Results of the EPA Method 1632 Validation Study

U.S. EPA Office of Water
Office of Science and Technology
Engineering and Analysis Division
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Disclaimer

This summary report has been reviewed by the Analytical Methods Staff in the Engineering and Analysis Division within the U.S. Environmental Protection Agency's (EPA's) Office of Water. Mention of company names, trade names, or commercial products in this report does not constitute endorsement or recommendation for use.

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1.0 Background

In 1993, EPA's Engineering and Analysis Division (EAD) began developing methods for the determination of metals at ambient water quality criteria levels. This method development initiative was driven by an increased emphasis on water quality-based permitting.

In October 1994, EAD began preliminary efforts aimed at developing an analytical method that would allow determination of arsenic at EPA's lowest water quality criterion of 0.018 Fg/L (18 ng/L). The objective of this effort was to develop a method capable of yielding a method detection limit (MDL) low enough to demonstrate that any measurement made at the water quality criterion is free from contamination. A target MDL was set at one tenth of EPA's water quality criterion (0.018 Fg/L x 0.10 = 0.0018 Fg/L or approximately 2 ng/L).

To meet this objective, EAD investigated two analytical techniques for the determination of arsenic. Both techniques involved hydride generation coupled with cryogenic concentration. In one technique, sample processing was followed by quartz furnace atomic absorption to measure arsenic concentrations. In the other technique, sample processing was followed by inductively coupled plasma/mass spectrometry (ICP/MS) analysis. Following a preliminary study of these techniques,[1] EAD developed draft *Method 1632: Determination of Inorganic Arsenic in Water by Hydride Generation Flame Atomic Absorption* in April 1995 (EPA 821-R-028). In January 1996, a revised version of Method 1632 was released to reflect the May 1995 publication of revised water quality criteria for some metals and to correct the calculation used to determine the relative percent difference between matrix spike and matrix spike duplicate QC samples.

In March 1996, EAD initiated a study to validate the January 1996 draft version of Method 1632. The purpose of this report is to document the results of this validation study.

2.0 Study Design and Objectives

The study described in this report was designed as a single laboratory study aimed at providing EAD with some level of verification that the procedures and QC acceptance criteria specified in the draft method could be met by environmental laboratories. Depending on laboratory costs and EPA budget constraints, the study was designed to be implemented in one or more laboratories. More extensive interlaboratory method validation studies may be performed at a later date, if warranted.

The study design is described fully in the *Study Plan for Validation of EPA Method 1632*, summarized below, and provided in Appendix A. The study was conducted in two phases.

The objective of Phase 1 was to use reagent water samples to achieve the method-specified MDL for arsenic (0.002 Fg/L) according to the instructions in 40 *CFR* Part 136, Appendix B-*Definition and Procedure for the Determination of the Method Detection Limit - Revision 1.11* (attached to Appendix A of this report) and the quartz furnace atomic absorption spectrometry procedures described in the January 1996 version of Method 1632. Reagent water was chosen as the sample matrix because it is homogeneous, readily available, and included as a matrix option in 40 *CFR* Part 136, Appendix B.

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[1] See *Study Plan for the Preliminary Development of a Method for Determination of Arsenic at Ambient Water Quality Criteria Levels*, September 1994. Available from the Sample Control Center (operated by DynCorp), 300 N. Lee Street, Alexandria, VA 22314, (703) 519-1140.

The objectives of Phase 2 were to verify that Method 1632 is capable of yielding a minimum level (ML) of 10 ng/L for arsenic, determine whether the QC acceptance criteria specified in Table 2 of Method 1632 are achievable, and identify any further method development needs. Performance of Phase 2 was contingent on successful completion of Phase 1.

3.0 Study Implementation

Two laboratories performed the Phase 1 and Phase 2 studies. These were Brooks Rand, Ltd. (Seattle, WA); and Frontier Geosciences (Seattle, WA). All analyses and data reporting were completed in May 1996. Day-to-day coordination of the study and review of study data was performed by the contractor-operated Sample Control Center (SCC).[2]

3.1 Phase 1 Methodology/Approach

Each laboratory was instructed to perform the MDL determination in accordance with the 40 *CFR* Part 136, Appendix B procedures. The laboratories analyzed a minimum of seven replicate samples spiked with arsenic. The spiking levels were recommended to be between one and five times the estimated MDL. To ensure that the spiking levels chosen were appropriate, the laboratories were required to perform the two-aliquot test described in Section 4b of 40 *CFR* Part 136, Appendix B. If this test indicated that the sample arsenic concentration was in the desired range for determining the MDL, the laboratory proceeded with the analysis of the five additional replicate samples for a total of seven samples. If the test indicated that the sample arsenic concentration was not in the correct range, the laboratory was required to repeat the test until the desired spike level was achieved.

3.2 Phase 2 Methodology/Approach

To achieve the Phase 2 objectives, the laboratories were required to analyze four spiked reagent water replicates and two spiked aqueous field sample replicates. The results of the spiked reagent water sample analyses were used to assess the precision and accuracy of arsenic determinations using Method 1632. The results of the spiked field sample analyses were used to assess the precision and accuracy of the method for determining arsenic in a real-world sample matrix. All method-specified QC requirements and analytical procedures were performed with the analyses. The results of associated QC analyses (e.g., blanks, calibration verification, etc.) were used to further assess the validity of the method.

Field samples were to be collected by each laboratory from a source known to contain arsenic at ambient concentrations that are at or below the levels of interest in this study. The laboratories, however, reported that they were unable to collect field samples that contained arsenic at concentrations low enough to allow spiking at the desired concentration (50 ng/L). Consequently, the laboratories were instructed to dilute a field sample with reagent water to lower the "ambient" arsenic concentration to one-fifth the desired spike level (10 ng/L).

4.0 Data Reporting and Validation

[2] The Sample Control Center is operated by DynCorp Environmental under EPA Contract No. 68-C3-0037.

All data from this study were submitted to SCC for review and validation. The laboratory reports included hardcopy summary level data, MDL results, and raw data. The data were reviewed in accordance with EPA's *Guidance on the Documentation and Evaluation of Trace Metals Data Collected for Clean Water Act Compliance Monitoring*.[3] This review included verification that (1) reagent water and ambient water samples were used as appropriate, (2) proper spike levels were used in the MDL studies and QC analyses, (3) the instruments were properly calibrated and that other method procedures were followed, and (4) the MDL was calculated per the MDL procedure specified in 40 *CFR* Part 136, Appendix B. All data were considered to be of acceptable quality with the exception noted in Section 5.2.

5.0 Results

Each laboratory submitted Phase 1 and Phase 2 analytical results according to the February 1996 study plan.

5.1 Phase 1 Results

The analytical and statistical results for Phase 1 are provided in Table 1. The MDL is calculated as the standard deviation of the seven replicate analyses multiplied by the students' t value for (n-1) degrees of freedom, where n equals the number of replicates. The students' t value for six degrees of freedom (seven replicates) is 3.143.

Brooks Rand, Ltd. and Frontier Geosciences reported arsenic MDLs (2.64 ng/L and 3.31 ng/L, respectively) which are higher than the MDL specified in the January 1996 draft version of Method 1632 (2 ng/L). Both MDLs, however, are well under the EPA water quality criterion of 18 ng/L.

Frontier Geosciences detected arsenic in its first blank at a concentration (3.81 ng/L) above the MDL. The arsenic concentration in the second reagent blank was determined to be 2.51 ng/L, which is below the MDL. Because Frontier Geosciences typically blank subtracts arsenic results, the reagent blank arsenic level did not interfere with the MDL determination.

5.2 Phase 2 Results

MLs were estimated by multiplying the MDL by 3.18 and rounding the resulting value to the nearest number in the series:

$$\boldsymbol{(1, 2, \text{ or } 5) \times 10^{n}}$$

where: n=a positive or negative integer, or zero
ML series: ..., 0.1, 0.2, 0.5, 1, 2, 5, 10, 20, 50, ...

The value 3.18 represents the ratio between the students' t multiplier used to determine the MDL (3.143) and the 10 times multiplier used in the American Chemical Society (ACS) Limit of

[3] *Guidance on the Documentation and Evaluation of Trace Metals Data Collected for Clean Water Act Compliance Monitoring*, Draft, January 1996 (EPA 821-B-96-002). Available from USEPA NCEPI, 11029 Kenwood Road, Cincinnati, OH 45242, (513) 489-8190.

Quantitation (i.e., 10 ÷ 3.143 = 3.18). For example, if the calculated MDL is 4.2, the ML will be equal to 4.2 x 3.18 which equals 13.4. The number in the ML series nearest to 13.4 then establishes the ML at 10 (where n=1).

Although both of the laboratories reported MDLs that were slightly higher than the MDL specified in the draft version of Method 1632, both laboratories' MDLs yield MLs of 10 ng/L, which is consistent with the ML specified in draft Method 1632. All laboratories were able to successfully calibrate to this ML during Phase 2 of the study.

The analytical and statistical results for Phase 2 are summarized in Table 2. This table also lists the target QC acceptance criteria and results for the initial precision and recovery (IPR), ongoing precision and recovery (OPR), calibration verification (CALVER), and matrix spike/matrix spike duplicate (MS/MSD) tests.

The two participating laboratories met all method-specified QC acceptance criteria with one exception. Frontier Geosciences reported an MS/MSD relative percent difference (RPD) that exceeds the method-specified criterion. Because Brooks Rand, Ltd.'s RPD is within criteria and all other results submitted by Frontier Geosciences are within criteria, the outlying RPD is considered an anomaly.

Table 1: Method Detection Limits for Arsenic by EPA Method 1632

				Concentration (ng/L) Replicate									
Laboratory	**Spike Levels**	**Blank 1**	**Blank 2**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**Mean**	**s**	**MDL**
Brooks Rand, Ltd.	5	3.81	2.51	7.23	7.92	6.58	6.01	8.18	8.05	7.96	2.06	0.8	2.64
Frontier Geosciences	7.5	2.41	2.29	8.33	6.21	6.29	6.55	8.38	5.97	7.78	7.07	1.1	3.31

Table 2: Minimum Levels and QC Acceptance Criteria Validation Results for Arsenic by EPA Method 1632

	ML (ng/L)	**IPR (%)**		**CALVER (%)**	**OPR (%)**	**MS (%)**	**MSD (%)**	**MS/MSD RPD**
		s	**X**					
Laboratory	***10***	***42***	***51-143***	***76-116***	***55-146***	***55-146***	***55-146***	***20***
Brooks Rand, Ltd.	10	3	106	92, 110	109, 106	93	92	1
Frontier Geosciences	10	2	86	99	107	103	77	27

6.0 Conclusion and Discussion

The two participating laboratories were unable to achieve the Phase 1 objective of confirming that EPA Method 1632 is capable of yielding an arsenic MDL of 2 ng/L. The results suggest that laboratories using this method will obtain slightly less sensitive results than were obtained by the laboratory EAD employed to establish the initial MDL and, therefore, the MDL specified in Method 1632 should be increased to 3 ng/L.

The Phase 2 results demonstrate that EPA Method 1632 is capable of achieving a 10 ng/L ML and that the QC acceptance criteria in EPA Method 1632 are reasonable. It should be possible for laboratories to meet these criteria on a routine basis by using this method. No additional method development needs were identified by either laboratory.

APPENDIX A

Study Plan for Validation of EPA Method 1632

Study Plan
for
Validation of EPA Method 1632

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Disclaimer

This document has been reviewed and approved by the Engineering and Analysis Division, U.S. Environmental Protection Agency. Mention of company names, trade names, or commercial products does not constitute endorsement or recommendation for use.

SECTION 1: INTRODUCTION

In 1993, EPA's Engineering and Analysis Division (EAD) began developing methods for determination of metals at ambient water quality criteria levels. This method development initiative was driven by an increased emphasis on water quality-based permitting.

In October 1994, EAD began preliminary efforts aimed at developing an analytical method that would allow determination of arsenic at EPA's lowest water quality criterion of 0.018 ug/L (18 ng/L). The objective of this effort was to develop a method capable of yielding a method detection limit (MDL) low enough to demonstrate that any measurements made at the water quality criterion were free from contamination. Such a demonstration would require an MDL that was no more than 1/10 EPA's water quality criterion (0.018 ug/L x 0.10 = 0.0018 ug/L or approximately 2 ng/L).

To meet this objective, EAD developed a study plan to investigate two possible techniques. Both techniques involved hydride generation coupled with cryogenic concentration. In one technique, sample processing was followed by hydrogen flame atomic absorption to measure arsenic concentrations. In the other technique, sample processing was followed by inductively coupled plasma/mass spectrometry (ICP/MS) analysis. Following a preliminary study of these techniques[4], EAD developed draft *Method 1632: Determination of Inorganic Arsenic in Water by Hydride Generation Flame Atomic Absorption* in April 1995 (EPA 821-R-028). In January 1996, a revised version of Method 1632 was released to reflect the May 1995 publication of revised water quality criteria for some metals and to correct the calculation used to determine the relative standard deviation between matrix spike and matrix spike duplicate QC samples. The purpose of this study plan is to document EAD's strategy for validating the January 1996 draft of Method 1632.

SECTION 2: OBJECTIVES

In order to minimize cost, the study will be pursued in two phases, each of which is designed to accomplish specific objectives. Objectives for each phase are summarized below.

2.1 Phase 1 Objectives

During initial development of Method 1632, EAD conducted an MDL study that demonstrated the procedures used in Method 1632 could achieve an MDL of 2 ng/L for arsenic. Based on these results, EAD drafted Method 1632. The purpose of Phase 1 of this study is confirm that Method 1632 is capable of yielding an arsenic MDL of 2 ng/L in a laboratory other than the laboratory EAD employed in the former study. If this MDL objective cannot be met, results of the study will be used as a basis to identify further method development efforts necessary to produce the desired MDL for arsenic.

[4] see *Study Plan for the Preliminary Development of a Method for Determination of Arsenic at Ambient Water Quality Criteria Levels*, September 1994. Available from DynCorp Environmental, 300 N. Lee Street, Alexandria, VA 22314, (703) 519-1140.

2.1.1 Data Quality Objectives for Phase 1

In addition to the overall objective described above, EAD has three principle data quality objectives (DQOs) for this phase of the study:

(1) The MDLs determined in this study must be within a factor of five of the level spiked in order to ensure that MDLs determined in the study are neither overstated nor understated.

(2) All data produced under this phase of the study must be generated in accordance with the analytical and QA/QC procedures defined in Method 1632. Alternatively, the data must be the result of pre-approved and documented changes to these procedures. This will allow EAD to use the results of this phase to identify the need for further revision of the method.

(3) All data produced under this phase of the study must be capable of being verified by an independent person reviewing the analytical data package.

2.1.2 Exceptions to QC Procedures

In order to meet these DQOs, the laboratory will be required to have a comprehensive QA program in place and operating throughout this study. This will ensure that the data produced are of the highest possible quality. During Phase 1 of the study, the laboratory will be required to follow all QC procedures defined in Method 1632 with the following exceptions:

- Demonstration of initial and ongoing precision and recovery will not be required.

- Performance of matrix spike and matrix spike duplicate analyses will not be required.

- Analysis of field blanks and equipment blanks will not be required.

- Instrument calibration must be performed at a range that will encompass the minimum level (ML) associated with the detection limit being studied.

All analyses performed in this study must be performed on a calibrated instrument, and calibration verification must be performed during each analytical batch.

2.2 Phase 2 Objectives

The second phase of this study will focus on validating the QC acceptance criteria that are specified in Method 1632. The primary objectives that will be pursued in Phase 2 are to:

(1) Verify that Method 1632 is capable of yielding a minimum level (ML) of 10 ng/L for arsenic. This level is below EPA's lowest water quality criterion of 18 ng/L.

(2) Determine if the IPR, calibration verification, OPR, and matrix spike QC acceptance criteria specified in Table 2 of the Method 1632 can be achieved for arsenic.

(3) Identify any further method development needs or areas in need of revision.

2.2.1 Data Quality Objectives for Phase 2

Data quality objectives for this phase of the study are as follows:

(1) All data produced under this phase of the study must be generated in accordance with the analytical and QA/QC procedures defined in Method 1632; alternatively, the data must be the result of pre-approved and documented changes to these procedures. This will allow EAD to use the results of this phase to identify the need for further revision of Method 1632.

(2) The QC data generated in this study must reflect careful laboratory attention to Method 1632. The QC data are not to be the result of repeated efforts on the part of the laboratory to achieve results that are within the QC limits currently stated in the method. Therefore, the laboratory will be instructed to utilize any stated QC specifications (i.e., limits) as data quality objectives (DQOs) rather than as definitive requirements of the study. The results of the laboratory's QC analyses will be used to confirm that the specifications provided in Method 1632 can be met, or alternatively, to identify specifications that may not be achievable.

(3) All data produced under this phase of the study must be capable of being verified by an independent review of the analytical data package.

SECTION 3: STUDY MANAGEMENT

The study described in this document will be managed by EAD's Analytical Methods Staff (AMS). Day-to-day management and coordination of study activities will be provided by the contractor-operated Sample Control Center (SCC) under AMS guidance. SCC will contract with one or more laboratories experienced in the determination of trace metals at WQC levels. The total number of laboratories participating in this study will be dependent upon laboratory capability, laboratory availability, cost, and scheduling constraints. SCC will coordinate laboratory analysis, receive and validate all analytical data, and perform statistical analyses. AMS will draw conclusions from the results and produce a report providing the results of the study. AMS will also share data and results with all interested parties upon request.

SECTION 4: TECHNICAL APPROACH

The technical approach detailed below is designed to be consistent with the technical approach previously used by EAD for validating the procedures outlined in the *Quality Control Supplement for Determination of Metals at Ambient Water Quality Criteria Levels* (the "QC Supplement"). That approach is detailed in the *Study Plan for Validation the Quality Control Supplement for Determination of Metals at Ambient Water Quality Criteria Levels*, dated June 1994.

4.1 Phase 1 Technical Approach

Phase 1 will focus on the performance of an MDL study in accordance with the procedure described in 40 *CFR* Part 136, Appendix B - *Definition and Procedure for the Determination of the Method Detection Limit - Revision 1.11*. This procedure, which is provided as Attachment 1 to this study plan, involves

the analysis of at least seven replicate samples that are known to contain the target analyte(s) at a concentration of one to five times the estimated MDL. For the purposes of this study, the estimated MDL is the previously determined MDL of 2 ng/L. Therefore, the laboratory will use choose a spike level that produces a concentration of 2 - 10 ng/L (1 - 5 times the estimated MDL of 2 ng/L).

In this phase of the study, reagent water will be spiked with arsenic to produce a synthetic sample that can be divided into at least seven replicates. In order to ensure that the laboratory is spiking at the appropriate level, it is recommended that the laboratory follow the two-aliquot test described in Section 4b of the 40 *CFR* Part 136 procedure. If these measurements indicate that the sample concentration is in the desired range for determination of the MDL, the laboratory may proceed with the five additional aliquots for a total of seven aliquots. *All* seven measurements will be used for calculation of the MDL. If the first two measurements indicate that the sample concentration is not in the correct range, the laboratory will be required to repeat Section 4b (analysis of two spiked aliquots) until the desired spike level is achieved. Application of the two aliquot test is designed to minimize the possibility of repeating the MDL study in order to obtain an MDL that is within a factor of five of the level spiked.

If the MDL resulting from the study is not within a factor of five of the level spiked, then the spiking, measurement, and calculation processes will be iterated until the measured MDL is within a factor of five, as given in the MDL procedure. If the laboratory obtains non-detect results during their MDL study, the laboratory must increase the spike level and repeat the test. The objective of these requirements is to ensure that MDLs resulting from the study are not artificially high or low due to inappropriate spiking levels. If appropriate spiking levels are chosen but yield MDLs greater than 2 ng/L, EAD will consider the need for further study or the identification of new analytical techniques.

The analytical portion of each MDL study will be performed in accordance with the procedures described in Method 1632, with the four exceptions noted in Section 2.1.2 above.

If the results of Phase 1 suggest that the MDL of 2 ng/L cannot be achieved using Method 1632, SCC will work with the laboratory(ies) to identify clarifications and/or revisions that must be made in order to yield the target detection levels. SCC will notify EAD of these results and any laboratory recommendations. EAD will make a final determination as to whether additional method development activities are needed before Phase 2 is commenced.

4.2 Phase 2 Technical Approach

The technical approach for Phase 2 will be centered around the use of Method 1632 to analyze four spiked reagent water replicates and two spiked aqueous field sample replicates. The results of the spiked reagent water analyses will be used to assess the precision and accuracy that can be achieved for arsenic determinations using Method 1632. The results of the spiked field sample replicates will be used to assess the precision and accuracy of the method in a real world matrix. *All* quality control requirements and analytical procedures stated in Method 1632 will be performed with each of these analyses. The results of any associated QC analyses (e.g., blanks, calibration verification, etc.) will be used to further assess the validity of the methods.

4.2.1 Matrix Spike and Matrix Spike Duplicate

The two spiked aqueous field sample replicates analyzed in this study (known as matrix spike and matrix spike duplicate samples) will be prepared by the laboratory. To do this, the laboratory shall collect a single sample from a source known to contain arsenic at ambient concentrations that are at or below the levels of interest in this study. This sample will then be divided into replicate aliquots and spiked in the laboratory to produce matrix spike (MS) and matrix spike duplicate (MSD) samples as described below and in Method 1632. The laboratory must collect and analyze a field blank with the field sample in order to demonstrate that the replicates used for preparation of the MS and MSD are free from contamination. Prior to collection of field samples, the laboratory shall verify that the sampling equipment is free from contamination by analyzing equipment blanks as described in Section 9.5.3 of Method 1632. When collecting field samples for this study, the laboratory may follow the procedures outlined in *EPA Method 1669: Sampling Ambient Water for Determination of Trace Metals at EPA Water Quality Criteria Levels* or in other documented sampling protocols known to be capable of yielding samples free from contamination at the levels of interest in this study. If an alternate documented sampling protocol is used, a copy of that protocol shall be provided with the results.

4.2.2 Minimum Level

In developing Method 1632, an interim minimum level (ML) of quantitation was derived by multiplying the MDL by 3.18. This 3.18 value is the ratio between the student t multiplier used to determine the MDL (3.143) and the 10 sigma multiplier used to establish the American Chemical Society (ACS) and International Union of Pure and Applied Chemistry (IUPAC) limit of quantitation (LOQ). Because EAD determined the MDL to be 2 ng/L, this value was multiplied by 3.18 to arrive at an interim ML of 6.36 ng/L. To facilitate calibration, the interim ML was rounded to 10 ng/L. This is consistent with OW's policy to round an interim ML to the nearest factor of 10 multiple of 1, 2, or 5. Although this policy suggests it is acceptable to round the interim ML to 5 ng/L, EAD chose to use to 10 ng/L as the ML in its draft version of Method 1632 because that level was sufficient to meet EAD's objective of making reliable determinations at EPA's lowest water quality criteria levels for arsenic.

4.2.3 Detailed Requirements

If the results of Phase 1 verify the MDL obtained by EPA, and hence the ML of 10 ng/L, then all Phase 2 QC analyses will be based on the requirements and concentrations specified in draft Method 1632. Specifically:

(1) The instrument will be calibrated at a minimum of three points, one of which must be the ML (10 ng/L) and one of which must be near the upper end of the linear dynamic range, as per Section 10.1 of Method 1632.

(2) Initial precision and recovery (IPR) and the ongoing precision and recovery (OPR) samples must be prepared by spiking reagent water with arsenic at 0.015 ug/L as required in Sections 9.2 and 9.6 of Method 1632.

(3) All blanks (laboratory, field, and equipment) must be demonstrated to be free from contamination below the MDL, as described in Section 9.5 of Method 1632.

(4) Matrix spike and matrix spike duplicate samples must be prepared by spiking field samples collected for Phase 2 at a concentration that is equal to five times the background

concentration or at five times the ML, whichever is greater (see Section 9.3.1.2). The field samples used for the performance of matrix spike and matrix spike duplicate analyses should be collected from sources known to contain arsenic at ambient concentrations that are at or below the levels of interest in this study.

All IPR, OPR, matrix spike, and matrix spike duplicate analyses performed during this phase of the study will be performed in accordance with the procedures described in Method 1632. If, during the course of analysis, the laboratory encounters difficulties that may be resolved through modification of the written procedures, the laboratory will be required to contact SCC, explain the problem, obtain approval for the deviation, evaluate the effectiveness of the deviation, and supply SCC with results and information that will enable SCC to modify the written procedures accordingly.

Note: If the results of Phase 1 do not verify the MDL or ML obtained by EAD in the previous study, and if EAD chooses to pursue Phase 2 without further method development activity, the MDL determined in Phase 1 of this study will be used to calculate a new interim ML for arsenic. As with the interim ML derived during the development of Method 1632, the new interim ML will be calculated by multiplying the MDL determined in Phase 1 by 3.18. This new interim ML would then be used to identify appropriate calibration levels and spike concentrations for the OPR, IPR, and MS/MSD samples.

SECTION 5: DATA REPORTING AND EVALUATION

The laboratory will be required to submit both summary level and raw data in hardcopy format. The laboratory will also be required to submit detailed explanations of any approved modifications to the analytical techniques specified in the referenced method and used in this study.

Upon receipt of the laboratory data package, SCC will review the data to ensure that the data were generated in accordance with the required procedures. The results of Phase 1 will be used to verify the MDL and ML listed in Method 1632 for arsenic. The results of the analyses performed in Phase 2 will be used to verify the IPR, OPR, calibration verification, and matrix spike QC specifications that are listed in Table 2 of Method 1632. Laboratory comments and suggestions will also be used to identify further revisions that should be made to Method 1632.

The laboratory shall report the following data, at a minimum:

(1) Summary reports of all analytical results. The Phase 1 summary report shall include an MDL summary table that groups data under the following categories: spiked concentration in each of the seven replicates, the mean of the seven measured concentrations, the standard deviation of these measurements, the student's t-value used, and the calculated MDL for the technique.

The Phase 2 summary report must contain a summary of analytical results for all QC and field samples. For the IPR analysis, the spiking level, individual results of the four replicates, and the mean recovery and relative standard deviation of the four replicates should be reported. For the OPR and CALVER analyses, the true (or expected) concentration of the QC sample, the measured concentration, and the percent recovery should be reported. For MS/MSD analyses, the background concentration of the field

sample, the spiking level, the individual results of the MS and MSD analyses, the percent recovery for the MS and MSD, the average concentration found in the MS/MSD samples, and the RPD between the MS and MSD should be reported. The results for all other QC, including calibration and blanks, should also be reported.

(2) A list of samples analyzed and a run chronology.

(3) Copies of all raw data, including quantitation reports, strip charts, spectra, bench sheets and laboratory notebooks showing tare and sample weights, sample volumes, solvent volumes and other data that will allow the final results reported to be traced back to the analytical steps performed. Each data element shall be clearly identified in the laboratory's data package.

(4) The MDL and the individual values that support the MDL, to three significant figures. All other data that support the MDL determination including calibration, blanks, and calibration verifications shall also be reported.

(5) A written report that details any problems associated with the performance of the MDL study or analysis of the samples. The written report should also provide comments on the performance of the method.

(6) A detailed written description of any approved modifications to the procedures specified in the referenced method that were used during the performance of this study.

SECTION 6: LIMITATIONS

The most significant limitation of the study is that it focuses only on the water quality criteria levels published by EPA; it does not address lower water quality criteria or criteria for other forms and species of arsenic that have been promulgated by states not covered under the National Toxics Rule or the Stay of Federal Water Quality Criteria for Metals. This limitation is consistent with and does not go beyond EAD's current mission to develop methods that will allow measurement of trace metals at the lowest water quality criteria levels published by EPA.

Other limitations are that this study plan does not attempt to validate the applicability of the procedures outlined in Method 1632 to effluent sample, marine samples, or to total recoverable arsenic. This study plan is limited to a validation of dissolved arsenic in ambient water samples. This approach is consistent with EAD's mission to prioritize dissolved metals in ambient waters over total recoverable metals and over determination of metals in effluent and marine samples.

Appendix A: Definition and Procedure for the Determination of the Method Detection Limit - Revision 1.11

(Federal Register, Vol. 49, No. 209, Friday, October 26, 1984)

Appendix B to Part 136 - Definition and Procedure for the Determination of the Method Detection Limit - Revision 1.11

"Definition"

The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.

"Scope and Application"

This procedure is designed for applicability to a wide variety of sample types ranging from reagent (blank) water containing analyte to wastewater containing analyte. The MDL for an analytical procedure may vary as a function of sample type. The procedure requires a complete, specific, and well defined analytical method. It is essential that all sample processing steps of the analytical method be included in the determination of the method detection limit.

The MDL obtained by this procedure is used to judge the significance of a single measurement of a future sample.

The MDL procedure was designed for applicability to a broad variety of physical and chemical methods. To accomplish this, the procedure was made device- or instrument-independent.

"Procedure"

1. Make an estimate of the detection limit using one of the following:

   (a) The concentration value that corresponds to an instrument signal/noise in the range of 2.5 to 5.

   (b) The concentration equivalent of three times the standard deviation of replicate instrumental measurements of the analyte in reagent water.

   (c) That region of the standard curve where there is a significant change in sensitivity, i.e., a break in the slope of the standard curve.

   (d) Instrumental limitations.

   It is recognized that the experience of the analyst is important to this process. However, the analyst must include the above considerations in the initial estimate of the detection limit.

2. Prepare reagent (blank) water that is as free of analyte as possible. Reagent or interference free water is defined as a water sample in which analyte and interferent concentrations are not detected at the method detection limit of each analyte of interest. Interferences are defined as systematic errors in the measured analytical signal of an established procedure

caused by the presence of interfering species (interferent). The interferent concentration is presupposed to be normally distributed in representative samples of a given matrix.

3. (a) If the MDL is to be determined in reagent (blank) water, prepare a laboratory standard (analyte in reagent water) at a concentration which is at least equal to or in the same concentration range as the estimated method detection limit. (Recommend between 1 and 5 times the estimated method detection limit.) Proceed to Step 4.

(b) If the MDL is to be determined in another sample matrix, analyze the sample. If the measured level of the analyte is in the recommended range of one to five times the estimated detection limit, proceed to Step 4.

If the measured level of analyte is less than the estimated detection limit, add a known amount of analyte to bring the level of analyte between one and five times the estimated detection limit.

If the measured level of analyte is greater than five times the estimated detection limit, there are two options.

(1) Obtain another sample with a lower level of analyte in the same matrix if possible.

(2) The sample may be used as is for determining the method detection limit if the analyte level does not exceed 10 times the MDL of the analyte in reagent water. The variance of the analytical method changes as the analyte concentration increases from the MDL, hence the MDL determined under these circumstances may not truly reflect method variance at lower analyte concentrations.

4. (a) Take a minimum of seven aliquots of the sample to be used to calculate the method detection limit and process each through the entire analytical method. Make all computations according to the defined method with final results in the method reporting units. If a blank measurement is required to calculate the measured level of analyte, obtain a separate blank measurement for each sample aliquot analyzed. The average blank measurement is subtracted from the respective sample measurements.

(b) It may be economically and technically desirable to evaluate the estimated method detection limit before proceeding with 4a. This will: (1) Prevent repeating this entire procedure when the costs of analyses are high and (2) insure that the procedure is being conducted at the correct concentration. It is quite possible that an inflated MDL will be calculated from data obtained at many times the real MDL even though the level of analyte is less than five times the calculated method detection limit. To insure that the estimate of the method detection limit is a good estimate, it is necessary to determine that a lower concentration of analyte will not result in a significantly lower method detection limit. Take two aliquots of the sample to be used to calculate the method detection limit and process each through

the entire method, including blank measurements as described above in 4a. Evaluate these data:

(1) If these measurements indicate the sample is in desirable range for determination of the MDL, take five additional aliquots and proceed. Use all seven measurements for calculation of the MDL.

(2) If these measurements indicate the sample is not in correct range, reestimate the MDL, obtain new sample as in 3 and repeat either 4a or 4b.

5. Calculate the variance (S^2) and standard deviation (S) of the replicate measurements, as follows:

$$S^2 = \frac{1}{n-1}\left[\sum_{i=1}^{n} X_1^2 - \frac{\left(\sum_{i=1}^{n} X_1\right)^2}{n}\right]$$

$$S = (S^2)^{\frac{1}{2}}$$

Where:

Xi; I = 1 to n, are the analytical results in the final method reporting units obtained from the n sample aliquots

S = refers to the sum of the X values from I=l to n.

6. (a) Compute the MDL as follows:

$$MDL = t_{(n-1,1-a=0.99)}\,(S)$$

where:

$t_{(n-1,1-a=.99)}$ = the students t value appropriate for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom. See Table.
S = standard deviation of the replicate analyses.
MDL = the method detection limit

(b) The 95% confidence interval estimates for the MDL derived in 6a are computed according to the following equations derived from percentiles of the chi square over degrees of freedom distribution ($_x^2$/df).

LCL = 0.64 MDL

UCL = 2.20 MDL

where: LCL and UCL are the lower and upper 95% confidence limits respectively based on seven aliquots.

7. Optional iterative procedure to verify the reasonableness of the estimate of the MDL and subsequent MDL determinations.

(a) If this is the initial attempt to compute MDL based on the estimate of MDL formulated in Step 1, take the MDL as calculated in Step 6, spike the matrix at this calculated MDL and proceed through the procedure starting with Step 4.

(b) If this is the second or later iteration of the MDL calculation, use S^2 from the current MDL calculation and S^2 from the previous MDL calculation to compute the F-ratio. The F-ratio is calculated by substituting the larger S^2 into the numerator S^2_A and the other into the denominator S^2_B The computed F-ratio is then compared with the F-ratio found in the table which is 3.05 as follows: if $S^2_A / S^2_B > 3.05$, then compute the pooled standard deviation by the following equation:

$$S_{pooled} = \left[\frac{6S_A^2 + 6S_B^2}{12}\right]^{\frac{1}{2}}$$

if $S^2_A/S^2_B>3.05$, respike at the most recent calculated MDL and process the samples through the procedure starting with Step 4. If the most recent calculated MDL does not permit qualitative identification when samples are spiked at that level, report the MDL as a concentration between the current and previous MDL which permits qualitative identification.

(c) Use the S_{pooled} as calculated in 7b to compute the final MDL according to the following equation:

MDL = 2.681 (S_{pooled})

where: 2.681 is equal to $t_{(12, 1-a =.99).}$

(d) The 95% confidence limits for MDL derived in 7c are computed according to the following equations derived from precentiles of the chi squared over degrees of freedom distribution.

LCL=0.72 MDL

UCL=1.65 MDL

where: LCL and UCL are the lower and upper 95% confidence limits respectively based on 14 aliquots.

Table of Students' t Values at the 99 Percent Confidence Level

Number of replicates	Degrees of freedom (n-1)	$t_{(n-1, .99)}$
7	6	3.143
8	7	2.998
9	8	2.896
10	9	2.821
11	10	2.764
16	15	2.602
21	20	2.528
26	25	2.485
31	30	2.457
61	60	2.390
00	00	2.326

"Reporting"

The analytical method used must be specifically identified by number or title ald the MDL for each analyte expressed in the appropriate method reporting units. If the analytical method permits options which affect the method detection limit, these conditions must be specified with the MDL value. The sample matrix used to determine the MDL must also be identified with MDL value. Report the mean analyte level with the MDL and indicate if the MDL procedure was iterated. If a laboratory standard or a sample that contained a known amount analyte was used for this determination, also report the mean recovery.

If the level of analyte in the sample was below the determined MDL or exceeds 10 times the MDL of the analyte in reagent water, do not report a value for the MDL.

[49 FR 43430, Oct. 26, 1984; 50 FR 694, 696, Jan. 4, 1985, as amended at 51 FR 23703, June 30, 1986]