Low Level Mercury Determination by Purge and Trap Cold Vapor Atomic Fluorescence Technique (CVAF) Using CETAC M-8000


1. Scope and Application

Matrices: The method is applicable to total and dissolved mercury in aqueous samples, tissue, sludge, sediment and soil.

Definitions: Refer to Alpha Analytical Quality Manual.

Three procedures for the analysis of mercury by cold vapor atomic fluorescence spectrometry are discussed in this SOP.

Method 1631 for aqueous samples

This procedure utilizes a bromine chloride digestion. Samples are then decolorized using hydroxylamine hydrochloride (optional) and analyzed following reduction with stannous chloride. Elemental mercury is then purged from solution and collected on a gold trap. The trap is heated to desorb mercury and analyzed by atomic fluorescence spectrometry. The reporting limit is 0.5 ng/L and the linear range of the analysis is 100 ng/L which may be extended with dilution.

Method 1631 for tissue (digestion II as outlined in Appendix to 1631)

This procedure is preferred for matrices containing organic materials, such as sludge and plant and animal tissues. An aliquot of sample is digested with HNO₃/H₂SO₄. The digestate is diluted with BrCl solution to destroy any remaining organic material. The reporting limit is 0.001 mg/Kg assuming 0.5g sample and 100% solids.

Method 1631 for sediment and soil (digestion I as outlined in Appendix to 1631)

This procedure is preferred for geological materials and is capable of rapid and complete dissolution of inorganic mercury. A sample aliquot is digested with HCl/HNO₃ followed by addition of BrCl to destroy any organic material. The reporting limit is 0.001 mg/Kg assuming 0.5g sample and 100% solids.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>CAS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mercury (Hg)</td>
<td>7439-97-6</td>
</tr>
</tbody>
</table>
2. Summary of Method

Mercury is determined by cold vapor atomic fluorescence spectrometry following digestion with an acidic bromine chloride solution. Bromine chloride is prepared by mixing potassium bromide with potassium bromate solutions with hydrochloric acid producing a yellow solution. Bromine chloride is known to oxidize inorganic and organomercury compounds.

If a yellow color does not persist after addition of bromine chloride then additional solution must be added until a yellow color persists. The same volume of bromine chloride solution is added to all samples, the method blank, LCS and standards. After digestion is complete, 12% hydroxylamine hydrochloride solution may be added (not required) to the sample, the sample shaken and allowed to stand for 5 minutes. As samples are diluted 1:10 at the instrument, there is adequate stannous chloride to reduce both the BrCl and mercury to Hg\(^0\).

Samples and standards are placed in the autosampler rack and analyzed by cold vapor atomic fluorescence spectrometry at a wavelength of 253.7 nm.

The data report packages present the documentation of any method modification related to the samples tested. Depending upon the nature of the modification and the extent of intended use, the laboratory may be required to demonstrate that the modifications will produce equivalent results for the matrix. Approval of all method modifications is by one or more of the following laboratory personnel before performing the modification: Area Supervisor, Department Supervisor, Laboratory Director, or Quality Assurance Officer.

This method is restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results with this method by performing an initial demonstration of capability, analyzing a proficiency test sample and completing the record of training.

After initial demonstration, ongoing demonstration is based on acceptable laboratory performance of at least a quarterly laboratory control sample or acceptable performance from an annual proficiency test sample. A major modification to this procedure requires demonstration of performance. The identification of major method modification requiring performance demonstration is directed by the Quality Assurance Officer and/or Laboratory Director on a case-by-case basis.

2.1 Method Modifications from Reference

New perfluoropolymer lined 250 mL bottles are used for aqueous sample collection for Method 1631E. These bottles are rinsed two times with Type I water, filled with DI water and 1 mL 0.2N BrCl and leached overnight. The bottles are rinsed two more times and placed in a new plastic bag for use. This cleaning procedure has been determined to be adequate through analysis of bottles blanks prepared for at least each lot of bottles.

3. Reporting Limits

The mercury aqueous is 0.0005 µg/L Method 1631.

The soil/sediment/tissue RL is 0.001 mg/Kg.

4. Interferences

4.1 Gold, silver and iodide are known interferences. Samples with iodide concentrations greater than 3 mg/L are pre-reduced with stannous chloride to clarify the brown color. It may be
necessary to clean the analytical system with 4N HCl following analysis of a sample with
iodide concentrations greater than 30 mg/L.

4.2 Sulfide concentrations up to 24 mg/L produce no interference problems.

4.3 High concentrations of gold and silver in a sample may suppress mercury reduction.

5. Health and Safety

The toxicity or carcinogenicity of each reagent and standard used in this method is not fully
established; however, each chemical compound should be treated as a potential health hazard.
From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by
whatever means available. A reference file of material safety data sheets is available to all
personnel involved in the chemical analysis. Additional references to laboratory safety are available
in the Chemical Hygiene Plan.

All personnel handling environmental samples known to contain or to have been in contact with
municipal waste must follow safety practices for handling known disease causative agents.

The use of laboratory equipment and chemicals exposes the analyst to several potential hazards.
Good laboratory techniques and safety practices shall be followed at all times. Eating, drinking,
smoking, or the application of cosmetics is not permitted in the laboratory area. Horseplay of any
kind is prohibited. Pipetting by mouth is not permitted. All Personal Protective Equipment (PPE)
must be removed before leaving the laboratory area and before entering the employee lounge or
eating area. Always wash your hands before leaving the laboratory. All relevant Material Safety
Data Sheets (MSDSs) are kept alphabetically in the centrally located file storage, in the common
area outside of the Information Technology (IT) offices.

Approved PPE, which includes Safety Glasses, Gloves and Lab Coats, must be worn at all
times when handling samples, reagents, chemicals, or when in the vicinity of others handling these items,
so that dermal contact is avoided. All standards, reagents and solvents shall be handled under a
hood using the proper PPE. All flammable solvents must be kept in the flammable storage cabinet,
and returned to the cabinet immediately after use. When transporting chemicals, use a secure
transporting devise and/or secondary outer container. Chemical storage is properly segregated and
adequately ventilated to reduce the possibility of hazardous reactions. Chemical storage in work
areas shall be kept to a minimum. Storage on bench tops or other work surfaces, except temporary,
is not permitted.

Spilled samples, solvents, reagents, and water must be cleaned up from bench tops, instruments
and autosampler surfaces immediately. A spill is considered a quantity of hazardous material if it is
two times greater than the normal working volume. Concentrated solvents, acids or bases present a
moderate to extreme hazard to the skin and mucous membranes. If contact with the skin occurs,
immediately flush with large volumes of water. In the case of acidic/basic spills, the Spill Kit
located in each laboratory shall be utilized before attempting to cleanup the spill. Although procedures are
designed to minimize the possibility of an accident, all injuries or accidents, regardless of the nature
or severity, are to be reported to the Department Manager Supervisor immediately. If an employee
discovers a potentially unsafe condition, this must be reported to the Department Manager
Supervisor immediately. No employee should feel compelled to work in a situation where they do
not feel entirely informed, trained, or safe.

Analytical instrumentation poses the unique possibility of exposure to high voltages. Other than the
routine instrument maintenance, as listed in the front of every Instrument Maintenance Logbook, at
no time shall an instrument operator attempt to maintenance an instrument alone, or without the
proper training, supervision or instruction. Caution must always be used in the presence of moving parts (autosamplers) and hot surfaces (injection ports).

Compressed gas cylinders shall only be moved with the dolly supplied for this specific purpose. The cap must be on the cylinder while it is being moved. The tank must be secured when in its final position. All spent tanks are to be returned in the same manner, and secured until removed by the vendor. Liquid argon or nitrogen represents a potential cryogenic hazard and safe-handling procedures must be used at all times.

6. Sample Collection, Preservation, Shipping and Handling

6.1 Sample Collection

Aqueous samples collected for Methods 1631 are collected in pre-cleaned fluoropolymer bottles with tightly fitting fluoropolymer caps. Atmospheric mercury is known to diffuse through polyethylene bottles at levels below 0.05 µg/L.

Fluoropolymer bottles supplied by the laboratory for sample collection by Methods 1631 must be tested prior to sampling. 5% of a new lot of bottles are tested by adding DI water and 0.25 mL of BrCl and letting stand overnight. Mercury concentrations in the bottles must be less than 0.5 ng/L.

Sediments and tissues are collected in amber glass jars.

6.2 Sample Preservation

Samples collected for Methods 1631 may be preserved with 5 mL/L of 12 N HCl or 5 mL/L of BrCl solution (Section 8.8) if only total Hg is being analyzed. Sample preservation at the laboratory is recorded in the Sample Preservation/Filtration Log Book in the Metals Laboratory.

Samples collected and preserved under these conditions are stable for 90 days for Method 1631E.

6.3 Sample Shipping

No special sample shipping requirements. Typical shipping procedures may be found in the Alpha Sample Receipt & Login SOP (08-01).

6.4 Sample Handling

Samples may be stored at room temperature in the laboratory. It is suggested that the sample containers for samples being analyzed by Methods 1631 be stored in new polyethylene bags until analysis to prevent possible contamination.

7. Equipment and Supplies

7.1 Instrument: CETAC M-8000 equipped with a PC loaded with instrumental software. The instrument is connected to a source of high-purity, mercury free argon regulated to 15 PSI.

7.2 Santoprene Peristaltic Pump Tubing: Various tubing sizes for reagent pump and autosampler rinse pump.

7.3 Glassware for Digestion: Pre-cleaned 50mL disposable polyethylene screw cap digestion tubes.

7.4 Other: Adjustable Eppendorf pipettes and replacement tips.
8. Reagents and Standards

ACS Trace Metal 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 lessening the accuracy of the determination. If the purity of a reagent is in question, analyze for contamination. If the concentration is less than the MDL then the reagent is acceptable.

Solutions below expire yearly unless noted and are stored at room temperature.

8.1 Deionized (DI) water: The Barnstead NANO-pure system provides Type I water used in the preparation of samples and standards.

8.2 Hydrochloric acid, concentrated (HCl): ACS reagent grade, Fisher #A508-212, or equivalent. Lots should be checked for purity prior to use and the results stored in a reagent check log book.

8.3 Nitric acid, concentrated (HNO₃): ACS reagent grade, Fisher #A509-212, or equivalent. Lots should be checked for purity prior to use and the results stored in a reagent check log book.

  8.3.1 2% HCl/2%HNO₃: Add 20mL concentrated HCl and 20mL concentrated HNO₃ to approximately 500mL DI and bring to 1L with DI. Larger volumes are prepared in a similar manner.

  8.3.2 10% HNO₃: Add 100 concentrated HNO₃ to approximately 500mL DI and bring to 1L with DI. Larger volumes are prepared in a similar manner.

8.4 Hydroxylamine hydrochloride (NH₂OH·HCl): ACS reagent grade, VWR #HX0770-1, or equivalent. Reagent expires 4 years from date received.

  8.4.1 12% Hydroxylamine Hydrochloride solution: Add 12g Hydroxylamine hydrochloride (NH₂OH·HCl) per 100 mL of DI. Prepare in 125 mL fluorocarbon lined bottle. Prepare every 6 months or as needed.

8.5 Stannous Chloride (SnCl₂·H₂O): ACS reagent grade, Fisher #T142-500, or equivalent. Reagent expires 4 years from date received.

  8.5.1 10% Stannous Chloride/7% HCl Solution: Add 100g SnCl₂ and 70 mL concentrated HCl to 500mL DI, dilute to 1 L with DI. Solution is stable for 3 days. Solution is purged with argon at 2L/minute for 30 minutes to remove Hg impurities if necessary.

8.6 Potassium Bromate (KBrO₃): ACS grade, Fisher #P207-250. Bake in muffle furnace at 250°C for 8 hours to remove mercury impurities if necessary. Reagent expires 4 years from date received.

8.7 Potassium Bromide (KBr): ACS grade, Fisher #P205-500. Bake in muffle furnace at 250°C for 8 hours to remove mercury impurities if necessary. Reagent expires 5 years from date received.

8.8 Bromine Chloride (0.2N BrCl) Solution: Prepare in BOD bottle or fluoropolymer bottle under fume hood by adding 2.7g KBr and 3.8g KBrO₃ to 250mL concentrated HCl and
mix. Solution will turn yellow. **Free Halogens are generated from this solution. Seal bottle when taking out of fume hood.** Prepare every 6 months or as needed.

8.9 **0.07N Bromine Chloride (BrCl) Solution:** Prepare in BOD bottle or fluoropolymer bottle under fume hood by diluting 300 mL of 0.2N BrCl to 1000mL DI. **Seal bottle when taking out of fume hood.** Prepare every 6 months or as needed.

8.10 **0.02N Bromine Chloride (BrCl) Solution:** Prepare in BOD bottle or PEF bottle under fume hood by diluting 100 mL of 0.2N BrCl to 1000mL DI. **Seal bottle when taking out of fume hood.** Prepare every 6 months or as needed.

8.11 **HNO₃/H₂SO₄ Solution:** In a hood, slowly add 300 mL of concentrated H₂SO₄ to 700 mL of concentrated HNO₃ in a fluoropolymer bottle. Prepare every 6 months or as needed.

8.12 **Stock and Working Standards:** Store standards at room temperature out of direct light. All stock and working calibration standards expiration dates are based on manufacturer expiration date or one year from date received.

8.12.1 **1000 mg/L Stock Calibration Mercury Standard:** Ultra Scientific #ICP-080, or equivalent.

8.12.1.1 **1000µg/L Working Standard:** Prepare by adding 0.1 mL of 1000 mg/L stock to a 100 mL volumetric flask containing 2% HCl. Bring to volume with DI water and pour into brown bottle. This standard is identified as **C-date-V** in the Mercury Standards Preparation Log.

8.12.1.2 **100 µg/L Intermediate Standard:** Prepare by adding 1 mL of the 1000 µg/L working standard to 15 mL graduated centrifuge tube containing 2% HCl. Bring to 10 ml final volume with DI water. This intermediate standard is used for calibration standards preparation and then discarded.

8.12.1.3 **5 µg/L Working Standard:** Prepare by adding 0.25 mL of 1000 µg/L working standard to a 50 mL graduated screw cap centrifuge tube containing 2% HCl. Bring to 50 mL final volume with DI water. This standard is identified as **C-date-VS** in the Mercury Standards Preparation Log.

8.12.2 **1000 mg/L Stock ICV Mercury Standard:** Inorganic Ventures #CGHG-1, or equivalent.

8.12.2.1 **1000 µg/L ICV Working Standard:** Prepare by adding 0.1 mL of 1000 mg/L ICV stock to a 100 mL volumetric flask containing 2% HCl. Bring to volume with DI water and pour into brown bottle. This standard is identified as **I-date-V** in the Mercury Standards Preparation Log.

8.12.2.2 **5 µg/L ICV Working Standard:** Prepare by adding 0.25 mL of 1000 µg/L working standard to a 50 mL graduated screw cap centrifuge tube containing 2% HCl. Bring to 50 mL final volume with DI water. This standard is identified as **I-date-VS** in the Mercury Standards Preparation Log.

8.13 **Calibration and Calibration Check Standards:** Store standards at room temperature out of direct light.

Calibration and calibration check standards are prepared in 50 ml polypropylene (or equivalent) screw cap digestion tubes containing about 50 mL of DI water and 0.5 mL of BrCl(Section 8.8) solution. The STD0 consists of 50mL DI and 0.5mL BrCl solution.

After addition of the working standard, calibration standards are brought to 50mL final volume.
with DI water and optionally decolorized with 0.1 mL of hydroxylamine hydrochloride solution (Section 8.4.1). If sample preparation required additional quantities of BrCl to maintain a yellow color, then the same amount of BrCl is added to calibration and calibration check standards.

8.13.1 Standards Preparation for Method 1631

<table>
<thead>
<tr>
<th>Standard ID</th>
<th>Vol. 5 µg/L Standard (Section 8.12.1.3) (mL)</th>
<th>Vol. STD5 (mL)</th>
<th>Final Concentration (µg/L)</th>
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<tbody>
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<td>STD0</td>
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<td>0.0</td>
</tr>
<tr>
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<td>-</td>
<td>0.25</td>
<td>0.0005</td>
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<td>-</td>
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<td>-</td>
<td>0.050</td>
</tr>
<tr>
<td>STD5</td>
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<td>-</td>
<td>0.100</td>
</tr>
<tr>
<td>ICV,CCV,MS</td>
<td>0.05</td>
<td>-</td>
<td>0.005</td>
</tr>
</tbody>
</table>

8.14 Argon Gas: Ultra-high purity

9. Quality Control

The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method.

9.1 Blanks

9.1.1 Method Blank

A method blank must be prepared once per every 20 samples or per digestion batch, whichever is more frequent. Prepare with same reagents as in the sample digests where applicable.

Mercury must not be detectable in the method blank at a concentration greater than the reporting limit.

For samples analyzed by Method 1631E, the mercury concentration in the Method Blank must be less than 0.5 ng/L or not to exceed one third of the regulatory limit if the data are to be used for regulatory purposes.

Corrective Action: May reanalyze once to determine if analytical error has occurred. Digestion of the method blank and all associated samples must be performed until the blank is in control. Samples cannot be analyzed until an acceptable method blank analysis is obtained. Exceptions may be made with approval of the Metals Department Manager, Laboratory Director or QAO, if the samples associated with the out of control method blank are non-detect for the elements of interest, or if sample concentrations are greater than 10x the blank levels. In such cases, the sample results are accepted without corrective action for the high method blank and the client is notified in a project narrative associated with the sample results.
9.1.2 Initial Calibration Blank (ICB)

An initial calibration blank must be analyzed immediately following the ICV (See 9.4).

An initial calibration blank may be analyzed immediately following calibration for Method 1631E.

Mercury must not be detectable in the ICB at a concentration greater than the reporting limit.

Corrective Action: May reanalyze once to determine if analytical error has occurred. If the concentration still exceeds the acceptance limit, stop and recalibrate the instrument. Samples cannot be analyzed until an acceptable ICB analysis is obtained. Exceptions may be made with approval of the Metals Department Manager, Laboratory Director or QAO, if the samples associated with the out of control blank are non-detect for mercury, or if sample concentrations are greater than 10x the blank levels. In such cases, the sample results are accepted without corrective action for the high blank and the client is notified in a project narrative associated with the sample results.

Note: The ICB is equivalent to a Reagent Blank for Method 1631E. The mercury concentration in the Reagent Blank is not to exceed 0.2 ng/L or one third of the regulatory limit.

9.1.3 Continuing Calibration Blank

A continuing calibration blank must be analyzed immediately following the CCB (see 9.5).

Mercury must not be detectable in the CCB at a concentration greater than the reporting limit.

Corrective Action: May reanalyze once to determine if analytical error has occurred. If the concentration still exceeds the acceptance limit, stop, recalibrate the instrument and reanalyze all associated samples. Samples cannot be analyzed until an acceptable CCB analysis is obtained. Exceptions may be made with approval of the Metals Department Manager, Laboratory Director or QAO, if the samples associated with the out of control blank are non-detect for the elements of interest, or if sample concentrations are greater than 10x the blank levels. In such cases, the sample results are accepted without corrective action for the high method blank and the client is notified in a project narrative associated with the sample results.

Note: The CCB is equivalent to a Method Blank for Method 1631E. Three Method Blanks must be analyzed with each batch.

9.2 Initial Precision and Recovery (IPR) for Soil/Sediment and Tissue

IPR is a one time initial demonstration of performance. Four aliquots of the appropriate reference matrix (Teflon chips for soil/sediment and chicken breast for tissue) spiked with 4.0 ng of Hg. The average % recovery must be 75-125% and the RSD between the replicates <20%.
9.3 LCS/Ongoing Precision and Recovery (OPR) for Soil/Sediment and Tissue

OPR/LCS is a test of the analytical system including prep. Analyze one aliquot of appropriate reference matrix spiked with 4.0 ng of Hg. Recovery must be 70-130%.

LCS/OPR for aqueous samples, recovery must be 77-123%

Corrective Action: Analysis according to the method may be repeated once to see if an analytical error has occurred. If the concentration still exceeds the acceptance limit, stop and recalibrate the instrument. Samples cannot be analyzed until an acceptable OPR analysis is obtained.

9.4 Initial Calibration Verification (ICV)

An initial calibration verification standard from a source different from that used to calibrate the instrument must be analyzed immediately following calibration as an independent check of instrument performance. Nominal acceptance limits are 85% - 115% of the true value.

Corrective Action: Analysis according to the method may be repeated once to see if an analytical error has occurred. If the concentration still exceeds the acceptance limit, stop and recalibrate the instrument. Samples cannot be analyzed until an acceptable ICV analysis is obtained.

9.5 Continuing Calibration Verification (CCV)

A continuing calibration verification standard must be analyzed after analysis of no more than 10 samples as an on-going check of instrument performance. Nominal acceptance limits are 85% - 115% of the true value.

Corrective Action: Analysis according to the method may be repeated once to see if an analytical error has occurred. If the concentration still exceeds the acceptance limit, stop, recalibrate the instrument and reanalyze all associated samples. Results cannot be accepted until an acceptable CCV analysis is obtained. Exceptions may be made with approval of the Metals Department Manager, Laboratory Director or QAO, if the samples associated with a high recovery CCV are non-detect. In such cases, the sample results are accepted without corrective action for the high CCV recovery and the client is notified in a project narrative associated with the sample results.

9.6 Matrix Spike/Matrix Spike Duplicate

An MS/MSD pair must be analyzed at a frequency of 1 per 10 samples. Spike samples at level in IPR/OPR (4.0 ng Hg for sediment/tissue, 0.005ug/L for aqueous). MS/MSD recovery criteria 70-130% and RPD <30% for sediment/tissue, 71-125% and RPD 24% for aqueous samples.

Corrective Action: For sediment/tissue, if MS/MSD fail and sample concentration is > ½ the spike concentration, the MS/MSD must be spiked at 2-5X the sample concentration and reanalyzed.

If the %RPD between the MS and MSD is not acceptable, a narrative is submitted with the data for inclusion on the final report.
9.7 Laboratory Duplicate

Duplicate analyses (matrix or sample duplicate) must be performed once per 20 samples 5% frequency), or per digestion batch, whichever is more frequent.

Acceptable relative percent differences (RPD) of duplicates is ≤20%. Acceptance criterion is not applicable to sample concentrations less than 5 times the reporting limit. Calculate the RPD as follows:

\[ \text{RPD} = \frac{R_1 - R_2}{\frac{R_1 + R_2}{2}} \times 100 \]

where:
- R1 = sample Replicate #1
- R2 = sample Replicate #2

Corrective Action: Include a project narrative.

9.8 Standard Reference Materials

Digest and analyze an appropriate reference material for the matrix, (animal tissue/plant tissue/soil/sediment). Recommended SRMs:

- Soil/solid – ERA D076 (Metals in Soil) or equivalent
- Sediment – NIST 2702 (Marine Sediment)
- Plant tissue – NIST 1515 (Apple Leaves)
- Animal tissue – NIST 2976 (Mussel tissue) or Tort-2 (Lobster tissue)

One SRM per batch must be analyzed and pass acceptance criteria

Corrective Action: Analysis according to the method may be repeated once to see if an analytical error has occurred. If the concentration still exceeds the acceptance limit, stop, recalibrate the instrument and reanalyze all associated samples. Results cannot be accepted until an acceptable SRM analysis is obtained. Exceptions may be made with approval of the Metals Department Manager, Laboratory Director or QAO, if the samples associated with a high recovery SRM are non-detect. In such cases, the sample results are accepted without corrective action for the high SRM recovery and the client is notified in a project narrative associated with the sample results.

9.9 Method-specific Quality Control Samples

Method 1631 requires that three calibration or system blanks be analyzed with the mean blank concentration used to blank correct all Data.

The average blank must be less than one third of the regulatory limit or 0.5 ng/L with the RSD less than <0.1 ng/L if the data is to be used for regulatory purposes.

Method 1631 requires that the recovery of mercury from the low calibration standard be within the range of 75% -125%.

The RSD of the mean calibration factor must be less than or equal to 15%.
9.10 Method Sequence

- Initial Calibration
- ICV
- ICB
- Method Blank
- IPR (LCS)
- SRM (sediment/tissue)
- Matrix Sample 1
- Matrix Duplicate
- Matrix Spike
- Matrix Spike Duplicate
- Samples 2-4
- CCV
- CCB
- Samples 5-14
- CCV
- CCB

10. Procedure

10.1 Equipment Set-up

Samples are prioritized by the Metals Department Manager or Preparation Group Leader for digestion based on hold time and client due date. The analyst must be familiar with instrument software and hardware as described in the user manuals supplied with the instrument, and have a completed IDC on file (Section 13.2) prior to any sample analysis.

10.1.1 Digestion I (Tissue/Sludge)

To a 50mL digestion tube, weigh 0.5 to 1.5 grams of material. Use less material if high organic content is expected.

Spike the OPR and MS/MSD samples with 0.08 mL of 5 ug/L intermediate (Section 8.12.2.2)

To each sample, add 10.0 mL of HNO3/H2SO4 (Section 8.11). Loosely cap with a watch glass. Carbohydrate based samples may react violently, allow these type of samples to react at room temperature for 4 hours prior to heating.

Place samples into digestion block. Monitor samples and remove from heat if excessive foaming occurs. Reflux for 2-3 hours.

After digestion, dilute samples with 0.02N BrCl (Section 8.10) and mix thoroughly. Allow samples to oxidize organic mercury for 4 hours prior to analysis.

Diluted digestates may be stored up to one year in glass or fluoropolymer containers.
10.1.2 Digestion II (Soil/Sediment)
To a 50mL digestion tube, weigh 0.5-1.5 grams of sample. Samples may be sieved if necessary to assure homogeneity.

Spike the OPR and MS/MSD samples with 0.08 mL of 5 ug/L intermediate (Section 8.12.2.2).

In a hood, add 8.0 mL concentrated HCl, then add 2.0 mL concentrated HNO₃. Allow to digest at room temperature for at least 4 hours, preferably overnight.

Dilute the digestate to 50 mL with 0.07N BrCl and shake thoroughly. Samples may be filtered through a 0.45µm filter or centrifuged for 20 minutes at 3000 RPM.

Diluted digestates may be stored up to one year in glass or fluoropolymer containers.

10.1.3 Aqueous Samples
To a 50mL digestion tube, add 50mL of sample and 0.25 mL of BrCl solution (Section 8.8). The sample should remain a yellow color. If not, add more BrCl solution to all samples, the Method Blank, LCS and all samples until yellow color persists.

Spike the MS/MSD and LCS with 0.05 L of 5ug/L Working Standard (Section 8.12.2.2).

Let stand for 12 hours and decolorize(optional) with 0.05mL of 12% hydroxylamine solution (Section 8.4.1).

10.2 Initial Calibration
The instrument is calibrated prior to sample analysis and at least once every 24 hours. Refer to Section 8.13 for the preparation of calibration standards for each determinative method.

For Method 1631, all standards and sample signals are blank corrected using the mean of the three calibration blanks analyzed at the beginning of the run. The instrument software calculates a mean calibration factor, calibration factor RSD and a recovery of the low calibration standard. The RSD of the mean calibration factor must be ≤ 15% and the recovery of the low calibration standard must be within the 75% - 125% range.

In all cases, a correlation coefficient ≥ 0.995 is required before the analysis of samples can begin.

10.3 Equipment Operation and Sample Processing
Power is turned on to the instrument, autosampler, PC and argon gas supply. Peristaltic pump tubing is inspected for wear and replaced if necessary.

10.3.1 STARTUP
Instrument startup (cold start).

Power up M-8000 and autosampler and open the QuickTrace software. If system is to be used for analysis in the ppb range a minimum of 15 minutes warm-up time is required. If system is to be run in the ppt range a minimum of 30 minutes warm-up time is required.
Instrument startup (warm start). The instrument and auto-sampler are on and stable. It is ok to leave the units powered up with the lamp and gas off.

Place the auto-sampler rinse tubing into the rinse bottle (2%HCl/2%HNO₃) (Section 8.3.2). Turn on the lamp and carrier gas. A minimum 15-minute warm-up time is required.

Verify that the sample capillary (inlet insert) is 0.5mm above the Gas/liquid separator (GLS) center post.

Open vents on waste container.

Inspect peristaltic pump tubing for flat spots replace if necessary. Place the peristaltic pump tubing in their appropriate shoes and bridge stops. Do not lock shoe clamps at this time.

Open instrument controls and start auto-sampler rinse pump if not already operating (click pump on and probe down).

Place the SnCl₂ capillary in the 10%SnCl₃/7% HCl (Section 8.5.1) and start the peristaltic pump at desired pump speed, which will usually match the method speed.

Lock down the peristaltic shoe clamps.

Inspect liquid flows. The GLS drain should be flowing smoothly with no build up or pulsing of liquid. The waste line from the peristaltic pump to the waste container should be liquid/gas etc... with no vibration. If this is not the case upon inspection, stop immediately and change GLS drain line and or waste line. The autosampler rinse station should have a convex liquid bubble adhering to the sample probe. If this is not the case, check that the rinse reservoir supply tubes are immersed in the rinse. If they are then check the rinse pump and pump tubing. Replace the tubing if necessary.

Wet the GLS center post. In instrument controls set the GLS gas flow to high and pump speed to 100%, pinch the drain line prior to the tee on the peristaltic pump drain tubing inlet side, let two or three bubbles go to the top of the GLS center post. Release the drain line and allow the liquid level to restore itself to normal operating levels before continuing to the next step. If the liquid does not bubble and the over flow sensor activates then clear the overflow and retry.

Connect the GLS exhaust tube (Nafion) or soda lime tubing to the GLS.

Place reagent capillaries in the reagent bottles.

Open the appropriate worksheet and verify that the gas flow and pump speed in the worksheet matches what is listed in >instrument>M-8000 controls, if the flow and speed are not the same make the necessary change in instrument controls or click the auto set icon on the menu bar. This will stabilize the instrument before auto zeroing and running a peak profile.

Zero the M-8000 using the auto zero.
Peak profile the high standard and verify baseline and sample integration times. Record hF units and concentration of the peak profile standard in a daily instrument logbook. Note: This operation should be performed on the highest standard.

Initiate sample analysis by clicking on the start button on the analysis page. If a sample concentration is greater than the highest standard concentration of the calibration curve, dilute the digestate and reanalyze.

10.3.2 SHUTTING DOWN:

Place the SnCl2 capillary in a beaker of 10% HNO3 and cap the SnCl2 bottle.

Rinse the system for a minimum of ten minutes with acid flowing.

Place the reagent capillaries in a beaker of DI water and rinse the system for one minute.

Raise sample probe via >instrument>auto-sampler controls (click probe up and pump off).

Remove reagent capillaries from DI water.

Allow the drain and waste lines to run completely dry.

Turn off peristaltic pump via >instrument>M-8000>pump off.

Release peristaltic shoe clamps and release the pump tubing from their bridge stops, release and relax peristaltic pump tubing.

Close vents on waste container.

Disconnect the GLS exhaust line (Nafion) or soda lime tubing from the GLS.

Turn off gas and lamp >instrument>M-8000>controls (note: you may want to turn off main supply gas at the Dewar or cylinder source).

If you are going to use the instrument the next day or in the near future, leave the software on the page >instrument>M-8000 controls>auto-sampler. It will then be ready for a warm start.

If you are not going to be using the instrument in the near future then exit the QuickTrace software and turn off the autodiluter, autosampler and M-8000 and pump.

The analysis method is selected and the autosampler template is selected. Once sample ID’s have been typed in, the file is saved as the LIMS workgroup number.

Following analysis, the data file is exported to the LIMS on the O:Metals\CETAC drive for data processing.
10.4 Continuing Calibration

Periodically and at the end of the analysis, CCV standards (Section 9.5) and CCB standards (Section 9.1.3) are analyzed.

10.5 Preventive Maintenance

Inspect pump tubing for signs of wear and replace (recommended at least monthly). Clean gas/liquid separator as needed. Change dryer tube annually.

11. Data Evaluation, Calculations and Reporting

All results for the metals elements of interests are reportable without qualification if digestion and analytical holding times are met, preservation (including cooler temperatures) are met, all QC criteria defined in the table below are met, and matrix interference is not suspected during digestion or analysis of the samples.

Sample concentrations for Method 1631 using the CETAC M-8000 are calculated based on peak area.

Sample concentrations are calculated as follows:

\[
\text{Sample Concentration} = \frac{(A_s - A_{mcb}) \times (V_f / V_i) \times DF}{CFm}
\]

Where:

- \(A_s\) = sample peak height or area
- \(A_{mcb}\) = Mean calibration blank peak height or area
- \(V_f\) = Final volume from preparation
- \(V_i\) = Initial volume from preparation
- DF = dilution factor
- CFm = mean calibration factor for the calibration curve

Note: The final volume from the sample preparation would reflect any changes in volume due to BrCl added to sample.

<table>
<thead>
<tr>
<th>QC Parameter</th>
<th>Acceptance Criteria</th>
</tr>
</thead>
<tbody>
<tr>
<td>Method Blank</td>
<td>&lt; reporting limit</td>
</tr>
<tr>
<td>OPR/LCS (sediment/tissue)</td>
<td>70-130% Recovery</td>
</tr>
<tr>
<td>OPR/LCS (aqueous)</td>
<td>77-123% Recovery</td>
</tr>
<tr>
<td>SRM (sediment/tissue)</td>
<td>% Recovery limits are specific to each SRM</td>
</tr>
<tr>
<td>Matrix Duplicate</td>
<td>(\leq 20%) RPD</td>
</tr>
<tr>
<td>Matrix Spike</td>
<td>70-130% Recovery (sediment/tissue)</td>
</tr>
<tr>
<td></td>
<td>71-125% Recovery (aqueous)</td>
</tr>
<tr>
<td>Matrix Spike Duplicate</td>
<td>(\leq 30%) RPD, 70-130% Recovery (sediment/tissue)</td>
</tr>
<tr>
<td></td>
<td>(\leq 24%) RPD, 71-125% Recovery (aqueous)</td>
</tr>
</tbody>
</table>
12. Contingencies for Handling Out-of-Control Data or Unacceptable Data

Section 9 outlines sample batch QC acceptance criteria. If non-compliant results are to be reported, the Metals Department Manager and/or the Laboratory Director must approve the reporting of these results. The laboratory Project Manager shall be notified, and may choose to relay the non-compliance to the client for approval, or other corrective action, such as re-sampling and re-analysis. The instrument analyst or Department Manager performing the secondary analytical review initiates a project narrative, and the narrative must clearly document the non-compliance and provide a reason for acceptance of these results.

13. Method Performance

13.1 Method Detection Limit Study (MDL) / Limit of Detection Study (LOD) / Limit of Quantitation (LOQ)

The laboratory follows the procedure to determine the MDL, LOD, and/or LOQ as outlined in Alpha SOP 1732. These studies performed by the laboratory are maintained on file for review.

13.2 Demonstration of Capability Studies

Refer to Alpha SOP 1739 for further information regarding IDC/DOC Generation.

13.2.1 Initial (IDC)

The analyst must make an initial, one-time, demonstration of the ability to generate acceptable accuracy and precision with this method, prior to the processing of any samples.

13.2.2 Continuing (DOC)

The analyst must make a continuing, annual, demonstration of the ability to generate acceptable accuracy and precision with this method.

13.3 Instrument Detection Limits

The instrument detection limit (IDL) is the smallest signal above the background noise that an instrument can detect. The IDL can be calculated taking the average of the standard deviations for three measurements of a reagent blank solution analyzed on three analytical runs on three non-consecutive days. Seven consecutive measurements must be taken per day. The IDL samples are not required to go through sample digestion. Each measurement must be performed as though it were a separate sample.

14. Pollution Prevention and Waste Management

The Hazardous Waste and Sample Disposal SOP (1797), must be referenced for disposal of used standards, solvents, acids, reagents or other chemicals.

Once sample batches have completed digestion, the sample containers are stored in the metals lab and held for 30 days. If there is no sample remaining in the sample collection bottle, it may be rinsed and thrown away.

Once the samples have been held for 30 days, any aqueous sample remaining must be disposed in a 55-gallon drum labeled “Corrosive Liquid”.
Once satisfactory inorganic element results have been generated, the digestates are held for 30 days, or longer if specified by a client contract, then discarded into a 55-gallon drum labeled “Corrosive Liquid”.

All reagent waste generated during digestion must be stored in satellite containers in the metals preparation laboratory.

Once the reagent waste satellite containers are full, they must be emptied into 55-gallon drums marked “Corrosive Liquid”.

Refer to Alpha’s Chemical Hygiene Plan and Waste Management and Disposal SOP for further pollution prevention and waste management information.

15. Referenced Documents

Chemical Hygiene Plan
SOP 1559 Sample Receipt & Log-In
SOP 1732 MDL/LOD/LOQ Generation
SOP 1739 IDC/DOC Generation
SOP 1797 Waste Management and Disposal SOP

16. Attachments

None.