

Standard Operating Procedure for Mercury Analysis

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University of Maryland Standard Operating Procedures for the Lake Michigan Mass Balance Project

Calibration Frequency And Procedures (Taken from QAPjP)

The detection limits of validated EPA methods for mercury quantification are orders of magnitude too high for Lake Michigan waters. For this reason, a peer reviewed method will be employed.

University of Maryland lab personnel will employ a Brooks-Rand Cold Vapor Atomic Fluorescence Spectrophotometer (CVAFS) Model-2 (Brooks-Rand, Ltd, Seattle, WA) to measure mercury. Commercially available, traceable HgNO₃ standard (from Fisher Scientific or comparable supplier), diluted using Class A volumetric equipment, will be used to calibrate the CVAFS. Working standards will be replaced at least monthly. An intercalibration with outside laboratories will be performed yearly to check our analytical procedure.

During each analysis session, the CVAFS will be initially calibrated with a four point curve spanning the anticipated range of sample signals. This calibration is achieved using a vapor mercury standard. As mercury is a liquid at room temperature it has a well-defined vapor pressure, which is temperature dependent. A temperature-controlled sealed container containing liquid mercury will therefore have a defined air concentration of mercury. This mercury-saturated air can be subsampled via a septum port using a gas tight chromatography syringe. Known aliquots of the air are then injected into the gas stream of the dual gold trap-CVAFS system, and trapped on the gold column just prior to the analyzer. Heating the column releases the Hg into the analyzer allowing quantification of the injected concentration. This method allows calibration of the instrument independent of the wet chemical manipulation-sparging techniques associated with mercury determination in water samples and allows a calibration curve to be established based on instrument sensitivity and linearity. Changes in CVAFS sensitivity will be monitored with single point standard injections after every five sample analyses. If CVAFS sensitivity drifts more than 10% during an analysis session - this would be atypical of the instrument - these single point standards will be used to recalibrate the analyzer.

Due to infrequent rapid temperature changes in the laboratory, obtaining a standard curve using the temperature dependent vapor mercury standard may be difficult. The technician under these circumstances is advised to proceed with the calibration verification (liquid standard) and sample analysis and wait until later in the day when the temperature has stabilized to run a vapor mercury standard curve. The calibration verification standard results are then checked using this curve. If specifications are not met, samples analyzed prior to the curve will be reanalyzed.

If the calibration QC requirement is not met, corrective measures will be taken. These include checking the integrity of the septum injection port and replacing if necessary; changing the injection needle to insure that this is not a source of error; check the stability of the gas flow within the analyzer and check and replace any tubing that might have become contaminated and might be leaching mercury into the system. The lamp and photomultiplier do deteriorate over the long-term (years) and this could be another source of variability. If none of these procedures results in a sufficient improvement in the calibration, the instrument will be returned to the manufacturer for checking and recalibration. All maintenance, calibration and repair will be logged in an equipment notebook. As the analyzer is kept on constantly, no specific recording of usage is maintained. Field equipment will be checked before and at the end of each cruise. The pump will be calibrated for flowrate at the beginning of the study. As filtration volume will be determined

volumetrically, small changes in the pump flowrate are not critical. The pump head and peristaltic tubing will be checked weekly during the cruises, and additional supplies will be on board. For the Go-Flo bottles, O-rings and the rubber tubing and the associated closing mechanisms are checked on a deployment basis. Spares are kept on board as maintenance can be performed, in the majority of cases, on board. In addition, there will be at least one additional Go-Flo, besides those being used, as a spare.

Analytical Procedures (Taken from QAPjP)

See Appendix 1 of our QAPjP for more detailed laboratory protocol for total mercury analyses. The protocol as written by Steve Claas for the University of Wisconsin-Madison Water Chemistry Program is essentially the same as that to be used at the University of Maryland. As this is the most recent detailed method, this should be considered the reference method. The CVAFS techniques have been developed based on techniques first initiated through the University of Connecticut (Bloom and Fitzgerald, 1988) and are generally used throughout the mercury research community for the analysis of mercury in environmental samples. The PI has been using similar techniques for the analysis of open ocean seawater, estuarine and freshwater samples for the last six years. The methods used are based on sample digestion methods described in Bloom and Crecelius (1983) and the CVAFS total mercury method of Bloom and Fitzgerald (1988). Deviations from these methods are described below.

- 1) The analyzer is kept on usually, so no warmup time is required.
- 2) A Hewlett-Packard integrator will be used instead of a strip chart recorder.
- 3) The calibration procedure is different from that used by the University of Wisconsin. See details above for the calibration procedure.
- 4) Analysis of water samples: Subsamples to be analyzed will be decanted from the 2 L Teflon bottle into a smaller, preweighed Teflon bottle for analysis. After tarring the sample, it will be wet oxidized with 100 μ L of BrCl solution for every 100 mL of sample. Samples will be sealed in double polyethylene bags and heated for at least an hour, and preferably overnight, at 70°C before prereduction and analysis. Aliquots of 125-500 mL, depending on expected mercury concentration, will be purged and trapped. Argon will be used as the carrier gas and the purge time will be such that 20 volumes of argon are purged through each sample volume.
- 5) Filters containing particulate will be unfrozen. Two mL of MilliQ water and 2 mL of BrCl reagent will be added and the bottle sealed. From this point the samples are treated in a similar fashion to the water sample, except 2 mL of hydroxylamine HCl is used to produce samples. The detection limit for both methods are similar, as the analytical techniques are comparable and the BrCl reagent is the primary source of the blank. For similar amounts of added BrCl, the blank should be comparable. The method has a mean detection limit of approximately 0.1 ng/L. Detection limits depend to a large extent on volume of sample analyzed and can be lowered by increasing the volume of the purged aliquot.

Standard Operating Procedure for Total Hg (Mason Lab Detailed Procedure) Analytical System

- 1.0 At start of day, turn on argon tanks for bubblers and analyzer. Pressure into analyzer should be b/w 50-60 units.
- 2.0 A column should be connected in line with crimped side facing integrator (First on, First off concept). Make sure that coils are covering gold and quartz wool or improper heating will result.
- 3.0 Run a standard curve by spiking you sample column with 20, 30, and 50 cc of mercury. Turn the integrator on by pressing <start> before each spike.
- 4.0 Turn on heating program by pressing <Program>, <1>, <On> on the Control Programmer. It will run through the heating program for 8 min.
- 5.0 Spikes of 20 to 50 cc should be run for most low level detection. For each spike, you must record the temperature and convert temperature to vapor pressure with the conversion chart on wall. A standard curve including 0 as a point should yield a correlation of 0.999 or better.
- 6.0 When done analyzing a sample, integrator is shut off by pressing <stop>.
- 7.0 Hg Collection System (Bubbler System)
 - 7.1 While standard curve is being run, the bubbler blanks can be run with the second set of columns.
 - 7.2 Rinse bubblers two to three times with Q-water, then fill to mark. Rinse spargers with Q-water, then replace bubblers.
 - 7.3 Stannous Chloride: The SnCl₂ pipette is labeled and should only be used for this reagent. Rinse the tip three to four times in 6N HCl then rinse one time with SnCl₂. All waste should be placed in labeled waste container. Spike 0.5 mL into each bubbler, then rinse tip again three to four times with HCl. Rinsing keeps the pipette tip clean (we do not change this tip) and it keeps the SnCl₂ from precipitating (it dissolves under acid conditions).
 - 7.4 Place lids firmly on bubblers so that no leaking occurs. Place clean gold traps onto bubblers, next to soda lime columns. (Columns should have crimped end facing bubbler-First on, First off). Turn the gas on to 60 units for larger bubblers and ~ 20 for small bubblers. Samples should bubble for about 20 min.
 - 7.5 After running Q-water blanks, a standard Hg spike should be run using the now blanked water. Standard Hg (~1ng/mL) is kept in the dark in the refrigerator. Only remove for use. Use 1 mL pipette labeled Hg Std only and take a pipette tip from the acid bath. Rinse with Q-water, then rinse once with standard before dispensing into bubblers. Hg waste and tip should go in flask labeled Hg waste. Ultimately, any Hg waste should be placed in labeled acid bottle at back of hood.
 - 7.6 After spiking with standard, spike bubblers with SnCl₂.

- 7.7 After standard is run, a blank should be run using the same blanked water. Only SnCl₂ should be added.
- 7.8 If standard and blank values are acceptable, then you are ready to run samples.
- 8.0 Water samples
- 8.1 For Reactive Hg, just add a known volume to each bubbler and spike with SnCl₂.
- 8.2 For Total Hg, rinse out acid cleaned 500 mL bottles with Q-water. (I usually rinse out about six and re-use them over again). This is done if your sample is in a 2 L bottle, as you only need 500 mL for analysis. If you are using smaller bottles this step is unnecessary. When running a duplicate, you will need two bottles per sample.
- 8.3 Rinse bottles once with sample, then fill with sample. Spike with BrCl. (Use pipette labeled BrCl and keep same tip; rinse with Q-water several times then one time with reagent prior to use). The volume of BrCl used will depend on how much mercury is in the sample (ie. rain samples usually get 1 mL BrCl). Tighten lids on samples, shake, then let sit for at least ½ hour.
- 8.4 After time has expired, add the same volume of Hydroxylamine HCl as BrCl to your samples, rinsing the tip in the same manner as your BrCl addition. Shake well; samples are ready for analysis.
- 8.5 To analyze samples, empty bubblers of old water. All waste from bubblers must be placed in container labeled SnCl₂. Rinse bubbler with sample. Record sample volume using balance. Again, samples need to be treated with SnCl₂ prior to analysis.
- 9.0 Filter samples
- 9.1 Filters should be placed into acid cleaned vials prior to analysis.
- 9.2 To each vial add 2 mL Q-water and 2 mL BrCl. Use Teflon coated forceps to push any unexposed filters into reagent and tighten caps. Shake gently and let stand for ½ hour.
- 9.3 Add 2 mL of Hydroxylamine HCl and shake well to neutralize.
- 9.4 To blanked bubblers, add 2 mL of sample (try to avoid getting filter paper pieces in pipette tip). Spike with SnCl₂.
- 10.0 End of the day
- 10.1 When finished running samples, empty bubblers into SnCl₂ waste container and rinse several times with Q-water. Fill again with Q-water and replace lids. If you are not going to use bubblers for an extended time period, top off with concentrated acid to clean.

- 10.2 All SnCl₂ waste should be placed in labeled flask in hood. When flask is full add some dissolved NaOH pellets to precipitate the SnCl₂. Let stand overnight. Before next use, decant clear liquid into sink being careful not to let any precipitate escape. When a substantial amount of precipitate has accumulated, empty flask into Hg/SnCl₂ bottle for proper waste disposal.
- 10.3 Shut off gas cylinders.