RSD)	Unit #1 (RSD)	Unit #2 (RSD)
Des Moines, IA, LFM	3%	2%	2%
Flagstaff, AZ, LFM	12%	1%	0%
Montpelier, VT, LFM	2%	2%	2%
Seattle, WA, LFM	2%	3%	2%
Tallahassee, FL, LFM	2%	NA ^(a)	NA

^(a) NA = calculation of RSD was not appropriate because results were below MDL of Thermo Orion ISE.

Table 6-4d. Relative Standard Deviation of Columbus, OH, Drinking Water Measurements

Sample Description	Reference Method (RSD)	Unit #1 (RSD)	Unit #2 (RSD)
City Water LFM - Outdoor Field Site	4%	5%	5%
City Water LFM - Indoor Field Site	4%	3%	4%
City Water LFM - Lab	4%	3%	3%
Well Water LFM - Indoor Field Site	13%	9%	8%
Well Water LFM - Outdoor Field Site	13%	10%	2%
Well Water LFM - Lab	13%	NA ^(a)	NA

^(a) NA = calculation of RSD was not appropriate because result was below MDL of Thermo Orion ISE.

6.4 Linearity

The linearity of the Thermo Orion ISE was assessed by using a linear regression of the PT results against the reference method results (Table 6-2a). Figure 6-1 shows a scatter plot of the results from the Thermo Orion ISE, versus the reference results.

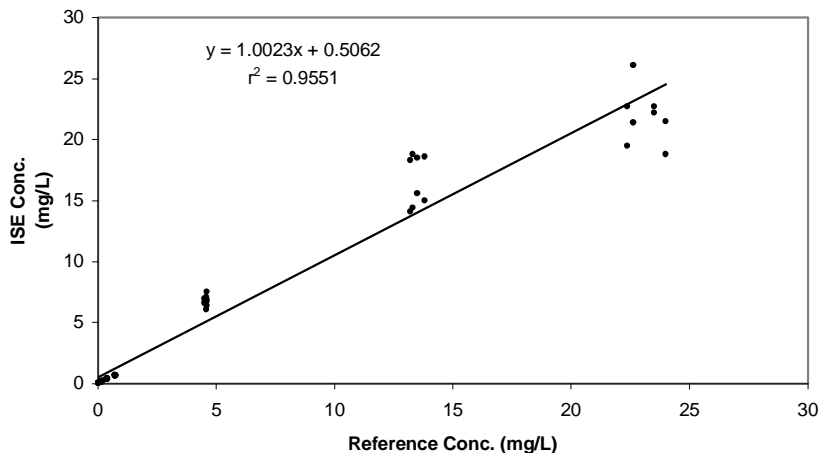


Figure 6-1. Linearity Results

A linear regression of the data in Figure 6-1 for the Thermo Orion ISE gives the following regression equation:

$$y \text{ (Thermo Orion ISE results in mg/L)} = 1.00 (\pm 0.055) x \text{ (reference result in mg/L)} + 0.506 (\pm 0.530) \text{ mg/L with } r^2 = 0.955 \text{ and } N = 65.$$

where the values in parentheses represent the 95% confidence interval of the slope and intercept. The slope is not significantly different from unity, the intercept is not significantly different from zero, and the r^2 value is above 0.950. From these regression parameters, the Thermo Orion ISE data indicate linearity; but, upon visual inspection, the three highest concentration PT samples (5.00, 15.0, and 25.0 mg/L) appear to be shifted with respect to the lower concentration PT samples (0.030 to 0.800 mg/L). Figure 6-2 shows separate regressions for both concentration ranges. The open circles represent data from the lower concentration samples and should be interpreted using the axes on the top and right of the plot. The closed circles represent data from the higher concentration samples and should be interpreted using the axes on the bottom and left.

A linear regression of the higher concentration data in Figure 6-2 gives the following regression equation:

$$y \text{ (Thermo Orion ISE results in mg/L)} = 0.804 (\pm 0.125) x \text{ (reference result in mg/L)} + 4.07 (\pm 1.96) \text{ mg/L with } r^2 = 0.889 \text{ and } N = 24.$$

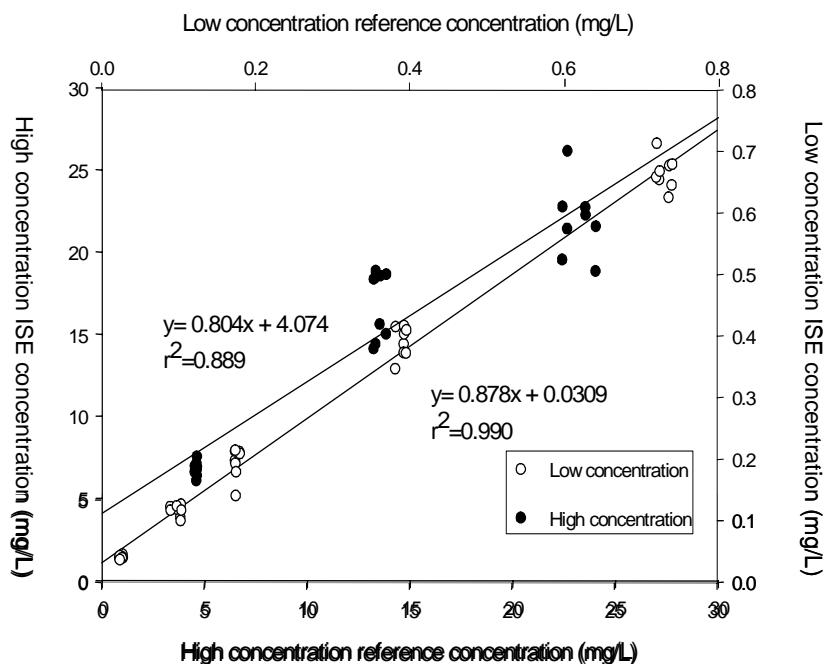


Figure 6-2. Linearity of High- and Low-Concentration Performance Test Samples

A linear regression of the lower concentration data in Figure 6-2 gives the following regression equation:

$$y \text{ (Thermo Orion ISE results in mg/L)} = 0.878 (\pm 0.029) x \text{ (reference result in mg/L)} + 0.031 (\pm 0.011) \text{ mg/L with } r^2 = 0.990 \text{ and } N = 40$$

where the values in parentheses represent the 95% confidence interval of the slope and intercept. The slopes of these regressions are not significantly different from one another, and both are significantly less than unity; but the intercepts of the two plots are significantly different from one another. The Thermo Orion ISE produced a linear response from 0.030 to 0.800 mg/L, with a high coefficient of correlation ($r^2 = 0.990$). The higher concentration samples display a higher degree of uncertainty, indicated by the relatively low coefficient of correlation ($r^2 = 0.889$). However, the scatter in the data does not cause the confidence intervals of the two intercepts to overlap. This underscores the need to encompass the likely concentration of the water samples with calibration standards slightly higher and lower in concentration to avoid systematic error due to calibration over a non-linear concentration range.

6.5 Method Detection Limit

The manufacturer's estimated detection limit for the Thermo Orion ISE is 0.020 mg/L cyanide. The MDL⁽⁴⁾ was determined by analyzing seven replicate samples at a concentration of 0.100 mg/L. Table 6-5 shows the results of the MDL assessment. The MDLs determined as described in Equation (6) of Section 5.4 were 0.040 and 0.023 mg/L for the two Thermo Orion ISEs.

Table 6-5. Results of Method Detection Limit Assessment

MDL Conc. (mg/L)	Unit #1 (mg/L)	Unit #2 (mg/L)
0.100	0.105	0.0985
0.100	0.122	0.115
0.100	0.118	0.122
0.100	0.126	0.115
0.100	0.089	0.113
0.100	0.102	0.113
0.100	0.107	0.119
Std Dev	0.013	0.007
t (n=7)	3.140	3.140
MDL	0.040	0.023

6.6 Inter-Unit Reproducibility

The inter-unit reproducibility of the two Thermo Orion ISEs tested during this verification test was assessed by using a linear regression of the results produced by one Thermo Orion ISE plotted against the results produced by the other Thermo Orion ISE. The results from all of the samples that had detectable amounts of cyanide (including the PT, surface, and drinking water samples) were included in this regression. Figure 6-3 shows a scatter plot of the results from both analyzers.

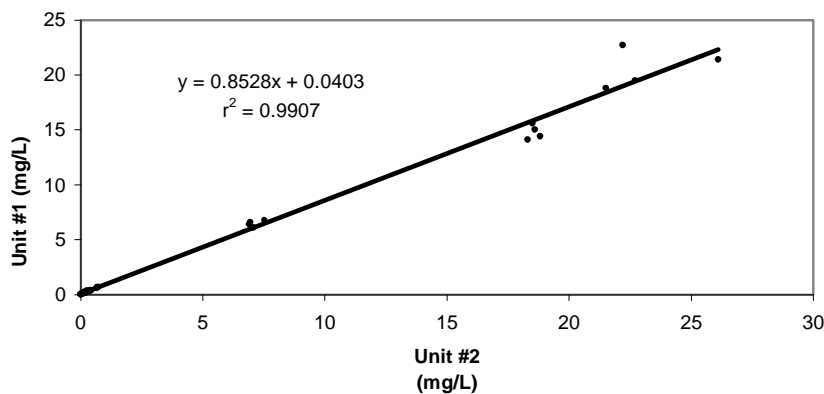


Figure 6-3. Inter-Unit Reproducibility Results

A linear regression of the data in Figure 6-2 for the inter-unit reproducibility assessment gives the following regression equation:

$$y \text{ (Unit \#1 result in mg/L)} = 0.853 (\pm 0.019) x \text{ (Unit \#2 result in mg/L)} + 0.040 (\pm 0.127) \text{ mg/L with } r^2 = 0.991 \text{ and } N = 80.$$

where the values in parentheses represent the 95% confidence interval of the slope and intercept. The slope is significantly different from unity, while the intercept is not significantly different from zero. These data indicate that the two Thermo Orion ISEs functioned somewhat differently from one another. This could be because each electrode was polished and calibrated individually before each analysis set. While the operator attempted to polish the two electrodes identically, the process is inherently difficult to reproduce. Other variables that may have caused different readings between the two Thermo Orion ISEs were the speed of the magnetic stirrer and the position of the electrode. All attempts were made to keep these variables constant, but slight variations are probable.

6.7 Lethal or Near-Lethal Dose Response

Samples at 50-, 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 Thermo Orion ISE. Tables 6-6a-c present the measured cyanide results from analysis of the lethal/near-lethal concentration samples for both the reference analyses and the Thermo Orion ISE. Results are shown in Table 6-6a for both analyzers that were tested. Table 6-6b presents the percent accuracy of the same results. The bias values were determined according to Equation (3), Section 5.1. The bias values shown in Table 6-6b ranged from 105 to 375%. While the results indicated that a high concentration of cyanide was present, the Thermo Orion ISE results at those concentrations were biased high. Table 6-6c shows the precision (in terms of %RSD) for the Thermo Orion ISE analysis of lethal/near-lethal concentration samples, which ranged from 5 to 38%.

Table 6-6a. Lethal/Near-Lethal Concentration Sample Results

Sample Concentration (mg/L)	Ref. Conc. (mg/L)	Unit #1 (mg/L)	Unit #2 (mg/L)
50.0	53.3	150	48.2
50.0	54.8	147	112
50.0	51.3	164	130
50.0	53.5	153	135
100	107	308	304
100	108	425	319
100	108	382	274
100	110	481	362
250	270	1,100	714
250	266	1,170	801
250	273	1,390	915
250	254	1,390	1,060

Table 6-6b. Percent Accuracy of Lethal/Near-Lethal Concentration Results

Sample Concentration (mg/L)	Unit #1 (bias)	Unit #2 (bias)
50.0	189%	105%
100	269%	191%
250	375%	228%

Table 6-6c. Relative Standard Deviation of Lethal/Near-Lethal Concentration Results

Sample Concentration (mg/L)	Reference Method (RSD)	Unit #1 (RSD)	Unit #2 (RSD)
50.0	3%	5%	38%
100	1%	18%	12%
250	3%	12%	17%

6.8 Field Portability

The Thermo Orion ISE was operated in laboratory and field settings during this verification test. It was packaged in a hard plastic carrying case equipped with a portable electrode stand that clipped onto the side of the carrying case. Thermo Orion also provided a battery-powered magnetic stirrer that was crucial for operating the technology in a field setting. This item is not normally provided when purchasing a Thermo Orion ISE and would need to be purchased separately. Tables 6-2d, 6-3d, and 6-4d show the results of the laboratory and field measurements. From an operational standpoint, the Thermo Orion ISE was easily transported to the field setting, and the samples were analyzed in the same fashion as they were in the laboratory. While no functional aspects of the Thermo Orion ISE were compromised by performing the analyses in the field setting, close attention had to be paid to bringing the calibration solutions to a similar temperature as the samples. This was done by letting the sample and calibration solutions equilibrate overnight at the indoor field location and for approximately one hour at the outdoor field location. The electrode equilibration time was similar for calibration solutions and samples analyzed indoors or outdoors.

Table 6-3d 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, well and city water samples were both dechlorinated as described in Section 3.5.2. In addition, because the well water sample had a pungent odor, lead carbonate was added to a small aliquot 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. When analyzing the Columbus, OH, city water LFM samples, the Thermo Orion ISE produced biases of less than 10% for both the measurements made indoors and outdoors at the field location. The bias in the Columbus, OH, city water indoor LFM samples (4%) were similar to the bias in the Columbus, OH, city water

LFM samples analyzed at the outdoor field location (9%). The biases were slightly larger (19 and 24%) when the analyses were performed at the laboratory. These data indicate that the Thermo Orion ISE was not significantly affected by the measurement location.

The Thermo Orion ISE produced biases of 22 to 100% when analyzing the Columbus, OH, well water. As discussed in Section 4.1, the well water biases were calculated using the fortified concentration of 0.200 mg/L cyanide rather than the well water reference LFM result. The well water sample analyzed indoors produced biases of 22 and 31%, and those measured outdoors produced biases of 41 to 51%. The apparent matrix interference in the well water continued to mask the cyanide in the LFM sample after it was spiked and analyzed at the indoor field setting because, by the time the well water LFM samples were analyzed by the Thermo Orion ISE at the laboratory five to six days after initial fortification, there was no detectable cyanide (100% bias from initial fortification). The concentration of cyanide in that same LFM aliquot was determined to be below detectable levels by 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 Thermo Orion ISE in the field setting cannot be meaningfully compared with the result produced from the identical samples analyzed with the Thermo Orion ISE in the laboratory.

6.9 Ease of Use

The instruction manual for the Thermo Orion ISE was clear and concise. The Thermo Orion ISE required calibration and electrode polishing before every sample set to ensure the most accurate measurements. It was convenient that calibration could be done with any concentration of cyanide by entering the concentration into the ion meter throughout the calibration process. During calibration and sample measurement, the Thermo Orion ISE displayed “ready” and beeped when the reading was stable. The pH was easily adjusted before analysis by the Thermo Orion ISE by adding 0.500 mL of alkaline reagent to 50.0 mL of sample. No tedious process of pH adjustment using a pH meter or paper and drop-by-drop addition of acid or base was necessary. One drawback of this type of technology was that the battery-powered stirrer would not operate at the slow speeds recommended while making ISE measurements. There was some agitation of the calibration and sample solutions when the stirrer was operating at its slowest setting. The carrying case featured a clip-on electrode stand for use during field operations.

6.10 Sample Throughput

Sample preparation, including accurately measuring volume and the addition of the Thermo Orion alkaline reagents, took one to two minutes per sample. However, the Thermo Orion ISE was calibrated with three calibration solutions before performing any sample analyses. Calibration took between 15 and 30 minutes depending on the length of time it took for solution equilibration with the electrode surface. Once the Thermo Orion ISE was calibrated, each sample took approximately five minutes to attain a stable reading. A typical sample set of 12 analyses plus calibration took approximately an hour and a half.

Chapter 7 Performance Summary

A three-point calibration using solutions of 0.030, 0.100, and 0.300 mg/L cyanide typically was used. The manufacturer suggested that the slope of the calibration linear regression be within the range of -54 to -60 mV per tenfold increase in cyanide concentration. Seventeen of 22 slopes attained usually were not within this range. However, analyzing samples using a calibration that produced a regression slope outside the acceptable range did not seem to negatively affect the accuracy of the results. Some of the most accurate results produced by the Thermo Orion ISE were produced on a day when the calibration regression slope was farthest from the acceptable range.

The biases ranged from 5 to 66% for the PT samples; 41 to 123% for the surface water samples; 14 to 100% for the drinking water samples from around the country; and 4 to 100% for the Columbus, OH, drinking water samples.

RSD ranged from 1 to 18% for the PT samples; 5 to 16% for the surface water samples; 0 to 2% for the drinking water samples from around the country; and 2 to 10% for the Columbus, OH, drinking water samples.

A linear regression of the linearity data for the Thermo Orion ISE gives the following regression equation:

$$y \text{ (Thermo Orion ISE results in mg/L)} = 1.00 (\pm 0.055) x \text{ (reference result in mg/L)} \\ + 0.506 (\pm 0.530) \text{ mg/L with } r^2=0.955 \text{ and } N=65.$$

where the values in parentheses represent the 95% confidence interval of the slope and intercept. The slope is not significantly different from unity, the intercept is not significantly different from zero, and the r^2 value is above 0.950. From these regression parameters, the Thermo Orion ISE data indicate linearity; but, upon visual inspection of the plot, the three highest concentration PT samples (5.00, 15.0, and 25.0 mg/L) appear to be shifted with respect to the lower concentration PT samples (0.030 to 0.800 mg/L). The data are more accurately described with two linear regressions, one for the high-concentration range and one for the lower concentration range. The slopes of these regressions are not significantly different from one another, and both are significantly less than unity; but the intercepts of the two plots are significantly different from one another. This underscores the need to encompass the likely concentration of the water samples with calibration standards slightly higher and lower in concentration to avoid systematic error due to calibration over a non-linear concentration range.

The MDLs for the Thermo Orion ISE were determined to be 0.04 and 0.02 mg/L.

A linear regression of the data for the inter-unit reproducibility assessment gives the following regression equation:

$$y \text{ (Unit \#1 result in mg/L)} = 0.853 (\pm 0.019) x \text{ (Unit \#2 result in mg/L)} + 0.040 (\pm 0.127) \text{ mg/L}$$

with $r^2=0.991$ and $N=80$.

where the values in parentheses represent the 95% confidence interval of the slope and intercept. The slope is significantly different from unity, while the intercept is not significantly different from zero. These data indicate that the two Thermo Orion ISEs functioned somewhat differently from one another, but that the difference is probably due to the operator's ability to reproduce the polishing technique.

When analyzing lethal/near-lethal concentrations of cyanide, the bias values ranged from 105 to 375%. While the results indicated that a high concentration of cyanide was present, the Thermo Orion ISE results at those concentrations were biased high.

From an operational standpoint, the Thermo Orion ISE was easily transported to the field setting, and the samples were analyzed in the same fashion as they were in the laboratory. While no functional aspects of the Thermo Orion ISE were compromised by performing the analyses in the field setting, close attention had to be paid to bringing the calibration solutions to a temperature similar to the samples.

The instruction manual for the Thermo Orion ISE was clear and concise. The Thermo Orion ISE required calibration and electrode polishing before each day. It was convenient that calibration could be done with any concentration of cyanide, but solutions needed to be prepared and transported to the field. The pH was easily adjusted before analysis by the Thermo Orion ISE by adding 0.500 mL of alkaline reagent to 50 mL of sample. One drawback of the Thermo Orion ISE was that the battery-powered stirrer would not operate at the slow speeds recommended while making ISE measurements. This probably increased the variability in the measurements made by the Thermo Orion ISE.

Sample preparation, including accurately measuring volume and adding the alkaline reagents, took one to two minutes per sample. Calibration took between 15 and 30 minutes. Each sample took approximately five minutes to attain a stable reading. A typical sample set of 12 analyses plus calibration took approximately an hour and a half.

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.