Methylmercury in Waters - PBM

Parameter

Methylmercury, MeHg.

Analytical Method

Distillation, Aqueous Ethylation, Purge & Trap, GC-Pyrolysis-CVAFS

Introduction

This method is applicable to the analysis of total or dissolved mono-methylmercury cation (methylmercury) in waters and seawaters.

Method Summary

This method is based on the procedures published in Method 1630 by the United States Environmental Protection Agency (US EPA).

Acid preserved samples are distilled under an inert gas flow. The pH of the distillate is adjusted to approximately 4.9 using an acetate buffer. The distillate is 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).

For dissolved analysis, samples are field-filtered through a 0.45 µm filter prior to preservation and distillation.

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 (µg/L)	EMS Analyte Code
Methylmercury (as MeHg) - Total	0.00006	HgMe
Methylmercury (as MeHg) - Dissolved	0.00006	code needed

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.

MDL values indicated above reflect the Method Limit from EPA 1630. Lower detection limit values may be achievable.

Analysis for total mercury may be used to determine compliance with methylmercury standards, if the total mercury concentration is shown to be lower than the methylmercury standard (with consideration of concentration unit differences as described above).

EMS Method Code(s)*

Code needed

*Refer to EMS Parameter Dictionary on the ministry website for all current EMS codes.

Matrix

Freshwater, Seawater, Groundwater, Wastewater.

Interferences and Precautions

Contaminants present in 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.

Nitric acid (HNO_3) will partially decompose methylmercury during the distillation process, therefore samples preserved with nitric acid cannot be analyzed for methylmercury.

The level of hydrochloric acid (HCl) in the sample must be controlled. If too little HCl is present, the distillation will not be quantitative, but too much HCl will result in co-distillation of HCl fumes which may interfere with the ethylation process. EPA 1630 states that freshwater samples should be preserved to 0.3% - 0.5% (v/v) 11.6 M HCl and seawater samples should be preserved to 0.1% - 0.2% (v/v) 9 M H_2SO_4.

High levels of inorganic mercury have been shown to cause positive artifact formation during the distillation process. In natural waters, approximately 0.01% - 0.05% of the ambient inorganic mercury in solution may be methylated by ambient organic matter during the distillation procedure. In most environmental waters, the percent methylmercury ranges from 1% - 30% of the total mercury, so this effect is trivial, and can be ignored in most cases. In extreme cases, this effect can be prevented using solvent extraction.

Sample Handling and Preservation

Sample Containers: Fluoropolymer (FLPE) bottle or borosilicate glass bottle with FLPE cap or FLPE lined cap.

Preservation: Samples should preferably be field preserved, or may be preserved at the lab within 48 hours of collection (for lab preservation, preserve within the original sample container, and equilibrate at least 16 hours before proceeding). For dissolved analysis, samples must be filtered prior to preservation. Field filtration is recommended (qualify if lab filtered).

Freshwater samples are preserved to pH < 2 with HCl (e.g. using 2 mL 1:1 HCl / 250 mL sample).

Seawaters are preserved to pH < 2 with H_2SO_4 (e.g. using 0.5 mL 1:1 M H_2SO_4 / 250 mL sample) to avoid interference from excess chloride.

Samples must be preserved within 48 hours of collection.

Stability

Holding Time: 180 days for preserved samples.

Storage: ≤6°C (store in an opaque container or in the dark). 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 US EPA Method 1630 for detailed step-by-step guidance on sample preparation and analysis by this method.

This method consists of five main processes conducted in series, for the preparation and analysis of water samples for methylmercury: Distillation, ethylation, purge and trap, Gas Chromatographic (GC) separation, and detection by pyrolysis with Cold Vapour Atomic Fluorescence Spectroscopy (CVAFS).

A 45 mL aliquot of preserved sample is dispensed into a distillation vessel where a complexing agent is added to improve the recovery of methylmercury. EPA 1630 recommends using a small amount (200 µL) of 1% ammonium pyrrolidinedithiocarbamate (APDC) but studies have shown that a dilute solution of L-cysteine instead of APDC can yield slightly better recoveries (Creswell et. al. 2015). The sample and complexing agent are then distilled using a heating block temperature of 125 ± 3°C under an inert gas flow of 60 ± 20 mL/min. The distillation is complete once 40 mL of distillate has been collected. Typically, the distillation will take between 2.5 to 4.0 hours, but the exact time required will vary based on the temperature, gas flow and sample matrix of each sample. Over-distillation may result in poor recoveries due to the co-distillation of HCl fumes, which can interfere with the ethylation procedure. The distillate must be analyzed within 48 hours. If analysis cannot be done immediately after distillation, the distillate can be stored in an opaque vessel or in the dark at >0 - 6°C until analysis.

Before proceeding with the ethylation process, the pH of the distillate must be checked. EPA 1630 states that the optimal pH for the ethylation reaction is pH 4.9. If the pH of the distillate is less than 3.5, over-distillation may have occurred. Although chloride and low pH can interfere with the ethylation reaction recent studies have shown that the reaction shows little to no variation in ethylation efficiency over the pH range of 3.0-5.0 in samples with low salinity and ionic strength as seen in distillates (Mansfield & Black 2015). Therefore it is not necessary to discard distillates that are below pH 3.5 as recommended by EPA 1630. The ethylation reaction is not affected by low initial pH as long as the buffered pH of the distillate is within an optimal pH range of approximately 4.0-5.0 before the addition of the ethylating reagent.

Transfer the distillate 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 2 M acetate buffer to each vessel, and check that pH is within 4.0 – 5.0 (additional buffer solution may be added if necessary). Note the exact final volume of the buffered distillate for calculation purposes (in case dilutions are required). Once the buffer and sample are mixed add 0.04 mL of freshly thawed 1% sodium tetraethylborate ($NaBEt_4$) then quickly seal the reaction vessel. The reagent amounts specified are per 45 mL sample volume. 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, with volatile ethylated mercury species collected on an adsorptive 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 form elemental mercury, which is detected and quantitated 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 performance 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 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)	One per batch (max 20 samples)	60 – 140%
Calibration Verification Standard (CVS) – 2nd source	One per initial calibration	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. Samples must be preserved with HCl (freshwaters) or H_2SO_4 (seawaters). Samples preserved with HNO_3 cannot be analyzed by this method.
2. A complexing agent must be added to the sample distillation vessel to ensure

distillation efficiency. Either ammonium pyrrolidinedithiocarbamate (APDC) or L-cysteine are recommended. Other complexing agents (e.g. $CuSO_4$) may be used if validated.

3. Distillation is to be carried out using a heating block temperature of 125 ± 3°C at 60 ± 20 mL/min inert gas flow.
4. Samples must be buffered using an acetate buffer (e.g. as per EPA 1630 sec 7.7) prior to the addition of the ethylating reagent.
5. Sodium tetraethylborate must be used as the ethylating reagent.
6. Sample analysis must follow the general principles and processes of the EPA 1630 method, including distillation, ethylation, and purge and trap with detection by GC-pyrolysis-CVAFS.
7. 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.
8. Sample Handling, Preservation, and Stability 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. 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
2. 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)
3. Creswell, J., P. Kilner and C. Davies (2015), *2015 Brooks Rand Instruments Interlaboratory Comparison Study for Total Mercury and Methylmercury (Intercomp 2015)*, Brooks Rand Instruments, Seattle, WA USA. http://www.brooksrandinc.com/content/uploads/2015/10/Interlaboratory-Comparison-Study-for-Total-Mercury-and-Methylmercury-report.pdf
4. Mansfield, C.R., & Black, F. J. (2015). *Quantification of monomethylmercury in natural waters by direct ethylation: Interference characterization and method optimization*. Limnol. Oceanogr.: Methods 13 (2), 81-91. doi: 10.1002/lom3.10009

Revision History

March 7, 2017 New BC Lab Manual method in support of 2017 CSR changes.