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Environmental Technology Verification Report

AS 75 ARSENIC TEST KIT

Prepared by



Battelle

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Environmental Technology Verification Report

ETV Advanced Monitoring Systems Center

AS 75 Arsenic Test Kit

by

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Notice

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Foreword

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

The Environmental Technology Verification (ETV) Program has been established by the EPA to verify the performance characteristics of innovative environmental technology across all media and to report this objective information to permittees, buyers, and users of the technology, thus substantially accelerating the entrance of new environmental technologies into the marketplace. Verification organizations oversee and report verification activities based on testing and quality assurance protocols developed with input from major stakeholders and customer groups associated with the technology area. ETV consists of 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/centers1.html>.

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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 Peters Engineering AS 75 arsenic test kit. The AS 75 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 75 arsenic test kit, made by Peters Engineering. 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 75 consists of the PeCo test kit, which measures the color change of a filter by visual comparison to a color chart, and an AS 75 tester, which measures the color change of the filter electronically. The AS 75 includes a 100-mL reaction bottle (Erlenmeyer flask), two filter holders, a 50-mL volumetric cylinder, a 10- and a 1-mL pipette, tweezers, gloves, two color charts, filters, cotton, a nine-volt battery, and chemicals and reagents (in tablet form) for 20 tests. The AS 75 can be used for 50-, 10-, 5-, or 1-mL samples; in this test all samples were 50 mL. The AS 75 tester is a hand-held, battery-powered electronic device recommended for determining low concentrations of arsenic in the field.



Figure 2-1. Peters Engineering AS 75 Arsenic Test Kit

60 ppb. The AS 75 tester can be used only in conjunction with the grey filter holder. For this reason, only the grey filter holder was used for this test.

To measure arsenic with the AS 75 tester, the Erlenmeyer flask is filled with the sample. The filter is placed into the test filter holder, reagent tablets are dropped in the sample, and the filter holder is placed on the flask. The filter is exposed to arsine gas evolved from the sample solution, resulting in a color change in the filter. When the reaction is complete, the filter is compared visually with the color charts provided with the PeCo test kit, or read by the AS 75 tester, to determine the amount of arsenic in the sample. The PeCo test kit color chart shows

discrete color spots corresponding to total arsenic concentrations of 10, 20, 30, . . . 100 parts per billion (ppb). In a few cases, the color formation on the filter appeared to be between two color gradations on the color chart. In these cases, the operator interpolated the results and reported an estimated value between the values assigned on the color chart.

The As 75 tester has a display resolution of 1 ppb and can provide arsenic readings below 10 ppb. The battery-operated AS 75 tester provides power for 260 hours under normal conditions, allowing for up to 1,200 measurements. The AS 75 tester (with the nine-volt battery) weighs 160 g (5.6 oz), and its dimensions are 120 mm by 60 mm by 26 mm (4.7 in by 2.4 in by 1 in).

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 both the visual (PeCo test kit) and electronic (AS 75 tester) arsenic results from the AS 75 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⁽²⁾ The AS 75 test kit comes with two types of filter holders and two corresponding color charts. The “grey type” can be used for both visual and electronic testing and was used throughout this verification. This filter holder and chart provide a measurement range of 10 to 100 ppb of arsenic. The “blue type” only can be used for visual testing and was not assessed during this test. The PeCo test kit does not require calibration for the visual test, but relies on comparing the filter color to a color chart provided with the kit to achieve semi-quantitative arsenic measurements. The AS 75 tester was calibrated prior to each sample analysis, as recommended by the vendor, by measuring a clean filter supplied with the kit. The AS 75 test kit was tested by analyzing laboratory-prepared performance test samples, treated and untreated drinking water, and fresh surface water, with both the test kit and the reference method.

3.2 Test Design

The AS 75 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 test kit were read visually using the PeCo test kit, as well as electronically with the AS 75 tester, and were recorded manually. The results from the test kits 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). 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 75 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 kits in order to analyze all the samples, so it is 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 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.

In a few instances, the test kit operator interpolated between the PeCo test kit's gradations in reporting an arsenic value. This is not unusual in the use of such kits, and typically resulted in an arsenic reading midway between two gradation values (e.g., 35 ppb, between gradations of 30 and 40 ppb).

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, 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 75 test kits and by 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 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 used 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 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 AS 75 test kit 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 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 75 test kit accuracy, linearity, and detection limit. To determine the detection limit of the AS 75 test kit, a solution with a concentration of 25 ppb (i.e., 2.5 times the vendor's estimated detection limit) 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 75 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 75 test kit. 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.

Table 3-1. Test Samples^a for Verification of the AS 75 Test Kit

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	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.

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 Columbus, 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 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.⁽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 with a minimum of five calibration standards with 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 AS 75 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 75 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

Test Day	Testing Location	Activity
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⁽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 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_L samples were analyzed to assess whether matrix effects influenced the results of the reference method. The percent recovery (R) of these LFM_L 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_L fell outside the range of from 85 to 115%, a matrix effect was suspected. As shown in Table 4-2, all of the LFM_L 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_L Analysis Results

LFM _L Sample ID	Date of Analysis	Unspiked Sample	Spiked Sample	Spiked Amount	Percent Recovery
		Arsenic (ppb)	Arsenic (ppb)	Arsenic (ppb)	
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.

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	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 AS 75 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 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 75 test kit and that from the reference method, and C_R is the reference measurement.

Because of the semi-quantitative nature of the PeCo test kit results, all of the data obtained by visual or electronic means were also 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 then 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% criteria, 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., <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 75 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^{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 75 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 test kit was assessed from the seven replicate analyses of a fortified sample with an analyte 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.⁽¹⁾ 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.⁽⁴⁾

5.5 Matrix Interference Effects

The effect of interfering matrix species on the response of the AS 75 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 75 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 AS 75 test kit data, and the inability of the operators to independently use the same test kits, quantitative assessments of operator bias could not be done. 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 75 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 75 test kit are presented in this section. Results are shown for both the PeCo test kit and the AS 75 tester.

6.1 Accuracy

Tables 6-1a-c present the measured arsenic results from analysis of the prepared, drinking water, and FW samples, respectively, for both the reference analyses and the PeCo test kit. PeCo test kit results are shown for both the technical and non-technical operators. Samples with no visible color development from the PeCo test kit were assigned a value of <10 ppb. Tables 6-1d-f list the corresponding measured arsenic results from analysis of the three types of water samples for both the reference method and the AS 75 tester. AS 75 tester results are shown for both the technical and non-technical operators. Although the AS 75 tester can display readings below 10 ppb, all such readings were reported as <10 ppb, because that is the low end of the measurement range of the AS 75 as used in this test (see Section 3.1).

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.

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

Sample	Non-Technical Arsenic (ppb)	Technical Arsenic (ppb)	Reference Method^a Arsenic (ppb)
Laboratory RB	<10	<10	<0.1
Laboratory RB	<10	<10	<0.1
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
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	<10	1.00
PT2-1	<10	<10	2.92
PT2-2	<10	<10	2.92
PT2-3	<10	<10	2.92
PT2-4	<10	<10	2.92
PT3-1	10	10	9.20
PT3-2	10	10	9.20
PT3-3	10	10	9.20
PT3-4	10	10	9.20
PT4-1	30	30	29.3
PT4-2	35	30	29.3
PT4-3	30	30	29.3
PT4-4	15	20	29.3
PT5-1	92	80	92.6
PT5-2	95	80	92.6
PT5-3	92	80	92.6
PT5-4	100	70	92.6
PT6-1	50	30	23.5
PT6-2	30	20	23.5
PT6-3	20	30	23.5
PT6-4	30	40	23.5
PT6-5	25	30	23.5
PT6-6	15	30	23.5
PT6-7	25	20	23.5

^a 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 PeCo test kit.

Table 6-1b. Results from Drinking Water Analyses for PeCo Test Kit

Sample	Non-Technical Arsenic (ppb)	Technical Arsenic (ppb)	Reference Method^a Arsenic (ppb)
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	<10	<10	0.87
DW-4	<10	<10	0.87
DW LFM _F	10	<10	10.6
Laboratory RB	<10	<10	<0.1
QCS	10	10	10.9
WW-1	65	60	86.6
WW-2	20	60	86.6
WW-3	60	60	86.6
WW-4	60	60	86.6
WW LFM _F	65	60	82.1
Laboratory RB	<10	<10	<0.1
QCS	10	10	10.9
TW-1	10	15	26.0
TW-2	20	15	26.0
TW-3	15	15	26.0
TW-4	15	15	26.0
TW LFM _F	20	<10	50.8

^a Only one aliquot of each sample was analyzed by the reference method. Multiple aliquots of each sample were analyzed by the PeCo test kit.

Table 6-1c. Results from Freshwater Analyses for PeCo Test Kit

Sample	Non-Technical Arsenic (ppb)	Technical Arsenic (ppb)	Reference Method Arsenic (ppb)
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 _F	<10	10	11.6
Laboratory RB	<10	<10	<0.1
QCS	10	10	9.43
LC-1	<10	<10	2.13
LC-2	<10	<10	1.30
LC-3	<10	<10	1.44
LC-4	<10	<10	1.37
LC-4 Duplicate	<10	<10	1.36
LC-3 LFM _F	10	10	12.0
Laboratory RB	<10	<10	<0.1
QCS	10	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 _F	<10	10	2.38

Table 6-1d. Results from Laboratory Performance Test Sample Analyses for AS 75 Tester

Sample	Non-Technical Arsenic (ppb)	Technical Arsenic (ppb)	Reference Method^a Arsenic (ppb)
Laboratory RB	<10	<10	<0.1
Laboratory RB	<10	<10	<0.1
Laboratory RB	<10	<10	<0.1
Laboratory RB	<10	<10	<0.1
Laboratory RB	<10	<10	<0.1
Laboratory RB	NA	<10	<0.1
QCS	<10	11	9.80
QCS	10	14	9.80
QCS	12	12	9.80
QCS	14	10	9.80
PT1-1	<10	<10	1.00
PT1-2	<10	<10	1.00
PT1-3	<10	<10	1.00
PT1-4	<10	<10	1.00
PT2-1	<10	<10	2.92
PT2-2	<10	<10	2.92
PT2-3	<10	<10	2.92
PT2-4	<10	<10	2.92
PT3-1	12	11	9.20
PT3-2	14	14	9.20
PT3-3	12	13	9.20
PT3-4	<10	11	9.20
PT4-1	34	38	29.3
PT4-2	39	40	29.3
PT4-3	39	35	29.3
PT4-4	31	>120	29.3
PT5-1	>120	>120	92.6
PT5-2	>120	>120	92.6
PT5-3	>120	>120	92.6
PT5-4	>120	>120	92.6
PT6-1	56	34	23.5
PT6-2	34	29	23.5
PT6-3	30	30	23.5
PT6-4	48	53	23.5
PT6-5	30	43	23.5
PT6-6	29	36	23.5
PT6-7	37	29	23.5

^a Only one aliquot of each sample was analyzed by the reference method. Multiple aliquots of each sample were analyzed by the AS 75 tester.

NA: Not analyzed.

Table 6-1e. Results from Drinking Water Analyses for AS 75 Tester

Sample	Non-Technical Arsenic (ppb)	Technical Arsenic (ppb)	Reference Method^a Arsenic (ppb)
Laboratory RB	<10	13	<0.1
QCS	11	28	10.9
DW-1	<10	<10	0.87
DW-2	<10	<10	0.87
DW-3	<10	21	0.87
DW-4	<10	<10	0.87
DW LFM _F	12	12	10.6
Laboratory RB	<10	<10	<0.1
QCS	<10	12	10.9
WW-1	57	66	86.6
WW-2	47	57	86.6
WW-3	58	66	86.6
WW-4	59	54	86.6
WW LFM _F	70	66	82.1
Laboratory RB	<10	<10	<0.1
QCS	13	12	10.9
TW-1	13	15	26
TW-2	28	15	26
TW-3	15	23	26
TW-4	15	14	26
TW LFM _F	42	36	50.8

^a Only one aliquot of each sample was analyzed by the reference method. Multiple aliquots of each sample were analyzed by the AS 75 tester.

Table 6-1f. Results from Freshwater Analyses for AS 75 Tester

Sample	Non-Technical Arsenic (ppb)	Technical Arsenic (ppb)	Reference Test Arsenic (ppb)
Laboratory RB	<10	<10	<0.1
QCS	12	11	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 _F	<10	<10	11.6
Laboratory RB	<10	<10	<0.1
QCS	10	10	9.43
LC-1	<10	<10	2.13
LC-2	<10	<10	1.30
LC-3	<10	<10	1.44
LC-4	10	<10	1.37
LC-4 Duplicate	<10	<10	1.36
LC-3 LFM _F	11	10	12.0
Laboratory RB	<10	<10	<0.1
QCS	13	11	9.81
LBC-1	<10	11	2.48
LBC-2	13	<10	2.60
LBC-3	11	<10	2.14
LBC-3 Duplicate	<10	<10	2.26
LBC-4	<10	<10	2.54
LBC-4 LFM _F	<10	13	2.38

Tables 6-2a-c show the percent accuracy of the PeCo test kit results. Shown in the second and third columns 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 <10 ppb. The percent bias values shown in Tables 6-2a-c can be summarized by the range of bias observed with different sample sets and arsenic concentrations. For example, for the PeCo test kit with the PT samples (Table 6-2a), biases of 2 to 9% were found with arsenic levels near 10 ppb, with greater variability (1 to 113%) at 23.5 to 92.6 ppb. With the drinking water samples (Table 6-2b), corresponding bias ranges were 6 to 8% near 10 ppb, and 21 to 77% at 26 to 86.6 ppb arsenic. With the FW samples, the bias range was 2 to 17% near 10 ppb (Table 6-2c).

Table 6-2a. Accuracy of the PeCo Test Kit with Laboratory Performance Test Samples

Sample	Bias ^a		Within Range (Y/N) ^b	
	Non-Technical	Technical	Non-Technical	Technical
Laboratory RB	— ^c	— ^c	Y	Y
Laboratory RB	— ^c	— ^c	Y	Y
Laboratory RB	— ^c	— ^c	Y	Y
Laboratory RB	— ^c	— ^c	Y	Y
Laboratory RB	— ^c	— ^c	Y	Y
QCS	2%	2%	Y	Y
QCS	2%	2%	Y	Y
QCS	2%	2%	Y	Y
QCS	2%	2%	Y	Y
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	9%	9%	Y	Y
PT3-2	9%	9%	Y	Y
PT3-3	9%	9%	Y	Y
PT3-4	9%	9%	Y	Y
PT4-1	2%	2%	Y	Y
PT4-2	20%	2%	Y	Y
PT4-3	2%	2%	Y	Y
PT4-4	49%	32%	N	N
PT5-1	1%	14%	Y	Y
PT5-2	3%	14%	Y	Y
PT5-3	1%	14%	Y	Y
PT5-4	8%	24%	Y	Y
PT6-1	113%	28%	N	N
PT6-2	28%	15%	N	Y
PT6-3	15%	28%	Y	N
PT6-4	28%	70%	N	N
PT6-5	6%	28%	Y	N
PT6-6	36%	28%	N	N
PT6-7	6%	15%	Y	Y

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

^b Y = result within $\pm 25\%$ of reference, or reference value within $<$ range; N = result not within $\pm 25\%$ of reference, or reference value not within $<$ range.

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

Table 6-2b. Accuracy of the PeCo Test Kit with Drinking Water Samples

Sample	Bias ^a		Within Range (Y/N) ^b	
	Non-Technical	Technical	Non-Technical	Technical
Laboratory RB	— ^c	— ^c	Y	Y
QCS	8%	8%	Y	Y
DW-1	— ^c	— ^c	Y	Y
DW-2	— ^c	— ^c	Y	Y
DW-3	— ^c	— ^c	Y	Y
DW-4	— ^c	— ^c	Y	Y
DW LFM _F	6%	— ^c	Y	Y
Laboratory RB	— ^c	— ^c	Y	Y
QCS	8%	8%	Y	Y
WW-1	25%	31%	Y	N
WW-2	77%	31%	N	N
WW-3	31%	31%	N	N
WW-4	31%	31%	N	N
WW LFM _F	21%	27%	Y	N
Laboratory RB	— ^c	— ^c	Y	Y
QCS	8%	8%	Y	Y
TW-1	62%	42%	N	N
TW-2	23%	42%	Y	N
TW-3	42%	42%	N	N
TW-4	42%	42%	N	N
TW LFM _F	61%	— ^c	N	N

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

^b Y = result within $\pm 25\%$ of reference, or reference value within $<$ range; N = result not within $\pm 25\%$ of reference, or reference value not within $<$ range.

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

Table 6-2c. Accuracy of the PeCo Test Kit with Freshwater Samples

Sample	Bias ^a		Within Range (Y/N) ^b	
	Non-Technical	Technical	Non-Technical	Technical
Laboratory RB	— ^c	— ^c	Y	Y
QCS	7%	7%	Y	Y
SR-1	— ^c	— ^c	Y	Y
SR-2	— ^c	— ^c	Y	Y
SR-2 Duplicate	— ^c	— ^c	Y	Y
SR-3	— ^c	— ^c	Y	Y
SR-4	— ^c	— ^c	Y	Y
SR-1 LFM _F	— ^c	14%	N	Y
Laboratory RB	— ^c	— ^c	Y	Y
QCS	6%	6%	Y	Y
LC-1	— ^c	— ^c	Y	Y
LC-2	— ^c	— ^c	Y	Y
LC-3	— ^c	— ^c	Y	Y
LC-4	— ^c	— ^c	Y	Y
LC-4 Duplicate	— ^c	— ^c	Y	Y
LC-3 LFM _F	17%	17%	Y	Y
Laboratory RB	— ^c	— ^c	Y	Y
QCS	2%	2%	Y	Y
LBC-1	— ^c	— ^c	Y	Y
LBC-2	— ^c	285%	Y	N
LBC-3	— ^c	— ^c	Y	Y
LBC-3 Duplicate	— ^c	— ^c	Y	Y
LBC-4	— ^c	— ^c	Y	Y
LBC-4 LFM _F	— ^c	320%	Y	N

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

^b Y = result within $\pm 25\%$ of reference, or reference value within $<$ range; N = result not within $\pm 25\%$ of reference, or reference value not within $<$ range.

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

Tables 6-2d-f show the results of evaluating the accuracy of the AS 75 tester. Shown in the second and third columns in each of Tables 6-2d-f are the percent bias values determined according to Equation 3, in Section 5.1. A percent bias could not be calculated for values reported as < 10 ppb. The percent bias values that are shown in Tables 6-2d-f for the AS 75 tester include a range of 2 to 52% at arsenic concentrations near 10 ppb, and 6 to more than 310% at concentrations of 23.5 to 92.6 ppb, for the PT samples (the highest percent bias resulting from an over-range reading on the tester) (Table 6-2d). With the drinking water samples (Table 6-2e), the AS 75 tester gave biases of 1 to 157% near 10 ppb, and 8 to 50% at 26 to 86.6 ppb. Very large biases were observed with sample DW-3 and with one laboratory RB (Table 6-2e). With the FW samples (Table 6-2f), the corresponding biases near 10 ppb were 6 to 33%.

Table 6-2d. Accuracy of the AS 75 Tester with Laboratory Performance Test Samples

Sample	Bias ^a		Within Range (Y/N) ^b	
	Non-Technical	Technical	Non-Technical	Technical
Laboratory RB	— ^c	— ^c	Y	Y
Laboratory RB	— ^c	— ^c	Y	Y
Laboratory RB	— ^c	— ^c	Y	Y
Laboratory RB	— ^c	— ^c	Y	Y
Laboratory RB	— ^c	— ^c	Y	Y
Laboratory RB	— ^c	— ^c	Y	Y
QCS	— ^c	12%	Y	Y
QCS	2%	43%	Y	N
QCS	22%	22%	Y	Y
QCS	43%	2%	N	Y
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	30%	20%	N	Y
PT3-2	52%	52%	N	N
PT3-3	30%	41%	N	N
PT3-4	— ^c	20%	Y	Y
PT4-1	16%	30%	Y	N
PT4-2	33%	37%	N	N
PT4-3	33%	20%	N	Y
PT4-4	6%	>310%	Y	N
PT5-1	>30%	>30%	N	N
PT5-2	>30%	>30%	N	N
PT5-3	>30%	>30%	N	N
PT5-4	>30%	>30%	N	N
PT6-1	138%	45%	N	N
PT6-2	45%	23%	N	Y
PT6-3	28%	28%	N	N
PT6-4	104%	125%	N	N
PT6-5	28%	83%	N	N
PT6-6	23%	53%	Y	N
PT6-7	57%	23%	N	Y

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

^b Y = result within $\pm 25\%$ of reference, or reference value within $<$ range; N = result not within $\pm 25\%$ of reference, or reference value not within $<$ range.

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

Table 6-2e. Accuracy of the AS 75 Tester with Drinking Water Samples

Sample	Bias ^a		Within Range (Y/N) ^b	
	Non-Technical	Technical	Non-Technical	Technical
Laboratory RB	— ^c	>12,900%	Y	N
QCS	1%	157%	Y	N
DW-1	— ^c	— ^c	Y	Y
DW-2	— ^c	— ^c	Y	Y
DW-3	— ^c	2,314%	Y	N
DW-4	— ^c	— ^c	Y	Y
DW LFM _F	13%	13%	Y	Y
Laboratory RB	— ^c	— ^c	Y	Y
QCS	— ^c	10%	N	Y
WW-1	34%	24%	N	Y
WW-2	46%	34%	N	N
WW-3	33%	24%	N	Y
WW-4	32%	38%	N	N
WW LFM _F	15%	20%	Y	Y
Laboratory RB	— ^c	— ^c	Y	Y
QCS	19%	10%	Y	Y
TW-1	50%	42%	N	N
TW-2	8%	42%	Y	N
TW-3	42%	12%	N	Y
TW-4	42%	46%	N	N
TW LFM _F	17%	29%	Y	N

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

^b Y = result within $\pm 25\%$ of reference, or reference value within $<$ range; N = result not within $\pm 25\%$ of reference, or reference value not within $<$ range.

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

Table 6-2f. Accuracy of the AS 75 Tester with Freshwater Samples

Sample	Bias ^a		Within Range (Y/N) ^b	
	Non-Technical	Technical	Non-Technical	Technical
Laboratory RB	— ^c	— ^c	Y	Y
QCS	29%	18%	N	Y
SR-1	— ^c	— ^c	Y	Y
SR-2	— ^c	— ^c	Y	Y
SR-2 Duplicate	— ^c	— ^c	Y	Y
SR-3	— ^c	— ^c	Y	Y
SR-4	— ^c	— ^c	Y	Y
SR-1 LFM _F	— ^c	— ^c	N	N
Laboratory RB	— ^c	— ^c	Y	Y
QCS	6%	6%	Y	Y
LC-1	— ^c	— ^c	Y	Y
LC-2	— ^c	— ^c	Y	Y
LC-3	— ^c	— ^c	Y	Y
LC-4	630%	— ^c	N	Y
LC-4 Duplicate	— ^c	— ^c	Y	Y
LC-3 LFM _F	8%	17%	Y	Y
Laboratory RB	— ^c	— ^c	Y	Y
QCS	33%	12%	N	Y
LBC-1	— ^c	344%	Y	N
LBC-2	400%	— ^c	N	Y
LBC-3	414%	— ^c	N	Y
LBC-3 Duplicate	— ^c	— ^c	Y	Y
LBC-4	— ^c	— ^c	Y	Y
LBC-4 LFM _F	— ^c	446%	Y	N

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

^b Y = result within $\pm 25\%$ of reference, or reference value within $<$ range; N = result not within $\pm 25\%$ of reference, or reference value not within $<$ range.

^c Non-detect, no calculation of bias can be made

In addition to the quantitative bias results, the qualitative accuracy comparison using Equation 4 in Section 5.1 was used. The fourth and fifth columns in Tables 6-2a-c show the assignment of each PeCo test kit 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 6-3a, which lists the overall percent of results meeting the $\pm 25\%$ criterion for each operator and sample type. Table 6-3a shows that the qualitative accuracy of the PeCo test kit for the PT samples was 86% for the non-technical operator and 83% for the technical operator. The qualitative accuracy for the drinking water samples was 67% for the non-technical operator and 52% for the technical operator. The qualitative accuracy for the FW samples was 96% for the non-technical operator and 92% for the technical operator. However, it should be noted that 79% of the FW reference results were < 10 ppb (Table 6-1c).

The fourth and fifth columns in Tables 6-2d-f show the assignment of each AS 75 tester 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 6-3b, which lists the overall percent of results meeting the $\pm 25\%$ criterion for each operator and sample type. Table 6-3b shows that the qualitative accuracy of the AS 75 tester for the PT samples (Table 6-2d) was 57% for the non-technical operator and 59% for the technical operator. The qualitative accuracy for the drinking water samples (Table 6-2e) was 62% for the non-technical operator and 57% for the technical operator. The qualitative accuracy for the FW samples (Table 6-2f) was 75% for the non-technical operator and 88% for the technical operator. However, it should be noted that 79% of the FW reference results were <10 ppb (Table 6-1f).

Table 6-3a. Summary of Qualitative Accuracy Results for PeCo Test Kit

	Percent Accurate Within 25% (Non-Technical Operator)	Percent Accurate Within 25% (Technical Operator)
Laboratory performance test samples	86%	83%
Drinking water samples	67%	52%
Freshwater samples	96%	92%

Table 6-3b. Summary of Qualitative Accuracy Results for AS 75 Tester

	Percent Accurate Within 25% (Non-Technical Operator)	Percent Accurate Within 25% (Technical Operator)
Laboratory performance test samples	57%	59%
Drinking water samples	62%	57%
Freshwater samples	75%	88%

6.2 Precision

Tables 6-4a and b, respectively, show the data used to evaluate the RSD of the PeCo 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. Percent RSD was not calculated if all of the results for a set of replicates were <10 ppb. The RSD ranged from 0 to 40% for the non-technical operator and 0 to 24% for the technical operator on the PT samples. The RSD for the drinking water samples was 27 to 41% for the non-technical operator and was 0% for the technical operator.

Tables 6-4c and d, respectively, show the data used to evaluate the RSD of the AS 75 tester results for the replicate laboratory PT and drinking water samples. Also shown in the tables is the percent RSD value for each set of replicate analyses. Percent RSD was not calculated if all of the results for a set of replicates were either <10 ppb or >120 ppb. A value of 5 ppb (i.e., half the

Table 6-4a. Precision Results for PeCo Test Kit from Laboratory Performance Test Samples

Sample	Reference Concentration (ppb)	Non-Technical Arsenic (ppb)	Technical^a Arsenic (ppb)
QCS	9.80	10	10
QCS		10	10
QCS		10	10
QCS		10	10
%RSD		0	0
PT1-1	1.00	<10	<10
PT1-2		<10	<10
PT1-3		<10	<10
PT1-4		<10 _b	<10 _b
%RSD			
PT2-1	2.92	<10	<10
PT2-2		<10	<10
PT2-3		<10	<10
PT2-4		<10 _b	<10 _b
%RSD			
PT3-1	9.20	10	10
PT3-2		10	10
PT3-3		10	10
PT3-4		10	10
%RSD		0	0
PT4-1	29.3	30	30
PT4-2		35	30
PT4-3		30	30
PT4-4		15	20
%RSD		31	18
PT5-1	92.6	92	80
PT5-2		95	80
PT5-3		92	80
PT5-4		100	70
%RSD		4	6
PT6-1	23.5	50	30
PT6-2		30	20
PT6-3		20	30
PT6-4		30	40
PT6-5		25	30
PT6-6		15	30
PT6-7		25	20
%RSD		40	24

^a For the purpose of calculating %RSD, all “less than” values are considered zero.

^b No %RSD could be calculated.

Table 6-4b. Precision Results for PeCo Test Kit from Drinking Water Samples

Sample	Reference Concentration (ppb)	Non-Technical Arsenic (ppb)	Technical^a Arsenic (ppb)
DW-1	0.87	<10	<10
DW-2		<10	<10
DW-3		<10	<10
DW-4		<10	<10
%RSD		_b	_b
WW-1	86.6	65	60
WW-2		20	60
WW-3		60	60
WW-4		60	60
%RSD		41	0
TW-1	26.0	10	15
TW-2		20	15
TW-3		15	15
TW-4		15	15
%RSD		27	0

^a For the purpose of calculating %RSD, all “less than” values are considered zero.

^b No %RSD could be calculated.

Table 6-4c. Precision Results for AS 75 Tester from Laboratory Performance Test Samples

Sample	Reference Concentration (ppb)	Non-Technical Arsenic (ppb)	Technical^a Arsenic (ppb)
QCS	9.80	<10	11
QCS		10	14
QCS		12	12
QCS		14	10
%RSD		38	15
PT1-1	1.00	<10	<10
PT1-2		<10	<10
PT1-3		<10	<10
PT1-4		<10 _b	<10 _b
%RSD			
PT2-1	2.92	<10	<10
PT2-2		<10	<10
PT2-3		<10	<10
PT2-4		<10 _b	<10 _b
%RSD			
PT3-1	9.20	12	11
PT3-2		14	14
PT3-3		12	13
PT3-4		<10	11
%RSD		37	12
PT4-1	29.3	34	38
PT4-2		39	40
PT4-3		39	35
PT4-4		31	>120
%RSD		11	>71
PT5-1	92.6	>120	>120
PT5-2		>120	>120
PT5-3		>120	>120
PT5-4		>120 _b	>120 _b
%RSD			
PT6-1	23.5	56	34
PT6-2		34	29
PT6-3		30	30
PT6-4		48	53
PT6-5		30	43
PT6-6		29	36
PT6-7		37	29
%RSD		28	25

^a For the purpose of calculating %RSD, all “less than” values are considered zero.

^b No %RSD could be calculated.

Table 6-4d. Precision Results for AS 75 Tester from Drinking Water Samples

Sample	Reference Concentration (ppb)	Non-Technical^a Arsenic (ppb)	Technical^a Arsenic (ppb)
DW-1	0.87	<10	<10
DW-2		<10	<10
DW-3		<10	21
DW-4		<10	<10
%RSD		_b	89
WW-1	86.6	57	66
WW-2		47	57
WW-3		58	66
WW-4		59	54
%RSD		10	10
TW-1	26.0	13	15
TW-2		28	15
TW-3		15	23
TW-4		15	14
%RSD		39	25

^a For the purpose of calculating standard deviation, all “less than” values are considered zero.

^b No %RSD could be calculated.

nominal MDL) was used when the replicate data included some non-detect values, and a value of 120 ppb was used in place of a reading of >120 ppb. The RSD ranged from 11 to 38% for the non-technical operator and 12 to >71% for the technical operator on the PT samples. The RSD for the drinking water samples was 10 to 39% for the non-technical operator and 10 to 89% for the technical operator.

6.3 Linearity

The linearity of the PeCo test kit and the AS 75 tester was assessed by means of a linear regression of the results against the reference method results, using the 27 data points from the PT samples (Tables 6-1a and 6-1d, respectively). In this regression, results reported as below detection limit by the PeCo test kit and the AS 75 tester were assigned a value of 5 ppb (i.e., half the detection limit). Results reported as >120 ppb by the AS 75 tester were assigned a value of 120 ppb for the regression. Figures 6-1 and 6-2 show scatter plots of the PeCo test kit and the AS 75 tester results, respectively, from the technical and non-technical operator versus the reference method results. The one-to-one line is also shown in Figures 6-1 and 6-2.

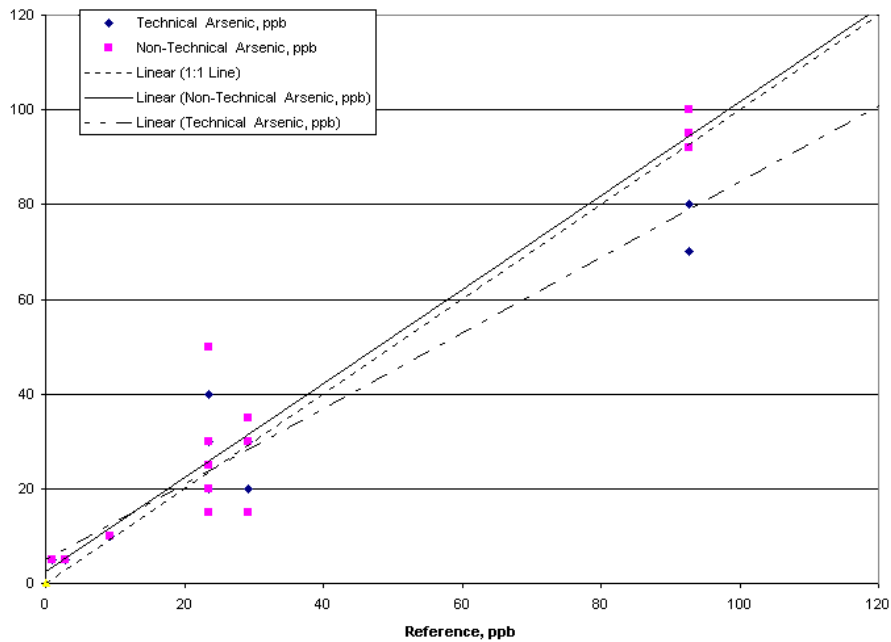


Figure 6-1. Comparison of PeCo Test Kit to Reference Method Results from PT Samples

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

with the PeCo test kit for the non-technical operator,
 $\text{ppb} = 0.99 (\pm 0.090) \times (\text{reference, ppb}) + 2.41 (\pm 3.55) \text{ ppb}$,
 with $r = 0.977$, and

with the PeCo test kit for the technical operator,
 $\text{ppb} = 0.80 (\pm 0.069) \times (\text{reference, ppb}) + 5.12 (\pm 2.70) \text{ ppb}$,
 with $r = 0.979$.

A linear regression of the data in Figure 6-2 gives the following regression equations:

with the AS 75 tester for the non-technical operator,
 $\text{ppb} = 1.27 (\pm 0.074) \times (\text{reference, ppb}) + 2.25 (\pm 2.93) \text{ ppb}$,
 with $r = 0.990$, and

with the AS 75 tester for the technical operator,
 $\text{ppb} = 1.28 (\pm 0.22) \times (\text{reference, ppb}) + 5.70 (\pm 8.69) \text{ ppb}$,
 with $r = 0.923$

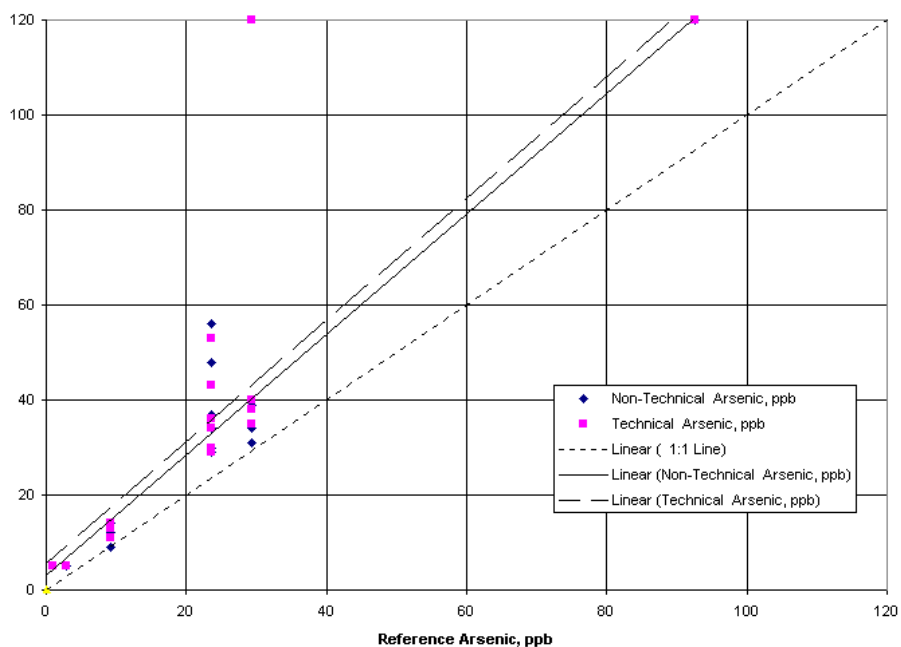


Figure 6-2. Comparison of AS 75 Tester to Reference Method Results from PT Samples

where the values in parentheses represent the 95% confidence interval of the slope and intercept. Only one of the calculated intercepts is significantly different from zero, and the r values are all 0.92 or higher. The slope for the non-technical operator with the PeCo test kit is not significantly different from 1.0. However, the other three slope values are all significantly different from 1.0.

6.4 Method Detection Limit

The manufacturer's estimated detection limit for the PeCo test kit and for the AS 75 tester is 10 ppb. An attempt was made to determine the MDL by analyzing seven replicate samples at a concentration of 25 ppb (i.e., 2.5 times the manufacturer's estimated detection limit). With the PeCo test kit, the results from both operators were somewhat erratic. The non-technical operator reported arsenic results ranging between 15 and 50 ppb, and the technical operator reported arsenic results between 20 and 40 ppb. These results were listed as PT-6 samples in Table 6-4a. Since the PeCo test kit is only semi-quantitative, no MDL was calculated from those data.

For the AS 75 tester, the MDL was calculated, based on the seven replicate analyses at 25 ppb listed in Table 6-4c. Those data, and the 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 AS 75 tester for the non-technical operator was 32.7 ppb and for the technical operator was 28 ppb.

Table 6-5. Method Detection Limit Results for the AS 75 Tester

	Non-Technical Arsenic (ppb)	Technical Arsenic (ppb)
PT6-1	56	34
PT6-2	34	29
PT6-3	30	30
PT6-4	48	53
PT6-5	30	43
PT6-6	29	36
PT6-7	37	29
Std. Deviation (S)	10.4	8.9
<i>t</i> at n=7 ^a	3.14	3.14
MDL ^b	32.7	28.0

^a *t* is the Student's value for a 99% confidence level, with seven samples.

^b MDL = *t* x S (see Section 5.4).

6.5 Matrix Interference Effects

Eight replicate samples with about 10 ppb arsenic and low amounts of interferences, and eight with high amounts of interferences, were analyzed. The technical operator only analyzed four of the eight samples with high levels of interferences. Tables 6-6a and b show the analytical results for the PeCo test kit from laboratory PT samples with low and high levels of interferences, respectively. The non-technical operator did not detect arsenic in any of the samples with low or high levels of interferences added to the matrix. The technical operator observed 10 ppb of arsenic in one of the samples with low levels of interferences, but did not detect arsenic in the other 11 samples.

Tables 6-6c and d show the corresponding analytical results for the AS 75 tester from laboratory PT samples with low and high levels of interferences, respectively. The non-technical operator did not detect arsenic in four of the samples with low levels of interferences, or in any of the samples with high levels of interferences added to the matrix. The technical operator reported 14 ppb of arsenic in one of the samples with low levels of interferences, but did not detect arsenic in any other samples.

The results in Tables 6-6c and d suggest that the non-technical operator achieved somewhat better detection of arsenic with the low interference levels with the AS 75 tester, compared to the high interference levels. However, this suggestion is not borne out by the technical operator's results. Furthermore, no clear effect of the interferences can be determined from the PeCo test kit data (Tables 6-6a and b) with either operator.

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

	Non-Technical Arsenic (ppb)	Technical Arsenic (ppb)
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

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

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

NA: Not analyzed.

Table 6-6c. Results from Laboratory Performance Test Samples with Low-Level Interferences for AS 75 Tester

	Non-Technical Arsenic (ppb)	Technical Arsenic (ppb)
LI-1	10	<10
LI-2	10	<10
LI-3	<10	<10
LI-4	10	<10
LI-5	<10	14
LI-6	10	<10
LI-7	<10	<10
LI-8	<10	<10

Table 6-6d. Results from Laboratory Performance Test Samples with High-Level Interferences for AS 75 Tester

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

NA: Not analyzed.

6.6 Operator Bias

The effect of operator skill level does not appear to be a major factor with this portable analyzer. The two operators' results track closely over a range of arsenic concentrations, and show similar degrees of variability in replicate analyses.

6.7 Rate of False Positives/False Negatives

Tables 6-7a and b and 6-8a and b, respectively, show the data and results for the rates of false positives and false negatives obtained from the PeCo test kit and AS 75. All performance test and environmental samples (Table 3-1) were considered for this evaluation.

Table 6-7a shows the false positive results for the PeCo test kit. The reference arsenic concentration was less than the target midpoint of 10 ppb for 44 samples of various types. For four samples, the non-technical operator reported concentrations of 10 ppb. In each instance, the value was less than 125% of the reference value. Similarly, the technical operator reported six readings of 10 ppb or more. In five of these instances, the value obtained by the technical operator was less than 125% of the reference value. The resulting false positive rates with the PeCo test kit are 0% for the non-technical and 3% for the technical operator.

Table 6-7b shows the false positive results for the AS 75 tester. Both operators reported a few readings exceeding 10 ppb. Most of these readings were less than 125% of the reference value. The rate of false positives was 2% for the non-technical operator and 13% for the technical operator with the As 75 tester.

Tables 6-8a and b show that 23 samples had reference arsenic concentrations greater than the target midpoint of 10 ppb. Table 6-8a gives the false negative results for the PeCo test kit. Table 6-8b gives the false negative results for the AS 75 tester. There were 0% false negatives from both operators on both of these devices.

Table 6-7a. Rate of False Positives from PeCo 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	<10	1.00	N	N
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	<10	2.92	N	N
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	10	10	9.20	N	N
DW-1	<10	<10	0.87	N	N
DW-2	<10	<10	0.87	N	N
DW-3	<10	<10	0.87	N	N
DW-4	<10	<10	0.87	N	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	NA	9.94	N	
HI-6	<10	NA	9.94	N	
HI-7	<10	NA	9.94	N	
HI-8	<10	NA	9.94	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

(continued)

Table 6-7a. Rate of False Positives from PeCo Test Kit (continued)

	Non-Technical Arsenic (ppb)	Technical Arsenic (ppb)	Reference Method Arsenic (ppb)	Non-Technical False Positive (Y/N)	Technical False Positive (Y/N)
LC-1	<10	<10	2.13	N	N
LC-2	<10	<10	1.30	N	N
LC-3	<10	<10	1.44	N	N
LC-4	<10	<10	1.37	N	N
LBC-1	<10	<10	2.48	N	N
LBC-2	<10	<10	2.60	N	N
LBC-3	<10	10	2.14	N	Y
LBC-4	<10	<10	2.54	N	N
Total number of applicable samples				44	40
Total false positive				0	1
Percent false positive				0%	3%

Y = yes

N = no

Table 6-7b. Rate of False Positives from AS 75 Tester

	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	<10	1.00	N	N
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	<10	2.92	N	N
PT3-1	12	11	9.20	N	N
PT3-2	14	14	9.20	Y	Y
PT3-3	12	13	9.20	N	Y
PT3-4	<10	11	9.20	N	N
DW-1	<10	<10	0.87	N	N
DW-2	<10	<10	0.87	N	N
DW-3	<10	21	0.87	N	Y
DW-4	<10	<10	0.87	N	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	14	9.91	N	Y
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	NA	9.94	N	
HI-6	<10	NA	9.94	N	
HI-7	<10	NA	9.94	N	
HI-8	<10	NA	9.94	N	

(continued)

Table 6-7b. Rate of False Positives from AS 75 Tester (continued)

	Non-Technical Arsenic (ppb)	Technical Arsenic (ppb)	Reference Method Arsenic (ppb)	Non-Technical False Positive (Y/N)	Technical False Positive (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
LC-1	<10	<10	2.13	N	N
LC-2	<10	<10	1.30	N	N
LC-3	<10	<10	1.44	N	N
LC-4	<10	<10	1.37	N	N
LBC-1	<10	11	2.48	N	Y
LBC-2	<10	<10	2.60	N	N
LBC-3	<10	<10	2.14	N	N
LBC-4	<10	<10	2.54	N	N
Total number of applicable samples				44	40
Total false positive				1	5
Percent false positive				2%	13%

Y = yes

N = no

Table 6-8a. Rate of False Negatives from PeCo Test Kit

	Non-Technical Arsenic (ppb)	Technical Arsenic (ppb)	Reference Method Arsenic (ppb)	Non-Technical False Negative (Y/N)	Technical False Negative (Y/N)
PT4-1	30	30	29.3	N	N
PT4-2	35	30	29.3	N	N
PT4-3	30	30	29.3	N	N
PT4-4	15	20	29.3	N	N
PT5-1	92	80	92.6	N	N
PT5-2	95	80	92.6	N	N
PT5-3	92	80	92.6	N	N
PT5-4	100	70	92.6	N	N
PT6-1	50	30	23.5	N	N
PT6-2	30	20	23.5	N	N
PT6-3	20	30	23.5	N	N
PT6-4	30	40	23.5	N	N
PT6-5	25	30	23.5	N	N
PT6-6	15	30	23.5	N	N
PT6-7	25	20	23.5	N	N
WW-1	65	60	86.6	N	N
WW-2	20	60	86.6	N	N
WW-3	60	60	86.6	N	N
WW-4	60	60	86.6	N	N
TW-1	10	15	26.0	N	N
TW-2	20	15	26.0	N	N
TW-3	15	15	26.0	N	N
TW-4	15	15	26.0	N	N
Total number of applicable samples				23	23
Total false negative				0	0
Percent false negative				0%	0%

Y = yes

N = no

Table 6-8b. Rate of False Negatives from AS 75 Tester

	Non-Technical Arsenic (ppb)	Technical Arsenic (ppb)	Reference Method Arsenic (ppb)	Non-Technical False Negative (Y/N)	Technical False Negative (Y/N)
PT4-1	34	38	29.3	N	N
PT4-2	39	40	29.3	N	N
PT4-3	39	35	29.3	N	N
PT4-4	31	11	29.3	N	N
PT5-1	>120	>120	92.6	N	N
PT5-2	>120	>120	92.6	N	N
PT5-3	>120	>120	92.6	N	N
PT5-4	>120	>120	92.6	N	N
PT6-1	56	34	23.5	N	N
PT6-2	34	29	23.5	N	N
PT6-3	30	30	23.5	N	N
PT6-4	48	53	23.5	N	N
PT6-5	30	43	23.5	N	N
PT6-6	29	36	23.5	N	N
PT6-7	37	29	23.5	N	N
WW-1	57	66	86.6	N	N
WW-2	47	57	86.6	N	N
WW-3	58	66	86.6	N	N
WW-4	59	54	86.6	N	N
TW-1	13	15	26.0	N	N
TW-2	28	15	26.0	N	N
TW-3	15	23	26.0	N	N
TW-4	15	14	26.0	N	N
Total number of applicable samples				23	23
Total false negative				0	0
Percent false negative				0%	0%

Y = yes

N = no

6.8 Other Factors

The operators felt that the AS 75 test kit was easy to use and free of maintenance. The kit is lightweight, easy to transport by car, and can easily be carried through fields and wooded areas. However, in one of the kits, the glass reaction bottle was blown over by the wind and broken. The color on the indicator paper is of the same color and shade as the color chart, making comparison easy. The color chart has cutout holes for the indicator paper, which assist in making comparisons. The reagents are solid tablets, which are easy to use and require no measuring or preparation. The AS 75 test kit instructions indicate that the tablets dissolve in ten minutes. The vendor was unable to provide newly prepared reagent tablets for this test, so previously prepared tablets from the vendor's stock were used. Operators found that the larger of the two reagent tablets required up to one and a half hours to dissolve. The time required to dissolve newly prepared tablets could not be determined in this test. The AS 75 test kit allows for the analysis of one sample at a time. When the analysis is complete, the reagent bottles are rinsed for reuse. The electronic AS 75 tester is light and easy to use and is capable of reading the filters within seconds. This kit requires no liquids or concentrated acids, making it safe and easy to carry in the field. The tablets contain no toxic materials.

6.8.1 Costs

The cost of the basic PeCo test kit capable of analyzing 100 samples is \$220. The cost of the electronic AS 75 tester is \$330. Refill packs for 100 additional tests cost \$60.

6.8.2 Data Completeness

All portions of the verification test were completed, and all data, except four samples containing high interferences that were to be recorded by the technical operator, were successfully acquired. Thus, data completeness was 98%, with the only missing data due to operator error.

Chapter 7

Performance Summary

The AS 75 arsenic test kit measures arsenic in water visually using the PeCo test kit, or electronically using the AS 75 tester. Both approaches were tested in this verification. Considering results from both technical and non-technical operators, the PeCo test kit gave accuracy (in terms of bias relative to reference results) of 2 to 9%, 6 to 8%, and 2 to 17% for samples near 10 ppb arsenic in the PT, drinking water, and FW sample sets, respectively. At higher arsenic concentrations (23.5 to 92.6 ppb), the PeCo test kit gave biases of 1 to 113% and 21 to 77% for samples in the PT and drinking water sets, respectively.

For the AS 75 tester, corresponding biases were 2 to 52%, 1 to 157%, and 6 to 33% for samples near 10 ppb in the PT, drinking water, and FW sets, respectively. At higher concentrations, the AS 75 tester showed biases of 6 to more than 310%, and 8 to 50% for samples in the PT and drinking water sets, respectively.

An additional criterion for accuracy was the percentage of AS 75 test kit results that were within 25% of the corresponding reference result, or within the corresponding “less-than” range. By this criterion, the qualitative accuracy of the PeCo test kit for the PT samples was 86% for the non-technical operator and 83% for the technical operator. The qualitative accuracy for the drinking water samples was 67% for the non-technical operator and 52% for the technical operator. The qualitative accuracy for the FW samples was 96% for the non-technical operator and 92% for the technical operator. The qualitative accuracy of the AS 75 tester for the PT samples was 57% for the non-technical operator and 59% for the technical operator. The qualitative accuracy for the drinking water samples was 62% for the non-technical operator and 57% for the technical operator, and for the FW samples was 75% for the non-technical and 88% for the technical operator.

With the PeCo test kit, the RSD ranged from 0 to 40% for the non-technical operator and 0 to 24% for the technical operator in replicate analyses of the PT samples. The corresponding RSD for the drinking water samples was 27 to 41% for the non-technical operator and was 0% for the technical operator. With the AS 75 tester, the RSD ranged from 11 to 38% for the non-technical operator and 12 to more than 71% for the technical operator on the PT samples. The RSD for the drinking water samples was 10 to 39% for the non-technical operator and 10 to 89% for the technical operator.

The linearity of response of the AS 75 was assessed using the PT samples containing from 1 to 93 ppb arsenic. The linear regression with the PeCo test kit for the non-technical operator was $\text{ppb} = 0.99 (\pm 0.090) x (\text{reference, ppb}) + 2.41 (\pm 3.55) \text{ ppb}$, with $r = 0.977$. With the PeCo test kit for the technical operator, it was $\text{ppb} = 0.80 (\pm 0.069) x (\text{reference, ppb}) + 5.12 (\pm 2.70) \text{ ppb}$, with $r = 0.979$. The linear regression with the AS 75 tester for the non-technical operator was $\text{ppb} = 1.27 (\pm 0.074) x (\text{reference, ppb}) + 2.25 (\pm 2.93) \text{ ppb}$, with $r = 0.990$. With the AS 75 tester for the technical operator, it was $\text{ppb} = 1.28 (\pm 0.22) x (\text{reference, ppb}) + 5.70 (\pm 8.69) \text{ ppb}$, with $r = 0.923$.

To assess the MDL of the AS 75, a total of seven replicate PT samples were analyzed at a concentration of 25 ppb. With the PeCo kit, the results from both operators were somewhat erratic. The non-technical operator reported arsenic between 15 and 50 ppb, and the technical operator reported arsenic between 20 and 40 ppb. No MDL was calculated for the PeCo kit, since it is a semi-quantitative test kit. For the AS 75 tester, the calculated MDL for the non-technical operator was 32.7 ppb, and for the technical operator was 28 ppb.

The AS 75 results did not show a significant effect of sample matrices containing low or high levels of sodium chloride, iron, sulfate, or acidity using either the PeCo test kit or the AS 75 tester.

The degree of technical training of the operators did not appear to be a major factor on the AS 75 results, with either the PeCo kit or the AS 75 tester.

The rates of false positives and false negatives of the AS 75 were assessed relative to the reference method using 10 ppb of arsenic as the decision level. The rate of false positives for the PeCo test kit was 0% for the non-technical and 3% for the technical operators. For the AS 75 tester, the false positive rate was 2% for the non-technical operator and 13% for the technical operator relative to the 10-ppb value. For both the PeCo test kit and the AS 75 tester, the rate of false negatives was 0% for both the non-technical and the technical operator.

The cost of the basic PeCo test kit capable of analyzing 100 samples is \$220. The cost of the electronic AS 75 tester is \$330. Refill packs for 100 additional tests cost \$60. The vendor was unable to provide newly prepared reagent tablets for this test, so previously prepared tablets from the vendor's stock were used. Operators found that the larger of the two reagent tablets required up to one and a half hours to dissolve. The time required to dissolve newly prepared tablets could not be determined in this test. The reagents are in tablet form and are ready to use, with no preparation required.

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.