SOP #BR-0006

Procedure for EPA Method 1631, Revision E: Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry

Brooks Rand Labs

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Written 05/30/00
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Reviewed _____
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VP of Analytical Services	5/24/10 Date
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Procedure for EPA Method 1631, Revision E: Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry

1.0. SCOPE AND APPLICATION

1.1. Method BR-0006 is the performance-based procedure followed at Brooks Rand Labs (BRL) as a modification of EPA Method 1631E. BRL has been performing mercury analysis by cold vapor atomic fluorescence since 1989, and during this time has identified several modifications to EPA Method 1631E that improve the quality of the data and the efficiency of the analytical process. These improvements and specific information about the equipment and forms used are detailed within this SOP, following the organizational format of Method 1631E. Unless specifically stated otherwise in this document, all apparatus, materials, reagents, standards, and procedures as stated in EPA Method 1631E are used at BRL.

1.2. Though EPA Method 1631E was written specifically for water samples, this method may be modified, as described in this SOP, for the analysis of many types of aqueous samples, including (but not limited to) chemicals, wastes, and biomonitoring samples (urine and plasma).

2.0. SUMMARY OF METHOD

2.1. Prior to instrumental analysis, the aqueous samples must be prepared according to the procedure discussed in EPA Method 1631E.

2.2. Refer to EPA Method 1631E, section 2.0, for the summary of the method employed at Brooks Rand Labs.

2.3. Refer to the Appendix at the end of this document for a summary of differences between EPA Method 1631, Revision E, and BRL SOP #BR-0006.

3.0. DEFINITIONS

3.1. A partial list of definitions is presented below. Most definitions can be found for specific terms in the sections where they are first mentioned. Many of the definitions mentioned in this method are based on those found in the glossary for EPA Method 1631E. Please refer directly to this method for a more detailed list.

3.2. May: This action is allowed, but not required.

3.3. May Not: This action is prohibited.

3.4. Must: This action is required.

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3.5. Shall: This action is required.

3.6. Should: This action is suggested, but is not required.

4.0. CONTAMINATION AND INTERFERENCES

4.1. Refer to EPA Method 1631E, section 4.0, for a detailed account of possible contamination routes and interferences that may be encountered during the analysis, and descriptions of how these may be avoided or minimized at BRL.

5.0. SAFETY

5.1. Refer to EPA Method 1631E, section 5.0, for safety issues associated with the use of this method.

5.2. Chronic mercury exposure may cause kidney damage, muscle tremors, spasms, personality changes, depression, irritability, and nervousness. Organo-mercurials may cause permanent brain damage. Because of this, only highly trained personnel familiar with the dangers and precautions to take when working with mercury compounds should ever handle standards and/or high level samples.

5.3. Material safety data sheets (MSDSs) are maintained for all chemicals used in this method. The MSDS sheets are stored in the sample receiving laboratory in appropriately marked binders.

5.4. Refer to the latest revision of the Chemical Hygiene Plan (CHP) for additional safety precautions and required protective equipment.

6.0. APPARATUS AND MATERIALS

6.1. Refer to EPA Method 1631E, section 6.0, for a list of materials used in this method.

6.2. Routine preventative maintenance for the equipment used in this procedure is described in detail in the standard operating procedure BR-1205 (Preventative Maintenance).

6.3. Detailed instructions for the decontamination of bottles and other equipment are described in BRL SOPs #BR-0400 (Decontamination of Sampling Containers) and #BR-0404 (Preventing Mercury Contamination of Samples).

6.4. Specific equipment used at BRL is listed below. Any modifications to EPA Method 1631E are described and explained.

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6.4.1. Brooks Rand Labs Model III Atomic Fluorescence Spectrophotometer (BRL part #07002): To achieve the low detection levels and small, interference-free sample aliquots claimed by this method, a very sensitive CVAFS detector is required. Such systems are built at BRL (Model III) based on the principals discussed in the literature. Refer to the "Brooks Rand LLC Model III Operations Manual" for instrument operating instructions. The initial setup of the instrument is governed by the range of the display of the signal height (0-2 million). The offset is set such that the peak area generated by the 500 pg standard is approximately 5000 to 7000.

6.4.2. Brooks Rand Labs Amalgamation Control Module (BRL part #02100): Controls the heating of the gold-coated sand traps to 450 ºC and then the cooling of the traps following desorption of Hg from the trap.

6.4.3. Brooks Rand Labs flow meter/needle valve (BRL part #08510): Capable of controlling and measuring gas flow to the purge vessel at 200-500 $mL \cdot min^{-1}$.

6.4.4. Teflon® adapters (BRL part #08401 through #08404) and tubing (BRL part #08405 through #08407): Connections between components and traps are made using 3.2-mm OD pre-cleaned Teflon® FEP tubing and Teflon® friction-fit or threaded tubing connectors.

6.4.5. Soda lime pre-trap (BRL part #03410): For preventing acid-fumes and moisture from degrading the gold-coated sand or gold wire traps. A 10 cm x 0.9 cm (diameter) Teflon® tube containing 2-3 grams of commercially available reagent grade, non-indicating, 6-12 mesh soda lime chunks, packed in between plugs of silanized glass wool. This trap is purged of Hg by placing it on the output of a clean cold vapor generator, partially filled with deionized water (DIW) and 500 µL stannous chloride ($SnCl_2$), and purging for a minimum of 15 minutes with nitrogen (N_2) at 400 mL/min. Bubbler blanks are analyzed first so that any indication of unclean pre-traps would be evident immediately.

6.4.6. Cold vapor generator (BRL part #03200): A 220-mL flask with a standard taper 24/40 neck, fitted with a sparging stopper having a coarse glass frit that extends to within 0.2 cm of the flask bottom.

6.4.7. Teflon® split bottle: Used for measurement and pre-reduction of original oxidized samples prior to analysis. A 125-mL blank tested Teflon® bottle with a unique identifier is permanently associated with a corresponding cold vapor generator.

6.4.8. Gold wire traps or gold-coated sand traps (BRL part #03010 or #03020): Used for trapping gaseous elemental mercury. Gold-coated sand traps made with gold-coated 40/100 mesh quartz sand are used to analyze water samples. Both gold-coated sand traps and gold wire traps are used to analyze air samples. Gold wire traps are made by forming 300 mg of 0.001 inch diameter gold wire into a

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plug that is inserted into quartz tubing. Figure 1 of this document shows the setup of the single-trap amalgamation system used at BRL.

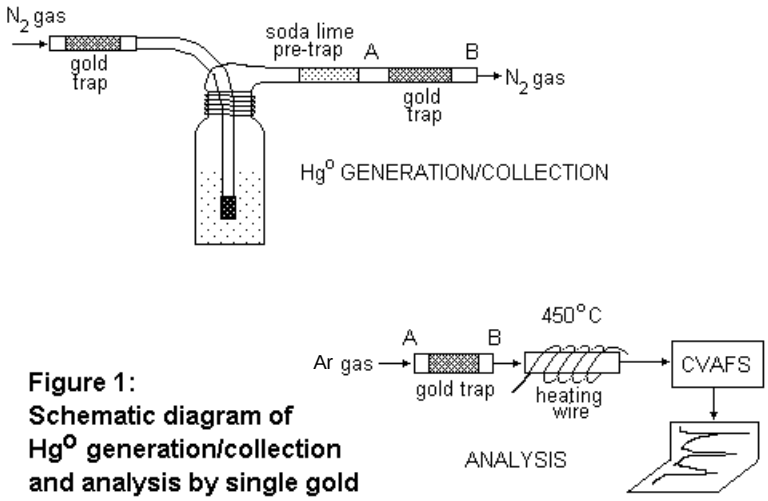

Figure 1: Schematic diagram of Hg^0 generation/collection and analysis by single gold amalgamation/CVAFS

6.4.9. Recorder: BRL uses direct data acquisition with the BRL Guru integration software instead of a chart recorder or integrator as described in EPA Method 1631E, section 6.6. The BRL Model III comes complete with the Hg Guru™ integrating software. Refer to the "Brooks Rand LLC Model III Operations Manual" for Hg Guru™ software/integrator operating instructions. Hg Guru™ software requires an IBM compatible computer (minimum requirements are a Pentium II® processor running at 400 MHz, a CD-ROM Drive, 128 MB RAM, and 50 MB free space on the hard-drive) and runs MS Windows® 98 or higher. Use of this integration software is faster, eliminates the expense of chart recorders and/or integrators, allows for storage of data in diskette form, and eliminates possible transcription errors.

6.4.10. Pipettes: All plastic pneumatic fixed volume and variable pipettes in the range of 10 µL to 5.0 mL.

6.4.11. Sampling Bottles: BRL uses clean and blank tested glass and fluoropolymer lined (FLPE) bottles for sample collection and preparation. For further information on the cleaning (or decontamination) and testing of bottles refer to SOP #BR-0400.

6.4.12. Nichrome wire coil (BRL part #08300) with plug (#08301): Used for heating the gold trap to thermally desorb the mercury.

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7.0. REAGENTS AND STANDARDS

7.1. Water: Reagent water is monitored for Hg on a daily basis when calibration blanks are analyzed. A minimum of four 100 mL aliquot of fresh reagent water, each with 0.5 mL $NH_2OH•HCl$ and 0.5 mL of $SnCl_2$, are analyzed at the beginning of the run sequence. The average results must be < 20 pg Hg with a standard deviation < 7.5 pg Hg. A high level of mercury detected in the reagent water analysis may also be attributed to the bubbler itself, the $SnCl_2$, or the soda lime pre-traps. Regardless of the source, all analysis is stopped until the source of contamination is determined and the problem is corrected. The results are stored with each batch.

7.2. Air: It is vital that the laboratory air be low in both particulate and gaseous mercury in order to reduce the risk of contamination. The BRL sample preparation lab clean room is equipped with a laminar flow hood that provides incoming air to the lab. Outside air, which is very low in Hg, is filtered through a particulate filter and then through HEPA filters before entering the mercury lab. Positive pressure is maintained to ensure that there is no incoming air through routes other than the laminar flow hoods. Sticky mats are located at the entrance as an additional precautionary measure. The mercury lab, the sample preparation lab, and the shipping and receiving area are monitored monthly for atmospheric mercury levels to ensure that these levels are sufficiently low for ultra-trace level mercury analysis. Air from each lab is pumped through a soda lime pre-trap and onto either a gold wire or gold-coated sand trap at a flow rate of 1 L/min until at least 20 L of air have been collected per trap. A warning level has been established at 15 ng Hg/m^3 with a shutdown control level at 25 ng Hg/m^3. Results from the monthly air tests are stored electronically on the BRL computer server.

7.3. Hydrochloric acid: Trace-metal purified reagent HCl is purchased and analyzed for Hg before use. In general, it is possible to obtain acid containing less than 5 pg/mL Hg. When a lot number meeting this specification is found, several cases are purchased. Generally, lower values can be obtained in this manner than by re-distilling acid in the laboratory. Only "trace-metal' grade acid should be used. Acids labeled as "ULTRA-PURIFIED" have historically had higher concentrations of mercury and should be avoided. All open cases of acids for trace metal work are stored in the locked storage area located in the north mezzanine level of the building.

7.4. Hydroxylamine hydrochloride ($NH_2OH•HCl$), stannous chloride ($SnCl_2$), and bromine monochloride (BrCl): Each of these reagents is prepared according to instructions listed in section 7.0 of Method 1631E. Reagent blanks must be analyzed each time that BrCl is made anew. The SnCl2 and $NH_2OH•HCl$ are tested daily whenever calibration blanks are analyzed.

Note: BrCl is tested whenever a new bottle is prepared prior to use with samples. During initial testing, reagent blanks are prepared in fluorinated polyethylene (FLPE) bottles at five different concentrations of BrCl (1.0%, 2.0%, 5.0%, and 10%). The BrCl is prereduced in the split bottle and then added to the bubbler with stannous chloride. A linear regression is performed to determine the level of contamination due to the bottles (b = y intercept) and the true

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concentration of Hg in the reagents. The acceptance criterion for the linear regression is an r^2 value ≤ 0.9 (If 2 or more of the points are less than the low standard, 25 pg Hg, then r^2 criteria may not be relevant and the lot of BrCl must be approved by QA). The amount of Hg per reagent unit (reagents used in a 1.0% BrCl method blank) must be ≤ 20 pg. If BrCl is prepared using the same lot of KBr and KBrO3 as a lot of BrCl already tested for linearity, then only two reagent blanks need be made at 10% BrCl to ensure the continued purity of the reagents. All lots of HCl are pretested and must already be shown to be pure prior to any use in reagents. As such, linearity testing of new BrCl is not required if only the HCl lot has changed.

7.5. Stock mercury standard: A commercially available 1000 µg/mL mercury standard that is traceable to NIST is used. This stock standard should be replaced by the manufacturer's expiration date.

7.6. Intermediate mercury standard solution: 0.100 mL of the stock solution is diluted to 100.0 mL with DIW containing 2.0 mL of BrCl. This solution contains 1000 ng/mL Hg, and must be kept refrigerated in a tightly closed Teflon® bottle. This solution should be replaced annually.

7.7. Mercury working standards: 2.50 mL of the intermediate mercury standard solution is diluted to 250 mL with high purity water containing 2.50 mL BrCl solution, to make a 10.0 ng/mL working solution (as discussed in EPA Method 1631E, section 7.9). A 1.00 ng/mL working standard should be made by diluting 0.250 mL of the intermediate mercury standard to 250 mL with DIW containing 2.50 mL BrCl solution. These working standards of 10.0 ng/mL and 1.00 ng/mL are added in appropriate aliquots to reagent water and analyzed to create the calibration curve and CCV samples.

7.8. Independent Calibration Verification (ICV) Standard: 0.250 mL of the standard reference material (SRM) NIST 1641d (mercury in water) is added 247.25 mL DIW and 2.5 mL BrCl for a final volume of 250 mL. After adjusting for the density of the SRM, the final value for this standard is 16.01 ng/L. NIST 1641d is purchased directly from the National Institute of Standards and Technology.

7.9. Nitrogen: Grade 4.8 (99.999% purity) minimum nitrogen that has been further purified by the removal of Hg using a gold coated sand trap.

7.10. Helium or Argon: Grade 4.8 (99.999% purity) minimum inert gas which has been further purified by the removal of Hg using a gold-coated sand trap.

8.0. SAMPLE COLLECTION, PRESERVATION, AND HANDLING

8.1. Refer to EPA Method 1631E, section 8.0, and EPA Method 1669 (*Sampling Ambient Water for Determination of Trace Metals at EPA Water Quality Criteria Levels*) for a detailed description of sample collection, preservation, and storage methods.

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9.0. QUALITY CONTROL

9.1. Refer to EPA Method 1631E, section 9.0, for a detailed description of the quality control procedures employed at BRL for this method. Consult Section 18 of this SOP for the current MDL (method detection limit) and ML (minimum limit) determined at BRL for the analysis of mercury using Method 1631E (Table 1). The ML is sometimes referred to as the method reporting limit (MRL). Acceptance criteria and corrective action procedures are listed in Table 2.

9.2. All quality control data should be maintained and available for easy reference and/or inspection.

9.3. Samples containing high analyte concentrations should be analyzed at a reduced volume. For all quantified results, peak areas obtained for samples must ultimately fall below the peak area obtained from the highest standard analyzed and above the peak area obtained from the lowest standard analyzed in the calibration curve.

9.4. Analysts who have not performed EPA Method 1631E previously at BRL must complete an initial demonstration of capability (IDOC) study, which includes the analysis of samples for MDL determination. Refer to Table 3 in Section 18 of this SOP for the general analytical sequence for the IDOC.

9.5. When analyzing client samples, BRL will follow the general analytical sequence found in Table 4 of Section 18 of this SOP. Note that in order to avoid potential carryover from high-level samples, samples projected to have only low levels of mercury (field blanks, method blanks, and samples otherwise expected to be low based on historical data or small amounts of particulate matter) should be analyzed at the beginning of the run sequence. Although EPA Method 1631E suggests (in section 9.1.7) that method blanks may be analyzed intermittently throughout the analysis, BRL analysts should analyze all method blanks at the beginning to avoid potential carryover and to verify that all method blanks meet criteria before proceeding with sample analysis. In addition, whereas Method 1631E only requires analysis of two CCV samples (at the start and at the end of the run sequence), it is BRL policy to run additional CCV samples (one after every 10 client samples) to ensure ongoing control of the system.

9.6. EPA Method 1631E states that spiking levels of the MS/MSD shall be equal to the regulatory compliance limit or 1-5 times the background concentration of the sample, whichever is greater. This is achieved in aqueous samples at BRL by analyzing the sample to be spiked prior to the addition of the spiking solution.

9.7. A minimum of 3 method blanks per batch of 20 client samples must be run. Method blanks must be prepared with the same lot of BrCl used to prepare the samples. Section 12.3 describes how the method blanks are used to correct results for samples prepared at BrCl concentrations other than 1.0%. Brooks Rand routinely prepares and analyzes 4 method blanks to allow for the possible outlier.

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10.0. CALIBRATION AND STANDARDIZATION

10.1. Refer to EPA Method 1631E, section 10.0, for a detailed description of instrument calibration.

10.2. Instrument Calibration: BRL has adopted the following procedure.

10.1.1. The mercury analyzers built and used at BRL are capable of achieving extremely low detection limits. As such, BRL calibrates its instruments down to 25 pg. The standards typically used to calibrate the instruments for total mercury at BRL are 25 pg, 100 pg, 500 pg, 2500 pg, and 10,000 pg. The standards are added to the split bottle, pre-reduced with $NH_2OH{\cdot}HCl$, and then poured into the bubbler. The calibration is based on the measured picograms of mercury in the bubbler and not on concentration.

10.2.2. Sections 9.0 and 10.0 of EPA Method 1631E do not state a frequency requirement for calibration. BRL performs a new calibration each day and whenever CCV recovery fails to meet the acceptance criteria as outlined in Method 1631E, Table 2. Additionally, analysis of the ICV standard must also meet the criterion in Table 2 for the calibration to be validated.

10.2.3. Section 9.4.1.3 of EPA Method 1631E suggests that the mean peak area for all bubbler blanks (including those analyzed during the analytical sequence to ensure that no carryover occurs from high-level samples) should be subtracted from all raw data before results are calculated. This does not allow for the continuous determination of whether QA results are in control, thereby forcing the analyst to analyze all samples prior to determining if all QA criteria are met. BRL subtracts the average peak area measurement of the first four bubbler blanks (or one blank for each split bottle and bubbler used in the analysis of samples) analyzed at the beginning of the analytical run from all raw data for result calculations. The acceptance criterion for the initial bubbler blanks (referred to as calibration blanks) is each ≤ 40 pg, average ≤ 20 pg, and standard deviation ≤ 7.5 pg. The criterion for subsequent bubbler blank checks is that each blank must be ≤ 40 pg and ± 20 pg from the calibration blank mean.

10.2.4. BRL uses the following equation to calculate the calibration factor (CF_x) for Hg in each of the standards:

$$CF_x = (C_x) / (A_x - A_{CB})$$

Where:
C_x = mass of Hg in standard analyzed (pg)
A_x = peak area for Hg in standard
A_{CB} = mean peak area for Hg in calibration blanks

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This calculation differs from the calculation given in 1631E in that the numerator and denominator are reversed.

11.0. PROCEDURE

11.1. Sample Preparation: Refer to EPA Method 1631E, section 11.0, for more detailed guidelines regarding sample preparation and analysis. Practices employed specifically by BRL are outlined below and in the appendix to this SOP.

11.1.1. Four method blanks are prepared with each batch of samples. All method blanks are preserved to 1% BrCl. This is allowable because BRL tests each new batch of BrCl made to prove that it maintains linearity with increased concentration.

11.1.2. The samples are then preserved to a percentage of BrCl that is dependant upon amount of particulate in sample. A clear sample would get 1% BrCl; a fairly clear sample with some particulate would get 2% BrCl; a sample with lots of particulate would get 5%. If a sample has a yellow tinge to it, an amber sticker is placed on top of the bottle to indicate that the coloration is due to the matrix and not necessarily due to any BrCl added to the sample during preparation. After the addition of BrCl, the samples are left to oxidize for at least 24 hours.

NOTE: When calculating the % BrCl in a sample, the amount of BrCl added to the sample must be accounted for in the total volume for any percentage of BrCl above 5%.

11.1.3. After a minimum of 24 hours, a 24 hour check is performed. The 24 hour check consists of looking at each sample individually to check that the sample is still yellow, which indicates the BrCl was added in excess. Any sample that is suspected of not having excess BrCl, or a sample with an amber sticker on top is tested with starch iodide indicator paper. If the paper turns purple, then the sample is presumed to be adequately preserved. If the paper stays white, more BrCl is added to the sample. If additional BrCl was added to any of the samples in a batch, a subsequent 24 hour check is required. If a batch is to be analyzed within less than 24 hours from prep, it should be heated for 4 hours at 65 ºC and the "24 hour" check should be performed prior to analysis.

11.1.4. Urine samples should be oxidized with 5% BrCl by default. They must be checked for excess BrCl using starch iodide paper as the BrCl color will be indistinguishable from the color of the urine itself.

11.2. Instrumental Analysis: BRL has adopted the following modifications from EPA Method 1631E.

11.2.1. Samples and standards are purged for 15 minutes at 400 mL/min. However, longer purge times may be necessary if the lab and/or sample

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temperature is < 16 °C. Lab temperature is maintained between 20 ºC to 25 ºC, so longer purging times are not generally necessary.

11.2.2. Four 100-mL aliquots of water are poured into each of the bubblers prior to calibration. 0.5 mL of $SnCl_2$ is added to each bubbler and the aliquots are used to condition the soda-lime pre-traps for a minimum of 15 minutes, as noted in 6.4.4 of this SOP. Following this pre-trap conditioning step, the purged water is discarded and 100 mL aliquots of DIW along with 0.5 mL $NH_2OH•HCl$ are poured from the four split bottles into their associated bubblers. 0.5 mL $SnCl_2$ is added to this water, which is then purged for 15 minutes onto a gold amalgamation trap and analyzed for Hg. A high level of mercury in the calibration blanks may be attributed to the split bottle, the bubbler, the reagents, or the soda lime pre-traps. Regardless of the source, all analysis using the contaminated bubbler/split bottle/trap combination is stopped until the source of contamination is determined and the problem is corrected. Use of all uncontaminated bubblers, split bottles, and traps may continue during this process.

11.2.3. All calibration standards and QC samples are added to 100 mL aliquots of DIW in a thoroughly rinsed split bottle prior to transfer to a bubbler for analysis.

11.2.4. Aliquots of the original oxidized sample of approximately 100 mL are weighed into split bottles. 0.5 mL of $NH_2OH•HCl$ is added directly to the split bottle and allowed to react for at least 5 minutes prior to transfer to the bubbler for purging onto a gold amalgamation trap for analysis. Split bottles and bubblers are rinsed a minimum of three times with DIW in between sample aliquots.

11.2.5. Urine samples should be pipetted into split bottles, as the density of urine is not equivalent to the density of water. A maximum of 25 mL will be used (giving an MRL/MDL 4x higher than for water samples). Urine samples can be analyzed in the same batch as water samples but must have QC performed on at least 1 urine sample.

11.2.6. As discussed in Method 1631E and in section 9.4 of this SOP, follow the attached analytical sequence (Table 4). Generally, analysts should follow the suggestion in Method 1631E that samples suspected to contain the lowest concentration of mercury (i.e., known blank samples) should be analyzed first followed by samples containing potentially higher levels (i.e., known influent samples).

11.2.7. As discussed in section 9.4 of this SOP, the analyst may choose to analyze CCV samples more frequently than required by Method 1631E. A CCV must be analyzed after every 10 client samples (not counting quality control samples) to verify ongoing control of the system.

11.2.8. The PMT and offset are recorded on the bench sheet at the beginning of each day after auto zeroing the instrument previous to measuring the noise. When the baseline shifts more than 100 units, the systems should be adjusted in the

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following manner. Auto zero the Model III. Compare the offset to the original offset for the day. If it is more than 100 units different than the original reading, adjust the PMT to obtain an offset that is within 100 units of the original reading. The PMT and offset must be recorded every time the instrument is auto zeroed regardless of if the PMT was adjusted.

11.2.9. BRL has found that checking for mercury carryover in a bubbler by analyzing a bubbler blank is not necessary unless an unusually high level sample has been purged. Carryover tests, performed using spikes of 10,000 pg, 20,000 pg, 40,000 pg, and 100,000 pg, resulted in carryover of less than 50 pg Hg from the bubbler and trap. To avoid carryover from the bubbler or split bottle, the analyst should rinse each bubbler and split bottle three times with DIW between all samples. To avoid carryover from the trap, the analyst should heat the mid- and downstream sections of any traps associated with a higher-level sample (such as any sample above the calibration range) for an additional 3 minutes following sample desorption. If a purged sample contains > 20,000 pg Hg, the analyst must follow the above corrective actions and analyze a bubbler blank and split bottle blank check using fresh DIW and the associated bubbler, split bottle and trap. The analysis of the split bottle blank should be performed on a different bubbler to facilitate proper contamination identification. Using previously purged DIW is not necessary for the bubbler blank. If any bubbler or split bottle blank fails (> 40 pg Hg and/or > ± 20 pg from average calibration blank on associated bubbler and trap), the analyst must identify and correct the source of contamination, and demonstrate that the bubbler and trap pass the blank criterion before sample analysis can continue using that bubbler, split bottle, and trap.

11.2.10. Any samples run in a bubbler, split bottle and/or on a trap associated with a carryover sample (e.g., a sample with > 20,000 pg Hg) must be reanalyzed, if sufficient sample volume exists.

11.2.11. After analysis is complete, split bottles and bubblers are rinsed with DIW three times and filled with DIW. Split bottles are stored tightly capped until further use. During the workweek, all bubblers are filled with DIW overnight and thoroughly rinsed prior to use in the morning. At the end of each week, the bubblers are filled with 10% (w/v) NaOH in DIW for approximately 1 hour or until all visible residue is removed and are then triple rinsed and filled with DIW. Purging the bubblers while soaking them with the 10% NaOH solution can help to expedite the process. This procedure should be done more frequently if the bubbler starts to appear dirty before the end of the week.

11.3. Gold traps should be tracked by unique identifiers so that any trap producing poor results can be quickly recognized and discarded. Occasionally due to inadvertent contact with halogen fumes, bubbler solution, organic fumes, or overheating, a sampling trap will become damaged, giving low and/or irreproducible results. Suspect traps should be checked with at least two consecutive standard runs before continued use. Traps should be replaced quarterly or as soon as possible after quality control results indicate their

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degradation. Additionally, traps should be replaced whenever integration peaks become abnormally shaped (no longer symmetrical with steep slopes).

11.4. Section 11.3.2 of Method 1631E states that before each trap is analyzed, argon should be passed through the trap for approximately two minutes to drive off condensed water vapor prior to heating and desorbing for three minutes. Historically, BRL has not experienced significant analytical problems associated with water vapor on traps. However, if the analyst observes peaks that desorb prior to the mercury peak, this technique may be employed.

12.0. DATA ANALYSIS AND CALCULATIONS

12.1. The following equations are used at BRL to calculate sample results.

12.2. To calculate the amount of mercury measured during an analytical run (P), employ the following formula:

$$P = Hg\ (pg) = CF_m\ (A_S - A_{CB})$$

Where:
CF_m = mean calibration factor
A_S = gross peak area measured in sample analysis
A_{CB} = mean peak area for Hg in calibration bubbler blanks

12.3. To determine the concentration of total mercury in a sample, the calculation is performed as follows:

$$Hg\ (\text{in ng/L or ppt}) = \{[(P/V_A)*V_D]-MB\}/\ V_O$$

Where:
P = Hg (pg) from equation in section 12.2
V_A = volume (mL) of the sample preparation that was analyzed
V_D = final dilution volume (mL) of the sample preparation
V_O = volume (mL) of the original sample used in the preparation
MB = multiple of the average result (in total pg Hg) for the 0.5% BrCl method blanks.

Note: The multiplier of the average 1.0% BrCl method blank result is based on the concentration of BrCl in the prepared sample. A multiplier of 1 is applied if the sample was prepared at 1.0% BrCl, 2 if the sample was prepared at 2.0% BrCl, 5 if the sample was prepared at 5.0% BrCl, etc. This is only allowed if the linear regression yielded by the initial reagent blank testing as described in Section 7.4 of this SOP yields the following: $r^2 \geq 0.9$ and $b \leq 0.2$ ng/L. Otherwise, method blanks must be prepared at each of the BrCl concentrations used to prepare the samples. (These

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criteria do not apply if the reagent blank units are less than 1 pg since all of the method blank testing results for the different BrCl concentrations would be below the MDL.)

12.4. It is BRL's policy to method blank correct sample results unless specifically requested not to do so by the client.

12.5. Method 1631E states that results below the ML should be reported as less than the level of the ML or as required by the regulatory authority, and that field blank results below the ML but above the MDL should be reported to 2 significant digits. Because BRL is not always aware of the original source of a sample or the specific needs or requirements of our clients, all results above the BRL determined MDL are reported to 3 significant digits.

13.0. METHOD PERFORMANCE

13.1. Refer to EPA Method 1631E, section 13.0, for information regarding the verification of this method.

13.2. The detection limits reported in Table 1 were achieved by performing a full MDL study as described in 40 CFR 136, Appendix B. The quality control acceptance limits reported in Table 2 are developed from the EPA methods and are validated as achievable at BRL in the control charts maintained for the method.

14.0. POLLUTION PREVENTION

14.1 Refer to EPA Method 1631E, section 14.0, for EPA recommendations regarding pollution prevention techniques.

14.2 Whenever feasible, lab personnel should use pollution prevention techniques to limit waste generation. The cost involved in purifying acids makes such recycling unpractical at BRL. Instead, every effort is made to reduce volumes necessary to still produce the best possible results. This analysis requires small amounts of acid to be used in the preparation of the samples (typically ~2.5 mL of BrCl per sample). When making standards, they should be prepared in volumes consistent with their use in the laboratory to minimize the volume of expired standards to be disposed.

15.0. WASTE MANAGEMENT

15.1. Refer to EPA Method 1631E, section 15.0, for information and references related to managing waste produced by application of this method.

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15.2. All waste is disposed of in accordance with state and federal regulations either by sewer disposal (only if concentrations are below the King County sewer limits) or through a licensed and bonded hazardous waste disposal facility such as Philips Services.

16.0. REFERENCES

16.1. EPA Method 1631, Revision E: Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry, August 2002 (including references cited in section 16.0).

16.2. Model III (CVAFS Mercury Analyzer) Operating Manual, September 2004. Brooks Rand LLC, 3958 6th Ave NW, Seattle, WA.

16.3. EPA Method 1669: Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels, July 1996.

17.0. GLOSSARY

17.1. Refer to EPA Method 1631E, section 17.0, for additional definitions of terms used throughout the text of 1631E.

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18.0. FIGURES (1631E), TABLES, AND BENCHSHEETS

18.1. BRL has adopted the following modifications to the figures illustrated in EPA Method 1631E, section 18.0.

18.1.1. Figure 1: Schematic Diagram of Bubbler Setup and Figure 2: Schematic Diagram of the Bubbler, Purge and Trap, Cold Vapor Atomic Fluorescence Spectrometer (CVAFS) System. Instead of the setup shown in these figures, BRL uses the setup illustrated in Figure 1 of this document, BR-0006, Section 6.3.6.

18.1.2. Figure 3: Schematic Diagram of the Flow-Injection, Cold Vapor Atomic Fluorescence Spectrometer (CVAFS) System. This system is not employed by BRL.

Table 1. Current Method Detection Limits and Minimum Levels Determined at Brooks Rand Labs for the Analysis of Total Mercury in Water Using EPA Method 1631

Matrix	Preparation Method	Method Detection Limit (MDL)[1]	Minimum Level (ML)[2]
Water	Digestion	0.15 ng/L	0.40 ng/L

NOTES:
1. MDL as determined by the procedure 40 CFR Part 136, Appendix B. MDL and ML reported here are for method blank corrected results.
2. At BRL the ML is often referred to as the method reporting limit (MRL).

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Table 2. Quality Control Criteria and Corrective Action Procedures for the Analysis of Total Mercury by CVAFS

QC Sample	Measure	Minimum Frequency	Criteria	Corrective Action
Calibration Blanks / Bubbler Blank	Contamination from split bottles / bubblers	1 per split bottle / bubbler used	each ≤ 40 pg avg ≤ 20 pg std ≤ 7.5 pg	Clean and test split bottles / bubblers until criteria met prior to any further analysis
Calibration Standards	Acceptability of the calibration curve	Daily (first batch of the day) or when ICV/CCV fail	RSD of response factors ≤ 15%; Recovery of Low Standard = 80 – 120%	Reanalyze suspect calib stand w/diff trap/bubbler. If criteria still not met, then remake standards and recalibrate the instrument.
Continuing Calibration Verification (CCV)	Accuracy	1 immediately after calibration followed by 1 every 10 samples and 1 at the end of each batch)	Recovery = 77 – 123%	Correct problem and reanalyze CCV. If criteria met, reanalyze samples backwards until 2 consecutive results w/RPD ≤ 20%. Otherwise, recalibrate system.
Carryover Check Bubbler Blank	Contamination due to carryover in the bubbler/trap	Perform on same bubbler/trap combination following any measured result ≥ 20,000 pg	≤ 40 pg (within ± 20 pg of avg bubbler blank before used for additional analyses)	Remake and condition the soda-lime trap. Clean and continue to test bubbler/trap combo until criteria met prior to further use. Samples analyzed using same bubbler and/or trap following a result ≥ 20,000 pg must be reanalyzed.
Method Blank (1% BrCl in reagent water)	Contamination from reagents, lab ware, etc.	3 per batch	Each MB ≤ 0.5 ng/L and StDev ≤ 2/3 the MDL or highest MB < 0.1 times the lowest reported result.	Correct problem until criteria met. All samples affected by high method blanks (sample < 10x the highest MB) must be qualified accordingly.
Independent Calibration Verification (ICV)	Independent check of system performance	1 per batch	Recovery = 85 – 115%	Correct problem prior to continuing analysis. Otherwise, recalibrate system.
Matrix Spike / Matrix Spike Duplicate	Accuracy and Precision within a given matrix	1 per 10 client samples	Recovery = 71 – 125%; RPD ≤ 24%	If **recoveries** similar but fail recovery criteria, an interference is present in the sample and the result must be qualified. If **RPD** criteria not met, then the system is not in control. Correct problem and reanalyze all associated samples.
Method Duplicate	Precision within a given matrix	As per client request	RPD ≤ 24% or if results < 5x the MRL then ± the MRL of one another	If **RPD** criteria not met, then the system is not in control. Correct problem and reanalyze all associated samples.

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Table 3. Quality Control Acceptance Criteria and General Analytical Run Sequence for the Initial Demonstration of Capability for the Analysis of Total Mercury.

Run	Run Name	Section Name	Analyze	Requirements
1	CB	Calibration	Split bottle blank	< 40 pg; ave. < 20 pg; stdev < 7.5 pg
2	CB		Split bottle blank	
3	CB		Split bottle blank	
4	CB		Split bottle blank	
5	25 pg std	Calibration	25 pg Hg	RSD of CF < 15%; recovery of low standard = 80-120%
6	100 pg std		100 pg Hg	
7	500 pg std		500 pg Hg	
8	2500 pg std		2500 pg Hg	
9	10000 pg std		10000 pg Hg	
10	IPR std (500 pg)	Initial Precision and Recovery	500 pg Hg	Ave. recovery 79-121%, RSD < 21%
11	IPR std (500 pg)		500 pg Hg	
12	IPR std (500 pg)		500 pg Hg	
13	IPR std (500 pg)		500 pg Hg	
14	Method Blank	Method Blanks for MDL	Method blanks prepared at same BrCl level as MDL samples	Each ≤ 0.5 ng/L StDev ≤ 0.07 ng/L
15	Method Blank			
16	Method Blank			
17	Method Blank			
18	MDL sample	Method Detection Limit	DIW + 0.1-0.5 ng/L	MDL ≤ 0.1 ng/L
19	MDL sample		DIW + 0.1-0.5 ng/L	
20	MDL sample		DIW + 0.1-0.5 ng/L	
21	MDL sample		DIW + 0.1-0.5 ng/L	
22	MDL sample		DIW + 0.1-0.5 ng/L	
23	MDL sample		DIW + 0.1-0.5 ng/L	
24	MDL sample		DIW + 0.1-0.5 ng/L	
25	CCV (500pg std)	Continuing Calibration Verification	500 pg Hg	Recovery 77-123%

Notes

1. All standards and samples are corrected for mean calibration blank.
2. All samples are corrected for mean method blank.

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Table 4. Quality Control Acceptance Criteria and General Analytical Run Sequence for the Analysis of Total Mercury.

Run	Run Name	Section Name	Analyze	Requirements
1 2 3 4	CB CB CB CB	Calibration Blanks	Split bottle blank Split bottle blank Split bottle blank Split bottle blank	Each < 40 pg; Ave. < 20 pg; StDev < 7.5 pg
5 6 7 8 9	25 pg std 100 pg std 500 pg std 2500 pg std 10000 pg std	Calibration	25 pg Hg 100 pg Hg 500 pg Hg 2500 pg Hg 10000 pg Hg	StDev < 15% of Ave. RF Recovery of 25 pg std = 80-120%
10	ICV (1000pg std)	Independent Calibration Verification	1000 pg (different standard)	Recovery 85-115%
11	CCV (500pg std)	Continuing Calibration Verification	500 pg Hg	Recovery 77-123%
12	Method Blank 01	Method Blank	1.0% BrCl MB	All MB ≤ 0.5 ng/L
13	CCB	Continuing Calibration Blank	Same split bottle and bubbler associated w/the 10000 pg std.	< 40 pg and within ± 20 pg of the average CB
14 15 16	Method Blank 02 Method Blank 03 Method Blank 04	Method Blank	1.0% BrCl MB 1.0% BrCl MB 1.0% BrCl MB	Each ≤ 0.5 ng/L StDev ≤ 0.07 ng/L
Next	Field, Equipment, or Bottle Blanks	Field, Equipment, or Bottle Blanks	Field, Equipment, or Bottle Blanks	< ML or < 1/5th of associated sample conc.
Next	1st Half of Samples (including MS1 and MSD1)	Sample Analyses Matrix Spike Matrix Spike Duplicate	Sample X X + spike X + dup. Spike Other Samples	 Recovery 71-125%; RPD < 24% Recovery 71-125%; RPD < 24%
Next	CCV (500pg std)	Continuing Calibration Verification	5.0 ng/L	Recovery 77-123%
Next	2nd Half of Samples (including MS2 and MSD2)	Sample Analyses Matrix Spike Matrix Spike Duplicate	Sample Y Y + spike Y + dup. Spike Other Samples	 Recovery 71-125%; RPD < 24% Recovery 71-125%; RPD < 24%
Last	CCV (500pg std)	Continuing Calibration Verification	500 pg Hg	Recovery 77-123%

Notes

1. All standards and samples are corrected for mean calibration blank.
2. All samples prepared with one level of BrCl are corrected by multiplication of the 1.0% BrCl MB result by the factor required to produce a result equivalent to that of the BrCl level used to oxidize the sample.
3. Field and equipment blanks are only analyzed if provided by clients. Bottle blanks are analyzed for the bottles provided by Brooks Rand Labs.
4. A carry-over blank is run following any high-level sample (≥20,000 pg measured). The carry-over blank is analyzed using the same split bottle, bubbler, and trap associated with the high-level sample.
5. Field blanks and other potentially low-level samples should be analyzed at the beginning of the analytical run; samples suspected to contain comparatively high levels of mercury should be run at the end of the sequence.
6. Reagent blanks must be analyzed when new BrCl is made and must average less than 20 pg of Hg per blank unit.
7. Equipment blanks are analyzed only on a project-specific basis.

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(Example Log)

Brooks Rand Labs

THg Water Prep Benchsheet

Prepped By: _____ Batch: _____ 1st - 24 hr Check Date/Time _____

Prep Date: _____ BrCl ID: _____ 2nd - 24 hr Check Date/Time _____

Prep Time: _____

					only fill out if additional BrCl is added		
Sample ID	Sample Aliquot (mL)	BrCl added (mL)	**%BrCl**	1st - 24 hr Check (initials)	Additional BrCl Added (mL)	2nd - 24 hr Check (initials)	**Adjusted %BrCl**

Comments:

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(Example Log) **Hg Analysis Sheet: T-Hg / Other: _____** Page 1 of____

Sequence:_____ Batch(es):_____

Analyst:_____ Date:_____ Instrument ID:_____

10ng/mL std ID: _____ 1ng/mL std ID: _____ ICV std ID: _____

$NH_2OH{\cdot}HCl$ #: _____ $SnCl_2$ #: _____

Initial offset: _____ Initial PMT: _____

Run #	Split Bottle	Trap	Bubb.	BRL Sample ID	Analy. Vol. (mL)	Dilution Factor	Analysis comments / For spiked QC: Source sample, standard ID, and spiked volume (mL)
1				SEQ-IBL1	---		
2				SEQ-IBL2	---		
3				SEQ-IBL3	---		
4				SEQ-IBL4	---		
5				SEQ-CAL1	0.025		1ng/mL
6				SEQ-CAL2	0.100		1ng/mL
7				SEQ-CAL3	0.050		10ng/mL
8				SEQ-CAL4	0.250		10ng/mL
9				SEQ-CAL5	1.00		10ng/mL
10				SEQ-ICV1	1.00		NIST 1641d
				SEQ-CCB1	---		

Comments:_____

_____

_____

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(Example Log) **Hg Analysis Sheet: T-Hg / Other: ____** Page ____ of ____

Sequence:____________________ Analyst:___________ Date:_____________

Run #	Split Bottle	Trap	Bubb.	BRL Sample ID	Analy. Vol. (mL)	Dilution Factor	Analysis comments / For spiked QC: Source sample, standard ID, and spiked volume (mL)

Comments:____

____

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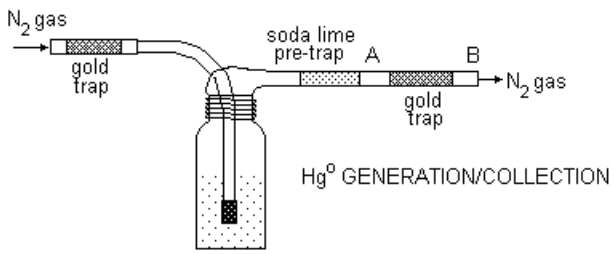
Appendix to Brooks Rand Labs Procedure for EPA Method 1631, Revision E (02/05)

Differences between EPA Method 1631, Revision E, and Brooks Rand Labs SOP #BR-0006

The following differences exist between EPA Method 1631, Revision E (with relevant sections marked in boldface), and the practices employed by Brooks Rand Labs (SOP #BR-0006):

- **Figures 1 and 2** (referenced within **sections 2.6 and 2.7**) give schematic diagrams of the bubbler, purge and trap, CVAFS analytical system. In contrast, Brooks Rand Labs (BRL) purges samples with nitrogen in bubblers onto sample traps. After samples are purged, the sample traps are disconnected from the bubbler system and desorbed using argon, as shown below:



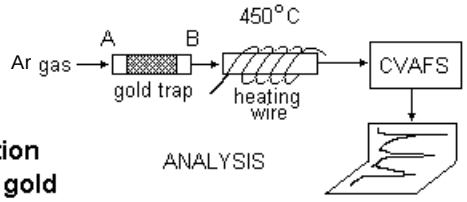


Figure 1: Schematic diagram of Hg^0 generation/collection and analysis by single gold amalgamation/CVAFS

- **Section 6.4.3** specifies the use of acid fume pretraps consisting of 8-14 mesh soda lime chunks and which are purged for 1 hour with nitrogen. BRL uses pretraps consisting of 6-12 mesh soda lime chunks and which are purged for 15 minutes with nitrogen.

- **Section 6.5** discusses the use of a dual-trap Hg(0) pre-concentration system. In contrast, BRL uses a single trap pre-concentration system. This allows for shorter analysis times without masking of potential problems on the sample collection trap.

- BRL uses direct data acquisition with the BRL "Hg Guru" integration software instead of a chart recorder or integrator as described in **section 6.6**.

- Method 1631E identifies two working standards at 10.0 ng Hg/mL and 0.10 ng Hg/mL (**sections 7.9 and 7.10**) used for instrument calibration. Instead of the 0.10 ng Hg/mL working standard, BRL uses a 1.0 ng Hg/mL standard, along with the 10 ng Hg/mL standard, for calibration.

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- **Section 9.3.1** states that the concentration of the spike for matrix spike (MS) and matrix spike duplicate (MSD) samples shall be at 1-5 times the background level of the native sample. After the determination of the concentration of the native sample, appropriate spike volumes will be added to an aliquot of the native sample in the Teflon split bottle prior to pre-reduction.

- **Section 9.4.1.3** specifies that the mean result for all bubbler blanks analyzed during an analytical batch should be subtracted from all raw data before results are calculated. Instead, BRL subtracts the average peak area measurement of the first four split bottle blanks analyzed prior to the calibration from all raw data. Split bottles are used for the measurement and/or transfer of all standards, client samples, and quality control samples to the bubblers.

- **Section 9.4.7** specifies that 5% of any lot of bottles should be tested. BRL has found that there is little variation within any given lot of FLPE bottles, glass bottles, or glass vials. Therefore, BRL randomly tests only 10% of the bottles or vials from the first opened case from each lot before accepting or rejecting the lot, up to a maximum of 10 cases per lot number. A minimum of 10% of the cases of any given lot number are tested. BRL uses the tighter acceptance criterion of THg ≤ 0.2 ng/L, as opposed to ≤ 0.5 ng/L, for passing a lot number of bottles. In addition, four method blanks are prepared with every batch (> 10% of any given batch) using the same bottles that the samples are collected and prepared in, which serves as a further indicator of any potential contamination due to the bottles.

- **Section 10.1** does not state a frequency requirement for calibration. BRL performs a new calibration at the beginning of each analytical day and whenever CCV recovery fails to meet the acceptance criteria as outlined in 1631E, Table 2.

- **Section 10.2.2.1** lists calibration points of 50 pg, 500 pg, 2500 pg, 5000 pg, and 10000 pg Hg created from aliquots of working standards discussed above. BRL uses a calibration curve with points of 25 pg, 100 pg, 500 pg, 2500 pg, and 10000 pg. These points are produced by adding 0.025 mL and 0.100 mL of a 1.0 ng Hg/mL standard (50 pg and 100 pg respectively) and by adding 0.050 mL, 0.250 mL, and 1.0 mL of a 10.0 ng Hg/mL standard (500 pg, 2500 pg, and 10000 pg respectively). BRL does not add aliquots of the working standard directly to the bubblers; instead aliquots of standards are added to approximately 100 mL of DI water in a split bottle prior to transfer to the bubbler.

- **Section 11.2.1.2** states that samples are purged with nitrogen for 20 minutes at gas flow rate of 300-400 mL/min. BRL purges all samples for 15 minutes at 400 mL/min. High-level standard recoveries and subsequent bubbler blanks indicate that 15 minutes is an adequate purge time to volatilize and collect mercury.

- BRL has not found the step described in section **11.3.2** (passing argon through the sample trap prior to desorption) to be necessary to eliminate condensed water vapor prior to trap desorption.

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