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1.0 OBJECTIVES

This standard operating procedure (SOP) describes procedures that Environmental Standards data reviewers will use to validate volatile organic data generated by SW-846 Method 8260B for the 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 Method 8260B 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. In addition, the usability of the volatile organic 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 Organic Data Review" (10/99; National Functional Guidelines). It should be noted that the National Functional Guidelines applies strictly to data generated by Contract Laboratory Program (CLP) protocol and it is not directly applicable to validation of data generated by SW-846 Method 8260B; 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 forms available in R:/Templates/Chemistry/XCELForms:

- Organic field duplicate comparison Rev1-01.xls
- Organic field quadruplicate comparison Rev1-01.xls
- Organic field triplicate comparison Rev1-01.xls

Chemistry Applications:

- FIT
- Mass Spec Database
- Methods Database
- Target Version 4.1 data processing software

3.0 REFERENCE DOCUMENTS

- US EPA Contract Laboratory Program National Functional Guidelines for Organic Data Review (10/99).

- SW-846 Method 8260B.

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

- Region II, Standard Operating Procedure for the Validation of Organic Data Acquired Using SW-846 Method 8260B (Rev. 2, 12/96).

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

4.0 PROCEDURE

4.1 EVALUATION OF METHOD COMPLIANCE

The data reviewer will assess the method compliance of the volatile data based on an evaluation of information presented in the data package deliverables. Compliance with SW-846 Method 8260B 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 (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 Organic Data Evaluation 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 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 requests will be discussed in the comments subsection of the QAR and will be included as an attachment to the QAR.

4.2 DETERMINATION OF DATA USABILITY

The data reviewer will determine the usability of the volatile organic data based on an evaluation of the information presented in the data package deliverables. The findings of the volatile organic 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 Organic Data Qualifier subsection of the QAR. Each qualification will indicate that the affected sample result(s) has been flagged with a representative qualifier code(s) in 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, common contaminants that were not qualified, unusable results (R/UR), tentative identifications of target compounds (N), estimated results (J/UJ), tentatively identified compounds (TICs), field duplicate comparison, and a general qualifier for all results reported below the quantitation 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 volatile organic data and the resultant qualifications will be as stated on the attached Table for the Validation of Volatile Organic Compounds Generated by SW-846 Method 8260B. It should be noted that the Project Manager should be consulted when the use of “professional judgement” is indicated on the attached table.

Table for the Validation of Volatile Organic Compounds Generated by SW-846 Method 8260B

Quality Control Item	Usability Criteria	Action(s)
Temperature and Conditions Upon Receipt (See Note #1 for additional information)	4±2°C. Aqueous samples should not have headspace.	If temperature is >6°C but ≤10°C, qualify positive results as estimated (“J”) and qualify “not-detected” results as estimated (“UJ”). If temperature is >10°C, qualify positive results as estimated (“J”) and qualify “not-detected” results as unusable (“UR”). If aqueous samples are received with headspace >pea-size but ≤5 mL, qualify positive results as estimated (“J”) and qualify “not-detected” results as estimated (“UJ”). If aqueous samples are received with headspace >5mL, qualify positive results as estimated (“J”) and qualify “not-detected” results as unusable (“UR”). Note the time of sample collection relative to receipt at the laboratory; use professional judgement if < 8 hours has elapsed from collect to receipt to determine if the qualification for elevated temperature applies.
Technical Holding Time (See Note #2 for additional information)	Chemically preserved (pH≤2 with HCl) aqueous samples analyzed for aromatic compounds should be analyzed within 14 days of collection. Preserved solid/soil samples should be analyzed within 14 days of collection. Unpreserved (pH>2) aqueous samples analyzed for aromatic compounds should be analyzed within 7 days of 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”).
GC/MS Tuning (BFB) (See Note #3 for additional information)	Ion abundances should meet the method acceptance criteria.	If mass calibration was not performed, qualify all associated data as unusable (“R/UR”). If mass assignment is in error, qualify all associated data as unusable (“R/UR”). Use professional judgement if abundance criteria are not met. (See Note #3.) Use professional judgement if samples are analyzed more than 12 hours after a compliant tune and there is no evidence of a compliant tune following the samples.

Table for the Validation of Volatile Organic Compounds Generated by SW-846 Method 8260B

Quality Control Item	Usability Criteria	Action(s)
Initial Calibration (See Note #4 for additional information.)	Average relative response factor (RRF) for each compound should be ≥0.050. %RSD should be ≤15% or a calibration curve should be generated. If a curve is generated, r (linear) or coefficient determination (COD; quadratic) should be ≥0.99.	If target compounds have an average RRF <0.050, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR"). If target compounds have 15%< %RSD ≤50%, qualify positive results as estimated ("J") and do not qualify "not-detected" results. If target compounds have 50%< %RSD ≤90%, qualify positive results as estimated ("J") and use professional judgement to qualify "not-detected" results. If target compounds have %RSD > 90%, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR"). Use professional judgement when evaluating correlation coefficients (r) and coefficients of determination (COD). If r (linear) or COD (quadratic) is <0.99 but ≥0.85, qualify positive results as estimated ("J") and do not qualify "not-detected" results. If r or COD is <0.85, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR"). If the initial calibration standards and the samples associated were not performed similarly (*e.g.,* the initial calibration standards were heated and the samples were not heated), qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ").

Table for the Validation of Volatile Organic Compounds Generated by SW-846 Method 8260B

Quality Control Item	Usability Criteria	Action(s)
Continuing Calibration Verification (CCV) (See Note #5 for additional information.)	CCV RRFs for target compounds should be ≥0.050. %drift or % difference (%D) should be ≤20%.	If target compounds have an RRF <0.050, qualify positive results as estimated (“J”) and qualify “not-detected” results as unusable (“UR”). If target compounds have 20%< %D ≤90% with the response indicating a sensitivity decrease, qualify positive results as estimated (“J”) and qualify “not-detected” results as estimated (“UJ”). If target compounds have %D>20% with a response indicating a sensitivity increase, qualify positive results as estimated (“J”) and use professional judgment to qualify “not-detected” results. If target compounds have %D>90%, with the response indicating a sensitivity decrease, qualify positive results as estimated (“J”) and qualify “not-detected” results as unusable (“UR”).
Internal Standards	Area counts of the internal standard peaks should be 50-200% of the internal standard area observed in the associated CCV standard. Retention time (RT) for any internal standard should not vary by more than ±30 seconds from RT in the associated CCV standard.	If a sample area count is outside of criteria (50-200% of associated CCV), qualify positive results for compounds quantitated using that internal standard as estimated (“J”) and qualify “not-detected” results for compounds quantitated using that internal standard as estimated (“UJ”). If extremely low sample area counts (<25%) are reported, qualify positive results for compounds quantitated using the extremely low internal standard as estimated (“J”) and qualify “not-detected” results for compounds quantitated using that internal standard as unusable (“UR”). If an internal standard RT varies by more than 30 seconds and no peaks are observed in the sample chromatogram, qualification is not necessary. Use professional judgement if peaks are observed in the sample chromatogram.

Table for the Validation of Volatile Organic Compounds Generated by SW-846 Method 8260B

Quality Control Item	Usability Criteria	Action(s)
Blanks (See Notes #6 and for additional information.)	Summarize all results greater than the method detection limit (MDL) in the blanks. The highest positive result associated with a sample should be utilized for evaluation of contamination.	If a target compound is detected in the blank but not in the associated sample(s), no action is required. If a sample result is ≤5× (10× for common contaminants) blank result, qualify the positive result as "not-detected" ("U*"). If the positive result qualified "U*" is <RL, the RL should be used as reported. If the positive result qualified "U*" is ≥RL, the value of the positive result should be used as the revised RL. If a sample result is >5× (10×) the blank result, qualification is not required. If gross contamination exists (*i.e.*, saturated peaks by GC/MS), qualify the positive results as unusable ("R") due to interference. If a TIC is observed in blank and sample, or if the TIC is a known laboratory artifact, qualify the TIC result as unusable ("R").
Surrogate Recovery	Use laboratory acceptance limits. Use 70%-130% as the default limits if the laboratory limits are unreasonable.	If recoveries of one or more surrogates > upper limit, qualify positive results as estimated ("J") and do not qualify "not-detected" results. If recoveries of one or more surrogates < lower limit, but ≥10%, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If recoveries of one or more surrogates <10%, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR").

Table for the Validation of Volatile Organic Compounds Generated by SW-846 Method 8260B

Quality Control Item	Usability Criteria	Action(s)
Matrix Spike/Matrix Spike Duplicate (MS/MSD)	For accuracy use recovery limits of 70-130%. 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 on %Rs) that are outside of criteria if the original concentration of a compound is >4× the spiking level for that compound. RPDs calculated using MS/MSD results can be used to evaluate precision. If the recovery is >130%, qualify the positive result in the native sample as estimated (“J”) and do not qualify the “not-detected” result. If the recovery is <70% but ≥30%, qualify the positive result in the native sample as estimated (“J”) and qualify the “not-detected” result in the native sample as estimated (“UJ”). If the recovery is <30%, qualify the positive result in the native sample as estimated (“J”) and qualify the “not-detected” result in the native sample as unusable (“UR”). If the precision exceeds the RPD criterion, qualify the positive result in the native sample as estimated (“J”) and do not qualify the “not-detected” result. If the precision criteria (see field duplicate usability criteria) for non-spiked compounds are not met, qualify positive results in the native sample as estimated (“J”) and qualify “not-detected” results in the native sample as estimated (“UJ”). If a field duplicate of the native sample was collected and analyzed, the field duplicate should also be qualified if the MS/MSD %Rs or RPD are outside of the criteria (as stated above for the native sample).
Laboratory Control Sample/Laboratory Control Sample Duplicate (LCS/LCSD)	For accuracy, use recovery limits of 70-130%. For precision, use RPD limit of 20% for aqueous samples and 40% for solid samples.	If the recovery is >130%, qualify positive results in all associated samples as estimated (“J”) and do not qualify “not-detected” results. If the recovery is <70% but ≥30%, qualify positive results in the associated samples as estimated (“J”) and qualify “not-detected” results as estimated (“UJ”). If the recovery is <30%, qualify positive results in the associated samples as estimated (“J”) and qualify “not-detected” results as unusable (“UR”). If the precision exceeds the RPD criterion, qualify positive results in the associated samples as estimated (“J”) and do not qualify “not-detected” results.

Table for the Validation of Volatile Organic Compounds Generated by SW-846 Method 8260B

Quality Control Item	Usability Criteria	Action(s)
Field Duplicate (See Note #7 for additional information.)	Use precision limits of 20% RPD (%RSD for triplicate and quadruplicate analyses) for aqueous samples and 40% RPD (%RSD for triplicate and quadruplicate analyses) for solid samples when sample results are ≥5× RL. Use limit of ± RL (±2× RL for solids) when at least one sample value is <5× RL. (Use one-half the RL as a numerical value for any "not-detected" results in the RPD calculations).	If the criteria are not met, qualify positive results for non-compliant compounds in original sample and its duplicate as estimated ("J") and qualify "not-detected" results as estimated ("UJ").
Target Compound Identification (See Note #8 for additional information.)	Relative Retention Time (RRTs) should be ±0.06 RRT units of the standard RRT. Mass spectra of sample and current laboratory-generated standard should match.	Use professional judgement when applying the qualitative criteria for GC/MS analysis of target compounds. If it is determined that incorrect identifications were made or positive results were not reported, professional judgment should be used to determine which of the following options should be used: (1) qualify affected results as unusable ("R"); (2) correct reported results based on the raw data; or (3) contact laboratory for clarification. If a positive result meets some qualitative criteria but an evaluation of all qualitative criteria is inconclusive (possibly due to mass spectral interferences), use professional judgment to determine if result should be qualified "N".
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%.

Table for the Validation of Volatile Organic Compounds Generated by SW-846 Method 8260B

Quality Control Item	Usability Criteria	Action(s)
Compound Quantitation (See Note #9 for additional information.)	Samples with results that exceed the instrument calibration range should be reanalyzed at a dilution.	If target compound results exceeds the instrument calibration range, qualify positive results as estimated ("J"). If a target compound result is <RL but ≥MDL, qualify positive results as estimated ("J"). Use professional judgment to determine whether sample reanalyses and dilutions should be compared to the original analysis. If the precision criteria (see field duplicate usability) between the original sample results and the reanalysis sample result are not met, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ").
System Performance (See Note #10 for additional information.)	Professional judgment should be used when assessing the degradation of the system performance during analyses.	Use professional judgement to qualify the data if it is determined that system performance degraded during sample analysis.
Overall Assessment of Data	Assess overall quality of the data. Review available materials to assess the quality, keeping in mind the additive 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 the Volatile Organic Data Generated by SW-846 Method 8260B

1. If several sample vials are received at the laboratory for one aqueous sample and the laboratory indicates that only one vial was received with head space, the data should not be qualified. It may be necessary to contact the laboratory to determine if the laboratory utilized a sample vial without head space.

2. If the pH is not checked by the laboratory, contact the Project Manager to determine if pH logs should be requested from the laboratory. If pH logs are not obtained, check the chain-of-custody (COC) to determine if the sample was properly preserved. Assume the pH is within the specified criteria if the COC indicates the sample was preserved and include a comment in the QAR indicating this.

   If a sample is acid-preserved (HCl for aqueous or sodium bisulfate for solids), the priority pollutant level (PPL) compound 2-chloroethyl vinyl ether may not be recovered because it is an acid-labile compound. This lack of recovery can be confirmed by examining the MS/MSD %Rs of an acid-preserved sample. In acid-preserved samples, qualify positive results for 2-chloroethyl vinyl ether as estimated (“J”) and qualify “not-detected” results for 2-chloroethyl vinyl ether as unusable (“R”).

3. Mass Tuning Criteria (alternate tuning criteria may be used by laboratory [*e.g.*, CLP, Method 524.2, or manufacturer instructions] provided that method performance is not adversely affected.)

Notes for the Validation of the Volatile Organic Data Generated by SW-846 Method 8260B

Mass	Intensity Required
50	15 to 40% of mass 95
75	30 to 60% of mass 95
95	base peak, 100% relative abundance
96	5 to 9% of mass 95
173	less than 2% of mass 174
174	greater than 50% of mass 95
175	5 to 9% of mass 174
176	greater than 95% but less than 101% of mass 174
177	5 to 9% of mass 176

If using professional judgement to determine an impact when ion abundance criteria are not met, the most important factors to consider are the empirical results that are relatively insensitive to location on the chromatographic profile and the type of instrumentation. Therefore, the critical ion abundance criteria for BFB are the m/z 95/96, 174/175, 174/176, and 176/177 ratios. The relative abundances of m/z 50 and 75 are of less importance.

4. If the initial calibration %RSD is >50%, the linearity of the first three initial calibration standards for the compound should be evaluated. If the first three initial calibration standards for the compound are linear (*i.e.*, r ≥0.99), do not qualify “not-detected” results. If the first three initial calibration standards for the compound are not linear, qualify “not-detected’ results as estimated (“UJ”).

Use professional judgement when evaluating the concentration intercept of a calibration curve. If the concentration intercept is positive, the samples should be evaluated for false positives. If the concentration intercept is negative, the samples should be evaluated for false negatives.

5. If instrument instability (*i.e.*, several continuing calibration standards with compounds exhibiting both increasing and decreasing sensitivity throughout an analytical sequence) is observed in the analysis of sequential continuing calibration standards, “not-detected” results may be qualified as estimated (“UJ”) due to instrument sensitivity of a continuing calibration standard response that is greater than the initial calibration standard response (increase in instrument sensitivity).

   If the continuing calibration standard is %D>20% in the direction of increased instrument sensitivity and it is determined that “not-detected” results should not be qualified, the data reviewer should note this in the QAR support documentation.

6. The frequency of equipment/rinse/storage blanks is determined during the sampling event. The results of a field/equipment/rinse blank should be applied to all samples collected using the same equipment (equipment/rinse blanks only) on the same day; unless only one was collected for a several-day sampling event. In instances when 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 for a contaminant.

Notes for the Validation of the Volatile Organic Data Generated by SW-846 Method 8260B

The following compounds are considered common laboratory contaminants/artifacts. If these compounds are reported as target compounds, the 10× rule applies for the evaluation of blank contamination. If these compounds are reported as TICs, they should be considered laboratory artifacts.

a. Common laboratory contaminants on CLP target compound list (TCL): methylene chloride, acetone, 2-butanone, and cyclohexane.
b Other common laboratory contaminants: CO_2 (m/z 44), siloxanes (m/z 73), diethyl ether, hexane, freons, and phthalates.
c. Solvent preservatives such as cyclohexene which is a methylene chloride preservative. Related by-products include cyclohexanone, cyclohexanone, cyclohexanol, chlorocyclohexene, and chlorocyclohexanol.
d. Aldol condensation reaction products of acetone include: 4-hydroxy-4-methyl-2-pentanone, 4-methyl-2-penten-2-one, and 5,5-dimethyl-2(5H)-furanone.
e. Silicon-containing compounds (*e.g.*, trimethyl silonol).

If a sample result qualified "U*" is < the RL and the laboratory did not report the RL on the data tables or Form the positive result (*e.g.*, 8 μg/L) should be replaced with the RL (*e.g.*, 10 μg/L).

7. 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. It is also expected that soil duplicate results will have a greater variance

than aqueous duplicate results.

8. Generally, all ions present in standard mass spectrum at relative intensity >10% should be present in the sample mass spectrum; however, the concentration of the compound should be considered when evaluating ions with a relative intensity of ≤30% in the standard mass spectrum. In addition, data for ions with a mz of ≤40 amu are often not collected and generally are not used for evaluation purposes.

Characteristic ions from the reference mass spectrum (three ions of greatest relative intensity or any ions over 30% relative intensity if less than three such ions occur in the reference spectrum) should maximize in the same scan or within one scan of each other. Relative intensities of these ions should agree within ±30% between the standard and the sample spectra.

Ions that are not present in the standard mass spectrum may be present in the sample mass spectrum without impacting the qualitative identification of the target compound. The presence of such ions at relative intensity 10% may be indicative of a coeluting compound. If feasible, the coeluting compound should be tentatively identified in order to evaluate whether the coeluting compound's mass spectrum contains any of the characteristic ions of the target compound. If a coeluting compound that has a mass spectrum containing characteristic ions of the target compound is tentatively identified, use professional judgment to evaluate the impact on the sample result.

Notes for the Validation of the Volatile Organic Data Generated by SW-846 Method 8260B

9. If a sample result exceeds the instrument calibration range (lower dilution analysis) or is less than the RL (secondary dilution), do not utilize this result when comparing an original analysis and a diluted reanalysis.

10. Poor chromatographic performance affects both qualitative and quantitative results. Indications of substandard performance include:

    - High background levels or shifts in absolute RT of internal standards
    - Excessive baseline rise at elevated temperatures
    - Extraneous peaks
    - Loss of resolution
    - Peak failing or peak splitting that may result in an inaccurate quantitation

11. The RL will be defined on a project-specific basis. If the project-required RL is lower than the low initial calibration standard concentration, the Project Manager should be consulted for instructions on how to apply qualification related to the RL.