DETERMINATION OF ARSENIC SPECIES BY HYDRIDE GENERATION CRYOGENIC TRAPPING GAS CHROMATOGRAPHY

MET-1632

ALS-KELSO

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Approved By: _____ Date: 1/13/14
Department Supervisor – Jeff Coronado

Approved By: _____ Date: 1/13/14
QA Manager – Suzanne LeMay

Approved By: _____ Date: 1/16/14
Laboratory Director – Jeff Grindstaff

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Standard Operating Procedure

for

DETERMINATION OF ARSENIC SPECIES BY HYDRIDE GENERATION CRYOGENIC TRAPPING GAS CHROMATOGRAPHY

1. SCOPE AND APPLICATION

1.1. This Standard Operating Procedure (SOP) describes the procedure used for the analysis of Total Inorganic Arsenic (TIA) and Arsenic species by atomic absorption spectrophotometry based upon EPA 1632. This procedure describes both the preparation and analysis procedures used to determine the target analytes and reporting limits listed.

1.2. This procedure is used to determine the analytes of interest in aqueous samples. The procedure may be applied to other miscellaneous sample matrices providing that the analyst demonstrates the ability of the procedure to give data of acceptable quality in that matrix. The Method Reporting Limits (MRLs) and Method Detection Limits (MDLs) for target analytes are presented in Table 1. This method is designed for the measurement of arsenic species in the range of 0.01-50 ug/L.

1.3. Hydride generation cryogenic trapping gas chromatography atomic absorption spectrophotometry (HG-CT-GC-AAS) is used for sensitive species-specific determination of arsenite [As(III)], monomethylarsonic acid [MMA], and dimethylarsinic acid [DMA]. It is also used for the determination of total inorganic arsenic [TIA]. Arsenate [As (V)] is determined as the difference between TIA and As(III): As(V) = TIA - As(III). The same analyzer may also be used for low level quantification of arsenic speciation in various solid digests and leachates.

1.4. In cases where there is a project-specific quality assurance plan (QAPP), the project manager identifies and communicates the QAPP-specific requirements to the laboratory. In general, project specific QAPP's supersede method specified requirements. An example of this are projects falling under DoD ELAP. QC requirements defined in ADM-DOD, *Department of Defense Projects - Laboratory Practices and Project Management* may supersede the requirements defined in this SOP.

2. METHOD SUMMARY

2.1. In this technique arsenic species are selectively volatilized from solution by controlling the pH of the sample solution and reducing them to their corresponding hydrides with borohydride. The arsines are purged from the solution by a helium gas flow and trapped in a liquid nitrogen cooled 'U' tube packed with 15% OV-3 on Chromasorb WAW-DMCS. Heating the column revolatilizes the arsines and allows for chromatographic separation based on boiling points. Once separated the arsines are carried into a quartz furnace with a hydrogen-air flame where they are atomized and detected via atomic absorption spectrophotometry.

3. DEFINITIONS

3.1. Analysis Sequence – Samples analyzed in a set are referred to as an analysis sequence. The sequence begins with instrument calibration followed by samples, interspersed with calibration standards (Calibration Verifications, Calibration Blanks, etc...) The sequence ends when the set of samples has been injected or when qualitative and/or quantitative QC criteria indicate an out-of-control situation.

3.2. Quality Control Sample (QCS) – The QCS solution is made from a second source stock solution and is used to verify the validity of the calibration standards. This standard is also known as Independent Calibration Verification (ICV).

3.3. Matrix Spike/Duplicate Matrix Spike (MS/DMS) Analysis – In the matrix spike analysis, predetermined quantities of target analytes are added to a sample matrix prior to sample preparation and analysis. The purpose of the matrix spike is to evaluate the effects of the sample matrix on the method used for the analysis. Sample duplicates are spiked, and analyzed as a MS/DMS pair. Percent recoveries are calculated for each of the analytes detected. The relative percent difference (RPD) between the duplicate spikes (or samples) is calculated and used to assess analytical precision.

3.4. Method Blank (MB) – The method blank is an artificial sample composed of analyte-free water or solid matrix and is designed to monitor the introduction of artifacts into the analytical process. The method blank is carried through the entire analytical procedure. Because water samples do not require digestion prior to analysis, method blank samples are equivalent to instrument blanks or calibration blanks.

3.5. Ongoing Precision Recovery (OPR) – A method blank spiked with known quantities of analytes, carried throughout the digestion procedure. This is also known as a laboratory Control Sample (LCS).

3.6. Continuing Calibration Verification (CCV) – is spiked reagent water (aqueous blank spike) and is used to determine that the instrument remains in control. This is also known as a calibration verification (CALVER).

3.7. Continuing Calibration Blank (CCB) – The continuing calibration blank is a volume of arsenic-free water (typically 50mL) analyzed in the same manner as samples. The purpose of the instrument blank is to determine the levels of contamination associated with the instrumental analysis itself, particularly with regard to the carry-over of analytes from standards or highly contaminated samples into subsequent sample analyses. This is also known as a calibration blank (CALBLK).

3.8. Initial precision and recovery (IPR) – Four aliquots of the ongoing precision and recovery standard analyzed to establish the ability to generate acceptable precision and recovery. IPR test are performed before a method is used for the first time and any time the methods or instrumentation is modified.

3.9. Field duplicates – two separate samples collected in separate sample bottles at the same time. Analysis of duplicates give a measure of the precision associated with sample collection and laboratory procedures.

3.10. Dissolved Inorganic Arsenic – All Potassium Borohydride (KBH_4) reducible As^{+3} and As^{+5} found in aqueous solution filtrate after passing the sample through a 0.45 um filter.

3.11. Total Inorganic Arsenic – All KBH_4 reducible As^{+3} and As^{+5} found in a sample. Total inorganic arsenic and total recoverable inorganic arsenic are synonymous.

4. INTERFERENCES

4.1. Little interference from environmental matrices (i.e. salts, chlorides, nitrates, and organics) has been noted. However high levels of transition metals or noble metals will dramatically inhibit the formation of arsenic hydrides, most likely by consumption of the borohydride, or by co-precipitation of reduced arsenic with other reduced metals. This is particularly a problem with respect to high dissolved Fe and Mn in reducing ground water and mine adduct samples.

4.2. If water is allowed to condense in the trap, multiple and irregular peaks occur in the region where Me_2AsH elutes. This may be overcome by heating the transfer line between the chromatographic column and the furnace. It was also observed that free chlorine (as contained in bad batches of HCl) completely suppresses the signal for all hydrides during cryotrapping. Thus, HCl with obvious green/yellow color must be avoided, and, if in doubt, it can be tested for free chlorine with iodide solution (formation of red/brown iodine). Hydrochloric acid can be purged in the hood of its free chlorine with N_2 (500 mL min^{-1} for 1 hour).

5. SAFETY

5.1. Follow all ALS safety practices as described in the ALS Safety Manual.

5.2. Each chemical compound or reagent should be treated as a potential health hazard. Exposure to these chemicals should be reduced to the lowest possible level. A reference file of material safety data sheets is available to all personnel involved in these analyses.

5.3. Hydrochloric Acid is used in this method. Hydrochloric acid is extremely corrosive and care must be taken while handling it. A face shield should be used while pouring acids. Safety glasses, lab coat and gloves should always be worn while working with these solutions.

5.4. Potassium Borohydride (KBH_4) is used in this method. KBH_4 is a flammable solid, water reactive substance and is harmful if inhaled, ingested, or absorbed. Safety glasses, lab coat and gloves should always be worn while working with this solution.

5.5. Arsenic standards are used in this method. Arsenic is harmful if inhaled, ingested, or absorbed. ALS purchases dilute standard solutions for this method. If primary solutions are prepared, they must be prepared in a hood. Safety glasses, lab coat and gloves should always be worn while working with arsenic standards.

6. SAMPLE COLLECTION, CONTAINERS, PRESERVATION, AND STORAGE

6.1. Aqueous samples must be collected in polyethylene or glass bottles washed with 4 N HCl using accepted clean techniques. Do not use HNO_3 cleaned bottles, as their surfaces are oxidizing with respect to As(III). Caution must be taken with glass as glass containers have been found to contaminate for arsenic.

6.2. Sample preservation must be performed in the field to reduce changes in Arsenic speciation that may occur during transport and storage. It is very difficult to preserve the original As(III)/As(V) ratio. River water tends to spontaneously reduce As(V) to As(III) and freezing of water tends to induce oxidation of As(III) to As(V), except in the case of very rapid freezing (in liquid nitrogen). Water samples are acidified to pH <2 with hydrochloric acid (3 mL 6M HCL/L) and stored at 0-4°C from the time of collection until analysis. If As species are not target analytes, the samples may be preserved upon receipt by the laboratory. Store the preserved sample for a minimum of 48 hours to allow the As adsorbed on the container walls to completely dissolve in the acidified sample. Holding time is 28 days from the time of collection until the time of analysis.

The best storage scheme is to quick freeze samples to -196°C in liquid nitrogen and store at -80°C (on dry ice) until analysis.

6.3. Current evidence suggests that HCl acidification is suitable for preserving arsenic speciation and it is valuable in preventing the precipitation of Fe(OH)3 which can both oxidize and co-precipitate As.

6.4. Tissue and solid samples are collected in plastic 4 oz jars and stored at <-18°C or freeze dried and stored at room temperature for up to a year prior to digestion and analysis.

7. REAGENTS AND STANDARDS

7.1. Reagent grade chemicals shall be used in all tests. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without increasing the MDL, or lowering the accuracy of the determination.

7.2. Reagent Water: 18 meg-Ω ultra pure deionized water starting from a pre-purified (distilled, R.O., etc.) source.

7.3. Arsenite (As(III)) Stock Solution: A 1,000 ppm stock solution is prepared by dissolving 0.173 g sodium meta-arsenite (>98.7%) in 100 mL of 0.1% ascorbic acid solution. This solution is kept refrigerated at 0°- 4° C in an amber bottle. This solution is stable and is good for 12 months. Arsenite 1,000 ppm stock solutions can also be purchased from Elements Inc., Shasta Lake, CA and Inorganic Ventures, Inc., Lakewood, NJ.

7.4. Arsenate (As(V)) Stock Solution: A 1,000 ppm stock solution is prepared by dissolving 0.416 g sodium arsenate (98.0%) in 100 ml reagent water. This solution is stable and is good for five years. Arsenate 1,000 ppm stock solutions can also be purchased from Elements Inc., Shasta Lake, CA and Inorganic Ventures, Inc., Lakewood, NJ

7.5. Monomethylarsonate (MMA) Stock Solution: A 1,000 ppm working standard is prepared by diluting 0.1866 g monomethylarsonic acid in 100 ml reagent water. This solution is good for five years. Monomethylarsonate stock solutions can also be purchased from High Purity Standards, Charleston, SC.

7.6. Dimethylarsinate (DMA) Stock Solution: A 1,000 ppm stock solution is prepared by dissolving 0.1842 g dimethylarsinic acid (98%) in 100 mL of water. This solution is good for five years. Dimethylarsinate stock solutions can also be purchased from High Purity Standards, Charleston, SC.

7.7. Working Standard A: An intermediate solution containing 10 mg/L of As(III), MMA, and DMA is made from measured aliquots of the above stock solutions (7.3, 7.5, 7.6) and diluted to measured volume with reagent water. A working standard containing 100 ug/L of As(III), MMA, and DMA is prepared from the intermediate solution.

7.8. Working Standard B: An intermediate solution containing 10 mg/L of TIA (5 mg/L As(III) and 5 mg/L As(V)), MMA, and DMA is made from a measured aliquot of the above stock solutions (7.3, 7.4, 7.5, 7.6) and diluted to measured volume with reagent water. A working standard containing 100 ug/L of TIA, MMA, and DMA is prepared from the intermediate solution.

7.9. Quality Control Sample (QCS) -The QCS must be prepared from a source different from that used to produce the calibration standards.

7.10. TRIS Buffer: To prepare pH 6.2 buffer solution, 394 g tris(hydroxymethyl)-aminomethane hydrochloride and 2.5 g reagent grade sodium hydroxide are dissolved in water to make 1000 mL of solution. This solution is good for five years.

7.11. Borohydride Solution: A 10% solution is prepared by dissolving 10 g KBH_4 into reagent water and diluting up to 100 ml with reagent water. This solution is stable for up to 3 days when kept covered and stored in the refrigerator overnight. For low level TIA determinations, KBH_4 is preferable over $NaBH_4$ since it was found to contain lower As blanks, dissolves much faster in water, forms a clear solution and liberates much less hydrogen.

7.12. 6 M Hydrochloric Acid: Equal volumes of reagent grade HCl and water are mixed to give a 6 M solution. This solution must be checked before use and should not have any measurable Arsenic.

7.13. 2M Hydrochloric Acid: Reagent grade HCl and water are combined in a 1:6 ratio to give a solution approximately 2M in HCl.

7.14. 0.1% EDTA: To prepare 1.0 liter of 0.1% EDTA, 0.416g of EDTA are dissolved in water and diluted up to measured volume.

7.15. 0.1M Phosphoric Acid: To prepare 1.0 liter of 0.1M phosphoric acid solution, 6.8ml of 85% H_3PO_4 are dissolved in water and diluted up to measured volume.

7.16. 0.1M Trifluoroacetic Acid: To prepare 1.0 liter of 0.1M trifluoroacetic acid solution, 11.4 grams of 99.5%+ CF_3COOH are dissolved in water and diluted up to measured volume.

7.17. 5M Potassium Hydroxide: To prepare 1.0 liter of 5M KOH, 316.9g of 88.5% KOH are dissolved in water and diluted up to measured volume.

7.18. Air: Breathing quality non-flammable gas.

7.19. Helium: High purity non-flammable gas.

7.20. Hydrogen: Ultra-high purity flammable gas.

Calibration Blank
Working Std A : *
Working Std A : 10 ng
Working Std A : 20 ng
Working Std A : 30 ng
Calibration Blank
Working Std B : CCV 10 ng
Calibration Blank
Ongoing Precision Recovery (OPR)
Method Blank 1
Method Blank 2
Method Blank 3
Up to 6 samples including QC (MS/MSD)
Working Std B : CCV 10 ng
Calibration Blank
Up to 10 samples including QC (MS/MSD)
Working Std B : CCV 10 ng
Calibration Blank

*Low point concentrations:

- As(III), tissue: 0.4ng or lower
- As(III), soil: 0.4ng or lower
- TIAs, soil: 0.5ng or lower
- TIAs, tissue: 2.0ng or lower
- MMA, tissue: 2.0ng or lower
- DMA, tissue: 4.0ng or lower
- MMA/DMA, soil: not performed

12. QUALITY CONTROL

12.1. Initial Precision and Recovery Validation

12.1.1. The accuracy and precision of the procedure must be validated before analysis of samples begins, or whenever significant changes to the procedures have been made. To do this, four water samples are spiked with the QCS solution, then prepared and analyzed.

12.2. Method Detection Limits and Method Reporting Limits

12.2.1. A method detection limit (MDL) study must be undertaken before analysis of samples can begin. To establish detection limits that are precise and accurate, the analyst must perform the following procedure. Spike seven blank matrix (water or soil) samples with MDL spiking solution at a level below the MRL. Follow the analysis procedures in Section 11 to analyze the samples.

12.2.2. Calculate the average concentration found (x) in µg/L, and the standard deviation of the concentrations (s) in µg/L for each analyte. Calculate the MDL for each analyte. Refer to CE-QA011, *Performing Method Detection Limit Studies and Establishing Limits of Detection and Quantification.* The MDL study must be verified annually.

12.2.3. Limits of Quantification (LOQ)

12.2.3.1. The laboratory establishes a LOQ for each analyte as the lowest reliable laboratory reporting concentration or in most cases the lowest point in the calibration curve which is less than or equal to the desired regulatory action levels, based on the stated project requirements. Analysis of a standard or extract prepared at the lowest point calibration standard provides confirmation of the established sensitivity of the method. The LOQ recoveries must be within 50% of the true values to verify the data reporting limit. Refer to CE-QA011, *Performing Method Detection Limit Studies and Establishing Limits of Detection and Quantification.*

12.2.4. The Method Reporting Limits (MRLs) used at ALS are the routinely reported lower limits of quantitation which take into account day-to-day fluctuations in instrument sensitivity as well as other factors. These MRLs are the levels to which ALS routinely reports results in order to minimize false positive or false negative results. The MRL is normally two to ten times the method detection limit.

12.3. Ongoing QC Samples required are described in the ALS-Kelso Quality Assurance Manual, in the SOP for Sample Batches, and in Method 1632. An analytical sequence must contain a calibration verification and a calibration blank every 10 samples. One MS/MSD pair must be analyzed for every 10 samples.

12.3.1. Method Blank

12.3.1.1. At least three method blanks are analyzed with every analytical sequence. If the method blank shows any hits above the reporting limit, corrective action must be taken. Corrective action includes recalculation, reanalysis, system cleaning, or re-extraction and reanalysis. For some project specific needs, exceptions may be noted and method blank results above the MRL may be reported.

12.3.1.2. Method Blanks for water samples are identical to calibration blanks.

12.3.2. Calibration blank – Analyze at least three calibration blanks per analytical sequence. One is required after calibration as well as after every CCV analysis. CCBs are equivalent to method blanks for water analysis only. For soils and other leachates 3 method blanks are required in addition to the CCBs. If the calibration blank exceeds the MRL, discontinue analysis, correct the problem, and recalibrate the instrument.

12.3.3. Calibration Verification – The calibration verification is verified daily and every 10 samples and at the end of the analytical run. Recovery of the CCV standard must be within the limits listed in Table 2

12.3.4. Ongoing and Precision Recovery (OPR) or Lab Control Sample (LCS)

12.3.4.1. CCV analysis is equivalent to the analysis of an aqueous OPR.

12.3.4.2. The OPR is composed of analyte-free water into which is spiked a number of appropriate target analytes. The OPR is designed to monitor the accuracy of the procedure. The concentration of the spike in the OPR matrix should be at 5 to 10 times the MRL or at levels specified by a project analysis plan.

12.3.4.3.An OPR must be prepared and analyzed with every batch of 20 (or fewer) samples. Calculate the OPR recovery as follows:

%R = X/TV x 100

Where X = Concentration of the analyte recovered
TV = True value of amount spiked

12.3.4.4.The acceptance criteria are given in Table 2. If the OPR fails acceptance criteria, corrective action must be taken. Corrective action includes recalculation or reanalysis.

12.3.5. Quality Control Sample (QCS)

12.3.5.1.The QCS is designed to verify the validity of the calibration. The QCS is analyzed on a quarterly basis, and whenever the calibration standards are re-prepared.

12.3.5.2.The QCS is prepared from a source different from that used to produce the calibration standards. The lab may use Certified Reference Materials (CRMs) or prepare a spike solution obtained from a second source to make the QCS.

12.3.5.3.The determined mean concentration from three analyses of the QCS must be within ± 10% of its stated value.

12.3.6. Matrix Spike

12.3.6.1.A matrix spike (MS) and duplicate matrix spike (DMS) must be prepared and analyzed with every batch of 10 (or fewer) samples. The MS/DMS is prepared by adding a known volume of the matrix spike solution to the sample and determining the spiked sample concentration. The spike must contain analytes at one to five times the background levels in the parent sample. Calculate percent recovery (%R) as:

$$\%R = \frac{X - X1}{TV} \times 100$$

Where X = Concentration of the analyte recovered
X1 = Concentration of unspiked analyte
TV = True value of amount spiked

12.3.6.2.Calculate Relative Percent Difference (RPD) as:

$$\%RPD = \frac{|R1 - R2|}{(R1 + R2)/2} \times 100$$

Where R1= Higher Result
R2= Lower Result

12.3.6.3. Following analysis of the MS the percent recovery is calculated and compared to acceptance limits in Table 2. If the recovery is within control limits the results may be reported. If not, and the QCS is within control limits, this indicates that the matrix potentially biases analyte recovery. Verify that the spike level is at least five times the background level. If not, the results are reported with a qualifier that the background level is too high for accurate recovery determination.

13. CALCULATIONS, DATA REDUCTION, AND REPORTING

13.1. Calculate the concentration of each arsenic species in each sample directly from the mean calibration factor.

Aqueous Samples:

$$Concentration\ (\mu g/L) = \frac{(As - Ab)}{(RFx)(V)}$$

Where A_s = peak area for arsenic species in sample
A_b = peak area for arsenic species in blank
RF_x = Response Factor Mean
V = Volume of sample

13.2. The concentration of As(V) is calculated by subtracting the value for As(III) from that of total inorganic As.

13.3. Nonaqueous Samples:

$$Concentration\ (mg/Kg) = \frac{(As - Ab)(D)}{(RFx)(W)}$$

Where A_s = peak area for arsenic species in sample
A_b = peak area for arsenic species in blank
RF_x = Response Factor Mean
D = Dilution Factor
W = Weight of sample extracted in grams. The wet or dry weight may be used, depending upon the specific client requirements.

13.4. Sample concentrations are reported when all QC criteria for the analysis has been met. Reported results not meeting QC criteria must be qualified with a standard ALS footnote.

13.5. Reporting

13.5.1. Refer to ADM-RG, *Data Reporting and Report Generation* for reporting guidelines.

13.5.2. Report results for each As species in ug/L or ug/g to three significant figures.

13.5.3. All sample results are reported blank corrected.

13.5.4. Reports are generated in the CAS LIMS by compiling the SMO login, sample prep database, instrument date, and client-specified report requirements (when specified). This compilation is then transferred to a file which Excel© uses to generate a report. The forms generated may be ALS standard reports, DOD, or client-specific reports. The compiled data from LIMS is also used to create EDDs.

13.5.5. As an alternative, reports are generated using Excel© templates located in R:\ICP\FORMS\Arsenic-1632. The analyst should choose the appropriate form and QC pages to correspond to required tier level and deliverables requirements. The results are then transferred, by hand or electronically, to the templates.

13.6. Data Review and Assessment

13.6.1. Following primary data interpretation and calculations, all data is reviewed by a secondary analyst. Following generation of the report, the report is also reviewed. Refer to ADM-DREV, *Laboratory Data Review Process* for details. The person responsible for final review of the data report and/or data package should assess the overall validity and quality of the results and provide any appropriate comments and information to the Project Chemist to inclusion in the report narrative.

14. CORRECTIVE ACTION

14.1. Refer to CE-QA008, *Nonconformance and Corrective Action* for procedures for corrective action. Personnel at all levels and positions in the laboratory are to be alert to identifying problems and nonconformities when errors, deficiencies, or out-of-control situations are detected.

14.2. Handling out-of-control or unacceptable data

14.2.1. On-the-spot corrective actions that are routinely made by analysts and result in acceptable analyses should be documented as normal operating procedures, and no specific documentation need be made other than notations in laboratory maintenance logbooks, runlogs, for example.

14.2.2. Documentation of a nonconformity must be done using a Nonconformity and Corrective Action Report (NCAR) when:

- Quality control results outside acceptance limits for accuracy and precision
- Method blanks or continuing calibration blanks (CCBs) with target analytes above acceptable levels
- Sample holding time missed due to laboratory error or operations
- Deviations from SOPs or project requirements
- Laboratory analysis errors impacting sample or QC results
- Miscellaneous laboratory errors (spilled sample, incorrect spiking, etc)
- Sample preservation or handling discrepancies due to laboratory or operations error

15. METHOD PERFORMANCE

15.1. Available method performance data is given in the reference method. In addition, this procedure was validated through single laboratory studies of accuracy and precision as specified in Section 12.1. The method detection limit(s) and method reporting limit(s) were established for this method as specified in Section 12.2.

16. POLLUTION PREVENTION AND WASTE MANAGEMENT

16.1. It is the laboratory's practice to minimize the amount of solvents, acids, and reagents used to perform this method wherever feasibly possible. Standards are prepared in volumes consistent with methodology and only the amount needed for routine laboratory use is kept on site. The threat to the environment from solvents and/or reagents used in this method can be minimized when recycled or disposed of properly.

16.2. The laboratory will comply with all Federal, State, and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions as specified in the ALS Environmental Health and Safety Manual.

17. TRAINING

17.1. Training outline

17.1.1. Review literature (see references section). Read and understand the SOP. Also review the applicable MSDS for all reagents and standards used. Following these reviews, observe the procedure as performed by an experienced analyst at least three times.

17.1.2. The next training step is to assist in the procedure under the guidance of an experienced analyst. During this period, the analyst is expected to transition from a role of assisting, to performing the procedure with minimal oversight from an experienced analyst.

17.1.3. Perform initial precision and recovery (IPR) study as described above for water samples. Summaries of the IPR are reviewed and signed by the supervisor. Copies may be forwarded to the employee's training file. For applicable tests, IPR studies should be performed in order to be equivalent to NELAC's Initial Demonstration of Capability.

17.2. Training is documented following ADM-TRAIN, ALS-Kelso Training Procedure.

17.2.1. NOTE: When the analyst training is documented by the supervisor on internal training documentation forms, the supervisor is acknowledging that the analyst has read and understands this SOP and that adequate training has been given to the analyst to competently perform the analysis independently.

18. METHOD MODIFICATIONS

18.1. This procedure uses Potassium Borohydride (KBH_4) instead of Sodium Borohydride ($NaBH_4$) as stated in the method. See Section 7.11.

18.2. The calibration blank is evaluated to the laboratory MRL. See Section 12.3.2.

18.3. In Section 11.2.1.1, the sample is purged for 3 minutes instead of 7 as stated in the method.

19. REFERENCES

19.1. *Chemical speciation of Arsenic in Water and Tissue by Hydride Generation Quartz Furnace Atomic Absorption Spectrometry,* Method 1632, Revision A, January 2001, U. S. Environmental Protection Agency Office of Water Engineering and Analysis Division.

19.2. Crecelius, E.A., Bloom, N.S., Cowan, C.E., and Jenne, E.A., *Speciation of Arsenic in Natural Waters and Sediments, Volume 2: Arsenic Speciation.* Final Report, prepared for Electric Power Research Institute, Palo Alto, CA by Battelle, Pacific Northwest Laboratories, Richland, WA, 1986.

20. CHANGES SINCE THE LAST REVISION

20.1. Sec. 11.1.2.3: Sample prep for MMAs and DMAs in tissue was changed to more closely follow EPA 1632. Tissue samples are prepped in the same manner as TIAs. The section has been revised to refer to section 11.1.2.1.

20.2. Section 12.3.2: Added calibration blank evaluation criterion.

20.3. Section 18: Added deviations from the reference method.

Table 1

TARGET COMPOUNDS, MRLs, and MDLs

Analyte	Method Detection Limit			Method Reporting Limit		
	Water ug/L	Tissue mg/Kg	Soil mg/Kg	Water ug/L	Tissue mg/Kg	Soil mg/Kg
IA	0.003	0.007	0.08	0.02	0.02	0.2
As^{+3}	0.003	0.02	0.04	0.02	0.04	0.1
MMA	0.002	0.008	Tbd	0.02	0.02	Tbd
DMA	0.006	0.02	Tbd	0.05	0.04	Tbd

Table 2

QC ACCEPTANCE CRITERIA

Aqueous Samples

IPR			QCS/ICV	CCV/OPR	MS/MSD	
Analyte	RPD %	% Rec			% R	%RPD
IA	<25	60-140	90-110%	80-120%	50-150	<35
As^{+3}	<25	40-160	90-110%	70-130%	30-170	<35
MMA	<20	70-130	90-110%	80-120%	60-140	<25
DMA	<30	50-150	90-110%	70-130%	40-160	<40

Tissue and Soil Samples

IPR			OPR	QCS/ICV	CCV/OPR	MS/MSD	
Analyte	RPD %	% Rec				% R	%RPD
IA	<25	60-140	50-150	90-110%	80-120%	50-150	<35
As^{+3}	<25	40-160	30-170	90-110%	70-130%	30-170	<35
MMA	<20	70-130	60-140	90-110%	80-120%	60-140	<25
DMA	<30	50-150	40-160	90-110%	70-130%	40-160	<40