Standard Operating Procedure for the Determination of Methyl Mercury in Water and Suspended Solids by Aqueous Phase Ethylation, Followed by Gas Chromatography Separation with Cold Vapor Atomic Fluorescence Detection.

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WDML SOP005

Application:

Applicable Matrices: This method may be used to determine methyl mercury (MeHg) concentrations in filtered or unfiltered water samples.

Minimum Reporting Limit: ≤0.040 ng/L (nanograms per liter).

Dynamic Range: This method is designed for the measurement of MeHg in the range of
0.040 - 5 ng/L. The upper range may be extended to higher levels by distilling a smaller sample volume or ethylating a smaller aliquot of the distillate.

Method Summary: Water samples are distilled to remove potential interferences. The pH of the distillate is adjusted to 4.9 using acetate buffer. The distillate is then ethylated using sodium tetraethyl borate (NaTEB) and allowed to react for 15 minutes. Following reaction with NaTEB the distillate is purged with grade 5 nitrogen gas (N_2) for 20 minutes and the ethylated mercury species are collected on a Carbotrap. The ethylated mercury species are thermally desorbed from the Carbotrap, separated using a gas chromatography (GC) column, reduced using a pyrolytic column, and detected using a cold vapor atomic fluorescence spectrometry (CVAFS).

Interferences:

The distillation procedure is intended to eliminate interferences from the water sample during the ethylation and analysis procedure.

Large amounts of water vapor absorbed onto the carbotraps during bubbling will cause an instrument response in excess of system sensitivity. The response from the water vapor will mask the response from the ethylated mercury species in the sample, resulting in loss of the sample.

Apparatus and instrumentation:

Flow meter(s) equipped with needle valves to maintain a N_2 flow of 250 mL/min.

Reaction vessels are 250 mL Erlenmeyer flask with the standard 24/40 tapered neck. A sparging stopper fitted with a special four-way valve is used to close the reaction vessel. The four-way valve allows the sample to react with the ethylating reagent in a closed environment, then to be purged onto the Carbotrap without opening the flask.

The Carbotraps are constructed of a 7 mm quartz tubes, 10 cm long with a constriction at 3 cm from the outlet end; about 0.2 g (3 cm in the tube) of Carbotrap (graphitized carbon black, Supelco 2-0287 or equivalent) is placed in the center and contained by quartz wool plugs at either end. Small pieces of 7 mm Teflon tubing are friction fit to the ends of the sample traps to provide a connection point between the sample trap and the reaction vessel and in the analytical train.

End plugs are created by heating ¼" Teflon tubing and sealing one end by pinching with pliers.

Sample volume is measured with an analytical balance capable of measuring to the
nearest 0.1 g.

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

A simple contact switch, connected to a timer, controls the analytical system. The timer is connected to a transformer, which is then connected to a Nichrome wire coil wrapped to fit around the Carbotrap. The Carbotrap is heated to 250^{o}C with a ramp time of 30 seconds. The detector analog output is captured by PeakSimple or similar chromatographic software.

The gas chromatographic column is a 4 mm i.d., 6 mm o.d., glass column 50cm long and filled with Chromosorb WAW-DMSC 60/80 mesh (Supelco 2-0152) enclosed in a glass sheath 2 cm in diameter and 25 cm long. This column is housed in a cylindrical oven connected to a transformer, which supplies a constant voltage to maintain a temperature of 95 +/- 5^{o}C.

The Pyrolytic column consists of a is a 7 mm quartz tube 15 cm in length with the center 4-5 cm filled with quartz wool. Small pieces of 7 mm Teflon tubing are friction fit to the ends of the pyrolytic column to provide a connection point

in the analytical train. A length of Nichrome wire is wrapped around the tube to cover the length of quartz wool. The wire is connected to a transformer that heats it to approximately 800^0C. The column reduces all oxidized mercury species to Hg^0.

The detector is a commercially available Model 2500 CVAFS Mercury Detector from Tekran (Toronto, ON) equipped with a mass flow controller capable of measuring 25 mL/min.

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 initial and date the reagent container.

Reagent water: Ultra pure reagent grade water shown to be > 18 MΩ starting from pre-purified source (distilled, RO, etc.). The water is delivered through a 0.2 uM filter. All water is obtained from a Millipore Academic water purification system.

Acetate buffer: Dispense approximately 50 mL of reagent water and 11.8 mL of glacial acetic acid into a 100 mL mercury clean class A volumetric flask. Add 27.2 g reagent grade sodium acetate to this solution and dilute to mark with reagent grade water. Transfer buffer to 125 mL mercury clean Teflon bottle for storage. This solution has an indefinite shelf life.

Ethylating Reagent: Sodium Tetraethyl Borate (NaTEB) is purchased in 1 gram (Strem 11-0575) sealed bottles and kept in the freezer. In a 125 mL Teflon bottle, dissolve 2 g Potassium Hydroxide (KOH) in 100 mL of reagent grade water and chill to 0^oC . When the KOH solution becomes slush remove a bottle of $NaBEt_4$ from the freezer, remove the tape seal and rinse the outside of the bottle with water. Open bottle and pour in about 5 mL of the KOH solution, recap and shake to dissolve. Pour the $NaBEt_4$ solution into the 125 mL bottle and shake to mix. Immediately, the 1% NaTEB in 2% KOH solution is divided equally into 9 clean 15 mL Teflon vials that are capped and frozen. The date prepared is written on the vial rack. This solution should be kept frozen and made fresh every 2 weeks. Never use NaTEB

solid or solutions that are yellow in color. *Note: NaTEB is toxic, gives off toxic gases (triethylboron) and is spontaneously combustible. Any NaTEB use should take place in a high-volume fume hood. To discard unused portions of ethylating reagent, empty bottles into a large beaker of 6N hydrochloric acid (HCl) inside a high volume fume hood. Place beaker on a hotplate and boil down to half-volume then discard the remaining solution as an acid waste. Triethylboron will boil off into the air where it is oxidized to boric acid.*

Argon (Ar): Ultra high purity grade 5.0 Ar is used as the carrier gas in the analytical system. The Ar is first passed through a gold bead trap attached to the outlet of the tank to remove any Hg.

25% $CuSO_4$ solution: In a 500 ml Teflon bottle, add 125 g $CuSO_4$ and bring up to 500 ml volume with reagent water. Shake well until all solids dissolve.

Standards

Upon receipt at the laboratory or on the day of preparation, standards should be labeled with the date received or made and the initials of the person preparing them. Highly concentrated stock solutions should be stored away from the main working areas to prevent contamination of the clean lab. Working standards and (if necessary) subsequent sub-stock dilutions should be made in a class A volumetric flask in a matrix of reagent grade water at a 2% and 0.2% concentration of glacial acetic acid and hydrochloric acid, respectively. This solution should be transferred to a Teflon bottle designated specifically for mercury standards, stored in an amber bag at 4^{o} C, and remade every 6 months. All standards must be assigned a unique letter-number-letter identification code and be entered into the laboratory database system. For working solutions of native MeHg, allow the solution to equilibrate for at least 24 hours and then determine the concentration by analysis via cold vapor atomic fluorescence spectrometry as follows:

1. Mass of mercury in the MeHg standard: To four 15 ml Teflon vials, add 8.0 ml of reagent grade water, 1.000 ml of the MeHg working standard, and 1.0 ml of BrCl.

2. Blank contribution of mercury: To four 15 ml Teflon vials, add 9.0 ml of reagent grade water and 1.0 ml of BrCl.

3. Store the vials in a rack, seal in a bag, and heat in an oven to 50^{o} C for eight hours.

4. Analyze the contents of the eight Teflon vials by EPA method 1631.

5. Analyze four 1.000 ml additions of the MeHg working standard to determine the $SnCl_2$ reducible fraction of Hg^{II}

6. Subtract the average blank mercury mass and the $SnCl_2$ reducible fraction of Hg^{II} from the total mercury mass determined MeHg working standard to determine the actual MeHg mass in the vials and subsequent concentration.

Sample Preservative, Containers, and Holding Times:

Samples are preserved by acidifying to 1% HCl with mercury clean HCl. After acidification samples should be kept in the dark to prevent photodegradation of methylmercury.

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 trace pure HCl heated to 65^{o}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, each bottle is filled to 25% with 1% trace pure HCl and 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 a 24 hr. soak is required.

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

Distillates should be analyzed within 48 hours of distillation.

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.

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 vinyl gloves and high volume hoods when preparing standards.

Strong acid solutions are employed in the cleaning of equipment and preparation of reagents. 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.

$NaTEB_4$ is toxic, gives off toxic gases (triethylboron) and is spontaneously combustible. Any $NaTEB_4$ use should take place in a high volume fume hood. To discard unused portions of ethylating reagent, in a high volume fume hood empty bottles into a large beaker of 6N hydrochloric acid (HCl). Place beaker on a hotplate and boil down to ½ volume then discard remaining solution as an acid waste. Triethylboron will bubble off to the air where it is oxidized to harmless boric acid.

Quality Control:

Ethylation blanks: Five ethylation blanks are prepared by adding approximately 100 mL of reagent grade water, 200 µL of acetate buffer, and 100 µL of NaTEB to separate reaction vessels. Ethylation blanks are used to measure and correct for bias created during the reaction and analysis processes.

Acceptance criteria: The maximum acceptable absolute concentration for any one ethylation blank must not exceed 2 picograms (pg).

Corrective actions: If the absolute concentration of any one ethylation blank exceeds 2 pg, another set of ethylation blanks should be run to ensure no operator error. If this second set of blanks is also out of control the analyst must isolate and correct the problem before continuing.

Standards: Create a standard curve by adding varying amounts of working standard (typically 200, 100, 50, 20, and 10 µL, but the range needs to cover the expected concentrations in the analytical batch) to approximately 100 mL of reagent water in each of the reaction vessels. Pipette 200 µL of acetate buffer and 100 µL of NaTEB to each of the reaction vessels. Check standards are analyzed throughout the run to verify that no instrument drift exists.

Acceptance criteria:

Peak areas obtained for the standards during the calibration are corrected for CH_3Hg^+ in the acetate buffer and the NaTEB by subtracting the average peak area of the ethylation blanks. Simple linear regression while forcing zero intercept is applied to the peak area / mass combinations to determine the best-fit line (DQO is r^2 equal to or greater than 0.995) and establish the equation used to determine the mass of the sample aliquot from its resulting peak area.

The check standards are evaluated with the following formula for percent recovery. The acceptance criterion for the check standards is 80 to 120 % of expected concentration.

$$\%R = ((PA_C - PA_{EB})/M)/(V_S * C_S) * 100$$

%R – Percent recovery
PA_C – Peak area of check standard
PA_{EB} – Average peak area of ethylation blanks
M – Slope of calibration line
V_S – Volume of standard added
C_S – Concentration of standard added

Corrective actions:

If the r^2 for the initial set of standards falls outside the acceptable range, another set of standards should be run to ensure no operator error. If this second set of standards is also out of control the analyst must isolate and correct the problem before continuing.

If the check standards fail to meet acceptance criteria, a set of standards equivalent to the first set of standards must be analyzed.

Method blank (MB): Method blanks are prepared according to MeHg_distillation_SOP. The method blanks are used to measure and correct for bias created during the distillation process.

Acceptance criteria:

The maximum acceptable absolute concentration for any one method blank must not exceed 5 picograms. The following formula is used to calculate the absolute MB concentration.

$[MB] = (PA_{MB}/M)/D$

[MB] = absolute concentration of the MB in ng
PA_{MB} = peak area of the MB
M = slope of calibration line
D = fraction distilled

Absolute MB concentrations are used to calculate an absolute detection limit for the day using the following formula.

$[DL] = 3 \times \sigma_{[\underline{MB}]}$

[DL] – absolute detection limit
$\sigma_{[\underline{MB}]}$ – standard deviation among absolute method blanks

A daily detection limit (DDL) is calculated for each sample from the absolute detection limit in a sample batch by the following formula and may not exceed 50 picograms per liter (pg/L).

$DDL = (([DL]/D) \times (V_D / V_A))/V_S$

DDL = daily detection limit
D = fraction distilled
V_D = total volume of distillate, in liters
V_A = volume of distillate analyzed, in liters
V_S = volume of sample, in liters

Corrective actions: If the distillation blanks fail to meet either of the acceptance criteria, the entire batch of samples must be distilled and analyzed again or flagged accordingly.

Matrix spikes: A matrix spike and matrix spike duplicate are prepared by adding a known concentration of working standard to a sample prior to distillation and treating like a sample from that point forward. Matrix spikes are used to evaluate the efficiency of the distillation and accuracy of the analysis.

Acceptance criteria: The percent recovery of the matrix spike and matrix spike duplicate must fall between 75 and 125% and the difference between the recoveries must not exceed 25%. Percent recovery is calculated as follows:

$$\%R = (MS - (S \times (V_{MS} / V_S)) / STD$$

%R - percent recovery
MS - mass of methylmercury in spiked sample
S - mass of methylmercury in unspiked sample
V_{MS} – volume of spiked sample
V_S – volume of unspiked sample
STD - mass of methylmercury added to sample

Corrective actions: There are 6 possible combinations when comparing the MS/MSD pair to the above listed acceptance criteria. The 6 combinations and the corresponding corrective actions are listed below.

Both recoveries are between 75 and 125%, and the difference is less than or equal to 25%. No corrective action.

Both recoveries are between 75 and 125%, but the difference is greater than 25%. All samples are flagged with S1.

Recovery for one is between 75 and 125%, one is outside this range, and the difference is less than or equal to 25%. All samples are flagged with S2.

Recovery for one is between 75 and 125%, one is outside this range, and the difference is greater than 25%. All samples are flagged with S3.

Both recoveries are outside acceptable range and the difference is greater than 25%. All samples are

distilled and analyzed again with resulting values flagged as R.

Both recoveries are outside acceptable range but the difference is less than or equal to 25%. All samples are flagged M.

Detailed procedure:

Helpful hints:

When working with detection limits in the parts per trillion range, protection of these samples from contamination cannot be over emphasized. The greatest difficulty in low level MeHg analysis is preventing the samples from becoming contaminated. Extreme caution must be used throughout the bottle preparation, collection, and distillation procedures to avoid contamination.

Extreme caution should be exercised during bubbler rinsing to avoid residual water in the four-way valve. If water is apparent in the valve, use a cotton swab to remove it before allowing flow through the carbotrap.

Sample preparation:

A typical water distillation contains 30 samples, four blanks, and three duplicate spikes. For suspended solids, the distillation contains 32 samples, two SRM, four blanks. The distillation method for suspended solids is similar to that of waters and details are published in DeWild *et al.* 2004. In small sample sets (< 16), four method blanks, and one duplicate spike should be included in each run.

1. Throughout the distillation process, it is important for the analyst to develop and maintain a structured and organized system. Each distillation and receiving vessel has a unique identification code etched onto the wall. The corresponding vials must be appropriately linked to each other, as well as back to the original sample. Good record keeping must occur not only throughout the distillation process, but must be similarly well documented in the Excel data sheet. See Appendix 1 for more details.

   Example: Sample Id → Distillation vial #001 → Receiving vial → #100

   A template of the Excel data sheet can be found at: HG4\hg4data\.

2. Before beginning sample setup, turn on the aluminum block heater so that it can reach temperature while samples are being prepared.

3. Arrange an adequate number of clean Teflon distillation and receiving vials into four wire racks.

4. Weigh approximately 60 grams of sample (or reagent water for method blanks) into each of the distillation vials. Be sure to homogenize the sample by inverting the sample bottle several times before dispensing to the distillation vial. Setup two samples in triplicate for the duplicate spike analysis. Be sure that you record the sample ID, distillation vial ID, distillation vial tare weight, and the sample mass into the appropriate places in the Excel data sheet.

5. To each of the distillation vials, add 1 ml of 25% $CuSO_4$ solution. The method blanks should be acidified with 600 µl of concentrated HCl.

6. Add 100 µl of the working standard to each of the duplicate spike samples.

7. Fit each distillation vial with a combined distillation cap/transfer tube assembly corresponding to the block position to be occupied by that vial (each cap has been engraved with a number between 1 and 40).

8. To each of the receiving vials, add 40 ml of reagent water. Be sure that you record the receiving vial ID and receiving vial tare weight.

9. Fit each receiving vial with a distillation cap corresponding to the rack position to be occupied by that vial (each cap has been engraved with a number between 1 and 40).

10. Place the distillation vials in the bore holes of the preheated (approximately 120º C) aluminum block. Attach an argon gas line to each of the distillation caps and ensure that gas flows through the sample.

11. In an ordered manner, thread the transfer tubes through the Teflon ports in the side of the cooler.

12. In the cooler, attach each transfer tube to the corresponding receiving vial. Ensure that gas flows in the reagent water of the receiving vial.

13. Throughout the distillation, check the temperature of the heating block often. Adjust to maintain a temperature of 121º C (± 5).

14. Check the distillation vials regularly. Samples are finished distilling when approximately 25% of the original sample is left.

15. Once a sample is finished, disconnect the transfer tube from the receiving vial and the gas line from the distillation cap. Cover the gas inlet port of the distillation cap quickly with a gloved finger to keep the sample in the vial from discharging.

16. Thoroughly rinse the combined distillation cap/transfer tube assembly with copious amounts of reagent water. Place the caps in the laminar flow hood to dry.

17. Once the entire distillation is finished, remove the receiving vials from the cooler and remove the distillation caps. Record the mass of the receiving vial in the Excel data sheet and attach a standard cap.

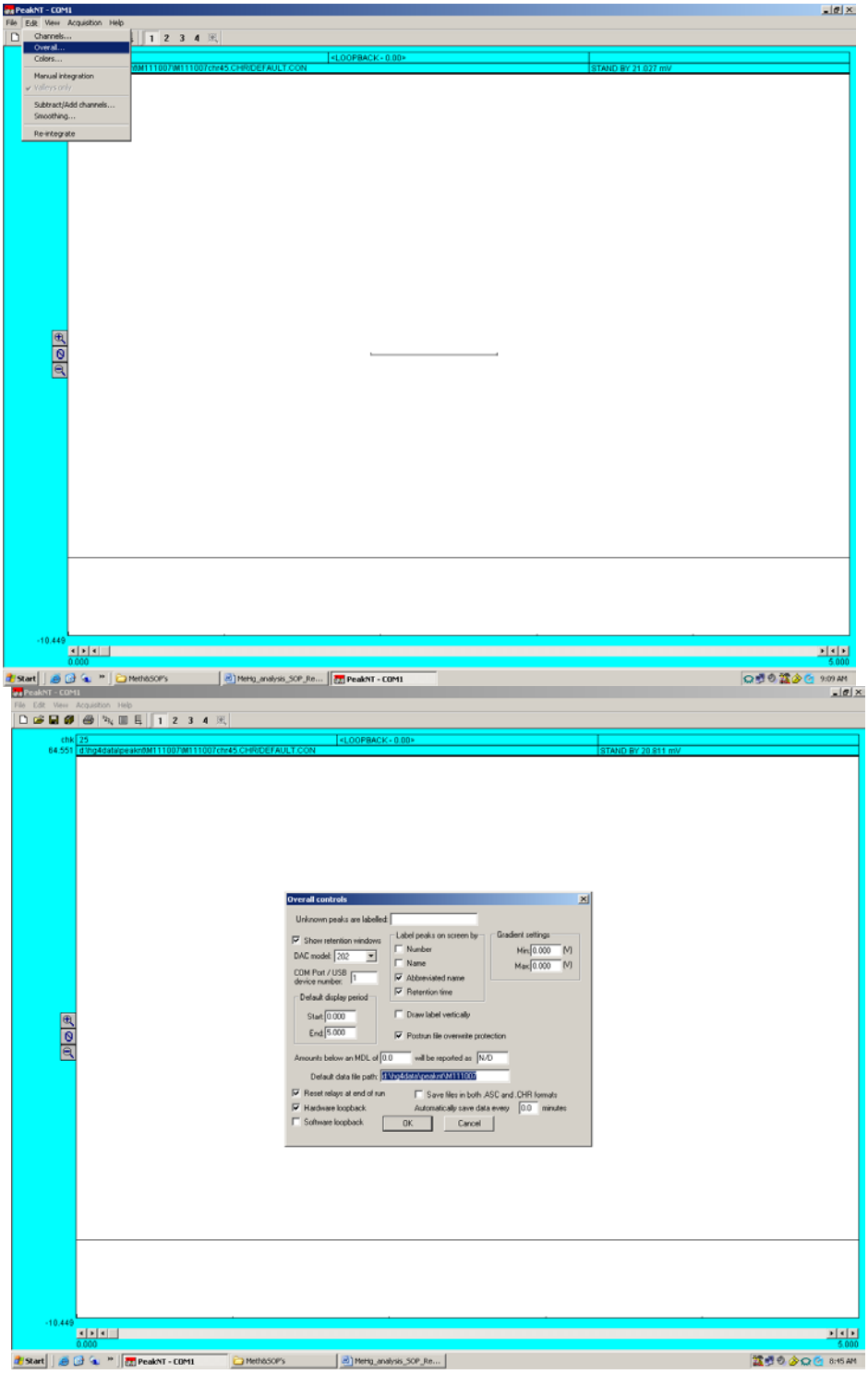
Initial setup and sample analysis:

Turn on the pyrolitic column and sample trap transformers, turn on the sample cooling fan, and check the detector to verify the flow rate is set at 25 mL/min and the baseline is near 0.0100.

Check the temperature of the GC column oven to verify it is at 95^0 C.

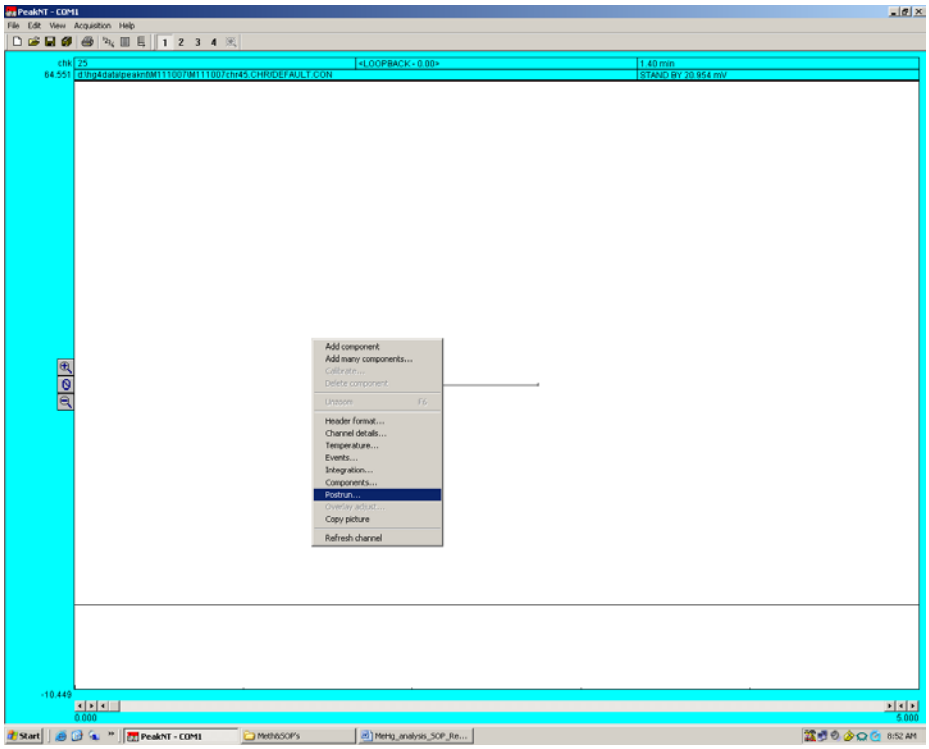
Log onto the computer and create a directory (*MMDDYY)* for the current day's analysis in the *PeakNT* folder.

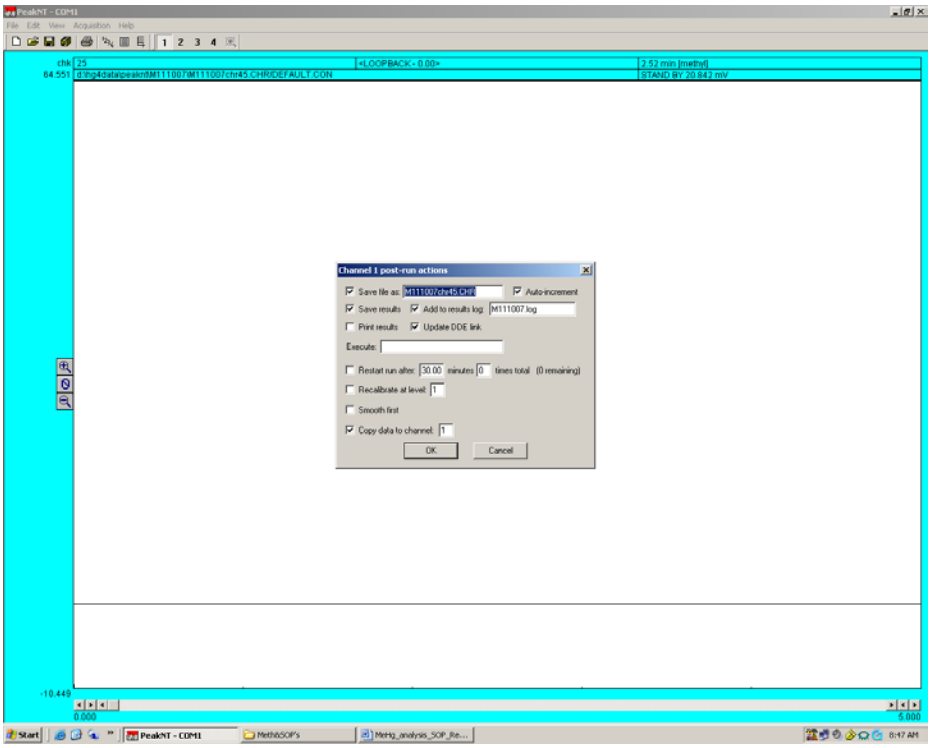
Open *Peak Simple* software, select the *Edit* pull-down menu, and choose the *Overall* option.



Change the default data path to the folder created in step 9.4.3.

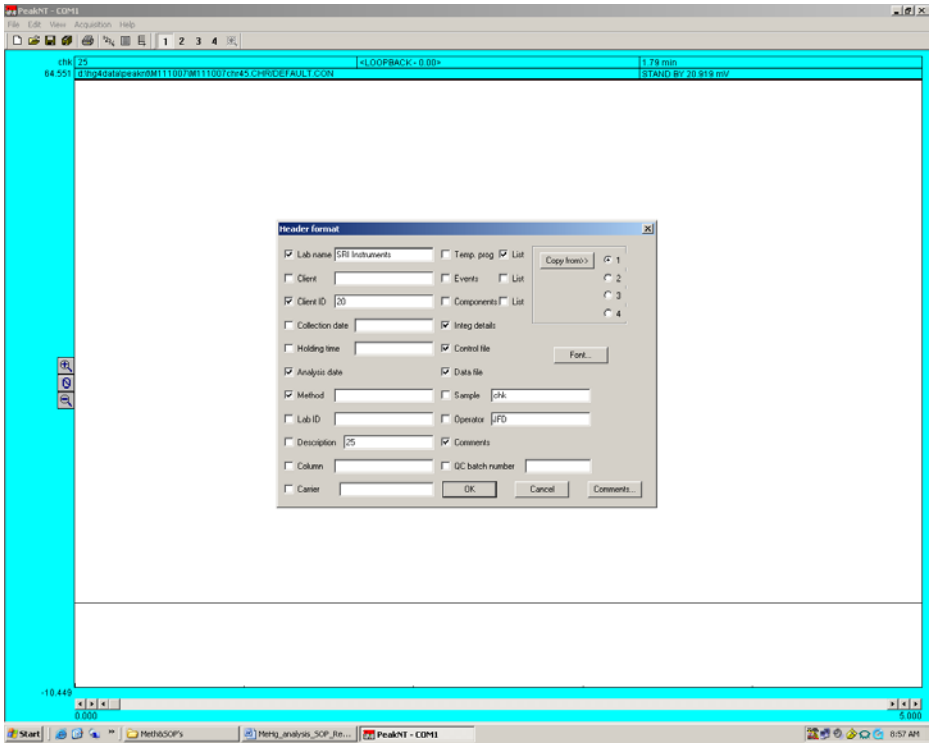
Use the right mouse button while in the Peak Simple window to access the drop-down menu and choose the post-run option.





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

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.



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

Remove the plugs from the ends of the first trap and place it into the analytical train by threading it, with the id number upstream, through the center of the Nichrome wire coil. Center the Nichrome wire over the graphitized carbon black and press switch closure button.

After the 7-minute cycle is complete repeat the steps in 9.4.7.1 for each of the remaining traps.

You need to have 5 traps burned before step 9.4.12 is complete. You have 10 traps and five bubblers. Sample reaction time is 15 minutes and bubbling time is 20 minutes -- the burning (analyzing) of 5 traps takes 35 minutes, you will be reacting, bubbling, and drying a round of samples while burning the previous round. This is the cycle you will follow throughout the day.

Thoroughly rinse the bubblers and sparging stoppers with reagent grade water.

Dispense approximately 100 mL of reagent grade water into each of the bubblers.

Pipette 200, 100, 50, 20 and 10 μl of working standard into bubblers 1,2,3,4 and 5 respectively. These bubblers represent your standard curve.

Pipette 200 μL of acetate buffer and 100 μL of NaTEB to each of the bubblers.

Note: The NaTEB needs to remain at near 0^0 C. It should be removed from the freezer approximately 5 minutes before being added to the bubbler and placed in the dark place to partially thaw.

Tighten the sparging stoppers, ensure the four-way valve is in the closed position, gently swirl the bubblers, and allow to react for 15 minutes. While the samples are reacting connect the N_2 line to the inlet of the stopper to purge the four-way valve of air and residual moisture.

After the reaction time has elapsed, remove the plugs from the ends of the Carbotraps, place them onto the outlet of the

bubbler with the id numbers downstream, turn the four-way valve to the open position, and allow to purge for 20 minutes.

After the 20 minute purge, turn the four-way valve to the closed position, remove the Carbotraps from the reaction vessel outlet, remove the N_2 line from the inlet of the four way valve, and place the Carbotrap on the end of the N_2 line with the id numbers downstream. Allow to dry for 7 minutes.

Thoroughly rinse the reaction vessels and sparging stoppers with reagent grade water.

Dispense approximately 100 mL of reagent grade water into each reaction vessel.

Repeat steps 9.4.11 – 9.4.14. These reaction vessels are your ethylation blanks.

While the ethylation blanks are reacting, remove the Carbotraps from the N_2 lines, attach the N_2 lines to the inlets of the four-way valves, and cap both ends of the Carbotraps. Analyze the Carbotraps used to collect the standards as in 9.4.7.1. Copy the peak area from the log file and paste it into the spreadsheet.

After the blanks have finished purging, thoroughly rinse the bubblers and sparging stoppers with reagent grade water and begin analyzing samples.

Place the distillation vessel on the balance and push the print button to record the ‘full wt’ (column J) in the analysis spreadsheet. The value will be recorded in whichever cell is highlighted at the time so be sure to highlight the correct cell. The table below outlines a typical analytical batch.

Round	Reaction vessel 1	Reaction vessel 2	Reaction vessel 3	Reaction vessel 4	Reaction vessel 5
Standards	200 µL	100 µL	50 µL	20 µL	10 µL
Blanks	EB1	EB2	EB3	EB4	EB5
Samples	MB1	MB2	MB3	MB4	S1
Samples	S2	S3	S4	CHK1	S5
Samples	S6	S7	S8	S9	S10
Samples	S11	S12	CHK2	S13	S14
Samples	S15	S16	S17	S18	S19
Samples	S20	CHK3	S21	S22	S23
Samples	S24	S25	S26	S27	S28
Samples	CHK4	S29	S30	S31	S32
Samples	S33	S34	S35	S36	CHK5

EBX - ethylation blank
MBX - method blank
SX - sample
CHKX – check standard

To analyze a sample, weigh the full receiving vessel, pour the aliquot to be analyzed (generally the entire contents unless high concentration expected) into the reaction vessel, weigh the vessel again, and proceed as in 9.4.11-9.4.14. After reaction and bubbling, burn the traps as in 9.4.7.1.

Calibration and performance documentation: During the analysis run, the analyst must evaluate the calibration data, ethylation blank values, MS/MSD recoveries, and check standard recoveries to ensure acceptance criteria (sec. 6.0) are being met. The spreadsheet created during the distillation of the samples is where this information is recorded. The following information must be recorded in the methyl mercury logbook.

Date of analysis.

Type and date prepared for reagents and standards used.

Name of analyst.

Identification of reaction vessel contents, volume analyzed, instrument response, and sample trap identification for each analysis performed.

Comments pertaining to special samples run, problem samples, corrective actions taken, and results of any

calculations performed to ensure acceptance criteria are being met.

Shutdown:

After all samples and standards have been run, thoroughly rinse the bubblers and sparging stoppers with reagent water. Fill the bubblers completely with reagent water. Replace the sparging stopper into the bubbler with the four way valve in the open position to allow the frit to fill with water. When the frit is filled turn the four-way valve to the closed position. Store the bubbler in the laminar flow hood.

Shut the N_2 flow off at the tank outlet.

Turn off the transformers for the pyrolytic column and sample trap and turn off sample cooling fan.

Reporting of results:

Reporting units: Methyl mercury in ng/L as Hg.

Reporting levels and significant figures:

Report to the nearest 0.01 ng/L for values less than 10 ng/L.

Report to three significant figures for values exceeding 10 ng/L.

Data transfer: After the data has been verified in the EXCEL spread sheet it may be transferred to the customer via e-mail, hard copy, or the internet.

Archiving: All raw data produced in the laboratory is archived in a filing cabinet located in the laboratory manager's office. Hard copies of EXCEL spreadsheets and data reports are archived with raw data. All electronic data is archived on the laboratory manager's computer, which is backed up to tape daily.

References:

Horvat, M., Liang, L., Bloom, N.S. 1993, Comparison of distillation with other current isolation methods for the determination of methyl mercury compounds in low level environmental samples. Part II. Water. Analytica Chimica Acta. 282: 153-168

Dewild, John F., Shane D. Olund, Mark L. Olson, Michael T. Tate. 2004. Methods for the Preparation and Analysis of Solids and Suspended Solids for Methylmercury, Book 5, Section A, Water Analysis. U.S. Geological Survey, Ch. 7, p. 21.

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