State of Connecticut

Department of Energy and Environmental Protection

Recommended Reasonable Confidence Protocols

Quality Assurance and Quality Control Requirements

Determination of Mercury by SW-846 Methods

7470 and 7471 Cold Vapor Atomic Absorption Spectroscopy

Version 3.0

May 2024

Written by the Connecticut DEEP QA/QC Workgroup

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1.0	First version for publication	7/05
2.0	Final version based upon public comments	July 2006
3.0	Updates to reflect CAM method updates to improve consistency between different states.	May 2024

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Acronym List

ACRONYM	DEFINITION
CASN	Chemical Abstracts Service Number
CCB	Continuing calibration blank
CCV	Continuing calibration verification
CVAA	Cold vapor atomic absorption
%D	Percent difference
DEEP	CT Department of Energy and Environmental Protection
EP	Environmental Professional
g	Grams
HCl	Hydrochloric acid
HNO_3	Nitric acid
ICB	Initial calibration blank
ICV	Initial calibration verification
LCS/LCSD	Laboratory control sample / Laboratory control sample duplicate
LLOQ	Lower limit of quantitation
MB	Method blank
MD	Matrix duplicate
mg/L	Milligram per liter
mg/kg	Milligram per kilogram
mL	Milliliter
MS	Matrix spike
nm	Nanometer
%R	Percent recovery
r/r^2	Correlation coefficient
RL	Reporting limit
RPD	Relative percent difference
RSR/RSRs	Remediation Standard Regulations
QA	Quality assurance
QC	Quality control
µg/L	Microgram per liter
µm	Micrometer

1.0 Quality Assurance and Quality Control Requirements for SW-846 Methods 7470/7471

1.1 Method Overview

SW-846 Methods 7470 and 7471are cold-vapor atomic absorption ("CVAA") procedures. Method 7470 is approved for determining the concentration of mercury (Hg) in mobility-procedure extracts, aqueous wastes, and ground waters. Method 7471 is approved for measuring total mercury (organic and inorganic) in soils, sediments, bottom-deposits, and sludge type materials. All samples must be subjected to an appropriate dissolution step prior to analysis. If this dissolution procedure is not sufficient to dissolve a specific matrix type or sample, then this method is not applicable for that matrix.

All method references are to the latest promulgated version of the method found in *Test Methods for Evaluating Solid Waste, SW-846*.

1.2 Summary of SW-846 Methods 7470/7471

Prior to analysis, samples must be digested according to the procedures discussed in Methods 7470 and 7471.

Both Method 7470 and 7471 CVAA techniques are based on the absorption of radiation at 253.7 nm by Hg vapor. The Hg is reduced to the elemental state (Hg^0) and aerated from solution in a closed system. The Hg vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance (peak height) is measured as a function of Hg concentration.

For soil/solid samples the typical sample aliquot is 0.2 grams. Due to the small sample-size it is critical that the sample be thoroughly homogenized. If Hg is an element of concern at the site, and sample heterogeneity is anticipated, then the Environmental Professional ("EP") and the laboratory should follow preemptive or corrective measures. Any corrective measure taken should be narrated in the laboratory report.

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.

1.3.1 Chemical Interferences

Potassium permanganate is added to eliminate possible interference from sulfide. Concentrations as high as 20 mg/L of sulfide as sodium sulfide do not interfere with the recovery of added inorganic Hg from reagent water.

Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/L had no effect on recovery of Hg from spiked samples.

Certain volatile organic materials that absorb at this wavelength may also cause interference. A preliminary run without reagents should determine if this type of interference is present.

Analysis of blanks provides information about the presence of contaminants. When potential interferences or high levels of target compounds are detected in blanks, the laboratory should try and find the source of the contamination and eliminate it. **Subtracting blank concentrations from sample results is not permitted.** Any method blank exceedances should be fully documented in the laboratory report narrative.

1.3.2 High Salt Concentrations

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. Care must therefore be taken to ensure that free chlorine is absent before the Hg is reduced and swept into the cell. This may be accomplished by using an excess of hydroxylamine sulfate reagent (25 mL). In addition, the dead air space in the biological oxygen demand ("BOD") bottle must be purged before adding stannous sulfate. Both inorganic and organic Hg spikes have been quantitatively recovered from seawater by using this technique.

1.4 Quality Control Requirements for SW-846 Methods 7470/7471

1.4.1 Reporting Limits/Lower Limits of Quantitation for Methods 7470 and 7471

The reporting limit ("RL"), or lower limit of quantitation ("LLOQ"), is dependent on the concentration of the lowest non-zero standard in the initial calibration or the low-level calibration verification ("LLCV"), analyzed under identical conditions as the sample, with adjustments made for the sample size, preparation factors, percent moisture, dilution factors, etc., as required. Table 1.0 lists approximate RL/LLOQs for using CVAA methods for the following sample matrices. Solid matrices in this table assume 100% solids.

Table 1.0: Typical Reporting Limits / Lower Limits of Quantitation[1]

Matrix	Typical Reporting Limit
Aqueous	0.2 µg/L
Soil and Sediment (assuming 100% solids)	0.1 mg/kg
[1]Note these values are intended to serve as guidance to EPs when planning analytical needs to achieve the data quality objectives to meet project-specific goals. These tables are not intended to dictate what RL/LLOQs laboratories must report.	

Moisture content of soils and sediments will raise the RL/LLOQ, as all results must be reported on a dry weight basis for these two matrices. Sample dilution or lower sample weight/volume will also cause the RL/LLOQs to be raised. It is the responsibility of the data user, in concert with the laboratory, to establish the range and required RL/LLOQ for the target analytes to meet the project Data Quality Objectives ("DQO"s). To meet the RLs/LLOQs applicable to project DQOs, it may be necessary to modify the analytical method to improve sensitivity. In such cases, the modifications must be noted in the laboratory report narrative.

1.4.2 General Quality Control Requirements

This protocol is restricted to use by, or under the supervision of, analysts who are experienced in using CVAA spectrometry as a quantitative tool and skilled in the correction of chemical and physical interferences described in this method.

Refer to SW-846 Chapter One for general quality control ("QC") procedures for all inorganic methods, including SW-846 Methods 7470 and 7471. These requirements ensure that each laboratory maintain a formal quality assurance program and records to document the quality of all inorganic data. These requirements ensure that each laboratory maintain a formal quality assurance ("QA") program and records to document the quality of all inorganic data and be certified by the Connecticut Department of Public Health for the analysis performed. QC procedures necessary to evaluate the instrument's operation may be found in SW-846 Chapter One and include evaluation of calibrations and performance of sample analyses. Instrument QC and method performance requirements for the CVAA system may be found in SW-846 Method 7470 and 7471.

The minimum requirements for the QA program include Initial Demonstration of Capability ("IDOC"), ongoing analysis of standards and blanks to confirm acceptable continuing performance, and analysis of laboratory control samples ("LCS") and/ or matrix spikes ("MS") to assess accuracy and analysis of LCS duplicates ("LCSD"), matrix spike duplicates ("MSD") and/or matrix duplicates ("MD") to assess precision. The use of site-specific MS/MSDs samples are required for solids samples (soil/sediment). However, site-specific MS/MSD or MS/MD samples are strongly recommended from each site and for each matrix type sampled. Evaluation of sample matrix effects on element recovery is key to making informed decisions. Percent recovery data from site-specific samples allow the

environmental professional (“EP”) to make informed decisions regarding contamination levels at the site. Batch MS/MSD or MS/MD results do not give any indication of site-specific matrix interferences or analytical problems related to the specific site matrices. Field, rinsate, or other blanks should not be used for MS/MSD/MDs. A laboratory may substitute a MS/MSD duplicate in lieu of the MS/MD.

Laboratories must document and have on file an IDOC for each combination of sample preparation and determinative method being used. An IDOC must be completed and documented when a method is initially started up, whenever a method is substantially modified, or new laboratory staff is trained to perform this Method. These data must meet or fall within the limits specified in Section 1.4 and Table 1A of this RCP. See SW-846 Chapter One and SW-846 Methods 7470 and 7471 for the procedure. The IDOC must include the following elements provided in Table 2.0:

Table 2.0: IDOC Requirements

QC Element	Performance Criteria
Initial Calibration	Table 1A
Continuing Calibration	Table 1A
Method Blanks	Table 1A
Percent Recovery for MS/LCS	Table 1A
Relative Percent Difference of Matrix Duplicate	Table 1A
Other Instrument QC Samples	Table 1A

Laboratories are required to generate laboratory specific performance criteria for LCS element recovery limits, MS/MSD element recovery and relative percent different (“RPD”) limits. These limits must be equal to or fall within the limits specified in Table 1A of this RCP.

1.4.3 Specific QA/QC Requirements and Performance Standards for SW-846 Methods 7470/7471

Specific QA/QC requirements and performance standards for SW-846 Methods 7470 and 7471 are presented in Table 1A. Strict compliance with the QA/QC requirements and performance standards for this method, as well as satisfying other analytical and reporting requirements will provide the EP with “Reasonable Confidence” regarding the usability of analytical data to support environmental decisions. The concept of "Reasonable Confidence" is explained on the DEEP website.

While optional, parties electing to utilize these protocols will be assured that agency reviewers will, generally, accept “Reasonable Confidence” data. To achieve “Reasonable Confidence” parties must:

1. Comply with the applicable QC analytical requirements prescribed in Table 1A for this test procedure;

2. Evaluate and narrate all protocol non-compliances and implement, as necessary, required corrective actions and analytical response actions for all non-conforming analytical performance standards; and

3. Retain reported and unreported analytical data and information for a period of 5 years or as required under applicable accreditation criteria.

Table 1A: Specific QA/QC Requirements and Performance Standards for Methods 7470 and 7471

Required QA/QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable	Required Corrective Action	Required Analytical Response Action
Initial Demonstration of Capability ("IDOC")	Laboratory Analytical Accuracy & Precision	(1) Must be performed prior to using method samples. (2) Must be performed for each matrix. (3) Must follow procedures in "Initial Demonstration of Capability" Section in the applicable EPA method.	No	Refer to "Initial Demonstration of Capability" Section in the applicable EPA method and Section 1.4.2 of this RCP.	NA
Preparation of Samples	Accuracy & Representativeness	All aqueous and solid samples must be prepared (digested) prior to analysis. See SW-846 Methods 7470 and 7471 for details. Note only one preparation required for each field sample.	No	NA	NA
Initial Calibration ("ICAL")	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 ≥0.995.	No	Perform instrument maintenance as necessary; re-optimize instrument, re-calibrate as required by SW-846 7470 and 7471	Suspend all analyses until initial calibration meets criteria.
Initial Calibration Verification ("ICV")	Laboratory Analytical Accuracy	(1) Frequency- immediately after each initial calibration and prior to sample analysis. (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	(1) Reanalyze ICV; if acceptable, no further action required. (2) If analysis is still outside of criteria, recalibrate and reanalyze ICV.	Suspend all analyses until ICV meets criteria

Required QA/QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable	Required Corrective Action	Required Analytical Response Action
Initial Calibration Blank ("ICB")	Laboratory Analytical Sensitivity (instrument drift & contamination)	(1) Frequency: Immediately after ICV (2) Matrix matched with standards and samples. (3) ICB must be <RL/LLOQ.	No	(1) Reanalyze ICB; if acceptable, no further action required. (2) If analysis is still outside of criteria, recalibrate and reanalyze ICV & ICB.	Suspend all analyses until ICB meets criteria.
Low-Level Calibration Verification ("LLCV")	Laboratory Analytical Sensitivity (Verify low-end of calibration range/verify RL/LLOQ)	(1) Frequency- daily prior to sample analysis if initial calibration did not contain a low-level standard at the RL/LLOQ. If initial calibration includes the RL/LLOQ 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/LLOQ for Hg. (4) Percent recovery must be 70-130%.	No	(1) Reanalyze LLCV; if acceptable, no further action required. (2) If reanalysis is still outside of criteria and concentrations of Hg are ≤10x RL/LLOQ in associated field samples, recalibrate and reanalyze LLCV and associated samples. (3) If concentrations of Hg are >10x RL/LLOQ in associated field samples, include explanation in laboratory report narrative; no further action required.	Suspend all analyses until LLCV meets criteria unless the concentrations of Hg are >10x RL/LLOQ in associated field samples. Report non-conformances in laboratory report narrative.
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	(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 report narrative.

Required QA/QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable	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) Hg concentration must be <RL/LLOQ. (3) Matrix matched with standards and samples.	No	(1) Reanalyze CCB; if acceptable, no further action required. (2) If reanalysis is still outside of criteria, recalibrate and reanalyze all associated samples since last compliant CCB-unless 3 applies. (3) If concentration of Hg in CCB is >RL/LLOQ but all associated sample results are either non-detected or >10x concentration of Hg in CCB, no corrective action required.	If 3 applies, include explanation in laboratory report narrative.
Method Blank ("MB")	Laboratory Method Sensitivity (contamination evaluation)	(1) Frequency- one per digestion batch of every ≤ 20 field samples (2) Must be digested with the samples using the same preparation method as the samples (3) Hg concentration must be <RL/LLOQ (4) Matrix specific and matched.	Yes	(1) Reanalyze MB; if acceptable, no further action required. (2) If reanalysis is still outside of criteria, re-digest and reanalyze all associated field batch samples -unless 3 applies. (3) If concentration of Hg in MB is >RL/LLOQ but all associated sample results are either non-detected or >10x concentration of Hg in MB, no corrective action required.	If 3 applies, include explanation in laboratory report narrative.

Required QA/QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable	Required Corrective Action	Required Analytical Response Action
Laboratory Control Sample ("LCS")	Laboratory Analytical Accuracy	(1) Frequency- one per digestion batch of ≤ 20 field samples or each batch (2) Must be matrix-matched by digesting with the samples using the same preparation method. It is recommended that 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 Hg at a known concentration and with 95% confidence limits. (3) Concentration level for aqueous LCS near midpoint of curve. (4) Percent recovery for Hg must be 80-120% for aqueous LCS and within vendor control limits (95% confidence limits) for solid (SRMs). (5) Prepared using second source standard. (6) Matrix specific (solid, aqueous, etc.)	Yes	(1) Reanalyze LCS; if acceptable, no further action required. (2) If reanalysis is still outside of criteria and LCSD is in-control for Hg, no corrective action required. (3) If LCS and LCSD are both outside of criteria, re-digest and reanalyze LCS/LCSD and all associated field samples in batch.	Report recovery non-conformances in laboratory report narrative.
LCS Duplicate ("LCSD")	Laboratory Analytical Accuracy & Precision	(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. It is recommended that a solid field samples as the "solid LCSD." An SRM is a soil or sediment matrix that contains Hg 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 Hg must be 80-120% for aqueous LCS and within vendor control limits (95% confidence limits) for solid LCS. (5) RPDs must be ≤20% for aqueous LCS/LCSD and ≤30% for solid LCS/LCSD.	Yes (if analyzed)	(1) Reanalyze LCSD; if acceptable, no further action required. (2) If reanalysis is still outside of recovery criteria and LCS is in-control for Hg, no corrective action required. (3) If LCSD and LCS are both outside of recovery criteria, re-digest and reanalyze LCS/LCSD and all associated field samples in batch.	Report recovery and RPD non-conformances in laboratory report narrative.

Required QA/QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable	Required Corrective Action	Required Analytical Response Action
Matrix Spike ("MS") (Site-Specific)	Method Accuracy in Sample Matrix	(1) Solid samples frequency- one per ≤ 20 field samples per matrix designated by data user on COC or at project set-up. Aqueous samples frequency- one per digestion batch of ≤ 20 field samples per matrix strongly recommended (designated by data user on COC or at project set-up). (2) Concentration levels near midpoint of curve. (3) Percent recoveries for Hg in solid samples must be 80-120% and aqueous samples must be 75-125%.	Yes ONLY when requested by data user	(1) Reanalyze MS; if acceptable, no further action required. (2) After reanalysis, if MS recovery is 30-74% or >125% and LCS was in-control, no corrective action is required. (3) If MS recovery is <30% and associated with non-detected results, re-digest (homogenize sample well) and reanalyze sample/MS pair. Report results and narrate.	(1) Report MS non-conformances in laboratory report narrative. (2)If re-digested due to recoveries <30%, report both sets of sample/MS data.
Matrix Spike Duplicate ("MSD") (site-specific) May elect to use in lieu of "MD"	Precisions in Sample Matrix	(1) Concentration levels near midpoint of curve. (2) Must contain all target elements. (3) Percent recoveries for Hg in solids must be 80-120% and aqueous samples must be 75-125%. (4) RPDs ≤20% (5) Field blanks, trip blanks, etc. cannot be used for MS/MSDs.	Yes ONLY when requested by data user	Check LCS; If recoveries are acceptable in LCS, narrate non-conformance.	Note non-conformances in laboratory report narrative.
Matrix Duplicate ("MD") (Site-Specific)	Method Precision in Sample Matrix	(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). (2) Prepare by digesting and analyzing an additional aliquot of the same field sample used for MS. (3) RPD for Hg must be ≤ 20% for aqueous and ≤ 35% for solids.	Yes ONLY when requested by data user	Narrate non-conformances	Report non-conformances in laboratory report narrative.

Required QA/QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable	Required Corrective Action	Required Analytical Response Action
General Reporting Issues	NA	(1) Non-detected values must be reported with the sample-specific RL/LLOQ for Hg using all appropriate preparation/dilution factors. (2) The lab must only report values ≥ the sample-specific RL/LLOQ. (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 RSR regulatory standards. (7) Concentrations below the reporting limit should be reported as “ND” with the sample specific RL/LLOQ also reported.	NA	NA	(1) The performance of dilutions must be documented in the laboratory report narrative or on the report form. Unless due to elevated concentrations of Hg, reasons for dilutions must be explained in the laboratory report narrative. (2) If samples are not preserved properly or are not received with an acceptable cooler temperature, not the non-conformances in the laboratory report narrative. (3) If samples are prepared and/or analyzed outside of the holding time, note the non-conformances in the laboratory report narrative. (4) Narrate any additional method non-compliance or sample-specific anomaly.

1.5 Routine Reporting Deliverables for Method 7470/7471

The following table (Table 3.0) lists the routine report deliverables. Note that while laboratories are not required to report certain items, they must keep the data on file and may be required to report all items in special circumstances.

Table 3.0: Report Deliverables

Parameter	Deliverable	Comments
Initial Calibration	NO	Correlation coefficient must meet QA/QC requirements
Initial Calibration Verification Standard	NO	ICV must pass
Initial Calibration Blank	NO	Note non-conformances in laboratory report narrative
Low Level Calibration Check Std	NO	Not required if low standard at RL/LLOQ
Continuing Calibration Verification	NO	CCV must pass
Continuing Calibration Blank	NO	Note non-conformances in laboratory report narrative.
Method Blanks	YES	Note non-conformances in laboratory report narrative. Flag all positive sample results above RL/LLOQ with “B” flag.
Lab Control Sample / LCS Duplicate	YES	Note non-conformances in laboratory report narrative
Site Specific Matrix Spike/ Matrix Duplicate	YES (If requested)	Note non-conformances in laboratory report narrative
General Reporting Issues	YES	Note non-conformances in laboratory report narrative
QA/QC Certification Form	YES	Signed by laboratory director or their designee.
Chain-of-Custody Form	YES	Signed by sample collector, courier, and laboratory

1.5.1 Reporting and Flagging of Results

The following rules apply to reporting results:

- Non-Detects: Report all non-detects and results below the reporting limit as “ND” (Not Detected at the specified RL/LLOQ). The RL/LLOQ for each element in each sample must be listed on the report and consider the exact sample mass, any dilution factors, percent moisture, etc.

- Elements detected above the RL/LLOQ in blanks and found in samples, also above the reporting limit, shall be flagged with a “B” suffix (e.g., 25B).

- All soil/sediment results shall be reported on a dry weight basis.

1.6 Sample Containers, Preservations, and Holding Times

Table 4.0 identifies the type of containers, preservation requirements, and holding times dependent upon analyte and matrix.

Table 4.0: Sample Containers, Preservation, and Holding Times

Matrix	Container[1,2]	Preservative[3]	Holding Time
Aqueous	500 mL plastic or glass	Nitric Acid to pH <2	28 days
Aqueous Dissolved Hg (Filtered)	500 mL plastic 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 HNO3 to pH <2	28 days
Soil/Sediment samples.	250 mL plastic or glass jar with Teflon or plastic lined cap.	Cool to 4 ± 2º C	28 days
High Concentration Waste Samples	Collect in glass jar with Teflon or plastic lined cap.	Cool to 4 ± 2º C	28 days

[1]The number of sampling containers specified is not a requirement. For specific analyses, the collection of multiple sample containers is encouraged to avoid resampling if sample is consumed or compromised during shipping and/or analysis.

[2]Plastic bottles must be acid rinsed and either high density polyethylene or Teflon.

[3]If 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.