Methylmercury in Soil/Sediment - PBM

Parameter

Methylmercury, MeHg

Analytical Method

Acidic Leach, Solvent Extraction, Aqueous Back-Extraction, Aqueous Ethylation, Purge & Trap, GC-Pyrolysis-CVAFS

Introduction

This method is applicable to the analysis of mono-methylmercury cation (methylmercury) in soils and sediments.

Soil and sediment samples contain relatively higher concentrations of inorganic mercury compared to water samples, which can form interfering artifacts when preparing samples by distillation. To minimize the risk of these interfering artifacts a solvent extraction is the preferred method for preparing soil/sediment samples for methylmercury analysis.

Method Summary

This method is based on the United States Geological Survey (USGS) procedures published by DeWild *et. al.* (Method 5A – 7).

Samples are prepared by leaching the soil/sediment with an acidic potassium bromide and copper sulfate solution to release organo-mercury species from inorganic complexes. Methylmercury is then extracted into dichloromethane. An aliquot of the dichloromethane extract is then back-extracted into ultra-pure deionized water by purging with argon. The water extract is then ethylated in a purge vessel using sodium tetraethylborate ($NaBEt_4$) to convert methylmercury to volatile methylethylmercury, which is then purged and collected on an adsorbent carbon trap. The methylethylmercury is thermally desorbed to a packed GC column for separation from other ethylated mercury species. The GC effluent is pyrolized to convert methylethylmercury to elemental mercury, with detection and quantitation by Cold Vapour Atomic Fluorescence Spectroscopy (CVAFS). Results are reported on a dry weight basis.

This method is performance-based. Laboratories may adopt alternative options to improve performance or efficiency provided that all stated performance requirements and prescribed (mandatory) elements are met.

MDL(s) and EMS Analyte Codes*

Analyte	Approx. MDL	CAS #	EMS Analyte Code
Methylmercury (as MeHg)	0.00008 mg/Kg	22967-92-6	HgMe

The BC CSR standards for methylmercury use “as MeHg” units. Data users should be aware that test results for methylmercury may sometimes be reported in “as Hg” units. Test results in “as Hg” units may be multiplied by 1.07x to convert to “as MeHg” units.

Analysis for unspeciated mercury in soils (i.e. sum of all species, using the BC SALM digestion method) may be used to determine compliance with methylmercury standards, if the total (unspeciated) mercury concentration is shown to be lower than the methylmercury standard (with consideration of concentration unit differences as described above).

EMS Method Code(s)*

Refer to EMS Parameter Dictionary on the ministry website for all current EMS codes or codes not provided.

Matrix

Soil, Sediment.

Interferences and Precautions

Contaminants present in solvents, reagents, sample containers or sample processing equipment may cause interferences or yield artifacts. Test method conditions must be suitably monitored by routine analysis of method blanks.

Interference (artifact formation) from high levels of inorganic mercury is avoided by preparing soil and sediment samples by solvent extraction instead of distillation.

Sample Handling and Preservation

Sample Containers: glass jar with Teflon™ lined lid, or plastic (e.g. HDPE)

Preservation: None

Stability

Holding Time: 28 Days

Storage: ≤ 6°C. Freezing is permitted, but is not recommended due to the potential for container breakage.

Procedure

This method provides a brief summary of the analytical method conditions for this test, but does not include all information necessary to conduct the test. Refer to USGS Method 5A-7 for detailed step by step guidance on sample preparation, and to US EPA Method 1630 for detail guidance on ethylation and analysis.

Prior to sub-sampling, soil/sediment samples must be well-mixed using a mercury-free spatula to ensure homogeneity prior to sub-sampling. Take a representative sub-sample and analyze for moisture content.

Accurately weigh a second sub-sample of 2.0 ± 0.2 g into a clean Teflon™ centrifuge tube for extraction. Add 10.0 mL of 18% potassium bromide (KBr) extraction solution and 2.0 mL of 1 M copper sulfate ($CuSO_4$) reagent to the sample. Cap the tube and briefly shake to mix, then let stand at room temperature for at least 1 hour. After the 1 hour leaching period, add 20 mL of dichloromethane (CH_2Cl_2) to each tube, cap and then shake vigorously for 1 additional hour. After shaking, centrifuge the samples at ~2000G (~3000 rpm for a typical benchtop centrifuge) for 20 minutes to break any emulsions. Use a Pasteur pipette to remove and discard the aqueous (top) layer. Prepare the back extraction vial (either Teflon or glass) by addition of 40mL of ultra-pure deionized water. Accurately transfer 2.00 mL of the organic layer into the back-extraction vial, then, in a fumehood, place the vial in a heating block or water bath set to 45°C. Purge the sample with mercury-free nitrogen gas at a flow rate of 100 mL/min until all the dichloromethane has been purged away. The extract is now ready for analysis and can be stored in an opaque container or in the dark at 4°C for up to 48 hours.

Transfer the water extract to an appropriate reaction vessel for the ethylation step (e.g. purge and trap bubbler or purge and trap vial). Add 0.3 mL of 2M acetate buffer to each vessel. Once the buffer and sample are mixed, add 0.05 mL of freshly thawed 1% sodium tetraethylborate ($NaBEt_4$) then quickly seal the reaction vessel. The reagent amounts specified are per 40-50 mL volume of aqueous extract. Allow a minimum of 17 minutes for the ethylation reaction to complete.

The reaction vessel is attached to a purge and trap system and is purged with mercury-free nitrogen, and the volatile ethylated mercury species are collected on a carbon trap. The trap is then dried to remove moisture using a secondary nitrogen flow. Once dried the ethylated mercury species are thermally desorbed from the carbon trap and separated using a packed GC column. The separated species are then pyrolized (>700°C) to elemental mercury, which is detected and quantified by cold vapour atomic fluorescence spectroscopy. A minimum 5 point linear calibration is recommended.

Performance Requirements

Any analytical method options selected for this analysis must meet or exceed the performance requirements specified below.

Accuracy and Precision requirements are distinct from daily QC requirements, and apply to measures of long term method performance (averages and standard deviations). Achievement of these requirements is to be demonstrated during initial and ongoing method re-validation studies. For Initial Validations, averages of at least 8 Lab Control Samples or RMs must be assessed. Ongoing Re-validations (performance reviews) should assess QC data encompassing longer timeframes (e.g. 6 months to 1 year). A minimum frequency of 2 years is recommended for Ongoing Re-validations.

Accuracy Requirement: Laboratories must demonstrate method accuracy (measured as average recovery) of 85-115% for Lab Control Samples or Certified Reference Materials at concentrations above ten times the MDL.

Precision Requirement: Laboratories must demonstrate method precision equal to or better than 15% relative standard deviation for clean matrix spikes at concentrations above ten times the MDL.

Sensitivity Requirement: Where possible, the method should support Reporting Limits (and MDLs) that are less than 1/5 of applicable numerical standards. The method is not fit-for-purpose if an MDL exceeds a guideline, standard, or regulatory criteria against which it will be used for evaluation of compliance.

Quality Control

Summary of QC Requirements		
QC Component	**Minimum Frequency**	**Minimum Data Quality Objectives**
Method Blank (MB)	One per batch (max 20 samples)	Less than reported DL
Lab Control Sample (LCS)	One per batch (max 20 samples)	70 – 130%
Lab Duplicates (DUP)	One per batch (max 20 samples)	30% RPD [or within 2x reported DL for low level results]
Matrix Spike (MS) or Reference Material (RM)	One per batch (max 20 samples)	60 – 140%
Calibration Verification Standard (CVS) – 2nd source	One per initial calibration	85 – 115%
Continuing Calibration Verification (CCV)	One per 20 samples and at the end of each run	85 – 115%
If DQOs are not met, repeat testing or report qualified test results. DQOs do not apply to MS results where sample background exceeds spike amount.		

Prescribed Elements

The following components of this method are mandatory:

1. A separate sub-sample must be used for moisture content analysis. Samples that have been dried cannot be analyzed by this method.
2. The minimum sample amount used for the extraction is 1.8 g wet weight, based on a nominal weight of 2.0 ± 0.2 g. This amount has been scaled up from the USGS reference method to improve homogeneity of sub-sampling.
3. Soil samples must utilize an aqueous acidic extraction to release methylmercury that may be bound to inorganic complexes, prior to solvent extraction.
4. Analysis of extracts by the EPA 1630 method (aqueous phase ethylation, purge and trap, with detection by GC-pyrolysis-CVAFS) is recommended, but alternate detection techniques may be used if DQOs and other prescribed elements are met.
5. Methods using detection by the EPA 1630 method must use an acetate buffer (see EPA 1630 sec 7.7) prior to ethylation with sodium tetraethylborate.
6. QC requirements from the Quality Control section must be completed as specified, and must pass all specified acceptance criteria, or sample data must be qualified.
7. Sample Handling, Preservation, and Stability section guidelines may not be modified.

Apart from these limitations, and provided performance requirements are met, laboratories may introduce modifications to this method in order to improve quality or efficiency. Laboratories must disclose to their clients where modified or alternative methods are employed.

References

1. DeWild, J.F., Olund, S. D., Olson, M. L., & Tate, M. T. (2004). *Methods for the Preparation and Analysis of Solids and Suspended Solids for Methylmercury*. Techniques and Methods 5-A7. Reston, VA: U.S. Department of the Interior, U.S. Geological Survey
2. U.S. Environmental Protection Agency, Office of Water (2001). *Method 1630: Methyl Mercury in Water by Distillation, Aqueous Ethylation, Purge and Trap and CVAFS*. (EPA-821-R-01-020). Washington, DC
3. Canadian Council of Ministers of the Environment, CCME. (2016). *Guidance Manual for Environmental Site Characterization in Support of Environmental and Human Health Risk Assessment*, Volume 4 Analytical Methods. (ISBN 978-1-77202-032-8)

Revision History

July 10, 2017 New BC Lab Manual Method in support of 2017 CSR updates.