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1.0 OBJECTIVES

This standard operating procedure (SOP) describes procedures that the Environmental Standards data reviewers will use to validate mercury data generated by SW-846 Methods 7470A/7471A for General Electric Company's Hudson River Design Support Sediment Sampling and Analysis Program. Validation will be performed to assess the compliance of the sample data to SW-846 Methods 7470A/7471A and/or other reference documents (*e.g.*, analytical SOPs) as applicable to General Electric Company's Hudson River Design Support Sediment Sampling and Analysis Program. In addition, the usability of the mercury data provided by the analytical laboratory(ies) will be determined based on the general guidance provided in the "US EPA Contract Laboratory Program National Functional Guidelines for Inorganic Data Review" (2/94; National Functional Guidelines). It should be noted that the National Functional Guidelines apply strictly to data generated by Contract Laboratory Program (CLP) protocol and are not directly applicable to validation of data generated by SW-846 Methods 7470A/7471A; this SOP presents the specific data qualification actions that will be used for validation.

The validation findings will be presented in a quality assurance review (QAR) that will be prepared for one or more sample delivery groups (SDGs). Copies of annotated analytical results summaries (Form I's), including any changes to the analytical results and data qualifier codes or a data summary spreadsheet of the qualified analytical results will be included in the analytical results section of the QAR.

2.0 EVALUATION TOOLS

Excel form available in R:/Templates/Chemistry/XCELForms:

- Inorganic field duplicate comparison Rev 1-01.xls
- Inorganic triplicate comparison Rev 1-01.xls
- Total versus dissolved comparison Rev 1-01.xls

Chemistry Applications:

- FIT
- Methods Database

3.0 REFERENCE DOCUMENTS

- US EPA Contract Laboratory Program National Functional Guidelines for Inorganic Data Review (2/94).
- SW-846 Methods 7470A/7471A.

- Region I, EPA – New England Data Validation Functional Guidelines for Evaluating Environmental Analyses (12/96).

- Region II, Standard Operating Procedure for the Validation of Inorganic Data Acquired Using SW-846 Methods 7470A/7471A (Rev. 2, 12/94).

- Region III, Modifications to National Functional Guidelines for Inorganic Data Review (9/94).

4.0 PROCEDURE

4.1 EVALUATION OF METHOD COMPLIANCE

The data reviewer will assess the method compliance of the mercury data based on evaluation of information presented in the data package deliverables. Compliance with SW-846 Methods 7470A/7471A and/or other reference documents (*e.g.*, analytical SOPs) as applicable to the General Electric Company's Hudson River Design Support Sediment Sampling and Analysis Program (as directed by the Project Manager) will be evaluated as part of the assessment. In addition, the deliverables will be evaluated for reporting errors and inconsistencies. The findings of the method compliance assessment will be described in terms of deficiencies and comments about the data/deliverables. The deficiencies/comments will be presented in three subdivisions (*i.e.*, correctable deficiencies, noncorrectable deficiencies, and comments) of the Inorganic Data Section of the QAR. Each deficiency and comment discussed in the QAR will indicate any subsequent impact on the usability of the data or will identify aspect(s) of the data that could not be evaluated due to the deficiency.

The data reviewer should contact the project laboratories to request the correction of deficiencies prior to submittal of the QAR (if feasible and sanctioned by the General Electric Company). At a minimum, corrections required to allow for a full evaluation of the usability of the data should be requested. Such correctable deficiencies may include sample result errors, missing data deliverables, or calculation errors that would require a significant amount of the data reviewer's time to correct. Any laboratory resubmittals as a result of such request will be discussed in the comments subsection of the QAR and will be included as an attachment of the QAR.

4.2 DETERMINATION OF DATA USABILITY

The data reviewer will determine the usability of the mercury data based on an evaluation of the information presented in the data package deliverables. The findings of the mercury data usability assessment will be presented in terms of data qualifications that the project team should consider in order to best utilize the data. These qualifications will be presented in the Inorganic Data Qualifier Section of the QAR. Each qualification will indicate that the affected sample result(s) has been flagged with representative qualifier code(s) in the General Electric Company's database to provide, at a glance, an indication of the quantitative and qualitative reliability of each analytical result. In general, the qualifier statements will be presented in the QAR in the following order: blank contamination, unusable results (R/UR), estimated results (J/UJ), field duplicate comparison, and a general qualifier for all results reported below the quantitation/reporting limit (if applicable to General Electric Company's Hudson River Design Support Sediment Sampling and Analysis Program).

The data reviewer's criteria for evaluating the usability of the mercury data and the resultant qualifications will be as stipulated on the attached Table for the Validation of Mercury Data Generated by SW-846 Methods 7470A/7471A. It should be noted that the Project Manager should be consulted when "professional judgement" use is indicated on the attached table.

Table for the Validation of Mercury Data Generated by SW-846 Methods 7470A/7471A

Quality Control Item	Usability Criteria	Action(s)
Temperature and Conditions Upon Receipt	Aqueous samples should be preserved to pH ≤2 with HNO_3. Solid/soil samples should be preserved to 4±2°C.	If pH is >2 and the laboratory did not adjust the pH and allow the sample to sit for 16 hours before digestion, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). Solid/soil samples should not be qualified due to out-of-criteria temperatures.
Technical Holding Time	All matrices should be analyzed within 28 days of sample collection.	If holding time is exceeded, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If holding time is grossly exceeded *i.e.*, twice the holding time), qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR").
Initial Calibration (See Note #1 for additional information.)	Calibration should be daily and each time the instrument is set up, with at least one blank and three standards. r (linear) should be ≥ 0.995.	Use professional judgement if the appropriate number of standards is not used or if the instrument was not calibrated daily and/or not calibrated each time set up. If the r is <0.995 but ≥0.850, qualify positive results as estimated ("J") and do not qualify "not-detected" results. If r is <0.850, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR").
Instrument Performance	Samples should not display negative results with an absolute value >2× the instrument detection limit (IDL).	If a negative result with an absolute value >2× IDL is observed, qualify the "not-detected" result as estimated ("UJ").

Table for the Validation of Mercury Data Generated by SW-846 Methods 7470A/7471A

Quality Control Item	Usability Criteria	Action(s)
Initial Calibration Verification (ICV)	For accuracy, use recovery limits of 80-120%.	Qualify samples for an entire analytical sequence. If the recovery is >120% but ≤135%, qualify positive results as estimated ("J") and do not qualify "not-detected" results. If the recovery is <80% but ≥65%, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If the recovery is <65%, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR"). If the recovery is >135%, qualify positive results as unusable ("R") and do not qualify "not-detected" results.
Continuing Calibration Verification (CCV)	For accuracy, use recovery limits of 80-120%.	Qualify samples analyzed before and after a non-compliant CCV. If the recovery is >120% but ≤135%, qualify positive results as estimated ("J") and do not qualify "not-detected" results. If the recovery is <80% but ≥65%, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If the recovery is <65%, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR"). If the recovery is >135%, qualify positive results as unusable ("R") and do not qualify "not-detected" results.

Table for the Validation of Mercury Data Generated by SW-846 Methods 7470A/7471A

Quality Control Item	Usability Criteria	Action(s)
CRDL/CRA Detection Limit (DL) standard (not required but frequently analyzed.) (See Note #2 and Note #7 for additional information.)	For accuracy, use recovery limits 75-125%.	Qualify samples analyzed before and after a non-compliant CRDL/CRA standard. If the recovery is >125% but ≤150%, qualify positive results ≤ 2 × the spike level as estimated ("J") and do not qualify "not-detected" results. If the recovery is <75% but ≥ 50%, qualify positive results ≤ 2 × the spike level as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If the recovery is <50%, qualify positive results ≤ 2 × the spike level as estimated ("J") and qualify "not-detected" results as unusable ("UR"). If the recovery is >150%, qualify positive results ≤ 2 × the spike level as unusable ("R"), qualify positive results >2× the spike level but ≤5× the spike level as estimated ("J"), and do not qualify "not-detected" results.
Initial Calibration Blank (ICB)/ Continuing Calibration Blank (CCB)/ Preparation Blank (PB)/Field Blank/Equipment Blank (See Note #3 and Note #7 for additional information.)	The highest positive result (greater than the IDL) associated with a sample should be summarized and utilized for the evaluation of contamination.	For ICBs and CCBs, qualify samples per analytical sequence; for PBs, field blanks, and equipment blanks, qualify per batch and/or SDG. If mercury is detected in blank but not in sample, no action is required. If a sample result is >MDL/IDL but ≤5× blank result, qualify the positive result as "not-detected" ("U*"). If sample is >5× blank result, qualification is not required. If a blank has a negative result with an absolute value >2 × IDL, qualify positive results ≤ 5 × the absolute value of the blank result as estimated ("J") and qualify "not-detected" results as estimated ("UJ").

Table for the Validation of Mercury Data Generated by SW-846 Methods 7470A/7471A

Quality Control Item	Usability Criteria	Action(s)
Laboratory Control Sample (LCS) (See Note #4 for additional information.)	For accuracy, use recovery limits of 80-120% for aqueous samples and 70-130% for solid samples.	For aqueous samples, if the recovery is >120% but ≤150%, qualify positive results as estimated ("J") and do not qualify "not-detected" results. For aqueous samples, if the recovery is <80%, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). For aqueous samples, if the recovery is >150%, qualify positive results as unusable ("R") and do not qualify "not-detected" results. For aqueous samples, if the recovery is <50%, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR"). For solid samples, if the recovery is >130%, qualify positive results as estimated ("J") and do not qualify "not-detected" results. For solid samples, if the recovery is <70% but ≥30%, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). For solid samples, if the recovery is <30%, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR").

Table for the Validation of Mercury Data Generated by SW-846 Methods 7470A/7471A

Quality Control Item	Usability Criteria	Action(s)
Matrix Spike/Matrix Spike Duplicates (MS/MSD) (See Note #5 for additional information.)	For accuracy use recovery limits of 75-125%. For precision, use RPD limits of 20% for aqueous samples and 40% for solid samples.	Data should not be qualified due to %Rs (or RPDs calculated using %Rs) that are outside of criteria if the original concentration of an analyte is >4× the spiking level for that analyte. RPDs calculated using MS/MSD results can be used to evaluate precision. If the recovery is >125%, qualify positive results in all associated samples as estimated ("J") and do not qualify "not-detected" results. If the recovery is <75% but ≥30%, qualify all positive results in all associated samples as estimated ("J") and qualify "not-detected" results in all associated samples as estimated ("UJ"). If the recovery is <30%, qualify positive results in all associated samples as estimated ("J") and qualify all "not-detected" results in all associated samples as unusable ("UR"). If the precision exceeds the RPD criterion, qualify positive results in all associated samples as estimated ("J") and do not qualify "not-detected" results.
Field Duplicate/Laboratory Duplicate (See Note #6 and Note #7 for additional information.)	Use default limits of 20% RPD (%RSD for triplicate analyses) for aqueous samples and 40% RPD (%RSD for triplicate analyses) for solids when sample results are ≥5× DL. Use default limit of ±DL for aqueous samples and ±2× DL for solid samples when at least one sample result is <5× DL.	If the criteria are not met, qualify positive results for the non-compliant analyte in original sample and its duplicate as estimated ("J") and qualify "not-detected" results as estimated ("UJ").

Table for the Validation of Mercury Data Generated by SW-846 Methods 7470A/7471A

Quality Control Item	Usability Criteria	Action(s)
Total vs. Dissolved Comparisons (See Note #7 for additional information.)	When the dissolved result is greater than the total result: use default limits of ± IDL when at least one result is <10× IDL. Use default limits of percent differences <10% when both results are ≥ 10× IDL.	If the criteria are not met, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If at least one result is <10× IDL and the differences is >5× IDL, qualify positive and "not-detected" results as unusable ("R/UR"). If both results are ≥10× IDL and the percent difference is >50%, qualify positive results as unusable ("R").
Percent Solids	Solid samples with less than 50% solid content require qualification.	If a solid sample has a percent solid content <50% but ≥10%, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). Use professional judgement if a solid sample has a percent solid content <10%.
Overall Assessment of Data	Assess overall quality of the data. Review available materials to assess the quality, keeping in mind the nature of the analytical problems.	Use professional judgement to determine the need to qualify data that were not qualified based on the QC previously discussed. Write a brief narrative to give the user an indication of the analytical limitation of the data. If sufficient information on the intended use and required quality of the data is available, include the assessment of the usability of the data within the given context.

Notes for the Validation of Mercury Data Generated by SW-846 Method 7470A/7471A

1. Use professional judgement when evaluating the concentration intercept of a calibration curve. If the concentration intercept is positive, samples should be evaluated for false positives. If the concentration intercept is negative, samples should be evaluated for false negatives. Furthermore, samples should not display negative values >2× the detection limit (DL).

   The laboratory may utilize a non-linear regression curve fit. Due to different software programs, it may not be possible to reproduce the laboratory results.

2. The action limit of 2× the spike level assumes that the spike level is based on the RL; therefore, if the RL is < the action limit, the CRDL/CRA standard results should be utilized to qualify the sample data. If the RL is > the action level, the CRDL/CRA standard results should not be utilized to qualify sample data.

3. Generally, if more than one blank is associated with a given sample, qualification should be based upon a comparison with the associated blank having the highest concentration of a contaminant. When evaluating blank contamination, sample weights, volumes, and initial dilution factors should be taken into account. Sample results should not be blank corrected.

   The frequency of equipment blanks is determined during the sampling event. The results of a equipment/rinse blank should be applied to all samples collected using the same equipment (equipment/rinse blanks only) on the same day (if only one blank was

Notes for the Validation of Mercury Data Generated by SW-846 Method 7470A/7471A

collected for a several-day sampling event; results would be applied to all samples in the SDG).

4. The spike level for the solid LCS should be comparable to the detection limit. Use professional judgement if the spike level is not comparable to the detection limit.

5. The laboratory may choose to analyze an matrix spike duplicate instead of a laboratory duplicate.

6. Duplicate samples may be collected and analyzed as an indication of overall precision. Field duplicate analyses measure both field and laboratory precision; therefore, the results may have more variability than laboratory duplicates that measure only laboratory performance. Field duplicate sample results should only be applied to the original sample and its field duplicate. Laboratory duplicate results should be applied to all samples in a batch. It is expected that soil duplicate results will have a greater variance than aqueous duplicate results.

7. The use of RL/DL in evaluating laboratory quality is as follows:

   - When evaluating negative values and total verses dissolved results, the DL should be used.
   - When evaluating field duplicates and laboratory duplicates, the RL/QL should be used.

Notes for the Validation of Mercury Data Generated by SW-846 Method 7470A/7471A

The DL is defined as the number that the positive results are reported down to; therefore, the DL may be the IDL, MDL, or RL.

The RL is defined as the quantitation limit or project-reporting limit. If the laboratory did not provide the RL then the IDL or MDL should be used.