

Determination of Mercury in Coal, Soil, Ashes, Rock, Sediment, and Plants by Direct Mercury Analyzer (DMA-80¹)

1. Introduction

This method describes how the quantitative amount of mercury (Hg) present is determined by atomic absorption upon the thermal decomposition of sample materials such as whole coal, soil, ash, rock, sediment and plants. Controlled heating of the sample in oxygen liberates Hg in a closed system. The sample is heated to dryness in the instrument and then thermally and chemically decomposed. The decomposition products are carried by flowing oxygen to the catalytic section of the furnace, where oxidation is completed and halogens as well as nitrogen and sulfur oxides are trapped. The remaining decomposition products are carried to the gold amalgamator that selectively traps Hg. After the system is flushed with oxygen to remove any remaining decomposition products, the amalgamator is rapidly heated, releasing Hg vapor. Flowing oxygen carries the Hg vapor through absorbance cells positioned in the light path of a single wavelength atomic absorption spectrophotometer. Absorbance peak height or peak area, as a function of Hg concentration, is measured at a wavelength of 253.7nm.

This method is similar to ASTM D6722-01 and U.S. EPA 7473.

2. Interfaces with Other Methods

EGL Method 26, Inorganic Sample Preparation.

EGL Method 29, Calibration of Laboratory Scales and Balances.

EGL Method 26, Solid Sample Preparation

3. Materials and Equipment

Milestone DMA-80 Direct Mercury Analyzer (DMA-80)

High purity oxygen

¹ Any use of trade, firm, or product names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

Reagents: None
Nickel Boats
Latex (or equivalent) gloves, and Personal Protection Equipment (PPE)

Standard Reference Materials (SRMs)
May include, but are not limited to:
Certified Coal Standards - ES6, ES2, CLB-1, Sarm20
Certified Soil Standards - NIST 2709, NIST 2711

Analytical Balance (4 place)

4. Procedure

The analysis proceeds by tuning the instrument for best stable response, calibrating the instrument with standards of known composition, and then analyzing the unknowns preferably in an automated routine to maximize reproducibility. This procedure provides concentrations of Hg in coal, soil, sediments, coal byproducts, plants and rocks.

Operating Conditions

The instrument should be turned on and 'warmed up' for an hour prior to analysis. High purity oxygen is required for analyses. Cleaned nickel boats are required for analysis. See the Instrument Manual at www.milestonesci.com for instrument settings and boat cleaning procedure.

Sample Analysis

Unknowns are analyzed only after an acceptable calibration curve has been established and verified for Hg.

Operational Checks

Operational checks will be used to determine if the DMA-80 is operational and capable of providing acceptable data. Operational checks are performed by analyzing an SRM at least every 10 samples, and analyzing a duplicate of an unknown at the end of the run. Acceptable tolerances are within 3 sigma of the error specified for the SRMs. Duplicates of unknowns must be within 10% of the original value.

5. Calibration and Quality Control Samples

Three blanks are run prior to calibration to condition the instrument. A suite of Standard Reference Materials (SRM's), or prepared aqueous standards are analyzed according to weight and/or calculated nanograms of Hg in ascending order up to 500 nanograms to achieve calibration. The calibration curve is typically a non-linear polynomial curve of more than four points with a correlation coefficient of 0.995 or greater. A calibration curve with a correlation coefficient of less than 0.995 is rejected, and a new calibration is performed. Following an acceptable calibration, verification of the calibration is performed as follows: one blank and one SRM are analyzed as unknowns to verify the calibration is within an acceptable tolerance of less than 0.5 ppb for the blank, and within the three sigma limits for the SRM. Records of the calibration curves and verification standard analyses are stored in computer files. Daily calibration is not required. However, calibration verification must be conducted prior to the start of each run to establish the instrument is operating optimally. The result for the first blank and SRM must be within established limits, or the calibration must be rejected and a new calibration curve is completed.

6. Limits, Precautions, and Interferences

Upper and lower concentration limits for the calibration are determined by the range of calibration standards used for Hg. Unknowns with high Hg concentrations that fall outside of the calibration range can be analyzed using reduced weights bringing the absolute amount of Hg within the calibration range. In accordance with EGL Method 26, all samples excluding water must be ground to -60 mesh for homogeneity. The lower reporting limit for the DMA-80 is 30.06 ppb as determined by the history of blank determinations. The lower reporting limit is updated on an annual basis.

Method limitation: Hg bound in silicates or other matrices may not thermally decompose, leading to incomplete (lower) Hg determinations.

Memory effects – Hg vapor may remain in the decomposition tube, amalgamator, or absorbance cells and then released in a subsequent analysis resulting in a positive bias. The instrument is programmed to clear the amalgamator and combustion tube of any potentially trapped gasses to avoid carryover of Hg to the next sample when the absolute amount of Hg is above 20ng.

7. Acceptance of Data

This procedure is considered acceptable by the satisfactory performance of the DMA-80 as determined by the calibration procedure described in Section 5. DMA-80 analyses determined under this procedure are quantitative. Acceptable tolerances are within 3 sigma of the error value for SRMs. One SRM is analyzed per 10 unknowns to verify precision and accuracy in each batch of samples. One duplicate of an unknown is analyzed with each sample batch. The duplicate of an unknown must be within 10% of the original value. Data are rejected if values for reference standards and duplicates fall outside of the specified margins. The following corrective actions are taken if data are rejected:

1. Check Calibration Standards – Prepare new calibration standards, or use new SRM standards and re-calibrate.
2. Check instrument settings – troubleshoot for proper gas flow, cell temperature, and lamp intensity.
3. Issues that are not resolved through steps one and two are reported to the laboratory supervisor, and instrument service may be needed. No further analysis will be conducted until the issue is resolved.

8. Data Handling and Transfer

Results are reported in parts per billion (ppb) by weight, equivalent to nanograms per gram (ng/g). Information obtained by this procedure is stored – 1. on the instrument's hard drive as raw data, and 2. transferred from the instrument by the analyst to an ExcelTM spreadsheet that includes the instrument, name of the analyst, element analyzed (Hg), date of analysis, and concentration of Hg. That spreadsheet is submitted to the Laboratory Information Management System (LIMS) and then reviewed and validated by the analyst.

9. References

ASTM (American Society of Testing and Materials) Methods ASTM D6722-01, Standard Test Method for Total Mercury in Coal and Coal Combustion Residues by Direct Combustion Analysis
U.S. EPA 7473, Mercury in Solids and Solutions by Thermal Decomposition, Amalgamation, and Atomic Absorption Spectrophotometry.

10. Attachments

None.

11. History of Changes

R0: Initial Issue