July 2002

Environmental Technology Verification Report

NANO-BAND™ EXPLORER Portable Water Analyzer

Prepared by

Battelle

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ETV Advanced Monitoring Systems Center

Nano-Band™ Explorer Portable Water Analyzer

by

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Notice

Foreword

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

The Environmental Technology Verification (ETV) Program has been established by the EPA to verify the performance characteristics of innovative environmental technology across all media and to report this objective information to permitters, buyers, and users of the technology, thus substantially accelerating the entrance of new environmental technologies into the marketplace. Verification organizations oversee and report verification activities based on testing and quality assurance protocols developed with input from major stakeholders and customer groups associated with the technology area. ETV consists of six 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. Information concerning this specific environmental technology area can be found on the Internet at http://www.epa.gov/etv/centers/center1.html.

Acknowledgments

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Contents

Figures

Tables

List of Abbreviations

AMS	Advanced Monitoring Systems
ASTM	American Society for Testing and Materials
DW	drinking water
EPA	U.S. Environmental Protection Agency
ETV	Environmental Technology Verification
FW	freshwater
HDPE	high-density polyethylene
HI	high interference
ICPMS	inductively coupled plasma mass spectrometry
LBC	Little Beaver Creek
LC	Lytle Creek
LFM	laboratory-fortified matrix
LI	low interference
MDL	method detection limit
NIST	National Institute of Standards and Technology
ppb	parts per billion
ppm	parts per million
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
RSD	relative standard deviation
RPD	relative percent difference
SR	Stillwater River
TSA	technical systems audit
TW	treated well water
WW	well water

Chapter 1
Background

The U.S. Environmental Protection Agency (EPA) has created the Environmental Technology Verification (ETV) Program to facilitate the deployment of innovative environmental technologies through performance verification and dissemination of information. The goal of the ETV Program is to further environmental protection by substantially accelerating the acceptance and use of improved and cost-effective technologies. ETV seeks to achieve this goal by providing high-quality, peer-reviewed data on technology performance to those involved in the design, distribution, financing, permitting, purchase, and use of environmental technologies.

ETV works in partnership with recognized testing organizations; with stakeholder groups consisting of buyers, vendor organizations, and permitters; and with the full participation of individual technology developers. The program evaluates the performance of innovative technologies by developing test plans that are responsive to the needs of stakeholders, conducting field or laboratory tests (as appropriate), collecting and analyzing data, and preparing peer-reviewed reports. All evaluations are conducted in accordance with rigorous quality assurance (QA) protocols to ensure that data of known and adequate quality are generated and that the results are defensible.

The EPA's National Exposure Research Laboratory and its verification organization partner, Battelle, operate the Advanced Monitoring Systems (AMS) Center under ETV. The AMS Center recently evaluated the performance of four portable analyzers for arsenic in water. This verification report presents the procedures and results of the verification test for the TraceDetect Nano-Band™ Explorer. The Nano-Band™ Explorer is a portable, rapid device designed for on-site analysis of arsenic in water.

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 Nano-Band™ Explorer. Following is a description of the Nano-Band™ Explorer, based on information provided by the vendor. The information provided below has not been verified in this test.

The Nano-Band™ Explorer uses an anodic stripping voltammetry technique in which information about an analyte is derived from the measurement of electric current as a function of applied potential. The measurement is performed in an electrochemical cell under polarizing conditions on a working electrode. Analysis involves reducing the analyte of interest and collecting it at the working electrode. The analyte is then stripped off (i.e., oxidized) and measured. The stripping step is much shorter than the reduction step, and the consequent increase in the signal-to-noise ratio allows low concentration solutions to be measured. The Nano-Band™ electrode is an array of 100 sub-electrodes, each less than 0.5 microns thick. The increased mass transport rate afforded by this array allows parts per billion (ppb) measurements in seconds. Iridium electrodes are used to measure lead, mercury, copper, zinc, cadmium, thallium, bismuth, tin, antimony, and silver. Gold electrodes are used to measure arsenic. The three-electrode cell combines a Nano-Band™ Explorer electrode with a reference and an auxiliary electrode. The auxiliary and reference electrodes manage the current as it is passed through the working electrode. The Nano-Band™ Explorer has a detection limit as low as 0.1 ppb for some metals and displays measurement results in real time using software run on a laptop computer (not included). The nominal detection limit for arsenic in this test was 4 ppb.

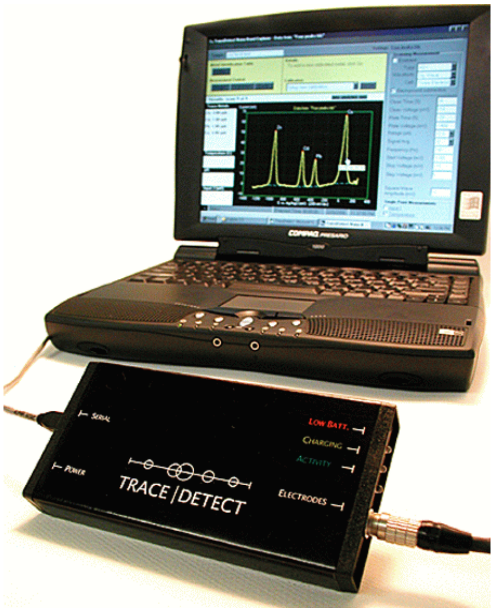

Figure 2-1. TraceDetect Nano-Band™ Explorer

The Nano Band™ Explorer is optimized for trace metals analysis. It can perform anodic and cathodic stripping voltammetry; normal square wave voltammetry; amperometry; cyclic voltammetry; temperature and pH measurements; and long-term data logging. The measurement system includes the Nano-Band™ Explorer, one reference and one auxiliary electrode, a measurement manual, a reference manual, Explorer software, a three-foot electrode cable, three conversion connectors, a temperature sensor, and an electrode cleaning kit.

Chapter 3
Test Design and Procedures

3.1 Introduction

This verification test was conducted according to procedures specified in the *Test/QA Plan for Verification of Portable Analyzers*.(1) The verification was based on comparing arsenic results from the Nano-Band™ Explorer to those from a laboratory-based reference method. The reference method for arsenic analysis was inductively coupled plasma mass spectrometry (ICPMS), performed according to EPA Method 200.8.(2) The Nano-Band™ Explorer was calibrated using standards supplied with the instrument. The Nano-Band™ Explorer was tested by analyzing laboratory-prepared performance test samples, treated and untreated drinking water, and fresh surface water, with both the Nano-Band™ Explorer and the reference method.

3.2 Test Design

The Nano-Band™ Explorer was verified in terms of its performance on the following parameters:

- Accuracy
- Precision
- Linearity
- Method detection limit (MDL)
- Matrix interference effects
- Operator bias
- Rate of false positives/false negatives.

Two units of the Nano-Band™ Explorer were tested independently by challenging them with samples representative of those likely to be analyzed using the Nano-Band™ Explorer. Each unit of the Nano-Band™ Explorer was used to analyze the full set of samples for arsenic. All preparation, calibration, and analyses were performed according to the manufacturer's recommended procedures. Results from the Nano-Band™ Explorer were recorded manually. The results from the Nano-Band™ Explorers were compared to those from the reference method to quantitatively assess accuracy, linearity, and detection limit. Multiple aliquots of performance test samples and drinking water samples were analyzed to assess precision.

Identical sets of samples were analyzed independently by two separate operators (a technical and a non-technical Battelle staff member), each using one of the Nano-Band™ Explorer units. The technical operator was a research technician at Battelle with three years of laboratory experience and a B.S degree. The non-technical operator was a part-time temporary helper at Battelle with a general education development certificate. During the field tests, the Nano-Band™ Explorer operated by the technical operator malfunctioned. The malfunction could not be resolved without the assistance of a vendor representative. Therefore, at the vendor’s request, the well water and freshwater samples were stored at 4°C until the instrument was repaired. Those samples were later analyzed in Battelle’s laboratories by a representative of the vendor.

Matrix interference effects were assessed by challenging the Nano-Band™ Explorer with performance test samples of known arsenic concentrations containing both low-level and high-level interferences. False positives and negatives were evaluated relative to the recently established 10-ppb maximum contaminant level for arsenic in drinking water. In addition to the analytical results, the time required for sample analysis and operator observations concerning the use of the instruments (e.g., frequency of calibration, ease of use, maintenance) were recorded.

3.3 Test Samples

Three types of samples were used in the verification test, as shown in Table 3-1: quality control (QC) samples, performance test (PT) samples, and environmental water samples.

The QC and PT samples were prepared from National Institute of Standards and Technology (NIST) traceable purchased standards. Under the Safe Drinking Water Act, the EPA lowered the maximum contaminant level for arsenic from 50 ppb to 10 ppb, effective in January 2006. Therefore, the QC sample concentrations for arsenic were targeted at that 10-ppb level. The PT samples were targeted to range from 10% to 1,000% of that level, i.e., from 1 to 100 ppb. The environmental water samples were collected from various drinking water and surface water sources. All samples were analyzed using the two Nano-Band™ Explorers and a reference method. Every tenth sample was analyzed twice by the reference method to document the reference method’s precision.

3.3.1 QC Samples

As Table 3-1 indicates, prepared QC samples included both laboratory reagent blanks (RB) and laboratory-fortified matrix (LFM) samples. The RB samples consisted of American Society for Testing and Materials (ASTM) Type II deionized water and were exposed to handling and analysis procedures identical to other prepared samples. These samples were used to help ensure that no sources of contamination were introduced during the sample handling and analysis. Two types of LFMs were prepared. The LFM_F samples consisted of aliquots of environmental samples that were spiked in the field to increase the analyte concentration by 10 ppb of arsenic. These samples were analyzed by the test kits in the field both before and after spiking. The spike solution for the LFM_F samples was prepared in the laboratory and brought to the field site. The LFM_L samples were aliquots of environmental samples that were spiked in the laboratory to

Table 3-1. Test Samples[a] for Verification of the Nano-Band™ Explorer

Type of Sample	Sample Characteristics	Concentration	No. of Samples
Quality Control	Reagent Blank (RB)[b]	~ 0	10% of all
	Laboratory Fortified Matrix (LFM_F)[b]	10 ppb above native level	1 per site
	LFM_L[b]	25 ppb above native level	6
	Quality Control Sample (QCS)[b]	10 ppb	10% of all
Performance Test	Prepared arsenic solution (PT6)	25 ppb	7
	Prepared arsenic solution (PT1)	1 ppb	4
	Prepared arsenic solution (PT2)	3 ppb	4
	Prepared arsenic solution (PT3)	10 ppb	4
	Prepared arsenic solution (PT4)	30 ppb	4
	Prepared arsenic solution (PT5)	100 ppb	4
	Prepared arsenic solution spiked with interference (LI)	10 ppb with low interference	8
	Prepared arsenic solution spiked with interference (HI)	10 ppb with high interference	8
Environmental	Columbus municipal drinking water (DW)	Unknown	4
	Well water (WW)	Unknown	4
	Treated well water (TW)	Unknown	4
	Stillwater River (SR)	Unknown	4
	Lytle Creek (LC)	Unknown	4
	Little Beaver Creek (LBC)	Unknown	4

[a] Listing is for clarity; samples were analyzed in random order for the verification testing.

[b] See Section 3.3.1 for descriptions of these samples.

increase the analyte concentration by 25 ppb of arsenic. These samples were used to help identify whether matrix effects influenced the reference analytical results. At least 10% of all the prepared samples analyzed were RBs, and at least one sample taken from each sampling site was an LFM_F.

Quality control standards (QCS) were used as calibration checks to verify that the Nano-Band™ Explorer and the reference instrument were properly calibrated and reading within defined control limits. These standards were purchased from a commercial supplier and were subject only to dilution as appropriate. Calibration of the Nano-Band™ Explorer and the reference instrument was verified using a QCS before and after the testing period, as well as after every tenth sample. An additional independent QCS was used in a performance evaluation (PE) audit of the reference method.

3.3.2 PT Samples

The two types of PT samples used in this verification test (Table 3-1) were prepared in the laboratory using ASTM Type II water as the water source. One type of PT solution contained arsenic at various concentrations and was prepared specifically to determine Nano-Band™ Explorer accuracy, linearity, and detection limit. To determine the detection limit of the Nano-Band™ Explorer, a solution with a concentration of 25 ppb pf arsenic was used. Seven non-consecutive replicate analyses of this solution were made to obtain precision data with which to estimate the MDL. Five other solutions were prepared to assess the linearity over a 1- to 100-ppb range of response to arsenic concentrations. Four aliquots of each of these solutions were prepared and analyzed separately to assess the precision of the Nano-Band™ Explorer, as well as the linearity.

The second type of PT sample was used to assess the effects of matrix interferences on the performance of the Nano-Band™ Explorer. These samples were solutions with 10-ppb concentrations of arsenic, spiked with potentially interfering species likely to be found in typical water samples. One sample (designated LI) contained low levels of interferences that consisted of 1 part per million (ppm) of iron, 3 ppm of sodium chloride, and 0.1 ppm of sulfide per liter at a pH of 6. The second sample (designated HI) contained high levels of interferences that consisted of 10 ppm of iron, 30 ppm of sodium chloride, and 1.0 ppm of sulfide per liter at a pH of 3. Eight replicate samples of each of these solutions were analyzed.

3.3.3 Environmental Samples

Drinking water samples listed in Table 3-1 include Columbus municipal water collected from a Battelle drinking fountain (DW), well water (WW), and treated well water (TW) from a school near Columbus, Ohio. The WW was pumped from a 250-foot well and collected directly from an existing spigot with no purging. The TW was treated by running the WW through a Greensand filtration system in the basement of the school. These samples were collected directly from the tap into 2-L high-density polyethylene (HDPE) containers. Four aliquots of each sample were analyzed in the field at the time of collection by each of the Nano-Band™ Explorers being verified. One aliquot of each sample was preserved with nitric acid and returned to Battelle for reference analysis. The remaining collected sample was stored at 4°C for later use, if necessary.

Freshwater (FW) samples from the Stillwater River (SR), Lytle Creek (LC), and the Little Beaver Creek (LBC) (in Ohio) were collected in 2-L HDPE containers. The samples were collected near the shoreline by submerging the containers no more than one inch below the surface of the water. Each body of water was sampled at four distinct locations. An aliquot of each sample was analyzed in the field at the time of collection by each test kit being verified. One aliquot of each sample was preserved with nitric acid and returned to Battelle for reference analysis. The remaining collected samples were stored at 4°C for later measurements, as required.

3.4 Reference Analysis

The reference arsenic analysis was performed using a Perkin Elmer Sciex Elan 6000 ICPMS according to EPA Method 200.8, Revision 5.5.(2) The sample was introduced through a peristaltic pump by pneumatic nebulization into a radiofrequency plasma where energy transfer processes cause desolvation, atomization, and ionization. The ions were extracted from the plasma through a pumped vacuum interface and separated on the basis of their mass-to-charge ratio by a quadrupole mass spectrometer. The ions transmitted through the quadrupole were registered by a continuous dynode electron multiplier, and the ion information was processed by a data handling system.

The ICPMS was tuned, optimized, and calibrated daily. The calibration was performed using a minimum of five calibration standards at concentrations ranging between 0.1 and 250 ppb and a required correlation coefficient minimum of 0.999. Internal standards were used to correct for instrument drift and physical interferences. These standards were introduced in line through the peristaltic pump and analyzed with all blanks, standards, and samples.

3.5 Verification Schedule

The Nano-Band™ Explorer verification test took place over a 19-day period from October 25 to November 12, 2001. The environmental samples were collected and analyzed over the seven-day period from November 2 through November 8, 2001. Table 3-2 shows the daily testing activities that were conducted during these periods. In all field locations, the samples were to be analyzed shortly after collection using the Nano-Band™ Explorer units by both the technical and the non-technical Battelle staff member. However, on November 2, the technical operator experienced mechanical failure of the Nano-Band™ Explorer electrode cable. That instrument was sent back to the manufacturer for repairs, and field sample collection and analysis continued with only the non-technical operator participating. Field samples were collected and stored at Battelle at 4°C until a representative from TraceDetect returned to Battelle on November 29 to analyze the remaining samples with the repaired instrument. Thus, the Battelle non-technical operator analyzed all test samples, whereas the Battelle technical operator analyzed the PT and DW samples, and the TraceDetect representative analyzed the WW, TW, LC, LBC, and SR samples. The reference analyses on all samples were performed on December 21, 2001, approximately six weeks after sample collection.

Table 3-2. Schedule of Verification Test Days

Test Day	Testing Location	Activity
10/25-11/12/01	Battelle	Preparation and analysis of PT and associated QC samples.[a]
10/25/01	Battelle	Collection and analysis of DW and associated QC samples within Battelle.[a]
11/02/01	Ohio Field Location	Collection and analysis of WW samples, TW samples and associated QC samples at Licking Valley Middle School.[b]
11/06/01	Ohio Field Location	Collection and analysis of environmental and associated QC samples at four locations on Little Beaver Creek.[b]
11/07/01	Ohio Field Location	Collection and analysis of environmental and associated QC samples at four locations on Lytle Creek.[b]
11/08/01	Ohio Field Location	Collection and analysis of environmental and associated QC samples at four locations on the Stillwater River.[b]
11/29/01	Battelle	Analysis of stored samples collected previously at Licking Valley, Little Beaver Creek, Lytle Creek, and Stillwater River by a TraceDetect representative.[c]

[a] Analyses performed by Battelle technical and non-technical operators.
[b] Analyses performed by Battelle non-technical operator only.
[c] Analyses performed by TraceDetect representative only.

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(3) and the test/QA plan for this verification test.(1)

4.1 QC for Reference Method

Field and laboratory RB samples were analyzed to ensure that no sources of contamination were present. The test/QA plan stated that, if the analysis of an RB sample indicated a concentration above the MDL for the reference instrument, any contamination source was to be corrected and proper blank readings achieved before proceeding with the verification test. A total of three field RB and one laboratory RB were analyzed. All of the blanks analyzed were below the 0.1-ppb reference MDL for arsenic.

The instrument used for the reference method was initially calibrated using 11 calibration standards, with concentrations ranging between 0.1 and 250 ppb of arsenic. The accuracy of the calibration also was verified after the analysis of every 10 samples by analyzing a 25-ppb QCS. If the QCS analysis differed by more than ±10% from the true value of the standard, the instrument was recalibrated before continuing the test. As shown in Table 4-1, the QCS analyses were always within this required range. The maximum bias from the standard in any QCS analysis was 6.04%.

$\mathrm{LFM_L}$ samples were analyzed to assess whether matrix effects influenced the results of the reference method. The percent recovery (R) of these $\mathrm{LFM_L}$ samples was calculated from the following equation:

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

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 analyte spike. If the percent recovery of an $\mathrm{LFM_L}$ fell outside of the range of 85 to 115%, a matrix effect was suspected. As shown in Table 4-2, all of the $\mathrm{LFM_L}$ results were well within this range, so no matrix effect on the reference analyses is inferred.

Table 4-1. Reference Method QCS Analysis Results

Sample ID	Date of Analysis	Measured Arsenic (ppb)	Actual Arsenic (ppb)	Percent Bias
QCS	12/21/01	24.1	25.0	3.56%
QCS	12/21/01	23.5	25.0	6.04%
QCS	12/21/01	23.8	25.0	4.64%
QCS	12/21/01	23.9	25.0	4.32%
QCS	12/21/01	24.4	25.0	2.52%

Table 4-2. Reference Method LFM_L Analysis Results

LFM_L Sample ID	Date of Analysis	Unspiked Sample Arsenic (ppb)	Spiked Sample Arsenic (ppb)	Spiked Amount Arsenic (ppb)	Percent Recovery
Laboratory RB	12/21/01	<0.1	23.8	25.0	95.3%
Field QCS	12/21/01	10.9	35.7	25.0	99.0%
DW LFM_F	12/21/01	10.6[a]	34.6	25.0	96.2%
LBC-3 Duplicate	12/21/01	2.26	26.6	25.0	97.5%
LC-4	12/21/01	1.37	26.3	25.0	99.7%
SR-4	12/21/01	1.88	26.4	25.0	98.0%

[a] Amount of arsenic in the sample after it was spiked in the field.

Duplicate samples were analyzed to assess the precision of the reference analysis. The relative percent difference (RPD) of the duplicate sample analysis was calculated from the following equation:

$$RPD = \frac{(C - CD)}{(C + CD)/2} \times 100 \qquad (2)$$

Where *C* is the concentration of the sample analysis, and *CD* is the concentration of the sample duplicate analysis. If the RPD was greater than 10%, the instrument was recalibrated before continuing the test. As shown in Table 4-3, the RPDs for the duplicate analysis were all less than 10%. The maximum RPD in any duplicate analysis was 4%.

Table 4-3. Reference Method Duplicate Analysis Results

Sample ID	Date of Analysis	Sample Arsenic (ppb)	Duplicate Sample Arsenic (ppb)	RPD
PT QCS	12/21/2001	9.80	9.81	0%
PT1 (tap)	12/21/2001	1.76	1.76	0%
WW-1	12/21/2001	86.6	86.1	1%
LBC-4	12/21/2001	2.54	2.44	4%
SR QCS	12/21/2001	9.33	9.37	0%

4.2 Audits

4.2.1 Performance Evaluation Audit

A PE audit was conducted to assess the quality of the reference measurements made in this verification test. For the PE audit, an independent, NIST-traceable, certified reference material was obtained from a different commercial supplier than the calibration standards and the field QCS. The PE standard was prepared from a Claritas PPT™ Grade standard purchased through SPEX CertiPrep. Accuracy of the reference method was determined by comparing the measured arsenic concentration using the verification test standards to those obtained using the independently certified PE standard. Percent difference was used to quantify the accuracy of the results. Agreement of the standard within 10% was required for the measurements to be considered acceptable. Failure to achieve this agreement would have triggered recalibration of the reference instrument with the original QC standards and a repeat of the PE comparison. As shown in Table 4-4, the PE sample result was well within this required range.

Table 4-4. Reference Method PE Audit Results

Sample ID	Date of Analysis	Measured Arsenic (ppb)	Actual Concentration Arsenic (ppb)	Percent Agreement
PE-1	12/21/01	23.7	25.0	5.2%

4.2.2 Technical Systems Audit

The Battelle Quality Manager conducted a technical systems audit (TSA) between October 22 and December 21, 2001, to ensure that the verification test was being performed in accordance with the test/QA plan(1) and the AMS Center QMP.(3) The standard solution preparation and PT sample preparation were observed on October 22, the environmental testing (drinking water) on October 25, the testing with PT samples on October 26, and the reference method performance on December 21. As part of the audit, the reference standards and method used were reviewed, actual test procedures were compared to those specified in the test/QA plan, and data acquisition and handling procedures were reviewed. Observations and findings from this audit were documented and submitted to the 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 was 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.(3) Once the assessment report was prepared, the 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 and the audit of data quality were sent to the EPA.

4.4 Data Review

Records generated in the verification test received a one-over-one review within two weeks of generation before these records were used to calculate, evaluate, or report verification results. Table 4-5 summarizes the types of data recorded. The review was performed by a Battelle technical staff member involved in the verification test, but not the staff member that 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 4-5. 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 or ETV field data sheets	Start/end of test event	Used to organize/check test results; manually incorporated in data spreadsheets as necessary
Test parameters (temperature, analyte/ interferant identities, and Nano-Band™ Explorer results)	Battelle	Laboratory record books or ETV field data sheets	When set or changed, or as needed to document test	Used to organize/check test results, manually incorporated in data spreadsheets as necessary
Reference method sample analysis, chain of custody, and results	Battelle	Laboratory record books, data sheets, or data acquisition system, as appropriate	Throughout sample handling and analysis process	Transferred to spreadsheets

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

Chapter 5
Statistical Methods

The statistical methods presented in this chapter were planned for verifying the performance factors listed in Section 3.2. In a few cases, qualitative comparisons are also reported.

5.1 Accuracy

When possible, accuracy was assessed relative to the results obtained from the reference analyses. Samples were analyzed by both the reference method and the portable analyzer being verified. For each sample, accuracy was expressed in terms of a relative bias (*B*) as calculated from the following equation:

$$B = \left| \frac{d}{C_R} \right| \times 100 \qquad (3)$$

where d is the difference between the reading from the Nano-Band™ Explorer and that from the reference method, and C_R is the reference measurement.

In addition, all of the data were judged by a qualitative measure that was not specified in the test/QA plan. If the result from the Nano-Band™ Explorer agreed within 25% of the reference result, the measurement was considered accurate; if it did not, the measurement was considered not to be accurate. The percentage of accurate measurements was determined for each of the three types of water samples as calculated from the following equation:

$$A = \frac{Y}{T} \times 100 \qquad (4)$$

where A is the percent of accurate measurements, Y is the number of measurements within the 25% criterion, and T is the total number of measurements. The criterion of 25% for agreement was based on the measurement resolution of the several portable arsenic analyzers tested and on scientific judgment of the required degree of accuracy for these analyzers. Readings below the detection limit (i.e., <4 ppb) were judged to be in agreement with the reference result if the reference value was in the specified “less than” range.

5.2 Precision

When possible, the standard deviation (*S*) of the results for the replicate samples was calculated and used as a measure of Nano-Band™ Explorer precision at each concentration.

$$S = \left[\frac{1}{n-1} \sum_{k=1}^{n} \left(C_k - \overline{C} \right)^2 \right]^{1/2} \tag{5}$$

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 instrumental precision at each concentration was reported in terms of the relative standard deviation (RSD), e.g.,

$$RSD = \left| \frac{S}{\overline{C}} \right| \times 100 \tag{6}$$

5.3 Linearity

Linearity was assessed by linear regression of Nano-Band™ Explorer results against the reference results, with linearity characterized by the slope, intercept, and correlation coefficient (r). Linearity was tested using PT samples over the range of about 1 to 100 ppb of arsenic.

5.4 Method Detection Limit

The MDL for the Nano-Band™ Explorer was assessed from the seven replicate analyses of a fortified sample with an analyte concentration of 25 ppb. This sample was used for assessment of the MDL of several portable analyzers in this verification. The 25-ppb concentration exceeds five times the 4-ppb nominal detection limit of the Nano-Band™ Explorer, as was called for in the test/QA plan.(1) An approved deviation to that effect was included in the verification file. The MDL was calculated from the following equation:

$$MDL = t \times S \tag{7}$$

where *t* (= 3.14) is the Student's *t* value for a 99% confidence level with n = 7, and *S* is the standard deviation of the replicate samples.(4)

5.5 Matrix Interference Effects

The effect of interfering matrix species on the response of the Nano-Band™ Explorer to arsenic is typically calculated as the ratio of the difference in analytical response to the concentration of interfering species. For example, if adding 500 ppb of an interfering species results in a difference of 10 ppb in the analytical result, the relative sensitivity of the Nano-Band™ Explorer to that interferant would be calculated as 10 ppb/500 ppb = 2%. In this test, three interfering species were added to the samples, all at either low or high concentrations (Section 3.3.2). Thus, it is not possible to determine which of these compounds would be responsible for any observed interferences. Only qualitative observations could be made assessing whether there was a positive or negative effect due to matrix interferences.

5.6 Operator Bias

The results obtained from each operator were compiled independently and subsequently compared. However, since each operator used only a single unit of the Nano-Band™ Explorer, operator bias could be assessed only by assuming that there were no unit-to-unit differences in performance. Furthermore, because of the malfunction in one of the Nano-Band™ Explorer electrode cables, and the subsequent completion of the bulk of the field sample analyses by the vendor representative three weeks after sample collection (see Section 3.5), no definitive comparison of operators could be made. Qualitative observations were made on the results from the three operators.

5.7 Rate of False Positives/False Negatives

The rates of false positives and false negatives of the Nano-Band™ Explorer were assessed relative to the 10-ppb target arsenic level. A false positive result is defined as any result reported to be equal to or greater than the guidance level (10 ppb) and greater than 125% of the reference value, when the reference value is less than that guidance level. Similarly, a false negative result is defined as any result reported below the guidance level and less than 75% of the reference value, when the reference value is greater than that guidance level. The rates of false positives and false negatives were expressed as a percentage of total samples analyzed for each type of sample.

Chapter 6
Test Results

The results of the verification test of the Nano-Band™ Explorer are presented in this section.

6.1 Accuracy

Tables 6-1a-c present the measured arsenic results from analysis of the PT, drinking water, and fresh water samples, respectively. Both reference analyses and Nano-Band™ Explorer results are shown in the tables, and Nano-Band™ Explorer results are shown for the vendor representative and both the Battelle technical and non-technical operators. All observed results were multiplied by 1.25 to account for the dilution of the samples from 40 mL to 50 mL by the addition of the reagents. Nano-Band™ Explorer readings of less than the nominal 4-ppb detection limit were assigned a value of <4 ppb.

The field spike results indicate apparent inconsistencies in some of the spike concentrations. The WW LFM_F and LBC-4 LFM_F samples apparently were not spiked in the field, and the TW LFM_F sample may have been spiked twice. However, these spiking errors have no effect on the usefulness of the data.

Tables 6-2a-c show the percent accuracy results of the Nano-Band™ Explorers. Shown in the second and third columns in each of Tables 6-2a-c are the percent bias values determined according to Equation 3, in Section 5.1. Bias was not calculated for values reported as <4 ppb. The bias values shown in Table 6-2a ranged from 3 to 64% for the non-technical operator and 1 to 64% for the technical operator for individual PT samples. The bias values ranged from 2 to 32% for the non-technical operator on individual well water samples, and 25 to 92% for the vendor representative for WW and TW samples stored at 4°C for three weeks (Table 6-2b). Percent bias values were up to 499% for the non-technical operator for individual FW samples, and up to 68% for the vendor representative for individual FW samples stored at 4°C and analyzed three weeks after collection (Table 6-2c).

Some of the highest bias values with the Nano-Band™ Explorer were found at the lowest arsenic concentrations. As a result, it is instructive to consider the accuracy results with concentrations near or above the 10-ppb maximum contaminant level for arsenic. With the PT samples (Tables 6-1a and 6-2a), biases of 5 to 42% were found with one QCS of 9.80 ppb. With the PT3 sample of 9.2 ppb, the non-technical operator reported all non-detects (<4 ppb), whereas the bias

Table 6-1a. Results from Laboratory Performance Test Sample Analyses

Sample	Non-Technical Arsenic (ppb)	Technical Arsenic (ppb)	Reference Method Arsenic (ppb)
Laboratory RB	<4	<4	<0.1
Laboratory RB	<4	<4	<0.1
Laboratory RB	NA	<4	<0.1
Laboratory RB	NA	<4	<0.1
Laboratory RB	NA	<4	<0.1
Laboratory RB	NA	<4	<0.1
QCS	12.3	8.66	9.80
QCS	10.3	5.73	9.80
QCS	NA	9.25	9.80
QCS	NA	13.8	9.80
QCS	NA	6.11	9.80
PT1-1	<4	<4	1.00
PT1-2	<4	<4	1.00
PT1-3	<4	<4	1.00
PT1-4	<4	<4	1.00
PT2-1	<4	<4	2.92
PT2-2	<4	<4	2.92
PT2-3	<4	<4	2.92
PT2-4	<4	<4	2.92
PT3-1	<4	11.5	9.20
PT3-2	<4	9.14	9.20
PT3-3	<4	7.53	9.20
PT3-4	<4	6.86	9.20
PT4-1	22.3	34.1	29.3
PT4-2	20.3	29.0	29.3
PT4-3	32.0	29.1	29.3
PT4-4	25.1	23.5	29.3
PT5-1	106	119	92.6
PT5-2	95.1	120	92.6
PT5-3	128	119	92.6
PT5-4	129	113	92.6
PT6-1	11.0	18.4	23.5
PT6-2	<4	8.38	23.5
PT6-3	8.5	17.1	23.5
PT6-4	<4	23.0	23.5
PT6-5	<4	20.3	23.5
PT6-6	<4	16.5	23.5
PT6-7	<4	16.3	23.5

NA: Not analyzed.

Table 6-1b. Results from Drinking Water Analyses

Sample	Non-Technical Arsenic (ppb)	Technical Arsenic (ppb)	Vendor Representative Arsenic [a]	Reference Method Arsenic (ppb)[b]
Laboratory RB	<4	<4	NA	<0.1
QCS	<4	<4	NA	10.9
DW-1	<4	<4	NA	0.87
DW-2	<4	<4	NA	0.87
DW-3	<4	<4	NA	0.87
DW-4	<4	<4	NA	0.87
DW LFM$_F$	<4	<4	NA	10.6
Laboratory RB	<4	NA	<4	<0.1
QCS	<4	NA	8.13	10.9
WW-1	88.1	NA	8.13	86.6
WW-2	74.1	NA	8.50	86.6
WW-3	71.4	NA	7.13	86.6
WW-4	70.4	NA	9.25	86.6
WW LFM$_F$	67.0	NA	9.38	82.1
Laboratory RB	<4	NA	<4	<0.1
QCS	<4	NA	<4	10.9
TW-1	22.3	NA	9.00	26.0
TW-2	30.0	NA	8.13	26.0
TW-3	29.8	NA	8.50	26.0
TW-4	27.1	NA	8.75	26.0
TW LFM$_F$	34.6	NA	26.6	50.8

[a] The operator was the vendor representative. These measurements were carried out three weeks after sampling on samples stored at 4°C.

[b] Only one aliquot of each sample was analyzed by the reference method (except for the laboratory RB). Multiple aliquots of each sample were analyzed by the Nano-Band™ Explorer.

NA: Not analyzed.

Table 6-1c. Results from Freshwater Analyses

Sample	Non-Technical Arsenic (ppb)	Vendor Representative Arsenic (ppb)[a]	Reference Method Arsenic (ppb)
Laboratory RB	<4	<4	<0.1
QCS	16.1	5.64	9.33
SR-1	<4	<4	1.73
SR-2	<4	<4	1.72
SR-2 Duplicate	4.86	<4	1.71
SR-3	<4	<4	2.03
SR-4	<4	<4	1.88
SR-1 LFM$_F$	8.56	4.13	11.6
Laboratory RB	<4	<4	<0.1
QCS	13.5	15.9	9.43
LC-1	<4	<4	2.13
LC-2	<4	<4	1.30
LC-3	<4	<4	1.44
LC-4	<4	<4	1.37
LC-4 Duplicate	<4	<4	1.36
LC-3 LFM$_F$	9.91	<4	12.0
Laboratory RB	<4	<4	<0.1
QCS	7.21	9.63	9.81
LBC-1	<4	<4	2.48
LBC-2	<4	<4	2.60
LBC-3	<4	<4	2.14
LBC-3 Duplicate	<4	<4	2.26
LBC-4	<4	<4	2.54
LBC-4 LFM$_F$	14.3	<4	2.38

[a] The operator was the vendor representative. These measurements were carried out three weeks after sampling on samples stored at 4°C.

Table 6-2a. Accuracy of the Nano-Band™ Explorer with Laboratory Performance Test Samples

Sample	Bias[a] Non-Technical	Bias[a] Technical	Within Range (Y/N)[b] Non-Technical	Within Range (Y/N)[b] Technical
Laboratory RB	–[c]	–[c]	Y	Y
Laboratory RB	–[c]	–[c]	Y	Y
Laboratory RB	NA	–[c]	NA	Y
Laboratory RB	NA	–[c]	NA	Y
Laboratory RB	NA	–[c]	NA	Y
Laboratory RB	NA	–[c]	NA	Y
QCS	25%	12%	Y	Y
QCS	5%	42%	Y	N
QCS	NA	6%	NA	Y
QCS	NA	40%	NA	N
QCS	NA	38%	NA	N
PT1-1	–[c]	–[c]	Y	Y
PT1-2	–[c]	–[c]	Y	Y
PT1-3	–[c]	–[c]	Y	Y
PT1-4	–[c]	–[c]	Y	Y
PT2-1	–[c]	–[c]	Y	Y
PT2-2	–[c]	–[c]	Y	Y
PT2-3	–[c]	–[c]	Y	Y
PT2-4	–[c]	–[c]	Y	Y
PT3-1	–[c]	25%	N	Y
PT3-2	–[c]	1%	N	Y
PT3-3	–[c]	18%	N	Y
PT3-4	–[c]	25%	N	Y
PT4-1	24%	17%	Y	Y
PT4-2	31%	1%	N	Y
PT4-3	9%	1%	Y	Y
PT4-4	14%	20%	Y	Y
PT5-1	15%	28%	Y	N
PT5-2	3%	29%	Y	N
PT5-3	38%	29%	N	N
PT5-4	39%	22%	N	Y
PT6-1	53%	22%	N	Y
PT6-2	–[c]	64%	N	N
PT6-3	64%	27%	N	N
PT6-4	–[c]	2%	N	Y
PT6-5	–[c]	14%	N	Y
PT6-6	–[c]	30%	N	N
PT6-7	–[c]	31%	N	N

[a] Percent bias calculated according to Equation 3, Section 5.1.

[b] Y = result within ±25% of reference, or reference value within < range; N = result not within ±25% of reference, or reference value not within < range.

[c] Non-detect, no calculation of bias can be made.

NA: Not analyzed.

Table 6-2b. Accuracy of the Nano-Band™ Explorer with Drinking Water Samples

Sample	Bias[a] Non-Technical	Bias[a] Technical	Bias[a] Vendor Respresentative[b]	Within Range (Y/N)[c] Non-Technical	Within Range (Y/N)[c] Technical	Within Range Vendor Representative[b]
Laboratory RB	–[d]	–[d]	NA	Y	Y	NA
QCS	–[d]	–[d]	NA	N	N	NA
DW-1	–[d]	–[d]	NA	Y	Y	NA
DW-2	–[d]	–[d]	NA	Y	Y	NA
DW-3	–[d]	–[d]	NA	Y	Y	NA
DW-4	–[d]	–[d]	NA	Y	Y	NA
DW LFM$_F$	–[d]	–[d]	NA	N	N	NA
Laboratory RB	–[d]	NA	–[d]	Y	NA	Y
QCS	–[d]	NA	25%	N	NA	Y
WW-1	2%	NA	91%	Y	NA	N
WW-2	14%	NA	90%	Y	NA	N
WW-3	18%	NA	92%	Y	NA	N
WW-4	19%	NA	89%	Y	NA	N
WW LFM$_F$	18%	NA	89%	Y	NA	N
Laboratory RB	–[d]	NA	–[d]	Y	NA	Y
QCS	–[d]	NA	–[d]	N	NA	N
TW-1	14%	NA	65%	Y	NA	N
TW-2	15%	NA	69%	Y	NA	N
TW-3	14%	NA	67%	Y	NA	N
TW-4	4%	NA	66%	Y	NA	N
TW LFM$_F$	32%	NA	48%	N	NA	N

[a] Percent bias calculated according to Equation 3, Section 5.1.

[b] The operator was the vendor representative. These measurements were carried out three weeks after sampling on samples stored at 4°C.

[C] Y = result within ±25% of reference, or reference value within < range; N = result not within ±25% of reference, or reference value not within < range.

[d] Non-detect, no calculation of bias can be made.

NA: Not analyzed.

Table 6-2c. Accuracy of the Nano-Band™ Explorer with Freshwater Samples

Sample	Bias[a] Non-Technical	Bias[a] Vendor Representative[b]	Within Range (Y/N)[c] Non-Technical	Within Range (Y/N)[c] Vendor Representative[b]
Laboratory RB	–[d]	–[d]	Y	Y
QCS	73%	40%	N	N
SR-1	–[d]	–[d]	Y	Y
SR-2	–[d]	–[d]	Y	Y
SR-2 Duplicate	184%	–[d]	N	Y
SR-3	–[d]	–[d]	Y	Y
SR-4	–[d]	–[d]	Y	Y
SR-1 LFM$_F$	26%	65%	N	N
Laboratory RB	–[d]	–[d]	Y	Y
QCS	43%	68%	N	N
LC-1	–[d]	–[d]	Y	Y
LC-2	–[d]	–[d]	Y	Y
LC-3	–[d]	–[d]	Y	Y
LC-4	–[d]	–[d]	Y	Y
LC-4 Duplicate	–[d]	–[d]	Y	Y
LC-3 LFM$_F$	17%	–[d]	Y	N
Laboratory RB	–[d]	–[d]	Y	Y
QCS	26%	2%	N	Y
LBC-1	–[d]	–[d]	Y	Y
LBC-2	–[d]	–[d]	Y	Y
LBC-3	–[d]	–[d]	Y	Y
LBC-3 Duplicate	–[d]	–[d]	Y	Y
LBC-4	–[d]	–[d]	Y	Y
LBC-4 LFM$_F$	499%	–[d]	N	Y

[a] Percent bias calculated according to Equation 3, Section 5.1.

[b] The operator was the vendor representative. These measurements were carried out three weeks after sampling on samples stored at 4°C.

[c] Y = result within ±25% of reference, or reference value within < range; N = result not within ±25% of reference, or reference value not within < range.

[d] Non-detect, no calculation of bias can be made.

results with the technical operator were 1 to 25%. At higher arsenic levels of 23 to 93 ppb, the non-technical operator's results show biases of 3 to 64%, as well as five non-detects. The vendor representative's results show biases of 1 to 64% for samples stored at 4°C and analyzed three weeks after collection. Drinking water samples (Tables 6-1b and 6-2b) of 10.6 and 10.9 ppb produced largely non-detects with the Nano-Band™ Explorer, with one analysis by the vendor representatives showing a bias of 25%. At arsenic levels of 26 to 87 ppb, biases with WW and TW samples were 2 to 32% for the non-technical operator and 48 to 92% for the vendor representative. For the FW samples (Tables 6-1c and 6-2c), bias values of 17 to 73% for the non-technical and 2 to 68% for the vendor representative were found at arsenic levels of 9.3 to 12 ppb.

In addition to the quantitative bias results, the qualitative accuracy was compared using Equation 4 in Section 5.1. The right-hand columns in Tables 6-2a-c show the assignment of each Nano-Band™ Explorer result, in terms of whether that result fell within 25% of the reference value. The results of this qualitative evaluation of accuracy are shown in Table 6-3, which lists the overall percentage of results meeting the ±25% criterion for each operator and sample type. Table 6-3 shows that the qualitative accuracy of the Nano-Band™ Explorer for the PT samples was 55% for the non-technical operator and 74% for the technical operator. The qualitative accuracy for the drinking water samples was 71% for both the non-technical and technical operators. The qualitative accuracy for the WW and TW samples was 79% for the non-technical operator and 21% for the vendor representative, and for the FW samples was 75% for the non-technical operator and 83% for the vendor representative.

Table 6-3. Summary of Qualitative Accuracy Results

	Percent Accurate Within 25% (Non-Technical Operator)	Percent Accurate Within 25% (Technical Operator)	Percent Accurate Within 25% (Vendor Representative[a])
Laboratory PT samples	55	74	NA
DW samples	71	71	NA
WW and TW samples	79	NA	21
FW samples	75	NA	83

[a] The operator was the vendor representative. These measurements were carried out three weeks after sampling on samples stored at 4°C.

NA: Not analyzed.

6.2 Precision

Tables 6-4a and b, respectively, show the data used to evaluate the RSD of the Nano-Band™ Explorer for the replicate laboratory PT and drinking water samples, along with the percent RSD for each set of replicate analyses determined according to Equation 6 in Section 5.2. Percent RSD was not calculated if all of the results for a set of replicates were below the nominal detection limit (i.e., <4 ppb). If some, but not all, of the results for a set of replicates were reported as <4 ppb, then those results were assigned a value of 2.0 ppb for calculation of precision. The RSD ranged from 13 to 91% for the non-technical operator and 3 to 37% for the technical operator on the PT samples (Table 6-4a). The RSD for the drinking water samples was 11 to 13% for the non-technical operator and 4 to 11% for the vendor representative (Table 6-4b). In general, better precision was found at higher arsenic concentrations, but the non-technical operator reported several non-detects even at 9.2 ppb (PT3) and 23.5 ppb (PT6) (Table 6-4a). Measuring samples stored at 4°C for three weeks, the vendor representative reported low readings with 86.6 ppb (WW) and 26 ppb (TW) samples (Table 6-4b).

Table 6-4a. Precision Results for Nano-Band™ Explorer from Laboratory Performance Test Samples

Sample	Reference Concentration (ppb)	Non-Technical[a] Arsenic (ppb)	Technical[a] Arsenic (ppb)
QCS	9.80	12.3	8.66
QCS		10.3	5.73
QCS		NA	9.25
QCS		NA	13.8
QCS		NA	6.11
%RSD		**13**	**37**
PT1-1	1.0	<4	<4
PT1-2		<4	<4
PT1-3		<4	<4
PT1-4		<4	<4
%RSD		—[b]	—[b]
PT2-1	2.9	<4	<4
PT2-2		<4	<4
PT2-3		<4	<4
PT2-4		<4	<4
%RSD		—[b]	—[b]
PT3-1	9.2	<4	11.5
PT3-2		<4	9.14
PT3-3		<4	7.53
PT3-4		<4	6.86
%RSD		—[b]	**24**
PT4-1	29.3	22.3	34.1
PT4-2		20.3	29.0
PT4-3		32.0	29.1
PT4-4		25.1	23.5
%RSD		**21**	**15**
PT5-1	92.6	106	119
PT5-2		95.1	120
PT5-3		128	119
PT5-4		129	113
%RSD		**14**	**3**
PT6-1	23.5	11.0	18.4
PT6-2		<4	8.38
PT6-3		8.5	17.1
PT6-4		<4	23.0
PT6-5		<4	20.3
PT6-6		<4	16.5
PT6-7		<4	16.3
%RSD		**91**	**26**

[a] For the purpose of calculating %RSD, all "less than" values are given the value of half the detection limit, i.e., as 2.0 ppb.

[b] No %RSD could be calculated.

NA: Not analyzed.

Table 6-4b. Precision Results for Nano-Band™ Explorer from Drinking Water Samples

Sample	Reference Concentration (ppb)	Non-Technical[a] Arsenic (ppb)	Technical[a] Arsenic (ppb)	Vendor Representative[c] Arsenic (ppb)
DW-1	0.87	<4	<4	NA
DW-2		<4	<4	NA
DW-3		<4	<4	NA
DW-4		<4	<4	NA
%RSD		–[b]	–[b]	NA
WW-1	86.6	88.1	NA	8.13
WW-2		74.1	NA	8.50
WW-3		71.4	NA	7.13
WW-4		70.4	NA	9.25
%RSD		**11**	NA	**11**
TW-1	26.0	22.3	NA	9.0
TW-2		30.0	NA	8.13
TW-3		29.8	NA	8.50
TW-4		27.1	NA	8.75
%RSD		**13**	NA	**4**

[a] For the purpose of calculating standard deviation, all “less than” values are considered as half the detection limit, i.e., as 2.0 ppb.

[b] No %RSD could be calculated.

[C] The operator was the vendor representative. These measurements were carried out three weeks after sampling on samples stored at 4°C.

NA: Not analyzed.

6.3 Linearity

The linearity of the Nano-Band™ Explorer was assessed by means of a linear regression of the Nano-Band™ Explorer results against the reference method results, using the 27 data points from the PT samples ranging from 1 to 93 ppb arsenic (Table 6-1a). In this regression, results reported as <4 ppb by the Nano-Band™ Explorer were assigned a value of 2 ppb, i.e., half the nominal detection limit. Figure 6-1 shows plots of the Nano-Band™ Explorer results from the technical and non-technical operators versus the reference method results. The one-to-one line is also shown in Figure 6-1. A linear regression of the data in Figure 6-1 gives the following regression equations:

> with the Nano-Band™ Explorer for the non-technical operator,
> ppb = 1.28 (±0.16) x (reference, ppb) - 10.73 (±6.37) ppb, with r = 0.956, and
>
> with the Nano-Band™ Explorer for the technical operator,
> ppb = 1.29 (±0.08) x (reference, ppb) - 5.56 (±3.29) ppb, with r = 0.988,

where the values in parentheses represent the 95% confidence interval of the slope and intercept. These two regression results are very similar for the two operators, despite the differences

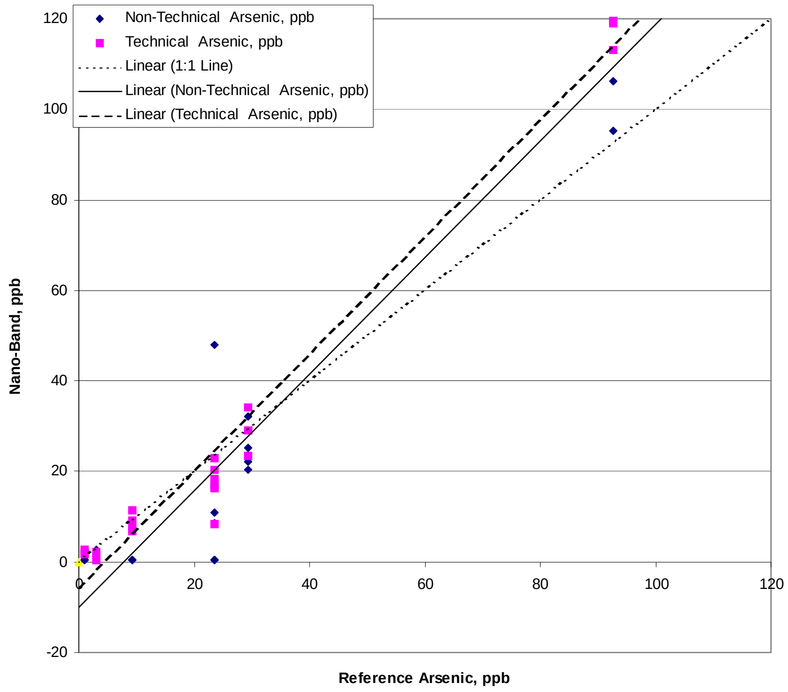

Figure 6-1. Comparison of Nano-Band™ Explorer to Reference Method Results from PT Samples

between their results noted above. Both regressions show a negative intercept, with a positive bias in Nano-Band™ Explorer results at the highest concentrations tested.

6.4 Method Detection Limit

The manufacturer's estimated detection limit for the Nano-Band™ Explorer is 4 ppb. The MDL was determined by analyzing seven replicate samples at a concentration of 25 ppb. The data and parameters needed for calculating MDL by Equation 7 in Section 5.4 are shown in Table 6-5. Shown are the values of S and *t* needed for the calculation and the resulting values for the MDL. The calculated MDL for the non-technical operator was 12.1 ppb, and, for the technical operator, it was 14.2 ppb.

Table 6-5. Method Detection Limit Results for the Nano-Band™ Explorer

	Non-Technical Arsenic (ppb)[a]	**Technical Arsenic (ppb)**[b]
PT6-1	11.0	18.4
PT6-2	<4	8.38
PT6-3	8.53	17.1
PT6-4	<4	23.0
PT6-5	<4	20.3
PT6-6	<4	16.5
PT6-7	<4	16.3
Std. Deviation (S)	3.85	4.54
t at n=7 [b]	3.14	3.14
MDL [c]	12.1	14.2

[a] For the purpose of calculating standard deviation, all "less than" values are considered as half the manufacturer's estimated detection limit, i.e., as 2 ppb.

[b] *t* is the Student's value for a 99% confidence level.

[c] MDL = *t* x S (see Section 5.4).

6.5 Matrix Interference Effects

Tables 6-6a and b show the analytical results from laboratory PT samples with low and high levels of interference, respectively. A total of eight replicate samples were analyzed with low amounts of interferences, and a total of eight samples were analyzed with high amounts of interferences. Both sets of PT samples (LI and HI) contained about 9.9 ppb of arsenic as determined by the reference method. The non-technical operator detected arsenic in none of these samples. On the other hand, for the samples with low levels of interferants, the technical operator observed values between 7.61 and 12.8 ppb, with an average value of 10.4 ppb of arsenic compared to the reference value of 9.91 ppb. Similarly, for the samples with high levels of interferants, the technical operator observed values between 8.45 and 13.9 ppb, with an average of 11.5 ppb compared to the reference value of 9.94 ppb. Clearly the results were quite different for the technical operator than for the non-technical operator. The results obtained by the technical operator do not indicate any significant effect from the interferants. The apparent negative effect of the interfering species for the non-technical operator may result from the operator's skill level rather than from the interfering compounds.

Table 6-6a. Results from Laboratory Performance Test Samples with Low-Level Interferences

	Non-Technical Arsenic (ppb)	Technical Arsenic (ppb)
LI-1	<4	11.6
LI-2	<4	12.2
LI-3	<4	10.2
LI-4	<4	7.70
LI-5	<4	12.8
LI-6	<4	12.3
LI-7	<4	8.59
LI-8	<4	7.61

Table 6-6b. Results from Laboratory Performance Test Samples with High-Level Interferences

	Non-Technical Arsenic (ppb)	Technical Arsenic (ppb)
HI-1	<4	12.6
HI-2	<4	11.5
HI-3	<4	11.1
HI-4	<4	11.6
HI-5	<4	8.91
HI-6	<4	8.45
HI-7	<4	13.9
HI-8	<4	13.8

6.6 Operator Bias

The use of only a single unit of the Nano-Band™ Explorer by each operator, the malfunction of one unit, and the subsequent completion of analyses by a vendor representative, prevent assessment of operator bias. However, the frequent non-detects reported by the non-technical operator with the PT samples (Sections 6.1, 6.2, and 6.4) and matrix interference samples (Section 6.5) suggest that the non-technical operator had greater difficulty with the Nano-Band™ Explorer than did the technical operator. None of the operators reported highly accurate results.

6.7 Rate of False Positives/False Negatives

Tables 6-7 and 6-8, respectively, show the data and results for the rates of false positives and false negatives obtained from the Nano-Band™ Explorer. All PT and environmental samples (Table 3-1) were considered for this evaluation.

6.7.1 False Positives

Tables 6-7a-b show that the reference arsenic concentration was less than the target midpoint of 10 ppb in 44 samples. The non-technical operator reported non-detects for all 44 of those samples. The Battelle technical operator reported 12 results that exceeded 10 ppb (Table 6-7a). Four of these results were greater than 125% of the reference value and are considered to be false positives. The vendor representative reported only non-detects for the FW samples he analyzed (Table 6-7b). As shown in Table 6-7c, the resulting rate of false positives for the technical operator was 13%, and the rate of false positives for the non-technical operator and the vendor representative was 0%.

6.7.2 False Negatives

Tables 6-8a-b show that 23 samples had reference arsenic concentrations greater than the target midpoint of 10 ppb. The non-technical operator reported five false negatives, including four non-detects at an arsenic concentration of 23.5 ppb (Table 6-8a). The technical operator had one false negative out of 15 samples (Table 6-8a), whereas the vendor representative had false negatives on all eight of the WW and TW samples that had been stored at 4°C after collection. As Table 6-8c shows, for these samples the non-technical operator had a false negative rate of 22%, the technical operator had a false negative rate of 7%, and the vendor representative had a false negative rate of 100%.

Table 6-7a. Rate of False Positives from Nano-Band™ Explorer: Performance Test, Interference, and Drinking Water Samples

	Non-Technical Arsenic (ppb)	Technical Arsenic (ppb)	Reference Method Arsenic (ppb)	Non-Technical False Positive (Y/N)	Technical False Positive (Y/N)
PT1-1	<4	<4	1.00	N	N
PT1-2	<4	<4	1.00	N	N
PT1-3	<4	<4	1.00	N	N
PT1-4	<4	<4	1.00	N	N
PT2-1	<4	<4	2.92	N	N
PT2-2	<4	<4	2.92	N	N
PT2-3	<4	<4	2.92	N	N
PT2-4	<4	<4	2.92	N	N
PT3-1	<4	11.5	9.20	N	N
PT3-2	<4	9.14	9.20	N	N
PT3-3	<4	7.53	9.20	N	N
PT3-4	<4	6.86	9.20	N	N
LI-1	<4	11.6	9.91	N	N
LI-2	<4	12.2	9.91	N	N
LI-3	<4	10.2	9.91	N	N
LI-4	<4	7.70	9.91	N	N
LI-5	<4	12.8	9.91	N	Y
LI-6	<4	12.3	9.91	N	N
LI-7	<4	8.59	9.91	N	N
LI-8	<4	7.61	9.91	N	N
HI-1	<4	12.6	9.94	N	Y
HI-2	<4	11.5	9.94	N	N
HI-3	<4	11.1	9.94	N	N
HI-4	<4	11.6	9.94	N	N
HI-5	<4	8.91	9.94	N	N
HI-6	<4	8.45	9.94	N	N
HI-7	<4	13.9	9.94	N	Y
HI-8	<4	13.8	9.94	N	Y
DW-1	<4	<4	0.87	N	N
DW-2	<4	<4	0.87	N	N
DW-3	<4	<4	0.87	N	N
DW-4	<4	<4	0.87	N	N

Y =yes
N = no

Table 6-7b. Rate of False Positives from Nano-Band™ Explorer: Freshwater Samples

	Non-Technical Arsenic (ppb)	Vendor Representative[a] Arsenic (ppb)	Reference Method Arsenic (ppb)	Non-Technical False Positive (Y/N)	Vendor Representative[a] False Positive (Y/N)
SR-1	<4	<4	1.73	N	N
SR-2	<4	<4	1.72	N	N
SR-3	<4	<4	2.03	N	N
SR-4	<4	<4	1.88	N	N
LC-1	<4	<4	2.13	N	N
LC-2	<4	<4	1.30	N	N
LC-3	<4	<4	1.44	N	N
LC-4	<4	<4	1.37	N	N
LBC-1	<4	<4	2.48	N	N
LBC-2	<4	<4	2.60	N	N
LBC-3	<4	<4	2.14	N	N
LBC-4	<4	<4	2.54	N	N

[a] The operator was the vendor representative. These measurements were carried out three weeks after sampling on samples stored at 4°C.

Y = yes
N = no

Table 6-7c. Summary of False Positives from Nano-Band™ Explorer

	Non-Technical	Technical	Vendor Representative
Total number of applicable samples	44	32	12
Total false positives	0	4	0
Percent false positives	0	13	0

Table 6-8a. Rate of False Negatives from Nano-Band™ Explorer: Performance Test Samples

	Non-Technical Arsenic (ppb)	Technical Arsenic (ppb)	Reference Method Arsenic (ppb)	Non-Technical False Negative (Y/N)	Technical False Negative (Y/N)
PT4-1	22.3	34.1	29.3	N	N
PT4-2	20.3	29.0	29.3	N	N
PT4-3	32.0	29.1	29.3	N	N
PT4-4	25.1	23.5	29.3	N	N
PT5-1	106	119	92.6	N	N
PT5-2	95.1	120	92.6	N	N
PT5-3	128	119	92.6	N	N
PT5-4	129	113	92.6	N	N
PT6-1	11.0	18.4	23.5	N	N
PT6-2	<4	8.38	23.5	Y	Y
PT6-3	8.53	17.1	23.5	Y	N
PT6-4	48	23.0	23.5	N	N
PT6-5	<4	20.3	23.5	Y	N
PT6-6	<4	16.5	23.5	Y	N
PT6-7	<4	16.3	23.5	Y	N

Y = Yes
N = No

Table 6-8b. Rate of False Negatives from Nano-Band™ Explorer: Freshwater Samples

	Non-Technical Arsenic (ppb)	Vendor Representative[a] Arsenic (ppb)	Reference Method Arsenic (ppb)	Non-Technical False Negative (Y/N)	Vendor Representative[a] False Negative (Y/N)
WW-1	88.1	8.13	86.6	N	Y
WW-2	74.1	8.50	86.6	N	Y
WW-3	71.4	7.13	86.6	N	Y
WW-4	70.4	9.25	86.6	N	Y
TW-1	22.3	9.00	26.0	N	Y
TW-2	30.0	8.13	26.0	N	Y
TW-3	29.8	8.50	26.0	N	Y
TW-4	27.1	8.75	26.0	N	Y

[a] The operator was the vendor representative. These measurements were carried out three weeks after sampling on samples stored at 4˚C.

Y = yes
N = no

Table 6-8c. Summary of False Negatives from Nano-Band™ Explorer

	Non-Technical	Technical	Vendor Representative
Total number of applicable samples	23	15	8
Total false negatives	5	1	8
Percent false negatives	22	7	100

6.8 Other Factors

The operators felt that the Nano-Band™ Explorer is a challenge to use. Often they observed peaks near the expected location of the arsenic peak that were not identified as, but may have been, arsenic. More in-depth knowledge of the Nano-Band™ Explorer beyond what is in the manual may have helped. The Nano-Band™ Explorer requires some technical ability that at times seemed beyond the capabilities of the non-technical operator. The non-technical operator could follow the directions for operating the Nano-Band™ Explorer, but had no idea how it was making the measurement or if the Nano-Band™ Explorer was operating properly. When the Nano-Band™ Explorer used by the technical operator malfunctioned, the operator was unable to troubleshoot the Nano-Band™ Explorer effectively, despite numerous telephone conversations with the manufacturer. At least currently, experience and knowledge are important factors in operating the Nano-Band™ Explorer. The Nano-Band™ Explorer is lightweight, easy to transport by car, and can be carried easily through fields and wooded areas. The instrument needs a clear flat surface so the reagents can be accurately measured and the burner safely operated. Seven samples can be prepared at the same time. Sample preparation takes approximately one hour, and the analysis can be performed in less than one minute per sample.

The Nano-Band™ Explorer requires some reagent preparation prior to entering the field. The reagents include acids and air-sensitive compounds that must be handled with care. The user should wear gloves during reagent preparation.

6.8.1 Costs

The Nano-Band™ Explorer sells for $8,000. This includes the battery-powered, rechargeable instrument that runs continuously for 40 hours and recharges in four hours; software; one Nano-Band™ Explorer electrode; auxiliary electrode; reference electrode; cleaning and reconditioning kit for the electrodes; and a temperature sensor. The price does not include a laptop computer necessary to run the instrument.

6.8.2 Data Completeness

All portions of the verification test were completed, and all data that were to be recorded were successfully acquired. The non-technical operator mistakenly analyzed only two of the required blanks and two of the required QCS samples; otherwise, data completeness was 100%. However, it was necessary for a representative of the vendor to analyze a portion of the field samples in the laboratory, after repairing the instrument operated by the technical operator. These tests were performed on samples preserved at 4°C and stored for three weeks prior to measurement.

Chapter 7
Performance Summary

The performance of Nano-Band™ Explorer evaluated in this verification test was inconsistent. An evaluation of the accuracy showed that the bias values for the individual PT samples ranged from 3 to 64% for the non-technical operator and 1 to 64% for the technical operator. The bias for the non-technical operator for the individual WW and TW samples was 2 to 32%, and up to 499% for the FW samples. Due to instrument failure, the technical operator did not analyze the WW, TW, or FW samples. These samples were stored at 4ºC for three weeks before analysis in the laboratory by the vendor representative. The bias for these individual samples was 25 to 92% for the WW and TW samples, and up to 68% for the FW samples. Similar ranges of bias were found when only samples containing 10 ppb or more of arsenic were considered.

An additional criterion for accuracy was the percentage of samples for which the Nano-Band™ Explorer result was within 25% of the reference result. By this criterion, the qualitative accuracy of the Nano-Band™ Explorer for the PT samples was 55% for the non-technical operator and 74% for the technical operator. The qualitative accuracy for the municipal drinking water samples was 71% for both the non-technical and technical operators. The qualitative accuracy for the WW and TW samples was 79% for the non-technical operator, and 21% for the vendor representative. The qualitative accuracy for the FW samples was 75% for the non-technical operator and 83% for the vendor representative.

The precision of the Nano-Band™ Explorer was determined by calculating the percent RSD of replicate analyses. The RSD ranged from 13 to 91% for the non-technical operator and from 3 to 37% for the technical operator on the PT samples. The RSD for the drinking water samples was 11 to 13% for the non-technical operator and 4 to 11% for the vendor representative.

The linearity of response of the Nano-Band™ Explorer was assessed using PT samples containing from 1 to 93 ppb arsenic. The linear regression for the Nano-Band™ Explorer for the non-technical operator was ppb = 1.28 (±0.16) × (reference, ppb) – 10.73 (±6.37) ppb with r = 0.956. The corresponding result for the technical operator was ppb = 1.29 (±0.08) × (reference, ppb) –5.56 (±3.29) ppb with r = 0.988.

The manufacturer's nominal detection limit for the Nano-Band™ Explorer is 4 ppb. The MDL was determined by analyzing seven replicate samples at a concentration of 25 ppb. The calculated MDL was 12.1 ppb for the non-technical operator and 14.2 ppb for the technical operator.

The Nano-Band™ Explorer did not appear to be affected by matrix interferences added to the samples. However, the data from the two operators were quite different, with the non-technical operator reporting no detectable arsenic in any of the 16 matrix test samples. In contrast, the technical operator reported an average value of 10.4 ppb of arsenic compared to the reference value of 9.91 ppb for the samples with low levels of interferants, and an average value of 11.5 ppb compared to the reference value of 9.94 ppb for the samples with high levels of interferants.

The rates of false positives and false negatives of the Nano-Band™ Explorer were assessed relative to the reference method using 10 ppb of arsenic as the decision level. The rate of false positives for the Nano-Band™ Explorer was 0% for the non-technical operator, 13% for the technical operator, and 0% for the vendor representative. The rate of false negatives was 22% for the non-technical operator, 7% for the technical operator, and 100% for the vendor representative (who analyzed WW and TW samples stored for three weeks at 4°C).

The Battelle operators felt that the Nano-Band™ Explorer is a challenge to use. The Nano-Band™ Explorer required some technical ability that at times seemed beyond the capabilities of the non-technical operator. However, none of the operators, including a representative of the Nano-Band™ Explorer's vendor, consistently achieved expected results in this test. The Nano-Band™ Explorer sells for $8,000. The samples take approximately one hour to prepare prior to analysis, seven samples can be prepared simultaneously, and the analysis takes less than one minute per sample.

Chapter 8
References

1. *Test/QA Plan for Verification of Portable Analyzers*, Battelle, Columbus, Ohio, Version 2.

2. U.S. EPA Method 200.8, *Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma Mass Spectrometry*, Revision 5.5, April 1991.

3. *Quality Management Plan (QMP) for the ETV Advanced Monitoring Systems Pilot*, Version 2.0, U.S. EPA Environmental Technology Verification Program, Battelle, Columbus, Ohio, October 2000.

4. *U.S. Code of Federal Regulations*, Title 40, Part 136, Appendix B.