

US EPA ARCHIVE DOCUMENT

July 2002

# Environmental Technology Verification Report

## AS-TOP WATER ARSENIC TEST KIT

Prepared by



Battelle

Under a cooperative agreement with



ET ✓ ET ✓ ET ✓

July 2002

# Environmental Technology Verification Report

ETV Advanced Monitoring Systems Center

## As-Top Water Arsenic Test Kit

by

Adam Abby  
Thomas Kelly  
Charles Lawrie  
Karen Riggs

Battelle  
Columbus, Ohio 43201

## Notice

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

## Foreword

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

The Environmental Technology Verification (ETV) Program has been established by the EPA to verify the performance characteristics of innovative environmental technology across all media and to report this objective information to permittees, buyers, and users of the technology, thus substantially accelerating the entrance of new environmental technologies into the marketplace. Verification organizations oversee and report verification activities based on testing and quality assurance protocols developed with input from major stakeholders and customer groups associated with the technology area. ETV consists of 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

The authors wish to acknowledge the support of all those who helped plan and conduct the verification test, analyze the data, and prepare this report. In particular we would like to thank A. J. Savage, Raj Mangaraj, Daniel Turner, and Bea Weaver of Battelle. We also acknowledge the assistance of AMS Center stakeholders Vito Minei, Dennis Goldman, Geoff Dates, and Marty Link, who reviewed the test/QA plan and verification reports.

## Contents

Notice .....	ii
Foreword .....	iii
Acknowledgments .....	iv
List of Abbreviations .....	viii
1. Background .....	1
2. Technology Description .....	2
3. Test Design and Procedures .....	3
3.1 Introduction .....	3
3.2 Test Design .....	3
3.3 Test Samples .....	4
3.3.1 QC Samples .....	4
3.3.2 PT Samples .....	6
3.3.3 Environmental Samples .....	6
3.4 Reference Analysis .....	7
3.5 Verification Schedule .....	7
4. Quality Assurance/Quality Control .....	9
4.1 QC for Reference Method .....	9
4.2 Audits .....	11
4.2.1 Performance Evaluation Audit .....	11
4.2.2 Technical Systems Audit .....	12
4.2.3 Audit of Data Quality .....	12
4.3 QA/QC Reporting .....	12
4.4 Data Review .....	12
5. Statistical Methods .....	14
5.1 Accuracy .....	14
5.2 Precision .....	15
5.3 Linearity .....	15
5.4 Method Detection Limit .....	15
5.5 Matrix Interference Effects .....	16

5.6	Operator Bias .....	16
5.7	Rate of False Positives/False Negatives .....	16
6.	Test Results .....	17
6.1	Accuracy .....	17
6.2	Precision .....	24
6.3	Linearity .....	24
6.4	Method Detection Limit .....	27
6.5	Matrix Interference Effects .....	27
6.6	Operator Bias .....	27
6.7	Rate of False Positives/False Negatives .....	29
6.8	Other Factors .....	29
	6.8.1 Costs .....	33
	6.8.2 Data Completeness .....	33
7.	Performance Summary .....	34
8.	References .....	36

**Figures**

Figure 2-1.	Envitop Ltd. As-Top Water Arsenic Test Kit .....	2
Figure 6-1.	Comparison of As-Top Water Test Kit Results to Reference Results from PT Samples .....	26

**Tables**

Table 3-1.	Test Samples for Verification of the As-Top Water Test Kit .....	5
Table 3-2.	Schedule of Verification Test Days .....	8
Table 4-1.	Reference Method QCS Analysis Results .....	10
Table 4-2.	Reference Method LFM <sub>L</sub> Results .....	10
Table 4-3.	Reference Method Duplicate Analysis Results .....	11
Table 4-4.	Reference Method PE Audit Results .....	11
Table 4-5.	Summary of Data Recording Process .....	13



Table 6-1a. Results from Laboratory Performance Test Sample Analyses ..... 18

Table 6-1b. Results from Drinking Water Analyses ..... 19

Table 6-1c. Results from Freshwater Analyses ..... 20

Table 6-2a. Accuracy of the As-Top Water Test Kit with Laboratory Performance Test Samples ..... 21

Table 6-2b. Accuracy of the As-Top Water Test Kit with Drinking Water Samples ..... 22

Table 6-2c. Accuracy of the As-Top Water Test Kit with Freshwater Samples ..... 23

Table 6-3. Summary of Qualitative Accuracy Results ..... 24

Table 6-4a. Precision Results for As-Top Water Test Kit from Laboratory Performance Test Samples ..... 25

Table 6-4b. Precision Results for As-Top Water Test Kit from Drinking Water Samples ..... 26

Table 6-5a. Results from Laboratory Performance Test Samples with Low-Level Interferences ..... 28

Table 6-5b. Results from Laboratory Performance Test Samples with High-Level Interferences ..... 28

Table 6-6. Rate of False Positives from As-Top Water Test Kit ..... 30

Table 6-7. Rate of False Negatives from As-Top Water Test Kit ..... 32

## List of Abbreviations

AMS	Advanced Monitoring Systems
ASTM	American Society for Testing and Materials
DW	drinking fountain 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
RPD	relative percent difference
RSD	relative standard deviation
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 permittees; and with the full participation of individual technology developers. The program evaluates the performance of innovative technologies by developing test plans that are responsive to the needs of stakeholders, conducting field or laboratory tests (as appropriate), collecting and analyzing data, and preparing peer-reviewed reports. All evaluations are conducted in accordance with rigorous quality assurance (QA) protocols to ensure that data of known and adequate quality are generated and that the results are defensible.

The EPA's National Exposure Research Laboratory and its verification organization partner, Battelle, operate the Advanced Monitoring Systems (AMS) Center under ETV. The AMS Center recently evaluated the performance of four portable analyzers for arsenic in water. This verification report presents the procedures and results of the verification test for the Envitop Ltd. As-Top Water arsenic test kit. The As-Top Water test kit is an inexpensive, 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 As-Top Water test kit for arsenic in water. Following is a description of the test kit, based on information provided by the vendor. The information provided below was not verified in this test.

The As-Top Water test kit is a field technology for determining total arsenic content in water samples. The test kit is self-contained and does not require additional analysis instruments. Analysis results are obtained in 30 minutes, and used equipment is recyclable. An instruction manual is included with each test kit.

The complete As-Top Water test kit contains reaction vessels, an As-1 filter sulphide trap, an indicator cap with test paper, an As-2 reduction reagent, an As-4 moistening solution, As-3 and As-5 reaction solutions, disposable pipettes, two measuring scoops, and a color comparison card. The color comparison card for the As-Top Water test kit reads 10 parts per billion (ppb), 30 ppb, 50 ppb, 70 ppb, 100 ppb, 300 ppb, and 500 ppb. The limit of detection of the test kit, as stated by the vendor, is 10 ppb for water samples.



**Figure 2-1. Envitop Ltd. As-Top Water Arsenic Test Kit**

To use the As-Top Water test kit, reagents are added sequentially to a 50-mL water sample in the reaction vessel. The test paper is moistened with As-4 reagent. The indicator cap containing the test paper is placed on the reaction vessel. After the reaction is complete, the test paper is compared visually to the color comparison card provided to determine the arsenic content of the sample.

---

## 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*.<sup>(1)</sup> The verification was based on comparing the arsenic results from the As-Top Water test kit 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.<sup>(2)</sup> The As-Top Water test kit does not require calibration, but relies on comparison of the color of the test paper to the color comparison card to achieve semi-quantitative arsenic measurements. The As-Top Water test kit was verified by analyzing laboratory-prepared performance test samples, treated and untreated drinking water, and fresh surface water, with both the As-Top Water test kit and the reference method.

### 3.2 Test Design

The As-Top Water test kit 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.

All preparation, calibration, and analyses were performed according to the manufacturer's recommended procedures. Results from the As-Top Water test kit were recorded manually. The results from the As-Top Water test kits were compared with 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). 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. Because the reagents of the As-Top Water test kits are consumed in use, it was not feasible for the two operators to switch kits as a means of quantitatively assessing operator bias. However, each operator used multiple As-Top Water test kits in order to analyze all the samples, so it was assumed that kit-to-kit variability was similar for both operators. Consequently, qualitative observations could be made on operator bias.

Matrix interference effects were assessed by challenging the As-Top Water test kit 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 test kit (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) 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 As-Top Water test kits 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 the other prepared samples. These samples were used to help ensure that no sources of contamination were introduced during sample handling and analysis. Two types of LFMs were prepared. The LFM<sub>F</sub> 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 used for the LFM<sub>F</sub> samples was prepared in the laboratory and brought to the field site. The LFM<sub>L</sub> samples were aliquots of environmental samples that were spiked in the laboratory to increase the analyte concentration by 25 ppb of arsenic. These samples were used to help identify whether matrix effects influenced the reference method 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<sub>F</sub>.

**Table 3-1. Test Samples<sup>a</sup> for Verification of the As-Top Water Test Kit**

Type of Sample	Sample Characteristics	Concentration	No. of Samples
Quality Control	Reagent Blank (RB) <sup>b</sup>	~ 0	10% of all
	Laboratory Fortified Matrix (LFM <sub>F</sub> ) <sup>b</sup>	10 ppb above native level	1 per site
	LFM <sub>L</sub> <sup>b</sup>	25 ppb above native level	6
	Quality Control Sample (QCS) <sup>b</sup>	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

<sup>a</sup> Listing is for clarity; samples were analyzed in random order for the verification testing.

<sup>b</sup> See Section 3.3.1 for descriptions of these samples.

---

Quality control standards (QCS) were used as calibration checks to verify that the As-Top Water test kits and the reference instrument were properly calibrated and reading within defined control limits. These arsenic standards were purchased from a commercial supplier and were subject only to dilution as appropriate. Calibration of the test kit 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 As-Top HE test kit accuracy, linearity, and detection limit. To determine the detection limit of the As-Top Water test kit, a solution with a concentration 2.5 times the vendor's detection limit of 10 ppb was used. Seven non-consecutive replicate analyses of this 25-ppb arsenic 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 arsenic concentrations. Four aliquots of each of these solutions were prepared and analyzed separately to assess the precision of the As-Top Water test kit, 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 As-Top Water test kit. These samples were solutions with known 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 set of the test kits 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. One aliquot of each sample was



---

analyzed in the field at the time of collection by each set of 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 sample was preserved and stored at 4°C for later use, if necessary.

### **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.<sup>(2)</sup> 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 via the peristaltic pump and analyzed with all blanks, standards, and samples.

### **3.5 Verification Schedule**

The 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 analyzed shortly after collection using the As-Top Water test kit by both the technical and the non-technical Battelle staff member. 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**

<b>Test Day</b>	<b>Testing Location</b>	<b>Activity</b>
10/25-11/12/01	Battelle	Preparation and analysis of PT and associated QC samples.
10/25/01	Battelle	Collection and analysis of DW and associated QC samples within Battelle.
11/02/01	Ohio Field Location	Collection and analysis of WW samples, TW samples, and associated QC samples at Licking Valley Middle School.
11/06/01	Ohio Field Location	Collection and analysis of environmental and associated QC samples at four locations on Little Beaver Creek.
11/07/01	Ohio Field Location	Collection and analysis of environmental and associated QC samples at four locations on Lytle Creek.
11/08/01	Ohio Field Location	Collection and analysis of environmental and associated QC samples at four locations on the Stillwater River.

---

## 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<sup>(3)</sup> and the test/QA plan for this verification test.<sup>(1)</sup>

#### 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 method, 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 was also verified after the analysis of every 10 samples by analyzing a 25-ppb QCS. If the QCS analysis differed by more than  $\pm 10\%$  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%.

LFM<sub>L</sub> samples were analyzed to assess whether matrix effects influenced the results of the reference method. The percent recovery ( $R$ ) of these LFM<sub>L</sub> samples was calculated from the following equation:

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

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 LFM<sub>L</sub> fell outside the range of from 85 to 115%, a matrix effect was suspected. As shown in Table 4-2, all of the LFM<sub>L</sub> sample results were well within this range, so no matrix effect on the reference analyses is inferred.

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:

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

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 4-1. 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<sub>L</sub> Analysis Results**

LFM <sub>L</sub> 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 <sub>F</sub>	12/21/01	10.6 <sup>a</sup>	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%

<sup>a</sup> Amount of arsenic in the sample after it was spiked in the field.

**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 supplier of 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 analysis 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<sup>(1)</sup> and the AMS Center QMP.<sup>(3)</sup> 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.<sup>(3)</sup> 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**

<b>Data to be Recorded</b>	<b>Responsible Party</b>	<b>Where Recorded</b>	<b>How Often Recorded</b>	<b>Disposition of Data<sup>a</sup></b>
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 As-Top Water test kit 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

<sup>a</sup> 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 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 test kit being verified. For each sample, accuracy was expressed in terms of a relative bias ( $B$ ) as calculated from the following equation:

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

where  $d$  is the difference between the reading from the As-Top Water test kit and that from the reference method, and  $C_R$  is the reference measurement.

Because of the semi-quantitative nature of the test kit results, it was not possible to make this determination for many of the results. For this reason, all of the data were judged by a qualitative measure that was not specified in the test/QA plan. If the result from the test kit 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:

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

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 those analyzers. Readings below the detection limit (i.e., <10 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 As-Top Water test kit precision at each concentration.

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

where  $n$  is the number of replicate samples,  $C_k$  is the concentration measured for the  $k^{\text{th}}$  sample, and  $\bar{C}$  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.,

$$\text{RSD} = \left| \frac{S}{\bar{C}} \right| \times 100 \quad (6)$$

## 5.3 Linearity

Linearity was assessed by linear regression of As-Top Water test kit results against the reference method results, with linearity characterized by the slope, intercept, and correlation coefficient ( $r$ ). Linearity was tested using PT samples over the range of 1 to 100 ppb of arsenic.

## 5.4 Method Detection Limit

The MDL for the As-Top Water test kit was assessed from the seven replicate analyses of a fortified sample with an arsenic concentration of 25 ppb, i.e., 2.5 times the vendor's estimated detection limit. This concentration differed from the approach stated in the test/QA plan, which called for a sample concentration of five times the estimated detection limit.<sup>(1)</sup> An approved deviation to that effect was included in the verification file. The MDL was calculated from the following equation:

$$\text{MDL} = t \times S \quad (7)$$

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.<sup>(4)</sup>

---

## 5.5 Matrix Interference Effects

The effect of interfering matrix species on the response of the As-Top Water test kit 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 test kit to that interferant would be calculated as  $10 \text{ ppb}/500 \text{ ppb} = 2\%$ . 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

To assess operator bias for the As-Top Water test kit, in all tests the results obtained from each operator were compiled independently and subsequently compared. However, because of the semi-quantitative nature of the test kit data, and the inability of the operators to independently use the same test kits, quantitative assessments of operator bias could not be made. Qualitative observations were made concerning the results from the two operators.

## 5.7 Rate of False Positives/False Negatives

The rates of false positives and false negatives of the As-Top Water test kit 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 As-Top Water test kit are presented in this section.

### 6.1 Accuracy

Tables 6-1a-c present the measured arsenic results from analysis of the prepared, drinking water, and FW samples, respectively. Both reference analyses and As-Top Water test kit results are shown in the tables, and As-Top Water test kit results are shown for both the technical and non-technical operators. Samples with no visible color development from the As-Top Water test kit were assigned a value of <10 ppb.

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

Tables 6-2a-c show percent accuracy of the As-Top Water test kit results listed in Tables 6-1a-c. Shown in the second and third columns in each of Tables 6-2a-d are the percent bias values determined according to Equation 3, in Section 5.1. Bias was not calculated for values reported as <10 ppb. The non-technical operator did not detect arsenic in any of the PT samples, even at concentrations exceeding 90 ppb (Table 6-2a). The percent bias values for the PT samples that are shown in Table 6-2a for the technical operator range from 2 to 2,900%. Percent bias values ranged from 6 to >9,900% for the non-technical operator and 6 to 65% for the technical operator for the drinking water samples (Table 6-2b) and from 6 to 630% for the non-technical operator and 2 to 2,106% for the technical operator for the FW samples (Table 6-2c). The extreme bias values resulted from indications of substantial arsenic concentrations (i.e., 10 or 30 ppb) by the As-Top HE for samples that contained very low arsenic levels (<0.1 to 2.1 ppb). Accuracy for the 10-ppb QCS samples was usually 2 to 8%, though several non-detects were reported from the As-Top HE with the QCS samples.

In addition to the quantitative bias results, the qualitative accuracy was compared using Equation 4 in Section 5.1. The fourth and fifth columns in Tables 6-2a-c show the assignment of each As-Top Water test kit result, in terms of whether that result fell within 25% of the

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

<b>Sample</b>	<b>Non-Technical Arsenic (ppb)</b>	<b>Technical Arsenic (ppb)</b>	<b>Reference Method<sup>a</sup> Arsenic (ppb)</b>
Laboratory RB	<10	<10	<0.1
Laboratory RB	<10	<10	<0.1
Laboratory RB	<10	<10	<0.1
QCS	<10	10	9.80
QCS	<10	10	9.80
PT1-1	<10	<10	1.00
PT1-2	<10	<10	1.00
PT1-3	<10	<10	1.00
PT1-4	<10	30	1.00
PT2-1	<10	<10	2.92
PT2-2	<10	<10	2.92
PT2-3	<10	<10	2.92
PT2-4	<10	30	2.92
PT3-1	<10	10	9.2
PT3-2	<10	10	9.2
PT3-3	<10	10	9.2
PT3-4	NA	10	9.2
PT4-1	<10	10	29.3
PT4-2	<10	10	29.3
PT4-3	<10	10	29.3
PT4-4	<10	<10	29.3
PT5-1	<10	10	92.6
PT5-2	<10	30	92.6
PT5-3	<10	100	92.6
PT5-4	<10	100	92.6
PT6-1	<10	<10	23.5
PT6-2	<10	<10	23.5
PT6-3	<10	30	23.5
PT6-4	<10	<10	23.5
PT6-5	<10	<10	23.5
PT6-6	<10	<10	23.5
PT6-7	<10	<10	23.5

<sup>a</sup> 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 As-Top Water test kit.

NA: Not analyzed.

**Table 6-1b. Results from Drinking Water Analyses**

<b>Sample</b>	<b>Non-Technical Arsenic (ppb)</b>	<b>Technical Arsenic (ppb)</b>	<b>Reference Method<sup>a</sup> Arsenic (ppb)</b>
Laboratory RB	10	<10	<0.1
QCS	10	<10	10.9
DW-1	<10	<10	0.87
DW-2	<10	<10	0.87
DW-3	30	<10	0.87
DW-4	10	<10	0.87
DW LFM <sub>F</sub>	10	10	10.6
Laboratory RB	<10	<10	<0.1
QCS	<10	10	10.9
WW-1	<10	30	86.6
WW-2	50	70	86.6
WW-3	50	70	86.6
WW-4	30	30	86.6
WW LFM <sub>F</sub>	30	100	82.1
Laboratory RB	<10	<10	<0.1
QCS	<10	<10	10.9
TW-1	<10	10	26.0
TW-2	<10	10	26.0
TW-3	<10	10	26.0
TW-4	<10	30	26.0
TW LFM <sub>F</sub>	<10	30	50.8

<sup>a</sup> Only one aliquot of each sample was analyzed by the reference method. Multiple aliquots of each sample were analyzed by the As-Top Water test kit.

**Table 6-1c. Results from Freshwater Analyses**

<b>Sample</b>	<b>Non-Technical Arsenic (ppb)</b>	<b>Technical Arsenic (ppb)</b>	<b>Reference Method Arsenic (ppb)</b>
Laboratory RB	<10	<10	<0.1
QCS	<10	<10	9.33
SR-1	<10	<10	1.73
SR-2	<10	<10	1.72
SR-2 Duplicate	<10	<10	1.71
SR-3	<10	<10	2.03
SR-4	<10	<10	1.88
SR-1 LFM <sub>F</sub>	10	<10	11.6
Laboratory RB	<10	<10	<0.1
QCS	10	10	9.43
LC-1	<10	30	2.13
LC-2	<10	10	1.30
LC-3	<10	<10	1.44
LC-4	10	10	1.37
LC-4 Duplicate	<10	30	1.36
LC-3 LFM <sub>F</sub>	10	30	12.0
Laboratory RB	<10	<10	<0.1
QCS	30	10	9.81
LBC-1	<10	<10	2.48
LBC-2	<10	10	2.60
LBC-3	<10	<10	2.14
LBC-3 Duplicate	<10	10	2.26
LBC-4	<10	10	2.54
LBC-4 LFM <sub>F</sub>	10	<10	2.38

**Table 6-2a. Accuracy of the As-Top Water Test Kit with Laboratory Performance Test Samples**

<b>Sample</b>	<b>Bias<sup>a</sup> Non-Technical</b>	<b>Bias<sup>a</sup> Technical</b>	<b>Within Range Non-Technical</b>	<b>Within Range Technical</b>
Laboratory RB	— <sup>c</sup>	—	Y <sup>b</sup>	Y <sup>b</sup>
Laboratory RB	—	—	Y	Y
Laboratory RB	—	—	Y	Y
QCS	—	2%	Y	Y
QCS	—	2%	Y	Y
PT1-1	—	—	Y	Y
PT1-2	—	—	Y	Y
PT1-3	—	—	Y	Y
PT1-4	—	2900%	Y	N
PT2-1	—	—	Y	Y
PT2-2	—	—	Y	Y
PT2-3	—	—	Y	Y
PT2-4	—	927%	Y	N
PT3-1	—	9%	Y	Y
PT3-2	—	9%	Y	Y
PT3-3	—	9%	Y	Y
PT3-4	NA	9%		Y
PT4-1	—	66%	N	N
PT4-2	—	66%	N	N
PT4-3	—	66%	N	N
PT4-4	—	—	N	N
PT5-1	—	89%	N	N
PT5-2	—	68%	N	N
PT5-3	—	8%	N	Y
PT5-4	—	8%	N	Y
PT6-1	—	—	N	N
PT6-2	—	—	N	N
PT6-3	—	28%	N	N
PT6-4	—	—	N	N
PT6-5	—	—	N	N
PT6-6	—	—	N	N
PT6-7	—	—	N	N

<sup>a</sup> Percent bias calculated according to Equation 3, Section 5.1.

<sup>b</sup> Y = result within ±25% of reference, or reference value within “less-than” range; N = result not within ±25% of reference, or reference value not within “less-than” range.

<sup>c</sup> Non-detect, no calculation of bias can be made.

NA: Not analyzed.

**Table 6-2b. Accuracy of the As-Top Water Test Kit with Drinking Water Samples**

<b>Sample</b>	<b>Bias<sup>a</sup> Non-Technical</b>	<b>Bias<sup>a</sup> Technical</b>	<b>Within Range Non-Technical</b>	<b>Within Range Technical</b>
Laboratory RB	>9,900%	— <sup>c</sup>	N <sup>b</sup>	Y <sup>b</sup>
QCS	8%	—	Y	N
DW-1	—	—	Y	Y
DW-2	—	—	Y	Y
DW-3	3,348%	—	N	Y
DW-4	1,049%	—	N	Y
DW LFM <sub>F</sub>	6%	6%	Y	Y
Laboratory RB	—	—	Y	Y
QCS	—	8%	N	Y
WW-1	—	65%	N	N
WW-2	42%	19%	N	Y
WW-3	42%	19%	N	Y
WW-4	65%	65%	N	N
WW LFM <sub>F</sub>	63%	22%	N	Y
Laboratory RB	—	—	Y	Y
QCS	—	—	N	N
TW-1	—	62%	N	N
TW-2	—	62%	N	N
TW-3	—	62%	N	N
TW-4	—	15%	N	Y
TW LFM <sub>F</sub>	—	41%	N	N

<sup>a</sup> Percent bias calculated according to Equation 3, Section 5.1.

<sup>b</sup> Y = result within ±25% of reference, or reference value within “less-than” range; N = result not within ±25% of reference, or reference value not within “less-than” range.

<sup>c</sup> Non-detect, no calculation of bias can be made.



**Table 6-2c. Accuracy of the As-Top Water Test Kit with Freshwater Samples**

Sample	Bias <sup>a</sup>		Within Range	
	Non-Technical	Technical	Non-Technical	Technical
Laboratory RB	— <sup>c</sup>	—	Y <sup>b</sup>	Y <sup>b</sup>
QCS	—	—	Y	Y
SR-1	—	—	Y	Y
SR-2	—	—	Y	Y
SR-2 Duplicate	—	—	Y	Y
SR-3	—	—	Y	Y
SR-4	—	—	Y	Y
SR-1 LFM <sub>F</sub>	14%	—	Y	N
Laboratory RB	—	—	Y	Y
QCS	6%	6%	Y	Y
LC-1	—	1308%	Y	N
LC-2	—	669%	Y	N
LC-3	—	—	Y	Y
LC-4	630%	630%	N	N
LC-4 Duplicate	—	2,106%	Y	N
LC-3 LFM <sub>F</sub>	17%	150%	Y	N
Laboratory RB	—	—	Y	Y
QCS	206%	2%	N	Y
LBC-1	—	—	Y	Y
LBC-2	—	285%	Y	N
LBC-3	—	—	Y	Y
LBC-3 Duplicate	—	342%	Y	N
LBC-4	—	294%	Y	N
LBC-4 LFM <sub>F</sub>	320%	—	N	Y

<sup>a</sup> Percent bias calculated according to Equation 3, Section 5.1.

<sup>b</sup> Y = result within ±25% of reference, or reference value within “less-than” range; N = result not within ±25% of reference, or reference value not within “less-than” range.

<sup>c</sup> Non-detect, no calculation of bias can be made.

reference value, or at least within the non-detect range. The results of this qualitative evaluation of accuracy are shown in Table 6-3, which lists the overall percent of results meeting the criterion for each operator and sample type. Table 6-3 shows that the qualitative accuracy of the As-Top HE test kit for the PT samples was 52% for the non-technical and 53% for the technical operators. The qualitative accuracy for the drinking water samples was 29% for the non-technical operator and 62% for the technical operator. The qualitative accuracy for the FW samples was 88% for the non-technical operator and 63% for the technical operator. The great majority of As-Top Water test kit results judged as qualitatively accurate were the result of sample arsenic concentrations below the As-Top Water estimated detection limit of 10 ppb. For the 25 samples with arsenic levels of 23.5 to 92.6 ppb (samples PT4, PT5, PT6, Tables 6-1a and 6-2a, and the

**Table 6-3. Summary of Qualitative Accuracy Results**

	<b>Percent Accurate Within 25% (Non-Technical Operator)</b>	<b>Percent Accurate Within 25% (Technical Operator)</b>
Laboratory performance test samples	52%	53%
Drinking water samples	29%	62%
Freshwater samples	88%	63%

WW and TW samples, Tables 6-1b and 6-2b), no results satisfying the 25% accuracy criterion were obtained by the non-technical operator, and only five such results were obtained by the technical operator.

## 6.2 Precision

Tables 6-4a and b, respectively, show the data used to evaluate the RSD of the As-Top Water test kit results for the replicate laboratory PT and drinking water samples, along with the percent RSD value for each set of replicate analyses. The percent RSD was determined according to Equation 6 in Section 5.2. Calculation of precision was complicated by the large number of <10 ppb results reported by the operators. No RSD value was calculated when all replicate results were reported as <10 ppb, but a value of 5 ppb was used (i.e., half the estimated detection limit) when only some of the replicate results were reported as <10 ppb. The non-technical operator did not detect arsenic in any of the PT samples, even at concentrations up to 92.6 ppb (Table 6-4a). The percent RSD ranged from 0 to 111% for the technical operator on the PT samples. The percent RSD for the drinking water samples was 63 to 95% for the non-technical operator and 46 to 67% for the technical operator.

## 6.3 Linearity

The linearity of the As-Top Water test kit was assessed by means of a linear regression of the As-Top HE test kit results against the reference method results, using the 27 data points from the PT samples (Table 6-1a). In this regression, results reported as below the 10-ppb vendor-estimated detection limit by the As-Top Water test kit were assigned a value of 5 ppb (i.e., half the 10-ppb detection limit). The linearity could not be assessed on the As-Top Water test kit using data from the non-technical operator, because that operator did not detect arsenic in any of the samples. Figure 6-1 shows a scatter plot of the As-Top Water test kit data from the technical operator versus the reference method results. A one-to-one line is also shown in Figure 6-1.

**Table 6-4a. Precision Results for As-Top Water Test Kit from Laboratory Performance Test Samples**

	Reference Concentration (ppb)	Non-Technical Arsenic (ppb)	Technical <sup>a</sup> Arsenic (ppb)
QCS	9.8	<10	10
QCS		<10	10
<b>%RSD</b>		— <sup>b</sup>	<b>0</b>
PT1-1	1.0	<10	<10
PT1-2		<10	<10
PT1-3		<10	<10
PT1-4		<10	30
<b>%RSD</b>		— <sup>b</sup>	<b>111</b>
PT2-1	2.9	<10	<10
PT2-2		<10	<10
PT2-3		<10	<10
PT2-4		<10	30
<b>%RSD</b>		— <sup>b</sup>	<b>111</b>
PT3-1	9.2	<10	10
PT3-2		<10	10
PT3-3		<10	10
PT3-4		NA	10
<b>%RSD</b>		— <sup>b</sup>	<b>0</b>
PT4-1	29.3	<10	10
PT4-2		<10	10
PT4-3		<10	10
PT4-4		<10	<10
<b>%RSD</b>		— <sup>b</sup>	<b>29</b>
PT5-1	92.6	<10	10
PT5-2		<10	30
PT5-3		<10	100
PT5-4		<10	100
<b>%RSD</b>		— <sup>b</sup>	<b>78</b>
PT6-1	23.5	<10	<10
PT6-2		<10	<10
PT6-3		<10	30
PT6-4		<10	<10
PT6-5		<10	<10
PT6-6		<10	<10
PT6-7		<10	<10
<b>%RSD</b>		— <sup>b</sup>	<b>110</b>

<sup>a</sup> For the purpose of calculating %RSD, all “less than” values are considered as half the detection limit, i.e., as 5 ppb.

<sup>b</sup> No %RSD could be calculated.

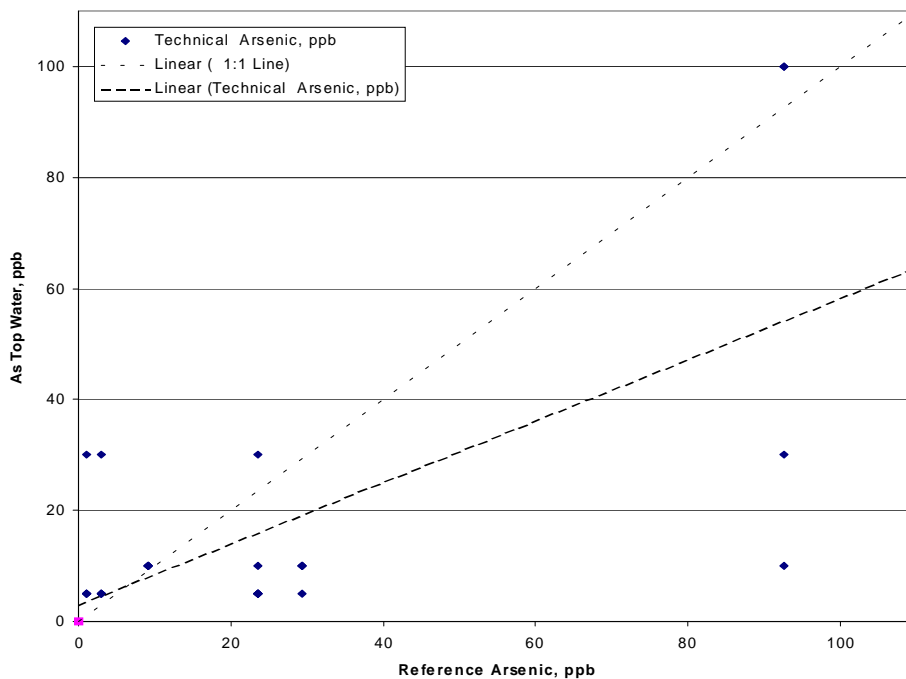
NA: Not analyzed

**Table 6-4b. Precision Results for As-Top Water Test Kit from Drinking Water Samples**

	<b>Reference Concentration (ppb)</b>	<b>Non-Technical<sup>a</sup> Arsenic (ppb)</b>	<b>Technical<sup>a</sup> Arsenic (ppb)</b>
DW-1	0.87	<10	<10
DW-2		<10	<10
DW-3		30	<10
DW-4		10	<10
%RSD		<b>95</b>	— <sup>b</sup>
WW-1	86.6	<10	30
WW-2		50	70
WW-3		50	70
WW-4		30	30
%RSD		<b>63</b>	<b>46</b>
TW-1	26.0	<10	10
TW-2		<10	10
TW-3		<10	30
TW-4		<10	10
%RSD		— <sup>b</sup>	<b>67</b>

<sup>a</sup> For the purpose of calculating standard deviation, all “less than” values are considered as half the detection limit, i.e., as 5 ppb.

<sup>b</sup> No %RSD could be calculated.



**Figure 6-1. Comparison of As-Top Water Test Kit Results to Reference Method Results from PT Samples**

---

A linear regression of the data in Figure 6-1 gives the following regression equations:

with the As-Top HE for the technical operator,  
 $\text{ppb} = 0.55 (\pm 0.26) x (\text{reference, ppb}) + 2.97 (\pm 10.2) \text{ ppb}$ ,  
with  $r = 0.66$

where the values in parentheses represent the 95% confidence interval of the slope and intercept. The slope is significantly different from 1.0, indicating non-linear performance, and the  $r$  value and Figure 6-1 confirm the scatter in the data.

#### **6.4 Method Detection Limit**

The manufacturer's estimated detection limit for the As-Top Water test kit is 10 ppb. An attempt was made to determine the MDL by analyzing seven replicate PT samples at a concentration of approximately 25 ppb arsenic. However, the non-technical operator did not detect arsenic in any of these samples, and the technical operator detected arsenic in only one of the seven samples, reporting the concentration to be 30 ppb. Because arsenic was not detected in all samples by either the technical or non-technical operator, no quantitative determination of MDL could be made. The results from the technical operator suggest a detection limit substantially greater than the estimated value of 10 ppb.

#### **6.5 Matrix Interference Effects**

Tables 6-5a and b show the analytical results from laboratory performance test samples containing about 10 ppb of arsenic with low and high levels of interferences, respectively. All data from the non-technical operator, and 13 of 16 results from the technical operator, were non-detects (<10 ppb). No obvious effect of interferences on As-Top Water test kit performance could be determined based on these results.

#### **6.6 Operator Bias**

The effect of operator skill level appears to be a significant factor with the As-Top Water test kit. The non-technical operator rarely detected arsenic in any samples, even those containing arsenic at over 90 ppb. The technical operator detected arsenic more frequently, though rarely at the same concentration determined by the reference method.

**Table 6-5a. Results from Laboratory Performance Test Samples with Low-Level Interferences**

	<b>Non-Technical Arsenic (ppb)</b>	<b>Technical Arsenic (ppb)</b>
LI-1	<10	<10
LI-2	<10	<10
LI-3	<10	10
LI-4	<10	<10
LI-5	<10	<10
LI-6	<10	<10
LI-7	<10	<10
LI-8	<10	<10

<sup>a</sup> Only one aliquot of LI solution was analyzed by the reference method. Eight aliquots of LI solution were analyzed by As-Top Water test kits.

**Table 6-5b. Results from Laboratory Performance Test Samples with High-Level Interferences**

	<b>Non-Technical Arsenic (ppb)</b>	<b>Technical Arsenic (ppb)</b>
HI-1	<10	<10
HI-2	<10	<10
HI-3	<10	<10
HI-4	<10	<10
HI-5	<10	<10
HI-6	<10	<10
HI-7	<10	10
HI-8	<10	10

<sup>a</sup> Only one aliquot of HI solution was analyzed by the reference method. Eight aliquots of HI solution were analyzed by As-Top Water test kits.

---

## 6.7 Rate of False Positives/False Negatives

Tables 6-6 and 6-7, respectively, show the data and results for the rates of false positives and false negatives obtained from the As-Top Water test kit. All PT and environmental samples were considered for this evaluation.

Table 6-6 shows that the reference method concentration was less than the target concentration of 10 ppb in 44 samples. The non-technical operator reported only two readings equal to or exceeding 10 ppb in the 43 samples he analyzed, and those readings were for samples containing 0.87 ppb arsenic according to the reference method. The result was a false positive rate of 5% for the non-technical operator. The technical operator reported eight samples with concentrations of 10 ppb or more, and exceeding by over 25% the arsenic concentrations according to the reference method. The false positive rate of the As-Top Water test kit with the technical operator was thus 18%.

Table 6-7 shows that 23 samples had reference method arsenic concentrations greater than the target level of 10 ppb. In 20 of these 23 samples, the As-Top Water test kit result was less than 10 ppb as measured by the non-technical operator. Thus, a false negative rate of 87% was obtained with the non-technical operator. For the technical operator, 7 of the 23 samples had a test result less than 10 ppb, resulting in a false negative rate of 30%.

## 6.8 Other Factors

The operators felt the As-Top Water test kit was easy to use and free of maintenance. The As-Top HE test kit is lightweight, easy to transport by car, and can easily be carried through fields and wooded areas. However, the color observed on the indicator cap was typically a greyish brown shade, unlike the shades of yellow on the color comparison card, which made comparing the indicator cap to the color comparison card difficult in this test.

The As-Top Water test kit allows analysis of one sample at a time. The reagents are ready to use, requiring no preparation. The reagents are measured with two separate scoops and a pipette provided in the As-Top Water test kit, allowing simple measurement of the reagents. The total time to add the reagents is less than five minutes, and the total reaction time for an analysis is 30 minutes. When the analysis is complete, the reagent bottles are rinsed for reuse.

The As-Top Water test kit uses both aqueous and solid reagents. The reagents contain no acutely toxic or hazardous materials. However, it is good practice to wear laboratory gloves when preparing the reagents.

**Table 6-6. Rate of False Positives from As-Top Water Test Kit**

	Non-Technical Arsenic (ppb)	Technical Arsenic (ppb)	Reference Method Arsenic (ppb)	Non-Technical False Positive (Y/N)	Technical False Positive (Y/N)
PT1-1	<10	<10	1.00	N	N
PT1-2	<10	<10	1.00	N	N
PT1-3	<10	<10	1.00	N	N
PT1-4	<10	30	1.00	N	Y
PT2-1	<10	<10	2.92	N	N
PT2-2	<10	<10	2.92	N	N
PT2-3	<10	<10	2.92	N	N
PT2-4	<10	30	2.92	N	Y
PT3-1	<10	10	9.20	N	N
PT3-2	<10	10	9.20	N	N
PT3-3	<10	10	9.20	N	N
PT3-4	NA	10	9.20		N
LI-1	<10	<10	9.91	N	N
LI-2	<10	<10	9.91	N	N
LI-3	<10	10	9.91	N	N
LI-4	<10	<10	9.91	N	N
LI-5	<10	<10	9.91	N	N
LI-6	<10	<10	9.91	N	N
LI-7	<10	<10	9.91	N	N
LI-8	<10	<10	9.91	N	N
HI-1	<10	<10	9.94	N	N
HI-2	<10	<10	9.94	N	N
HI-3	<10	<10	9.94	N	N
HI-4	<10	<10	9.94	N	N
HI-5	<10	<10	9.94	N	N
HI-6	<10	<10	9.94	N	N
HI-7	<10	10	9.94	N	N
HI-8	<10	10	9.94	N	N
DW-1	<10	<10	0.87	N	N
DW-2	<10	<10	0.87	N	N
DW-3	30	<10	0.87	Y	N
DW-4	10	<10	0.87	Y	N
SR-1	<10	<10	1.73	N	N
SR-2	<10	<10	1.72	N	N
SR-3	<10	<10	2.03	N	N
SR-4	<10	<10	1.88	N	N

NA: Not analyzed.

(continued)



**Table 6-6. Rate of False Positives from As-Top Water Test Kit (continued)**

	<b>Non-Technical Arsenic (ppb)</b>	<b>Technical Arsenic (ppb)</b>	<b>Reference Method Arsenic (ppb)</b>	<b>Non-Technical False Positive (Y/N)</b>	<b>Technical False Positive (Y/N)</b>
LC-1	<10	30	2.13	N	Y
LC-2	<10	10	1.30	N	Y
LC-3	<10	<10	1.44	N	N
LC-4	<10	10	1.37	N	Y
LBC-1	<10	<10	2.48	N	N
LBC-2	<10	10	2.60	N	Y
LBC-3	<10	10	2.14	N	Y
LBC-4	<10	10	2.54	N	Y
Total number of applicable samples				43	44
Total false positive				2	8
Percent false positive				5%	18%

Y = yes

N = no

NA: Not analyzed.

**Table 6-7. Rate of False Negatives from As-Top Water Test Kit**

	<b>Non-Technical Arsenic (ppb)</b>	<b>Technical Arsenic (ppb)</b>	<b>Reference Method Arsenic (ppb)</b>	<b>Non-Technical False Negative (Y/N)</b>	<b>Technical False Negative (Y/N)</b>
PT4-1	<10	10	29.3	Y	N
PT4-2	<10	10	29.3	Y	N
PT4-3	<10	10	29.3	Y	N
PT4-4	<10	<10	29.3	Y	Y
PT5-1	<10	10	92.6	Y	N
PT5-2	<10	30	92.6	Y	N
PT5-3	<10	100	92.6	Y	N
PT5-4	<10	100	92.6	Y	N
PT6-1	<10	<10	23.5	Y	Y
PT6-2	<10	<10	23.5	Y	Y
PT6-3	<10	30	23.5	Y	N
PT6-4	<10	<10	23.5	Y	Y
PT6-5	<10	<10	23.5	Y	Y
PT6-6	<10	<10	23.5	Y	Y
PT6-7	<10	<10	23.5	Y	Y
WW-1	<10	30	86.6	Y	N
WW-2	50	70	86.6	N	N
WW-3	50	70	86.6	N	N
WW-4	30	30	86.6	N	N
TW-1	<10	10	26.0	Y	N
TW-2	<10	10	26.0	Y	N
TW-3	<10	10	26.0	Y	N
TW-4	<10	30	26.0	Y	N
Total number of applicable samples				23	23
Total false negative				20	7
Percent false negative				87%	30%

Y = yes

N = no

---

### **6.8.1 Costs**

The cost of the As-Top Water test kit was not provided by the vendor. Consequently, no estimate of per test cost can be made.

### **6.8.2 Data Completeness**

All portions of the verification test were completed, and all data that were to be recorded were successfully acquired. One 10-ppb PT sample was not analyzed by the non-technical operator because he ran out of reagents. With that exception, data completeness was 100%.

---

## Chapter 7

### Performance Summary

Frequent non-detect results were obtained with the As-Top Water, especially by the non-technical operator. As a result, quantitative evaluations could not be made for all performance parameters.

In considering accuracy, percent bias values ranged from 2 to 2,900% for the technical operator for the PT samples, whereas the non-technical operator did not detect arsenic in any PT sample, including those containing over 90 ppb arsenic. For the drinking water samples, the percent bias ranged from 6 to >9,900% for the non-technical operator and 6 to 65% for the technical operator. For the FW samples, percent bias was 6 to 630% for the non-technical operator and 2 to 2,106% for the technical operator. Accuracy was also considered more qualitatively by determining the percentage of samples for which the As-Top Water test kit results were within 25% of the reference method result, or at least within a comparable non-detect range. By this criterion, the qualitative accuracy of the As-Top Water test kit for the PT samples was 52% for the non-technical and 53% for the technical operator. The qualitative accuracy for the drinking water samples was 29% for the non-technical operator and 62% for the technical operator. The qualitative accuracy for the FW samples was 88% for the non-technical operator and 63% for the technical operator. Most of the As-Top Water test kit results that met the qualitative accuracy criteria were non-detects; and, with samples of 23.5 to 92.6 ppb arsenic, very few As-Top Water test kit results met the 25% accuracy criterion.

Calculating precision also was complicated by the large number of non-detect results reported by the operators. In many cases, the percent RSD could not be calculated quantitatively because all As-Top Water test kit results were <10 ppb. The non-technical operator did not detect arsenic in any of the PT samples. The RSD ranged from 0 to 111% for the technical operator on the PT samples. The RSD for the drinking water samples was 63 to 95% for the non-technical operator and 46 to 67% for the technical operator.

The linearity of response of the As-Top Water test kit was assessed using PT samples containing from 1 to 93 ppb arsenic. The linear regression for the As-Top Water results for the technical operator was  $\text{ppb} = 0.55 (\pm 0.26) \times (\text{reference, ppb}) + 2.97 (\pm 10.2) \text{ ppb}$ , with  $r = 0.66$ . The linearity could not be assessed on the As-Top Water data from the non-technical operator because arsenic was not detected in any of the PT samples.

A quantitative assessment of the MDL could not be made for the As-Top Water because arsenic was only rarely detected with the As-Top Water test kit by either operator in 25-ppb samples.

---

Results obtained suggest a detection limit for the As-Top Water test kit substantially higher than the 10 ppb estimated by the manufacturer.

The As-Top Water test only rarely detected arsenic present at 10-ppb levels in matrices containing low or high levels of sodium chloride, iron, sulfide, or acidity. No obvious effect of interferences could be determined based on these results.

In terms of operator bias, the operator skill level appeared to be a significant factor with the As-Top Water test kits. The non-technical operator rarely detected arsenic in any samples, even those containing over 90 ppb of arsenic, while the technical operator detected arsenic more frequently.

The rates of false positives and false negatives of the As-Top Water test kit were assessed relative to the reference method, using 10 ppb of arsenic as the decision level. The rate of false positives of the As-Top Water test kit was 5% for the non-technical operator and 18% for the technical operator. The rate of false negatives was 87% for the non-technical operator and 30% for the technical operator.

The cost of the As-Top Water test kit was not provided by the vendor, so no estimate of per-test cost can be made. The As-Top Water test kit allows analysis of one sample at a time, requiring a total of 35 minutes for reagent addition and reaction. The reagents are ready to use, requiring no preparation. Two measuring scoops of different sizes and a pipette are included in the As-Top Water test kit, allowing for simple measurement of the reagents.

---

## 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.