Data Review/Authorization Procedures for the Volatile Organic Laboratory

FLORIDA DEPARTMENT OF ENVIRONMENTAL PROTECTION

CHEMISTRY PROGRAM, DEP LABORATORY

TALLAHASSEE, FLORIDA

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Data Review/Authorization Procedures for the Volatile Organic and Laboratory

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Data Review/Authorization Procedures for the Volatile Laboratory

1. SCOPE AND APPLICATION

1.1. The procedures provided in this SOP detail the required steps, responsible parties, and authorization necessary for data review and reporting in the volatile organic (VOC) laboratory. Many aspects of the data review process are already covered in the method and general SOPs. This SOP has additional detailed information not found in the method SOPs due to the more comprehensive nature of this data review document. The associated method SOPs covered by this Data Review and Authorization Procedure include:

- **VO-002:** Measurement of VOCs in Water by GC/MS.
- **VO-003:** Measurement of VOCs in Sediment and Waste by GC/MS
- **VO-004:** *Measurement of Acrylonitrile and Acrolein in Sediments and Waste by P&T/GC/MS.*
- **VO-005:** TCLP and SPLP using Zero Headspace Extraction
- **VO-006:** Measurement of Polar VOCs in Wastewater by GC/MS

1.2. The Quality Assurance/Quality Control SOP **VO-001** includes a detailed discussion of Laboratory Quality Control and Assurance, MDL determination, Method Validation, Calculations, and Definitions and Acronyms. While this SOP will describe data review aspects of QA/QC, please refer to the SOP **VO-001** for more specific details.

1.3. The procedures and requirements for qualifying data are provided in SOP **LB-027,** *Standard Operating Procedure for Reporting Qualified Data.* The qualifier requirements in the SOP **LB-027** will supersede the requirements provided in this SOP.

1.4. The procedures and requirements for manual peak integration are provided in SOP **CM-018**, *Laboratory Policy Regarding Manual Chromatographic Peak Integration.* The integration requirements in the SOP **CM-018** will supersede the requirements provided in this SOP.

1.5. The procedures for determining how to report significant figures are provided in SOP **LB-024** *Significant Figure Policy.* In general, the VOC data is reported with two significant figures, but there are exceptions where the data will support three significant figures and is requested by the client.

1.6. This Data Review and Authorization SOP does not include:

- Data review of field sampling operations.
- Data review of sample receipt or transport operations.
- Final job review and event level review.

2. SAMPLE PREPARATION REVIEW, COMMENTING, AND QUALIFICATION

The primary responsible parties for reviewing sample preparation are the Analyst and Analyst Supervisor. They have the responsibility to review all documents relevant to preparation of samples.

2.1. Review the project (job) folder for special instructions or conditions noted during sample receipt and log-in. The project folder must be reviewed at each step of the process, including log-in, sample preparation, sample analysis, and data review. The log-in information and chain-of-custody are available electronically in the Laboratory Information Management System (LIMS). Consider special instructions when making any determinations. Consult the Organic Section Manager or Customer if the instructions are not legible or not understood.

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2.2. Review the backlog report to verify that the correct test was requested in the LIMS. Consult the Analyst or Receiving Room Supervisors if there are discrepancies.

2.3. Confirm that the sample matrix is consistent with the test requested. The test may have to be changed if there is a sample matrix mismatch with the requested test. Consult the Analyst and Receiving Room Supervisors if there are discrepancies.

2.4. Review the sample preparation records and verify that the correct preparation was used for the analytical samples. If samples were prepared incorrectly, then re-prepare all affected samples using the appropriate preparation method. Verify that all preparation steps are documented. The following log books are used to record information that may be relevant to the preparation of VOC samples:

- Toploading Balance Calibration Log
- Analytical Balance Calibration Log
- Instrument Temperature Calibration Log
- pH Meter Calibration Log
- LIMS Analytical Standard Preparation Log
- Volatiles Sediment and Waste Preparation Log
- TCLP and SPLP Sample Preparation Log by EPA Methods 1311 and 1312

2.5. Note any observations recorded in the sample screening records such as unusual odors, colors, viscosity, solubility, or reactions during sample preparation or extraction. Consider these observations in making any determinations and evaluate potential ramifications to the reported data.

2.6. Verify that the appropriate matrix and surrogate spike solutions and spike levels were used. Check the expiration date of all working standards and solutions**. If any of the working solutions have expired, then the samples must be re-prepared or the data must be flagged with the qualifier "J" and an explanation must be placed in the sample comment field.**

2.7. Verify that the preparation holding times were achieved. **If not, then flag the data with the qualifier "Q" for each analyte reported beyond the holding time and add a comment explaining the holding time exceedance.**

3. SAMPLE ANALYSIS REVIEW, COMMENTING, AND QUALIFICATION

The primary responsible parties for review of the sample analysis are the Analyst and Analyst Supervisor. The Supervisor or a Senior Analyst must provide a duplicate check of the sample analysis. The following items must be checked for every analytical batch of samples.

3.1. Ensure that a valid instrument calibration is on file and complies with method specifications for all parameters analyzed. **If not, then re-analyze the sample batch after producing a valid instrument calibration.**

3.2. For samples analyzed by GC/MS, check the background-subtracted tune of the mass spectrometer instrument with the tuning compound bromofluorobenzene (BFB) every 12 hours and ensure that the mass spectrometer meets all of the method tuning requirements. If the criteria in Table 1 are not achieved, then re-analyze the samples analyzed during the time period when the instrument was not tuning properly. **If any of the reanalyzed samples exceed the analysis holding time, then consult the Supervisor about reporting either the original results with a qualifier "J" or the reanalysis results beyond holding time with a qualifier "Q". Include a comment in the final report explaining the qualifier used.**

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Table 1.-BFB m/z Abundance Criteria

Mass, m/z	Abundance Criteria†	Abundance Criteria**
50	15-40 % of mass 95	8-40 % of mass 95
75	30-60 % of mass 95	30-66 % of mass 95
95	Base peak, 100 %	Base peak, 100 %
96	5-9 % of mass 95	5-9 % of mass 95
173	<2 % of mass 174	<2 % of mass 174
174	>50 % of mass 95	50-120 % of mass 95
175	5-9 % of mass 174	4-9 % of mass 174
176	>95 % but < 101 % of mass 174	93-101 % of mass 174
177	5-9 % of mass 176	5-9 % of mass 176

† BFB Criteria for Agilent 5975 instruments.
** BFB Criteria for Agilent 5977 High Efficiency Source instruments, based on CLP-SOW.

3.3. Ensure that the appropriate Quality Control (QC) samples were analyzed for the analysis batch including tune blanks, method blanks, calibration checks, duplicate laboratory fortified blanks, and duplicate matrix spike samples. Refer to the Method Standard Operating Procedures and the corresponding EPA methods for details on the analysis requirements. If there are problems with the QC samples, then re-prepare the samples. **If the samples have expired, then continue with the re-analysis, but flag the data with a "Q" qualifier.**

3.4. A hardcopy of the sample field sheets, preparation log sheets, sample screening results, analytical batch run sequence, sample quantitation data, and chromatograms must be compiled into a job folder. An associated QC folder containing a hardcopy of the QC quantitation data, chromatograms, batch run sequence, and QC statistical results must also be compiled daily in a QC folder for each instrument used to report data.

3.5. All computer file names, folder file names, as well as, marks or comments on the data hardcopies must conform to the conventions used in the laboratory. These conventions are stipulated in the method SOPs and the Laboratory Comprehensive Plan.

3.6. Ensure that calibration check standards pass for all parameters reported. For the VOC tests, a calibration check standard must be analyzed every 12 hours and must comply with method specifications. If not, then re-analyze the affected samples with valid calibration check standards or add the qualifier "J" and an appropriate comment if re-analysis is not feasible.

3.7. Check the internal standards, surrogates, lab fortified blank recoveries, matrix spike recoveries, and precision. Ensure that all values are within the QC acceptance ranges. For the 8260D analysis, the internal standard recovery must be between 50-200%. The recovery limits for the surrogates and CCV compounds are 80 to 120%. The recovery limits for the spike compounds are approximately 70-130%. Most compounds are set to 70-130 limit range except for the light gases and ketones, which have a somewhat larger range that is determined based on statistical measurements. A comment must be included in the report for any compounds outside of the acceptance ranges and the data must also be qualified accordingly. **Failing recovery or precision values require qualification, regardless if the failure is high or low for a non-detect. All QA/QC failures for detected compounds require "J" qualification, except for the one condition where the spike level is less than the background analyte level. In this case a comment is added indicating that the matrix spike accuracy could not be assessed. Always include a comment in the final report explaining the use of qualifiers.**

3.8. Check the internal standard area counts and retention times in the GC/MS data. Confirm that the internal standard recoveries and retention times comply with method specifications. If not, then re-analyze the affected samples.

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3.9. Check the precision of all field and laboratory duplicates. If the degree of replication is not within the warning acceptance range of ± 20%, then attempt to identify the problem. Precision values greater than ± 30% must be appropriately qualified and commented. If the problem is with the instrumentation, then re-analyze the sample batch. If the problem is with one of the duplicate samples, then reanalyze the duplicates, if possible.

3.10. Check the laboratory blanks, trip blanks, field blanks and equipment blanks for evidence of contamination with one or more target compounds. If laboratory contamination is suspected, then determine whether the contamination occurred during sample preparation or analysis. Reanalyze the affected samples if the contamination is from the laboratory and can be eliminated. Use the following criteria for qualifying sample results when there is blank contamination with a target compound:

3.10.1. **No qualifier is needed** when the target compound concentration in the blanks is less than 10% found in the sample. No comment is needed to explain the blank detection.

3.10.2. **Report the result with the qualifier "V"** when the target compound concentration in the blanks is more than 10% found in the sample. Blank detects below the reporting limit must be monitored, but are not normally subject to this rule. Sample results more than 10 times the amount of blank contamination do not require qualification. Include a comment in the final report explaining the use of this qualifier.

3.10.3. **Elevate the MDL** when the target compound concentration in the blank is due to a background level in the laboratory that cannot be immediately remediated. This is usually determined during the initial method validation, but can also occur if there is a change in the method, equipment, reagents, or a temporary background contamination. Some analytical methods routinely have a measurable blank signal above the instrument's inherent detection capabilities.

3.11. For all positive results, check the integration of the peak area by ensuring that the baseline was drawn appropriately. For some types of matrix interference, it may be necessary to use background subtraction to alleviate the spectral interference from the mass spectrum of the target analyte. Ensure that the peak integration technique was utilized appropriately as specified in SOP **CM-018**. If a parameter cannot be accurately quantified due to matrix interference, then the result for the affected parameter must be flagged as an estimate (i.e., append the qualifier "J" to the final result). Include a comment in final report explaining the use of this qualifier.

3.12. Evaluate the analytical batch for carryover contamination by checking all samples that follow a highly contaminated sample. Rerun all samples with suspected or potential carryover contamination.

3.13. Two criteria must be satisfied to verify identification of a compound: 1) elution of the sample component in the relative retention time window as the standard component and 2) for the VOC analysis, correspondence of the mass spectrum for the analyte. Closely evaluate the Total Ion Chromatogram and associated single ion chromatograms for all reported analytes. Do not rely on the instrument generated reports without reviewing the chromatograms and mass spectra. Manually mark all positives on the hardcopy to indicate that they have been verified as follows:

- **P or Pos** – Positive result.
- "√" Mark – Results have been reviewed and checked for correctness.
- **NP, FP, or "X" Mark)** – Not Positive (False Positive) result.
- **BDL –** Below Detection Limit
- **RR** – Rerun Analysis.

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3.14. Ensure that the proper dilution levels were used for sample analysis. Dilute and re-analyzed any samples that contain analytes at concentrations higher than the calibration range. Use the following criteria for reporting:

3.14.1. **No qualifier is needed** for concentrations greater than the PQL and less than the maximum calibration point.
3.14.2. **Report the MDL with qualifier "U"** for concentrations less than the MDL.
3.14.3. **Report the result with qualifier "T"** for concentrations reported less than the MDL. This qualifier is used only when there is strong evidence to support reporting a positive result and under consultation with the Analyst Supervisor.
3.14.4. **Report the result with qualifier "I"** for concentrations equal to the MDL and less than the PQL.
3.14.5. **Report the result with qualifier "J"** for concentrations greater than the maximum calibration point.

3.15. Review all sample calculations. Make sure any dilution factors and dry-weight corrections were properly applied.

3.16. Review all sample dilution results for consistency. In some cases it is necessary to report results from multiple analytical data sets in order to report all of the parameters within calibration range.

3.17. If a sample with CCV, LCS or process errors is not or cannot be re-analyzed, then report the analytes with the appropriate qualifier and add a comment to the report explaining the use of the qualifier.

3.18. A library search must be performed on unknowns higher than the internal standard peak height. For library searches (i.e., tentatively identified parameters), exercise caution when utilizing the search results and make sure to examine the library spectra against the sample spectra. Report library searches with an estimated concentration. Remember: Do not rely on the library search program over your scientific judgment. Look at the spectra; you may have additional information about the sample that will lead to a different conclusion than what the search program provides.

3.19. Ensure appropriate qualifiers are used. Refer to the *Department of Environmental Protection: Standard Operating Procedure for Reporting Qualified Data* (DEP SOP **LB-027**) for details on the use and the reporting priority of these qualifiers.

3.20. Evaluate the analytical results against any field information and make certain that the transcribed information is correct and consistent with the laboratory findings. The final results should not be posted until all inconsistencies are accounted for. If a library search for non-target analytes was performed, then review the guidelines. Ensure that these guidelines were properly followed.

3.21. Check field preservation records (e.g., log-in details and sample prep records) for any indication that the samples were improperly preserved at collection. **If samples were received improperly preserved, then all data must be flagged with a "Y" qualifier.**

4. REPORTED DATA REVIEW, COMMENTING, AND QUALIFICATION

The primary responsible parties for reviewing reported data are the Analyst and Analyst Supervisor. The Environmental Manager provides a secondary check for the items noted by an asterisk "*".

4.1. Data must be reported with two significant figures, unless the method indicates otherwise. *****

4.2. When samples with the same Field ID are analyzed by multiple groups, cross check the data of both groups for possible discrepancies, particularly when both report the same compound. *****

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4.3. Compare field and laboratory duplicate results. *****

4.4. Compare effluents with backgrounds were the effluent concentrations will usually be higher than background concentrations. *****

4.5. Compare results with any information known about the sites history. *****

4.6. Confirm the sample preparation dates and the analysis dates. The collection time must come before sample preparation which must come before analysis. *****

4.7. Ensure appropriate qualifiers are used and that comments are entered when needed.***** Frequently used comments are:

4.7.1. Insufficient sample was available to perform duplicate matrix spikes.
4.7.2. The MDLs are elevated due to low percent solids of the sample matrix.
4.7.3. The MDLs are elevated due to required dilution of the sample matrix.
4.7.4. The MDL for "compound name" is elevated due to the presence of "compound name" in the method blank.
4.7.5. The MDLs are elevated due to required dilution as a result of sample foaming.
4.7.6. The accuracy and precision of "compound name" in the matrix spikes are out of routine statistical limits due to matrix interference.
4.7.7. Recovery of "compound name" in the matrix spikes could not be assessed due to an elevated level of the compound in the sample matrix.
4.7.8. Precision for "compound name" is not available due to no recoveries in the duplicate matrix spikes
4.7.9. Tentative identification: total other purgeable aliphatic compounds = est. 10 µg/L.
4.7.10. Tentative identification: total other purgeable aromatic compounds = est. 10 µg/kg.
4.7.11. Tentative identification: total other purgeable petroleum compounds = est. 10 µg/kg.
4.7.12. Sample was received with headspace.
4.7.13. The compound "name" has the qualifier "J" due to the level in the sample exceeding the calibration range.
4.7.14. Quality control failure(s) observed.
4.7.15. V – qualifier due to detection of "compound name" in the method blank.
4.7.16. Q – sample expired upon receipt.
4.7.17. Q – sample was reported beyond normal holding time due to need for reanalysis.
4.7.18. Q – sample is a PT study with an arbitrary expiration date.
4.7.19. J – estimation is due to the surrogate recovery for "compound name" exceeding the routine statistical limits as a result of matrix interference.

4.8. Verify that sample identifier information in the LIMS matches that in the reported data package.

4.9. Evaluate the analytical results against any field information. If anything looks suspicious, further research, as necessary, before posting results. *****

5. FINAL AUTHORIZATION OF SAMPLES AND JOBS

The primary responsible party for authorizing samples is the analyst supervisor or designate. The primary responsible party for authorizing a job is the Environmental Manager.

5.1. After completion of the above data review process, the supervisor (or designate) must authorize the results by affixing their name and the date of review to the data package. Authorization of the data indicates that the checks in the proceeding sections were performed. The LIMS incorporates electronic features and functions for Review and Authorization. The original hardcopy file for each job is also initialed and dated upon authorization of the sample results.

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5.2. The job is forwarded through the Environmental Manager to the Section Administrator (or designate) for final approval and submission to the client.

5.3. If any data review check results in a corrective action(s), then the Supervisor (or designate) must indicate the corrective action(s) performed and affix their signature and date to indicate that the specified corrective action was initiated and completed satisfactorily.

6. REFERENCES

6.1. Florida Department of Environmental Protection, Comprehensive Quality Assurance Plan, Bureau of Laboratories, DEP, 2021.

6.2. Florida Department of Environmental Protection Laboratory Safety SOP Manual, **OG-001**.

6.3. Florida Department of Environmental Protection Laboratory SOP **VO-001,** *Data Quality Assurance/Quality Control Measurements in the Volatile Organics (VOC) Laboratory.*

6.4. Florida Department of Environmental Protection Laboratory SOP **VO-002,** *Measurement of VOCs in Water by GC/MS.*

6.5. Florida Department of Environmental Protection Laboratory SOP **VO-003,** *Measurement of VOCs in Sediment and Waste by GC/MS.*

6.6. Florida Department of Environmental Protection Laboratory SOP **VO-004,** *Measurement of Acrylonitrile and Acrolein in Sediments and Waste by P&T/GC/MS.*

6.7. Florida Department of Environmental Protection Laboratory SOP **VO-005,** *TCLP and SPLP Sample Preparation using Zero Headspace Extraction.*

6.8. Florida Department of Environmental Protection Laboratory SOP **VO-006,** *Measurement of Polar VOCs in Wastewater by GC/MS.*

6.9. Florida Department of Environmental Protection Laboratory SOP **LB-002,** *Non-Conformance Reporting System.*

6.10. Florida Department of Environmental Protection Laboratory SOP **CM-018,** *Data Laboratory Policy Regarding Manual Chromatographic Peak Integration.*

6.11. Florida Department of Environmental Protection Laboratory SOP **LB-027,** *Data Standard Operating Procedure for Reporting Qualified Data.*

6.12. Florida Department of Environmental Protection Laboratory SOP **LB-006,** *Standard Operating Procedure for Records Storage and Retention.*

6.13. Florida Department of Environmental Protection Laboratory SOP **LB-024,** *Significant Figures: Policy of the DEP Bureau of Laboratories.*

7. APPENDIX OF CHANGES

7.1 Listing of SOP Version Edits

12/04/2014 Updated version number, updated SOP reference information, removed the methyl mercury test and associated references, updated listing of log books, updated the qualifier comments, and updated the references.

12/07/2015 Updated the log, removed an obsolete test, corrected typos, and updated the references.

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12/12/2017 Updated references.

01/04/2019 Corrected minor typos and updated references.

01/24/2020 Corrected minor typos and updated references.

02/04/2021 Minor formatting edits, updated the version number, and updated references.

01/19/2022 Updated version number, references, and BFB tuning criteria in Table 1.

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