

Analytical Methods Support Document For Arsenic In Drinking Water

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This report is issued in support of a proposed National Primary Drinking Water Regulation for arsenic. It is intended for public comment and does not represent final agency policy. EPA expects to issue a final version of this report in 2001, reflecting corrections due to public comment on the proposed rule and supporting documents.

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Executive Summary

Under the Safe Drinking Water Act of 1974, the EPA Office of Ground Water and Drinking Water (OGWDW) is responsible for ensuring that public water systems provide safe drinking water. As part of that responsibility, OGWDW establishes maximum contaminant levels or treatment technology requirements for specific contaminants that may have adverse human health effects.

Arsenic is trace metal found in aquatic environments that can cause a variety of adverse health effects in humans and other organisms. There are both natural and anthropogenic sources of arsenic in natural waters.

In order to establish a regulatory limit for arsenic in drinking water, EPA has evaluated the sensitivity of analytical techniques that are currently available for SDWA compliance monitoring of arsenic. One aspect of that evaluation is to determine the Practical Quantitation Limit (PQL), which has previously been defined by EPA as the lowest concentration of an analyte that can be reliably measured within specified limits of precision and accuracy during routine laboratory operation conditions (52 FR 25699, July 8, 1987). The PQL is a means of integrating information on the performance of the approved analytical methods into the development of a drinking water regulation.

In 1994, EPA derived a PQL for arsenic that was based on data collected by the Agency from performance evaluation studies that addressed low levels of arsenic. In response to concerns from the water utility industry, the results of that derivation and a separate evaluation conducted by the American Water Works Association (AWWA) were reviewed by the EPA Science Advisory Board (SAB) in 1995. The SAB noted that the acceptance limits for the laboratory data used by EPA to derive the PQL in 1994 were wider than those for other metal contaminants that had been regulated and recommended that EPA not accept less precision and accuracy for arsenic for the purpose of protection at a certain risk level.

Subsequent to that recommendation, EPA has conducted additional performance evaluation studies focused on levels of arsenic below 6 µg/L and determined a new PQL for arsenic. The process employed by EPA in 1999 utilized:

- data from six low-level(<6 µg/L) arsenic performance evaluation studies
- acceptance limits similar to other low level inorganics, and
- linear regression analysis to determine the point at which 75% of EPA and State laboratories fell within the acceptance range.

This process yielded a PQL of 3 µg/L at the ± 30% acceptance limit. While the PQL represents a stringent target for laboratory performance, the Agency believes that most laboratories using appropriate quality assurance and quality control procedures will be able to achieve this level on a routine basis. The process used was consistent with the derivations of PQLs for other contaminants regulated under the SDWA and consistent with the 1995 recommendations of the EPA Science Advisory Board.

Analytical Methods Support Document for Arsenic in Drinking Water

1.0 Introduction

1.1 What is the Purpose of this Document?

This document has been developed by EPA in support of the rulemaking process for arsenic in drinking water. The Agency is proposing a Maximum Contaminant Level Goal (MCLG) and revising the existing MCL for arsenic. The purposes of this document is the:

- identification of available and acceptable analytical methods for measuring arsenic in drinking water; and
- the determination of the practical quantitation limit (PQL) for arsenic in drinking water.

1.2 What are the Statutory Requirements?

The Safe Drinking Water Act (Section 1401) directs EPA to promulgate national primary drinking water regulations (NPDWRs) which specify either MCLs or treatment techniques for drinking water contaminants (42 USC 300g-1). EPA is required to set an MCL “if, in the judgement of the Administrator, it is economically and technologically feasible to ascertain the level of a contaminant in water in public water systems” [SDWA §1401(1)(C)(i)]. Alternatively, “if, in the judgement of the Administrator, it is not economically or technologically feasible to so ascertain the level of such contaminant,” the Administrator may identify known treatment techniques, which sufficiently reduce the contaminant in drinking water, in lieu of an MCL [SDWA §1401(1)(C)(ii)]. In addition, the NPDWRs are required to include “criteria and procedures to assure a supply of drinking water which dependably complies with such maximum contaminant levels; including accepted methods for quality control and testing procedures to insure compliance with such levels ...” [SDWA §1401(1)(D)]. Hence, the purpose of this document is identify acceptable test methods which can be used for the measurement of arsenic in drinking water and determine the lower limits of quantitation (based on routine use).

2.0 Analytical Methods

Why Does EPA List Methods to Measure Arsenic in Drinking Water?

The Safe Drinking Water Act (SDWA) requires that EPA set a Maximum Contaminant Level (MCL) and a Maximum Contaminant Level Goal (MCLG) for each regulated contaminant. In establishing and meeting the MCL and/or the MCLG, it is critical that reliable analytical method(s) are identified, approved and published in order for public water systems (PWSs) to monitor their compliance with SDWA regulations. This chapter addresses the (a) analytical methods that may be applicable to the measurement arsenic in drinking water samples and (b) the practical level of quantitation that can be expected with the currently approved methods. As part of identifying and approving analytical methods for each regulated contaminant, EPA documents the steps taken by the Agency to ensure that reliable methods are available to measure arsenic in drinking water.

What Criteria Does EPA Use to Select Analytical Methods?

In selecting appropriate analytical methods for SDWA compliance monitoring, EPA considers the following technical and economic criteria:

- The sensitivity of the method;
- The reliability (or bias and precision) of the analytical results;
- The specificity or selectivity of the method in the presence of interferences;
- The operating range of the method;
- The availability of equipment and trained personnel to implement a national monitoring program;
- The rapidity of analysis to permit routine use; and
- The cost of analysis to the water supply system.

Each of these criteria is discussed in more detail below.

Sensitivity

To be useful for Safe Drinking Water Act compliance monitoring, analytical methods must be sufficiently sensitive to measure the presence and concentration of a contaminant of concern. For the Safe Drinking Water Act, EPA evaluates the overall sensitivity of the techniques. In previous regulations, EPA used two measures of analytical capability, the Method Detection Limit (MDL) and the Practical Quantitation Level (PQL).

- ▶ The MDL is a measure of an individual laboratory's sensitivity and is defined as "the minimum concentration of a substance that can be reported with 99% confidence that the analyte concentration is greater than zero (40 CFR Part 136 Appendix B)." MDLs can be operator, method, laboratory, and matrix specific. The MDL is experimentally determined from at least seven replicate analyses of samples that are comprised of low-level analyte spikes in reagent grade water. Due to normal day-to-day and run-to-run analytical variability, MDLs may not be reproducible within a laboratory or between laboratories.
- ▶ In the preamble to a November 13, 1985 rulemaking (50 FR 46906), the PQL was defined as "the lowest concentration of an analyte that can be reliably measured within specified limits of precision and accuracy during routine laboratory operating conditions." In an effort to integrate this analytical chemistry data into regulation development, the Agency uses the PQL to estimate or evaluate the minimum, reliable quantitation level that most laboratories can be expected to meet during day-to-day operations. The PQL is one of the factors considered in the determination of an MCL. The derivation of the PQL for arsenic is discussed in more detail in section 2.7.

Reliability

An analytical method is said to be reliable if it consistently gives similar results when similar samples are analyzed over a long period of time. Two specific measures of reliability are *bias* and *precision*. The bias of an analytical measurement is the relationship between the

measured value and the "true" value for a given sample. Because the true concentration of many environmental contaminants cannot be known exactly, bias is often measured as the recovery of an analyte that has been spiked into a reference sample such as reagent-grade water. Bias as percent recovery is calculated as the concentration of the analyte found, divided by the concentration that was added to the sample. Under ideal circumstances, the recovery will be 100%.

$$\% \text{ Recovery} = \frac{\text{Concentration Found}}{\text{Concentration Added}} \times 100$$

The term "accuracy" has been used in the past to express this same concept, however, more recently, accuracy has been used to encompass the concepts of both bias and precision.

Precision is the degree of agreement between repeated measurements of a specified parameter in identical samples. It is a measure of the reproducibility of a method, and when three or more measurements have been performed, it can be expressed in terms of the relative standard deviation (RSD), or the coefficient of variation (C_v).

$$RSD = C_v = \frac{SD}{\text{mean concentration}} \times 100$$

Specificity

Specificity, or selectivity, is the ability of the method to determine the analyte of interest in the presence of other contaminants and interferences. Specificity can be achieved through a variety of means, including the use of:

- Detectors that respond to the analyte but not to the interference;
- Detectors, such as mass spectrometers, which can distinguish the analyte on the basis of its molecular ion and any fragmentation patterns;
- Sample preparation and extraction steps that separate the analyte from interfering compounds; and
- Cleanup procedures that selectively remove the co-contaminants or interferences.

Operating Range

A method must not only be sensitive enough to detect analytes at or below the MCL, it must also have a wide enough operating range to be practical for compliance monitoring. As a general rule, EPA has considered the range from detection of the analyte to 1.5 times the MCL to be appropriate. However, methods that can operate in the concentration range expected in most compliance monitoring samples are also considered.

Availability of Equipment and Personnel

EPA weighs multiple factors when selecting analytical methods, including the availability of the test methods used for compliance monitoring purposes, as well as the availability of the

equipment, facilities, and trained personnel necessary to perform the analyses. Some compliance monitoring measurements must be conducted at the utility's facility because the act of shipping the sample may change the conditions being measured. Other parameters may be measured either at the utility's facility or in an off-site laboratory. Some equipment and techniques, which are relatively new, may not be appropriate for compliance monitoring since the availability of trained personnel and equipment would be limited.

Rapidity of Analysis

Tests that can be run in a short period of time can provide important feedback to utility plant personnel and allow corrective actions to be taken when problems are noted. Methods that can be easily automated or that can be performed with less technician involvement may be responsive to compliance reporting and may be more cost-effective. Thus, EPA considers the time required for analyses as part of its selection criteria.

Costs

EPA evaluates the costs of analysis by considering a wide range of variables, including:

- Instrumentation costs - are additional equipment and instrumentation required that are not used for other analyses?
- Costs associated with collecting an appropriate sample for analysis - are special equipment, bottles, preservatives, storage requirements, or shipping procedures required?
- Routine operating costs - what expendable supplies, necessary reagents, and maintenance costs are required?
- Costs of the quality control procedures specified in the method - are replicate measurements of the sample required? Is the operating range so narrow that numerous dilutions may be necessary? Are appropriate performance evaluation materials available (to both the laboratories and to EPA)?
- Labor costs - does the method involve lengthy labor-intensive procedures? Does it require specially-trained analysts?

Using these evaluation criteria, an electronic literature search was conducted to identify analytical methods that might be used to measure the concentration of arsenic in drinking water. The remainder of Chapter 2 addresses the following aspects of these methods:

- Inventory of methods
(Methods currently approved by EPA and methods not yet approved)
- Performance capabilities of the methods
- Skill requirements
- Practical availability of methods
- Anticipated unit costs
- Practical performance and analytical uncertainties
- The Practical Quantitation Limit (PQL)

2.1.0 What is the Inventory of Analytical Methods for Arsenic in Drinking Water?

This section provides information on a number of common analytical methods that may be used to accurately measure low concentrations ($< 10 \mu\text{g/L}$) of arsenic in drinking water. In the context of this report, “common analytical methods” refers to those methods that have been promulgated and/or published by various EPA offices or consensus organizations, i.e., the American Society for Testing and Materials (ASTM), and the American Public Health Association (APHA), the American Water Works Association (AWWA), and the Water Environment Federation (WEF). The common analytical methods published by EPA, ASTM, APHA, and AWWA are generally within the analytical capabilities of most EPA, state, utility, and commercial laboratories.

In identifying analytical methods appropriate for measuring arsenic in drinking water, it is important that the measurement technique reflect what is needed to demonstrate compliance with the MCL. The current MCL for arsenic is based on the total arsenic present in an unfiltered water sample. When samples are filtered to remove particulate or colloidal material, arsenic associated with the particulates or colloids is lost to the analysis. Whereas analysis of an unfiltered water sample yields the concentration of arsenic present in the dissolved and suspended fractions, analysis of a filtered water sample only yields the concentration of arsenic present in the dissolved fraction. Because the current MCL for arsenic is based on total arsenic, some of the technologies that measure only dissolved arsenic species may not be suitable for demonstrating compliance. This factor was taken into consideration in reviewing available analytical methods for measuring arsenic in drinking water.

Newer technologies and procedures such as chelation/liquid-liquid extraction-atomic absorption spectrometry, chelation-gas chromatography, ion chromatography-inductively-coupled plasma/mass spectrometry (IC-ICP/MS), and other experimental techniques were not reviewed for this report. Although these newer methods and techniques may offer significantly lower detection limits than the more traditional arsenic methods, their relative cost, equipment requirements, and required level of expertise, generally make these methods unsuitable for routine compliance monitoring at this time.

2.1.1 What Methods Are Currently Approved by EPA for Measuring Arsenic?

Eight methods are currently approved in 40 CFR 141.23 (l) for the analysis of arsenic in drinking water. Table 2.1 lists the approved methods and the method detection limits (MDLs) that are typical of the approved methodologies.

Three of the approved methods are multi-element or multi-analyte, meaning other analytes besides arsenic can be measured during the analysis. Whereas two of the three methods (EPA 200.7 and SM 3120B) are Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) techniques, EPA 200.8 is an Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) technique. The primary advantage of using a multi-analyte method is if the same method is approved for compliance monitoring of one or more other regulated analytes, compliance monitoring requirements for this metal will result in minimal additional analytical costs.

The remaining five analytical methods approved by EPA for the measurement of arsenic in drinking water are all element-specific or single-analyte techniques (can only measure arsenic). These single-analyte techniques include EPA 200.9, SM 3113 B, SM 3114 B, ASTM D 2972-93 B and ASTM D 2972-93 C). Three of the five single-analyte methods, EPA 200.9, SM 3113 B, and ASTM 2972-93 C, are graphite furnace atomic absorption (GFAA) techniques that have traditionally been used to quantify arsenic in drinking water. Two of these GFAA methods, EPA 200.9 and SM 3113 B, employ the use of stabilized temperature platform graphite furnace atomic absorption (STP-GFAA) technology that significantly reduces interferences and improves analytical sensitivity. ASTM 2972-93 C employs regular hollow graphite tubes with off-the-wall atomization. In reality, any of the GFAA methods can be adapted to stabilized temperature platform (STP) technology, provided that the furnace and background correction system are compatible with STP graphite tubes. Users of GFAA should consult their instrument manufacturer for further guidance on this issue.

Two of the five single-analyte methods, SM 3114 B and ASTM 2972-93 B, utilize gaseous hydride atomic absorption (GHAA). These methods employ zinc in hydrochloric acid or sodium borohydride to convert arsenic to its volatile hydride. In ASTM 2972-93 B, the arsenic hydride is removed from the sample by a flow of nitrogen into an argon- or nitrogen-entrained hydrogen flame where it is determined by atomic absorption at 193.7 nm. In SM 3114 B, the volatile hydrides may also be swept into an entrained hydrogen flame, or alternatively, into a quartz atomization cell positioned in the optical path of an atomic spectrophotometer. Quartz atomization cells provide the most sensitive arsenic hydride determinations and minimize background noise associated with hydrogen flames. In both methods, the absorption of the light source is proportional to the arsenic concentration. Both hydride methods provide method-specific sample digestion procedures that are required prior to analysis.

Table 2.1
Analytical Methods Currently Approved for the Analysis of Arsenic in Drinking Water

Method		Technique	MDL (µg/L)
Multi-Analyte Methods	EPA 200.8 ¹	Inductively coupled plasma/mass spectrometry (ICP/MS)	1.4
	EPA 200.7 ²	Inductively coupled plasma/atomic emission spectrometry (ICP/AES)	8
	SM 3120 B ³	ICP/AES	50
Single-Analyte Methods	EPA 200.9 ⁴	Graphite furnace atomic absorption spectrometry (GFAA)	0.5
	SM 3113 B ⁵	GFAA	1
	ASTM D 2972-93, Test Method C ⁶	GFAA	5
	SM 3114 B ⁷	Gaseous hydride atomic absorption (GHAA)	0.5
	ASTM D 2972-93, Test Method B ⁸	GHAA	1

¹ **EPA Method 200.8**, "Determination of Trace Elements In Water and Wastes By Inductively Coupled Plasma-Mass Spectrometry," Revision 5.4, Methods for the Determination of Metals in Environmental Samples-Supplement I, EPA/600/R-94-111, May 1994.

² **EPA Method 200.7**, "Determination of Metals and Trace Elements In Water and Wastes By Inductively Coupled Plasma-Atomic Emission Spectrometry, Revision 4.4, EMMC Version, Methods for the Determination of Metals in Environmental Samples-Supplement I, EPA/600/R-94-111, May 1994.

³ **Standard Methods 3120 B**, "Inductively Coupled Plasma (ICP) Method" Standard Methods for the Examination of Water and Wastewater, 19th ed., American Public Health Association, 1995.

⁴ **EPA Method 200.9**, "Determination of Trace Elements By Stabilized Temperature Graphite Furnace Atomic Absorption," Revision 2.2, Methods for the Determination of Metals in Environmental Samples-Supplement I, EPA/600/R-94-111, May 1994.

⁵ **Standard Methods 3113 B**, "Electrothermal Atomic Absorption Spectrometric Method," Standard Methods for the Examination of Water and Wastewater, 19th ed., American Public Health Association, 1995.

⁶ **ASTM D 2972-93, Test Method C** "Atomic Absorption, Graphite Furnace," Annual Book of ASTM Standards, Waster and Environmental Technology," Vol. 11.01, 1998, American Society for Testing and Materials, Philadelphia, PA.

⁷ **Standard Methods 3114 B**, "Manual Hydride Generation/Atomic Absorption Spectrometric Method," Standard Methods for the Examination of Water and Wastewater, 19th ed., American Public Health Association, 1995.

⁸ **ASTM D 2972-93, Test Method B**, "Atomic Absorption, Hydride Generation," Annual Book of ASTM Standards, Waster and Environmental Technology," Vol. 11.01, 1998, American Society for Testing and Materials, Philadelphia, PA.

2.1.2 What Other Methods Are Available for Measuring Arsenic?

The Agency conducted a literature search to find other methods available for measuring arsenic in drinking water. Table 2.2 lists the results of that literature search. The two multi-analyte techniques cited include SW-846 Method 6020 and EPA 200.15. SW-846 Method 6020

is an ICP-MS technique that is very similar to the approved EPA 200.8. EPA 200.15 is an ICP-AES technique which employs ultrasonic nebulization to introduce the aqueous sample into the plasma (refer to Section 2.2.2 for further details).

There are four other single-analyte EPA methods for the analysis of arsenic. These single-element methods include SW-846 Method 7060A, SW-846 7062, EPA 1632 and SW-846 7063. SW-846 Method 7060A is a GFAA method which employs "off-the-wall" atomization. It may be used for STP-GFAA, provided that the instrumentation and background correction systems are compatible with stabilized temperature platform graphite tubes. GFAA users should consult their instrument manufacturer for additional information on this issue and for information on the appropriate furnace temperature program(s) for STP-GFAA operation. Although use of "off-the-wall" atomization may not be as sensitive as STP-GFAA, larger injection volumes, multiple injections, and/or sample concentration techniques may be used to achieve the required level of detection.

EPA has two alternative gaseous hydride or GHAA methods, SW-846 Method 7060A and EPA 1632. As with the approved GHAA methods, the volatile hydrides formed by reaction with sodium borohydride are swept into a quartz cell positioned in the optical path of an atomic spectrophotometer. In each case, the absorption of the light source is proportional to the arsenic concentration. EPA 1632 provides for the direct analysis of drinking water (Refer to Section 2.2.3 below for further details on this method).

Finally, SW-846 Method 7063 provides an alternative analysis procedure that uses an anodic stripping voltammetry (ASV) technique to quantify free, dissolved arsenic in aqueous samples. The chief advantage of this technique is that it does not require expensive instrumentation and has utility for field analysis.

**Table 2.2 - Other Analytical Methods for Arsenic
(Not Currently Approved for Drinking Water Analysis)**

Method		Technique	MDL (µg/L)
Multi-Analyte Methods	SW-846 6020 ¹	ICP-MS	0.4
	EPA 200.15 ²	ICP-AES	3
Single Analyte Methods	SW-846 7060A ³	GFAA	1
	SW-846 7062 ⁴	GHAA	1
	EPA 1632 ⁵		0.002
	SW-846 7063 ⁶	ASV	0.1

¹ **SW-846 Method 6020**, "Inductively Coupled Plasma-Mass Spectrometry," Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, Third Edition, Update II, September 1994.

² **EPA 200.15**, "Determination of Metals and Trace Elements In Water By Ultrasonic Nebulization Inductively Coupled Plasma-Atomic Emission Spectrometry" Methods for the Determination of Metals in Environmental Samples-Supplement I, EPA/600/R-94-111, May 1994.

³ **SW-846 Method 7060A**, "Arsenic (Atomic Absorption, Furnace Technique)," Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, Third Edition, Update II, September 1994.

⁴ **SW-846 Method 7062**, "Antimony and Arsenic (Atomic Absorption, Borohydride Reduction)," Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, Third Edition, Update II, September 1994. ⁵ **EPA Method 1632**, "Determination of Inorganic Arsenic In Water by Hydride Generation Quartz Furnace Atomic Absorption," EPA/821/R-96-013, July 1996.

⁶ **SW-846 Method 7063**, "Arsenic in Aqueous Samples and Extracts by Anodic Stripping Voltammetry (ASV)," Test Methods for Evaluating Solid Wastes, Physical/Chemical Methods, Third Edition, Update III, December 1996.

2.2.0 What are the Performance Capabilities of the Analytical Methods?

2.2.1 Inductively Coupled Plasma - Mass Spectrometry (ICP-MS) (EPA 200.8, SW-846 6020)

Description of ICP-MS

Inductively Coupled Plasma Mass Spectrometry methods provide for the multi-element determination of metals in solution. An aqueous solution of sample is introduced by pneumatic nebulization into a radio frequency plasma where energy transfer processes causes desolvation, atomization, and ionization. The ions are extracted from the plasma through a differentially pumped vacuum interface and separated on the basis of their mass-to-charge ratio by a quadrupole mass spectrometer. The ions transmitted through the mass spectrometer are detected by a continuous electron multiplier or Faraday detector. The mass spectrometer can be operated in two different modes, full-scan and selective ion monitoring. In the full-scan mode, the detector scans across a wide range of masses that encompass many target analytes. The selective ion monitoring mode restricts the detector to a few specific masses that are characteristic of the analyte of interest. By selecting a narrow subset of all possible masses, the detector spends more time

looking for those specific masses than in the full-scan mode, thereby increasing its sensitivity for those target analytes. Selective ion monitoring can be used to obtain an MDL as low as 0.4 µg/L for total recoverable arsenic and 0.1 µg/L arsenic for direct analysis (EPA Method 200.8, Table 7, May 1994).

Performance data for EPA 200.8

Performance data for arsenic in drinking water generated by EPA Method 200.8 are summarized in Table 2.3 and 2.4. In table 2.3, single laboratory data for a drinking water sample are shown. Five replicates were analyzed to determine the background concentration for total recoverable arsenic. Two further pairs of duplicates were fortified at 50 µg/L and 200 µg/L. The mean percent recovery, the standard deviation of the percent recovery, and the relative percent difference between the duplicate fortified samples were determined and are shown in table 2.3.

Table 2.3 Precision and Accuracy Data for Total Recoverable Arsenic in Drinking Water by EPA 200.8				
Sample Conc. (µg/L)	Spike Conc. (µg/L)	Average Recovery (%)	Standard Deviation of Percent Recovery	RPD Between Duplicate Spike Determinations
< 1.4	50	99.7	0.8	2.2
< 1.4	200	102.5	1.1	2.9

Data obtained from single-laboratory testing of the method for drinking water analysis using the direct analysis procedure (i.e., no sample digestion) are provided in table 2.4. Three different drinking water samples from US EPA Regions IV, VI, and X were fortified at 1 µg/L. Four replicates were analyzed to establish the background concentrations and four spiked aliquots were analyzed to determine the mean percent recovery for each matrix.

Table 2.4 Precision and Accuracy Data For Arsenic (Direct Analysis) Via EPA 200.8			
	Region IV	Region VI	Region X
Mean Background Conc. (µg/L)	< MDL	2.4	1.0
Average Mean Recovery for 1 µg/L spike (n=4)	93%		
Standard Deviation of the Mean Recovery	8.5%		

2.2.2 Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) (EPA 200.15, EPA 200.7 and SM 3120 B)

Description of ICP-AES

Inductively coupled plasma-atomic emission spectrometry methods provide for the multi-element determination of metals in solution using sequential or simultaneous instruments. The instruments measure characteristic atomic-line emission spectra by optical spectroscopy. Aqueous samples are introduced into the instrument via a peristaltic pump or by pneumatic nebulization. The resulting aerosol is desolvated before being transported to the plasma torch. Element-specific emission spectra are produced by a radio-frequency inductively coupled plasma and are dispersed by a grating spectrometer. The intensities of the line spectra are monitored at specific wavelengths by a photosensitive device. Quantitation of the target analyte(s) is performed by comparing the spectral intensity for each element to known calibration standards. Background correction is required to compensate for variable background contribution.

Two modifications to ICP-AES allow for greater sensitivity. These modifications include (1) the use of the axial torch configuration and/or (2) the use of ultrasonic nebulization. Using the axial torch configuration, the torch is in a horizontal position, rather than in a vertical position. The source path length is increased by viewing axially or down the end of the torch. This longer path length increases analyte emission and improves sensitivity. "Trace ICP" as it is sometimes called, has detection limits typically ten times lower than standard ICP-AES.

Ultrasonic nebulization is a new sample introduction technique, which provides greater sensitivity due to the more efficient transport of the analyte(s) into the plasma torch. Ultrasonic nebulization ICP-AES (referred to as UNICP-AES) is the same as traditional ICP-AES except for the difference in the way the sample is introduced into the plasma torch. UNICP-AES employs an ultrasonic nebulizer to introduce the sample aerosol into the plasma, instead of pneumatic nebulization or a peristaltic pump. In reality, any ICP-AES instrument can be converted to UNICP by simply attaching a ultrasonic nebulizer. Stand-alone module kits are commercially available that can provide ultrasonic nebulization capabilities to any ICP. Ultrasonic nebulization can improve detection limits on any ICP-AES by a factor of 5 to 10, owing to the greater efficiency with which the sample is transported into the plasma. EPA method 200.15, which employs ultrasonic nebulization, has reported a method detection limit of 2 µg/L for direct analysis and 3 µg/L for a total recoverable digestion.

Performance Data for Method 200.7

In a single laboratory evaluation of EPA method 200.7, one drinking water sample (tap water) and one ground water sample (well water) were analyzed for arsenic. Five replicate aliquots of each sample were prepared, analyzed, and the average of the five determinations used to define the background concentrations. Two pairs of duplicates were fortified at 50 and 200 µg/L and the mean percent recovery, standard deviation of the percent recovery, and the relative percent difference between the duplicate fortified samples calculated. The results of this evaluation are summarized in Table 2.5.

Table 2.5 Accuracy and Precision Data for EPA 200.7							
		Accuracy and Precision for 50 µg/L Spike Concentration			Accuracy and Precision for 200 µg/L Spike Concentration		
Matri x	Conc. (µg/L)	Average Recovery (%) (n = 2)	Standard Deviation	RPD	Average Recovery (%) (n = 2)	Standard Deviation	RPD
Tap Water	< 8	108	1.4	3.7	101	0.7	2.0
Well Water	< 8	107	0.7	1.9	104	0.4	1.0

Performance Data For SM 3120 B

As a guide to the generally expected precision and bias of this method, a linear regression equation was developed for total recoverable arsenic over the concentration range of 69-1887 µg/L;

$$X = 1.0437C - 12.2$$

$$S = 0.1239X + 2.4$$

$$SR = 0.0874X + 6.4$$

where: X = mean recovery, µg/L

C = true value, µg/L

S = multi-laboratory standard deviation, µg/L

SR = single analyst standard deviation, µg/L

Performance Data for EPA 200.15

Performance data from a single laboratory analysis using EPA Method 200.15 for five different drinking water supplies (two ground waters, two surface waters, and a river water) are summarized in Table 2.6. Each sample was analyzed five times to determine the background concentration. Each sample was spiked at 30 µg/L arsenic and analyzed in duplicate.

Table 2.6 Accuracy and Precision Data for EPA 200.15				
Matrix	Sample Conc. (µg/L)	Spike Conc. (µg/L)	Average Spike Recovery (%) (n = 2)	RPD Between Duplicate Spike Determinations
Region II Tap Water	< 3	30	118	1.1

Region V Tap Water	< 3	30	110	2.7
Region VI Tap Water	5.2	30	110	10.7
Region X Tap Water	< 3	30	122	9.0
Region V River Water	< 3	15	108	6.8

2.2.3 Gaseous Hydride/Atomic Absorption Spectrometry (GHAA) (SM 3114 B, ASTM 2972-93 B, SW-846 7062, EPA 1632)

Description of GHAA

The Gaseous Hydride/Atomic Absorption Spectroscopic methods operate on the following principal. Trivalent arsenic is converted to its volatile hydride (arsine) by reaction with zinc and hydrochloric acid or sodium borohydride. The volatile hydrides are swept into an argon-hydrogen flame or into a heated quartz cell positioned in the optical path of an atomic absorption spectrophotometer. A light beam from a hollow cathode lamp or electrodeless discharge lamp (EDL) containing the element of interest is directed through the flame or quartz cell, into a monochromator, and into a detector that measures the amount of light absorbed by the arsine. In this respect, GHAA is the same as flame or furnace atomic absorption. For total or total recoverable arsenic, the sample is first acid digested or placed in a special reaction vessel to destroy organic arsenic compounds and oxidize the arsenic to arsenic (V). The arsenic (V) is then reduced to arsenic (III) by reaction with potassium iodide or tin chloride, then converted to their volatile hydrides with zinc or borohydride.

Each of the methods cited above provide method-specific digestion procedures to prepare the sample for hydride analysis, except EPA Method 1632. Method 1632 is discussed in detail below. As noted in *Technical Notes on Drinking Water Methods, October 1994*, irrespective of the sample turbidity, drinking water samples analyzed for arsenic by gaseous hydride must be digested prior to analysis. SM 3114 B provides a persulfate digestion that is effective in converting organic arsenic compounds to the arsenic (V) oxidation state. The perchloric acid digestion provided in the method should be avoided due to safety concerns (Refer to *Technical Notes on Drinking Water Methods, October 1994*). ASTM 2972-93 B provides two sulfuric/nitric acid digestion procedures depending on whether zinc or sodium borohydride is used in the hydride generation step. SW-846 Method 7062 references SW-846 Method 3010A, a separate total metals hotplate digestion procedure using nitric acid. SW-846 Method 7062 also employs an automated analysis system for automated sample analysis.

EPA 1632 is a GHAA method developed by the US EPA Office of Water in 1996, and provides for the direct analysis of dissolved and total arsenic in aqueous samples. This method does not require a separate preliminary digestion procedure, and in the context of the method, total arsenic and total recoverable arsenic are synonymous. An aliquot of sample is placed in a special reaction vessel and 6 M HCL is added. A 4% sodium borohydride solution is added to the sample to convert organic and inorganic arsenic to volatile arsines, which are purged into a cryogenic trap containing 15% OV-3 on Chromasorb®. The trapped arsines are thermally desorbed from the trap and swept into a quartz furnace containing an air-hydrogen flame. The sample absorbance is

recorded and compared with the response of known calibration standards. Use of a quartz furnace in conjunction with cryogenic trapping allows for the detection of arsenic down to 10 ng/L, a detection limit significantly lower than those provided by the other hydride methods.

Performance Data for SM Method 3114B

Single-laboratory, single-operator data were collected for As (III) and organic arsenic by both manual and automated methods. Recovery values (%) from seven replicates are given in Table 2.7. The concentration of spikes and the identity of the organic arsenic compound(s) were not provided.

Table 2.7 Recovery Data for Arsenic (III) and Organic Arsenic for Aqueous Matrices Using Manual GHAA or Automated GHAA (SM 3114B)		
Method/Digestion	Percent Recovery for As III (%)	Percent Recovery for Organic As (%)
Manual with digestion	91.8	87.3
Manual without digestion	109.4	19.4
Automated with digestion	99.8	98.4
Automated without digestion	92.5	10.4

Performance Data for ASTM D 2972-93 Test Method B

The single operator and overall precision of ASTM D 2972-93 B is summarized in Table 2.8. The reported precision and bias data is for reagent water and also water for which the matrix is not specified.

Table 2.8 Precision and Bias Data for Arsenic Trioxide Atomic Absorption, Hydride Generation (ASTM D 2972-93 B)					
Water Type	Spike Conc. (µg/L)	Conc. Found (µg/L)	Overall Standard Deviation (S_o) (µg/L)	Single Operator Standard Deviation (S_o) (µg/L)	% Bias
Reagent Water, Type II	3.0	3.16	0.76	0.74	+5
	10.0	9.74	0.93	0.97	-3
	18.0	17.67	1.81	1.93	-2
Water of Choice ¹	3.0	2.70	0.70	0.48	-10
	10.0	8.76	1.93	0.94	-12
	18.0	18.07	2.93	2.22	+0.4

¹ Specific sample matrix not provided.

Performance Data for EPA 1632

A method detection limit of 0.002 µg/L and a minimum level of 0.01 µg/L is reported for EPA method 1632. Average recovery is 59 to 143 % and the standard deviation is less than 42 %. Method 1632 is designed for the measurement of dissolved an total arsenic in the range of 0.002 µg/L to 0.01 µg/L.

2.2.4 Graphite Furnace Atomic Absorption Spectrometry (GFAA) (EPA 200.9, SM 3113 B, ASTM 2972-93 C, SW-846 7060A)

Description of GFAA

In the graphite furnace atomic absorption spectrometry technique, a small volume of sample (typically 5 to 50 µL) is injected into a graphite tube positioned in the optical path of an atomic absorption spectrophotometer. An electrical furnace is used to heat the tube sequentially through drying, charring, and finally, an atomization step. A light beam from a hollow cathode lamp or electrodeless discharge lamp (EDL) containing the element of interest is directed through the tube, into a monochromator, and into a detector that measures the amount of light absorbed by the free ground state atoms. The amount of light absorbed by the free ground state atoms is directly proportional to the concentration of the analyte in solution within the linear calibration range of the instrument. Because the greater percentage of analyte atoms are vaporized and dissociated within the light beam passing through the graphite tube, greater analytical sensitivity is obtained and lower detection limits are possible as compared with flame atomic absorption. The limit of detection can be extended by increasing the injection volume or by using a multi-injection technique. These techniques effectively increase the total amount of analyte placed in the tube resulting in greater absorbance.

GFAA may be divided into two basic techniques, depending on the type of graphite tube used in the method. In standard GFAA, the sample is pipetted directly into a graphite tube and the tube is electrically heated to effect atomization of the analyte. This type of GFAA is known as “off-the-wall-atomization.” ASTM 2972-93 C and SW-846 7060A utilize standard graphite tubes and “off-the-wall-atomization.”

A newer technique utilizes stabilized temperature graphite furnace atomic absorption (STP-GFAA). In this technique, a small platform (L'vov platform or similar device) is inserted into the graphite tube. The sample is pipetted directly onto the platform. As with plain graphite tube, the platform tube is serially heated to dry, char, and atomize the analyte. With the platform tube, atomization is more consistent and controlled, resulting in increased atomization efficiency. Because the sample is more efficiently atomized on the stabilized platform than in the standard graphite tube, the detection of lower concentrations is possible, down to 0.5 µg/L. EPA 200.9 and SM 3113 B employ STP-GFAA, although any method can be adapted for this technology provided the background correction system and furnace are compatible with the platform tube and the furnace temperature programs are adjusted appropriately. Users of GFAA should consult their instrument manufacturer for further guidance on this issue. As noted above, the detection limits for any of the GFAA methods, including EPA 200.9, can be lowered by employing multiple

injections (thereby increasing the total sample volume injected into the graphite tube). Adjustment to the furnace heating program would be required to sequentially dry each injection aliquot prior to charring and atomization.

Performance data for EPA 200.9

Single-laboratory test data for EPA method 200.9 is shown for aqueous media (including drinking water, pond water, and well water) in Table 2.9. For each aqueous matrix, five replicates were analyzed, and an average of the replicates was used for determining the sample background concentration. Four samples were spiked at 10 µg/L. The percent relative standard deviation was calculated for the spiked samples. The average recovery is also reported.

Table 2.9 Accuracy and Precision Data for Aqueous Samples for EPA 200.9					
Matrix	Ave. Conc. (µg/L)	% RSD	Fortified Conc. (µg/L)	% RSD at Fortified Conc.	Average Percent Recovery
Pond Water	3.2	4.1	10	0.8	100.5
Drinking Water	0.5	10.5	10	0.6	88.4
Well Water	0.9	14.2	10	2.1	101.6

Performance data for SM Method 3113B

Table 2.10 provides interlaboratory single-analyst precision and interlaboratory overall precision data for this method. The samples were analyzed by injecting a measured volume of the sample into the furnace device.

Table 2.10 Precision Data for SM 3113 B				
Matrix	Spike Conc. (µg/L)	Single-Analyst Precision % RSD	Overall Precision % RSD	Relative Error %
Lab Pure Water	9.78	40	43	36
Lab Pure Water	227	10	18	3
Drinking Water	9.78	25	26	1
Drinking Water	227	6	12	7
Surface Water	9.78	15	37	22
Surface Water	227	8	13	10

Performance Data for ASTM: D 2972-93 C

The precision of the ASTM D 2972-93 C was tested by twelve laboratories using reagent water and water whose matrix was not specified. Since each analysis was performed once, the single operator precision data could not be calculated. The precision and bias data are shown in Table 2.11.

Table 2.11 Precision and Bias Data for Arsenic for ASTM D 2972-93 C				
Matrix	Spike Conc. (µg/L)	Average Conc. Measured (µg/L)	Overall Standard Deviation (S)	Bias, %
Reagent Water, Type II	6.0	5.35	1.14	-11.0
Reagent Water, Type II	22.0	23.10	2.96	+5.0
Reagent Water, Type II	72.0	71.30	6.68	-1.0
Water of Choice ¹	6.0	5.21	0.89	-13.0
Water of Choice ¹	22.0	23.20	3.28	+5.4
Water of Choice ¹	72.0	71.30	6.21	-1.0
¹ The precision data as provided in this method are not matrix-specific, therefore the data apply to the overall precision and bias for all matrices.				

Performance Data for SW-846 Method 7060A (These data are referenced from EPA 206.2)

Table 2.12 contains precision and accuracy data from a single laboratory using spiked tap water for SW-846 method 7060A.

Table 2.12 Accuracy and Precision Data for Arsenic for SW-846 Method 7060A		
Spike Concentration (µg /L)	Standard Deviation	Percent Recovery
20	±0.7	105
50	±1.1	106
100	±1.6	101

2.2.5 Anodic Stripping Voltammetry (ASV) (SW-846 Method 7063)

Description of ASV

Anodic stripping voltammetry provides an alternative analytical technique for measuring free dissolved arsenic in drinking water. The ASV method is equally sensitive for As (III) and As (V) and is suitable for measuring low-levels of free arsenic from 0.1 to 300 µg/L. In this method, free dissolved arsenic [as As (III) and/or As (V)] is quantified by anodic stripping, at a potential of +145 mV with respect to the saturated calomel electrode, from a conditioned gold plated electrode. The analysis by ASV involves three major steps. First, a glassy carbon electrode (GCE) is prepared for use by plating on a thin film of gold onto the electrode. The plated electrode is then conditioned, and finally, the arsenic concentration in the sample is determined by comparing the sample response to external standards. Dissolved antimony and bismuth are positive interferences. Dissolved copper at a concentration > 1 mg/L is also a positive interference.

Performance Data for SW-846 7063

In a single laboratory evaluation, aqueous standards were spiked with known concentrations of As (III) and As (V), and the accuracy and precision of the analysis by ASV were determined for each spike concentration. Table 2.13 summarizes these results.

Table 2.13 Performance Data for SW-846 Method 7063 (Reagent Water)					
Arsenic as As (III)			Arsenic as As (V)		
Spike Conc. (µg/L)	Recovery (%)	RSD (%)	Spike Conc. (µg/L)	Recovery (%)	RSD (%)
0.7	102	14	0.7	99	10
7.0	98	2	7.0	100	10
70	100	5	70	99	2

In a single-laboratory evaluation, the performance of EPA method 7063 was compared with graphite furnace atomic absorption (GFAA) by analyzing spiked environmental water samples. The results of this evaluation are summarized in Table 2.14.

Table 2.14 Results for EPA Method 7063 (ASV) Compared With GFAA			
Water Sample ID	Arsenic Added (µg/L)	ASV Result (µg/L)	GFAA Result (µg/L)
A12545	5.00	5.11	5.08
A12582	10.0	10.0	9.91
A22949	50.0	48.2	54.0

2.3.0 What Are the Anticipated Unit Cost and Cost of Instrumentation?

In identifying analytical methods for compliance monitoring, the Agency takes into consideration the cost of the analysis and the cost of instrumentation. The affordability of the analysis and/or the instrumentation used for analysis can impact whether or not compliance monitoring will be successful.

Cost of Analysis

Seven randomly-chosen commercial laboratories were contacted by telephone to obtain cost information on the analysis of drinking water for arsenic. In addition to the phone survey, drinking water analysis price lists were collected from the Internet. Table 2.15 summarizes the results of the phone survey and the Internet search.

Table 2.15 Methods and Cost for Measuring Arsenic in Drinking Water				
Data Source	Lab No.	Technique Cited	Method Cited	Cost/Sample (\$)
Phone	1	ICP-AES	200.7	25
Phone	2	ICP/MS	200.8	10
Phone	3	GFAA	200.9	15
Phone	4	ICP-AES	200.7	15
Phone	5	GFAA	200.9	15
Phone	6	GFAA	200.9	24-50
Internet	7	GFAA	200.9	24
Internet	8	ICP-AES	200.7	12
Internet	9	ICP-AES	200.7	10
Internet	10	GFAA	200.8	25
Internet	11	GFAA	200.8	38

As can be seen from table 2.15, six of the eleven laboratories use GFAA for measuring arsenic in drinking water, with a cost per analysis ranging from \$15 to \$50. It should be noted that several of the laboratories offered significant discounts for multiple metal analyses. For a single analyses for arsenic only, the higher price would apply. Four of the laboratories cited the use of ICP-AES, Method 200.7. The cost of these analyses ranged from \$10 to \$25. However, it should be noted that this method is essentially the same as Method 200.15, except the latter method employs ultrasonic nebulization, which allows for lower detection limits. Finally, one laboratory cited the use of ICP-MS, Method 200.8, with a cost of \$10 per sample. None of the

laboratories contacted used gaseous hydride or ASV. The Agency estimates that the cost of gaseous hydride would be approximately the same as GFAA analyses because both techniques involve approximately the same level of effort. The cost of ASV analyses is estimated to be \$15-20 per sample.

Cost of Instrumentation

Table 2.16 cites the approximate cost of instrumentation needed for the various techniques. The cost information cited in table 2.16 was taken from a paper prepared by K.J. Irgolic (reference provided below).

Table 2.16 Approximate Cost of Instrumentation (Irgolic, 1994)	
Instrumentation	Approximate Cost (\$)
ICP-MS	200,000
ICP-AES	80,000
GFAA	80,000
GHAA	60,000
ASV	30,000
Irgolic, K.J., 1994. Determination of Total Arsenic and Arsenic Compounds in Drinking Water. Pp 51-60 in <i>Arsenic: Exposure and Health</i> , W.R. Chappell, C.O. Abernathy, and C.R. Cothorn, eds. Northwood, U.K.: Science and Technology Letters.	

2.4.0 What Methods Meet the Skill Requirements?

The Agency has identified five different analytical techniques used for monitoring of arsenic in drinking water. These techniques include:

- Inductively coupled plasma-mass spectrometry (ICP-MS);
- Inductively coupled plasma-atomic emission spectrometry (ICP-AES);
- Graphite furnace atomic absorption (GFAA);
- Gaseous hydride atomic absorption, (GHAA); and
- Anodic stripping voltammetry (ASV).

Except for ICP-MS (see discussion below), which is a relatively new technique, the skill requirements for the remaining techniques (i.e., GFAA, GHAA, ICP-AES and ASV) are within the capabilities of most environmental laboratories. Most modern environmental testing laboratories already have the necessary skills to analyze drinking water by GFAA and/or ICP-AES. GFAA has been in use for more than 20 years for measurement of low-level concentrations of metals, and many laboratories routinely use this technique to measure metals such as lead, selenium, thallium, and arsenic. Stabilized temperature graphite furnace atomic absorption (STP-

GFAA) has been available for at least ten years. Use of STP-GFAA does not require any additional skills beyond those required to operate an atomic spectrophotometer.

ICP-AES has also become a routine analytical tool used by many laboratories. ICP-AES offers the advantage of simultaneous multi-element analysis, thereby reducing analysis time and cost. The only disadvantage of ICP-AES is the level of detection cited by the methods are in the range of 8 to 50 $\mu\text{g/L}$. Ultrasonic nebulization ICP-AES, which is a more efficient technique for introducing the sample into the argon plasma, can increase sensitivity by 5 to 10-fold. As indicated earlier, detection limits in the range of 2 to 3 $\mu\text{g/L}$ are possible for arsenic. A modular ultrasonic nebulizer can be purchased to equip older, direct aspiration instruments with ultrasonic nebulization capability. Because ultrasonic nebulization is an alternative sample introductory technique, no additional skills beyond those required to operate the system are required. Therefore, the skills necessary to operate GFAA and ICP-AES already exist in many laboratories, and these techniques are suitable for measuring arsenic in drinking water.

Anodic stripping voltammetry (ASV) offers a less costly alternative for measuring low-concentrations of dissolved arsenic in drinking water. This technique does not require expensive equipment, (as compared with ICP-AES or GFAA) and the necessary equipment can be obtained from commercial suppliers. The skill requirements to perform this analysis are not significant, and may be considered to be equivalent to mercury cold-vapor or other spectrophotometric techniques. In addition to low cost and ease of use, this method also has utility for field monitoring of drinking water. For these reasons, ASV is cited as an inexpensive option for measuring arsenic. It should be noted again that the ASV technique only measures free arsenic species in the dissolved fraction.

Four gaseous hydride/atomic absorption spectroscopic methods (GHAA) are available for the determination of arsenic in drinking water. With the exception of EPA 1632, these methods do not require a high degree of skill. These techniques are based on the formation of volatile hydrides, which are swept into a hydrogen/argon flame or heated quartz cell positioned in the optical path of an atomic absorption spectrophotometer. The equipment required for this analysis can be constructed from common laboratory equipment, or can be purchased from commercial suppliers. The level of skill required for this technique is about equal to that required for graphite furnace atomic absorption. It should also be noted that GHAA has been routinely used for the analysis of selenium, arsenic, and mercury for over ten years and is still a viable option for measuring arsenic in drinking water.

EPA Method 1632, also a GHAA technique recently developed by the Office of Water, has the chief advantage of a very low detection limit (MDL $\sim 0.002 \mu\text{g/L}$ and a minimum level of $\sim 0.01 \mu\text{g/L}$). However, this method does require a level of expertise significantly greater than the other hydride techniques. In this method, the volatile arsines are purged from the sample and trapped on a liquid nitrogen-cooled, packed glass trap. The trapped arsines are then thermally desorbed into a quartz cell of an atomic absorption spectrophotometer for detection. Although this method does require a greater level of skill, the detection of ultra-low concentrations of arsenic in drinking water justifies its use for monitoring purposes. It should also be noted that other methods for measuring arsenic are provided that require a lower skill level.

ICP-MS is a relatively new technique, that is both technically and economically feasible for routine compliance monitoring of arsenic. Although the availability of ICP-MS is currently limited, due to the high initial cost of instrumentation, the use of ICP-MS will continue to expand in response to market forces that favor multi-elements techniques at low levels of detection. The high level of skill and operator training required for this technique is justified because the method provides simultaneous multi-analyte analysis capabilities and ultra-low detection limits.

2.5.0 What is the Practical Availability of the Methods?

The Agency evaluated the practical availability of the methods by analyzing what methods were reported for the analysis of arsenic in last six EPA Water Supply (WS) studies (WS 030-036). By far, the most common technique cited by the participating laboratories was GFAA (EPA Methods 200.9 and SM 3113B were the most frequently cited methods overall). As discussed above, GFAA is routinely used in most environmental laboratories, and is generally available to most laboratories involved in drinking water analysis. ICP-MS was cited by two participants (EPA 200.8), indicating that this technique is being utilized for drinking water analyses, on a limited scale.

Gaseous hydride (GHAA) was also frequently cited (SM 3114 B and ASTM D 2972-93 were the hydride methods cited most often). As noted above, laboratories that have atomic absorption capabilities (either graphite furnace or flame AA) may also perform gaseous hydride analysis. Except for Method 1632, the necessary equipment to conduct hydride analysis is not extensive, and can often be assembled from common laboratory glassware and equipment. In addition, hydride systems may be purchased from commercial suppliers.

ICP-AES and ASV methods were not cited by participating laboratories. This is probably due to the fact that GFAA or GHAA are the current methods of choice for low-level analysis of arsenic. ASV is a new technique recently promulgated into the Third Update to SW-846 (December 1996) after WS 36. It still may not be well known to many laboratories, and it is not currently an approved method for drinking water. Given the relatively simple instrumentation requirements for this method, this method should gain in popularity, especially among small laboratories not having atomic absorption or ICP capabilities. ASV offers a less-costly analytical option for measuring arsenic in drinking water. As noted earlier, the disadvantage of the ASV technique, as written, is only free dissolved arsenic species are quantified. The use of both UNICP-AES and ICP-AES using axial torch configuration for measuring low-concentrations of metals in drinking water will increase in the future. Given the technical advances in ICP-AES, detection limits comparable to GFAA may be possible at some point in the future. Potentially lower detection limits and the multi-analyte capabilities of ICP-AES may increase the popularity of this technique in the future.

2.6.0 What Are the Practical Performance and Analytical Uncertainties?

The available performance data for the techniques discussed in this report are included in Section 2.2 of this report. In general, the detection limits, precision, and accuracy for most of the methods are satisfactory for monitoring arsenic in drinking water at the current MCL of 50 ug/L. At a lower MCL, the ICP-AES methods may lack the sensitivity needed for compliance monitoring. Each method provides information on possible interferences that may impact the

analytical result and describes the appropriate corrective actions. Both GFAA and ICP-AES instruments employ background correction systems to correct for nonspecific background interferences. The use of the method of standard additions (MSA) may also be used to quantify samples having matrix interference.

Based on the analytical techniques reported by laboratories involved in the WS studies, GFAA appears to be the current method of choice for measuring arsenic in drinking water. GFAA has been available for over twenty years and offers a relatively simple technique for measuring arsenic. Samples with turbidity less than 1 NTU may be analyzed directly, and do not require a preliminary digestion. The chief advantage of this technique is that it offers low detection limits, which may be extended if necessary by injecting a larger sample volume or by the use of multiple injections. This technique also offers spectral specificity by measuring the absorbance of light at a wavelength specific for the metal. Molecular or non-specific absorption (interferences) may be reduced or eliminated by the use of matrix modifiers and/or one of several background correction system currently available (deuterium arc, Zeeman, and Smith-Hieftje). Most instruments are equipped with an autosampler that allows the analysis of up to thirty to forty samples with minimal operator attendance. The primary disadvantage of this technique is that it is a single-analyte method (as compared with multi-analyte techniques such as ICP-AES and ICP-MS) and thus requires more time to complete.

Gaseous hydride also provides many of the advantages of GFAA, including very low detection limits, analytical specificity, and general availability. Next to GFAA, gaseous hydride was the most frequently cited method for measuring arsenic in WS PE studies. Most laboratories having flame or GFAA capabilities can perform these methods, as the necessary equipment is not extensive or expensive. Similar to GFAA, this technique is element-specific and therefore requires more time to complete. Except for Method 1632, all the gaseous hydride methods require a preliminary digestion to convert the arsenic to the proper oxidation state. This additional step would presumably add to the analysis time and cost of the analyses. Method 1632 employs a special reaction vessel and an aliquot of sample is treated with 6 N HCL and a 4% sodium borohydride solution to convert organic and inorganic arsenic to volatile arsines.

ICP-MS was cited by only a few WS study participants, most likely because this technique is relatively new and because of the high initial cost of the instrumentation. In addition, the level of expertise required to operate this instrumentation is high. However, the advantages of this technique include very low detection limits (equal to or better than GFAA) and multi-analyte capability. Although this technique may not be used extensively at the present time, the use of this method would be expected to increase with time given the competitive advantage offered by this technique. Laboratories having ICP-MS capability or considering purchasing ICP-MS instrumentation may use this technique for monitoring arsenic and other metallic contaminants.

ICP-AES was not cited for measuring arsenic in drinking water by WS PE participants. This is probably due to the fact that until recently, ICP-AES has not provided adequate sensitivity for monitoring arsenic at drinking water levels. However, recent advances in ICP-AES, including the use of ultrasonic nebulization and the axial-viewing plasma torch, have significantly reduced detection limits down to GFAA levels. Based on these technical advances, the use of ICP-AES would be expected to increase because of the multi-analyte capability of this technique provides.

As long as the laboratory can demonstrate acceptable detection limits through MDL studies, use of ICP-AES for monitoring of arsenic is a viable alternative.

Finally, anodic stripping Voltammetry (ASV) is provided as an alternative determinative method for measuring arsenic. The advantages of this technique is that it does not require expensive instrumentation, is easy to perform, provides very low detection limits, and can be performed in the field. The primary disadvantage of this method is that it would require a preliminary total metals digestion prior to analysis. If the total arsenic concentration is below the level of concern, then use of this method may be applicable in cases where the arsenic concentration is known to be low or non-detect.

2.7.0 What Is the Practical Quantitation Limit for Arsenic ?

To be useful for Safe Drinking Water Act (SDWA) compliance monitoring, analytical methods must be sufficiently sensitive to measure the presence and concentration of the contaminant of concern. In determining the analytical capabilities and sensitivities required to detect SDWA analytes, EPA considers both the method detection limit (MDL) and the practical quantitation limit (PQL). Generally, EPA defines the MDL as the minimum concentration of a substance that can be measured and reported with 99 percent confidence that the true value is greater than zero (40 CFR Part 136 Appendix B). The MDL may be operator-specific, method-specific, laboratory-specific and matrix-specific. MDLs may not be reproducible within a laboratory or even between laboratories due to the day-to-day analytical variability that can occur.

In an attempt to incorporate this analytical variability into regulation development, the Agency uses the PQL to estimate or evaluate the minimum, reliable quantitation level that most laboratories can be expected to meet during day-to-day operations. According to the July 17, 1992 final rule for Phase V synthetic organic chemicals (SOCs) and inorganic chemicals (IOCs),

"integrating the analytical chemistry data into regulation development becomes especially important where MCLGs are zero or at very low concentrations, near or below the detection limit. The PQL yields a limit on measurement and identifies specific precision and accuracy requirements which EPA uses to develop regulations. As such, PQLs are a regulatory device rather than a standard that labs must specifically demonstrate they can meet." (57 FR 31776)

The following sections of this document discuss what variables are incorporated into the PQL, what information is used to derive a PQL, and more specifically, the 1994 and 1999 EPA PQL derivations for arsenic.

2.7.1.0 What do Practical Quantitation Limits Consider?

EPA defined the Practical Quantitation Limit (PQL) as the lowest concentration of an analyte that can be reliably measured within specified limits of precision and accuracy during routine laboratory operation conditions (52 FR 25699, July 8, 1987). As stated before, the PQL is a means of integrating information on the performance of the approved analytical methods into the development of a drinking water regulation. The PQL incorporates the following:

- quantitation,
- precision and bias,
- normal operations of a laboratory, and
- the fundamental need to have a sufficient number of laboratories available to conduct compliance monitoring analyses.

The EPA uses two main approaches to determine a PQL for a SDWA analyte. One approach is to use the data from Water Supply (WS) studies. This method is used in most cases when sufficient WS data are available to calculate a PQL. The WS data approach, which is discussed in more detail in Sections 2.7.2 and 2.7.3, was used to determine the PQLs for Phase V inorganic chemicals such as antimony, beryllium, cyanide, nickel and thallium (July 17, 1992 57 FR 31776 at 31800).

In the absence of WS data, the second approach that EPA uses is the multiplier method. In this approach, the PQL is calculated by multiplying the EPA-derived MDL by a factor between 5 and 10. The exact multiplier varies and sometimes depends on the degree of concern about the specific contaminant. It is important to note that the multiplier approach has not been used for derivation of the PQL for arsenic. Instead, the arsenic PQL derivation relies on actual data from WS studies.

2.7.2.0 How Are Water Supply Studies Conducted?

Water Supply (WS) laboratory performance evaluation studies have been an integral part of EPA's certification program for drinking water laboratories for over 20 years. Historically, WS studies have been conducted semi-annually by EPA for all current and proposed drinking water contaminants. WS study samples are sent to all laboratories that conduct drinking water analyses, including utility laboratories, commercial laboratories, and State and EPA Regional laboratories. Each WS study includes samples or sample concentrates that are analyzed both for all SDWA analytes and for analytes that are being considered for regulation under the SDWA.

During these WS studies, EPA's National Exposure Research Laboratory (NERL) in Cincinnati, Ohio, sends participating laboratories a set of stable sample concentrates in sealed glass ampules, a data reporting form, and appropriate instructions. Each laboratory produces the study samples by diluting a measured quantity of the specific concentrates to volume with reagent water. The laboratory then analyzes the samples using the specified procedures. The completed reporting form is sent to EPA for evaluation and a fully detailed report is returned to each laboratory. The responsible state or EPA office contacts those laboratories that demonstrate potential problems.

Currently, the WS studies serve five main purposes:

- evaluate and certify laboratories conducting drinking water analyses.
- provide large-scale testing of the analytical methods and/or analytes that may be subject to future regulation.
- provide the Office of Ground Water and Drinking Water with performance evaluation data to demonstrate that the method can be used by a large number of laboratories.
- provide a database for method validation.

- provide inter-laboratory data from which to statistically determine PQLs.

2.7.3.0 How Are WS Studies Evaluated and What Criteria Are Used to Determine a PQL?

2.7.3.1 Evaluation of WS Studies

For each analyte in the WS study, EPA evaluates the results using Kafadar's biweight estimates of the mean and standard deviation from all the study data, and separately, from the data reported by EPA and state laboratories. Where acceptance limits have not been specified by regulations, and where there are data from at least 13 EPA and state laboratories, the biweight estimates from the EPA and state laboratory data are used to calculate a 95 percent prediction interval. If there are no regulatory limits, but fewer than 13 EPA and state laboratories reported data, then the prediction interval is calculated from the biweight estimates made from all the study data reported for the analyte.

For each analyte, 95 percent of the study data from laboratories operating in a state of statistical control, i.e., "in control," should theoretically be within the 95 percent prediction interval. Since 1986, such prediction intervals, or the limits set in regulations, have been used as the acceptance limits to judge laboratory performance in WS studies.

The recovery of an analyte is defined as the estimated biweight mean divided by the true concentration of the analyte in the study, and can be calculated as follows:

$$\% \text{ recovery} = \frac{\text{measured concentration}}{\text{spiked concentration}} \times 100$$

Using the recovery of an analyte instead of the mean concentration facilitates comparisons across WS studies performed at different true concentrations.

2.7.3.2 Criteria Used by EPA to Select a PQL

The statistical derivation of the PQL involves determining the concentration of an analyte at which a set percentage of the laboratories achieve results within a specified range of the spiked value. Historically, the percentage of laboratories has been set at 75%, while a range of acceptance limits around the spiked value has been used. In many cases, EPA derives PQLs only from the data submitted by the EPA Regional and State laboratories that participate in the WS studies. When the PQL is derived from WS data generated by the EPA Regional and State laboratories, the PQL is considered representative of the performance of the best laboratories, not average laboratory performance.

A PQL derived from WS data in such a manner is considered a stringent target for routine laboratory performance because:

- WS samples are prepared in reagent water and therefore do not contain the matrix interferences that may occur in field samples.

- Laboratories analyze only a small number of samples for the study and are aware that the samples are for the purposes of performance evaluation (i.e., they are not "blind" samples).

In deriving a PQL from WS study data, the Agency sets a fixed percentage acceptance window around the spiked value of the WS samples and plots the percentage of laboratories achieving results within that window against the spiked concentration of the study samples. The data are subjected to a linear regression analysis which can be used to determine the concentration at which a specific percentage of laboratories will achieve acceptable results.

2.7.4.0 What PQL Value Did EPA Derive in 1994?

In 1994, EPA drafted a document entitled "*Draft Methods and Analytical Support Document for Arsenic*" (EPA, 1994). Within this draft document EPA discussed the process by which the Agency derived the 1994 PQL for arsenic. EPA evaluated the data from Water Supply Studies 20 through 33. Of those WS studies, only WS 30 to 33 contained arsenic at the relatively low levels at which EPA was considering regulating this contaminant. Based on the combined results of WS 30, 32, and 33, the Agency performed regression analyses to derive equations for the mean concentration of arsenic recovered and the standard deviation as a function of the spiked value of the WS samples themselves. The data from WS study 31 were not used because EPA determined that the samples were mixed incorrectly and therefore the results were not reliable.

EPA used the spiked value of the lowest concentration sample in the three WS studies (1.5 µg/L) to solve these two equations and then determined the percent recovery and the relative standard deviation. Those values were then used to determine a 95% confidence interval around the calculated mean recovery of arsenic, expressed as the mean percent recovery plus and minus two standard deviations. In the case of WS 30, 32, and 33, EPA determined that the mean percent recovery of arsenic across all three studies was 110%, with a 95% confidence interval of 23% to 197%. Thus, if the results for each laboratory were expressed as a recovery (not a concentration), then 95% of the results should fall within the 23% to 197% limits.

The 1994 support document stated that these limits (23% to 197%) do *not* establish the limits for acceptable performance by a single laboratory in the combined studies. Rather, the limits place bounds on the variability that can be expected in these studies. Any results that fall outside of these limits would be considered to be aberrant data and would not be used by EPA for additional evaluations, including those for the PQL.

According to the EPA 1994 draft document, these unusually wide confidence limits were believed to be a result of the manner in which the regression line was calculated. The regression line was calculated from three mean recoveries and standard deviations from WS 30, 32 and 33, and not from the actual results from each of the laboratories that participated in the studies. The individual results from each laboratory were not available at the time of the calculations. Therefore, the usefulness of the regression equations in determining the acceptance limits was considerably reduced.

To more substantially assess the acceptance limits, EPA then plotted the data from WS studies 20 through 33 (except 31). In those graphs, the spiked value of arsenic (on the x axis) was

plotted against the percentage of laboratories achieving results at specified acceptance limits (on the y axis).

The WS 20 data utilized in 1994 now appear to contain a calculation error and the original data set was no longer available in an electronic format. Therefore, the Agency has replotted the results from the WS studies used in 1994 for this report, but without the data from WS 20 (nor WS 31). The results, shown in Figures 2.1 and Figure 2.2 below, were plotted at both the $\pm 40\%$ and $\pm 30\%$ acceptance limits.

Figure 2.1
Spiked Value of Arsenic versus the Percentage of Labs within Acceptance Range
at the $\pm 40\%$ Acceptance Limit for the 1994 PQL Determination

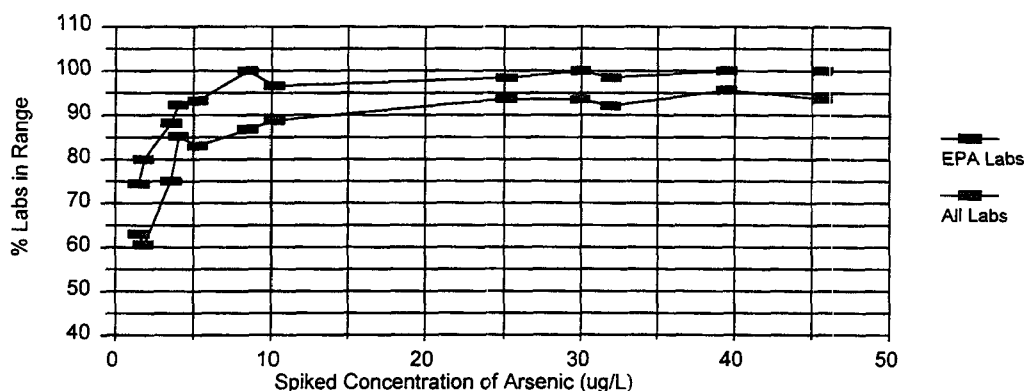
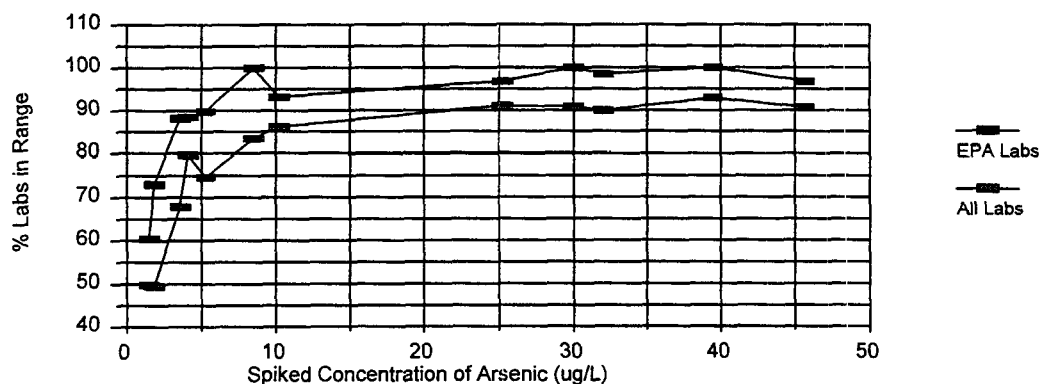
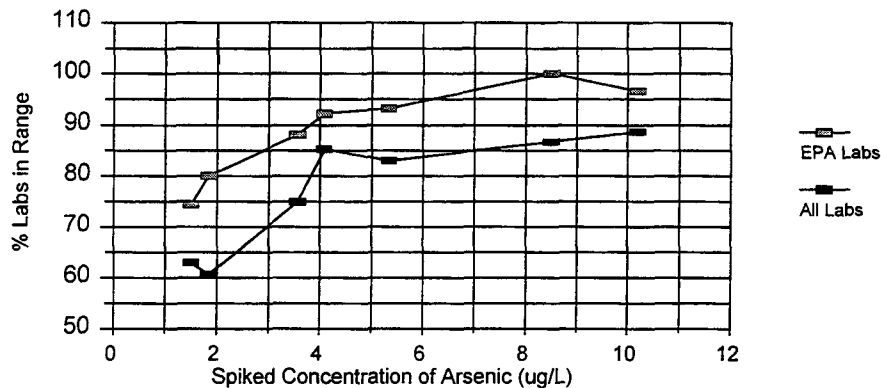


Figure 2.2
Spiked Value of Arsenic versus the Percentage of Labs within Acceptance Range
at the $\pm 30\%$ Acceptance Limit for the 1994 PQL Determination



As can be seen in both Figures 2.1 and 2.2, the relationship between laboratory performance and concentration generally levels off above about 10 µg/L of arsenic. Therefore, the results in Figure 2.1 below 12 µg/L are shown in closeup in Figure 2.3.

Figure 2.3
Low-Level Arsenic versus the Percentage of Labs within Acceptance Range
at the $\pm 40\%$ Acceptance Limit for the 1994 PQL Determination



Based on a graph similar to Figure 2.3, in 1994, EPA concluded that a PQL of 2 µg/L, with a minimum acceptance limit of $\pm 40\%$, was the point at which 75% of the EPA and State laboratories had the ability to measure arsenic at low concentrations.

2.7.5.0 What Were the Findings of the 1994 AWWA Evaluation of the Arsenic PQL Study?

In February 1994, the American Water Works Association (AWWA) submitted a report to EPA entitled *"An Evaluation of the Practical Quantitation Level (PQL) for Arsenic,"* authored by Dr. Andrew Eaton. The report was prepared for the AWWA Water Industry Technical Action Fund in response to the 1994 EPA derivation of a 2 µg/L for arsenic (at $\pm 40\%$ acceptance limit).

The study described in the report involved 14 utility laboratories chosen by the author of the study. Those laboratories were chosen because they had *"demonstrated experience in performing arsenic analysis by graphite furnace or hydride generation atomic absorption spectroscopy."* In addition, the study involved eight commercial laboratories that were chosen based on several selection criteria, including the detection limits reported by the laboratories, performance on arsenic WS samples, geographic distribution, and price.

The study design differs from that employed by EPA for the low-level arsenic WS studies described here. The study focused on two analytical techniques for arsenic, graphite furnace atomic absorption (GFAA) and gaseous hydride atomic absorption (GHAA). Some laboratories performed analyses by both techniques. In the case of the commercial laboratories that participated, they were paid for the analyses and were unaware that the samples were part of a

performance evaluation study. The study involved the preparation of samples spiked with arsenic at five concentrations, ranging from 1 µg/L to 10 µg/L.

The samples were prepared in a manner designed to investigate the possible effects of total dissolved solids (TDS) and total organic carbon (TOC) on the analysis of arsenic in water. As a result, the laboratories received samples of four matrix types, described below, spiked with arsenic at five concentrations:

- reagent water
- high TDS and high TOC
- low TDS and low TOC, and
- high TDS and low TOC

The spiking concentrations were approximately 1, 2, 4, 6, and 10 µg/L. Each laboratory was also sent a set of samples with no spiked arsenic (as a blank) and a set of samples prepared from reagent water and spiked at 25 µg/L. Each laboratory analyzed the samples in duplicate and reported both replicate results. The report describes a variety of statistical manipulations that were used to analyze the study results.

The conclusion of the study was that the PQL should be set at 4 µg/L, because at 4 µg/L:

"a competent laboratory should be able to measure arsenic to an accuracy of better than 25%."

The AWWA report goes on to state that:

"below this concentration, precision and bias degrade substantially, indicating that reliable interlaboratory measurements are not routinely possible below 4 µg/L."

In 1994, EPA graphed the results of the AWWA study for each matrix at various acceptance windows. Those graphs have been replotted as Figures 2.4 through 2.8 of the current report, using the summary data from the AWWA report.

Figure 2.4
Spiked Reagent Water Data from the AWWA Study

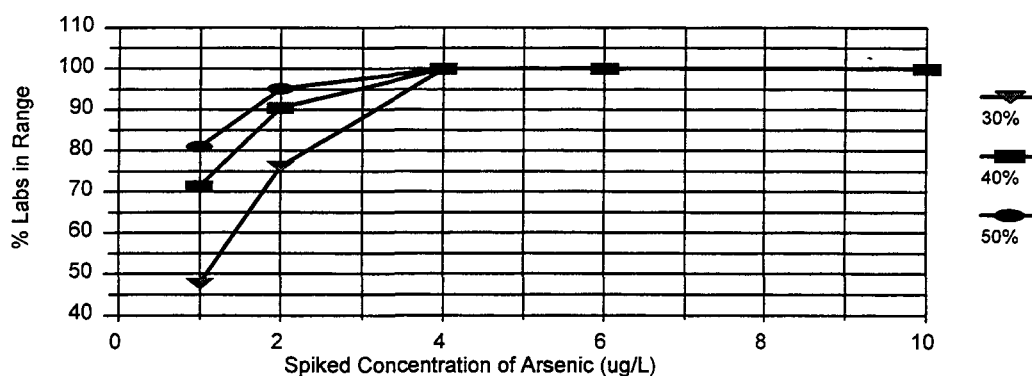


Figure 2.5
High TDS/High TOC Data from the AWWA Study

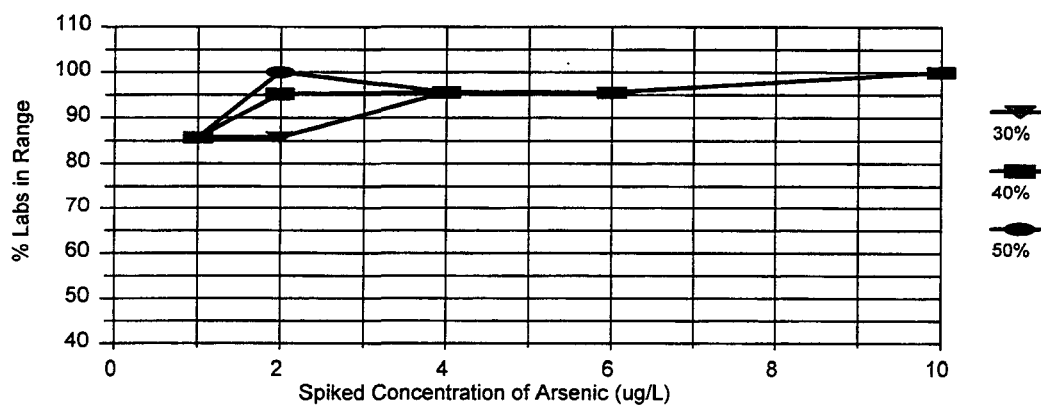


Figure 2.6
Low TDS/Low TOC Data from the AWWA Study

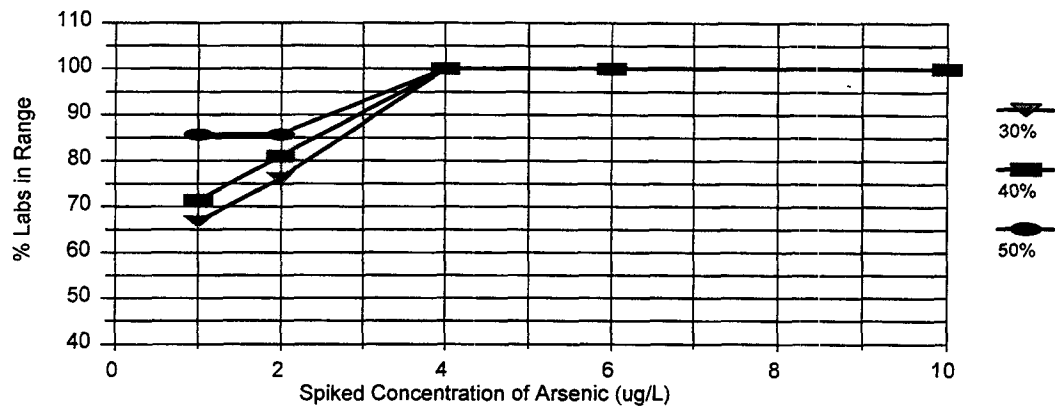


Figure 2.7
High TDS/Low TOC Data from the AWWA Study

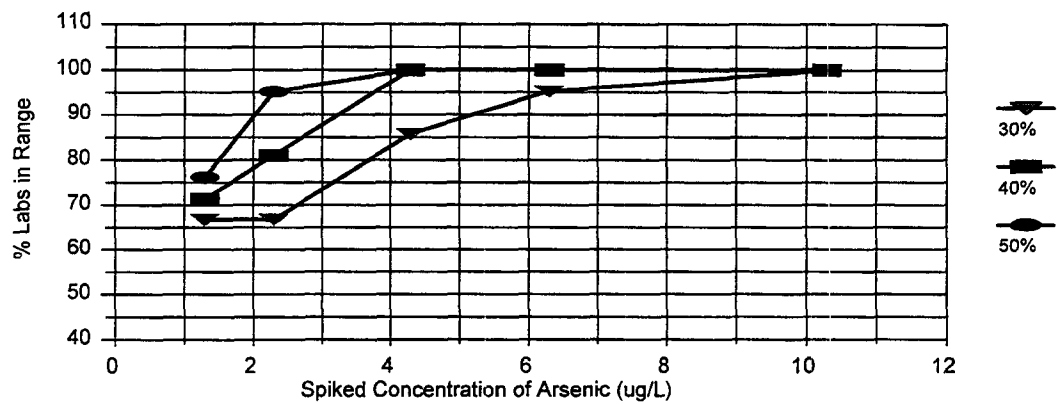
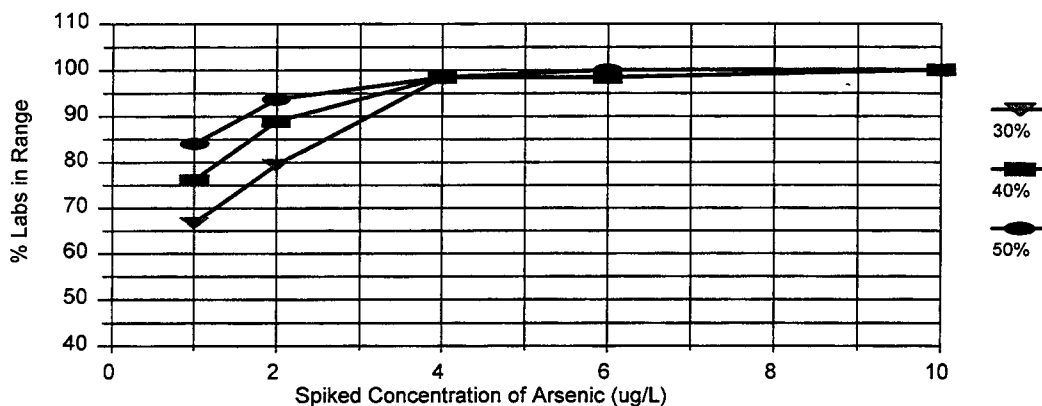


Figure 2.8
Combined Data from All Matrices in the AWWA Study



Not surprisingly, the AWWA data indicate that laboratory performance was best in spiked reagent water. However, the performance in the high TDS/high TOC water sample was also very good, with about 85% of the laboratories achieving acceptable results at the $\pm 30\%$ acceptance limits in the lowest arsenic concentration in the AWWA study. Performance in the low TDS/low TOC and high TDS/low TOC samples was noticeably lower than the other matrices at all the acceptance limits. Nevertheless, as can be seen in Figure 2.7, even at the $\pm 30\%$ acceptance limit, using the same approach that EPA used in 1994, it would appear that about 75% of the laboratories could achieve acceptable results at approximately 3 $\mu\text{g/L}$.

2.7.6.0 What Were the Recommendations from the EPA Science Advisory Board?

In August 1994, the Office of Ground Water and Drinking Water presented information on the arsenic PQL to the EPA Science Advisory Board (SAB), including the 1994 EPA report on the PQL and the AWWA study results. In July 1995, the SAB recommended that the PQL for arsenic be established using acceptance limits similar to those used for other inorganics, $\pm 20\%$ to $\pm 30\%$. The SAB noted that the analytical methods for arsenic had

"been in wide use for some time," and were "relatively straightforward, using direct injection without derivatization or extraction steps."

Therefore, the SAB believed that laboratories would be able to perform within the acceptance limits for other metals. Table 2.17 contains the acceptance limits for other inorganics regulated under the SDWA (40 CFR 141.23).

In addition, the SAB reviewed the plot in the 1994 EPA report of percent of laboratories passing versus the arsenic concentration. This plot was similar to Figure 2.1 of the current report,

except for the results for WS 21 that were deleted from the plot in the current report. Based on their review, the SAB concluded that:

"the arsenic method begins to deteriorate rapidly below a level of 4 to 6 $\mu\text{g/L}$."

The SAB further recommended that EPA not accept less precision and accuracy when setting low-level PQLs in order to support a risk management decision to protect to a certain risk level.

Table 2.17 Acceptance Limits, PQLs, and MCLs for Other Inorganics			
Contaminant	Acceptance Limit¹	PQL (mg/L)²	MCL (mg/L)³
Antimony	$\pm 30\%$	0.006	0.006
Barium	$\pm 15\%$	0.15	2
Beryllium	$\pm 15\%$	0.001	0.004
Cadmium	$\pm 20\%$	0.002	0.005
Chromium	$\pm 15\%$	0.01	0.1
Mercury	$\pm 30\%$	0.0005	0.002
Selenium	$\pm 20\%$	0.01	0.05
Thallium	$\pm 30\%$	0.002	0.002
¹ Acceptance limits for the listed inorganics are found at CFR 141.23 (k) (3)(ii). ² The PQL for antimony, beryllium and thallium was published in 57 FR 31776 at 31801 (July 17, 1992). The PQL for barium, cadmium, chromium, mercury and selenium was published in 66 FR 3526 at 3459 (January 30, 1991). ³ The MCLs for inorganics are listed at 40 CFR 141.62.			

2.7.7.0 What Were EPA's Next Steps in Deriving a PQL for Arsenic?

2.7.7.1 Additional WS Studies

As part of EPA's efforts to develop SDWA regulations for arsenic and evaluate the arsenic PQL, the Agency conducted a series of WS studies (WS 30 - 33) involving water samples containing less than 6 $\mu\text{g/L}$ of arsenic. In these WS studies for arsenic, the laboratories did not receive sample concentrates in sealed ampules. Rather, each laboratory received a sample that was prepared in reagent-grade water and acidified with nitric acid. As a result, the sample was ready for direct analysis by each laboratory. These low-level arsenic WS studies began prior to the 1994 PQL derivation, and the data from WS 30, 32, and 33 were evaluated as part of the 1994 PQL derivation.

Three additional low-level arsenic WS studies were conducted, including WS 34, 35, and 36. For the 1999 PQL derivation, the data from WS studies 30, 32, 33, 34, 35, and 36 were evaluated. As in 1994, the data from WS study 31 were not used because EPA determined that

the spike samples were mixed incorrectly and therefore the results were not reliable. The results submitted by all laboratories are summarized in Table 2.18, listed in order by the WS study number. Table 2.18 also provides the spiked value of arsenic in each study, the number of results reported in each study, the number of results reported as either "greater than" or "less than" some value, and the number of strictly numerical results. The results of these low-level arsenic studies were *not* used in the laboratory certification process.

As can be seen from Table 2.18, as many as 8% (54 of 728) of the laboratories reported results as "less than" or "greater than" values in some studies. The reasons for reporting results may be specific to each laboratory and cannot be deduced from the WS study results themselves. However, the "less than" results are likely a function of laboratory-specific reporting conventions. There was only one value reported as "greater than," and it was reported as ">1" in WS 33 by one state laboratory.

Table 2.18 Summary of WS Study 30 to 36 Results for All Laboratories					
WS Study #	Year	Arsenic Spiked Value (µg/L)	Total Number of Results Reported	Number of results reported as ">" or "<"	Number of Numerical Results*
30	1992	1.84	728	54	674
32	1993	1.5	499	41	458
33	1993	4.09	403	14	389
34	1994	3.22	538	0	538
35	1994	2.49	427	15	412
36	1995	5.71	498	7	491
* The number of numerical results is simply the difference between the total number of results reported and the number of results that were reported as "greater than" or "less than" values.					

2.7.7.2 What Analytical Methods Were Used?

Among the many factors that may influence the results of a given WS study are the analytical methods that are used by the participating laboratories. EPA approves methods for the analysis of both regulated and unregulated drinking water contaminants, including arsenic. During the three-year span of the six WS studies used in this evaluation, EPA revoked approval status for three methods used by study participants, Method 206.2 on July 14, 1994 (59 FR 35891), and Methods 206.3 and 206.4 on December 5, 1994 (59 FR 62456).

EPA withdrew approval for Method 206.2 along with methods for other analytes because:

"...those methods are outdated and the Agency has either proposed or already approved equivalent, updated versions of these methods that are published in the American Society for Testing and Materials (ASTM) and 18th edition of Standard Methods for the Examination of Water and Wastewater."

Approval for Method 206.3 was withdrawn for similar reasons, in that it referred to a method in the 14th edition of *Standard Methods for the Examination of Water and Wastewater*, which was outdated long before 1994.

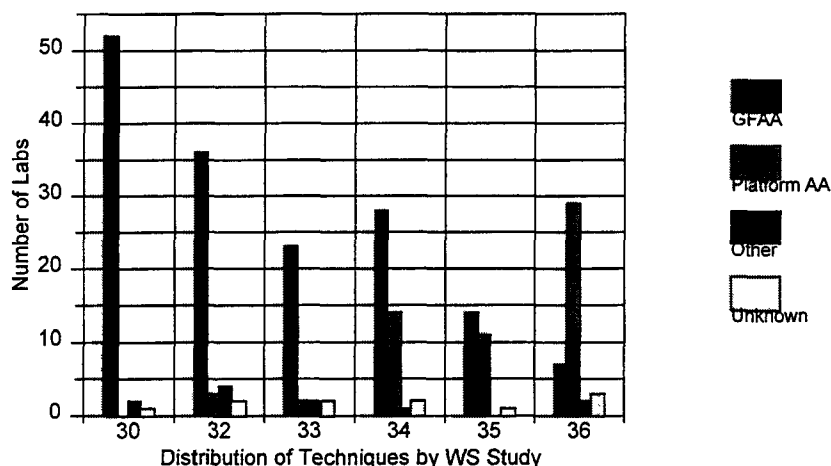
EPA withdrew approval for Method 206.4 because of concerns about the sensitivity of this colorimetric technique. In the December 5, 1994 notice where approval was withdrawn, the Agency concluded that because the detection limit is near the MCL for arsenic,

"...colorimetric measurements do not provide a reliable indication of variability of, or trends in, ambient concentrations of arsenic in the water supply when these concentrations are less than the MCL. EPA believes that the detection limit deficiency warrants withdrawal of colorimetric methods for arsenic."

It is important to note that the withdrawal of approval for Methods 206.2 and 206.3 was *not* based on concerns with the performance of the analytical techniques that underlie these methods, but rather with the written descriptions of the methods. In fact, the techniques used, graphite furnace atomic absorption spectrometry (GFAA) and gaseous hydride atomic absorption spectrometry (GHAA), are the same techniques employed in the ASTM and Standard Methods procedures that remain on the list of approved methods for arsenic published in the December 1994 notice. ASTM D-2972-93C and SM 3113B are GFAA procedures, while ASTM D-2972-93B and SM 3114B are GHAA procedures. Therefore, no attempt was made to differentiate among methods used by the EPA and State laboratories in deriving the PQL. The derivation of the PQL used the EPA and State laboratory data for all methods reported to be used, regardless of the current approval status for those methods.

Figure 2.9 illustrates the distribution of the analytical techniques used by the EPA and State laboratories in WS 30 to 36. The results for "GFAA" include the traditional graphite furnace atomic absorption (GFAA) techniques of graphite tube atomization and a L'vov graphite platform in the tube. The results for "Platform AA" include the stabilized temperature platform GFAA technique described in EPA Method 200.9. The results for "other" techniques in this figure include the use of inductively couple plasma/atomic emission spectroscopy (ICP/AES), inductively couple plasma/mass spectrometry (ICP/MS), and any other technique identified by the laboratories participating in the WS study. The "unknown" technique data represent those laboratories that did not report any information on the method used.

Figure 2.9
Distribution of Analytical Techniques by WS Study



As can be seen, the use of the traditional GFAA techniques predominated the results from the early low-level arsenic WS studies. However, by the time of WS 34 in 1994, the use of the stabilized temperature platform technique in EPA Method 200.9 had grown to represent a substantial portion of the results from the EPA and State laboratories, eventually surpassing the other GFAA techniques for low-level arsenic samples by WS 36.

2.7.7.3 What Data Were Used in the 1999 PQL Derivation?

The data used for this evaluation of the PQL were taken from WS studies 30, 32, 33, 34, 35, and 36. Table 2.19 summarizes the results of the six WS studies, providing the study number, the spiked value for the WS sample, the number of results from EPA and State laboratories, the number of results from all other laboratories, and the arsenic results evaluated using three numerical acceptance criteria, $\pm 20\%$, $\pm 25\%$, $\pm 30\%$. The results reported as either "greater than" or "less than" (see Table 2.18) were *not* included in this evaluation, and are not displayed in Table 2.19. Table 2.20 summarizes the same data as Table 2.19, but presented in order of increasing spiked value of the arsenic concentration.

As can be seen from the data in Table 2.19 or Table 2.20, the "other" laboratories performed noticeably less well overall than the EPA Regional or State laboratories. In only one instance (WS study 33) did at least 75% of the other laboratories achieve acceptable results with a spiked value of 4.09 $\mu\text{g/L}$. The $\pm 20\%$ acceptance criterion produced only two instances where at least 75% of the EPA Regional and State laboratories achieved acceptable results, in WS Study 33, with a spiked value of 4.09 $\mu\text{g/L}$, and in WS 36, with a spiked value of 5.71 $\mu\text{g/L}$. As a result, no further consideration was given to the $\pm 20\%$ criterion in this evaluation. Both the other criteria, $\pm 25\%$ and $\pm 30\%$, resulted in at least 75% of the EPA and State laboratories achieving acceptable results in the last four studies that were evaluated (WS 33-36).

Table 2.19 Evaluation of Arsenic Data from WS Studies Using Different Acceptance Criteria (listed in order by study number)									
WS #	Spiked Value (µg/L)	# Results from EPA and State Labs	# Results from Other Labs	± 20% Acceptance Criterion		± 25% Acceptance Criterion		± 30% Acceptance Criterion	
				% EPA and State Passing	% Other Passing	% EPA and State Passing	% Other Passing	% EPA and State Passing	% Other Passing
30	1.84	55	619	64	37	71	42	73	48
32	1.50	45	413	58	35	60	43	60	49
33	4.09	29	360	76	63	79	69	83	76
34	3.22	45	493	62	55	76	63	82	68
35	2.49	26	386	69	47	77	58	81	65
36	5.71	42	449	79	61	88	69	91	73
Values in bold are those instances where at least 75% of the laboratories achieved results within the acceptance criterion.									

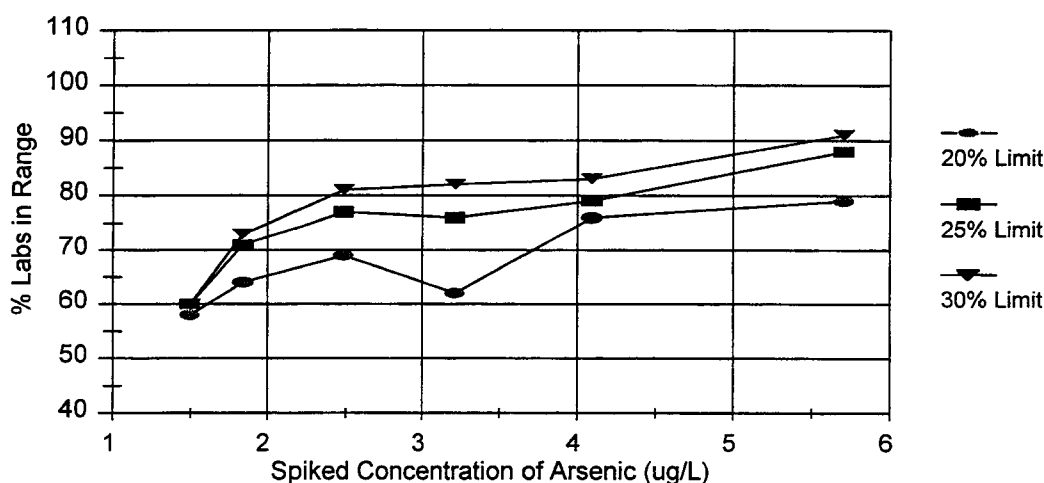
Table 2.20 Evaluation of Arsenic Data from WS Studies Using Different Acceptance Criteria (listed in order of increasing arsenic concentration)									
WS #	Spiked Value (µg/L)	# Results from EPA and State Labs	# Results from Other Labs	± 20% Acceptance Criterion		± 25% Acceptance Criterion		± 30% Acceptance Criterion	
				% EPA and State Passing	% Other Passing	% EPA and State Passing	% Other Passing	% EPA and State Passing	% Other Passing
32	1.50	45	413	58	35	60	43	60	49
30	1.84	55	619	64	37	71	42	73	48
35	2.49	26	386	69	47	77	58	81	65
34	3.22	45	493	62	55	76	63	82	68
33	4.09	29	360	76	63	79	69	83	76
36	5.71	42	449	79	61	88	69	91	73
Values in bold are those instances where at least 75% of the laboratories achieved results within the acceptance criterion.									

2.7.7.4 Visual Examination of the Graphical Data

The percentages of the acceptable results for the EPA and State laboratories in WS 30-36 (excluding 31) were plotted against the spiked value of arsenic concentrations, using the $\pm 20\%$, $\pm 25\%$, and $\pm 30\%$ acceptance criteria (see Figure 2.10). Simple visual examination of the data for the $\pm 25\%$ and $\pm 30\%$ acceptance limits suggests that the percentage of laboratories achieving acceptable results reaches 75% at an arsenic concentration between 2.0 and 2.5 $\mu\text{g/L}$. In fact, this visual approach is the technique that EPA used in 1994 to derive the PQL for arsenic (see the discussion in Section 2.7.4). For the 1994 PQL determination, a horizontal line representing 75% of the laboratories achieving acceptable performance was drawn on a plot similar to Figure 2.1, and the intersection of that line with the laboratory performance data for a $\pm 40\%$ acceptance limit was translated into an arsenic concentration by drawing a vertical line down to the x-axis.

One of the pitfalls of applying the simple visual approach to the data from multiple WS studies is that it assumes that there is a unique concentration that corresponds to the percentage of acceptable laboratories. As can be seen in Figure 2.10, this assumption does not necessarily hold true. For example, the performance of the EPA and State laboratories declined noticeably in WS 32, using all three sets of acceptance limits in the figure. The effect is most evident for the $\pm 20\%$ acceptance limit, where there are three points where the 65% acceptable results line crosses the curve. The effect is also evident for the $\pm 25\%$ acceptance limit, where there are two points that intersect at about the 75% acceptable results line. Obviously, it would be difficult to use simple visual examination to determine the appropriate choice of points.

Figure 2.10
Plot of Percentage of EPA and State Laboratories Achieving Acceptable Results Versus WS Study Concentration of Arsenic in $\mu\text{g/L}$



2.7.7.5 Statistical Analysis of the Data (Linear Regression Results)

One approach that can be used to overcome the potential problem from using the simple visual approach is to perform regression analyses of the observed results from the WS studies. As with the visual approach, the linear regression includes the inherent assumption that there is a

unique concentration that corresponds to the percentage of acceptable laboratories. However, the linear regression approach both formalizes that assumption and provides a means to address it. The data for the EPA Regional and State laboratories shown in Table 2.19 (or 2.20) were used to develop a linear regression of the percentage of laboratories achieving acceptable results against concentration of the WS samples. The WS sample concentration is the independent variable and the percentage of acceptable results is the dependent variable. Separate regression equations were calculated for the 25% and 30% acceptance criteria. The equations take the form of:

$$y = mx + b$$

where:

- y = percentage of labs achieving acceptable results (i.e., within the acceptance window)
- x = concentration of arsenic in the WS sample in $\mu\text{g/L}$ (spiked concentration of arsenic)
- m = slope of the regression line
- b = y-intercept value (in percent)

The use of regression techniques assumes that the data from the various WS studies form a single continuous data set. In reality, the study results do not form a continuous data set, but represent results from samples spiked at specific discrete concentrations of arsenic and analyzed a few at a time over a long period. However, through the use of a linear regression, the data can be used to create a model (the regression line) that may be useful in predicting accuracy and precision as a function of the concentration of the samples. The regression determines the linear relationship that best fits the observed results, in effect smoothing the curve and ensuring that there is a unique concentration that corresponds to any percentage of acceptable laboratories.

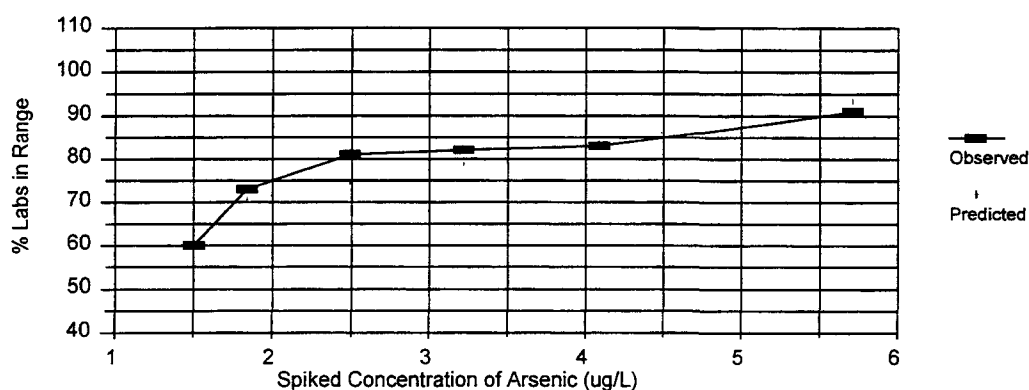
Calculating the regression equations also provides the correlation coefficient (r) for the regression, which is a measure of the degree to which the actual data fit the linear model represented by the regression line. An r value of 1 indicates a perfect fit with a positive slope of the data to the model. A value, p , can also be calculated for the regression that indicates the probability of concluding the null hypothesis (in this case that the spiked value concentration is linearly correlated with the percentage of labs achieving acceptable results) is false, when in fact the null hypothesis is true, for the given data set. In statistical terms, p indicates the probability of a Type I error. The results for the two regression equations are shown in Table 2.21.

Table 2.21 PQL Regression Results		
Regression Term	25% Acceptance Criterion	30% Acceptance Criterion
m	0.053417	0.056820
b	0.583847	0.603158
r	0.903153	0.855845
p	0.0034	0.0079

The r values shown in Table 2.21, 0.903 and 0.856, indicate that the data fit the linear model fairly well. The p values in Table 2.21 indicate that there is statistically significant evidence (over 99% confidence) that the spiked value and the percentage acceptable are linearly correlated.

In Figure 2.11, the observed data for the $\pm 30\%$ acceptance limit have been plotted against the WS sample concentration along with the results predicted from the linear regression line. As can be seen, the predicted success rate for the EPA and State laboratories is noticeably lower than the observed success rate in the region from about 2 to 3 $\mu\text{g/L}$. While attempts might be made to model the observed results using a second order (non-linear) regression, the Agency does not believe that there is a scientifically valid reason to do so. A similar plot could be developed for the $\pm 25\%$ acceptance limit and would illustrate a similar difference between the observed and predicted results for that limit.

Figure 2.11
Observed and Predicted Results for EPA and State Laboratories for the $\pm 30\%$ Limit



As noted earlier, one advantage of the linear regression approach is that it provides a model of the relationship between the sample concentration and laboratory success that, by definition, has only one concentration that corresponds to a given success rate. Two such models have been developed for these WS data, e.g., the two regression equations described in Table 2.21.

At the $\pm 25\%$ and the $\pm 30\%$ acceptance limits, the concentration corresponding to exactly 75% of the EPA Regional and State laboratories achieving acceptable results can be calculated using the regression equations by setting y equal to 0.75 and solving that the equation for x , as shown below, where the definitions of the terms remain the same.

$$x = \frac{y - b}{m}$$

The results of those calculations are shown in Table 2.22.

Table 2.22 Calculated PQLs for Arsenic	
For $\pm 25\%$ Acceptance Criterion	For $\pm 30\%$ Acceptance Criterion
3.11 $\mu\text{g/L}$	2.58 $\mu\text{g/L}$

When rounded to the appropriate level of significance, i.e., no decimal places, both the values in Table 2.22 round to 3 $\mu\text{g/L}$. It is important to note that the statistical evaluations of the WS study data sets described in Section 2.7.4 were not conducted as part of this derivation of the PQL, nor were any outlier tests performed on the data from the EPA and State laboratories. There were several reasons why these tests were not performed. First, and foremost, the assumption inherent in the use of just the data from the EPA and State laboratories is that these laboratories perform better than the aggregate performance exhibited by all laboratories. Secondly, the use of a fixed acceptance window already addresses any outlier values to some degree. For example, if one EPA or State laboratory result was determined to be an outlier from the distribution of results of *all* laboratories, then that same results would certainly fall outside of the $\pm 25\%$ or $\pm 30\%$ acceptance window around the spiked value. The only EPA and State laboratory data that were not included in this derivation of the PQL were those values that were not numerical values, e.g., one "greater than" value and 11 "less than" values.

2.7.8.0 What Other Factors Did EPA Consider When Determining the PQL for Arsenic?

There are several other factors that EPA considered in establishing the 1999 PQL for arsenic. These factors include:

- What are the acceptance limits for other inorganics?
- Does the MCLG have any bearing on what PQL is chosen?
- Does the 1999 PQL preclude the use of any currently approved methods?
- What is the estimated laboratory capacity at a particular PQL?

2.7.8.1 What are the acceptance limits for other inorganics?

As can be seen in the earlier discussion, the exact value of the PQL for a given contaminant is a function of the acceptance limit placed on laboratory performance. The data in Table 2.22 indicate that the PQL could be set a 3 $\mu\text{g/L}$ using either the $\pm 25\%$ or $\pm 30\%$

acceptance limit. In selecting a specific acceptance limit for arsenic, EPA reviewed the limits established for other metals. Table 2.23 shows the acceptance limits and the PQLs that have been determined for other inorganics regulated under the SDWA. These values are the same data shown in Table 2.17, but displayed in order of decreasing PQL and units of $\mu\text{g/L}$ (to allow comparison with the PQL derived for arsenic for this report).

In general, as the PQL decreases, the acceptance limits increase. The exceptions are for cadmium and beryllium, where it was not necessary to use wider limits to establish the PQLs. There are no metals that use an acceptance limit of $\pm 25\%$.

Table 2.23 Acceptance Limits, PQLs, and MCLs for Other Metals (in order of decreasing PQL)			
Contaminant	Acceptance Limit¹	PQL ($\mu\text{g/L}$)²	MCL ($\mu\text{g/L}$)³
Barium	$\pm 15\%$	150	2,000
Chromium	$\pm 15\%$	10	100
Selenium	$\pm 20\%$	10	50
Antimony	$\pm 30\%$	6	6
Thallium	$\pm 30\%$	2	2
Cadmium	$\pm 20\%$	2	5
Beryllium	$\pm 15\%$	1	4
Mercury	$\pm 30\%$	0.5	2
¹ Acceptance limits for the listed inorganics are found at CFR 141.23 (k) (3)(ii). ² The PQL for antimony, beryllium and thallium was published in 57 FR 31776 at 31801 (July 17, 1992). The PQL for barium, cadmium, chromium, mercury and selenium was published in 66 FR 3526 at 3459 (January 30, 1991). ³ The MCLs for inorganics are listed at 40 CFR 141.62.			

Based on the 1995 recommendation of the EPA Science Advisory Board to use acceptance limits for arsenic that are similar to those for other SDWA metals, the $\pm 30\%$ acceptance limit was chosen for arsenic, since no other metals use a $\pm 25\%$ limit *and* the $\pm 30\%$ limit yields the same PQL value as the $\pm 25\%$ limit, e.g., both values round to 3 $\mu\text{g/L}$.

2.7.8.2 Does the MCLG Have Any Bearing on What PQL is Chosen?

Currently, there is no MCLG for arsenic. However, EPA has abided by the 1995 SAB recommendation that the Agency not include risk management issues in the policy decision of setting the PQL. The PQL has been established based on the ability of the EPA and State laboratories to achieve acceptable performance in a series of low-level arsenic WS studies, as described previously.

2.7.8.3 Does the 1999 PQL Preclude the Use of Any Currently Approved Methods?

One factor that may influence the results of a given WS study are the analytical methods that are used by the participating laboratories. If the WS studies used to derive a particular PQL are based on results from only one or two of the approved methods, does the established PQL preclude the use of other approved methods?

The distribution of analytical techniques that were used in WS 30 to 36 was shown in Figure 2.9 (see Section 2.7.7.2). The predominant analytical technique employed by EPA and State laboratories in WS studies 30 to 33 was one of two forms of graphite furnace atomic absorption (GFAA). The majority of the EPA and State laboratories participating in these early WS studies used either graphite tube atomization (so called "off-the-wall" atomization of the sample) or a L'vov graphite platform in the tube (platform atomization). A much smaller number of EPA and State laboratories reported using techniques such as (GHAA), inductively coupled plasma (ICP), and ICP-MS during these studies. Beginning with WS 34, a large percentage of the laboratories began using the stabilized temperature platform GFAA method, EPA Method 200.9, with a corresponding reduction in the reported use of the other two forms of GFAA used in the earlier WS studies. Despite these changes, GFAA in one form or another was the predominant analytical technique used for these analyses.

At present, EPA has approved eight analytical methods for arsenic under 40 CFR 141.23. The methods include those developed by EPA, as well as by two voluntary consensus organizations, the American Society for Testing and Materials (ASTM) and the American Public Health Association (APHA, the publishers of *Standard Methods for the Examination of Waters and Wastes*). Table 2.24 lists the currently approved methods and provides the published method detection limit (MDL) for each method.

The published MDL, which represents a snapshot of the performance in a single laboratory, should only be used as guidance in choosing an analytical procedure for a specific application. If the purpose of the analysis is to monitor compliance with an arsenic PQL of 3 µg/L, then the data in Table 2.24 would lead one to not choose one of the ICP-AES methods, since the published MDLs are greater than the PQL. If the new MCL for arsenic were set close to the PQL, the currently approved ICP-AES method would not be reliable for compliance monitoring and would be removed from the list. Depending on the final MCL for arsenic, EPA method 200.15 (UNICP-AES) with method detection limits of 2 to 3 µg/L could be approved for compliance monitoring.

Since the PQL of 3 µg/L was derived from data, where GFAA and STP-GFAA were the predominant methods used, it is obvious these methods have the analytical capabilities to reach a PQL of 3 µg/L. Because GHAA and ICP-MS have method detection limits similar to GFAA and STP-GFAA, these techniques should be technically reliable and have no difficulty measuring a PQL of 3 µg/L.

Table 2.24 Approved Analytical Methods for Arsenic (40 CFR 141.23)				
Analytical Technique	Published MDL (µg/L)	EPA Method	Standard Method	ASTM Method
Inductively coupled plasma - atomic emission spectroscopy (ICP-AES)	8 (EPA) 50 (SM)	200.7	3120B	---
Inductively coupled plasma - mass spectrometry (ICP-MS)	1.4	200.8	---	---
Stabilized temperature platform - graphite furnace atomic absorption (STP-GFAA)	0.5	200.9	---	---
Graphite furnace atomic absorption (GFAA)	1 (SM) 5 (ASTM)	---	3113B	D-2972-93 C
Gaseous hydride atomic absorption (GHAA)	0.5 (SM) 1 (ASTM)	---	3114B	D-2972-93 B

In addition, EPA as a whole, may be in the process of adopting a performance-based measurement system (PBMS) approach to environmental monitoring. At the writing of this report, the PBMS approach has not yet been implemented in the water program. If at some point in the future PBMS is implemented, the regulated entity would be free to choose any analytical technique as long as that technique met or exceeded the performance capabilities of the approved techniques. A laboratory would be given considerable latitude to develop or modify methods to achieve appropriate performance. For example, under a PBMS approach, if a laboratory could modify an existing ICP-AES technique and achieve sufficient sensitivity, the laboratory would be allowed to employ that method for compliance monitoring. Thus, the issue of "approved" methods may take on less significance than at present.

Moreover, in adopting the PBMS approach, EPA must provide data quality objectives (DQOs) for analyses to be conducted for compliance monitoring purposes. The DQOs can then be used by the regulated community or their contract laboratories in their choice of analytical methods. The PQL provides the DQO for monitoring arsenic, in that it stipulates the accuracy that must be achieved at a concentration of interest, i.e., $\pm 30\%$ at the PQL.

2.7.8.4 What is the Estimated Laboratory Capacity at the PQL?

The PQL serves a secondary function in EPA's drinking water regulations in that the acceptance limits used to establish the PQL become the acceptance limits for the routine WS studies conducted to certify drinking water laboratories. Thus, in order to achieve passing results for a given future WS study, a laboratory will have to achieve results with $\pm X\%$ of the spiked value on the study samples. For an arsenic PQL established at 3 µg/L using $\pm 30\%$ acceptance limits, the $\pm 30\%$ limits will be used as the WS study acceptance limits.

The importance of the WS study acceptance limit is that it affects the number of laboratories that are able to maintain their certification status in any future WS study. As noted in

Section 2.7.3.2, a PQL derived from EPA and State laboratory data sets a stringent target for routine laboratory performance. However, the vast majority of SDWA compliance monitoring results are *not* generated by those EPA and State laboratories. The majority of the results are generated by laboratories operated by the water utilities themselves or by commercial environmental laboratories, many of whom specialize in drinking water analyses.

Because many states are authorized by EPA to operate their own drinking water certification programs, national figures on the number of certified drinking water laboratories are not readily available. Moreover, they are subject to some degree of change with time. However, EPA has used information from the WS study program to estimate the likely pool of laboratories.

Based on the data for WS studies 30-36 (Tables 2.19 and 2.20), there were between 360 and 619 results submitted by "other" laboratories, i.e., non-EPA and non-State laboratories. The 619 figure is from the oldest study, WS 30, and the number of laboratories in the other WS studies fell in a narrower range of 360 to 493. The most recent study used for the 1999 PQL derivation was WS 36, which was completed in 1995 and had 449 results from other laboratories. Again, it should be noted that WS studies 30-36 were the only low-level arsenic studies conducted by EPA to date and they had spike concentrations that ranged from 1.50 to 5.71 µg/L. Participation in these low-level arsenic studies was strictly voluntary and did not affect the certification status of the laboratories.

As of this writing, the most recent WS study to be completed was WS 41, in 1998. In that study, 929 out of 1938 laboratories reported results for arsenic. While this suggests a large increase in the potential pool of laboratories, it is critical to note that the WS studies since WS 36 have not involved low levels of arsenic. Since WS study 36, most studies were conducted in the range of 25 to 150 µg/L of arsenic. For WS 41, the spiked value of arsenic was 65.6 µg/L, well above the likely PQL. Because the low-level arsenic WS studies were voluntary, only those laboratories with the instrumentation and the willingness to participate did so. Therefore, EPA does not believe that the 929 laboratories that submitted arsenic results in WS 41 represent a likely estimate of the laboratory capacity. Rather, the likely available analytical capacity lies somewhere between the 360 laboratories that participated in WS 33 and the 929 laboratories in WS 41.

One of the factors that certainly influences laboratory capacity for any analyte is the instrumentation required for the analysis. In the case of arsenic, analyses at a PQL of 3 µg/L would likely require the use of one of three analytical techniques: graphite furnace atomic absorption spectroscopy (GFAA), gaseous hydride atomic absorption spectroscopy (GHAA), or inductively-coupled plasma/mass spectrometry (ICP-MS).

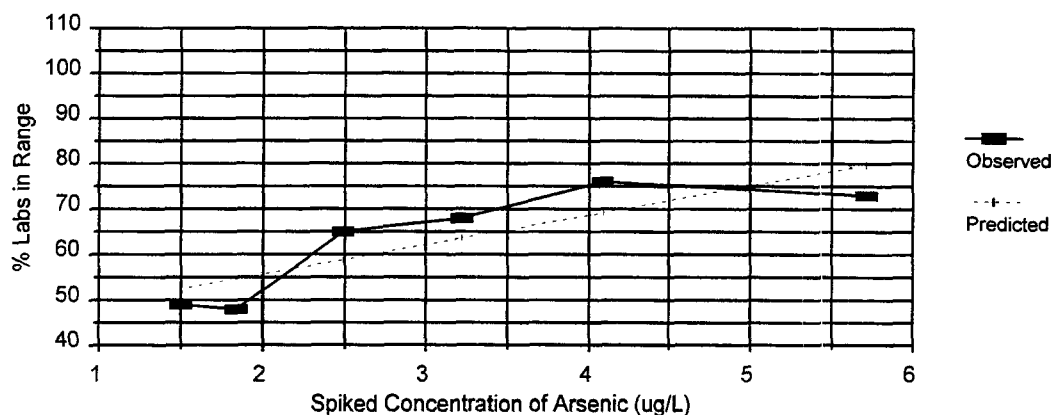
In order to estimate the laboratory capacity for arsenic using these techniques, EPA reviewed recent WS study results for other, already regulated metals that utilize these techniques. The two metals chosen were cadmium and antimony with PQLs of 2 and 6 µg/L, respectively. Table 2.25 illustrates the breakdown of methods and instrumentation used for the cadmium results reported in WS 41 and for the antimony results reported in WS 40, the two most recent WS studies.

Table 2.25 Methods, Instrumentation, and WS Study Participants for Cadmium and Antimony		
Method Number	Instrumentation	Number of Participants
<i>Cadmium Results for WS 41 (spiked concentration 18.2 µg/L)</i>		
EPA 200.7	ICP-AES	349
EPA 200.8	ICP-MS	106
EPA 200.9	STP-GFAA	204
SM 3113B	GFAA	228
Total (ICP-MS + GFAA)		538
<i>Antimony Results for WS 40 (spiked concentration 13.0 µg/L)</i>		
EPA 200.8	ICP-MS	111
EPA 200.9	STP-GFAA	388
SM 3113B	GFAA	281
ASTM D3697-92	GHAA	7
Total (ICP-MS + GFAA)		780

Although 349 laboratories reported results for cadmium in WS 41 using ICP-AES, this technique is not likely to be sensitive enough for use in the analysis of arsenic at or near the PQL of 3 µg/L. Conversely, GHAA is a technique that is ideal for low-level arsenic determinations, but based on the WS 40 results for antimony, laboratories may not have made significant investments in this instrumentation. Therefore, only the data for ICP-MS and GFAA were summed for each of the studies in Table 2.25. Those results indicate that there were at least 780 laboratories with the analytical instrumentation necessary to measure arsenic at the 3 µg/L PQL in 1998 when WS 40 and WS 41 were conducted.

As can be seen in Tables 2.19 and 2.20, not all laboratories with the instrumentation and the willingness to participate in the voluntary low-level arsenic WS studies achieved acceptable results. In fact, not all the EPA and State laboratories achieved acceptable results. While past performance is not necessarily an accurate predictor of future success, EPA used the data in Table 2.20 to estimate the percentage of a theoretical pool of laboratories that would pass an arsenic WS study at or near the PQL. EPA plotted the data in Table 2.20 for the other laboratories against the spiked concentration of arsenic, as was done for the EPA and State laboratories. A linear regression was also performed in a similar fashion. Both the observed and predicted performance are shown in Figure 2.12.

Figure 2.12
Observed and Predicted Results for Other Laboratories for the $\pm 30\%$ Limit



Unlike Figure 2.11, the purpose of this graph is *not* to estimate the PQL for arsenic, but rather, to indicate the percentage of laboratories that would achieve acceptable results at a given PQL. Drawing a horizontal line from the point where the observed results intersect the vertical line representing 3 $\mu\text{g/L}$ suggests that about 67% of the other laboratories would achieve acceptable results at that concentration (compared to at least 75% of the EPA and State laboratories in Figure 2.11).

The predicted line is based on a linear regression, and it falls below the observed results between 2.5 and 4.5 $\mu\text{g/L}$. The reason for this is the relatively poorer performance of the other laboratories in the two lowest concentration and one highest concentration WS studies in the data set. The terms of the regression equation for other laboratories are shown in Table 2.26, in a similar fashion as for the EPA Regional and State laboratory data presented in Table 2.21.

Table 2.26 Regression Equation Terms for Other Laboratory Data	
Regression Term	At $\pm 30\%$ Acceptance Criterion
m	0.064639
b	0.428593
r	0.846080
p	0.0120

These terms can be used to form a similar equation, but instead of setting $y = 0.75$, and solving for x , the concentration term, x was set to 3 $\mu\text{g/L}$, and the equation was solved for the percentage of acceptable laboratories. Thus, the equation $y = mx + b$ yields a value for y of 0.6225, or approximately 62%.

Based on this regression, EPA assumed that approximately 62% of other laboratories would achieve acceptable results at 3 µg/L. The Agency multiplied this percentage by the numbers of laboratories that participated in three different WS studies to derive the three estimates of laboratory capacity that are shown in Table 2.27.

Table 2.27 Estimates of Laboratory Capacity for Arsenic Analyses at a PQL of 3 µg/L and a ± 30% Acceptance Limit		
Source of Data for Estimate	Total Number of Laboratories	Estimated Laboratory Capacity at 62% Passing
WS 36 - most recent low-level arsenic study	449	278
WS 41 laboratories reporting cadmium results using ICP-MS and GFAA	538	333
WS 40 laboratories reporting antimony results using ICP-MS and GFAA	780	483

Although there is considerable variability among these estimates of the number of other laboratories, EPA expects that there would still be at least several hundred laboratories available in which to conduct nationwide monitoring for arsenic. EPA also believes that all three of these estimates are conservative since they are based on historical data from laboratories that have voluntarily participated in WS studies. EPA expects that once the PQL for arsenic is established, additional laboratories will participate in the WS studies and the environmental laboratory community will continue to develop their capabilities for the analysis of arsenic at the PQL.

2.7.8.5 Conclusions

In an effort to incorporate analytical variability into regulation development, the Agency uses the PQL to estimate or evaluate the ability of most laboratories to produce reliable quantitative results for SDWA contaminants during day-to-day operations. The process employed by EPA in 1999 to determine PQL for arsenic utilized:

- Data from low-level (<6 µg/L) arsenic WS studies 30, 32, 33, 34, 35 and 36;
- Acceptance limits similar to other low- level inorganics; and
- Linear regression analysis to determine the point at which 75% of EPA Regional and State laboratories fell within the acceptance range.

This process yielded a PQL of 3 µg/L at the ± 30% acceptance limit. While the PQL represents a stringent target for laboratory performance, the Agency believes that most laboratories using appropriate quality assurance and quality control procedures will be able to achieve this level on a routine basis. The process used was consistent with the derivations of

PQLs for most of the other contaminants regulated under the SDWA and consistent with the 1995 recommendations of the EPA Science Advisory Board.

The predominant analytical technique used in WS studies 30-36 was some form of GFAA with a minor component of ICP-MS. A rough estimation of the non-EPA laboratory capacity at this PQL was determined using data from WS study 36 and information from more recent WS studies for other metals regulated at similar low levels (i.e., antimony and cadmium). The Agency conservatively estimates that at least several hundred (~ 300) non-EPA laboratories should be able to achieve acceptable performance at a PQL of 3 µg/L with the ± 30% acceptance limit.

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