Chapter O

Mercury in plants and animal tissue by thermal decomposition-atomic spectrometry

By Philip L. Hageman

U.S. Geological Survey Open File Report 02-223-O

Analytical methods for chemical analysis of geologic and other materials, U.S. Geological Survey

Contents

Table

Mercury in plants and animal tissue by thermal decomposition-atomic spectrometry

By Philip L. Hageman

Code: T30

Approved: 5/21/02

Principle

In the analytical laboratory prepared samples (ground to - 80 mesh and homogenized) are weighed into nickel alloy sample boats on an analytical balance and placed in the auto-sampler tray of the DMA- 80 instrument. Once introduced into the instrument, the sample is dried and decomposed by heating in an oxygen environment inside a quartz decomposition tube. Combustion gases are purged with oxygen from the combustion chamber and subject to further decomposition by exposure to a catalytic column (catalyst tube). The resulting combustion products are then exposed to the gold amalgamation trap where mercury vapor is selectively collected. Mercury on the trap is rapidly desorbed by heating and final mercury concentration quantified by atomic absorption spectrometry (TD-AAS) using a wavelength of 254 nm. Further details and specifics of sample collection, sample preparation procedures, and the determination of mercury in environmental samples are given in Crock (1996), Crock and others (1999), Kennedy and Crock (1986), and Hageman (this volume).

Interferences

Because samples are thermally decomposed and analyzed directly, this method has minimal interferences. This procedure requires no wet chemistry digestion or reagent driven chemical reduction, and thus, these potential interference and contamination sources are eliminated. However, memory effects or carryover can be experienced if analyzing samples with low mercury concentrations after analyzing samples with high mercury concentration. Adjusting sample weights, batching, or running blanks between samples can minimize this effect. An additional source of carryover contamination can come from sample boats that are re-used in this procedure. In order to prevent this, boats should be heated (700° C.) in a muffle furnace for one-hour prior to re-use. As in any mercury method, contamination from ambient (background) mercury needs to be minimized, and the analyst must eliminate all possible sources of mercury contamination to the sample and the laboratory environment if reliable mercury analyses are to be achieved. Mercury is ubiquitous in the environment and contamination can be derived from many sources including sample collection procedures, sample preparation protocols, and sample handling and storage. In the laboratory, mercury contamination can come from the ambient air, carrier gas, and lab ware. Prior to use in this procedure, all glassware, including the sample collection bottles, should be washed with detergent and rinsed. All washed glassware should then be rinsed with nitric acid (10% HNO_3) and triple rinsed with DI water. Clean glassware should then be placed in heated storage (≈95° C) until needed in order to prevent re-contamination with mercury. Finally, the analyst should never use polymer containers as storage vessels because mercury has the ability to diffuse across these materials and thus contaminate adjoining containers or the laboratory environment.

Scope

This method is designed for the determination of total mercury in plant material and animal tissue. According to the manufacturer, the instrument detection limit (IDL) for solid samples is 0.11 ng mercury. A Lower Reporting Limit (LRL) was determined by analyzing empty sample boats after matrix calibration and using a weight of 1.0g for the empty boats. Using this procedure, the LRL for plant samples is 0.12 ppb (µg/kg) and 0.25 ppb (µg/kg) for animal tissue samples. A maximum of 40 samples can be analyzed per run and approximately 15 samples can be analyzed per hour.

Apparatus

- DMA-80 automatic mercury analyzer including sample boats and auto sampler tray (Milestone Inc.).
- Analytical balance capable of weighing to 0.0001g.

Reagents

- High purity oxygen (Hg free)
- *Nitric acid wash*: Dilute 100 mL research grade HNO_3 to 1 L with DI water.
- Water used in sample preparation or any part of this procedure should be deionized (DI) and mercury-free. The DI water should have a resistance of >17 mega-ohms.

Safety precautions

Because of the toxic nature of mercury, all established safety procedures should be used. These requirements include the use of protective eyewear, laboratory coat, and gloves. All chemical and reagent handling activities should be performed in a chemical hood. See the *CHP and MSDS* for further information concerning first-aide treatment and disposal procedures for nitric acid or any other chemical products used in this method. The DMA-80 instrument should be vented to an exhaust hood in order to safely vent combustion products and any residual mercury vapors that may be generated by the DMA-AAS system.

Procedure for analysis of plants and animal tissue

In order to determine mercury in plant material and animal tissue, the samples must be carefully collected and prepared. After preparation, homogenized samples are incrementally weighed to (± 0.0001 g) into the sample boats using an analytical balance. Weights for each sample are entered into the instrument program. After weighing and entering all sample weights and loading the weighed samples in the auto-sampler tray, the loaded tray is inserted into the instrument, which has been warmed up for about 45 minutes. All analytical parameters specific for the run such as dry time, combustion time and temperature, wait time etc. are entered into the run program of the DMA-80. The analyst must understand that analytical parameters are matrix specific and require different settings due to differences in sample weight, organic content, moisture content, combustibility, etc. For plant material and animal tissue samples that were used for this validation, the settings used were as follows: *Drying time:* 10 seconds, Decomposition time: 2 minutes 30 seconds, *Wait time:* 40 seconds (i.e. 10/2:30/40). Other instrument specific parameters are set with consideration of sample size, matrix, and expected mercury concentration in the sample (high/low). For these general analytical settings, the analyst should refer to the DMA Operating Manual, version 3.23 (2001). After loading the samples and setting the instrument parameters, the analyst then either creates a new calibration curve or checks and uses a previously established curve which has been stored in the program from a previous run. (Complete calibration instructions are found in the following section).

Standardization

Solid reference materials, with certified mercury values are used for calibration. The reference material chosen should be a standard reference material (SRM), and must be matrix matched to the samples being analyzed (i.e., as similar to the samples being analyzed as possible). To calibrate the instrument, the SRM is weighed into a sample boat (±0.0001 g) on an analytical balance. This procedure is repeated producing calibration samples of varying weights. Calibration sample weights and certified mercury concentration of the SRM are entered into the run program in the software. The instrument then analyzes each calibration standard and a calibration curve and working range for the samples is created by the instrument software plotting the absorbance of the standards versus the nanograms of mercury. For daily calibration, a new calibration curve is not required if a matrix matched, full calibration curve which covers the proposed working range has been previously established. A calibration check of the curve can be made by analysis of a high and low concentration standard. If the concentration of the calibration standards are (± 10%) of their true value, the curve can be considered valid and may be used for analysis. If these criteria are not met, a new calibration curve should be established. Following calibration, any sample exceeding the upper calibration limit must be reanalyzed using a smaller aliquot of sample (this requires re-weighing of sample). For quality control, each batch of samples should include analysis of at least one method blank (taken through the entire sample preparation and analytical procedure), one reference sample, and one duplicate sample. Periodically, spiked samples and/or check standards should be analyzed in order to verify performance and analytic stability of the instrument.

Calculation

The instrument data analysis program prepares a calibration curve based on the analyses of matrix matched calibration standards and determines sample concentration by use of a regression equation.

Assignment of Uncertainty

Table 1 shows the analytical results of selected reference materials, and method blanks obtained by use of this procedure.

Table 1.—Analytical performance summary for mercury in plants and animal tissue by DMA-AAS

[Concentration in μg/kg] See page ix of the introduction to this Methods Manual for an explanation of the abbreviations used in the analytical performance summary tables.

Reference	*Description*	*n*	*Mean*	*s*	*pv*	*% RSD*	*% R*
NIST 1566b	oyster	9	39	1.0	35[2]	2.64	111
NIST SRM 2976	mussel	9	70	4.4	61[2]	6.33	115
NRCC TORT 1	lobster	9	309	13.6	330[1]	4.40	94
NRCC DOLT 2	dogfish	9	2378	179	2140[1]	7.85	111
NIST SRM 1570a	spinach leaves	9	29	1.42	30[2]	4.97	97
NIST SRM 1547	peach leaves	9	33	3.62	31[2]	10.9	106
NIST SRM 1515	apple leaves	9	46	4.39	44[2]	9.61	104

[1]National Research Council Canada, Institute for Environmental Chemistry, Ottawa, Canada
[2]National Institute of Technology, Standard Reference Material Program, Gaithersburg, MD 20899

Table 1.—Continued—Duplicate samples results not yet available

Table 1.–Continued--Method blank results 3s values are considered the lower limit of detection (LOD), and 5s values are considered the lower limit of determination (LLD)

Method blank	*n*	*Mean*	*s*	*3s*	*5s*
Animal tissue	13	0.10	0.05	0.15	0.25
Plants	13	0.06	0.024	0.072	0.12

Bibliography

Crock, J.G., 1996, Mercury: Chapter 29, *in*, Methods of Soil Analysis, Part 3: Chemical Methods, D.L. Sparks, Editor, Number 5 in the Soil Science Society of America Book Series, soil Science Society of America, Inc., Madison, WI, pp. 769-791.

Crock, J.G., Arbogast, B.F. and Lamothe, P.J., 1999, "Laboratory Methods for the Analysis of Environmental Samples," in G. S. Plumlee, and M.J. Logsdon (Eds.), *The Environmental Geochemistry of Mineral Deposits, Part A. Processes, Techniques, and Health Issues*: Society of Economic Geologists, *Reviews in Economic Geology*. 6A: 265-287.

Hageman, Philip L., Mercury in Water by Continuous Flow Cold-Vapor Atomic Fluorescence Spectrometry, (this volume).

Kennedy, K.R. and Crock, J.G., 1987, Determination of Mercury in Geological Materials by Continuous-Flow, Cold-Vapor, Atomic Absorption Spectrophotometry: Analytical Letters, 20, p. 899-908.

Milestone, Inc., 2001, DMA 80 Operating Manual Version 3.23, 160B Shelton Rd., Monroe, CN 06468