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Environmental Technology Verification Report

WTW MEASUREMENT SYSTEMS
CYANIDE ELECTRODE CN501
with Reference Electrode R503D
and Ion Pocket Meter 340i

Prepared by
Battelle



Under a cooperative agreement with



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Environmental Technology Verification Report

ETV Advanced Monitoring Systems Center

WTW MEASUREMENT SYSTEMS
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with Reference Electrode R503D
and Ion Pocket Meter 340i

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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 WTW Measurement Systems Cyanide Electrode CN501 with the Reference Electrode R503D and Ion Pocket Meter 340i (referred to as the WTW ion selective electrode [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 WTW ISE. Following is a description of the WTW ISE, based on information provided by the vendor. The information provided below was not verified in this test.

The WTW 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 a digital readout when the WTW ISE is inserted into an unknown solution.



Figure 2-1. WTW Measurement Systems ISE

WTW ISE accessories include a hard carrying case, an electrode stand, a one-meter cable, and a reference electrode filling solution. List price for the provided items was \$985 for the Ion Pocket Meter 340i and carrying case, \$596 for the Cyanide Electrode CN501, and \$121 for the electrode stand. The WTW ISE operates on four AA batteries and has dimensions of 6.9 x 3.2 x 1.5 inches.

To analyze water samples for cyanide with the WTW ISE it has to first be calibrated using calibration solutions of known concentrations of cyanide in 0.100 M sodium hydroxide (NaOH). After calibration, a 50.0-mL sample is stirred with a magnetic stirrer; the WTW ISE is lowered into the sample; and, when a stable reading 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 0.200 mg/L as the maximum concentration of cyanide that can be present in drinking water. In drinking and surface water under ambient conditions, cyanide evolves from aqueous hydrogen cyanide, sodium cyanide, potassium cyanide, and other metal or ionic salts where cyanide is released when dissolved in water. Heavier cyanide complexes (e.g., iron) are bound tightly, requiring an acid distillation to liberate the toxic free cyanide ion, a step not verified as part of this test since field portability would have been eliminated. Because disassociation of the free cyanide ion is unlikely under ambient conditions, the heavier 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 WTW 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 WTW 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 WTW ISE and the reference method provided the basis for the quantitative performance evaluations.

The WTW 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 WTW 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 WTW 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 WTW ISE with a variety of test samples, including sets of drinking and surface water samples representative of those likely to be analyzed by the WTW ISE. The results from the WTW 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 WTW 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 WTW 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 WTW ISE also was quantitatively evaluated with samples prepared in an American Society for 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 2.00 mg/L. The LFM spiking concentration anticipated in the test/QA plan⁽¹⁾ was 0.200 mg/L. However, because manufacturer's estimated limit of detection for the WTW ISE was reported as 0.200 mg/L, the LFM samples for this technology were made at 2.00 mg/L. This was done so the WTW ISE was not tested in drinking water matrices at concentrations near the detection limit. Before this adjustment in the test/QA plan was made, the surface water and two sets of drinking water (Seattle, WA, and Montpelier, VT) LFM samples had already been analyzed after being fortified at 0.200 mg/L. The drinking water samples were analyzed again after being fortified at 2.00 mg/L, but the surface water samples were not. 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 WTW ISE. The QCSs for the WTW 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 protocols. Section 4.1 describes these samples in more detail.

QCSs were analyzed (without defined performance expectations) by the WTW ISE to demonstrate their proper functioning to the operator. A QCS was analyzed before and after each sample batch (typically consisting of 12 water 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 or 2.00 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 | 0.800 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 | 2 |
| | | 0.200 and 2.00 mg/L LFM | 4 |
| | Southwestern U.S. | Background | 1 |
| | | 2.00 mg/L LFM | 4 |
| | Midwestern U.S. | Background | 1 |
| | | 2.00 mg/L LFM | 4 |
| | Southeastern U.S. | Background | 1 |
| | | 2.00 mg/L LFM | 4 |
| Northeastern U.S. | Background | 2 | |
| | 0.200 and 2.00 mg/L LFM | 4 | |
| Columbus, OH, Area Drinking Water | Residence with city water | Background | 6 |
| | | 2.00 mg/L LFM | 12 |
| | Residence with well water | Background | 6 |
| | | 2.00 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 WTW ISE's accuracy, linearity, and detection limit. Seven non-consecutive replicate analyses of a 0.800-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 WTW ISE when cyanide is present in drinking water at lethal and near-lethal concentrations (>50 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 WTW 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 or 2.00 mg/L of cyanide to

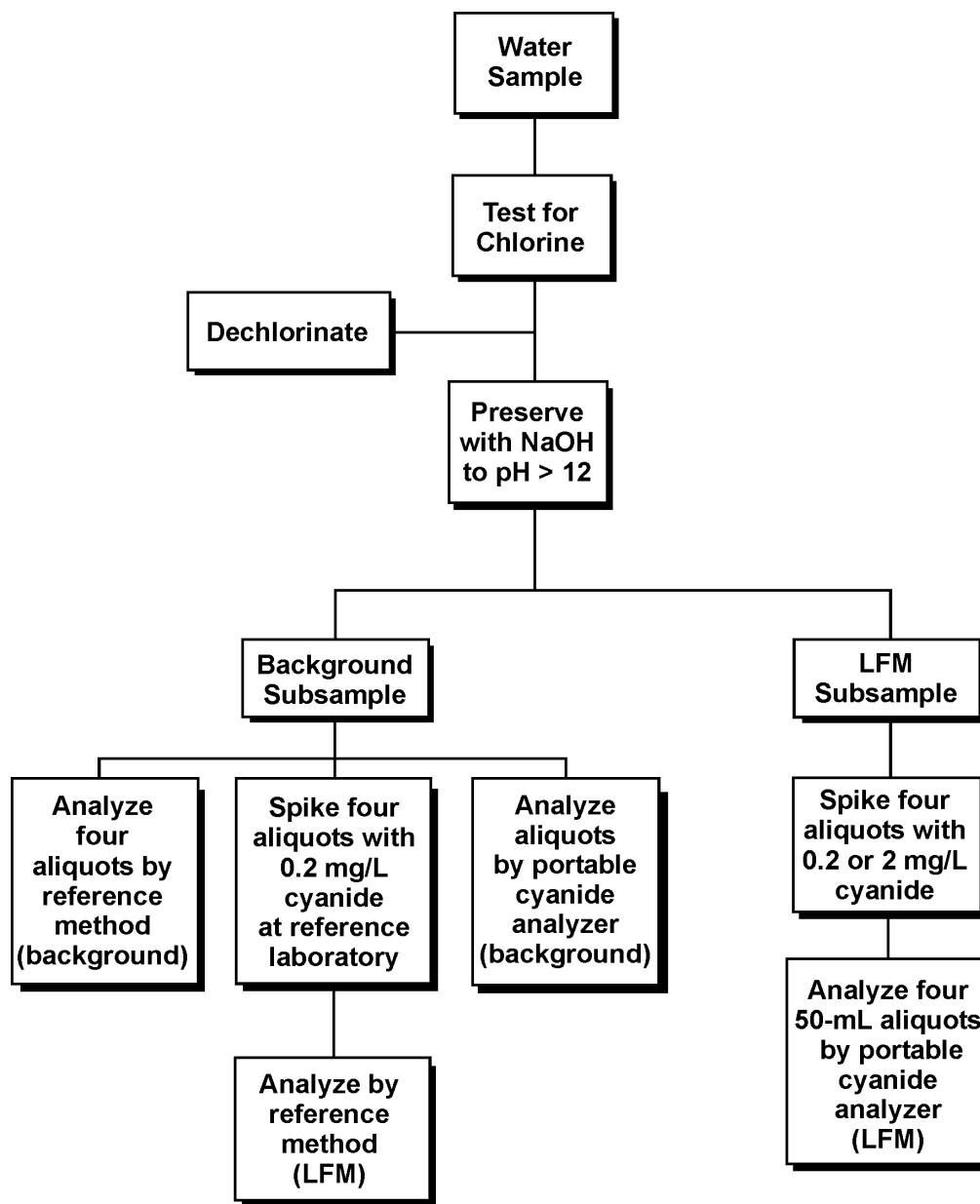


Figure 3-1. Sampling through Analysis Process

provide LFM aliquots, and the other subsample remained unspiked (background). One 50-mL aliquot was taken from each subsample and analyzed for cyanide by the WTW ISE four separate times (background samples). 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 or 2.00 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 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 sample 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 WTW 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 WTW ISE at the indoor and outdoor field locations and the laboratory location.

3.5 Test Procedure

3.5.1 Calibration and Maintenance

The WTW ISE required a daily calibration using three calibration solutions. Solutions of 0.200, 2.00, 20.0, and 200 mg/L were used depending on the expected concentration of the samples to be analyzed. The 2.00- and 20.0-mg/L calibration solutions were always used, but the third calibration solution (0.200 or 200 mg/L) was chosen based on whether the samples were expected to be on the high end of the calibration range or on the low end. For example, the 0.200-, 2.00-, and 20.0-mg/L calibration solutions were used most often for calibration because most of the QC, PT, surface, and drinking water samples were below 20.0 mg/L cyanide. However, when the water samples with lethal/near lethal concentrations (50.0 to 250 mg/L) were

analyzed, the 200-mg/L calibration solution was used instead of the 0.200-mg/L calibration solution. The operator also polished the WTW 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 deionized 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 chlorine was not present. However, when the LFM samples were analyzed with the colorimetric technologies being evaluated, 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, 0.500 mL of alkaline reagent provided by WTW ISE was added to 50.0 mL of each sample to be analyzed by the WTW 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 WTW ISEs were tested independently. Each WTW 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 WTW 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 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:

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

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 analytical problem was suspected. As shown in Table 4-2, only the percent recovery for the LFM

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% |
| Tallahassee, FL, LFM | 0.200 | 0.161 | 80% | 2% |
| Seattle, WA, LFM | 0.200 | 0.173 | 87% | 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.

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 reference LFM result after the eight- to 10-day delay was within 15% of the result obtained from the LFM sample spiked just minutes before reference analysis. However, the well water reference LFM result fortified eight to 10 days prior to analysis was less than the MDL for the reference method. The combination of the poor recovery (53%) of cyanide obtained immediately upon spiking and the complete loss of the reference method's ability to detect the cyanide fortified eight to 10 days before strongly suggests the presence of a time-dependent matrix interference in the well water. In response to this finding, the biases for the well water samples were calculated using the fortified concentration of cyanide (0.200 mg/L) rather than the reference LFM result.

4.2 Audits

4.2.1 Performance Evaluation Audit

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

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

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 of 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 WTW 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 WTW ISE and those from the reference method, and \bar{C}_R is the average of the reference measurements. Accuracy was assessed independently for each WTW 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 WTW 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 analyzer 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 analyte concentration measured by the reference method as independent variable and the reading from the WTW 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 WTW ISE was assessed from the seven replicate analyses of a fortified sample with a cyanide concentration of approximately four times the vendor's estimated detection limit (see Table 3-1). The test/QA plan⁽¹⁾ called for the use of five times that concentration, but the *Code of Federal Regulations* procedure for determining MDLs recommends using a solution in the range of three to five times that concentration. Since the 0.800-mg/L PT solution was already prepared, and it was within the recommended range, it was used for the MDL determination. The MDL 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 WTW ISE was reported separately.

5.5 Inter-Unit Reproducibility

The results obtained from two identical WTW ISEs were compiled independently for each WTW ISE and compared to assess inter-unit reproducibility. The results were interpreted using a linear regression of one WTW ISE's results plotted against the results produced by the other WTW ISE. If the WTW 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 WTW 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 WTW 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 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 WTW 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 WTW 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 WTW 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. To simulate the situation that a field technician would be in when using this technology, one calibration was performed; and then the samples were analyzed, regardless of whether the slope value was within the recommended range. As shown in Table 6-1, the slopes were usually in or within 10% of this range.

Table 6-1. Calibration Results

| Date | Calibration Solutions (mg/L) | Unit #1 ^(a) (slope) | Unit #2 ^(a) (slope) |
|--------------------------|------------------------------|-----------------------------------|-----------------------------------|
| 1/14/2003 | 0.200, 2.00, 20.0 | -58.2 | -56.6 |
| 1/16/2003 | 0.200, 2.00, 20.0 | -51.7 | -56.1 |
| 1/17/2003 | 0.200, 2.00, 20.0 | -55.2 | -54.4 |
| 1/21/2003 | 0.200, 2.00, 20.0 | -57.6 | -56.0 |
| 1/27/2003 | 0.200, 2.00, 20.0 | -57.9 | -50.1 |
| 1/28/2003 ^(b) | 0.200, 2.00, 20.0 | -58.3 | -58.4 |
| 1/28/2003 ^(b) | 0.200, 2.00, 20.0 | -53.4 | -50.0 |
| 1/29/2003 ^(b) | 0.200, 2.00, 20.0 | -55.7 | -52.8 |
| 1/29/2003 ^(b) | 0.200, 2.00, 20.0 | -53.1 | -50.8 |
| 2/3/2003 | 0.200, 2.00, 20.0 | -52.6 | -55.1 |
| 2/4/2003 | 2.00, 20.0, 200 | -51.9 | -50.9 |

^(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.

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 WTW ISE. Results are shown for both WTW ISEs that were tested (labeled as Unit #1 and #2).

Tables 6-3a-d present the percent accuracy of the WTW 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. However, in instances when the LFM samples resulted in a non-detect reading due to a matrix effect, 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. For example, the biases ranged from 2 to 17% for the PT samples, 31 to 128% for the surface water samples, 2 to 39% for the drinking water samples from around the country, and 3 to 44% for the Columbus, OH, water samples. 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 2 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 WTW 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 for WTW 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 23% for the PT samples; 5 to 10% for the surface water samples; 2 to 13% for the drinking water samples from around the country; and 2 to 10% for all of the Columbus, OH, drinking water samples.

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

| Concentration (mg/L) | Ref. Conc. (mg/L) | Unit #1 (mg/L) | Unit #2 (mg/L) |
|----------------------|-------------------|----------------------|----------------------|
| 0.030 | 0.027 | <0.200 | <0.200 |
| 0.030 | 0.023 | <0.200 | <0.200 |
| 0.030 | 0.026 | <0.200 | <0.200 |
| 0.030 | 0.023 | <0.200 | <0.200 |
| 0.100 | 0.102 | <0.200 | <0.200 |
| 0.100 | 0.089 | <0.200 | <0.200 |
| 0.100 | 0.097 | <0.200 | <0.200 |
| 0.100 | 0.103 | <0.200 | <0.200 |
| 0.200 | 0.173 | 0.200 | 0.185 ^(a) |
| 0.200 | 0.179 | 0.192 ^(a) | 0.159 ^(a) |
| 0.200 | 0.173 | 0.190 ^(a) | 0.147 ^(a) |
| 0.200 | 0.174 | 0.150 ^(a) | 0.110 ^(a) |
| 0.400 | 0.381 | 0.347 | 0.383 |
| 0.400 | 0.392 | 0.358 | 0.370 |
| 0.400 | 0.392 | 0.334 | 0.335 |
| 0.400 | 0.395 | 0.320 | 0.352 |
| 0.800 | 0.736 | 0.773 | 0.723 |
| 0.800 | 0.724 | 0.713 | 0.637 |
| 0.800 | 0.720 | 0.696 | 0.607 |
| 0.800 | 0.740 | 0.703 | 0.613 |
| 5.00 | 4.60 | 4.65 | 4.63 |
| 5.00 | 4.50 | 5.04 | 4.64 |
| 5.00 | 4.60 | 5.02 | 4.61 |
| 5.00 | 4.58 | 4.90 | 4.83 |
| 15.0 | 13.3 | 15.7 | 13.4 |
| 15.0 | 13.8 | 15.4 | 12.9 |
| 15.0 | 13.5 | 14.6 | 13.1 |
| 15.0 | 13.2 | 14.6 | 12.6 |
| 25.0 | 22.6 | 23.4 | 21.1 |
| 25.0 | 23.5 | 23.8 | 21.3 |
| 25.0 | 22.4 | 23.8 | 21.3 |
| 25.0 | 24.0 | 23.9 | 22.3 |

^(a) Result below the WTW ISE detection limit of 0.200 mg/L, but still reported because of its close proximity to that limit.

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 | <0.200 | <0.200 |
| Alum Creek Background | <0.005 | <0.200 | <0.200 |
| Alum Creek Background | <0.005 | <0.200 | <0.200 |
| Alum Creek Background | <0.005 | <0.200 | <0.200 |
| Alum Creek LFM ^a | 0.166 | 0.249 | 0.357 |
| Alum Creek LFM ^a | 0.183 | 0.222 | 0.373 |
| Alum Creek LFM ^a | 0.173 | 0.204 | 0.340 |
| Alum Creek LFM ^a | 0.151 | 0.205 | 0.335 |
| Olentangy River Background | <0.005 | <0.200 | <0.200 |
| Olentangy River Background | <0.005 | <0.200 | <0.200 |
| Olentangy River Background | <0.005 | <0.200 | <0.200 |
| Olentangy River Background | <0.005 | <0.200 | <0.200 |
| Olentangy River LFM ^(a) | 0.174 | 0.295 | 0.430 |
| Olentangy River LFM ^(a) | 0.178 | 0.252 | 0.389 |
| Olentangy River LFM ^(a) | 0.171 | 0.245 | 0.394 |
| Olentangy River LFM ^(a) | 0.176 | 0.242 | 0.379 |

^(a) These drinking water LFM samples were analyzed before the fortification amount of cyanide was changed from 0.200 mg/L to 2 mg/L.

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

| Sample Description | Ref. Conc. (mg/L) | Unit #1 (mg/L) | Unit #2 (mg/L) |
|-----------------------------------------------|----------------------|----------------------|----------------------|
| Des Moines, IA, Background | <0.005 | <0.200 | <0.200 |
| Des Moines, IA, LFM | 1.73 | 2.11 | 1.26 |
| Des Moines, IA, LFM | 1.73 | 1.97 | 1.28 |
| Des Moines, IA, LFM | 1.83 | 1.64 | 1.08 |
| Des Moines, IA, LFM | 1.81 | 1.61 | 1.21 |
| Flagstaff, AZ, Background | <0.005 | <0.200 | <0.200 |
| Flagstaff, AZ, LFM | 1.57 | 1.87 | 1.22 |
| Flagstaff, AZ, LFM | 1.32 | 1.69 | 1.27 |
| Flagstaff, AZ, LFM | SL ^(b) | 1.72 | 1.21 |
| Flagstaff, AZ, LFM | 1.69 | 1.68 | 1.32 |
| Montpelier, VT, 0.200 mg/L LFM ^(a) | 0.167 | 0.192 ^(c) | 0.193 ^(c) |
| Montpelier, VT, 0.200 mg/L LFM ^(a) | 0.176 | 0.200 | 0.200 |
| Montpelier, VT, 0.200 mg/L LFM ^(a) | 0.168 | 0.193 ^(c) | 0.191 ^(c) |
| Montpelier, VT, 0.200 mg/L LFM ^(a) | 0.168 | 0.196 ^(c) | 0.193 ^(c) |
| Montpelier, VT, Background | <0.005 | <0.200 | <0.200 |
| Montpelier, VT, Background | <0.005 | <0.200 | <0.200 |
| Montpelier, VT, LFM | 1.67 | 2.25 | 1.45 |
| Montpelier, VT, LFM | 1.76 | 2.13 | 1.43 |
| Montpelier, VT, LFM | 1.68 | 2.10 | 1.29 |
| Montpelier, VT, LFM | 1.68 | 2.05 | 1.21 |
| Seattle, WA, 0.200 mg/L LFM ^(a) | 0.177 | 0.209 | 0.208 |
| Seattle, WA, 0.200 mg/L LFM ^(a) | 0.174 | 0.203 | 0.214 |
| Seattle, WA, 0.200 mg/L LFM ^(a) | 0.170 | 0.207 | 0.214 |
| Seattle, WA, 0.2 mg/L LFM ^(a) | 0.172 | 0.217 | 0.216 |
| Seattle, WA, Background | <0.005 | <0.200 | <0.200 |
| Seattle, WA, Background | <0.005 | <0.200 | <0.200 |
| Seattle, WA, LFM | 1.77 | 2.13 | 1.42 |
| Seattle, WA, LFM | 1.74 | 2.04 | 1.23 |
| Seattle, WA, LFM | 1.70 | 2.06 | 1.26 |
| Seattle, WA, LFM | 1.72 | 1.88 | 1.17 |
| Tallahassee, FL, Background | <0.005 | <0.200 | <0.200 |
| Tallahassee, FL, LFM | 1.57 | 1.82 | 1.10 |
| Tallahassee, FL, LFM | 1.61 | 1.65 | 1.06 |
| Tallahassee, FL, LFM | 1.65 | 1.59 | 1.07 |
| Tallahassee, FL, LFM | 1.59 | 1.57 | 1.10 |

^(a) These drinking water LFM samples were analyzed before the fortification amount of cyanide was changed from 0.200 mg/L to 2.00 mg/L.

^(b) SL= sample lost due to a laboratory error.

^(c) Result below the WTW ISE detection limit of 0.200 mg/L, but still reported because of its close proximity to that limit.

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

| Sample Description | Ref. Conc.^(a) (mg/L) | Unit #1 (mg/L) | Unit #2 (mg/L) |
|--------------------------------------------|--------------------------------------------|---------------------------|---------------------------|
| City Water Background - Outdoor Field Site | <0.005 | <0.200 | <0.200 |
| City Water Background - Indoor Field Site | <0.005 | <0.200 | <0.200 |
| City Water Background - Lab | <0.005 | <0.200 | <0.200 |
| City Water Background - Lab | <0.005 | <0.200 | <0.200 |
| City Water Background - Lab | <0.005 | <0.200 | <0.200 |
| City Water Background - Lab | <0.005 | <0.200 | <0.200 |
| City Water LFM - Outdoor Field Site | 1.76 | 2.43 | 2.38 |
| City Water LFM - Outdoor Field Site | 1.67 | 2.71 | 2.38 |
| City Water LFM - Outdoor Field Site | 1.65 | 2.51 | 2.13 |
| City Water LFM - Outdoor Field Site | 1.78 | 2.24 | 2.26 |
| City Water LFM - Indoor Field Site | 1.76 | 2.26 | 2.15 |
| City Water LFM - Indoor Field Site | 1.67 | 2.33 | 2.07 |
| City Water LFM - Indoor Field Site | 1.65 | 2.36 | 2.22 |
| City Water LFM - Indoor Field Site | 1.78 | 2.23 | 2.49 |
| City Water LFM - Lab | 1.76 | 1.92 | 2.25 |
| City Water LFM - Lab | 1.67 | 1.91 | 2.63 |
| City Water LFM - Lab | 1.65 | 2.03 | 2.22 |
| City Water LFM - Lab | 1.78 | 1.70 | 2.25 |
| Well Water Background - Outdoor Field Site | <0.005 | <0.200 | <0.200 |
| Well Water Background - Indoor Field Site | <0.005 | <0.200 | <0.200 |
| Well Water Background - Lab | <0.005 | <0.200 | <0.200 |
| Well Water Background - Lab | <0.005 | <0.200 | <0.200 |
| Well Water Background - Lab | <0.005 | <0.200 | <0.200 |
| Well Water Background - Lab | <0.005 | <0.200 | <0.200 |
| Well Water LFM - Outdoor Field Site | 1.00 | 1.98 | 1.58 |
| Well Water LFM - Outdoor Field Site | 1.21 | 2.06 | 1.66 |
| Well Water LFM - Outdoor Field Site | 1.14 | 2.07 | 1.64 |
| Well Water LFM - Outdoor Field Site | 0.91 | 2.10 | 1.63 |
| Well Water LFM - Indoor Field Site | 1.00 | 2.69 | 2.65 |
| Well Water LFM - Indoor Field Site | 1.21 | 2.92 | 2.89 |
| Well Water LFM - Indoor Field Site | 1.14 | 3.09 | 2.57 |
| Well Water LFM - Indoor Field Site | 0.91 | 2.55 | 2.27 |
| Well Water LFM - Lab | 1.00 | 2.03 | 2.40 |
| Well Water LFM - Lab | 1.21 | 1.75 | 2.38 |
| Well Water LFM - Lab | 1.14 | 1.75 | 2.29 |
| Well Water LFM - Lab | 0.91 | 1.65 | 2.08 |

^(a) The same reference LFM samples are used for the outdoor, indoor, and laboratory analysis locations

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

| Sample Concentration (mg/L) | Unit #1 (bias) | Unit #2 (bias) |
|-----------------------------|-------------------|----------------|
| 0.030 | NA ^(a) | NA |
| 0.100 | NA | NA |
| 0.200 | 12% | 17% |
| 0.400 | 13% | 8% |
| 0.800 | 4% | 12% |
| 5.00 | 7% | 2% |
| 15.0 | 12% | 4% |
| 25.0 | 3% | 7% |

^(a) NA = calculation of bias not appropriate when result was outside the detectable range of the WTW ISE.

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

| Sample Description | Unit #1 (bias) | Unit #2 (bias) |
|---------------------|----------------|----------------|
| Alum Creek LFM | 31% | 109% |
| Olentangy River LFM | 48% | 128% |

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

| Sample Description | Unit #1 (bias) | Unit #2 (bias) |
|------------------------------------------------|----------------|----------------|
| Montpelier, VT, 0.2.00 mg/L LFM ^(a) | 15% | 14% |
| Seattle, WA, 0.200 mg/L LFM ^(a) | 2% | 2% |
| Montpelier, VT, LFM | 26% | 21% |
| Seattle, WA, FM | 17% | 27% |
| Tallahassee, FL, LFM | 6% | 33% |
| Flagstaff, AZ, LFM | 39% | 32% |
| Des Moines, IA, LFM | 14% | 32% |

^(a) These drinking water LFM samples were analyzed before the drinking water fortification amount of cyanide was changed from 0.200 mg/L to 2.00 mg/L.

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

| Sample Description | Unit #1 (bias) | Unit #2 (bias) |
|----------------------------------------------------|-----------------------|-----------------------|
| City Water LFM - Lab | 12% | 36% |
| City Water LFM - Indoor Field Site | 35% | 30% |
| City Water LFM - Outdoor Field Site | 44% | 33% |
| Well Water LFM - Lab ^(a) | 11% | 14% |
| Well Water LFM - Indoor Field Site ^(a) | 40% | 30% |
| Well Water LFM - Outdoor Field Site ^(a) | 3% | 19% |

^(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 2.00 mg/L rather than the reference LFM result.

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% | 18% | 10% |
| 0.100 | 7% | 16% | 23% |
| 0.200 | 2% | 13% | 21% |
| 0.400 | 2% | 5% | 6% |
| 0.800 | 1% | 5% | 8% |
| 5.00 | 1% | 4% | 2% |
| 15.0 | 2% | 4% | 3% |
| 25.0 | 3% | 1% | 2% |

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% | 10% | 5% |
| Olentangy River LFM | 2% | 10% | 6% |

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

| Sample Description | Reference Method (RSD) | Unit #1 (RSD) | Unit #2 (RSD) |
|---------------------------------------------|------------------------|---------------|---------------|
| Montpelier, VT, 0.2 mg/L LFM ^(a) | 2% | 2% | 2% |
| Seattle, WA, 0.2 mg/L LFM ^(a) | 2% | 3% | 2% |
| Montpelier, VT, LFM | 2% | 4% | 9% |
| Seattle, WA, LFM | 2% | 5% | 8% |
| Tallahassee, FL, LFM | 2% | 7% | 2% |
| Flagstaff, AZ, LFM | 12% | 5% | 4% |
| Des Moines, IA, LFM | 3% | 13% | 7% |

^(a) These drinking water LFM samples were analyzed before the drinking water fortification amount of cyanide was changed from 0.200 mg/L to 2.00 mg/L.

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 - Lab | 4% | 7% | 8% |
| City Water LFM - Indoor Field Site | 4% | 2% | 8% |
| City Water LFM - Outdoor Field Site | 4% | 8% | 5% |
| Well Water LFM - Lab | 13% | 9% | 6% |
| Well Water LFM - Indoor Field Site | 13% | 9% | 10% |
| Well Water LFM - Outdoor Field Site | 13% | 2% | 2% |

6.4 Linearity

The linearity of the WTW 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 WTW ISE, versus the reference results.

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

$$y \text{ (WTW ISE results in mg/L)} = 0.99 (\pm 0.02) x \text{ (reference result in mg/L)} + 0.075 (\pm 0.200) \text{ mg/L with } r^2 = 0.993 \text{ and } N = 64.$$

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 0.990, indicating that the WTW ISE was linear over the entire range of PT concentrations (0.030 to 25.0 mg/L).

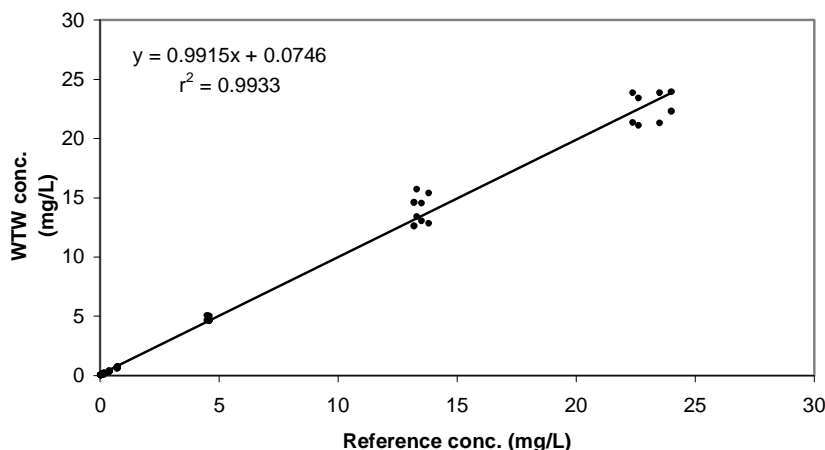


Figure 6-1. Linearity Results

6.5 Method Detection Limit

The manufacturer’s estimated detection limit for the WTW ISE is 0.200 mg/L cyanide. The MDL⁽⁴⁾ was determined by analyzing seven replicate samples at a concentration of 0.800 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 0.221 and 0.271 mg/L for Unit #1 and Unit #2, respectively.

Table 6-5. Results of Method Detection Limit Assessment

| MDL Conc. (mg/L) | Unit #1 (RSD) | Unit #2 (RSD) |
|------------------|---------------|---------------|
| 0.800 | 0.773 | 0.723 |
| 0.800 | 0.713 | 0.637 |
| 0.800 | 0.696 | 0.607 |
| 0.800 | 0.703 | 0.613 |
| 0.800 | 0.625 | 0.507 |
| 0.800 | 0.584 | 0.508 |
| 0.800 | 0.592 | 0.487 |
| Std Dev | 0.070 | 0.086 |
| t (n=7) | 3.140 | 3.140 |
| MDL | 0.221 | 0.271 |

6.6 Inter-Unit Reproducibility

The inter-unit reproducibility of the WTW ISE was assessed by using a linear regression of the results produced by one WTW ISE plotted against the results produced by the other WTW 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 6-2 shows a scatter plot of the results from both analyzers.

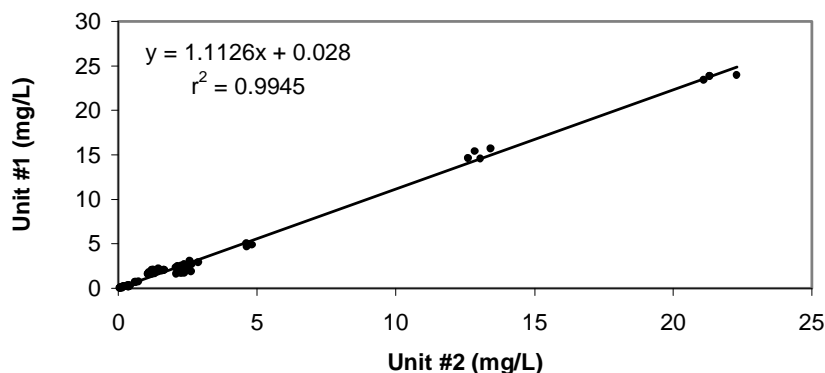


Figure 6-2. Inter-Unit Reproducibility Results

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

$$y \text{ (Unit \#1 result in mg/L)} = 1.113 (\pm 0.017) x \text{ (Unit \#2 result in mg/L)} + 0.028 (\pm 0.095) \text{ mg/L with } r^2 = 0.995 \text{ and } N = 92.$$

where the values in parentheses represent the 95% confidence interval of the slope and intercept. While the slope is significantly different from unity, further analysis of the data revealed that the deviation is heavily influenced by the 15.0- and 25.0-mg/L concentration levels. If only the PT samples with cyanide concentrations of 0.200 through 5.00 mg/L are included in this regression, the slope is unity, and the intercept is near zero. These data indicate that the two WTW ISEs functioned similarly to one another except at the two highest PT sample concentration levels. The inclusion of these data caused approximately 10% deviation from a slope of unity.

6.7 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 WTW 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 WTW ISE. Results are shown in Table 6-6a for both WTW ISEs. 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 3 to 34%, and the RSD of these results are shown in Table 6-6c and

ranged from 2 to 19%. The WTW ISE performed as well when analyzing water samples at lethal/non-lethal concentrations as it did at much lower concentrations.

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 | 58.5 | 49.5 |
| 50.0 | 54.8 | 54.6 | 47.1 |
| 50.0 | 51.3 | 55.2 | 48.0 |
| 50.0 | 53.5 | 52.1 | 47.7 |
| 100 | 107 | SL ^(a) | 111 |
| 100 | 108 | 116 | 109 |
| 100 | 108 | 115 | 110 |
| 100 | 110 | 105 | 116 |
| 250 | 270 | 438 | 383 |
| 250 | 266 | 383 | 313 |
| 250 | 273 | 316 | 317 |
| 250 | 254 | 285 | 338 |

^(a) SL = sample lost due to a laboratory error.

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

| Sample Concentration (mg/L) | Unit #1 (bias) | Unit #2 (bias) |
|-----------------------------|----------------|----------------|
| 50.0 | 5% | 10% |
| 100 | 6% | 3% |
| 250 | 34% | 27% |

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

| Prepared Concentration (mg/L) | Reference Method (RSD) | Unit #1 (RSD) | Unit #2 (RSD) |
|-------------------------------|------------------------|---------------|---------------|
| 50.0 | 3% | 5% | 2% |
| 100 | 1% | 5% | 3% |
| 250 | 3% | 19% | 9% |

6.8 Field Portability

The WTW ISE was operated in laboratory and field settings during this verification test. It was packaged in a hard plastic carrying case, which weighed about five pounds when fully loaded with its contents. WTW also provided an electrode stand and a battery-powered magnetic stirrer that were crucial for operating the analyzer in a field setting. These items are not routinely provided with the WTW ISE and would have to be purchased separately. The electrode stand and magnetic stirrer did not fit into the carrying case, but could easily be carried to the field. Tables 6-2d, 6-3d, and 6-4d show the results of the laboratory and field measurements. From an operational standpoint, the WTW 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 WTW 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. 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 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, city and well 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.

The Columbus, OH, well water LFM samples resulted in biases ranging from 3 to 40%. Very low biases (3 and 19%) were attained from the samples that were analyzed outside in frigid temperatures. The biases of the well water sample analyzed indoors were 30 and 40%, and those measured in the laboratory were 11 and 14%. There was no clear trend for biases from indoor and outdoor locations. The analyses performed outdoors by the WTW ISE resulted in biases as low or lower than those performed indoors. The apparent matrix interference that affected the reference LFM results did not seem to affect the results from the WTW ISE. One possible reason is that the LFM samples for the WTW ISE were fortified with 2.00 mg/L, ten times the fortification amount for the other technologies being verified.

The Columbus, OH, city water LFM samples resulted in biases from 30 to 44%, except for the 12% bias of Unit #1 operated in the laboratory. These data indicate that the WTW ISE functioned similarly in a laboratory and a field setting.

6.9 Ease of Use

The instruction manual for the WTW ISE was not easy to understand. It took consultation with a WTW representative to assemble and operate the WTW ISE properly. However, after that initial consultation with WTW, which included approximately a one-hour telephone call, the WTW ISE was easy to operate. The WTW ISE required calibration and electrode polishing before every

sample set to ensure the most accurate measurements. Although the manual describes a five-point calibration at 16 levels, the calibration concentrations were pre-programmed into the ISE meter so only 0.200-, 2.00-, 20.0-, or 200-mg/L calibration solutions could be used. A sample could be analyzed as long as the pH was above 12. No pH adjustment was necessary. One drawback of this technology was that the battery-powered stirrer would not operate at the slow speeds recommended for use while making ISE measurements. There was some agitation of the calibration and sample solutions when the stirrer was operating at its slowest setting.

6.10 Sample Throughput

The WTW 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 WTW 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

Upon calibration with three calibration solutions performed as suggested by the manufacturer's instructions, the WTW 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. The slopes attained were usually in this range or within 10% of this range. Regardless of whether the slope was within the suggested range, one calibration was performed and then the samples were analyzed.

The biases for the WTW ISE ranged from 2 to 17% for the PT samples; 31 to 128% for the surface water samples; 2 to 39% for the drinking water samples from around the country; and 3 to 44% for the Columbus, OH, drinking water samples.

The RSDs ranged from 1 to 23% for the PT samples; 5 to 10% for the surface water samples; 2 to 13% for the drinking water samples from around the country; and 2 to 10% for all of the Columbus, OH, drinking water samples.

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

$$y \text{ (WTW ISE results in mg/L)} = 0.99 (\pm 0.02) x \text{ (reference result in mg/L)} \\ + 0.075 (\pm 0.200) \text{ mg/L with } r^2 = 0.993 \text{ and } N = 64.$$

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 0.99.

The MDLs for the WTW ISE were determined to be 0.221 and 0.271 mg/L.

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

$$y \text{ (Unit #1 result in mg/L)} = 1.113 (\pm 0.017) x \text{ (Unit #2 result in mg/L)} + 0.028 (\pm 0.095) \\ \text{mg/L with } r^2 = 0.995 \text{ and } N = 92.$$

where the values in parentheses represent the 95% confidence interval of the slope and intercept. While the slope is significantly different from unity, further analysis of the data revealed that the deviation is heavily influenced by the 15- and 25-mg/L concentration levels.

When analyzing lethal/near-lethal concentrations of cyanide, the bias values ranged from 3 to 34%, and the RSDs of these results ranged from 2 to 19%.

From an operational standpoint, the WTW 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 WTW 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 operator found the instruction manual for the WTW ISE difficult to understand. Consultation with the supplier was required for explanation before the technician could properly assemble and operate the WTW ISE. The WTW ISE required calibration and electrode polishing before every sample set to ensure the most accurate measurements. The calibration concentrations were pre-programmed into the ISE meter so only 0.2-, 2-, 20-, or 200-mg/L calibration solutions could be used. These solutions needed to be prepared and transported to the field. No pH adjustment was necessary once the sample was preserved to a pH greater than 12.0. One drawback of the WTW ISE was that the battery-powered stirrer would not operate at the slow speeds recommended.

The WTW ISE was calibrated with three calibration solutions before performing any sample analyses. Calibration took between 15 and 30 minutes. Once the WTW 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 8 References

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