State Of Connecticut
Department of Environmental Protection

Recommended Reasonable Confidence Protocols

Quality Assurance and Quality Control Requirements

Determination of Mercury By SW-846 Methods 7470/7471 Cold Vapor Atomic Absorption Spectroscopy

Version 2.0
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Written by the Connecticut DEP 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

1.0 QA/QC Requirements for Methods 7470/7471

1.1 Method Overview

Methods 7470 and 7471are cold-vapor atomic absorption procedures. Method 7470 is approved for determining the concentration of mercury 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 Method

1.2.1 Prior to analysis, samples must be digested according to the procedures discussed in the methods.

1.2.2 Both methods are cold-vapor atomic absorption techniques, based on the absorption of radiation at 253.7-nm 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.

1.2.3 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 mercury is a compound of concern at the site, and sample heterogeneity is anticipated, then the following preemptive or corrective measures should be considered by the EP and the laboratory:

- Direct the laboratory to use a larger sample size, up to 10 grams, for the analysis to enhance sensitivity and precision. The laboratory must adjust the concentration/volume of all reagents to accommodate the analytical requirements of the larger sample size. The laboratory must also demonstrate the applicable laboratory specific QC-limits and performance criteria using the larger sample size. Note that increasing the sample size may also increase any potential interferences, and may not always be practical.

- Direct the laboratory to analyze multiple replicates of the sample to better assess the variability of the site.
- Utilize more effective field sample homogeneity techniques prior to submitting samples to the laboratory.
- Increase the frequency of field duplicates.

1.2.4 Method 7471A in SW-846 calls for analysis of soil/solid samples in triplicate. The DEP does not require this for routine analysis of soil/sediment samples. In certain instances, however, triplicate analyses may be warranted where site homogeneity is in question.

1.3 Reporting Limits for Methods 7470 and 7471

The reporting limit (RL) for mercury is based upon the lowest standard in the calibration curve, the exact sample weight /volume, any dilutions, and percent moisture for soil/sediments.

Sample preservation, container and analytical holding time specifications for surface water, groundwater, soil, and sediment matrices for trace metals are listed in Table 2A of this document. Moisture content of soils and sediments will raise the RL, 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's to be raised.

1.4 Interferences

1.4.1 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 mercury from reagent water.

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

1.4.3 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 mercury 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 BOD bottle must be purged before adding stannous sulfate. Both inorganic and organic mercury spikes have been quantitatively recovered from seawater by using this technique.

1.4.4 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.

1.5 General Quality Control Requirements

Each laboratory is required to operate a formal quality assurance program and be certified by the Connecticut Department of Public Health for the analysis performed. The minimum requirements include initial demonstration of laboratory proficiency, ongoing analysis of standards and blanks to confirm acceptable continuing performance, and analysis of laboratory control samples (LCS) to assess precision and accuracy. The use of site specific matrix spikes and matrix duplicates is highly recommended. Evaluation of sample matrix effects on mercury recovery is key to making good decisions.

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 Section 1.5 and Table 1A. See Section 4.4.1 of SW-846 Chapter One for the procedure. The Initial Demonstration of Proficiency must include the following elements:

Table 1.1 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

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

1.6.1 General Quality Control Requirements for Determinative Inorganic Methods

Refer to SW-846 Chapter One for general quality control procedures for all inorganic methods, including SW-846 Methods 7470/7471. These requirements ensure that each laboratory maintain a formal quality assurance program and records to document the quality of all inorganic data.

Quality Control procedures necessary to evaluate the instrument's operation may be found in Chapter One, Section 2.0, and include evaluation of calibrations and performance of sample analyses.

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

Specific QA/QC requirements and performance standards for SW-846 Methods 7470/7471 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 DEP decisions.

While optional, parties electing to utilize these protocols will be assured that "Reasonable Confidence" data, will be generally accepted by agency reviewers. In order 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, as necessary, compliance with performance standards prescribed in Table 1A for this test method; and

3. Adopt the reporting formats and elements specified in Section 1.7 of this method.

1.6.3 Site Specific Matrix Spike (MS) and Matrix Duplicate (MD) Samples

It is strongly recommended that site specific MS/MD samples be analyzed from each site, and each matrix type sampled. Percent recovery data from site specific samples allow the

EP to make intelligent decisions regarding contamination levels at the site. Batch MS/MD results do not give any indication of site specific matrix interferences or analytical problems related to the specific site matrices and are in general discouraged. Field blanks, rinsate blanks, etc. should not be used for MS/MD's. A laboratory may substitute a matrix spike/matrix spike duplicate in lieu of the MS/MD.

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

Required QA/QC Parameter	**Data Quality Objective**	**Required Performance Standard**	**Required Deliverable**	**Recommended Corrective Action**	**Analytical Response Action**
Preparation of Samples	Accuracy and Representativeness	All samples must be digested prior to analysis. See Methods 7470 and 7471 for details. Note only one preparation required for each field sample.	NO	See Section 1.2.3 for guidance on obtaining representative soil results.	
Initial Calibration	Laboratory Analytical Accuracy	1) Daily prior to sample analysis. 2) Minimum of calibration blank plus five calibration standards. 3) Linear curve with "r" ≥ 0.995. Can use second order fit if "r " ≥ 0.995.	NO	Re-optimize instrument and recalibrate as necessary.	Sample analysis cannot proceed without valid initial calibration.
Initial Calibration Verification (ICV)	Laboratory Analytical Accuracy	1) Daily immediately after calibration and prior to sample analysis. 2) 2nd source std 3) ICV ±10% of true value.	NO	Re-calibrate/Re-analyze ICV as required by method.	Suspend all analyses until problem corrected and ICV meets criteria.
Initial Calibration Blank (ICB)	Evaluation of instrument drift, sensitivity, and contamination.	1) Daily immediately after ICV. 2) Matrix matched with standards and samples. 3) ICB must be < RL	NO	Re-calibrate/Re-analyze ICB as required by method.	
Low Level Calibration Check Standard	Instrument sensitivity to support RL	Only required if low calibration standard not at or below RL 1) Daily prior to sample analysis 2) Std concentration at RL for all analytes 3) Recovery ±30% of true value.	NO	Recalibrate/Narrate	Report non-conformances in narrative.

TABLE 1A Specific QA/QC Requirements and Performance Standards for Methods 7470/7471* (continued)

Required QA/QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable	Recommended Corrective Action	Analytical Response Action
Continuing Calibration Verification (CCV)	Laboratory Analytical Accuracy	1) Every 10 samples and at end of analytical sequence. 2) Can be same source or second source. 3) Recovery ±20% of true value	NO	Recalibrate/Re-analyze all samples since last compliant CCV	Report non-conformances in narrative. .
Continuing Calibration Blank (CCB)	Evaluation of instrument drift, sensitivity, and contamination.	1) Every 10 samples immediately after CCV. 2)) Matrix matched with standards and samples. 3) CCB must be < RL	NO	Recalibrate/Re-analyze all samples since last compliant CCV	Report non-conformances in narrative.
Method Blanks	Laboratory Contamination Evaluation	1) Digested every 20 or every batch, whichever is greater. 2) Matrix specific and matrix matched 3) Mercury must be <RL	YES	Locate source of contamination and correct problem. Reprepare samples unless all analyte concentration >10x method blank level	Report non-conformances in case narrative.

TABLE 1A Specific QA/QC Requirements and Performance Standards for Methods 7470/7471* (continued)

Required QA/QC Parameter	**Data Quality Objective**	**Required Performance Standard**	**Required Deliverable**	**Recommended Corrective Action**	**Analytical Response Action**
Laboratory Control Sample (LCS)	Laboratory Method Accuracy	1) Every 20 samples or each batch, whichever is more frequent 2) Standard source can be initial calibration source. 3) Matrix specific (solid, aqueous, etc). 4) LCS recoveries ±20% for aqueous media and within vendor control (95% confidence limits) for solids.	YES	Redigest and reanalyze all samples.	Report non-conformances in narrative.
Site Specific Matrix Spike	Accuracy in Sample Matrix	1) Every 20 samples or batch per matrix* 2) Percent recovery limits must be between 75-125%.	Yes* (*If analyzed)	If recoveries >30% and LCS in limits note in narrative If MS recoveries <30%, reprepare and reanalyze samples	Note outliers in narrative
Site Specific Matrix Duplicate (Lab may substitute MSD in lieu of sample duplicate)	Precision in Sample Matrix	1) Every 20 samples or batch per matrix* 2) For aqueous samples RPD ± 20% if conc. >5x the RL. If conc. < 5x RL, the limit is ± RL 3) For solids RPD ±35% if conc >5x the RL. If conc. < 5x the RL, limit is ± the RL.	Yes* (*If analyzed)	If LCS in criteria, narrate outliers.	Note outliers in narrative

TABLE 1A Specific QA/QC Requirements and Performance Standards for Methods 7470/7471* (continued)

Required QA/QC Parameter	**Data Quality Objective**	**Required Performance Standard**	**Required Deliverable**	**Recommended Corrective Action**	**Analytical Response Action**
General Reporting Issues	N/A	1) The laboratory should report only concentrations detected above the sample specific RL. 2) Concentrations below the reporting limit (RL) should be reported as "ND" with the sample specific RL also reported 3) Dilutions: If analyte above linear range, dilute and reanalyze for those analytes. 4) Soils/sediments reported on a dry weight basis. 5) RL must be verified daily with a standard analyzed at the RL. May be part of initial calibration.	YES	N/A	

<u>Notes for Table 1A:</u>

* Refers to latest published version of SW-846 Method 7470/7471.
RPD = Relative Percent Difference
%RSD = Relative Percent Standard Deviation

r = Correlation Coefficient
EP = Environmental Professional
N/A = Not Applicable

1.7 Reporting Limits for Methods 7470 and 7471

The Reporting Limit (RL) is based upon the lowest standard in the initial calibration or by analysis of a low standard after calibration., taking into account exact sample weight or volume, any dilutions, percent moisture, etc. It is the responsibility of the environmental professional (EP) to specify to the laboratory the detection limits required for the samples. In order to meet the limits it may be necessary to modify the analytical method by using increased sample volume or mass, concentration of the digestate, etc. In such cases the modifications must be noted in the narrative.

1.8 Routine Reporting Deliverables for Method 7470/7471

The following table (Table 1.2) 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.

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 Reporting Limit). The reporting limit for each compound in each sample must be listed on the report and take into account the exact sample mass, any dilution factors, percent moisture, etc.

Compounds detected above the reporting limit 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.

Table 1.2 Report Deliverables

PARAMETER	DELIVERABLE	COMMENTS
Initial Calibration	NO	
Initial Calibration Verification Standard (ICV)	NO	ICV must pass
Initial Calibration Blank (ICB)	NO	Note non-conformances in narrative
Low Level Calibration Check Std	NO	Not required if low standard at RL
Continuing Calibration Verification (CCV)	NO	CCV must pass
Method Blanks	YES	Note non-conformances in narrative. Flag all positive sample results above RL with “B” flag.
Lab Control Sample (LCS)	YES	Note non-conformances in narrative
Site Specific Matrix Spike/ Matrix Duplicate	YES (If requested)	Note non-conformances in narrative
General Reporting Issues	YES	Note non-conformances in narrative
QA/QC Certification Form	YES	Signed by laboratory director or his/her designee.

Table 2A Sample Containers, Preservation, and Holding Times

MATRIX	CONTAINER	PRESERVATIVE	HOLDING TIME
Aqueous	500 mL plastic† or glass (1)	Nitric Acid 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 4 ± 2º C.	28 days

Notes:
1. If dissolved metals are to be determined, the samples must be filtered within 24 hours of collection through a 0.45 µm membrane filter prior to acidification.

† Plastic bottles must be acid rinsed and either high density polyethylene or Teflon

The number of sample containers is optional. Laboratories should supply enough containers to allow for any reanalysis or breakage.