Analysis of Total Mercury in Solid Samples by Atomic Adsorption following Direct Combustion with the Nippon MA-2 Mercury Analyzer

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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 solid samples. This SOP describes the preparation of the sample and subsequent analysis. The Nippon MA-2 is a direct combustion instrument designed to analyze total mercury in solid samples. The solid sample is combusted at high temperature (850°C) in the presence of interference-reducing reagents, releasing mercury from the matrix as reduced gaseous mercury. In the resulting gas, matrix interference is further eliminated by catalytic treatment, adjusted to appropriate pH in a phosphate buffer, and then passed through a gold amalgam trap to quantitatively capture gaseous mercury. Lastly, the gold trap is heated, releasing the bound mercury into the sample stream, and detected by cold vapor atomic adsorption. Quality assurance and control protocols are employed throughout sample preparation and analysis, including: laboratory practices to prevent sample contamination, analytical blanks, method and analytical replication, and analysis of certified reference materials (CRM).

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 as that 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. The powdered analytical reagents are very fine and pose a severe harmful particulate inhalation hazard. Due care must be exercised in handling these reagents, and should include the use of a fume hood when working with a large volume of reagents, containment in sealed bags before disposal, and regular cleaning of surfaces with a dust vacuum. Additionally, extremely high temperatures are used to heat the catalyst,

ceramic combustion boats, and reagents prior to use. These will remain hot minutes (boats) to hours (reagents and instrument) after heating; use caution in handling these items. The automated sample loader and tray start moving without warning during analysis and are a mechanical hazard.

Reagents

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.

Additive B: Purchased from Nippon in 500 g quantities and is composed of aluminum oxide. Before use, heat to 750°C for 1 hr in a 250 ml crucible to volatilize residual mercury and water. Leave in furnace until cool and transfer back into original container if not immediately used. Label container as "combusted" and date.

Additive M: Purchased from Nippon in 500 g quantities and is composed of sodium carbonate and calcium hydroxide. Before use, heat to 750°C for 1 hr in 250 ml crucible to volatilize residual mercury and water. Leave in furnace until cool and transfer back into original container if not immediately used. Label container as "combusted" and date.

Phosphate Buffer Solution: Purchased from Nippon in single use packages. In a clean 1L PETG bottle add approximately 500 ml of reagent grade water. Dump the contents of one package of Phosphate Buffer Powder to the water, and fill to the 1L mark. Shake until all the reagent dissolves. Phosphate buffer should be labeled with the date made and stored in the refrigerator. Phosphate buffer should be made fresh every 12 months or if it becomes turbid.

Standard Solutions

Mercury stock standard is purchased from Nippon. Working standards are prepared in a class A volumetric flask in a 0.001% L-cysteine, 0.2% Nitric acid matrix; do not use standards prepared in any other matrix because acids and free halogens substantially interfere with instrument performance. Standards solutions of 10, 100, and 10000 ng/ml meet most analytical needs of the instrument.

Instrument Operation

Interferences

The instrument is extremely sensitive to acid and free halogens, which degrade the catalyst and gold trap. It is very important to reduce/eliminate exposure to these factors throughout analysis and storage. Saline sediments (such as marine sediments) and potentially acidified samples should be analyzed sparingly with the Nippon or with an alternative method.

Start up

Prior to operation, the analyst needs to prepare the instrument for analysis. If necessary, start the software with the shortcut located on the desktop. If the instrument is off, turn it on with the switch near the mains and allow the combustion tube to come to temperature (850°C). The Nippon operates in one of two modes (low mode and high mode), and the analyst must choose the mode appropriate to the samples prior to analysis. When set to low mode, the Nippon can analyze mercury mass ranging 0.2 – 20 ng and is generally used for sediments. When set to high mode, the Nippon can analyze mercury mass ranging 2 – 200 ng and is generally used for highly contaminated sediments or biota. To set the mode of the instrument, go to the “run” drop down menu, select “mode”, and select the appropriate radio button (“low” for low mode, “high1” for high mode). Open the template file that contains the most recent calibration for the mode that will be used (it is not necessary to calibrate the instrument with every use). Low mode uses LOW CAL.ma2 file and high mode uses the HIGH CAL.ma2 file. Once the template is open, save as a run file, using the date followed by a brief description of the samples analyzed for a file name. On the instrument diagram, make sure that the heat mode is in “mode 2” and the measurement mode is correct for the intended analysis.

Empty the gas washing bottle (left bottle) of buffer solution, and drain residual moisture from the dehumidifying bottle (right bottle). Fill the gas washing bottle with 2 cm of phosphate buffer solution, being sure to leave the dehumidifying bottle open to vent head space (otherwise buffer solution will be forced upstream into the end cap and require shut down and cleaning). If necessary, remove combustion boats from the sample tray, empty the spent reagents into a large Ziplock bag, and vacuum residual reagent dust from boats. Gently vacuum any reagent dust that has collected on interior components of the autosampler, including the sample changing tray and surrounding areas (tray removal function possible in the “run” drop down menu). Clear the instrument of residual mercury by running the purge function (select the PURGE option in the sample table from the NAME drop down menu). Repeat purge until at baseline level (peak area < 0.005).

Preparation for Sample Analysis

It is important that the combustion boats are mercury and acid free. Prior to use, newly acid washed boats should be heated in the oven at 550°C for 2 hours, and boats not used in the previous 3 days should be clean burned in the instrument. If the boats have been recently used, randomly select 3 boats and clean burn (without reagents) them to ensure that there is no significant carryover (peak area < 0.01) from previous analyses. If the boats fail this criterion, repeat with 3 additional boats. If contamination persists the entire lot of boats needs to be clean burned before use.

When the boats are verified mercury-clean, analyze three reagent blanks and three relevant CRM samples. If the instrument has been inactive for an extended period of time (>2 weeks) analyze two check standards to verify calibration. Analysis requires the addition of solid reagents to the combustion boats. For the analysis of standards, add additive B, 10 – 1000 µl of standard, additive B to cover, and finally fill the boat with additive M. For the analysis of solid samples, add additive M, 10 – 50 mg sample, additive M to cover the sample, additive B, and finally fill the boat with additive M. Following analysis, if the initial reagent blanks are sufficiently low (< 0.05 ng/boat), the CRM is within the accepted range (± 20% recovery), and the check standard recovery is within 10%, proceed with sample analysis. In the case of an elevated reagent blank or the failed recovery of a CRM or check standard, repeat the measurement. A repeated failure rules out analyst error and indicates that the instrument is not performing properly; samples should not be analyzed until the issue is corrected.

Sample Analysis

Samples may be analyzed once the preceding instrumental control has been demonstrated. Analytical sample mass should be 10 – 50 mg. Every analytical batch of ten samples will include at least one sample analyzed in triplicate, one CRM analysis, and two reagent blanks. The reagent blanks, preceded by an instrumental purge, are located in the middle and at the end of the sample set. Biological samples are prone to carryover; an instrument purge should follow the analysis of every biological sample. A typical analytical batch for sediments is described below:

Sample 1
Sample 1
Sample 1
Sample 2
Sample 3
Sample 4
Sample 5
Purge
Blank 1
Sample 6
Sample 7
Sample 8
Sample 9
Sample 10
CRM
Purge
Blank 2

Data Capture and Processing

Data from analysis appears in the run list in the sample page and is written to the "DEPOSIT.MA" file. In the run list, copy the columns for sample ID, sample mass analyzed, and mercury mass. Paste these data into the appropriate Excel spread sheet template (HIGH CAL.xls or LOW CAL.xls) for processing and save with the file name as the analytical date followed by a brief description of the samples (i.e. 012309 GL MERCURY SEDS.xls). Following the analysis, also save the DEPOSIT.MA file as the same name. It is important to save the existing DEPOSIT.MA file before starting a new analysis; the data will be overwritten.

Instrument Shutdown

The heaters operate at a high temperature and should be turned off following sample analysis. To shut the heaters off following an analytical run, turn the instrument off with the power switch. If the batch is to finish unattended, use the "start sleep" function found in the run menu. Select the samples you wish to run but do not start (the run will start automatically). Select start sleep and choose the option that fits your situation. You can choose to turn heaters off following the run, and if a run is scheduled for the following day enter the time that the heaters will begin to warm again.

For extended periods of inactivity (>3 months) prepare the instrument for long-term storage. Turn off the main power to the instrument. After the instrument completely cools, remove the end cap and combustion tube (see chapter six in the user manual). Rinse the combustion tube with copious volumes of reagent water, dry completely, cap, store in an airtight bag, and record the period of use for the combustion tube. Acid wash the end cap (see below). Empty the buffer and drying bottles, rinse and fill the buffer bottle with reagent grade water, and plug the inlet hole. Empty the spent reagents from the sample boats, acid wash, and store. Finally, vacuum the residual reagent dust from the instrument.

Quality Assurance and Control Protocols

Acid Washing

All acid-washing is done in a 10% HNO_3 solution. Wash glass equipment and ceramic combustion boats for at least 2 and 24 hours, respectively. Rinse glass equipment well with mercury-clean water and let dry before use. Following acid washing, boats need to be soaked in mercury-clean water for a minimum of 24 hours to become fully rinsed, dried for 3 days, and heated to 550°C for 2 hours before use.

Standard Reference Material

Three CRMs of a similar matrix to the samples should be run in the initial instrument setup and one CRM for every ten samples analyzed after that. Recovery of the CRM must be within 80 – 120% of its certified value. Repeat the CRM in the case of failure. A second failure indicates the instrument is not performing properly and the problem needs to be corrected and the samples repeated.

Sample Precision

The relative standard deviation of samples analyzed in triplicate should be less than 15%. In the case of failure repeat the sample (if possible) in addition to another sample from the same set in triplicate. Repeated triplicate failure should be brought to the attention of the quality assurance officer.

Sample Carryover

The purge function of the instrument clears the sample train (without a combustion boat) of residual mercury and indicates the level of carryover from previous sample analyses. A purge mass should not exceed 10% of the mass of mercury measured in any previous sample, up to the previous purge. When a purge exceeds 10% of a previous mercury mass, repeat that sample in a subsequent batch bracketed with purges. If significant carryover persists in a sample set (common in biological samples), mercury concentrations tend to be extremely variable among the sample set, or sample mass is extremely limited, each sample should be analyzed bracketed with purges.

Reagent Blank

Reagent blanks analyzed before and throughout analytical batches measure the mercury concentration present in the additives M and B. Reagent blanks analyzed in the initial setup of the instrument should be < 0.05 ng/boat. Reagent blanks analyzed throughout sample analysis are preceded by an instrumental purge to clear the sample train of residual mercury. Reagent blanks in an

analytical batch that exceed 10% of a previous sample mercury mass (up to the last reagent blank) indicate contamination of the additive source, the combustion boat, or the sample train. Repeat the samples preceding a failed reagent blank up to the last passing reagent blank. If the reagent blanks continue to fail repeated analysis, either the sample train, combustion boats, or reagents have become contaminated; the source of the contamination should be identified and corrected.

Instrument Calibration

A standard curve should be (1) created with mercury masses appropriate to the measurement mode, (2) calculated with a polynomial best fit equation with while forcing an intercept of zero, and (3) have an r^2 value greater than 0.995. The mass of mercury in analyzed samples should not exceed the standard curve. Instrumental response tends to be relatively stable over multiple days, therefore daily calibration is not necessary. However, after long periods of inactivity (>2 weeks) instrumental calibration should be verified (± 10%) prior to sample analysis by analysis of a known mass of mercury from a standard solution.

Quick Reference Guide for mercury analysis with the Nippon MA-2

- Turn instrument on with switch near mains
- Drain and fill buffer
- Remove sample tray and vacuum interior of instrument
- Start software and select appropriate calibration file (generally low cal for sediments, high cal for biological)
- Once heaters are at operating temperature, begin initial purge and boat blanks
- Analyze reagent blanks, CRM, and check standards. Add the reagents in the appropriate order (M, Sample or CRM, M, B, and M: or B, standard, B, and M)

TYPE	QA/QC CRITERIA
Instrument purge	Acceptable when peak area is < 0.005
3-6 (10%) Empty boat blanks	Acceptable if peak area is < 0.01
3 Reagent blanks	Acceptable if mass is < 0.05 ng/boat
3 CRM	Acceptable if recovery is 80 – 120%
2 Check Standards	Acceptable if recorvery is 90 – 110%

- Once the startup criteria is met, begin analysis of samples that include one triplicate, one CRM, and two reagent blanks that are preceded with purges for every ten samples
- An example of a typical 10 sample batch is as follows:

TYPE	QA/QC CRITERIA
Sample 1 in triplicate	RSD < 15%
Samples 2-5	Within confines of standard curve mass
Instrument purge	Mass < 10% preceding samples
Reagent blank	Mass < 10% preceding samples
Samples 6-10	Within confines of standard curve mass
Instrument purge	Mass < 10% preceding samples
CRM	80 – 120% recovery
Reagent blank	Mass < 10% preceding samples

- Continue subsequent analytical batches as long as CRM recovery is within 20% of certified value
- Copy and paste data into excel spread sheet and save the spread sheet as well as the DEPOSIT.MA file with the analytical date as the file name (012309.xxx)
- Turn the instrument off following analysis (use start sleep function if the instrument will be unattended)

Appendix 1. Definitions of equations

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

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

$$\text{Sample Concentration} = \frac{(\text{Hg per Aliquot}) - (\text{Mean Reagent Blank Hg})}{(\text{Sample Mass})}$$