Analysis of Total Mercury in Water by Manual Purge and Trap Capture and Cold Vapor Atomic Fluorescence Detection

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Scope and Application

The following standard operating procedure (SOP) is used by the U.S. Geological Survey's Mercury Research Laboratory (MRL) to determine total mercury (HgT) concentrations in water. This SOP describes the preparation of the sample and subsequent analysis. Samples are collected into Teflon bottles and preserved to 1% v/v with MRL-supplied Hydrochloric Acid. Bromine Monochloride (BrCl) is added to the sample and heated to 50°C for five days to release matrix-bound mercury and oxidize all forms of mercury to the Hg^{2+} oxidation state. Immediately prior to analysis, the BrCl is neutralized by the addition of Hydroxylamine Hydrochloride ($NH_2OH*HCl$). Following neutralization, Stannous Chloride ($SnCl_2$) is added to the sample to reduce the mercury from Hg^{2+} to Hg^0. The volatile Hg^0 is purged from the sample and captured onto a gold bead trap (sample trap). The Hg^0 is thermally desorbed from the sample trap and captured onto a second gold trap (analytical trap). The Hg^0 is desorbed from the analytical trap and detected by cold vapor atomic fluorescence spectrometry (CVAFS) with a Tekran 2500. Quality assurance and control protocols are employed throughout sample preparation and analysis, including: laboratory practices to prevent sample contamination, method blanks, analytical replication and matrix spikes, and analysis of quality control standards (QCS).

Laboratory Safety

Analysts who use the MRL must have read, understood, and signed the Chemical Hygiene Plan for the MRL prior to potential exposure to any chemicals. The analyst must have a thorough understanding of the required safety protocols for the lab chemicals prior to their use of the lab. Adequate personal protection equipment such as safety glasses, gloves, and chemical resistant clothing must be worn when exposure to hazardous chemicals are possible. Caution should always be exercised; chemicals are present in the laboratory and often in use by other analysts. Hazardous chemicals should only be handled by adequately trained personnel under a high volume fume hood with extreme caution.

Multiple safety concerns are present in the conduct of this method; detailed information is included for each reagent specific to the method later in this SOP, and additional safety information can be found in the safety data sheets (SDS) located in the lab. Mercury is a toxic metal and caution should be exercised to limit exposure during daily operations. While samples and working standards are relatively low in concentration, concentrated stock solutions containing elevated HgT levels are occasionally encountered. Concentrated HgT stock solutions should only be handled by experienced lab personnel. Additionally, other hazardous chemicals used in this method include concentrated strong acids, $SnCl_2$, and BrCl (a strong oxidizer).

Equipment

Trace level mercury analyses of samples at parts per billion concentrations are susceptible to contamination. Equipment that comes into contact with samples or reagents should be free of residual mercury and can consist of (but not be limited to) Teflon, glass, and polycarbonate containers. Brand new and previously used Teflon equipment should be washed in acid before use. The equipment is first rinsed with tap water, and then cleaned by immersing in 4 N HCl heated to 65°C for at least 12 hours (48 hours for new Teflon equipment). Immediately following removal from the bath, equipment is completely immersed in reagent-grade water and then additionally triple-rinsed in reagent-grade water. After rinsing, each container is air dried under a mercury-free class 100 laminar flow hood. Dry equipment is stored double bagged in zip-type bags.

Reagents and Standards

Reagents

All reagents and/or dry chemicals used to make reagents must be of the highest purity available from the vendor and shown to be low in mercury. Upon receipt at the laboratory, containers will be marked with the date of receipt and stored in the appropriate areas. When reagents are mixed for use in this method, the person who mixes them will record the chemical contents and concentration, and initial and date the reagent container. Reagents and manufacture instructions follow below.

Reagent water (Milli-Q water): Ultra-pure reagent grade water containing less than 0.1 ng/L Hg with a resistance greater than 18 MΩ-cm. The water is delivered through a 0.2 µm filter, as obtained from a Millipore Academic water-purification system or equivalent.

Hydrochloric Acid (HCl): EM Science Omni Pure HCl (containing less than 5 ng/L Hg) or equivalent.

Bromine Monochloride (BrCl): Dissolve 27.0 g of reagent grade Potassium Bromide (KBr) in a new 2.5 L bottle of concentrated HCl. Place a Teflon coated stir bar into the bottle and stir for 1 hour or until dissolved. Slowly add 38.0 g reagent grade Potassium Bromate ($KBrO_3$) to the bottle while stirring. CAUTION: This needs to be done slowly and in a fume hood because large quantities of free halogens are produced. Addition of $KBrO_3$ to the solution should produce a color change from orange to red to yellow. Cap bottle loosely, stir for an additional hour, and remove stir bar. BrCl is stored in the original acid container in the acid cabinet. Replace the original acid label with a preprinted BrCl label and record your initials and the date made.

30% w/v Hydroxylamine Hydrochloride ($NH_2OH*HCl$): Dissolve 120 g of $NH_2OH*HCl$ in a Teflon bottle containing 400 mL of reagent grade water. Hydroxylamine hydrochloride typically contains significant amounts of HgT and needs to be treated to reduce the contamination to acceptable levels (< 0.02 ng/ml). Add 50 µL $SnCl_2$ to the solution and purge with Nitrogen gas (300 mL/min for 1 hour). After the solution has been purged, analyze 0.1 ml in reagent water. If necessary, repeat the $SnCl_2$ addition and purging steps until the solution is below the acceptable level. Store the $NH_2OH*HCl$ solution in the refrigerator when not in use.

20% w/v Stannous Chloride ($SnCl_2$): Add 200 g $SnCl_2$ to 100 mL concentrated HCl in a 1 L Teflon bottle. Add 900 mL reagent water. Purge for 1 hour with Nitrogen gas at 300 mL/min. Store the $SnCl_2$ solution in the refrigerator when not in use.

Soda Lime: Purchased from Alpha Aesar, 4-8 mesh.

Argon (Ar): Grade 5.0 (ultra high purity) Argon gas that is scrubbed of gaseous mercury by passing through a gold bead trap.

Nitrogen (N_2): Nitrogen gas is provided by a Peak Scientific nitrogen generator (model NM32LA) and is scrubbed of gaseous mercury by passing through a gold bead trap.

Analytical and Quality Control Standards

Upon receipt at the laboratory and on the day of preparation, mercury standard solutions should be labeled with the concentration, date received/prepared, and analyst initials. All standards must also be assigned a unique letter-number-letter identification code and must be entered into the laboratory database system. Concentrated (> 10 ng/ml) standard solutions should be stored outside of the main laboratory area to avoid contamination of the lab. Dispose of the working and concentrated mercury solutions in the appropriate waste container when expired (>6 months old for working solutions) or when the solution no longer contains BrCl (yellow color has faded to clear).

Two standard solutions from different sources are required for analysis: (1) an “analytical standard” which is used to calibrate the instrument and for matrix spikes, and (2) a “quality control standard” (QCS) which is prepared from a different source of mercury standard than the working standard and functions as an independent check against the working standard and to verify instrument calibration throughout an analysis.

Stock mercury standard solutions: The stock mercury standard solutions are commercially available mercury standards verified against a NIST standard reference material.

Working mercury standard solutions: The working mercury solutions are used in the daily operation of the instrument and is prepared from the stock solutions. For typical environmental samples (>1 ng/L), a working analytical solution of 10 ng/ml and QCS working solution of 5 ng/L are used. When low level samples (< 1 ng/L) are expected for an entire run, a working analytical solution of 1 ng/ml and QCS working solution of 1 ng/L are used.

Analytical working standard solution: The analytical working standard is prepared at 1 or 10 ng/ml (subsequent dilutions of the stock should follow a similar preparation). Dispense approximately 50 mL of reagent grade water and 3 mL of BrCl into a 100 mL mercury clean class A volumetric flask. Pipette the appropriate volume of stock solution (or diluted stock solution) and bring to volume with reagent water. Store the standard in a designated Teflon mercury standard bottle, and label with concentration, bottle identification code, date prepared, and analyst initials. Enter the working standard solutions into the lab database. This working standard must be compared to the previous working standard and agree within $\pm$ 5%. Prepare fresh every 6 months.

QCS working solution: The working solution of the QCS is prepared at 1 or 5 ng/L and in a manner similar to a typical water sample. Prepare the QCS working solutions in a matrix of Milli-Q water that is 1% HCl and 0.4% BrCl. The QCS solutions should be prepared in 5 L batches. To a 1 L volumetric flask, add approximately 500 ml of water, and the appropriate volumes of HCl, BrCl, and the stock QCS mercury standard. Fill to 1 L and add to a rinsed 5 L Teflon bottle. Using the same volumetric flask, add the remaining 4 L of reagent water to the 5 L Teflon bottle. Distribute the bulk QCS into individual rinsed 250 ml Teflon sample bottles (5 ng/L solutions) or ashed 250 mL amber glass bottles (1 ng/L solutions). The new QCS working solutions should be analyzed on the day it is made and the concentration should agree with the previous QCS (± 5%).

Sample Preparation

Water samples (filtered or unfiltered) are collected into Teflon bottles and preserved to a 1% v/v with MRL-supplied Hydrochloric Acid. Samples with high visible levels of dissolved organic carbon are placed in an ultraviolet light box until colorless (this step may be skipped if the samples are colorless or nearly so). Prior to analysis, BrCl is added to the sample (1.2% BrCl v/v) to oxidize all mercury to Hg^{2+}. The HgT contribution to the sample from the BrCl is determined by CVAFS analysis, and the final sample concentration is corrected. Following bromination, samples are placed into a convection oven and heated to 50°C for five days. If the yellow color remains after five days, this indicates excess BrCl in the sample and it is ready for analysis. If the yellow color is absent, additional BrCl is added and the sample is again placed in the oven overnight. Immediately prior to analysis the BrCl in the sample is neutralized with a 30% NH_2OH*HCl solution; add 30 μL of NH_2OH*HCl per mL of BrCl.

Instrument Operation

The manual method of HgT analysis is a two-step process: (1) purging Hg^0 from the analyte onto gold traps using a set of five purging flasks, and (2) desorption of Hg^0 from gold traps and subsequent detection with a Tekran 2500. During analysis, these steps are generally occurring simultaneously. Each setup of five flasks and their respective traps are a "round" of analysis.

Instrument Start Up

1. Turn on the nitrogen generator. Open the needle valve under the hood to supply gas to the rotometers.

2. Check that the lamp light is off on the detector. If the lamp light is on, the voltage to the lamp needs to be adjusted.

3. Adjust the mass-flow controller on the detector to read 30 mL/min.

4. Check the baseline at the detector. Acceptable baseline readings are 0.005 – 0.0250. If the baseline is out of range, adjust with the offset knob.

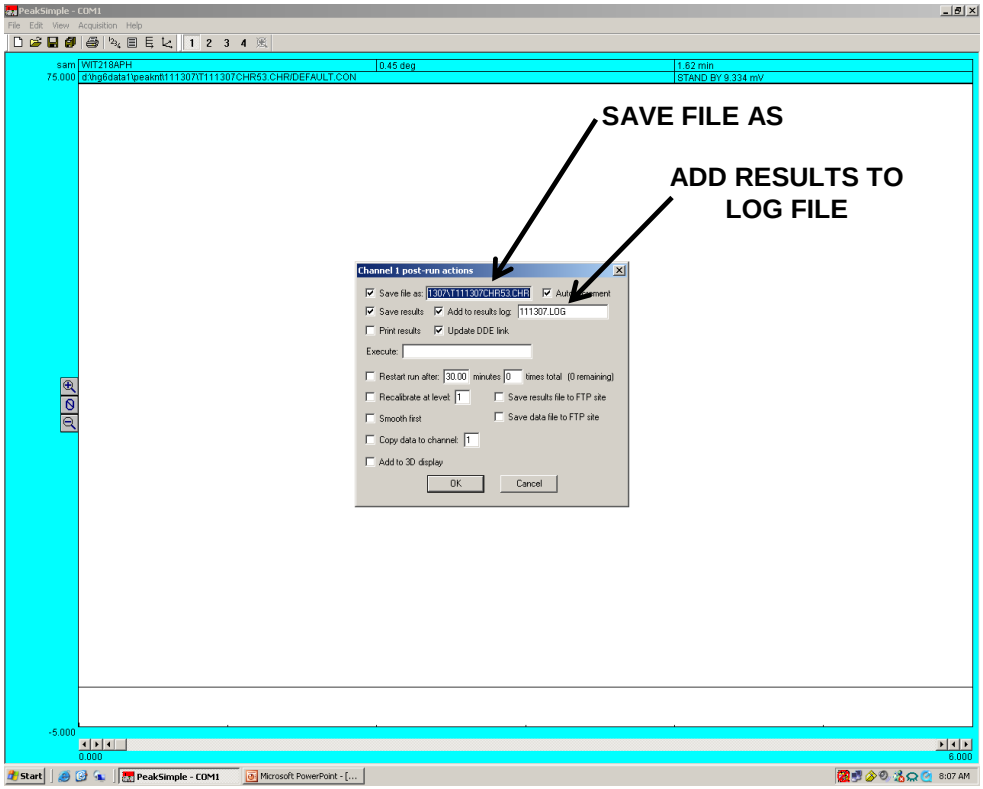
5. Log onto the computer and open the "PeakNT folder on the desktop. Within the PeakNT folder, open the current year folder and create a new folder named for the analytical days date (MMDDYY). This folder will hold the log file for the chromatogram output; when analysis starts a log file will be created by PeakSimple.

6. Open the PeakSimple integration software. Click the Edit pull-down menu and choose the "Overall" option. A popup window will appear.

7. Change the data path to the folder created previously in the PeakNT folder.

8. Use the right mouse button while in the PeakSimple window to access a dropdown menu and choose the post-run option. A popup window will appear.

9. Modify both the "save file as" and "add results to log file" windows. In the "save file as" window adjust the folder and chromatogram names to represent present date and reset the CHR number to 00 (d:\hg6data1\peaknt\MMDDYY\TMMDDYYCHRXX.CHR). The .log file also needs to be updated to represent the current date in the "save file as" window (MMDDYY.log).


SAVE FILE AS
ADD RESULTS TO LOG FILE
Channel 1 post-run actions
Save file as:
Save results
Add to results log:
111307.LOG
Print results
Update DDE link
Execute:
Restart run after:
minutes
times total (0 remaining)
Recalibrate at level:
Smooth first
Copy data to channel:
Add to 3D display
Save results file to FTP site
Save data file to FTP site
OK
Cancel

Gold Trap Loading

Following section describes the general procedure for loading a gold trap.

1. Add the analyte (sample, standard, QCS…) to the purge flask.

    a. With the exception of concentrated analytical standard, always neutralize the BrCl in samples and QCS solutions before purging. Excess BrCl in a purged solution will damage the gold bead traps.

    b. The medium in the purging flasks should always be acidified with HCl. For the initial calibration standards, add 5 ml of HCl to each flask. Samples and QCS are already preserved to the proper concentration and no additional acid is needed.

2. Add 500 μL of $SnCl_2$ to each flask and promptly put the impinger in the purge flask.

3. Attach Soda Lime traps to the impingers.

4. Remove the Teflon plugs from clean-burned gold traps and attach the gold trap to the outlet of the Soda Lime traps. Orientate the trap so the identification number is downstream.

5. Purge for 20 minutes at 300 ml/min.

6. Cap the trap with Teflon plugs and proceed to analysis.

Gold Trap Desorption

Following section describes the general procedure for desorbing a gold trap.

1. Remove the existing clean-burned sample trap from the desorption unit and cap with plugs.

2. Install the loaded sample trap into the Nichrome wire coil. Orientate the identification number downstream. Make sure the coil is centered over the gold beads.

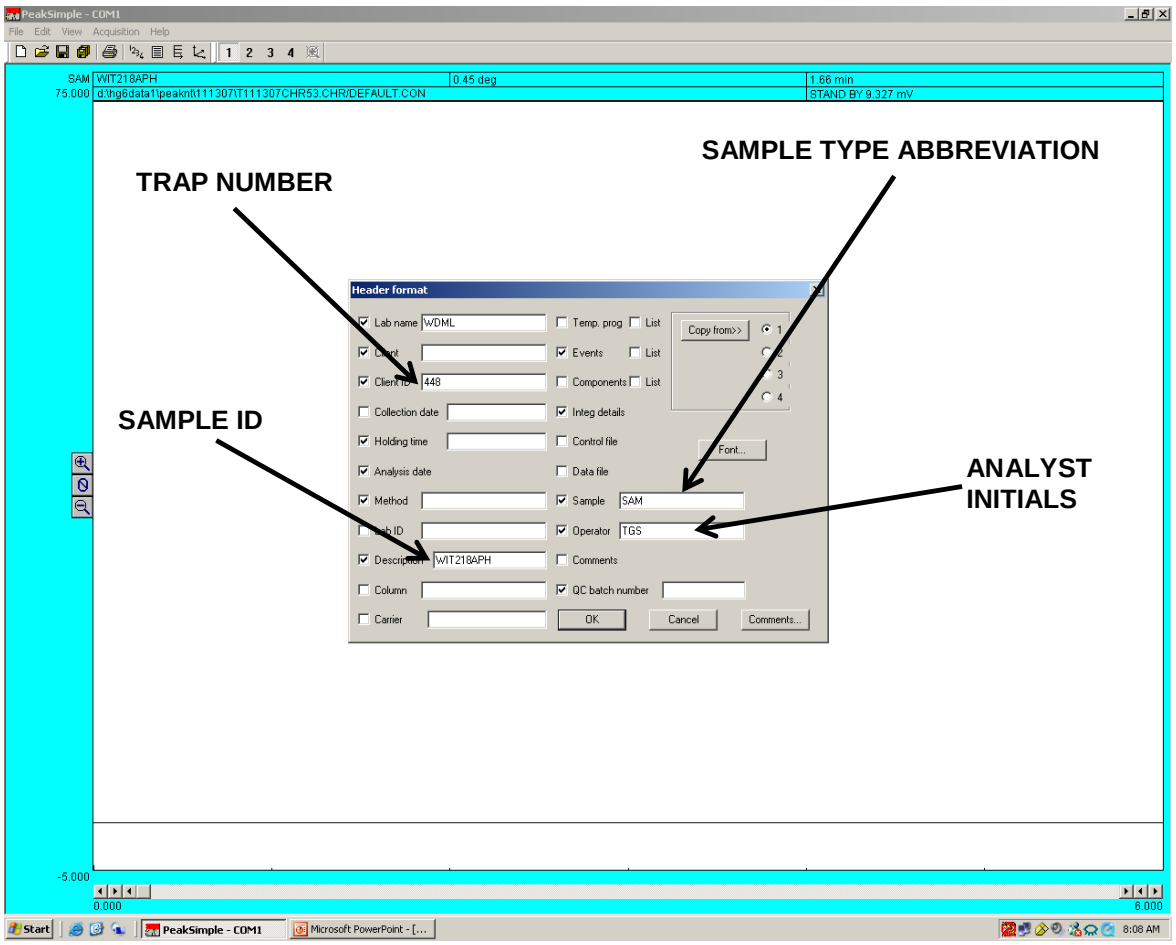
3. Attach the Teflon ports to the trap.

4. On the ChronTrol unit, press (in sequence) “Program 3” and then “On”. The ChronTrol timer is programmed to control the heating of the Nichrome coils, the cooling fans, and will trigger the PeakSimple software to begin a chromatogram.

5. Update the header format specific to that trap in the PeakSimple software. Use the right mouse button while in the PeakSimple window to access the drop-down menu and choose the Header option. Change the “Client ID” field to the present trap number. Change the “Description” window to the sample ID (sample barcode, standard volume, blank). Change the “Sample” window to the present sample type abbreviation (see figure below). Also verify that the “Operator” window contains the correct initials for the analyst.

6. Sample types as follows:

Abbreviation	Sample Type
GCB	Gold clean burn
MQ	Milli-Q blank
BB	Calibration blank
STD	Standard
QC	Quality control
SAM	Environmental sample
MS	Matrix spike
BAT	Bath blank
AC	Preservative acid



Preparation of Gold Traps and Purge Flasks for Calibration and Analysis

Prior to instrument calibration and sample analysis, the gold traps and purge flasks must be cleaned of residual mercury. Specific details for gold trap desorption and loading are given above.

1. Desorb ("clean burn") a set of ten sample traps to remove any residual mercury.

2. Empty the Soda Lime traps and refill with fresh reagent.

3. Empty and rinse the purge flasks and impingers with Milli-Q. Fill the flasks with approximately 125 mL of Milli-Q.

4. Add 5 mL of concentrated HCl and 500 μL of $SnCl_2$ to each flask.

5. Put the impingers into the purge flasks and attach a Soda Lime trap to the outlet of each impinger.

6. Install a gold trap to only one of the flasks (the rest of the flasks can purge without a gold trap). This is a Milli-Q blank and is used as a daily measure of the background mercury levels in our reagent water system.

7. Attach the gas supply lines to the inlet port of the impingers and purge the flasks for 20 minutes. Remove trap and analyze.

Instrument Calibration

1. Prepare five calibration blanks. Add 500 μL of $SnCl_2$ to the purged Milli-Q that is in each of the flasks. Attach the Soda Lime and gold traps and purge for 20 minutes. Remove traps and analyze.

2. Select a QCS solution. Neutralize the BrCl in the QCS with 30 μL of the NH_2OH*HCl solution. The yellow solution should turn clear. Allow it to react for five minutes.

3. Analyze a calibration curve and the neutralized QCS solution. Create a four point calibration curve with the working standard. For typical environmental samples create a calibration curve that spans 0.1 – 1.0 ng of mercury. For low-level analysis, create a calibration curve that spans 0.025 – 0.200 ng of mercury. In the remaining flask, weigh approximately 40 mL of the appropriate QCS (dump out an equivalent volume of purged reagent water to maintain a 125 mL volume).

4. Add 500 μL of $SnCl_2$ to each flask, attach the soda lime and gold traps, and purge for 20 minutes. Remove traps and analyze.

5. Proceed to analysis of samples only if: (1) the daily detection limit is < 0.04 ng/L, (2) the r^2 of the calibration curve is > 0.995, and the QCS is ± 10% of the accepted value.

Sample Analysis

On a typical eight hour analytical day 20 samples are analyzed. Analysis is conducted in 2 batches of 10 samples, followed by a pause between the batches for equipment blanks and quality control checks. Each batch of 10 samples is analyzed twice in alternating sets of five, resulting in duplicate analyses for each sample. A typical analytical day is described in the figure below.

1. Select 10 samples for analysis and record the sample ID's in the Excel spread sheet. Weigh the samples and record the full weight in the Excel spread sheet.

2. Neutralize the BrCl with an appropriate volume of $NH_2OH*HCl$ (30 μl per 1 mL of BrCl). Allow five minutes for the reaction to occur.

3. Dump the reagent water out of the purge flasks. Weigh approximately 125 mL of five of the ten samples into the purge flasks (set A). Record the mass of sample analyzed in the Excel spread sheet.

4. Add 500 mL of $SnCl_2$ to each of the purge flasks.

5. Attach the Soda Lime and gold traps to the impingers and purge for 20 minutes.

6. Remove the traps and analyze.

7. While the gold traps from set A are analyzing, prepare the second set of five samples (set B) in the flasks by following steps 3 – 6.

8. Continue setting up rounds of samples until all 10 samples have been analyzed twice.

9. Review the initial results from the first batch of 10 samples as they appear. Check that all samples are within the calibration curve. If a sample exceeds the calibration on its initial analysis, reduce the volume appropriately for the duplicate analysis.

10. Review that analytical duplicates are within 10% of each other. If sample duplicates are greater than 10%, the sample needs to be reanalyzed until a relative standard deviation of the sample is < 10% or the sample is consumed.

11. Set up a round of equipment blanks after the final round of samples. This allows time for the final round of sample traps to be desorbed and cleans the flasks for the upcoming Matrix Spike, QCS, and rerun round.

12. After the samples have been successfully analyzed (passing all quality control criteria), empty the sample bottles and record the sample bottle tare weight in the Excel spread sheet.

	Bubbler 1	Bubbler 2	Bubbler 3	Bubbler 4	Bubbler 5
Milli-Q blank and flask purge	Milli-Q Blank	Flask Purge	Flask Purge	Flask Purge	Flask Purge
Calibration Blanks	Calibration Blank 1	Calibration Blank 2	Calibration Blank 3	Calibration Blank 4	Calibration Blank 5
Instrument Calibration and QCS	1 ng Analytical Standard	0.5 ng Analytical Standard	0.25 ng Analytical Standard	0.10 ng Analytical Standard	40 mL QCS
Sample set A	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
Sample set B	Sample 6	Sample 7	Sample 8	Sample 9	Sample 10
Sample set A (duplicates)	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
Sample set B (duplicates	Sample 6	Sample 7	Sample 8	Sample 9	Sample 10
Equipment Blanks	Equipment Blank 1	Equipment Blank 2	Equipment Blank 3	Equipment Blank 4	Equipment Blank 5
Matrix Spike QCS Reruns	Matrix Spike	40 mL QCS	Sample Rerun or Equipment Blank	Sample Rerun or Equipment Blank	Sample Rerun or Equipment Blank
Sample set C	Sample 11	Sample 12	Sample 13	Sample 14	Sample 15
Sample set D	Sample 16	Sample 17	Sample 18	Sample 19	Sample 20
Sample set C (duplicates)	Sample 11	Sample 12	Sample 13	Sample 14	Sample 15
Sample set D (duplicates)	Sample 16	Sample 17	Sample 18	Sample 19	Sample 20
Equipment Blanks	Equipment Blank 1	Equipment Blank 2	Equipment Blank 3	Equipment Blank 4	Equipment Blank 5
Matrix Spike QCS Reruns	Sample Rerun or Equipment Blank	Sample Rerun or Equipment Blank	Matrix Spike	40 mL QCS	Sample Rerun or Equipment Blank

Matrix Spike, Quality Control Standard, and Sample Reruns

1. Select one sample to be analyzed as a matrix spike from the previously analyzed batch. Try to select a sample with a response between 0.25 – 0.5 ng. Pour the sample into the purge flask and add a volume of the analytical standard that approximately doubles the expected response. Record the sample ID, sample volume, and analytical standard volume in the Excel spread sheet.

2. Pour approximately 40 mL of the QCS into a purge flask. Record the appropriate information into the Excel spread sheet.

3. If necessary, utilize the three remaining purge flasks for other samples from the batch that have failed duplicate analysis. Otherwise, set them up as equipment blanks.

4. Add 500 μL $SnCl_2$ to each flask and purge as previously described.

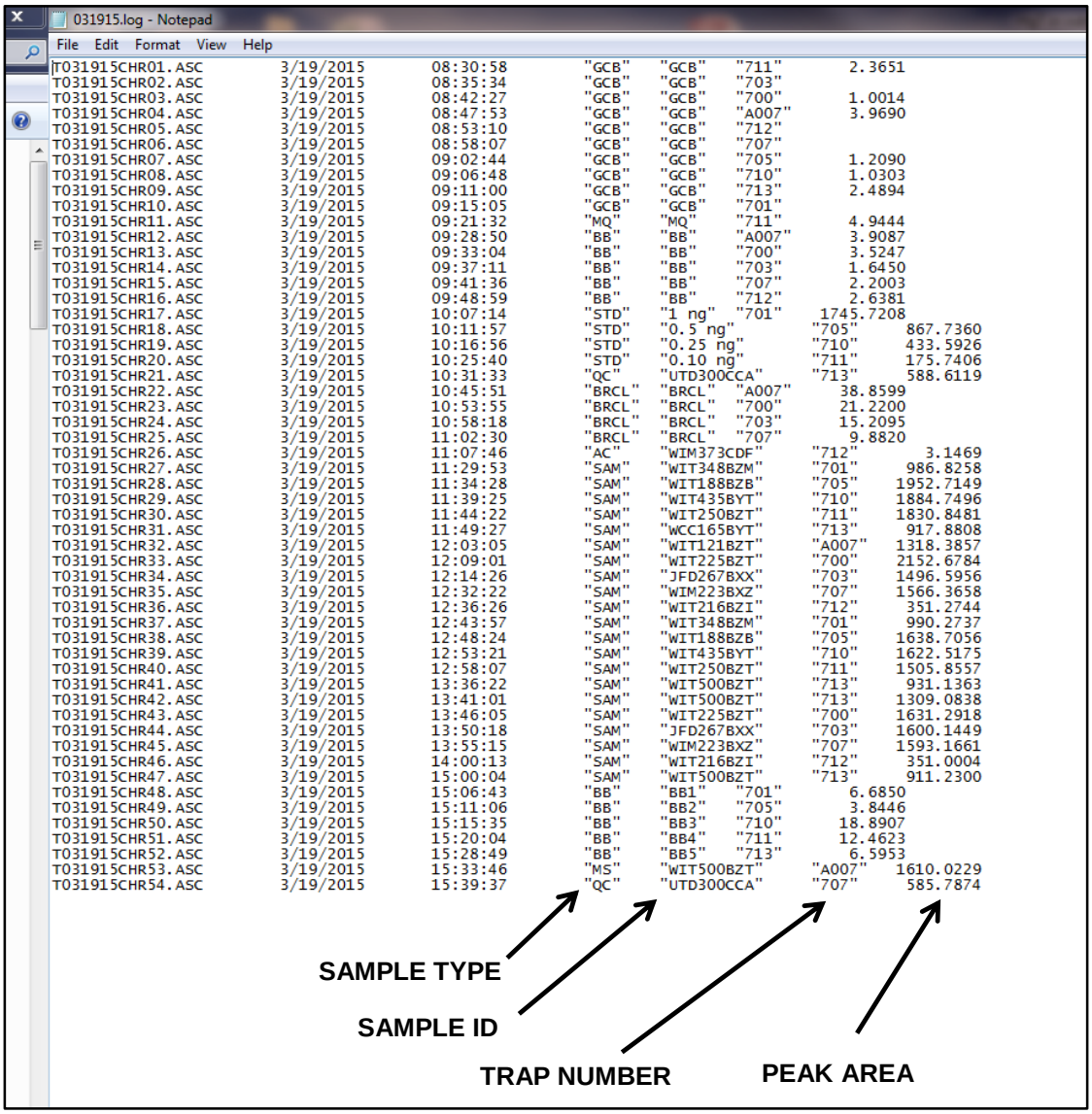
5. The matrix spike recovery should be within 10% of expected value. If the matrix spike fails, set up an additional round and repeat the matrix spike in the same sample as well as in another sample from the batch.

6. The QCS sample should be within 10% of expected value. If a QCS check fails, repeat the original QCS. In the case of subsequent QCS check failures, analyze the original QCS solution along with a new QCS solution.

7. Only proceed to the second batch of 10 samples after the first batch has been successfully analyzed.

Data Capture and Management

1. As the analysis progresses, data will appear in the log file that you created during instrument start up. To open this file, click the PeakNT folder shortcut on the desktop. Within the PeakNT folder, open the folder named for the current year, and then the folder for the day of analysis. The log file should appear as the first file in the list (MMDDYY.log). Header information and the output for each chromatogram are recorded as a new line of text in the log file (see figure below). Once opened, the log file does not update, so as new data are made the file will have to be re-opened.



2. Data from the analysis should be recorded into an Excel spread sheet. Open the Excel template spread sheet for analysis (HG6Data→Total Mercury Data→HgT Method Template.xlsx) and save in the folder with the current year. Name the new Excel file as “T” and then with the current date (eg. T031915.xlsx).

3. In the Excel spread sheet, under the “Analysis” tab, fill out the header information, instrument calibration information, calibration blank information, sample type description, sample identification code, analytical volume, and gold trap number. As the analysis progresses, copy the peak area from the log file and paste it into the Excel spread sheet. See Appendix 1 for an example of a completed analysis spread sheet.

4. In the Excel spread sheet, under the “BrCl” tab, fill out the sample type description, sample identification code, sample full and empty weights, BrCl date and volume, and the BrCl mercury concentration. The BrCl volume and mercury concentrations need to be queried from the Merlins data base. See Appendix 2 for an example of a completed BrCl spread sheet.

5. Instrument calibration statistics and quality control parameters (duplicate sample differences, matrix spike recoveries, and QCS recoveries) will automatically update and can be viewed in the Analysis tab.

Instrument Shutdown

1. Close the Nitrogen gas valve under the hood. Turn off the Nitrogen generator (as long as it is not being elsewhere in the lab).

2. Remove the Soda Lime traps from the impingers.

3. Rinse the purge flasks and impingers with Milli-Q. Fill the flasks to approximately 95% volume with Milli-Q, and add 5 mL of concentrated HCl to each flask.

4. Replace the impinger, cap the inlet and outlet, and store under the laminar flow hood.

5. Leave the final desorbed trap in the analytical train to avoid contamination from ambient air. Reduce gas flow on the detector to the minimum flow possible (approximately 2 mL/min).

Quality Assurance and Control Protocols

Analytical Precision: Every sample should be analyzed in duplicate. For samples with concentrations exceeding 0.12 ng/L, the acceptance criterion of duplicate analysis is less than 10% percent difference. In the case of failure, the sample is reanalyzed until a relative standard deviation less than 10% is achieved or the sample is consumed.

For samples with a concentration less than 0.12 ng/L, the acceptance criterion of duplicate analyses is an absolute difference less than 0.02 ng/L. In the case of failure, the sample is reanalyzed until a standard deviation less than 0.02 is achieved or the sample is consumed.

Repeated failure of sample duplication should be brought to the attention of the quality assurance officer.

Matrix Interference: One sample should be analyzed as an instrument spike for every 10 samples analyzed to assess for matrix interference. Ideally, select a sample with a response between 0.25 – 0.5 ng and add a volume of working standard that approximately doubles instrument response. The recovery of the spike should be 90-110% of the known addition. In the case of failure, repeat the matrix spike in the original sample as well as in another sample from the batch. Repeated failure is an indication of matrix interference and should be brought to the attention of the quality assurance officer.

Instrumental Carryover: Instrumental carryover is assessed with equipment blanks that are analyzed throughout the run. Equipment blank is defined as a previously purged flask that has had 500 μL of $SnCl_2$ added and no new analyte. If an equipment blank is found to contain more than 25 pg of mercury during the course of the analysis, the purging flask is considered contaminated; sample purged in that bubbler should be rerun if possible or carefully evaluated by the quality control officer.

Instrument Calibration Blanks: Instrument calibration blanks are analyzed prior to instrument calibration, and function to assess background mercury levels in the purging flasks, reagents, Soda Lime traps, and analytical train. Calibration blanks are analyzed following an initial round of equipment blanks. Calibration blanks across all five flasks should result in a daily detection limit less than 0.04 ng/L. If this criterion is not met, repeat the calibration blanks in a subsequent round of analysis or correct the problem as necessary.

Instrument Calibration: In the course of analysis of typical environmental samples, calibrate the instrument with a 4 point standard curve and conduct regular checks of instrument calibration throughout the run. Create a standard curve from the analytical standard with masses that span 0.1 – 1.0 ng of mercury. A calibration curve is calculated from linear regression (forced zero

intercept) and must have an r^2 value greater than 0.995. Checks of calibration with the 5 ng/L QCS are conducted immediately after calibration, and after each batch of samples. The recovery of the QCS must be within 10% of the accepted value.

When low levels of mercury (< 1 ng/L) are expected in an entire run of samples, calibrate the instrument with a 4 point standard curve using a low level analytical standard. Create the curve with masses that span 0.025 – 0.2 ng of mercury. Checks of calibration with a 1 ng/L QCS are conducted throughout the run. The same acceptance criteria apply for the low-level calibration curve and QCS checks as do for a typical calibration.

If a QCS check fails, repeat the original QCS. In the case of subsequent QCS check failures, analyze the original QCS solution along with a new QCS solution. Repeated failures indicate that the instrument may require recalibration or that the analytical process is not functioning properly and may need to be corrected.

Maintenance

Purge Flasks: Over time the purge flasks and impinger stems will become coated with a cloudy residue. To prevent/remove this precipitate, fill the flasks with a 2% NaOH solution, install the impingers, and let them soak overnight. Conduct weekly or as needed.

Soda Lime traps: Replace the Soda Lime in the traps daily. Take the traps apart and acid wash weekly.

Nichrome coil: The Nichrome coils for the sample and analytical traps should reach a temperature of 450°C during desorption. Check the temperature of the coils monthly with a blank quartz tube and high temperature thermometer.

Rotometers: Check the flow rate of the nitrogen purge gas quarterly. The flow rate across all five rotometers should be 250 – 300 ml/min.

Detector lamp voltage: Check the lamp light on the front of the detector daily. If it is on, adjust the voltage of the lamp driver on the control board to a voltage of approximately 8. Lamp life is usually 4-6 months. If the lamp voltage will not adjust, the lamp is degraded and needs to be replaced. Seek the assistance of an experienced analyst to adjust lamp voltage or lamp replacement; Instructions can also be found in the Tekran user manual.

Technical Details

Analytical train: A CronTrol model XT multi outlet timer controls the analytical system. The timer is connected to 2 variable current transformers and 2 cooling fans. The transformers are connected to Nichrome coils that are wrapped to fit around the sample traps and the analytical trap. First the sample trap is heated to 450°C with a ramp time of 2 minutes. Then the analytical trap is heated. After the heating of each coil, the corresponding fan is activated to help cool the trap.

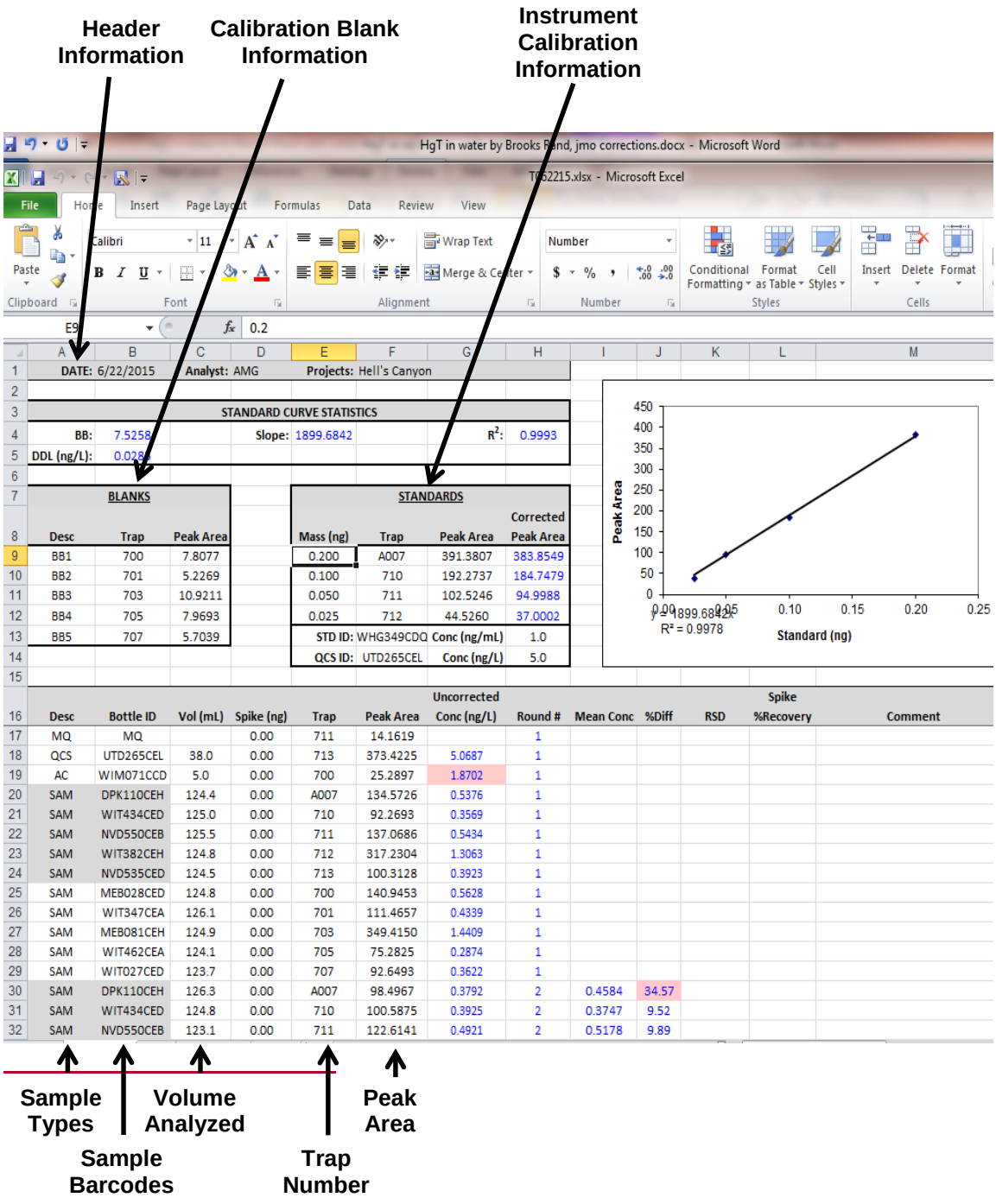
Detector: The detector is a commercially available Model 2500 CVAFS Mercury Detector from Tekran (Toronto, ON) equipped with a mass flow controller capable of maintaining 30 mL/min.

Peak Capture: Peak areas from the instrument response are captured utilizing Peak NT software.

Gold traps: Gold coated bead traps are used for the sample and analytical traps. Gold traps are made at MRL from custom made quartz tubes and gold coated glass beads purchased from Brooks-Rand.

Method source: U.S. Environmental Protection Agency, 2002, Method 1631: Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry: EPA-821-R-02-019, Office of Water, 38 p.

APPENDIX 1. Example of a completed analysis data sheet for water analysis.



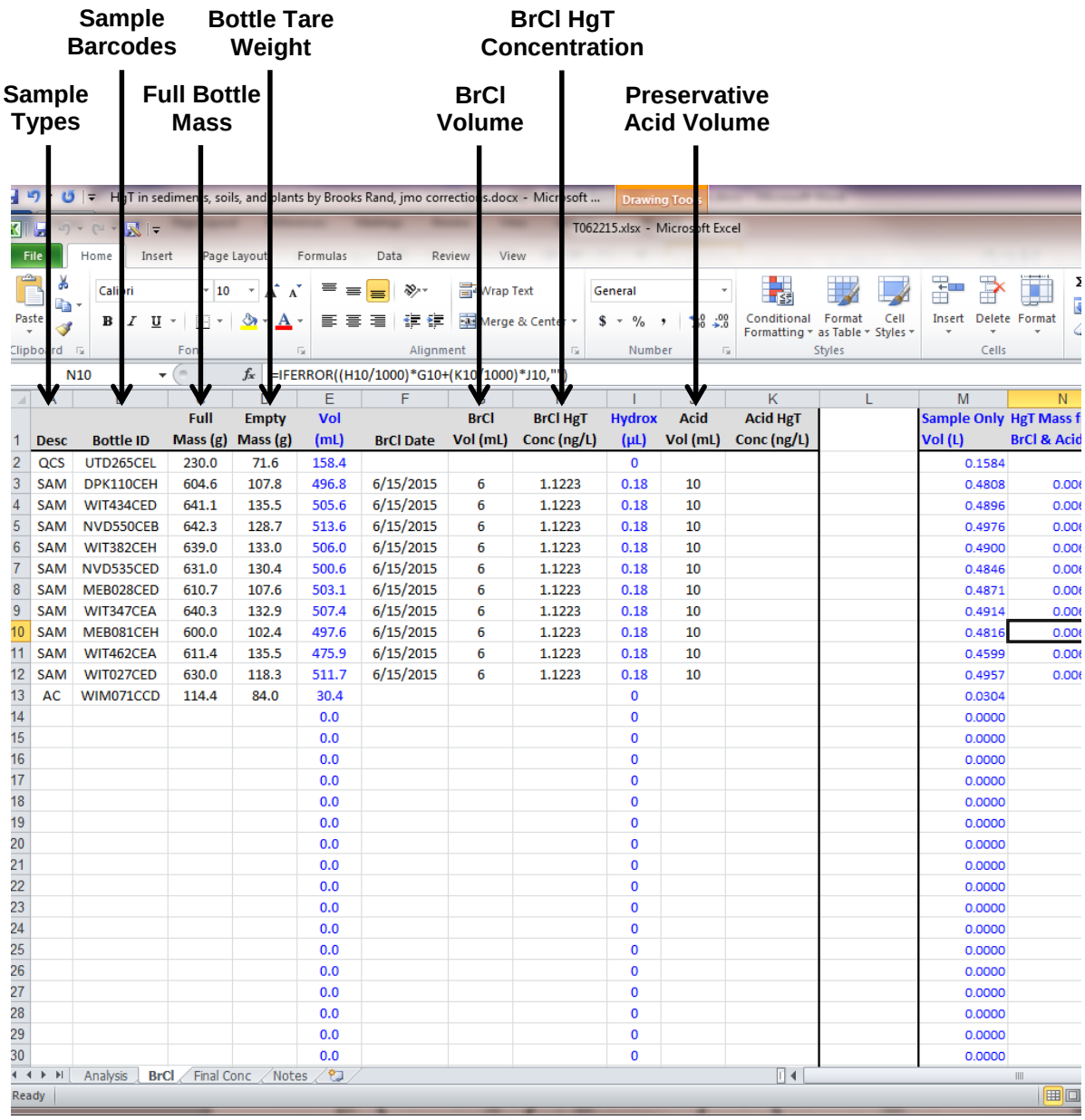
Desc	Trap	Peak Area
BB1	700	7.8077
BB2	701	5.2269
BB3	703	10.9211
BB4	705	7.9693
BB5	707	5.7039

Mass (ng)	Trap	Peak Area	Corrected Peak Area
0.200	A007	391.3807	383.8549
0.100	710	192.2737	184.7479
0.050	711	102.5246	94.9988
0.025	712	44.5260	37.0002

STD ID: WHG349CDQ Conc (ng/mL) 1.0
QCS ID: UTD265CEL Conc (ng/L) 5.0

Desc	Bottle ID	Vol (mL)	Spike (ng)	Trap	Peak Area	Uncorrected Conc (ng/L)	Round #	Mean Conc	%Diff	RSD	Spike %Recovery	Comment
MQ	MQ		0.00	711	14.1619		1					
QCS	UTD265CEL	38.0	0.00	713	373.4225	5.0687	1					
AC	WIM071CCD	5.0	0.00	700	25.2897	1.8702	1					
SAM	DPK110CEH	124.4	0.00	A007	134.5726	0.5376	1					
SAM	WIT434CED	125.0	0.00	710	92.2693	0.3569	1					
SAM	NVD550CEB	125.5	0.00	711	137.0686	0.5434	1					
SAM	WIT382CEH	124.8	0.00	712	317.2304	1.3063	1					
SAM	NVD535CED	124.5	0.00	713	100.3128	0.3923	1					
SAM	MEB028CED	124.8	0.00	700	140.9453	0.5628	1					
SAM	WIT347CEA	126.1	0.00	701	111.4657	0.4339	1					
SAM	MEB081CEH	124.9	0.00	703	349.4150	1.4409	1					
SAM	WIT462CEA	124.1	0.00	705	75.2825	0.2874	1					
SAM	WIT027CED	123.7	0.00	707	92.6493	0.3622	1					
SAM	DPK110CEH	126.3	0.00	A007	98.4967	0.3792	2	0.4584	34.57			
SAM	WIT434CED	124.8	0.00	710	100.5875	0.3925	2	0.3747	9.52			
SAM	NVD550CEB	123.1	0.00	711	122.6141	0.4921	2	0.5178	9.89			

APPENDIX 2. Example of a completed BrCl data sheet for water analysis.



	Desc	Bottle ID	Full Mass (g)	Empty Mass (g)	Vol (mL)	BrCl Date	BrCl Vol (mL)	BrCl HgT Conc (ng/L)	Hydrox (µL)	Acid Vol (mL)	Acid HgT Conc (ng/L)		Sample Only Vol (L)	HgT Mass f BrCl & Acid
2	QCS	UTD265CEL	230.0	71.6	158.4				0				0.1584	
3	SAM	DPK110CEH	604.6	107.8	496.8	6/15/2015	6	1.1223	0.18	10			0.4808	0.00
4	SAM	WIT434CED	641.1	135.5	505.6	6/15/2015	6	1.1223	0.18	10			0.4896	0.00
5	SAM	NVD550CEB	642.3	128.7	513.6	6/15/2015	6	1.1223	0.18	10			0.4976	0.00
6	SAM	WIT382CEH	639.0	133.0	506.0	6/15/2015	6	1.1223	0.18	10			0.4900	0.00
7	SAM	NVD535CED	631.0	130.4	500.6	6/15/2015	6	1.1223	0.18	10			0.4846	0.00
8	SAM	MEB028CED	610.7	107.6	503.1	6/15/2015	6	1.1223	0.18	10			0.4871	0.00
9	SAM	WIT347CEA	640.3	132.9	507.4	6/15/2015	6	1.1223	0.18	10			0.4914	0.00
10	SAM	MEB081CEH	600.0	102.4	497.6	6/15/2015	6	1.1223	0.18	10			0.4816	0.00
11	SAM	WIT462CEA	611.4	135.5	475.9	6/15/2015	6	1.1223	0.18	10			0.4599	0.00
12	SAM	WIT027CED	630.0	118.3	511.7	6/15/2015	6	1.1223	0.18	10			0.4957	0.00
13	AC	WIM071CCD	114.4	84.0	30.4				0				0.0304	
14					0.0				0				0.0000	
15					0.0				0				0.0000	
16					0.0				0				0.0000	
17					0.0				0				0.0000	
18					0.0				0				0.0000	
19					0.0				0				0.0000	
20					0.0				0				0.0000	
21					0.0				0				0.0000	
22					0.0				0				0.0000	
23					0.0				0				0.0000	
24					0.0				0				0.0000	
25					0.0				0				0.0000	
26					0.0				0				0.0000	
27					0.0				0				0.0000	
28					0.0				0				0.0000	
29					0.0				0				0.0000	
30					0.0				0				0.0000	

Appendix 4. Definition of equations.

$$\text{BrCl Corrected Sample Hg Concentration} = \frac{\left(\text{Uncorrected Sample Hg Concentration}\right)\left(\text{Sample Volume}\right) - \left(\text{Mass of Hg From BrCl}\right)}{\left(\text{Sample Volume}\right)}$$

$$\text{Uncorrected Sample Hg Concentration} = \frac{\left(\frac{\left(\text{Sample Peak Area}\right) - \left(\text{Mean Calibration Blank Peak Area}\right)}{\left(\text{Slope of Calibration}\right)}\right)}{\left(\text{Volume Analyzed}\right)}$$

$$\text{Hg Spike Percent Recovery} = \frac{\left(\text{Hg Mass of Spiked Sample Aliquot}\right) - \left(\left(\text{Hg Concentration of Unspiked Sample Aliquot}\right)\left(\text{Volume of Spiked Sample Aliquot}\right)\right)}{(\text{Spike Mass})} \text{ X } 100$$

$$\text{Percent Relative Standard Deviation} = \frac{\left(\text{Standard Deviation of Triplicate Hg Concentrations In Sample}\right)}{\left(\text{Mean of Triplicate Hg Concentrations In Sample}\right)} \times 100$$

$$\text{Duplicate Percent Difference} = \frac{\left(\text{Hg Concentration of Sample}\right) - \left(\text{Hg Concentration of Duplicate}\right)}{(\text{Mean of Sample and Duplicate Hg Concentration})} \text{ X } 100$$

$$\text{Percent Recovery} = \frac{(\text{Analyzed Concentration})}{(\text{Known Concentration})} \times 100$$