



Massachusetts Department of Environmental
Protection Bureau of Waste Site Cleanup

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| WSC-CAM | Section: III B |
| July 1, 2010 | Revision No. 1 |
| Final | Page 1 of 22 |

Quality Control Requirements and Performance Standards for the ***Analysis of Mercury by Cold Vapor Atomic Absorption (CVAA) Spectrometry*** in Support of Response Actions under the Massachusetts Contingency Plan (MCP)

WSC – CAM – III B

Quality Control Requirements and Performance
Standards for the ***Analysis of Mercury by Cold
Vapor Atomic Absorption (CVAA) Spectrometry*** in
Support of Response Actions under the Massachusetts
Contingency Plan (MCP)



Quality Control Requirements and Performance Standards for the ***Analysis of Mercury by Cold Vapor Atomic Absorption (CVAA) Spectrometry*** in Support of Response Actions under the Massachusetts Contingency Plan (MCP)

III. Metals Methods

B. Quality Control Requirements and Performance Standards for WSC-CAM-III B (Mercury by CVAA)

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ACRONYM LIST

| | |
|------------------|---|
| CAM | Compendium of Analytical Methods |
| CASN | Chemical Abstracts Service Number |
| CCB | Continuing calibration blank |
| CCV | Continuing calibration verification |
| CVAA | Cold vapor atomic absorption spectrometry |
| HNO ₃ | Nitric acid |
| LLCV | Low-level Calibration Verification |
| ICB | Initial calibration blank |
| ICV | Initial calibration verification |
| IDP | Initial demonstration of proficiency |
| IRAs | Immediate Response Actions |
| LCS/LCSD | Laboratory control sample / Laboratory control sample duplicate |
| MassDEP | Massachusetts Department of Environmental Protection |
| MB | Method blank |
| MCP | Massachusetts Contingency Plan |
| MD | Matrix duplicate |
| MS | Matrix spike |
| MOHML | Massachusetts Oil and Hazardous Materials List |
| %R | Percent recovery |
| r | Correlation coefficient |
| RAO | Response Action Outcome |
| RCs | Reportable Concentrations |
| RL | Reporting limit |
| RPD | Relative percent difference |
| RQs | Reportable Quantities |
| QA | Quality assurance |
| QC | Quality control |

UNITS:

| | |
|-------|------------------------|
| g | Gram |
| mg/L | Milligram per liter |
| mg/Kg | Milligram per kilogram |
| mL | Milliliter |
| µg/L | Microgram per liter |
| µm | Micrometer |
| nm | Nanometer |

| | | |
|--|--------------|----------------|
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1.0 Quality Control Requirements and Performance Standards for WSC-CAM-III B

1.1 Overview of WSC-CAM-III B

WSC-CAM-III B, *Quality Control Requirements and Performance Standards for the Analysis of Mercury by Cold Vapor Atomic Absorption (CVAA) Spectrometry in Support of Response Actions under the Massachusetts Contingency Plan (MCP)*, is a component of MassDEP's Compendium of Analytical Methods (CAM). Effective July 1, 2010, this revised CAM protocol, WSC-CAM-III B, replaces the original Mercury CAM document, WSC-CAM-III B (effective date, August 13, 2004). Refer to WSC-CAM-I A for an overview of the CAM process. Please note that while this protocol must be followed on and after the effective date of July 1, 2010 for the purpose of "Presumptive Certainty," the revised protocol may be used optionally prior to its effective date upon its publication on April 15, 2010.

This document provides Quality Control (QC) requirements and performance standards to be used in conjunction with the required analytical methods SW-846 7470A & 7471B, analysis for mercury in aqueous and solid samples using cold vapor atomic absorption (CVAA) spectrometry. The QC requirements and performance standards specified in this document in Table III B-1 together with the analytical procedures described in EPA SW-846 Methods 7470A *Mercury Liquid Waste (Manual Cold-Vapor Techniques)* & 7471B, *Mercury in Solid or Semisolid Waste (Manual Cold-Vapor Techniques)* constitute the WSC-CAM-III B protocol. All protocols included in the CAM are considered "methods" published by the MassDEP pursuant to the provisions of 310 CMR 40.0017(2). Use of EPA SW-846 7470A & 7471B is a "Presumptive Certainty" requirement of WSC-CAM-III B. It should be noted that if the laboratory utilizes the analytical procedures in SW-846 Method 7471A instead of 7471B, it is NOT acceptable to answer "YES" to Question B on the MassDEP Analytical Protocol Certification Form since there are analytical procedural differences between 7471A and 7471B (i.e., 7471B requires the use of a well-homogenized 0.6 gram aliquot instead of three 0.2 gram aliquots). Sample preservation, container and analytical holding time specifications for aqueous, soil, and sediment matrices for Mercury analyzed in support of MCP decision-making are presented in Appendix III B-1 of this document and Appendix VII-A of WSC-CAM-VII A *Quality Assurance and Quality Control Guidelines for the Acquisition and Reporting of Analytical Data in Support of Response Actions Conducted Under the Massachusetts Contingency Plan (MCP)*. Data reporting requirements are also provided in WSC-CAM-VII A.

Overall usability of data produced using this CAM protocol should be evaluated for compliance with project-specific data quality objectives, regardless of "Presumptive Certainty" status. For more guidance on data usability, refer to MassDEP Policy #WSC-07-350, *MCP Representativeness Evaluations and Data Usability Assessments*.

1.1.1 Reporting Limits for Mercury by WSC-CAM-III B

The reporting limit (RL) for Mercury using WSC-CAM-III B is dependent on the concentration of the lowest non-zero standard in the initial calibration or low-level calibration verification (LLCV), analyzed under identical conditions as the sample, with adjustments made for the sample size, preparation factors, percent solids, dilution factors, etc., as required. The CAM RLs for Mercury using the WSC-CAM-III B protocol are:



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- 0.2 µg/L for aqueous samples (surface water, groundwater and drinking water); and
- 0.1 mg/Kg for soil/sediment samples (assuming 100% solids).

For “Presumptive Certainty” purposes, if the typical CAM RLs are not achieved, respond “NO” to Question G of the “MassDEP MCP Analytical Protocol Certification Form” and address the CAM RL exceedance in the laboratory narrative.

Reporting limits lower than the above referenced CAM RLs for Mercury may be required to satisfy project requirements. The RL (based on the concentration of the lowest calibration standard or the LLCV) for Mercury must be less than or equal to the MCP standards or criteria that the contaminant concentrations are being compared to (e.g., Method 1 Standards, benchmark values, background, etc.). Meeting MCP standards or criteria may require analytical modifications to improve sensitivity. All such modifications must be described in the laboratory narrative.

1.1.2 Initial Demonstration of Proficiency for WSC-CAM-III B

Each laboratory that uses the WSC-CAM-III B protocol is required to operate a formal quality assurance program. The minimum requirements of this program consist of an initial demonstration of laboratory proficiency, ongoing analysis of standards and blanks to confirm acceptable continuing performance, the preparation/analysis of laboratory control samples (LCS) and/or matrix spikes (MS) to assess accuracy and LCS duplicates or matrix duplicates (MD) to assess precision.

Laboratories must document and have on file an Initial Demonstration of Proficiency for each combination of sample preparation and determinative method being used. These data must meet or exceed the performance standards as presented in Table III B-1 of this protocol. Procedural requirements for performing the Initial Demonstration of Proficiency can be found in SW-846 Chapter One, Section 4.4.1, Section 9.4 of SW-846 Method 7000B, and Section 9.2 of SW-846 Method 7471B. The data associated with the Initial Demonstration of Proficiency must be kept on file at the laboratory and made available to potential data users on request. The data associated with the Initial Demonstration of Proficiency for WSC-CAM-III B must include the following:

| QC Element | Performance Criteria |
|---|--|
| Initial Calibration | See WSC-CAM-III B, Table III B-1, for Performance Criteria |
| Continuing Calibration | |
| Method Blanks | |
| % Percent Recovery for LCS & MS | |
| Relative Percent Difference (RPD) for LCS Duplicate or MD | |

Laboratories are encouraged to actively monitor pertinent QC performance standards described in Table III B-1 to assess analytical trends (i.e., systematic bias, etc) and improve overall method performance by preempting potential non-conformances.



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For the WSC-CAM-III B protocol, laboratory-specific control limits must meet or exceed (demonstrate less variability than) the performance standards for each QC element listed in Table III B-1. It should be noted that the performance standards listed in Table III B-1 are based on multiple-laboratory data, which are in most cases expected to demonstrate more variability than performance standards developed by a single laboratory.

This protocol is restricted to use by, or under the supervision of, analysts who are experienced in using CVAA spectrometry as a quantitative tool for environmental analyses.

1.2 Summary of SW-846 Methods 7470A and 7471B

SW-846 Method 7470A is a CVAA procedure for determining the concentration of total Mercury (organic and inorganic forms) in mobility-procedure extracts, aqueous wastes, surface water and groundwater. SW-846 Method 7471B is a CVAA procedure for determining total mercury (organic and inorganic forms) in soils, sediments, bottom deposits, and sludge-type materials. Prior to analysis, the liquid samples must be pretreated according to the procedure described in Section 7.0 of SW-846 Method 7470A and solid samples are prepared using an appropriate dissolution step, as described in Section 11.0 of SW-846 Method 7471B.

Quantitation is based on the absorption of radiation at the 253.7-nm wavelength by mercury vapor. The mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance (peak height) is measured as a function of mercury concentration.

1.3 Method Interferences

Samples submitted to a laboratory for trace metal analysis may become contaminated by numerous routes during both sampling and analysis. Potential sources of contamination may include:

- Metallic or metal-containing containers and sampling equipment,
- Laboratory acids or reagents,
- Improperly cleaned or stored equipment, and
- Atmospheric inputs such as dirt and dust.

Refer to SW-846 Methods 7470A and 7471B for further information on method interferences and contamination. Several common interferences and corrective measures are summarized as follows.

- Potassium permanganate is added to eliminate possible interference from sulfide. Concentrations as high as 20 mg/Kg of sulfide, as sodium sulfide, do not interfere with the recovery of inorganic mercury added to reagent water.
- Seawaters, brines, and industrial effluents high in chlorides require additional permanganate (as much as 25 mL) because, during the oxidation step, chlorides are converted to free chlorine, which also absorbs radiation of 253.7 nm, thereby giving a potential high bias for Mercury. An excess of hydroxylamine sulfate reagent (25 mL) can be added to ensure that free chlorine is absent before the mercury is reduced and swept into the cell.



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1.4 Quality Control Requirements for WSC-CAM-III B

1.4.1 General QC Requirements

For general quality control procedures for all inorganic methods, including SW-846 Methods 7470A/7471B, refer to SW-846 Chapter One. General QC procedures to evaluate the instrument's operation can also be found in SW-846 Chapter One, Section 2.0, and include evaluation of calibrations and performance of sample analyses.

1.4.2 Specific QC Requirements and Performance Standards for WSC-CAM-III B

Specific QC requirements and performance standards for Mercury using the WSC-CAM-III B protocol are presented in Table III B-1. Refer to WSC-CAM-VII A for field QC requirements. ***Note that a project-specific matrix spike (MS) must be performed for Mercury to evaluate accuracy in a solid matrix (soil/sediment) at a frequency of one per 20 samples per matrix.*** Strict compliance with the QC requirements and performance standards, as well as satisfying the CAM's other analytical and reporting requirements will provide a data user with "Presumptive Certainty" in support of Response Actions under the MCP. The concept of "Presumptive Certainty" is explained in detail in Section 2.0 of WSC-CAM-VII A.

While optional, parties electing to utilize these protocols will be assured of "Presumptive Certainty" of data acceptance by agency reviewers. In order to achieve "Presumptive Certainty" for analytical data, parties must:

- (a) Use the analytical method specified for the selected CAM protocol;
- (b) Incorporate **all** required analytical QC elements specified for the selected CAM protocol;
- (c) Implement, as necessary, required corrective actions and analytical response actions for **all** non-conforming analytical performance standards;
- (d) Evaluate and narrate, as necessary, **all** identified CAM protocol non-compliances; and
- (e) Comply with **all** the reporting requirements specified in WSC-CAM-VII A, including retention of reported and unreported analytical data and information for a period of ten (10) years.

In achieving "Presumptive Certainty" status, parties will be assured that analytical data sets:

- ✓ Satisfy the broad QA/QC requirements of 310 CMR 40.0017 and 40.0191 regarding the scientific defensibility, precision and accuracy, and reporting of analytical data; and
- ✓ May be used in a data usability and representativeness assessment, as required in 310 CMR 40.1056(2)(k) for Response Action Outcome (RAO) submittals, consistent with the guidance described in MassDEP Policy #WSC-07-350, *MCP Representativeness Evaluations and Data Usability Assessments*.



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1.5 Special Analytical Considerations for WSC-CAM-III B

- Matrix Spike (MS) Recovery – **A MS is required for WSC-CAM-III B for solid matrices (soil/sediment) at a frequency of one per 20 samples per matrix.** Consistent with USEPA Region I data validation guidance, MassDEP requires rejection of non-detected metals results with <30% recovery in the MS. If the MS recovery is <30% and non-detected results were found for mercury, the laboratory must follow the required corrective actions listed on Table III B-1.
 - Laboratories are not required to monitor whether or not matrix spikes are performed on soil/sediment samples at a frequency of one per 20 samples per matrix. This is the responsibility of the data user.
 - For “Presumptive Certainty” purposes, if the data user does not submit a soil/sediment sample for MS analysis, Question H of the “MassDEP MCP Analytical Protocol Certification Form” must be answered NO and this must be noted in the laboratory narrative.
- Soils/Sediments – Because of the small sample size generally used for solid sample analyses (0.6-grams), “as-received” field samples of solid or semisolid materials must be thoroughly homogenized in the laboratory prior to mercury analysis to obtain a representative aliquot for analysis. If mercury is a contaminant of concern (COC) at an MCP site or if poor precision and/or accuracy (that would adversely effect MCP decision making) associated with sample matrix heterogeneity is anticipated, then the following corrective measures should be considered by the data user:
 - Direct the laboratory to use a larger sample aliquot (up to 10 grams) to enhance sensitivity and/or precision. The laboratory must adjust the concentration/volume of all reagents for the larger sample aliquot.
 - Direct the laboratory to prepare and analyze replicate aliquots (two or more) for each field sample to better assess variability, associated with sample matrix heterogeneity.
 - Use more effective field sample homogenization procedures (prior to submitting sample to laboratory for mercury analysis).
 - Increase frequency of field duplicate collection and analysis to improve understanding of heterogeneity and representativeness.
 - If overall site heterogeneity for mercury is a specific concern (i.e. distribution of mercury contamination is inconsistent with the conceptual site model), it is recommended that the number of field samples be increased to improve the representativeness of mercury results for site assessment and characterization.

1.6 Analyte List for WSC-CAM-III B

The MCP analyte list for WSC-CAM-III B consists of Mercury, total (organic and inorganic), CASN 7439-97-9.

It is the responsibility of the data user, in concert with the laboratory, to establish the range and required RL for the target analyte. Sources of various MassDEP standards and criteria are as follows:

- Reportable Quantities (RQs) and Concentrations (RCs) as described in 310 CMR 40.1600, The Massachusetts Oil and Hazardous Materials List (MOHML), in Subpart P of the MCP may be found at the following URL: <http://www.mass.gov/dep/cleanup/laws/regulati.htm#mcp>



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- An online searchable Oil & Hazardous Materials List of RQs and RCs values may be found at the following URL:
<http://public.dep.state.ma.us/momhl/hazmat.aspx>.
- An updated list of MCP Method 1 Standards may be found at the following URL:
<http://www.mass.gov/dep/cleanup/laws/standard.htm>

Mercury has promulgated MCP Method 1 groundwater/soil standards.



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Table III B-1: Specific QC Requirements and Performance Standards for Mercury (SW-846 7470A & 7471B) Using WSC-CAM-III B

| Required QC Parameter | Data Quality Objective | Required Performance Standard | Required Deliverable? | Rejection Criteria per WSC-07-350 ¹ | Required Corrective Action | Required Analytical Response Action |
|--|--|--|-----------------------|--|---|--|
| Initial Demonstration of Proficiency (IDP) | Laboratory Analytical Accuracy & Precision | (1) Must be performed prior to using method on samples. (2) Must be performed for each matrix. (3) Must follow procedures in Section 9.2 of SW-846 7471B and Section 9.4 of SW-846 7000B. | No | NA | Refer to Section 9.2 of SW-846 7471B, Section 9.4 of SW-846 7000B, and Section 1.1.2 of this protocol. | NA |
| Preparation of Samples | Accuracy and Representativeness | (1) All aqueous and solid samples must be prepared (digested) prior to analysis. See SW-846 7470A and 7471B for details. | No | NA | NA | NA |
| Initial Calibration | Laboratory Analytical Accuracy | (1) Frequency: Daily prior to sample analysis. (2) Minimum calibration blank plus 5 calibration standards (multi-point); high level standard in calibration defines the upper end of the linear calibration range. (3) Linear regression with correlation coefficient $r \geq 0.995$. | No | NA | Perform instrument maintenance as necessary; re-optimize instrument; re-calibrate as required by SW-846 7470A and 7471B. | Suspend all analyses until initial calibration meets criteria. |
| Initial Calibration Verification (ICV) | Laboratory Analytical Accuracy | (1) Frequency: Immediately after each initial calibration. (2) Prepared using standard source different than used for initial calibration. (3) Concentration level near midpoint of curve. (4) Percent recovery must be between 90-110%. | No | NA | (1) Reanalyze ICV; if acceptable, no further action required. (2) If reanalysis is still outside of criteria, recalibrate and reanalyze ICV. | Suspend all analyses until ICV meets criteria. |
| Initial Calibration Blank (ICB) | Laboratory Analytical Sensitivity (instrument drift & contamination) | (1) Frequency: Immediately after ICV. (2) Prepared using same concentration of acids as calibration standards. (3) Mercury must be <RL. | No | NA | (1) Reanalyze ICB; if acceptable, no further action required. (2) If reanalysis is still outside of criteria, recalibrate and reanalyze ICV & ICB. | Suspend all analyses until ICB meets criteria. |



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| Required QC Parameter | Data Quality Objective | Required Performance Standard | Required Deliverable? | Rejection Criteria per WSC-07-350 ¹ | Required Corrective Action | Required Analytical Response Action |
|---|--|--|-----------------------|--|---|---|
| Low-Level Calibration Verification (LLCV) | Laboratory Analytical Sensitivity (verify low-end of calibration range / verify RL) | (1) Frequency: Daily prior to sample analysis if initial calibration did not contain a low-level standard at the RL. If initial calibration includes the RL as the low-level standard in the initial calibration curve, then LLCV is not required. (2) Prepared using same source as initial calibration standards. (3) Concentration level must be at the level of the RL for mercury. (4) Percent recovery must be 70-130%. | No | NA | (1) Reanalyze LLCV; if acceptable, no further action required. (2) If reanalysis is still outside of criteria and concentrations of mercury are $\leq 10x$ RL in associated field samples, recalibrate and reanalyze LLCV and associated samples. (3) If concentrations of mercury are $> 10x$ RL in associated field samples, include explanation in laboratory narrative; no further action required. | Suspend all analyses until LLCV meets criteria unless the concentrations of mercury are $> 10x$ RL in associated field samples. |
| Continuing Calibration Verification (CCV) | Laboratory Analytical Accuracy | (1) Frequency: Every 10 samples and at the end of the analytical run. (2) Prepared using same source as initial calibration standards. (3) Concentration level near midpoint of curve. (4) Percent recovery must be 80-120%. | No | NA | (1) Reanalyze CCV; if acceptable, no further action required. (2) If reanalysis is still outside of criteria, recalibrate and reanalyze all associated samples since last compliant CCV – unless (3) applies. (3) If recovery is high ($> 120\%$) and all associated sample results are non-detected, no corrective action required. | If (3) applies, include explanation in laboratory narrative. |



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| Required QC Parameter | Data Quality Objective | Required Performance Standard | Required Deliverable? | Rejection Criteria per WSC-07-350 ¹ | Required Corrective Action | Required Analytical Response Action |
|------------------------------------|--|---|-----------------------|--|--|--|
| Continuing Calibration Blank (CCB) | Laboratory Analytical Sensitivity (instrument drift & contamination) | (1) Frequency: Every 10 samples following CCV and at the end of the analytical run. (2) Prepared using same concentration of acids as calibration standards. (3) Mercury must be <RL. | No | NA | (1) Reanalyze CCB; if acceptable, no further action required. (2) If reanalysis still outside of criteria, recalibrate and reanalyze all associated samples since last compliant CCB – unless (3) applies. (3) If concentration of mercury in CCB is >RL but all associated sample results are either non-detected or >10x concentration of mercury in CCB, no corrective action required. | If (3) applies, include explanation in laboratory narrative. |
| Method Blank (MB) | Laboratory Method Sensitivity (contamination evaluation) | (1) Frequency: One per digestion batch of ≤20 field samples. (2) Must be digested with the samples using the same preparation method as the samples. (3) Mercury must be <RL. | Yes | NA | (1) Reanalyze MB; if acceptable, no further action required. (2) If reanalysis is still outside of criteria, redigest and reanalyze MB and all associated field samples in batch – unless (3) applies. (3) If concentration of mercury in MB is >RL but all associated sample results are either non-detected or >10x concentration of mercury in MB, no corrective action required. | If (3) applies, include explanation in laboratory narrative. |



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| Required QC Parameter | Data Quality Objective | Required Performance Standard | Required Deliverable? | Rejection Criteria per WSC-07-350 ¹ | Required Corrective Action | Required Analytical Response Action |
|---------------------------------|--|--|-----------------------|--|--|--|
| Laboratory Control Sample (LCS) | Laboratory Analytical Accuracy | (1) Frequency: One per digestion batch of ≤ 20 field samples. (2) Must be matrix-matched by digesting with the samples using the same preparation method. CAM requires a solid Standard Reference Material (SRM) be prepared and analyzed with solid field samples as the "solid LCS." An SRM is a soil or sediment matrix that contains mercury at a known concentration and with 95% confidence limits. (3) Concentration level for aqueous LCS near midpoint of curve. (4) Percent recovery for mercury must be 80-120% for aqueous LCS and within vendor control limits (95% confidence limits) for solid LCS. | Yes | Aqueous LCS: Recovery <50%: mercury results in associated samples may be rejected. | (1) Reanalyze LCS; if acceptable, no further action required. (2) If reanalysis is still outside of criteria and LCSD is in-control for mercury, no corrective action required. (3) If LCS and LCSD are both outside of criteria, redigest and reanalyze LCS/LCSD and all associated field samples in batch. | Report recovery exceedances in laboratory narrative. |
| LCS Duplicate (LCSD) | Laboratory Analytical Accuracy & Precision | (1) Frequency: One per digestion batch of ≤ 20 field samples ONLY if not performing project-specific MD. (2) Must be matrix-matched by digesting with the samples using the same preparation method. CAM requires a solid SRM be prepared and analyzed with solid field samples as the "solid LCSD." An SRM is a soil or sediment matrix that contains mercury at a known concentration and with 95% confidence limits. (3) Concentration level must be same as LCS. Analyze immediately following LCS. (4) Percent recovery for mercury must be 80-120% for aqueous LCS and within | Yes ONLY if no MD | Same as above for LCS for recovery evaluation | (1) Reanalyze LCSD; if acceptable, no further action required. (2) If reanalysis is still outside of recovery criteria and LCS is in-control for mercury, no corrective action required. (3) If LCSD and LCS are both outside of recovery criteria, redigest and reanalyze LCS/LCSD and all associated field samples in batch. | Report recovery and RPD exceedances in laboratory narrative. |



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| Required QC Parameter | Data Quality Objective | Required Performance Standard | Required Deliverable? | Rejection Criteria per WSC-07-350 ¹ | Required Corrective Action | Required Analytical Response Action |
|---|-----------------------------------|--|---|---|--|---|
| | | <p>vendor control limits (95% confidence limits) for solid LCS.</p> <p>(5) RPDs must be ≤ 20 for aqueous LCS/LCSD and ≤ 30 for solid LCS/LCSD.</p> | | | | |
| Matrix Spike (MS) Project-Specific | Method Accuracy in Sample Matrix | <p>(1) Solid Samples (Soil/Sediment) <u>Frequency</u>: One per 20 field samples per matrix; designated by data user on COC or at project set-up.</p> <p><u>Aqueous Samples Frequency</u>: One per digestion batch of ≤ 20 field samples per matrix strongly recommended (designated by data user on COC or at project set-up).</p> <p>(2) Concentration levels near midpoint of curve.</p> <p>(3) Percent recovery for mercury must be 75-125%.</p> | Yes ONLY when requested by the data user | Recovery <30%: affects non-detects for mercury in all associated samples. | <p>(1) Reanalyze MS; if acceptable, no further action required.</p> <p>(2) After reanalysis, if MS recovery is 30-74% or >125% and LCS was in-control, no corrective action is required.</p> <p>(3) If MS recovery is <30% and associated with non-detected results, redigest (homogenize sample well) and reanalyze sample/MS pair. Report results and narrate.</p> | <p>Report MS exceedances in laboratory narrative.</p> <p>If redigested due to recoveries <30%, report both sets of sample/MS data.</p> |
| Matrix Duplicate (MD) Project-Specific | Method Precision in Sample Matrix | <p>(1) Frequency: One per digestion batch of ≤ 20 field samples per matrix is strongly recommended (designated by data user on COC or at project set-up).</p> <p>(2) Prepare by digesting and analyzing an additional aliquot of the same field sample used for MS.</p> <p>(3) RPD for mercury must be ≤ 20 for aqueous and ≤ 35 for solids.</p> | Yes ONLY when requested by the data user | NA | Narrate. | Report exceedances in laboratory narrative. |



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Table III B-1: Specific QC Requirements and Performance Standards for Mercury (SW-846 7470A & 7471B) Using WSC-CAM-III B

| Required QC Parameter | Data Quality Objective | Required Performance Standard | Required Deliverable? | Rejection Criteria per WSC-07-350 ¹ | Required Corrective Action | Required Analytical Response Action |
|--------------------------|------------------------|--|-----------------------|--|----------------------------|---|
| General Reporting Issues | NA | (1) Non-detected values must be reported with the sample-specific RL for mercury using all appropriate preparation/dilution factors. (2) The laboratory must only report values \geq the sample-specific RL. (3) Sample concentrations that exceed the highest calibration standard must be diluted and reanalyzed to fall within the linear calibration range. (4) Results for soils/sediments must be reported on a dry-weight basis for comparison to MCP regulatory standards. (5) Results must be reported with 2 or more "significant figures" if \geq RL. If reporting values below the RL, report with 1 or more "significant figures". ² (6) Refer to Appendix III B-1 for chain-of-custody requirements regarding preservation, cooler temperature, and holding times. | NA | NA | NA | (1) The performance of dilutions must be documented in the laboratory narrative or on the report form. Unless due to elevated concentrations of mercury, reasons for dilutions must be explained in the laboratory narrative. (2) If samples are not preserved properly or are not received with an acceptable cooler temperature, note the non-conformances in the laboratory narrative. (3) If samples are prepared and/or analyzed outside of the holding time, note the non-conformances in the laboratory narrative. (4) Narrate any additional method non-compliance or sample-specific anomaly. |

¹As per Appendix IV of MassDEP Policy #WSC-07-350, *MCP Representativeness Evaluations and Data Usability Assessments*, September 2007, if these results are observed, data users should consider nondetect results as unusable and detected results as estimated with a significant low bias.

²Reporting protocol for "significant figures" is a policy decision included for standardization and consistency for reporting of results and is not a definition of "significant" in the scientific or mathematical sense.



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2.0 Data Usability Assessment

Specific guidance applicable to all Class A, B or C RAO Statements, including partial RAOs, for preparation of Representativeness Evaluations and Data Usability Assessments pursuant to 310 CMR 40.1056(2)(k) of the MCP is provided in *MCP Representativeness Evaluations and Data Usability Assessments* (Policy #WSC-07-350). This document provides general information regarding the purpose and content of these required evaluations as a component of and in support of an RAO submittal. The most current version of this document may be found at the following URL: <http://www.mass.gov/dep/cleanup/laws/policies.htm#finpol>

Overall usability of data produced using this CAM protocol should be evaluated for compliance with project-specific data objectives using MassDEP Policy #WSC-07-350, regardless of “Presumptive Certainty” status.

3.0 Reporting Requirements for WSC-CAM-III B

3.1 General Reporting Requirements for WSC-CAM-III B

General environmental laboratory reporting requirements for analytical data used in support of assessment and evaluation decisions at MCP disposal sites are presented in WSC-CAM-VII A, Section 2.4. This guidance document provides limited recommendations for field QC, as well as the required content of the laboratory report, which includes:

- Laboratory identification information,
- Analytical results and supporting information,
- Sample- and batch-specific QC information,
- Laboratory Report Certification Statement,
- Copy of the Analytical Protocol Certification Form,
- Laboratory narrative contents, and
- Chain-of-custody form requirements.

3.2 Specific Reporting Requirements for WSC-CAM-III B

Specific QC requirements and performance standards for WSC-CAM-III B are presented in Table III B-1. Specific reporting requirements for WSC-CAM-III B are summarized below in Table III B-2 as “Required Analytical Deliverables (**YES**)”. These routine reporting requirements must always be included as part of the laboratory deliverable for this method. It should be noted that although certain items are not specified as “Required Analytical Deliverables (**NO**)”, these data must be available for review during an audit and may also be requested on a client-specific basis.

Soil and sediment results must be reported on a dry-weight basis. Refer to ASTM Method D2216, Determination of Moisture Content of Soils and Sediments, for more detailed analytical and equipment specifications.



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Table II B-2 Routine Reporting Requirements for WSC-CAM-III B (SW-846 7470A/7471B)

| Parameter | Required Analytical Deliverable |
|---|--|
| Initial Calibration | NO |
| Initial Calibration Verification (ICV) | NO |
| Initial Calibration Blank (ICB) | NO |
| Low-Level Calibration Verification (LLCV) | NO |
| Continuing Calibration Verification (CCV) | NO |
| Continuing Calibration Blank (CCB) | NO |
| Method Blank (MB) | YES |
| Laboratory Control Sample (LCS) | YES |
| LCS Duplicate | YES |
| Matrix Spike (MS) | YES <i>(if requested by data user)</i> |
| Matrix Duplicate (MD) | YES <i>(if requested by data user)</i> |
| Identification and Quantitation | NO |
| General Reporting Issues | YES |

3.2.1 Sample Dilution

Under circumstances that sample dilution is required because the concentration of mercury exceeds the concentration of the highest calibration standard or due to matrix interference, the RL for mercury must be adjusted (increased) in direct proportion to the Dilution Factor (DF).

The revised RL for the diluted sample, RL_d :

$$RL_d = DF \times \text{Lowest Calibration Standard for Mercury}$$

It should be understood that samples with elevated RLs as a result of a dilution may not be able to satisfy MCP standards/criteria in some cases if the RL_d is greater than the applicable MCP standard or criterion to which the concentration is being compared. All dilutions must be fully documented in the laboratory narrative.



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Appendix III B-1

Sample Collection, Preservation, and Handling Procedures for Mercury Analyses

Sample preservation, container and analytical holding time specifications for aqueous, soil, and sediment matrices for Mercury analyzed in support of MCP decision-making are summarized below and presented in Appendix VII A-1 of WSC-CAM-VII A, *Quality Assurance and Quality Control Guidelines for the Acquisition and Reporting of Analytical Data Conducted in Support of Response Actions Conducted Under the Massachusetts Contingency Plan (MCP)*. Additional guidance may be found in SW-846, Chapter Three.



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| Matrix | Container ¹ | Preservation ⁴ | Holding Time ² |
|--------------------------------------|--|---|---------------------------|
| Aqueous Total Mercury | 500 mL glass or Polyethylene Bottle | HNO ₃ to pH <2 | 28 days |
| Aqueous Dissolved Mercury (Filtered) | 500 mL glass or Polyethylene Bottle | Filter (0.45 µm) on site or at the laboratory (prior to acid preservation) within 24 hours of collection; then preserve with HNO ₃ to pH <2 | 28 days |
| Soil and Sediments | 4-ounce glass jar with teflon-lined cap | Cool to ≤ 6°C | 28 days ³ |
| Concentrated Waste | 125 mL wide-mouth glass or polyethylene bottle | Cool to ≤ 6°C | 28 days |

¹The collection of multiple sample containers per sample location may be required to collect enough sample for matrix QC.

²Holding Time begins from time of sample collection. As per Appendix IV of MassDEP Policy #WSC-07-350, *MCP Representativeness Evaluations and Data Usability Assessments*, September 2007, if the holding time is exceeded by >2x, data users should consider non-detect results as unusable and detected results as estimated (low bias).

³Alternatively, soil and sediment samples for mercury analyses may be held for up to one (1) year if frozen within 24 hours of collection at <-10°C. Sampling container should only be filled to 2/3 of capacity to avoid breakage caused by expansion during freezing. Preparation must commence within 24 hours of thawing. Temperature must never be allowed to go below -20°C to avoid damage to container seals and breakage.

⁴If samples were received by the laboratory on the same day of collection and were stored and transported to the laboratory on ice, cooler temperatures above 6°C are acceptable.



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Appendix III B-2

Data Deliverable Requirements for Data Audits



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If requested by MassDEP, submission of the information listed below may be required to perform a data audit to verify compliance with the analytical methods and to evaluate accuracy and reliability of the reported results. These deliverables represent a “full data package” including all sample documentation from receipt through preparation, analysis, and data reporting. The laboratory must ensure that these deliverables are available, in the event a data audit is performed. The laboratory is required to retain these deliverables for a period of 10 years from the date generated.

| DELIVERABLE REQUIREMENTS FOR DATA AUDITS WSC-CAM-III B (Mercury by CVAA: SW-846 7470A/7471B) | |
|---|---|
| Laboratory Narrative | Must comply with the required laboratory narrative contents as described in WSC-CAM-VII A |
| Sample Handling Information | Chain-of-custody (external and internal), sample receipt logs (cooler temperatures and sample pH), correspondences |
| Miscellaneous Logs | Dry weight logs; Analytical logs; Freezer logs |
| Initial Calibration Data | Raw instrument data for initial calibration, including calculation of linear or non-linear regression and correlation coefficient values; Concentrations of calibration standards used |
| Initial Calibration Verification and Initial Calibration Blank Data | Percent recoveries for all ICVs; ICV source & true value; Results and raw instrument data for ICV and ICB |
| Low-Level Calibration Verification, Continuing Calibration Verification, and Continuing Calibration Blank Data | Percent recoveries for all LLCV and CCV; LLCV and CCV source & true value; Results and raw instrument data for LLCV, CCV, and CCB |
| Sample Results | Sample result forms with dilution factors, units, reporting limits, method reference, date of preparation, date of analysis; Raw instrument data; Percent solids results; Sample preparation logs (initial and final weights/volumes; preparation method reference) |
| Method Blank Results | Method Blank results, units, reporting limits; Raw instrument data; Preparation logs |
| LCS/LCS Duplicate Results and/or SRM results | Summary of results, including concentrations detected, concentrations spiked or known (vendor limits) if SRM, percent recoveries and RPDs; Raw instrument data; Preparation logs |
| MS Results – if analyzed MD Results – if analyzed | Summary of results, project-specific sample ID, unspiked sample concentration, concentration detected, concentration spiked, percent recoveries and RPDs; Raw instrument data; Preparation logs |



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Appendix III B-3

Analysis Sequence for Mercury by WSC-CAM-III B

Typical analytical sequence for Mercury by CVAA using WSC-CAM-III B:

- Initial Calibration
- ICV
- ICB
- LLCV – only required if low-level standard in initial calibration curve is not at the level of the RL
- CCV – initial
- CCB – initial
- MB
- LCS
- LCSD – only required if not performing a project-specific MD
- 7 samples – include the project-specific MS and/or MD if applicable
- CCV
- CCB
- 10 samples
- CCV
- CCB
- Etc. (continue 10 samples and CCV/CCB pairs)
- CCV – ending
- CCB – ending