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

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Principle of Operation

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. A more detailed description of the principle of operation is available in chapter two of the manufacturer's instruction manual.

Safety Concerns

Multiple safety concerns are present in the operation of this instrument. Although mercury is a dangerous neurotoxic metal, concentrations encountered in the samples and standards generally measured on this instrument are relatively low. However, caution should still be exercised to limit chronic mercury exposure. 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. Finally, the powdered analytical reagents are very fine and pose a severe harmful particulate inhalation hazard (see attached MSDS for further details). Due care must be exercised in handling these reagents, and should include the use of appropriate precautions (particulate filter fume hood, appropriate disposal, and regular cleaning of surfaces with dust vacuum).

Instrument Operation

This document is intended as an additional standard operating procedure (SOP) designed to guide the user through mercury analysis specific to the Wisconsin District Mercury Laboratory. A condensed version is also provided following the detailed SOP, and is intended as a quick reference bench guide for the analyst. However, the analyst is required to be familiar with the detailed SOP as well as the original user's manual provided by Nippon which will be referred to when appropriate.

Start up

If the instrument is off, turn it on with the switch near the mains. If necessary, start the software (click on shortcut located on the desktop, "MA2000") and open the appropriate (HIGH CAL or LOW CAL) template file. The template files include a standard curve that was successfully used on the instrument for the previous analysis; it is not necessary to calibrate the instrument with every use.

The LOW CAL file operates from 0.2 – 20 ng and is generally used for sediment analysis, while the HIGH CAL file operates from 2 – 200 ng and is generally used for biological analysis. Choose the correct analysis mode ("low mode" for LOW CAL function, and "high1 mode" for HIGH CAL function) by clicking the drop down menu "run", select "mode", and choose radio button. On the instrument diagram, make sure that the heat mode is in "mode 2" and the measurement mode is correct for the intended analysis. If the instrument is "cold" allow it to come up to operating temperature.

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 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 sample tray, empty the spent reagent-sample mixture 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 instrument, 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 10% of combustion boats (3-6) to be used for the analysis 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 3-6 additional boats, and if contamination persists the entire lot of boats needs to be clean burned before use.

When the boats are clean analyze three reagent blanks, at least three relevant standard reference material (SRM) samples, and two check standards. Analysis requires the addition of solid reagents to the combustion boats and is further described in chapter 5 of the instruction manual. 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 covering the sample, additive B covering that, and finally fill the boat with additive M. Following analysis, if the initial reagent blanks are sufficiently low (< 0.05 ng/boat), the SRM 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, and SRM or check standard

recovery failure, 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 SRM 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. If necessary, additional purges may be added to a batch. A typical analytical batch 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
SRM
Purge
Blank 2

Instrumental Shutdown

Short-term Instrument Shutdown (< 2 weeks): 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 to 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.

Long-term Instrument Shutdown (> 2 weeks): For extended periods of inactivity, the instrument must be prepared for storage. First, follow the short-term

instructions for shutdown. 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 residual reagent dust from the instrument.

Quality Assurance and Control Protocols

Standard Reference Material

Recovery of the reference material must be within 80 – 120% of its certified value. Repeat the SRM in the case of failure. A second failure indicates the method in not performing properly and the problem needs to be corrected and the samples repeated.

Sample Precision

The relative standard deviation of samples 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 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, mercury concentrations tend to be extremely low, and/or sample volume is extremely limited, increase the frequency of purges to reduce inter-sample carryover.

Reagent Blank

Reagent blanks analyzed before and throughout analytical batches measure the mercury concentration present in the additives M and B. If any one of the three initial reagent blanks exceeds 0.05 ng/boat, reanalyze three reagent blanks using the same boats. Repeated failure of initial reagent blanks indicate the additive is contaminated and should be combusted again before future use. Reagent blanks throughout the analytical batch are preceded by an instrumental purge to

clear the sample train of residual mercury, reducing sample carryover. Reagent blanks within an analytical batch exceeding 0.05 ng/boat indicate contamination of additive source or persistent systemic contamination. Repeat the preceding samples of a failed reagent blank up to the last passing reagent blank (< 0.05 ng/boat) or instrumental purge with a peak area < 0.005; if sample carryover is suspected in this batch, the samples should be bracketed with purges. If reagent blanks continue to fail the repeated analysis, the additive has become contaminated and should be combusted.

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 an intercept of zero, and (3) have an r^2 value greater than 0.995. The mass of mercury in analyzed samples should occur within the levels of the standard curve. Instrumental response tends to be relatively stable over multiple days, therefore daily calibration is not necessary. However, instrumental calibration should be verified (± 10%) prior to sample analysis by analysis of a known mass of mercury from a standard solution.

Additional Instructions

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.

Reagents

Before use, heat reagents 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.

Standard Solution

Mercury standards are prepared in a 0.001% L-cysteine, 0.2% Nitric acid solution; do not use standards prepared in any other matrix as that 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.

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, and mercury mass. Paste these data into the appropriate excel spread sheet template (HIGH CAL or LOW CAL) for processing and save with the file name as the analytical date (012309.xxx). Following analysis, also save the DEPOSIT.MA file as the same name.

Maintanence Schedule

Daily Gently vacuum the interior components of the instrument to minimize dust build up. Change buffer solution. Visually inspect the downstream components (end cap, bubblers, gold amalgam trap, cell, and connecting tubing) for deposits and clean or replace as necessary. .

Monthly Acid-wash the end cap and inspect the end of the combustion tube for deposited material. Replace combustion tube and clean as necessary. Acid-wash combustion boats as described below.

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. Cleaning the combustion tube requires special precautions and is described previously in this text, and in detail (chapter 6) in the supplied instruction manual.

Quick Reference Guide for HgT analysis with the Nippon MA-2 Mercury Analyzer

- 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, SRM, and check standards. Add the reagents in the appropriate order (M, Sample or SRM, 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 SRM	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 SRM, 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 < 0.05 ng/boat
Samples 6-10	Within confines of standard curve mass
Instrument purge	Mass < 10% preceding samples
SRM	80 – 120% recovery
Reagent blank	

- Continue subsequent analytical batches as long as SRM 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)