

Determination of Total Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry.

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WDML SOP001

1. Scope and Application:

- 1.1. **Applicable Matrices:** This method may be used to determine mercury in filtered or unfiltered water samples.
- 1.2. **Minimum Reporting Limit:** The minimum reporting limit for this method is 0.04 ng/L (nanograms per Liter).
- 1.3. **Dynamic Range:** This method is designed for the measurement of total mercury (Hg) in the range of 0.04 - 8 ng/L. The upper range may be extended to higher levels with the selection of a smaller sample volume.

2. Summary of Method: Bromine Monochloride (BrCl) is added to the sample container to oxidize all forms of Hg to the Hg^{II} oxidation state. After 5 days at 50°C, the BrCl is neutralized by the addition of Hydroxylamine Hydrochloride (NH₂OH·HCl). Following neutralization, Stannous Chloride (SnCl₂) is added to the sample to reduce the Hg from Hg^{II} to Hg⁰. The Hg⁰ is purged onto gold-coated glass bead traps (sample). The mercury vapor is thermally desorbed to a second gold trap (analytical) and from that detected by cold vapor atomic fluorescence spectrometry (CVAFS). Samples high in organic matter may require initial pretreatment in an ultra violet (UV) digester to remove the organic color from the sample.

3. Safety Issues: Before beginning any of the procedures involved in this method, each individual must read and sign the Chemical Hygiene Plan developed for the lab. Specific safety concerns for each chemical can be found in the Material Safety Data Sheets for that chemical – all of which are located in the laboratory. Two extremely important areas for this method are addressed below.

- 3.1. Chronic mercury exposure may cause kidney damage, muscle tremors, spasms, personality changes, depression, irritability and nervousness. Due to the toxicological and physical properties of Hg, only highly trained personnel using extremely cautionary procedures should handle high concentration standards. These cautionary measures include use of gloves and high volume hoods when preparing standards.
- 3.2. Strong acid solutions are employed in the cleaning of equipment, preparation of reagents and in sample preservation. Proper acid handling techniques should be employed whenever acids are being used. These techniques include the use of acid resistant clothing and the utilization of high volume fume hoods.

4. Sample Preservative, Containers, and Holding Times:

- 4.1. Samples are preserved to 1% v/v with the addition of 6N omni pure Hydrochloric Acid (HCl).
- 4.2. Sample containers will consist of Teflon bottles cleaned at the laboratory. New Teflon bottles are rinsed with tap water, and cleaned by immersing in 4 N omni pure HCl heated to 65°C for at least 48 hour. Immediately following removal from the bath, the bottles are immersed in fresh reagent grade water and rinsed at least 3 times with reagent grade water. Following the rinsing step, approximately 100 mL of 1% omni pure HCl is added to each sample bottle and the bottles are

tightly capped. The exterior of the bottles is allowed to air dry under a mercury-free class 100 laminar flow hood. Dry equipment is double bagged in new zip-type bags with the unique identifier and date cleaned written on the outer bag. After the initial 48 hr. cleaning, only 24 hr. is required.

4.3. Properly preserved samples may be held for up to 6 months at the laboratory.

5. Reagents and Standards:

- 5.1. 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 initial and date the reagent container.
 - 5.1.1. Reagent water: Ultra pure reagent grade water shown to be $> 18 \text{ M}\Omega$ starting from pre-purified source (distilled, RO, etc.). The water is delivered through a $0.2 \text{ }\mu\text{M}$ filter. All water is obtained from a Millipore Academic water purification system.
 - 5.1.2. Hydrochloric Acid: EM Science omni pure HCl (containing less than 5 ng/L Hg) or equivalent.
 - 5.1.3. Bromine monochloride (BrCl): Dissolve 27 g of reagent grade Potassium Bromide (KBr) in a 2.5 L bottle of concentrated HCl. Place a Teflon coated stir bar into the bottle and stir for 1 hour. Slowly add 38 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. As you add the KBrO_3 to the solution, the color should change from yellow to red to orange. Cap bottle loosely and allow to stir for an additional hour. The BrCl is analyzed for Hg prior to adding to samples.
 - 5.1.4. Hydroxylamine Hydrochloride ($\text{NH}_2\text{OH}\cdot\text{HCl}$): Dissolve 30 g of $\text{NH}_2\text{OH}\cdot\text{HCl}$ in a Teflon bottle containing 100 mL of reagent water. The solution should be purged with Hg free N_2 at 100 mL/min for 1 hour. Prepare fresh every 6 months.
 - 5.1.5. Stannous chloride (SnCl_2): Add 100 g SnCl_2 to 50 mL concentrated HCl in a 500 mL Teflon bottle. Add 450 mL reagent water. Purge for 1 hour with Hg free N_2 at 100 mL/min. Prepare fresh every 6 months
 - 5.1.6. Nitrogen (N_2): Grade 5.0 (ultra high purity) that is passed through a gold bead trap attached to the outlet of the tank to remove any Hg.
 - 5.1.7. Argon (Ar): Grade 5.0 (ultra high purity) that is passed through a gold bead trap attached to the outlet of the tank to remove any Hg.
- 5.2. Standards: Upon receipt at the laboratory or on the day of preparation, containers should be labeled with the date received or made and the initials of the person preparing them. The stock and substock standards should be stored outside of the clean laboratory to prevent contamination of the entire lab.
 - 5.2.1. Stock standard (1000 mg/L): Commercially available Hg standard verified against a NIST standard reference material. All subsequent standards are prepared using the stock standard. Before preparing other standards, ensure the expiration date of the stock standard has not been exceeded.

- 5.2.2. Substock standard (1000 ng/mL): Dispense approximately 50 mL of reagent grade water and 5 mL of BrCl into a 100 mL mercury clean class A volumetric flask. Pipette 100 μ L of the stock standard (1000 mg/L) and bring to volume with reagent water. To clean the volumetric flask, fill to approximately 20 % total volume with 50% HNO₃, place the ground glass stopper on its side over the opening to prevent pressure buildup, and heat to near boiling on a hotplate for 4 hours.
- 5.2.3. Working standard (10 ng/mL): Dispense approximately 50 mL of reagent grade water and 3 mL of BrCl into a 100 mL mercury clean (sec. 5.2.2) class A volumetric flask. Pipette 1.0 mL of the substock standard (1000 ng/mL) and bring to volume with reagent water. This working standard must be compared to the previous working standard and agree within \pm 5%. Prepare fresh every 6 months.
- 5.3. Quality control sample (QCS): The quality control sample will be prepared from a Hg source different from that used to prepare the standards routinely used for analysis. The QCS is used during analysis runs to verify calibration of the detector. Due to the fact that Hg source standards are only commercially available in concentrated solutions serial dilutions are necessary. The serial dilutions necessary are outlined below.
- 5.3.1. Quality control stock standard (10,000 mg/L): Commercially NIST certified standard reference material 3133. All subsequent quality control standards and samples are prepared using this stock standard. Before preparing other standards, ensure the expiration date of the stock standard has not been exceeded.
- 5.3.2. Quality control substock standard (10,000 ng/mL): Dispense approximately 50 mL of reagent grade water and 5 mL of BrCl into a 100 mL mercury clean (sec. 5.2.2) class A volumetric flask. Pipette 100 μ L of the quality control stock standard (10,000 mg/L) and bring to volume with reagent water.
- 5.3.3. Quality control working standard (10 ng/mL): Dispense approximately 50 mL of reagent grade water and 3 mL of BrCl into a 100 mL mercury clean (sec. 5.2.2) class A volumetric flask. Pipette 100 μ L of the quality control substock standard (10,000 ng/mL) and bring to volume with reagent water. This quality control working standard must be compared to the previous quality control working standard and agree within \pm 5%. Prepare fresh every 6 months.
- 5.3.4. Quality control sample (5 ng/L):
- 5.3.4.1. Dispense approximately 750 mL of reagent grade water and 50 mL of concentrated HCl into a mercury clean (sec. 5.2.2) 1.0 L class A volumetric flask. Pipette 20 mL of BrCl into the volumetric and dilute to volume. Pour this solution into a mercury clean 5 L Teflon bottle.
- 5.3.4.2. Dispense approximately 750 mL of reagent grade water into the same volumetric flask used in sec 5.3.4.1. Pipette 2.5 mL of the quality control working standard into the volumetric and dilute to volume. Add this solution to the 5 L bottle from sec. 5.3.4.1.
- 5.3.4.3. Fill the same volumetric used previously to volume and add to the 5 L bottle containing the HCl, BrCl, and the quality control working standard. Repeat an additional 2 times to bring the final volume to 5 L.
- 5.3.4.4. The QCS is then split into 20 – 250 mL mercury clean Teflon bottles. A new QCS needs to be prepared when 500 mL of the previous QCS remains. The new QCS must be verified against the previous QCS and agree within \pm 5%.

6. **Quality Control:** Each analyst must demonstrate the ability to generate acceptable accuracy and precision with this method. This includes the ability to reproduce standards, establish acceptable daily detection limits (DDL), produce acceptable relative percent differences between replicates, and produce spike recoveries that meet acceptance criteria.

6.1. **Bubbler blanks:** A bubbler blank is prepared by adding 500 μL of SnCl_2 to a bubbler containing approximately 125 mL of mercury free water. The water in the bubbler can be reagent grade water or sample water but must first be reduced with SnCl_2 and purged for 20 minutes to remove all Hg. Blanks are used to determine the amount of Hg contributed from the SnCl_2 . Blanks are critical to the reliable determination of Hg at low levels. Frequent analysis of bubbler blanks is required to demonstrate freedom of system contamination and the absence of carry over from one sample or standard to the next.

- 6.1.1. **Acceptance criteria:** No bubbler blank may contain more than 25 pg of Hg. A daily detection limit (DDL) is calculated each day prior to analysis of samples. The DDL is computed using the following formula:

$$\text{DDL} = ((3 \times \sigma) / M) / 0.125 \text{ L}$$

DDL = standard deviation among peak areas for a set of bubbler blanks purged simultaneously on all bubblers

M = slope of the calibration curve (sec. 6.2.1)

The acceptable value for the DDL must be 0.04 ng/L or less.

- 6.1.2. **Corrective Actions:**

6.1.2.1. If a bubbler blank is found to contain more than 25 pg Hg at the beginning of the day, another set of bubbler blanks should be run to ensure the entire system has been purged and that the value is true. If this second set of blanks is also out of control the analyst must isolate and correct the problem before continuing.

6.1.2.2. If a bubbler blank is found to contain more than 25 pg Hg, during the course of the day's analyses, the system is out of control and data produced on that bubbler should be rerun or carefully evaluated and flagged as being suspect.

6.1.2.3. If the DDL exceeds 0.04 ng/L, another set of bubbler blanks should be run to ensure the entire system has been purged and that the value is true. If this second set blanks is also out of control, the analyst must isolate and correct the problem before continuing.

6.2. **Standards:** A standard is prepared by adding a known volume of working standard and 500 μL of SnCl_2 to a bubbler containing approximately 125 mL of mercury free water. The water in the bubbler can be reagent grade water or sample water but must first be reduced with SnCl_2 and purged for 20 minutes to remove all Hg.

- 6.2.1. **Acceptance criteria:** A slope and R^2 is calculated using the response from the detector to 4 different standards (sec. 7.6.11) using simple linear regression while forcing 0 intercept. The R^2 among the standards must be greater than 0.995.

6.2.2. **Corrective action:** If the R^2 of the standards fails to meet acceptance criteria, an additional set of standards must be run to ensure no operator error exists. If the second set of standards still does not meet acceptance criteria, the analyst must isolate and correct the problem before continuing.

- 6.3. Quality control sample: A QCS must be analyzed prior to sample analysis. A QCS is also analyzed approximately every tenth sample and at the end of the day.
- 6.3.1. Acceptance criteria: The recovery of the QCS must be between 90 and 110% (4.5 and 5.5 ng/L) of the expected value.
- 6.3.2. Corrective actions:
- 6.3.2.1. If the initial QCS analysis fails to meet acceptance criteria, an additional QCS must be run to ensure no operator error exists. If the second QCS still does not meet acceptance criteria, the analyst must isolate and correct the problem before beginning analysis.
- 6.3.2.2. If the QCS, analyzed subsequent to a batch of samples, fails to meet acceptance criteria, an additional QCS must be run to ensure no operator error exists. If the second QCS still does not meet acceptance criteria, the instrument is recalibrated and the QCS is analyzed until statistical control has been reestablished. After control has been reestablished, all routine samples analyzed since the last acceptable QCS measurement are reanalyzed or flagged appropriately.
- 6.3.2.3. If the QCS analyzed prior to or subsequent to a batch of samples fails to meet the acceptance criteria, the samples in that batch must be reanalyzed or flagged appropriately.
- 6.4. Duplicates: All samples are run in duplicate provided there is sufficient volume.
- 6.4.1. Acceptance criteria:
- 6.4.1.1. For samples with concentrations exceeding 0.12 ng/L the acceptance criteria is a relative percent difference (RPD) of $\leq 10\%$.
- $$\text{RPD (\%)} = ((|X_1 - X_2|) / \text{Mean}) \times 100$$
- X1 = Measured value of first replicate*
X2 = Measured value of second replicate
- 6.4.1.2. For samples with concentrations $\leq 0.12\text{ng/L}$ the acceptance criteria is an absolute difference (AD) of $\pm 0.02 \text{ ng/L}$.
- 6.4.2. Corrective action:
- 6.4.2.1. If the RPD or the AD between the two replicates is greater than 10% or 0.02 ng/L, respectively, the sample is analyzed a third time.
- 6.4.2.2. If the relative standard deviation (RSD) between the three replicates is greater than 10%, the sample is flagged and/or analyzed a fourth time.
- $$\text{RSD (\%)} = (\sigma / \text{mean}) \times 100$$
- $\sigma = \text{standard deviation among three replicates}$
- 6.5. Matrix spike: A matrix spike is prepared by adding a known concentration of working standard to a sample. A matrix spike must be analyzed each run or every tenth sample whichever is greater.

6.5.1. Acceptance criteria: Percent recovery for a matrix spike must fall between 90 and 110%.

$$\% \text{ Recovery} = ((M_{MS} - (C_S \times V_S)) / M_S) \times 100$$

M_{MS} = Mass of mercury in spiked aliquot

C_S = Average concentration of sample to which spike was added

V_S = Volume of sample aliquot spiked

M_S = Mass of spike added

6.5.2. Corrective actions:

6.5.2.1. If the percent recovery falls outside the range of 90 to 110%, that same sample should be spiked again to rule out operator error. Another sample from the batch should also be spiked to evaluate the remaining samples in the batch.

6.5.2.2. If percent recovery for the second spike falls outside the range of 90 to 110%, the batch of samples analyzed for that day are flagged identifying probable matrix interference.

7. Sample Preparation and Analysis:

7.1. Low level mercury analysis is a very sensitive procedure and can be influenced by many factors. Following are some common interferences and some helpful hints to consider before attempting this analysis.

7.1.1. Interferences:

7.1.1.1. Free halogens: The destruction of the gold traps occurs if they are exposed to free halogens resulting in inefficient mercury amalgamation. A soda lime trap installed directly upstream of the sample traps during purging limits exposure of the gold traps to free halogens in the sample.

7.1.1.2. Water vapor: Water vapor collected on the gold traps during the purging step results in a false peak during analysis. A soda lime trap installed directly upstream of the sample traps during purging dries the purge gas.

7.1.2. Helpful hints: Protecting samples from contamination cannot be over emphasized when working with detection limits in the parts per trillion range. Extreme caution must be used throughout the preparation, collection and analysis procedures to avoid contamination.

7.1.2.1. It is very important that the laboratory air be low in both particulate and gaseous Hg. The mercury in the air can be reduced with the use of gold-coated cloth at the intakes of the laminar flow hoods.

7.1.2.2. If cloudy residue becomes apparent on the inside of the bubblers, dissolve approximately 2 grams of Potassium Hydroxide in 250 mL of reagent water and allow to soak for 1 hr.

7.2. General description: Bromine Monochloride (BrCl) is added to the sample container to oxidize all forms of Hg to the Hg^{II} oxidation state. After 5 days at 50°C, the BrCl is neutralized by the addition of Hydroxylamine Hydrochloride (NH₂OH·HCl). Following neutralization, Stannous Chloride (SnCl₂) is added to the sample to reduce the Hg from Hg^{II} to Hg⁰. The Hg⁰ is purged onto gold-coated glass bead traps (sample). The mercury vapor is thermally desorbed to a second gold trap (analytical) and from that detected by cold vapor atomic fluorescence spectrometry

(CVAFS). Samples high in organic matter may require initial pretreatment in an ultra violet (UV) digester to remove the organic color from the sample.

7.2.1. Apparatus and Instrumentation

7.2.1.1. Sample preparation

7.2.1.1.1. Ultraviolet light (UV) oxidation: Samples with a high degree of organic color are placed in a UV digestion box until colorless. The digestion box consists of a large box lined with aluminum foil, shiny side out, and contains one 600W UV light. This step may be skipped if the samples are colorless or nearly so. Samples are exposed to UV light when the organic color in the sample may interfere with the color produced from the addition of BrCl (Olson et al 1997).

7.2.1.1.2. BrCl oxidation: After the UV oxidation or a determination that UV treatment is not necessary, the sample is oxidized with the addition of BrCl. The amount of BrCl that is necessary to oxidize the samples may vary from < 1% up to 5% in some cases. To insure complete oxidation, brominated samples are placed into a stainless steel convection oven and heated to 50°C for five days. If the yellow color remains, this indicates excess BrCl in the sample. If the yellow color is absent, additional BrCl is added and the sample is again placed in the oven overnight. Additions of BrCl must be repeated until the sample color indicates the presence of excess BrCl. The BrCl needs to be analyzed prior to each addition to document the amount of Hg added to the sample. Volume of BrCl added, date added, name of person performing the addition and Hg concentration of the BrCl added must be recorded in the database on the day of the addition.

7.2.1.1.3. Neutralization: Excess BrCl in the sample needs to be reduced to limit the presence of free halogens. To reduce the BrCl add 30 µL of NH₂OH·HCl for every 1 mL of BrCl added to the sample. Swirl the sample. The yellow color will disappear, indicating the reduction of the BrCl. Allow the sample to react another 5 min before analysis. Only neutralize samples immediately prior to analysis. Once samples are neutralized, they must be analyzed the same day or flagged appropriately.

7.2.1.2. Purging and preconcentration:

7.2.1.2.1. Regulator capable of supplying 30 psi of pressure.

7.2.1.2.2. Various sizes of Teflon tubing and fittings.

7.2.1.2.3. Flow meter(s) capable of maintaining a N₂ flow of 300 mL/min.

7.2.1.2.4. Needle valve to shut off N₂ flow to bubblers.

7.2.1.2.5. Gold coated glass bead traps: Gold coated glass bead traps are constructed of a 7 mm quartz tube, 4" long and with a constriction at 1¼" from the outlet end. A quartz plug is placed into the inlet end, about 0.7 g (3.5 cm in the tube) of gold coated beads are added and the inlet end is plugged with another piece of quartz wool. Female fittings for gold traps are made from small pieces of 6 mm i.d. monobarb Teflon tubing. Heating ¼" Teflon tubing and sealing one end by pinching with a pliers until cool creates end plugs.

7.2.1.2.6. Bubblers: Bubblers are 250 mL borosilicate glass flasks with the standard 24/40 tapered neck. The sparging stopper has a coarse glass frit that extends to the bottom of the flask.

7.2.1.2.7. Soda lime traps: Soda lime traps are constructed of a 10 mm i.d. Teflon tube with removable custom machined Teflon end plugs. With one end plug installed, place some quartz wool in the end, fill with 4-8 mesh soda lime, and install the final plug. The traps are pre-purged for 20 min before collection of a sample onto a gold trap. Traps should be repacked with fresh soda lime daily.

7.2.1.3. Desorption and analysis

7.2.1.3.1. All-plastic pneumatic fixed-volume and variable pipettes in the range of 5 μ L to 10 mL.

7.2.1.3.2. Analytical balance capable of measuring to the nearest 0.1 g.

7.2.1.3.3. 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.

7.2.1.3.4. 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.

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

7.3. Detailed Procedure:

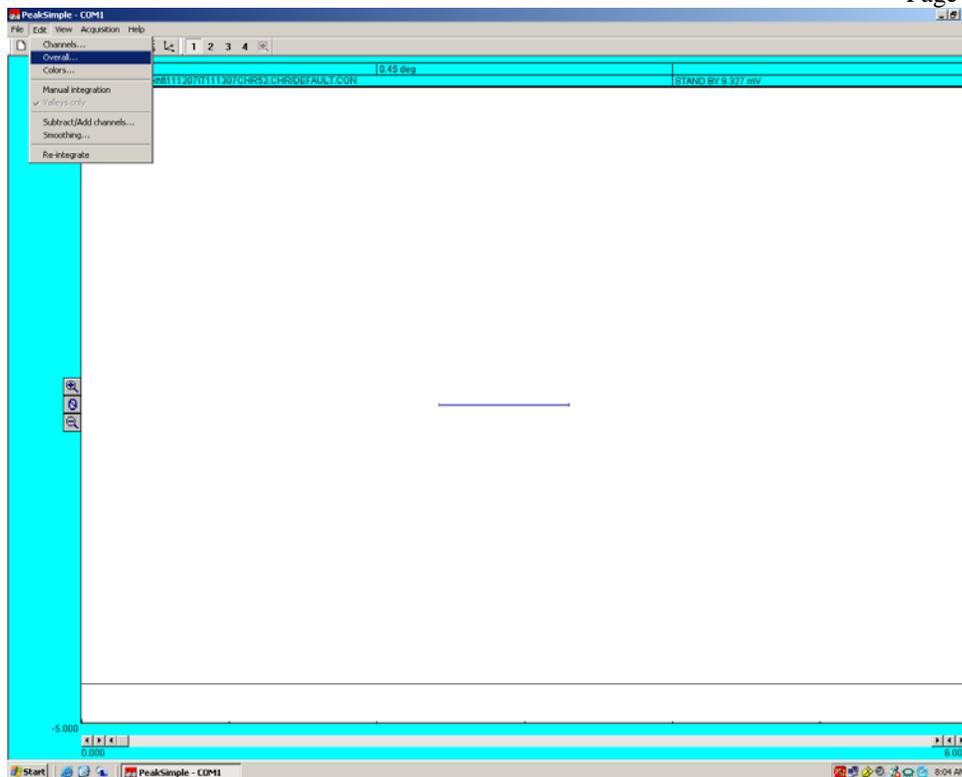
7.3.1. Check pressure in Argon tank to verify adequate volume for the day's analyses.

7.3.2. Adjust mass flow controller at detector to read 30.0 mL/min.

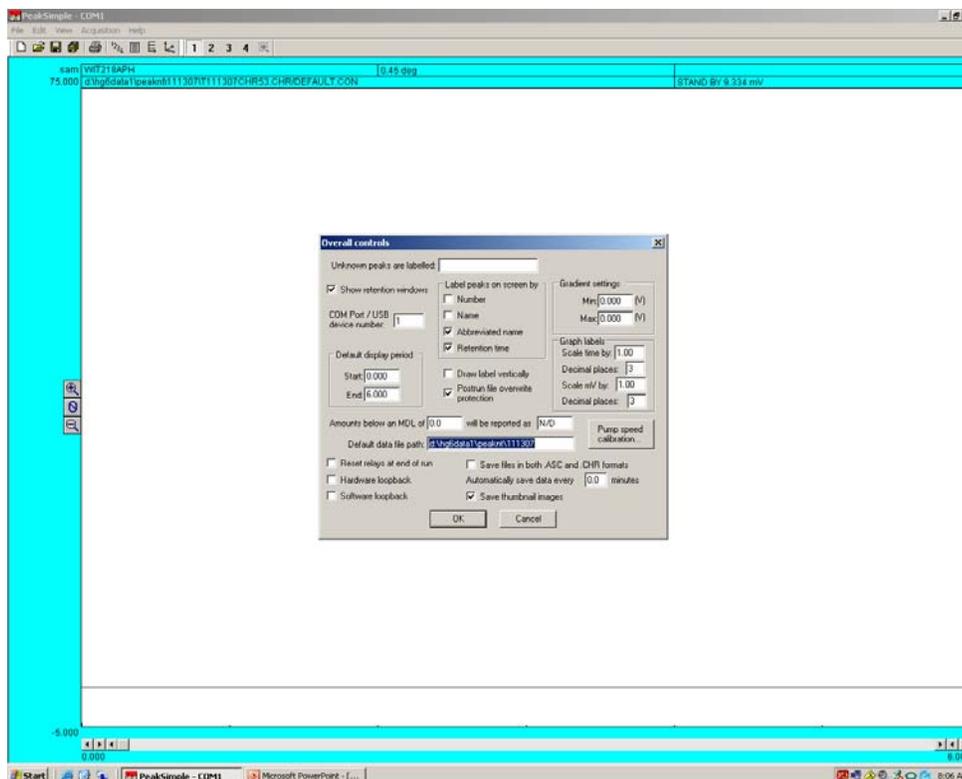
7.3.3. Check baseline at detector, acceptable baseline readings are from 0.0050 and 0.0250. If the baseline is out of that range, adjust by turning the offset knob.

7.3.4. Log onto the computer and create a directory (*MMDDYY*) for the current day's analysis in the *PeakNT* folder.

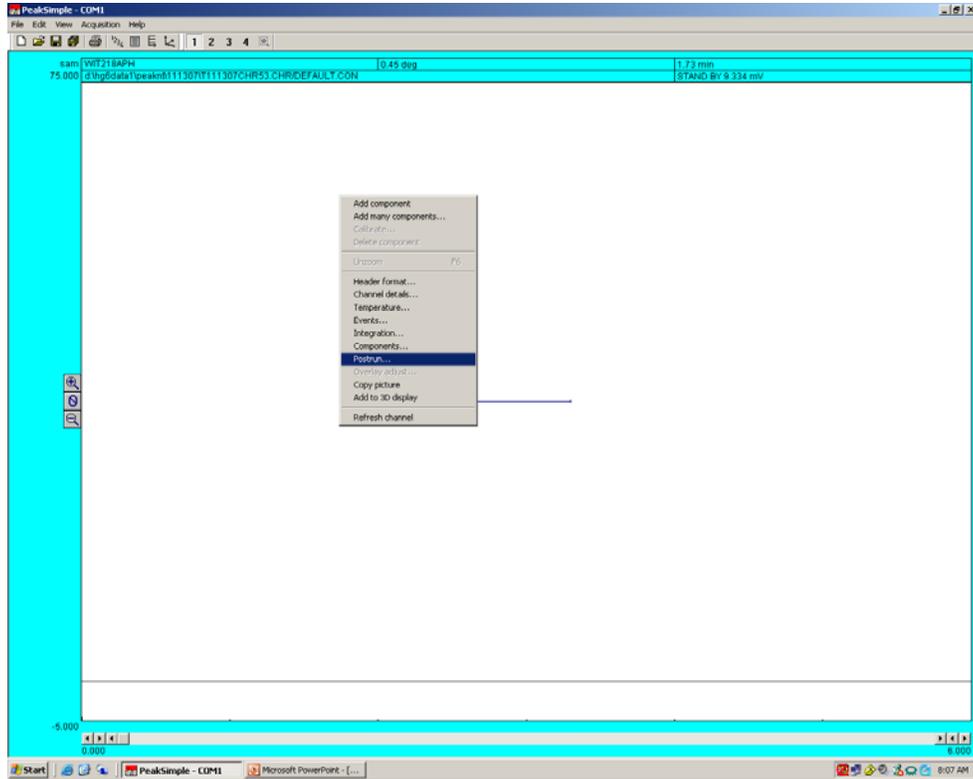
7.3.5. Open *Peak Simple* software and utilizing the *Edit* pull-down menu choose the *Overall* option.



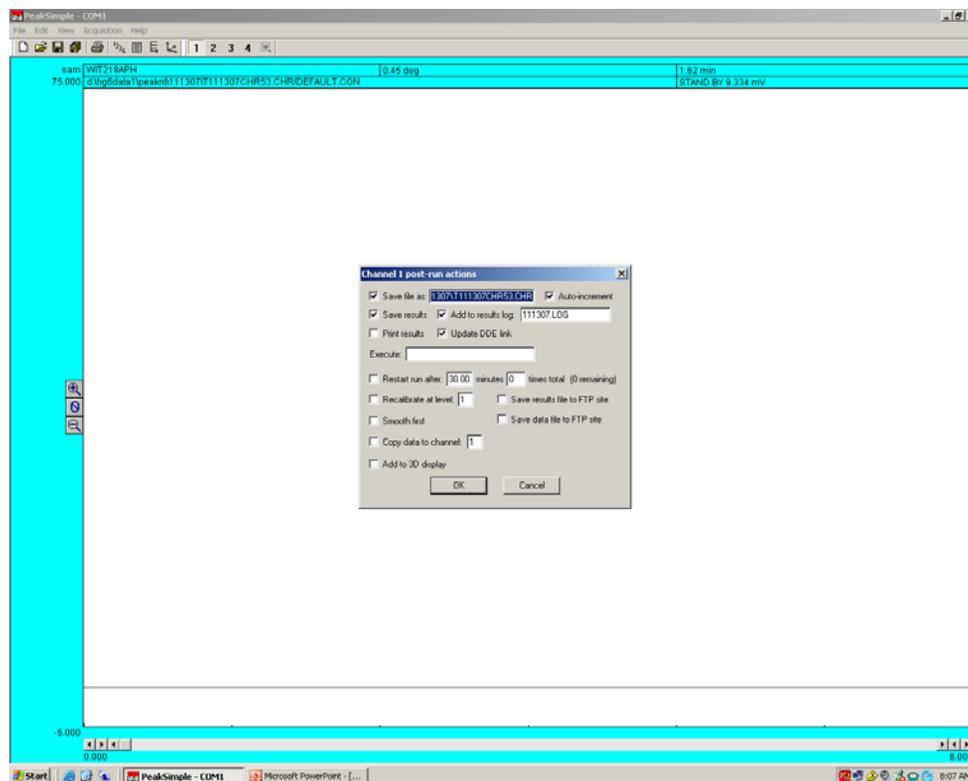
Change the default data path to the folder created in step 7.3.4.



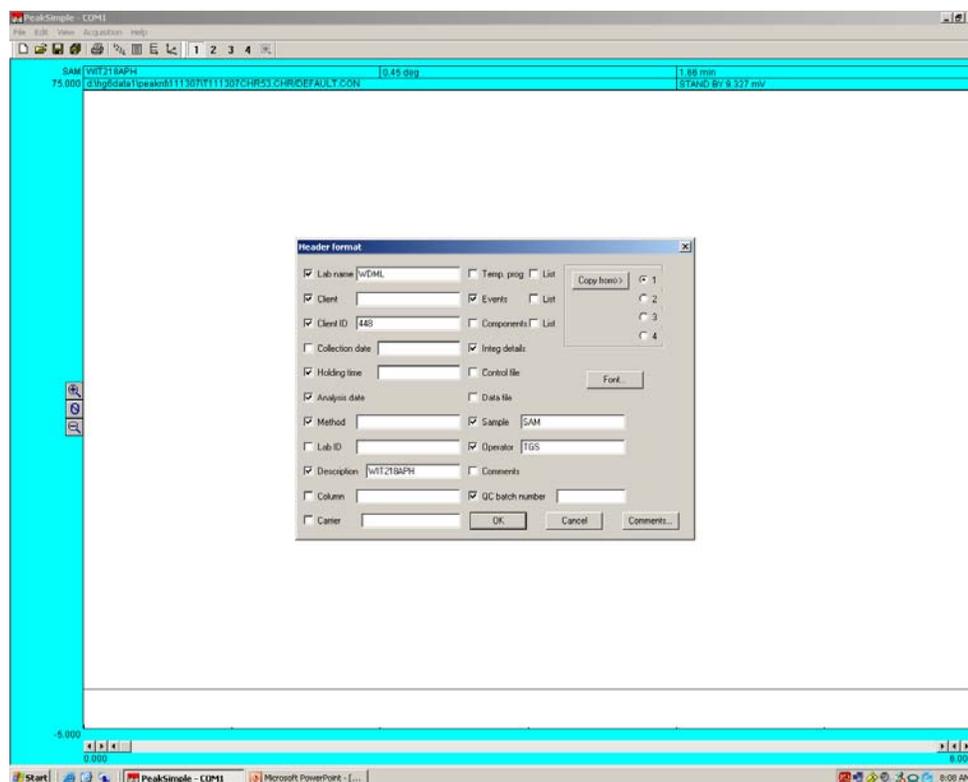
7.3.6. Use the right mouse button while in the Peak Simple window to access the drop-down menu and choose the post-run option.



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**\T**MMDDYY**CHR**XX**.CHR). The .log file also needs to be update to represent the current date in the “save file as” window (**MMDDYY**.log).



7.3.7. Prior to analyzing each trap, use the right mouse button while in the Peak Simple window to access the drop-down menu and choose the *Header* option. Change the “Client ID” field to the present trap number, the “Description” window to the sample ID, and the “Sample” window to the present sample type. Also verify that the “Operator” window contains the correct initials for the analyst.



7.3.8. Sample types are as follows:

Abbreviation	Type of analysis
BB	Bubbler blank
STD	Standard
QCS	Quality control sample
SAM	Environmental sample
MS	Matrix spike
BAT	Bath blank
AC	Preservative acid

7.3.9. Start heating the set of eight sample traps to remove any mercury accumulated since their last use. While these traps are being cleaned proceed with step 7.3.10.

7.3.9.1. Remove the plugs from the ends of the first trap and place it into the analytical train by threading it, with the id number downstream, through the center of the Nichrome wire coil. Center the Nichrome wire over the gold beads and press, in sequence, the buttons labeled **Prog**, **3**, and **run** on the Control timer.

7.3.9.2. After the 5-minute cycle is complete repeat the steps in 7.3.9.1. for each of the remaining traps.

Note: There are 10 traps and five bubblers. The purging of samples takes 20 minutes and the analysis of 5 traps takes 25 minutes, a round of samples will be purging while the previous round is being analyzed. This is the cycle you will follow throughout the day. The table below outlines a typical analytical batch.

Round	Bubbler 1	Bubbler 2	Bubbler 3	Bubbler 4	Bubbler 5
Blanks	BB1	BB2	BB3	BB4	BB5
Standards/QCS	1.00 ng	0.500 ng	0.250 ng	0.100 ng	QCS
Sample set A	S1	S2	S3	S4	S5
Sample set B	S6	S7	S8	S9	S10
Sample set A	S1	S2	S3	S4	S5
Sample set B	S6	S7	S8	S9	S10
Blanks	BB1	BB2	BB3	BB4	BB5
MS/QCS/RERUNS	MS	RERUN/BLANK	RERUN/BLANK	QCS	RERUN/BLANK
Sample set C	SPIKE	QCS	OOPS	OOPS	OOPS
Sample set D	S9	S10	S11	S12	S12
Sample set C	S13	S14	S15	S16	S16
Sample set D	S9	S10	S11	S12	S12
Blanks	S13	S14	S15	S16	S16
MS/QCS/RERUNS	RERUN/BLANK	MS	RERUN/BLANK	RERUN/BLANK	QCS

BB = bubbler blank

SX = sample

SPIKE = matrix spike

RERUN = sample whose replicates do not meet acceptance criteria

7.3.10. While the gold traps are being purged of residual mercury, proceed with two rounds of bubbler blanks. The first round cleans the bubblers and reagent water of residual mercury and is not analyzed for mercury content; the second round is analyzed as analytical blanks.

7.3.10.1. Remove the Teflon plugs from the inlet and outlet of the sparging stopper and thoroughly rinse the bubblers and stoppers with reagent grade water.

7.3.10.2. Dispense approximately 125 mL of reagent grade water into each of the bubblers and add 5 mL concentrated HCl and 500 μ L SnCl₂.

7.3.10.3. Attach the nitrogen lines (with the attached pretrap) to the inlet of the stoppers and the soda lime traps to the outlet of the stoppers, and then tighten the stoppers to the bubblers. Attach a cleaned gold trap to the end of a soda lime trap (with the id number downstream) of one of the bubblers, and the SnCl₂ purge line to the end of that gold trap. Place the other end of the purge line into the SnCl₂ bottle and purge at 300 mL/min with nitrogen for 20 minutes to volatilize residual mercury. Purging SnCl₂ is only necessary once at the beginning of an analytical session and does not need to be repeated with every round.

7.3.10.4. Following this initial purging, begin the analytical bubbler blank round. Shut off the flow of gas to the bubblers, add 500 μ L of SnCl₂, attach a clean gold trap to the end of each soda lime trap (with the id number downstream), and turn on the flow of gas to the bubblers.

7.3.10.5. When the 20-minute purging cycle for the bubbler blanks has elapsed, remove the gold traps from the end of the soda lime traps, cap both ends of the gold traps, and shut-off the flow to the bubblers.

7.3.10.6. Analyze the gold traps as in 7.3.9.1-7.3.9.2.

7.3.11. While the analytical blanks are being analyzed proceed with the standard curve round.

7.3.11.1. Pipette 100, 50, 25, and 10 μL of the working standard into bubblers 1, 2, 3, and 4, respectively. Add 500 μL of SnCl_2 to each bubbler, attach a clean gold trap to the end of the soda lime trap (with the id number downstream), and turn on the flow of gas to the bubblers.

7.3.11.2. When the 20-minute purging cycle for the standard curve has elapsed, remove the gold traps from the end of the soda lime traps, cap both ends of the gold traps, and shut-off the flow to the bubblers.

7.3.11.3. Analyze the gold traps as in 7.3.9.1-7.3.9.2.

7.3.12. While the traps for the standard curve are being analyzed proceed with the QCS round.

7.3.12.1. Add approximately 60 mL of the QCS (sec. 6.3) to about 60 mL of mercury free water (purged water remaining from the previous round) in bubbler 1. Add 500 μL of SnCl_2 to each bubbler, attach a clean gold trap to the end of each soda lime trap (with the id number downstream), and turn on the flow of gas to the bubblers. The QCS establishes system control when it meets the acceptance criteria outlined in sec. 6.3. The additional bubbler blanks demonstrate the amount of carry-over if any exists.

7.3.12.2. When the 20-minute purging cycle for the standard curve has elapsed, remove the gold traps from the end of the soda lime traps, cap both ends of the gold traps, and shut-off the flow to the bubblers.

7.3.12.3. Analyze the gold traps as in 7.3.9.1-7.3.9.2.

7.3.13. When the QCS has been analyzed and found to be within acceptance criteria, neutralize the samples to be analyzed that day with hydroxyl amine. After the reaction time (minimum of 5 minutes) has elapsed proceed with the rest of the rounds as indicated in the chart.

7.3.13.1. To analyze a sample, pour off the volume of water in the bubbler from the previous round, tare the bubbler on the balance, add approximately 125 mL of sample to the bubbler, add 500 μL of SnCl_2 , and proceed as above. If the sample is suspected to have a relatively high mercury content, reduce the volume poured into the bubbler (be sure to pour out only as much volume from the previous round as you plan to add).

7.3.13.2. All samples need to fall within the linear range established by the standards, if the sample peak area is greater than the highest standard, either a higher standard needs to be analyzed or the result is ignored and the sample is analyzed using a smaller volume.

8. Calibration and performance documentation: During the analysis run, the analyst must evaluate the calibration data, bubbler blank values, QCS recovery, and RPDs for duplicate analyses to ensure acceptance criteria (sec. 6.0) are being met. The following information must be recorded on the analysis spreadsheet.

- 8.1.1. Date of analysis.
 - 8.1.2. Type and date prepared for reagents and standards used.
 - 8.1.3. Name of analyst.
 - 8.1.4. Identification of bubbler contents, volume analyzed, instrument response, and sample trap identification for each analysis performed.
 - 8.1.5. Comments pertaining to special samples run, problem samples, corrective actions taken, and results of any calculations performed to ensure acceptance criteria are being met.
- 8.2. Shut-down:
- 8.2.1. After the last sample has been purged, the following steps must be performed to properly store the bubblers until the next analysis run.
 - 8.2.1.1. Shut off N₂ flow at the needle valve and at the tank regulator.
 - 8.2.1.2. Remove the N₂ line from the inlet and the soda lime trap from the outlet of the bubblers.
 - 8.2.1.3. Thoroughly rinse the bubblers and the sparging stoppers with copious amounts of reagent grade water.
 - 8.2.1.4. Fill the bubblers to approximately 95% volume with reagent grade water, add 5 mL of concentrated HCl.
 - 8.2.1.5. Carefully replace the sparging stopper, cap the inlet and outlet of the bubbler and return to the laminar flow hood.
 - 8.2.2. After the last sample trap has been analyzed, leave the trap in the analytical train to avoid contamination from room air. Reduce flow at the mass flow controller to the minimum flow allowable (approximately 2 mL/min).
- 8.3. Maintenance, maintenance records and Responsibilities
- 8.3.1. Gold traps attached to regulators on the N₂ and Ar tanks should be burned clean every time a tank is changed.
 - 8.3.2. Nichrome wire temperature should be checked quarterly.
 - 8.3.3. Detector lamp driver voltage should be checked quarterly. If voltage exceeds 12.5, the lamp should be adjusted or replaced according to manufacturer's guidelines.
- 8.4. Calculations
- 8.4.1. Uncorrected concentrations: The uncorrected (for additions of mercury from preservation and bromination) concentrations must be calculated during analysis to ensure acceptance criteria are being met. The following formula is used to calculate the uncorrected concentration for environmental and QC samples.

$$C = ((PA_s - BB_m) / M) / V_s$$

C = concentration in ng/L

PA_s = peak area of sample, in PA units

BB_m = mean bubbler blank, in PA units (sec. 6.1)

M = Slope from calibration curve

V_s = volume of sample purged, in liters

- 8.4.2. Final (corrected) concentrations: The raw data from the Peak NT software is imported into an EXCEL spreadsheet which calculates final concentrations using the same basic formula as above. The uncorrected value is then adjusted by subtracting additional Hg added to the sample during bromination.
- 8.5. Data validation and evaluation: After the data has been entered into the EXCEL spreadsheet, someone other than the analyst must verify that no values have been incorrectly entered in the spreadsheet. The data is then evaluated carefully by the QC officer to ensure all data quality objectives have been met for the batch.
- 8.6. Reporting:
- 8.6.1. Reporting units: Total mercury as ng/L Hg.
- 8.6.2. Reporting levels and significant figures:
- 8.6.2.1. Report to the nearest 0.01 ng/L for values less than 10 ng/L.
- 8.6.2.2. Report to three significant figures for values exceeding 10 ng/L.
- 8.6.3. Data transfer: After the data has been verified in the EXCEL spread sheet it may be uploaded into the database and transferred to the customer via e-mail, hard copy, or the internet.
9. Archiving: All raw data produced in the laboratory is archived electronically and backed up daily. Hard copies of EXCEL spreadsheets and data reports are archived electronically on the drive of the laboratory operations manager's computer and backed up daily.
10. References
- 10.1. Method source:
- 10.1.1.1.1. 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.
- 10.1.1.1.2. Olson, M.L. Cleckner, L.B., Hurley, J.P., Krabbenhoft, D.P., Heelan, T.W. 1997, Resolution of matrix effects on analysis of total and methyl mercury in aqueous samples from the Florida Everglades: Fresenius Journal Analytical Chemistry. 358: 392-396
- 10.2. Deviations from source method and rationale:
- 10.2.1. Method 1631 states that a 100 mL aliquot of sample should be poured into a clean 125 mL bottle before bromination and neutralization. To avoid the potential contamination associated with this transfer, this procedure recommends bromination and neutralization in the original sample bottle. Bromination in the original sample container also has the benefit of stripping any mercury that may have adhered to the container wall.

- 10.2.2. Gold coated glass bead traps are used in place of sand traps. There are two advantages to glass beads 1) less back pressure and 2) the ability to handle higher temperatures during analysis which provides cleaner burning traps (Olson et al 1997).
11. To increase the confidence in the analytical result obtained using this procedure, all samples are analyzed in duplicate, which is not required in Method 1631.
12. Method 1631 establishes bubbler blank control limits at 50 pg. This method sets the control limits for bubbler blanks at 25 pg.