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Environmental Technology Verification Program

Advanced Monitoring Systems Center

Generic Verification Protocol for Portable Technologies for Detecting Cyanide in Water

GENERIC VERIFICATION PROTOCOL

for

PORTABLE TECHNOLOGIES FOR DETECTING CYANIDE IN WATER

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FOREWORD

This generic verification protocol is based upon a peer-reviewed test/quality assurance (QA) plan entitled "Test/QA Plan for Verification of Portable Technologies for Detection of Cyanide in Water (dated January 8, 2003)." The test/QA plan was developed with vendor and stakeholder input by the ETV Advanced Monitoring Systems Center. Peer reviewers for the test/QA plan were Billy Potter, U.S. EPA, National Exposure Research Laboratory; Ricardo DeLeon, Metropolitan Water District of Southern California; William Burrows, U.S. Army Center for Environmental Health Research; and Kenneth Wood, DuPont Corporate Environmental Engineering Group. In preparing this generic verification protocol, specific names of individuals involved, vendor and technology names, test dates, and similar details in the test/QA plan were revised to be generic. The experimental design in the protocol is the same as that in the peer-reviewed test/QA plan.

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ACRONYMS

AMS	Advanced Monitoring Systems
ASTM	American Society for Testing and Materials
EPA	Environmental Protection Agency
ETV	Environmental Technology Verification
HCl	hydrogen chloride
HDPE	high-density polyethylene
ID	identification
ISE	ion selective electrode
KI	potassium iodide
L	liter
LFM	laboratory fortified matrix
MDL	method detection limit
mg	milligram
NaOH	sodium hydroxide
NIST	National Institute of Standards and Technology
PE	performance evaluation
PT	performance test
QA	quality assurance
QC	quality control
QCS	quality control standard
QMP	Quality Management Plan
RB	reagent blank
TSA	technical systems audit

1 INTRODUCTION

1.1 Test Description

This protocol provides generic procedures for conducting a verification test of portable technologies for detecting cyanide in water. Verification tests are conducted under the auspices of the U.S. Environmental Protection Agency (EPA) through the Environmental Technology Verification (ETV) program. The purpose of ETV is to provide objective and quality-assured performance data on environmental technologies, so that users, developers, regulators, and consultants can make informed decisions about purchasing and applying these technologies.

Verification tests are performed by Battelle, of Columbus, Ohio, which is managing the ETV Advanced Monitoring Systems (AMS) Center through a cooperative agreement with EPA. The scope of the AMS Center covers verification of monitoring technologies for contaminants and natural species in air, water, and soil. In performing verification tests, Battelle follows the procedures specified in this protocol and will comply with the data quality requirements in the "Quality Management Plan (QMP) for the ETV Advanced Monitoring Systems Center."[1]

1.2 Test Objective

The objective of the verification test described in this protocol is to quantify the analytical and operational performance characteristics of portable technologies for detecting cyanide in water under a specific set of test conditions. The portable technologies shall be tested to assess their ability to measure cyanide in a variety of quality control (QC), performance evaluation (PE), drinking, and surface water samples. The cyanide technologies may be test kits that record a color change in the presence of cyanide or ion selective electrodes (ISEs).

1.3 Roles and Responsibilities

Verification tests are performed by Battelle with the participation of the vendors whose technologies are being verified. The organization chart in Figure 1 shows the responsibilities of individuals from Battelle, the vendor companies, and the EPA. These responsibilities are detailed in the following paragraphs.

1.3.1 Battelle

The AMS Center's Verification Test Coordinator has overall responsibility for ensuring that the technical, schedule, and cost goals established for the verification test are met. More specifically, the Verification Test Coordinator will:

- Assemble a team of qualified technical staff to conduct the verification test
- Direct the team in performing the verification test in accordance with this protocol
- Ensure that all procedures specified in this protocol and the QMP are followed
- Prepare and revise the draft verification reports and verification statements in response to reviewers' comments
- Respond to any issues raised in assessment reports and audits, including instituting corrective action as necessary
- Coordinate distribution of the verification reports and statements
- Serve as the primary point of contact for vendor representatives
- Ensure that confidentiality of vendor information is maintained.

The Verification Testing Leader for the AMS Center provides technical guidance and oversees the various stages of verification testing. The Verification Testing Leader will:

- Support the Verification Test Coordinator in organizing the test

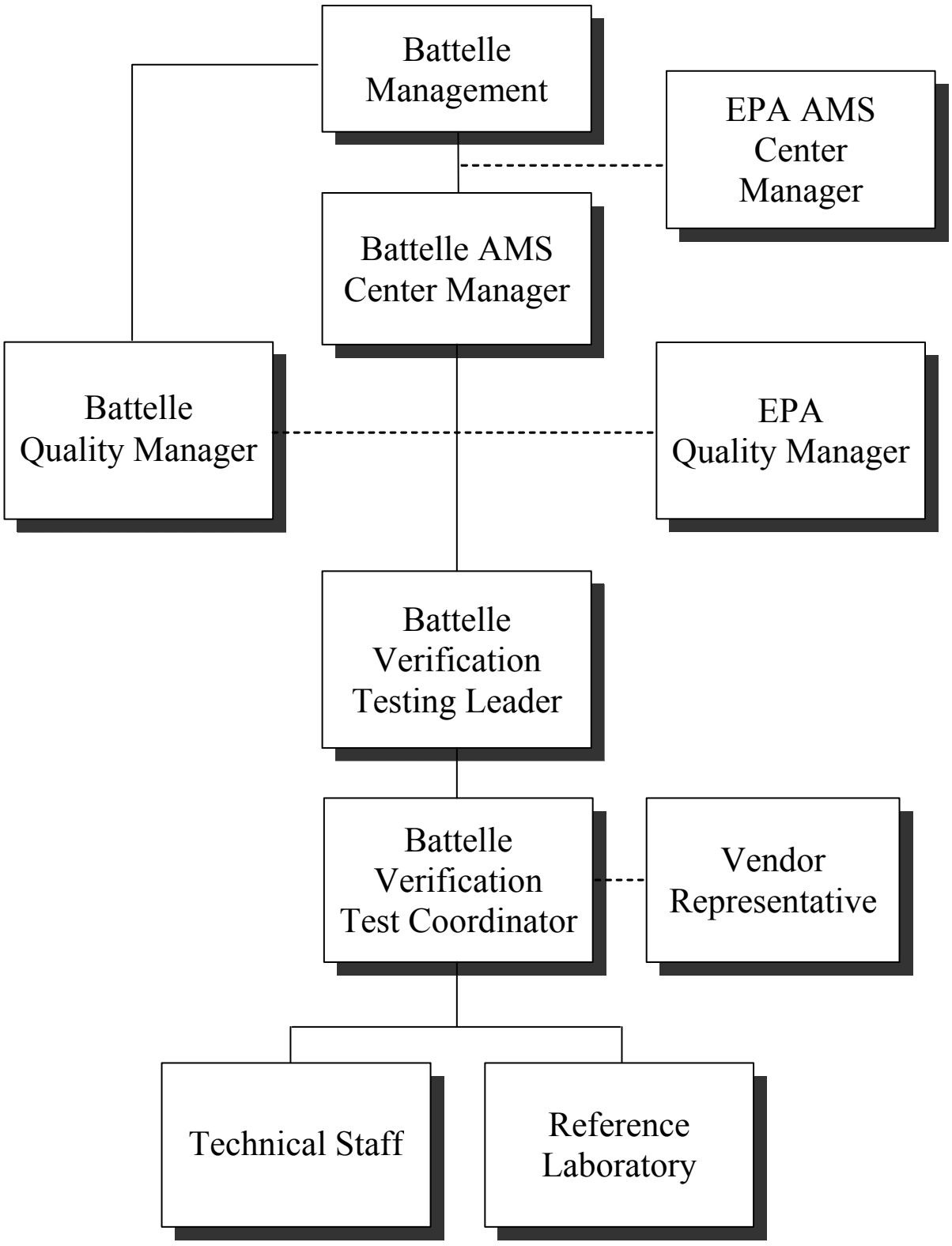

Figure 1. Organization Chart for the Verification Test

- Review the draft verification reports and statements.

The Battelle AMS Center Manager will:

- Review the draft verification reports and verification statements
- Ensure that necessary Battelle resources, including staff and facilities, are committed to the verification test
- Ensure that vendor confidentiality is maintained
- Support the Verification Test Coordinator in responding to any issues raised in assessment reports and audits
- Maintain communication with EPA's technical and quality managers
- Facilitate a stop work order if Battelle or EPA quality assurance (QA) staff discovers adverse findings.

Technical and temporary staff will test the technologies. Their responsibilities include:

- Assisting in the collection of samples
- Analyze samples for the verification test as described in this protocol.

The Battelle Quality Manager will:

- Conduct a quality review of reference laboratory documentation
- Conduct a technical systems audit (TSA) once during the verification test
- Audit at least 10% of the verification data
- Prepare and distribute an assessment report for each audit
- Verify implementation of any necessary corrective action
- Notify Battelle's AMS Center Manager about the need for a stop work order if self audits indicate that data quality is being compromised
- Provide a summary of the QA/QC activities and results for the verification reports
- Review the draft and final verification reports and statements
- Have overall responsibility for ensuring that this protocol is followed.

1.3.2 Vendors

Vendor representatives will:

- Provide two off-the-shelf models of the technology to be verified for the duration of the verification test
- As desired, familiarize Battelle personnel on the operation and maintenance of the technology prior to testing
- If desired, provide a representative to operate the technologies during the verification test
- Review their respective draft verification report and statement.

1.3.3 EPA

EPA's AMS Center Quality Manager will:

- Direct the performance, at the EPA's discretion, of external TSAs during the verification test
- Notify the EPA AMS Center Manager of the need for a stop work order if the external audit indicates that data quality is being compromised
- Prepare and distribute an assessment report summarizing results of the external audit, if one is performed
- Review the draft verification reports and statements.

EPA's AMS Center Manager will:

- Notify the Battelle AMS Center Manager of the need for a stop work order if the external audit indicates that data quality is being compromised
- Review the draft verification reports and statements
- Oversee the EPA review process of the verification reports and statements
- Coordinate the submission of verification reports and statements for final EPA approval.

1.3.4 Reference Laboratory

Analytical laboratories at Battelle, a subcontractor, and/or a partnering organization will serve as a reference laboratory to:

- Perform reference analyses of all test and QA samples of unknown concentrations
- Submit the results of the reference analyses in an agreed-upon format to the Verification Test Coordinator.

To be selected to perform the reference analyses during the verification test, a commercial laboratory or a partnering organization will demonstrate its competence to perform the needed cyanide analysis by providing Battelle with copies of its method/standard operating procedure, QA manual, state government certifications/approvals for cyanide analysis, and staff training records, where available. The Battelle Quality Manager will review these documents. Additionally, Battelle will prepare and blindly submit several samples of potassium cyanide to the laboratory as a proficiency test. Battelle will prepare these samples at concentrations unknown to the prospective laboratory. The laboratory's reported concentrations of the submitted QC standards will need to be within 25% of their known concentrations. If the prospective laboratory does not comply fully with each of the above requirements, another laboratory will be selected and its competence verified in a similar manner.

2 VERIFICATION APPROACH

2.1 Introduction

Cyanide is present in various forms in water. Verification tests will focus on detecting the free cyanide ion (CN^-), which in this document is referred to as "cyanide." At high doses, this form of cyanide inhibits cellular respiration and, in some cases, can result in death. In drinking and surface water under ambient conditions, cyanide evolves from aqueous hydrogen cyanide, sodium cyanide, potassium cyanide, and other ionic complexes where cyanide is released easily when dissolved in water. Because of the toxicity of cyanide to humans, the EPA

has set 0.2 milligrams per liter (mg/L) as the maximum concentration of cyanide that can be present in drinking water.

EPA Method 335.1, "Cyanides Amenable to Chlorination,"[2] shall be used as the reference method to verify the portable cyanide technologies. This method measures the concentration of the cyanide ion in water samples under ambient conditions.

Portable cyanide technologies (colorimetric test kits or ISEs) shall analyze prepared, surface, and drinking water samples. The results shall be compared to those from the reference method, and the technologies shall be evaluated in terms of

- Accuracy
- Precision
- Linearity
- Method detection limit
- Operator bias (test kits only)
- Inter-unit reproducibility
- Matrix interferences
- Portability
- Response of analyzer at cyanide concentrations dangerous to human health (lethal/near lethal dose)
- Sample throughput
- Ease of use and reliability.

2.2 Experimental Design

The verification test shall involve challenging the technologies with a variety of test samples, including sets of drinking and surface water samples representative of those likely to be analyzed using these technologies. All samples shall be analyzed by the technologies being verified and by a standard reference method.

The results from the technologies shall be compared to those from the reference method to quantitatively assess accuracy, linearity, and detection limit. Multiple aliquots of each test

sample shall be analyzed separately to assess precision of both the technologies being verified and the reference method.

Technologies designed for use by nontechnical operators (colorimetric test kits only) shall be tested independently by two separate operators (technical and nontechnical) to determine operator bias on analyzer performance. The vendor shall have the option of providing a representative or of familiarizing Battelle staff to serve as the technical operator. The nontechnical staff operator shall have little prior knowledge of the analyzer being verified and little or no previous laboratory experience. Both operators shall analyze all of the test samples. Each operator shall manipulate the water samples and reagents to generate a solution that can be probed photometrically. Then, each operator shall analyze that solution using both units of a given vendor's analyzer. More than one technical and/or nontechnical operator may be used by Battelle. The operators shall be uniquely identified in the verification report so it is clear which operator produced what data. The performance of two units of each portable cyanide technology shall be verified. Results for the two units shall be reported and compared to assess unit-to-unit reproducibility.

Matrix interferences shall be assessed by separately evaluating accuracy, precision, and linearity on distinctly different sample matrices, such as samples prepared in pure water with varying cyanide concentrations and drinking and surface water samples both spiked with cyanide and left unspiked. Sample throughput shall be estimated based on the time required to analyze a sample set. Performance parameters, such as ease of use and reliability, shall be based on documented observations of the operators and Verification Test Coordinator. Each analyzer shall be used in a field environment, as well as in a laboratory setting, to assess the impact of field conditions on performance.

Because cyanide is particularly toxic, ETV stakeholders and other end users of these technologies are interested in their response when the cyanide is present in drinking water at lethal and near-lethal concentrations (>50 mg/L). To address the toxicity of cyanide at lethal and near-lethal concentrations (>50 mg/L), three test samples, prepared in American Society for Testing and Materials (ASTM) Type II water, at concentrations of 50, 100, and 250 mg/L shall be analyzed. While typically the technologies are not designed to quantitatively measure these extreme concentrations, the operators and Verification Test Coordinator shall make qualitative

observations of their operation while analyzing such samples. Observations of unusual operational characteristics (rate of color change, unusually intense color, unique digital readout, etc.) shall be documented and reported so the end user can be made aware of what analyzer performance characteristics may serve as indicators of lethal or near-lethal concentrations.

The results from each technology shall be reported individually. No direct comparison shall be made between technologies, but each technology shall undergo identical testing so it is convenient for end users to evaluate the ETV testing results.

2.3 Test Samples

Test samples used in the verification test shall include QC samples, performance test (PT) samples, drinking water, and surface water samples. Table 1 shows the number and type of samples to be analyzed for colorimetric test kits and Table 2 shows the number and type of samples to be analyzed for ISEs. The QC and PT samples will be prepared from purchased standards. The QC sample concentrations will be targeted to the EPA maximum contaminant level in drinking water, which, for cyanide, is 0.2 mg/L. The PT samples will cover the range from 0.03 mg/L to 0.8 mg/L for the colorimetric test kits. The ISEs will be tested with PT samples ranging from 0.03 mg/L to 25 mg/L. The performance of the colorimetric test kits and ISEs also will be evaluated with three samples at concentrations that could be lethal if a volume the size of a typical glass of water was ingested. To evaluate the field portability of the technologies, some of the drinking water samples will be analyzed in a field setting. Other drinking and surface water samples will be shipped to Battelle and analyzed blindly in a laboratory setting. All the samples will be analyzed by both units of each analyzer undergoing testing and by a standard reference method.

Table 1. Summary of Colorimetric Test Kit Verification Test Samples

Type of Sample	Sample Characteristics	Concentration	No. of Samples
Quality Control	Reagent blank (RB)	~ 0	10% of all
	Laboratory fortified matrix (LFM)	0.200 mg/L	4 per water source (listed below)
	Quality control standard (QCS)	0.200 mg/L	10% of all
Performance Test	For the determination of method detection limit	0.100 mg/L[(a)]	7
	Cyanide spike	0.030 mg/L	4
	Cyanide spike	0.100 mg/L	4
	Cyanide spike	0.200 mg/L	4
	Cyanide spike	0.400 mg/L	4
	Cyanide spike	0.800 mg/L	4
Lethal / Near-Lethal	Cyanide spike	50.0 mg/L	4
	Cyanide spike	100 mg/L	4
	Cyanide spike	250 mg/L	4
Surface Water	Reservoir source	Background	4[(a)]
		0.200 mg/L LFM	4
	River source	Background	4[(a)]
		0.200 mg/L LFM	4
Drinking Water from Around the U.S.	Northwestern U.S.	Background	1[(a)]
		0.200 mg/L LFM	4
	Southwestern U.S.	Background	1[(a)]
		0.200 mg/L LFM	4
	Midwestern U.S.	Background	1[(a)]
		0.200 mg/L LFM	4
	Southeastern U.S.	Background	1[(a)]
		0.200 mg/L LFM	4
	Northeastern U.S.	Background	1[(a)]
		0.200 mg/L LFM	4
Residential Drinking Water	Residence with city water	Background	6
		0.200 mg/L LFM	12
	Residence with well water	Background	6
		0.200 mg/L LFM	12

[(a)] Additional analysis may be required (see Section 2.3.3).

Table 2. Summary of Ion Selective Electrode Verification 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 (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 spike	0.030 mg/L	4
	Cyanide spike	0.100 mg/L	4
	Cyanide spike	0.200 mg/L	4
	Cyanide spike	0.400 mg/L	4
	Cyanide spike	0.800 mg/L	4
	Cyanide spike	5.00 mg/L	4
	Cyanide spike	15.0 mg/L	4
	Cyanide spike	25.0 mg/L	4
Lethal / Near-Lethal	Cyanide spike	50.0 mg/L	4
	Cyanide spike	100 mg/L	4
	Cyanide spike	250 mg/L	4
Surface Water	Reservoir source	Background	4[(a)]
		0.200 mg/L LFM	4
	River source	Background	4[(a)]
		0.200 mg/L LFM	4
Drinking Water from Around the U.S.	Northwestern U.S.	Background	1[(a)]
		0.200 mg/L LFM	4
	Southwestern U.S.	Background	1[(a)]
		0.200 mg/L LFM	4
	Midwestern U.S.	Background	1[(a)]
		0.200 mg/L LFM	4
	Southeastern U.S.	Background	1[(a)]
		0.200 mg/L LFM	4
	Northeastern U.S.	Background	1[(a)]
		0.200 mg/L LFM	4
Residential 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

[(a)] Additional analysis may be required (see Section 2.3.3).

2.3.1 QC Samples

Prepared QC samples will include laboratory reagent blank (RB) samples, laboratory fortified matrix (LFM) samples, and quality control standards (QCS). RB samples will be analyzed to ensure that no sources of contamination are present. If the analysis of an RB sample indicates a concentration above the MDL for the technology being verified, contamination will be suspected. The RB samples will be prepared from ASTM Type II deionized water and be handled and analyzed identically to other prepared samples, including the addition of all reagents. These samples will be used to help ensure that no sources of contamination are introduced in the sample handling and analysis procedures. Any contamination source(s) will be corrected, and proper blank readings will be achieved.

The LFM samples will be prepared as aliquots of drinking and surface water samples spiked with potassium cyanide to increase the analyte concentration by 0.2 mg/L. In the case of the drinking water samples to be analyzed in the field, the spike solution used to prepare the LFM will be prepared in the laboratory and brought to the field site. For the rest of the samples, the LFM will be prepared similarly, but within a Battelle laboratory, not in a field setting. Since no cyanide is expected to be detectable in the drinking and surface water samples, four LFM samples will be analyzed for each source of water. These samples will be used to help determine whether matrix interferences have an influence on the analytical results.

Quality control standards (QCS) will be used to ensure the proper functioning of the technologies being verified. The QCSs will be purchased from a commercial supplier and subject only to dilution as appropriate. A QCS will be analyzed before and after the testing period, as well as after every tenth sample. Although no performance expectations will be defined, measurement results that are not within 25% of the expected value may indicate technology failure; the technology vendor should be contacted and appropriate remedial action taken. ISEs, for example, may be polished by the operator and recalibrated when response to QCSs is more than 25% different from the expected value. Additional standards also will be purchased from an independent supplier for use in a PE audit.

2.3.2 PT Samples

PT samples will be prepared in the laboratory using ASTM Type II deionized water as the water source and will include only cyanide at various concentrations. These samples will be used specifically to help determine the analyzer accuracy, linearity, and detection limit. To determine the detection limit of the technologies, a solution with a concentration three to five times the vendor's reported detection limit will be used. Seven nonconsecutive replicate analyses of this solution will be made to obtain precision data with which to determine the method detection limit (MDL). Additionally, solutions will be prepared to assess the linearity over a broad concentration range. Four aliquots of each of these solutions will be analyzed separately to assess the precision of the technologies. The concentrations of the PT samples are listed in Tables 1 and 2. The operators will analyze the PT samples blindly in a random order to minimize any bias that could occur.

2.3.3 Drinking and Surface Water Samples

Water samples, including drinking water (well and local distribution sources) and fresh surface water will be collected from a variety of sources and used to evaluate technology performance. In general, water samples of approximately 8 L will be collected. The water samples may not be characterized in any way (for hardness, alkalinity, etc.) other than for cyanide concentration. They will be split into two subsamples (see Figure 2). One subsample will be spiked with 0.2 mg/L cyanide to provide LFM aliquots, and the other will remain unspiked. Four 400-mL aliquots to be used for analysis by the vendors' test kits (~10 mL per replicate analysis) and ISEs (~100 mL total needed) will be taken from each subsample. Also taken from each subsample will be four 500-mL aliquots that will be used for analysis by the reference method. Cyanide is not expected to be detectable in any of the drinking or surface water samples analyzed during this test. To avoid replicating nondetectable concentrations, only one unspiked aliquot of each source of water will be analyzed if cyanide is not detectable in the first aliquot analyzed by each participating technology. If there is detectable cyanide in that initial aliquot, three additional aliquots of that sample will be analyzed in addition to four LFM

aliquots. Four LFM aliquots will be prepared and analyzed for every drinking and surface water source, regardless of the concentration of the initial aliquot. Each aliquot analyzed by the technologies being verified will also be analyzed by the reference method.

Surface water samples will be collected near the shoreline by submerging the containers no more than one inch below the surface of the water. City water samples will have completed the water treatment process, but not have yet entered the water distribution system. These samples will be adjusted with sodium hydroxide (NaOH) at a pH of greater than 12, and the samples will be analyzed within 14 days. Once the samples arrive at Battelle, they will be split into unspiked background and LFM subsamples as described above and analyzed.

Residential drinking water (both well and city water) samples will be used to verify the field portability of the technologies. Residential drinking water samples will be analyzed three different ways to verify each technology's performance. Twenty-four liters of water will be collected from an outside spigot at participating residences and split into three approximately 8-L samples. The first sample will be analyzed outdoors at the residence under the current weather conditions (meteorological conditions at the time of field sampling and analysis will be documented), the second sample will be brought inside the residence and allowed to equilibrate to room temperature before testing, and the third sample will be transported to Battelle for testing in the laboratory. Each 8-L sample will be split and analyzed as described above. If any of the samples cannot be analyzed within 24 hours of sampling, they will be preserved with NaOH to a pH greater than 12 at 4EC.

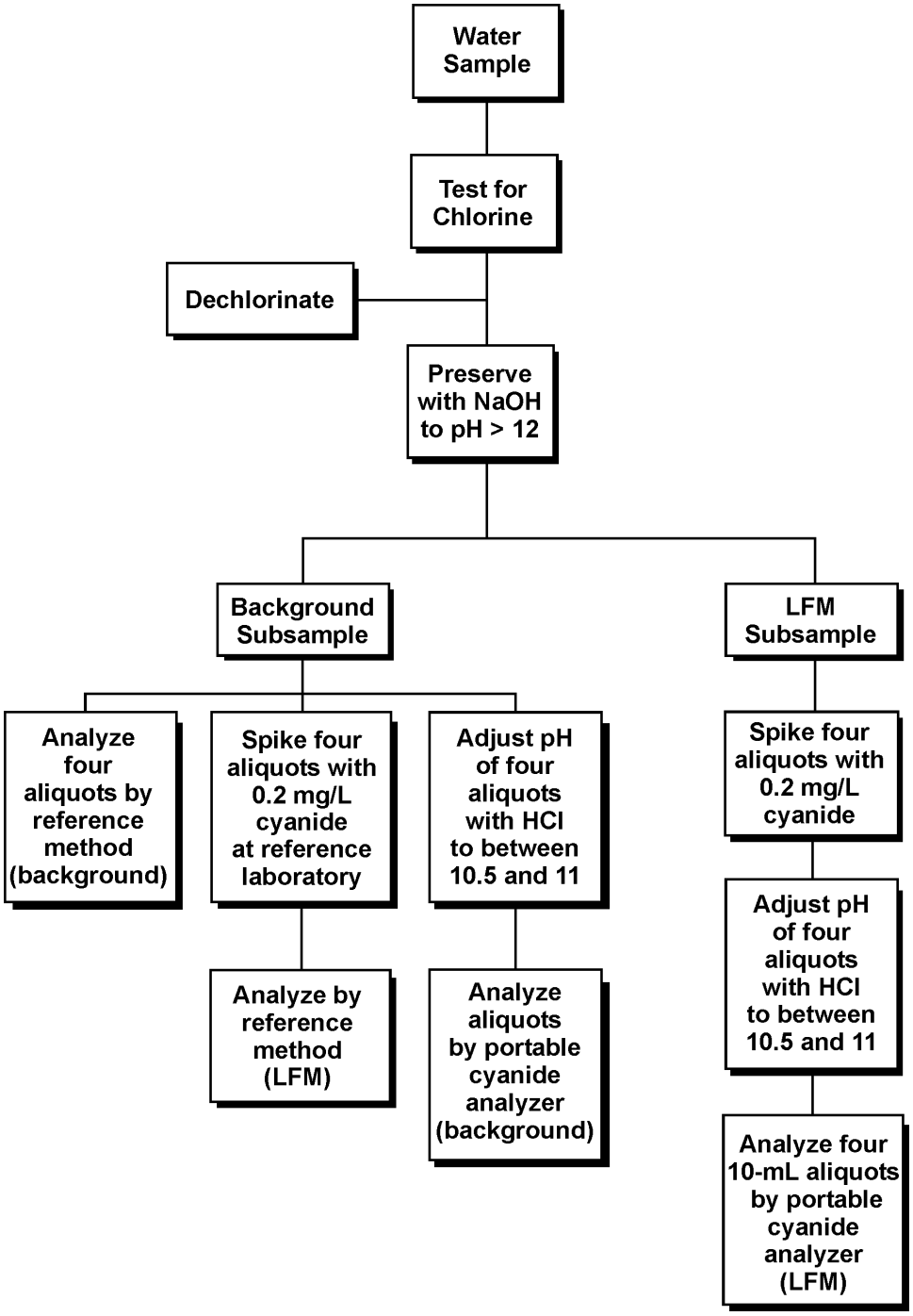

Figure 2. Sampling through Analysis Process

2.4 Reference Method

Technology verification will involve, in part, comparing the results from each analyzer being verified to the results obtained from an appropriate reference method. The reference method chosen for comparison to both ISE and colorimetric test kits is an EPA standard method for the analysis of water. Samples will be analyzed using visible spectroscopy according to EPA Method 335.1, "Cyanides Amenable to Chlorination."[2] This method incorporates two determinations of total cyanide. One determination is made after the free cyanide in the sample has been chlorinated to cyanogen chloride, which degrades quickly; and the second is made without chlorination. The concentration of free cyanide is given by the difference of the two measurements of total cyanide.

2.5 Sample Preparation and Storage

QC and PT samples will be prepared from commercially available National Institute of Standards and Technology- (NIST-) traceable standard material. The standard will be dissolved and diluted to appropriate concentrations using ASTM Type II water in Class A volumetric glassware. The QC and PT samples will be prepared at the start of testing, preserved with NaOH, and stored at 4EC for a maximum of 30 days.

Surface and drinking water samples will be stored in high-density polyethylene (HDPE) containers. Because free chlorine will degrade cyanide during storage, at the time of sampling, all of the samples will be tested for free chlorine with potassium iodide (KI) starch paper and dechlorinated, as necessary. The presence of chlorine is indicated if the KI paper changes to a bright blue color. If chlorine is present, ascorbic acid will be added a few crystals at a time until there is no further color change on the KI paper. Analysis of the samples will then proceed. For the residential drinking water samples, sample analysis will be performed at the time of collection. The rest of the surface and drinking water samples and all of the samples to be analyzed by the reference method will be stored until analysis at 4EC and adjusted, as necessary, with NaOH to a pH of greater than 12. The reference analyses will be performed within 14 days of collection, or the field sampling will be repeated.

2.6 Sample Identification

All test samples will be placed in uniquely identified sample containers for subsequent analysis. The sample containers will be identified by a unique identification (ID) number. A master log of the samples and ID numbers for each analyzer will be kept by Battelle. The ID number, date, person collecting, sample location, and time of collection will be recorded on a chain-of-custody form for all field samples.

2.7 Sample Analysis

2.7.1 Reference Method

The reference method will be operated according to the recommended procedures in the instruction manual, and samples will be analyzed according to EPA Method 335.1, "Cyanides Amenable to Chlorination."[2] Results from the reference method will be recorded electronically and compiled by the laboratory performing the analyses into a report format, including the sample ID and the analyte concentration for each sample.

2.7.2 Portable Cyanide Technologies

Each vendor will be required to provide two portable cyanide technologies for testing. Each analyzer will be subjected to the test procedure independently, and separate verification results will be reported for each unit. Those results will then be compared to assess unit-to-unit reproducibility. Each analyzer will be used to analyze the full set of samples. The sample set will include replicates of each of the PT, QC, and drinking and surface water samples. In the case of the colorimetric test kits, the complete set of samples will be analyzed twice for each technology, once by a nontechnical Battelle staff member and once by a technical staff member using the same sample aliquot. Because the ISEs are designed for a technical user, only a technical operator will perform the analyses for those technologies. For both types of technologies, the analyses will be performed according to the manufacturer's recommended

procedures as described in the user's instructions or manual or during training provided to the Battelle staff. Similarly, calibration and maintenance of the technologies will be performed as specified by the manufacturer.

Results from the technologies being verified will be recorded manually on appropriate data sheets. In addition to the analytical results, the data sheets will include records of the time required for sample analysis and operator observations concerning the use of the analyzer (e.g., frequency of calibration, ease of use, maintenance).

3 STATISTICAL CALCULATIONS

3.1 Accuracy

Accuracy of the technologies being verified will be assessed relative to the results obtained from the reference analyses. Samples will be analyzed by both the reference method and the technologies being verified. The results for each set of analyses will be averaged, and the accuracy will be expressed in terms of a relative average bias *(B)* as calculated from the following equation:

$$B = \frac{\bar{d}}{\overline{C_R}} \times 100 \qquad (1)$$

where $\bar{d}$ is the average difference between the readings from the analyzer being verified and those from the reference method, and $\overline{C_R}$ is the average of the reference measurements. Accuracy will be assessed independently for each analyzer to determine inter-unit reproducibility. Additionally, the results will be analyzed independently for the readings obtained from the two operators to determine if significant operator bias exists.

3.2 Precision

The standard deviation *(S)* of the results for the replicate samples will be calculated and used as a measure of analyzer precision at each concentration.

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

where n is the number of replicate samples, C_k is the concentration measured for the k^{th} sample, and $\overline{C}$ is the average concentration of the replicate samples. The analyzer precision at each concentration will be reported in terms of the relative standard deviation, e.g.,

$$RSD = \left| \frac{S}{\overline{C}} \right| \times 100 \quad (3)$$

3.3 Linearity

Linearity will be assessed by linear regression with the analyte concentration measured by the reference method as independent variable, and the reading from the analyzer being verified as dependent variable. Linearity will be expressed in terms of the slope, intercept, and coefficient of determination (r^2).

3.4 Method Detection Limit

The MDL for each analyzer will be assessed from the seven replicate analyses of a fortified sample with an analyte concentration of three to five times the vendor's estimated detection limit (see Tables 1 and 2). The MDL will be calculated from the following equation:

$$MDL = t \times S \quad (4)$$

where *t* is the Student's value for a 99% confidence level, and *S* is the standard deviation of the replicate samples. The MDL values for the two units of each technology will be reported as separate results.

3.5 Operator Bias

To assess operator bias for each technology, the results obtained from each operator will be compiled independently and subsequently compared. The existence of operator bias will be assessed by comparing the linear regression results of the nontechnical operator plotted against the results of the technical operator.

3.6 Inter-Unit Reproducibility

The results obtained from two identical units of each analyzer will be compiled independently for each analyzer and for each operator and compared to assess inter-unit reproducibility. The results will be interpreted by comparing the linear regression of the two units, plotted against each other.

3.7 Matrix Interferences

The potential effect of the sample matrix on the analyzer performance will be evaluated qualitatively by comparing the accuracy and precision results for the natural and cyanide-fortified surface and drinking water samples to those for the PT samples.

3.8 Portability

The results obtained from the measurements made on drinking water samples in the laboratory and field settings will be compiled independently for each analyzer and for each operator and compared to assess the accuracy of the measurements under the different analysis conditions, including the pertinent meteorological conditions such as ambient temperature and water temperature.

3.9 Lethal or Near-Lethal Dose Response

Extremely high-concentration water samples that are near-lethal or lethal if consumed will be analyzed. The operators and Verification Test Coordinator will make qualitative observations of their operation while analyzing such samples. Observations of unusual operational characteristics (rate of color change, unusually intense color, unique digital readout, etc.) will be documented and reported. If applicable, technologies will be assessed using the relative average bias, described in Section 3.1.

4 MATERIALS AND EQUIPMENT

In general, the verification test relies on the materials and equipment provided by the vendors. Battelle will provide the following equipment and materials.

4.1 Laboratory Supplies

The following laboratory supplies are needed to prepare the PT and QC samples:

- ASTM Type II water
- 4-L, 1-L, 250-mL, and 100-mL Class A volumetric flasks

- 10-mL Class A volumetric pipets
- 10-mL and 50-mL disposable pipets
- 0.5-mL and 1.0-mL micropipets
- micropipet tips
- NIST-traceable reference standard for target analyte
- HDPE containers
- NaOH for preservation and pH adjustment where applicable
- Hydrogen chloride (HCl) for pH adjustment where applicable
- pH meter
- Personal protective equipment.

4.2 Field Supplies

Battelle will provide the following supplies for collecting field samples:

- ASTM Type II water
- 125-mL, 500-mL, 1-L, and 8-L HDPE containers
- 1-mL micropipet
- 1-mL micropipet tips
- 10-mL and 50-mL disposable pipets
- HDPE volumetric flasks of various volumes
- Coolers and blue ice packs for sample storage
- Thermometer
- Lead carbonate

- KI starch paper
- Lead acetate paper
- pH meter
- Ascorbic acid
- NaOH for preservation and pH adjustment where applicable
- HCl for pH adjustment where applicable
- Personal protective equipment.

5 QUALITY ASSURANCE /QUALITY CONTROL

The QA/QC activities associated with the verification test will focus primarily on reference analysis, sample preparation and handling, and data recording and analysis. An independent audit covering each of these areas will be performed by the Battelle Quality Manager to ensure the quality of the verification test.

5.1 QC of Reference Method

Analysis of QC samples throughout the verification test will be used to document the performance of the reference method. Prepared QC samples will include QCSs, RB samples, and LFM samples. The reference technology will be calibrated according to the procedures described in the reference method. In addition, the accuracy of the reference method will be tested before the beginning and after the conclusion of each testing day as well as after every tenth sample with an appropriate QCS. The reference method will be required to measure the concentrations of the QCS to within 25% of the known concentration. If the difference is larger than 25%, the data collected since the most recent QCS will be flagged; and proper maintenance will be performed to regain accurate cyanide measurement.

RB samples will be analyzed to ensure that no sources of contamination are present. If the analysis of an RB sample indicates a concentration above the MDL for the reference method, contamination will be suspected. The RB samples will be prepared from ASTM Type II deionized water and be handled and analyzed identically to other prepared samples, including the addition of all reagents. These samples will be used to help ensure that no sources of contamination are introduced in the sample handling and analysis procedures. Any contamination source(s) will be corrected, and proper blank readings will be achieved.

The LFM samples will be prepared as aliquots of drinking and surface water samples spiked with potassium cyanide to increase the analyte concentration by 0.2 mg/L. In the case of the drinking water samples to be analyzed in the field, the spike solution used to prepare the LFM will be prepared in the laboratory and brought to the field site. For the rest of the samples, the LFM will be prepared similarly, but within a Battelle laboratory, not in a field setting. Since no cyanide is expected to be detectable in the drinking and surface water samples, four LFM samples will be analyzed for each source of water. These samples will be used to help determine whether matrix interferences have an influence on the analytical results of the reference method. The percent recovery of the spiked solution will be calculated from the following equation:

$$R = \frac{C_s - C}{s} \times 100 \qquad (5)$$

where C_s is the analyzed concentration of the spiked sample, C is the analyzed concentration of the unspiked sample, and s is the concentration equivalent of the cyanide spike. If the percent recovery of an LFM falls outside the range from 75 to 125%, a matrix interference will be suspected.

5.2 Audits

5.2.1 Performance Evaluation Audit

A PE audit will be conducted to assess the quality of the reference measurements made in the verification test. A PE audit involves challenging the analyzer used for the reference method

with standards that are independent of those used to calibrate the technologies being tested. For the PE audit, an independent standard will be obtained from a source other than the one that supplied the QCS. QC and PE standards will be measured using the reference method, and the results will be compared once during the verification test. Agreement of the standards within 25% is required for the measurements to be considered acceptable. Failure to achieve this agreement will trigger a repeat of the PE comparison. Failure in the second comparison requires obtaining another set of standards and repeating the performance audit.

A second type of PE will involve selecting the reference laboratory. Battelle will submit various solutions with known concentrations of cyanide to prospective commercial laboratories to test their ability to accurately measure cyanide. After the reference laboratories report the cyanide concentrations in those solutions to within 25% of the known concentration, the Battelle Quality Manager will conduct an audit of its quality documents. If there are areas of concern with the quality documents, the commercial laboratories will be notified, and if they are willing to adapt Battelle's procedures, will be considered for use.

5.2.2 Technical Systems Audit

The Battelle Quality Manager will conduct a TSA at least once during the course of the verification test. The purpose of this audit is to ensure that the verification test is performed in accordance with this protocol and the AMS Center QMP.[1] In this audit, the Battelle Quality Manager will review the reference standards and methods used, compare actual test procedures to those specified in this protocol, and review data acquisition and handling procedures. An independent TSA also may be performed by EPA Quality Management staff during the verification test, at EPA's discretion.

5.2.3 Data Quality Audit

At least 10% percent of the data generated during the verification test will be audited. Battelle's Quality Manager will trace 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 will be checked.

5.2.4 Assessment Reports

Each assessment and audit will be documented in accordance with Section 3.3.4 of the QMP for the AMS Center.[1] The results of the TSA will be sent to the EPA. Assessment reports will include the following:

- Identification of any adverse findings or potential problems
- Response to adverse findings or potential problems
- Recommendations for resolving problems
- Confirmation that solutions have been implemented and are effective
- Citation of any noteworthy practices that may be of use to others.

5.3 Corrective Action

The Battelle or EPA Quality Manager, during the course of any assessment or audit, will identify to the technical staff performing experimental activities any immediate corrective action that should be taken. If serious quality problems exist, the Battelle Quality Manager is authorized to stop work. Once the assessment report has been prepared, the Verification Test Coordinator will ensure that a response is provided for each adverse finding or potential problem and implement any necessary follow-up corrective action. The Battelle Quality Manager will ensure that follow-up corrective action has been taken.

6 DATA ANALYSIS AND REPORTING

6.1 Data Acquisition

A variety of verification test data will be acquired and recorded electronically or manually by Battelle staff. Operation and maintenance data, sampling procedures, and test results will be documented on data sheets or in laboratory record books. Results from the reference method will be compiled in electronic format.

6.2 Data Review

Records generated during the verification test by any Battelle staff will be reviewed by a more senior Battelle staff member within two weeks of generation, before these records are used to calculate, evaluate, or report verification results. Table 3 summarizes the types of data to be recorded. These records may include laboratory record books or reference method analytical results. Battelle, contractor, and/or vendor staff will be consulted as needed to clarify any issues about the data records. The review will be documented by the person performing it by adding his/her initials and date to a hard copy of the record being reviewed. This hard copy will then be returned to the Battelle staff member who generated or who will be storing the record.

6.3 Reporting

The data obtained in the verification test will be compiled separately for each vendor's analyzer, and the statistical calculations described in Section 3 will be applied to each data set without reference to any other vendor's results. At no time will data from different vendor's technologies be compared or ranked. Following completion of the statistical calculations, a draft verification report will be prepared for each vendor's technology, describing the verification test procedures and documenting the performance observed. The draft verification reports will be

submitted to the respective vendors for review and comment. Battelle will consider the comments provided by each vendor when revising the verification reports, but does not guarantee that revisions made to the final verification reports will reflect those comments. After vendor review, the revised reports will be submitted to EPA and AMS Center stakeholders for peer review. The reports will be revised again to address the peer review comments and submitted for final EPA approval.

In parallel with preparation of the verification reports will be preparation of the verification statement for each technology. The verification statement is a two- to three-page summary of the technology, the test procedures, and the test results. Each draft verification statement will be submitted to the respective vendor for review, and then will follow the same revision and EPA review process as the reports. Upon approval by EPA, each verification statement will be signed by a senior manager of Battelle and by an EPA laboratory director. Battelle will reserve the right to post the final verification reports and statements on the ETV Web site (http://www.epa.gov/etv). Original signed verification statements will be provided to the respective vendors for use in marketing their products.

Table 3. Summary of Data Recording Process for the Verification Test

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, and at each change of a test parameter	Used to organize/check test results; manually incorporated in data 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 in data spreadsheets as necessary
Reference method analytical data	Battelle	Laboratory record books	At least at the time of sampling	Used to organize/check test results; manually incorporated in data spreadsheets as necessary
Reference method sample analysis, chain of custody, and results	Contracted laboratory	Laboratory record books, data sheets, or data acquisition system, as appropriate	Throughout sample handling and analysis process	Transferred to spreadsheets/agreed upon report

(a) All activities subsequent to data recording are carried out by Battelle.

7 HEALTH AND SAFETY

7.1 Laboratory Standard/Performance Test Sample Preparation

All solid and highly concentrated aqueous solutions of potassium cyanide and NaOH will be handled inside a laboratory hood with the hood sash set to the lowest height that allows for safe manipulation of materials. The following guidelines should be adhered to:

- Personal protective equipment will include safety glasses with side shields, a laboratory coat, and nitrile lab gloves. Gloves will be immediately changed if they become contaminated. (The same gloves can be used for NaOH.)
- All contaminated waste will be handled as hazardous waste and sent out through Battelle Waste Operations.

7.2 Field Handling of Test Solutions

Cyanide and NaOH solutions will be handled in the field by taking the following precautions:

- All containers will be stored and transported in double containment.
- Safety goggles, nitrile gloves with long cuffs, and a chemical-resistant disposable lab coat will be worn when handling either chemical. Gloves will be immediately changed if they become contaminated.

8 REFERENCES

1. "Quality Management Plan (QMP) for the ETV Advanced Monitoring Systems Center," Version 3.0, Environmental Technology Verification Program, prepared by Battelle, Columbus, Ohio, December 2001.
2. U.S. EPA Method 335.1, "Cyanides, Amenable to Chlorination," in *Methods for the Chemical Analysis of Water and Wastes*, EPA/600/4/l-79-020, Revised, March 1983.