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Data Validation Guidelines Module 4: Data Validation Procedure for Organic Analysis by GC

Environmental Data Quality Workgroup

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Data Validation Guidelines Module 4

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Module 4: Data Validation Procedure for Organic Analysis by GC (SW-846 8000 Series)

1.0 Purpose

This document provides guidance on the validation of organic contaminants by SW-846 Series 8000 methods when analyzed on a Gas Chromatograph (GC):

- 1,2-Dibromoethane and 1,2-Dibromo-3-Chloropropane by Microextraction and GC Method 8011;
- Nonhalogenated Organics by GC Method 8015;
- Aromatic and Halogenated Volatiles by GC Using Photoionization and/or Electrolytic Conductivity Detectors Method 8021;
- Organochlorine Pesticides by GC Method 8081;
- Polychlorinated Biphenyls (PCBs) by GC Method 8082;
- Organophosphorus Compounds by GC Method 8141; and
- Chlorinated Herbicides by GC Using Methylation or Pentafluorobenzylation Derivatization Method 8151;

Note: With the exception of EPA 8000D, this document does not identify specific Series 8000 method versions. Consult the project UFP-QAPP to determine specific requirements for analysis and validation. The language within this document is only to be used as guidance and the QAPP shall always supersede this document.

The objective of this procedure is to provide the end user with a clear understanding of the quality and limitations of the data through documented validation procedures and to encourage consistency in the validation technique and reporting for data generated for Department of Defense (DoD) projects for organic constituents when analyzed on GC.

This document assumes the user is familiar with data validation conventions and qualifiers used in the *DoD General Data Validation Guidelines Version 1 (2019*). This document is also not intended to obviate the need for professional judgment during the validation process.

This document references the *Uniform Federal Policy for Quality Assurance Project Plans (UFP-QAPP) Optimized Worksheets (March 2012)*. Other QAPP formats are equally acceptable.

2.0 Procedure

This guidance can be applied to organic contaminant data generated in support of DoD projects that was produced on GC. This guidance should be implemented by personnel familiar with the methodology contained herein.

Data validation personnel are responsible for implementing this procedure for validation of data and generation of data validation reports for GC organic contaminant data.

2.1 Introduction

This document was written with primary consideration to the latest SW-846 8000 series GC method versions with Quality Control (QC) criteria identified in the DoD Quality Systems Manual (QSM). Actual validation should proceed using the acceptance criteria for the method version specified in the laboratory data deliverable or in the QAPP.

Appendix A summarizes the QC checks and the required frequency and acceptance criteria for Method 8000D and the QSM version 5.3 requirements.

2.2 Deliverables

Laboratory data deliverables consist of a combination of forms and raw data. The manner in which laboratories label their forms is not dictated nor specified. **The labeling convention below is used for simplicity.**

- Cover Sheet
- Case Narrative
- Sample Receipt and Conditions Summary
- Sample Results Summary
- Surrogate Recovery Summary
- Laboratory Control Sample/Laboratory Control Sample Duplicate
- Matrix Spike/Matrix Spike Duplicate Recovery Summary
- Method Blank Summary
- Instrument Performance Check Summary (where applicable)
- Initial Calibration Summary
- Initial/Continuing Calibration Verification Summary
- Retention Time/Internal Standard Summary
- Sequence and preparation logs

2.3 Validation Stages

The types of laboratory data deliverables, staged data validation, and the relationship between the two are outlined in the *DoD General Data Validation Guidelines Version 1*.

Stage 1 data validation consists of a review of sample results form, associated sample receipt summaries (chain of custody), and field QC data.

Stages 2A and **2B** data validation consist of review of summary forms only.

Stages 3 and **4** data validation require review of both summary forms and all associated raw data.

Both the laboratory deliverable and the level of validation should be specified in the QAPP or other planning documents. Data review guidelines and how they apply to the different validation stages are indicated in the following sections.

Note: Any required stage of validation that reveals significant deviations from project requirements may require a higher stage of validation to uncover the source. Data validators are encouraged to communicate with their points of contact identified in the QAPP (such as the UFP-QAPP Worksheet #6) to resolve discrepancies.

3.0 Stage 1 Validation

The following documents should be reviewed for *representativeness* (compliance with required analytical protocols outlined in QAPP), *completeness, and project sensitivity needs:*

- Cover Sheet
- Table of Contents
- Case Narrative
- Sample results form or equivalent Laboratory Report

- Chain of Custody (CoC) forms, Laboratory Receipt Checklists, and other supporting records
- Field QC forms and supporting records

Stage 1 is the validation of investigative and field QC samples.

3.1 Sample Results

Examine the Laboratory Report sample results summary (can be called by many names, such as Form I) and verify the following information:

- Holding times have been met, as applicable
- All sample identification labels are unique, and match the CoC
- All project GC analytes have been analyzed and are reported
- Second (dissimilar) Column results are consistent with QAPP requirements
- All laboratory reported Limits of Detection (LODs) and Limits of Quantitation (LOQs) are equal to or less than QAPP required LODs/LOQs
- All project required LOQs have been met and achieved LOQs are less than the project required action levels
- All reported units (e.g., mg/kg) are accurate and reflect the requirements of the project, and units are consistent with the type of sample matrix
- All required field QC samples (such as trip blanks, equipment blanks, reagent blanks, and field duplicates) have been included in the Laboratory Report at the frequency specified in the QAPP
- Soil samples have been reported on a dry weight basis, unless specified by the QAPP to report on a wet weight basis
- Each laboratory report has a case narrative that explains non-conformities with the data
- All sample collection date/time information matches the CoC or any inconsistency is appropriately documented

The following statements apply to sample results (assuming no other qualifications due to data quality issues):

Qualification of data is based upon the reporting requirements of the QAPP.

The QSM requires reporting non-detects as U-qualified at the LOD and requires reporting detects between the DL and LOQ with a J qualification. There are several ways that a project team may change these reporting requirements for project-specific reasons which are outlined in the QAPP. Though not recommended for typical projects, these changes include reporting non-detects as U-qualified at the DL; reporting non-detects and detects below the LOD as non-detects with U qualification at the LOD; or reporting non-detects and detects below the LOQ as non-detects with U qualification at the LOQ. These varying reporting conventions are summarized in the following table:

Table I: Reporting Requirements

Reporting Requirements (listed below)	**Non-detects or results Below (<) DL**	**Results Below (<) LOD**	**Results Below (<) LOQ**
Standard QSM Reporting	LOD value U	Reported Result J	Reported Result J
*Reporting results to DL	DL value U	Reported Result J	Reported Result J
Reporting results to LOD	LOD value U	LOD value U	Reported Result J
Reporting results to LOQ	LOQ value U	LOQ value U	LOQ value U

***Note:** non-detects reported at the DL have a 50% false negative rate. For further discussion please see *Fact Sheet: Detection and Quantitation – What Project Managers and Data Users Need to Know*, DoD Environmental Data Quality Workgroup, October 2017.

Evaluation of the Laboratory Report

Any samples received for analysis that were not analyzed should be noted in the data validation report, along with the reason(s) for failure to analyze the samples, if the reason(s) can be determined; conversely, samples that were analyzed by GC but were not requested should also be noted.

Analytes that have project action levels less than the laboratory's LOD may reveal a severe deficiency in the data and a failure to meet project goals, and such instances should be noted in the data validation report. Errors in reported units and case narrative non-conformities that call into question the quality of the data should also be discussed in the data validation report.

Errors in quantitation limits or missing or misidentified samples may require a higher than Stage 1 validation. Data validators are encouraged to reach out to their point of contact (QAPP Worksheet #6) when preparing the data validation report.

3.2 Chain of Custody (CoC)

Examine the CoC form (some information may be included on Laboratory Receipt Checklists) for legibility and check that all GC analyses requested on the CoC have been performed by the laboratory. Ensure that the CoC Sample Identification on the laboratory sample results summary (Form I [or equivalent]) matches the Sample Identification on the CoC. Ensure the CoC was signed and dated during transfers of custody. Read the laboratory case narrative for additional information.

Evaluation of the CoC

Any discrepancies in sample identification between the CoC and sample results form should be noted in the data validation report with the correct sample identification in the report and on the appropriate summary form, if the correct sample identification can be determined. These edit corrections should also be verified in any associated electronic data deliverables (EDDs).

If the receiving laboratory transferred the samples to another laboratory for analysis, both the original CoCs and transfer CoCs should be present. Document in the data validation report if the transfer CoCs are not present or if there is missing information (such as location of the laboratory). Make note in the data validation report when signatures of relinquish and receipt of custody were not present.

3.2.1 Sample Preservation, Handling, and Transport

Evaluate sample handling, transport, and laboratory receipt from the CoC and laboratory receipt checklists to ensure that the samples have been properly preserved and handled. The project QAPP (such as UFP-QAPP Worksheet #19) should provide specific preservation requirements. The following are general guidance if project specifications were not stipulated.

Typically, organic samples do not require chemical preservation. An exception is 3 mL 10% sodium thiosulfate solution is added per gallon (or 0.008%) to aqueous samples with residual chlorine present. Addition of sodium thiosulfate solution to sample container may be performed in the laboratory prior to field use. Reference the QAPP for specific preservation requirements.

- Organic contaminant samples are to be shipped in amber bottles with PTFE-lined lids
- All samples are to be shipped in coolers that are maintained at ≤ 6 degrees Celsius (°C)

Evaluation of Preservation, Handling, and Transport

If the temperature of receipt is > 6°C but ≤ 15ºC, detects should be flagged as estimated **J-** and non-detects as estimated **UJ**.

If the temperature of receipt is > 15°C, detects should be flagged as estimated **J-** and non-detects as **X**, exclusion of data recommended.

On occasion, the samples may be delivered to the laboratory within a few hours of collection and before the temperature of the cooler is able to reach 6ºC. For those instances, if cooling has begun, but the temperature is > 6ºC, special note should be made but no qualification should be required.

If the temperature is below 0°C, special note should be made but no qualification should be required.

In the event that both a cooler temperature and a temperature blank were measured, the temperature blank should be evaluated for temperature compliance as it best represents the condition of the samples; however, both temperatures shall be noted in the data validation report.

If the temperature upon receipt at the laboratory was not recorded, note this in the data validation report and assume that a temperature non-conformance occurred. Detects should be flagged as estimated J- and non-detects flagged X, exclusion of data recommended.

If the receiving laboratory transferred the samples to another laboratory for analysis, apply the same temperature criteria to both the transfer CoC and the original CoC.

If aqueous samples known to contain chlorine were not chemically preserved with sodium thiosulfate, apply professional judgment to qualify the sample results.

3.2.2 Holding Times

Holding times for organics are measured from the time of collection (as shown on the CoC) to the time of sample analysis as shown on the sample results summary (Forms I or equivalent) or extraction log (if applicable). Based on input from the DoD Environmental Data Quality Workgroup (EDQW) holding time exceedances are calculated as follows:

Total holding time is based on the timeframe (i.e., hours, days, or months) of the requirement. The following example gives guidance on how holding time exceedances are measured:

For a test with a recommended maximum holding time measured in **days**, the holding time is tracked by the **day**.

- An exceedance of holding time for a sample with a 14-day holding time will occur when the 15th day is reached. Therefore, a sample with a 14-day holding time collected at 8:30 AM on April 4th must be analyzed or extracted before 12:00 AM April 19th (midnight, the start of the 15th day), or an exceedance has occurred.

Samples and extracts must be stored refrigerated to ≤ 6°C until the time of analysis. The holding time for aqueous samples is 7 days from the collection date to the beginning of extraction, and 40 days from extraction to analysis. The holding time for solid samples is 14 days from the collection date to the beginning of extraction, and 40 days from extraction to analysis. The holding time for aqueous waste samples is 7 days from collection to leaching, 7 days from leaching to the beginning of extraction, and 40 days from extraction to analysis. The holding time for solid waste samples is 14 days from collection to leaching, 7 days from leeching to the beginning of extraction and 40 days from extraction to analysis.

There is no specified holding time for PCB Aroclor samples. The QAPP should specify the holding time requirements.

Evaluation of Holding Time

If the holding time is exceeded, qualify all associated detects as estimated **J-** and all associated non-detects as estimated **UJ** and document that holding times were exceeded.

If holding times are grossly exceeded (defined as > 14 days to extraction for aqueous samples and > 28 days for solid samples), detects should be qualified as estimated **J-** and non-detects as **X**, exclusion of data recommended.

For PCB Aroclor samples, the above holding times for organic contaminants can be used for guidance if specific holding times are not listed in the QAPP. Exceedances do not require qualification of the data but should be noted in the data validation report.

3.3 Field QC

Field QC can consist of various blanks, field duplicates, and field replicates. The purpose of blanks is to identify potential cross-contamination at different stages of sampling and cleaning of equipment for reuse. Duplicates and replicates help a project identify reproducibility among samples at the project site.

3.3.1 Field Blanks

Not every field blank type may be utilized during any given sampling event and there may be more blank types than described in this document. Field blanks may be varied throughout the

sampling events of a project. The types of blanks and their collection frequency should be stipulated in the QAPP. Generally, the blanks are collected once a day or one per twenty field investigative samples, by each sampling team, and may be matrix dependent.

Below are the common types of field blanks utilized in the collection of organic contaminants analyzed by GC.

Trip blanks are included for aqueous volatile analytes only. Volatile organic compounds detected in trip blanks indicate the possibility of contamination of site samples or cross-contamination between site samples due to sample handling and transport while in the cooler. A trip blank is usually included for every cooler that transports volatile samples.

An **ambient blank** is sample collected on site, without the need of equipment, filled directly into a sample container. Ambient blanks are included for volatile analysis only. Analytes detected in ambient blanks indicate the possibility of cross-contamination between the air matrix and the matrix being collected for testing.

An **equipment blank** (also called a **rinse or rinsate blank**) is an aliquot of reagent water subjected to all aspects of sample collection. Analytes detected in equipment blanks indicate the possibility of cross-contamination between samples due to improper equipment decontamination. Equipment blanks are usually collected at a frequency of one per twenty investigative samples, or as specified in the QAPP.

A **source blank** (also called a **reagent blank**) may be collected from each source of water used during each sampling event. This type of field blank may be analyzed to assess whether the chemical nature of the water used in decontamination may have affected the analytical results of site samples. A source blank is usually collected once per source prior to sample collection.

Evaluation of Field Blanks

Check that all coolers containing samples to be analyzed for volatile organic contaminants by GC contained a trip blank. If a cooler requiring a trip blank did not have an associated trip blank, no qualification of the samples transported in the cooler is necessary, but the incident should be discussed in the data validation report along with other required types of field blanks that were found missing. The point of contact (QAPP Worksheet #6) should be notified within the required time frame as required by the QAPP.

Determine which field blanks apply to samples in the sample delivery group (SDG) from the CoC. If the applicability of multiple field blanks cannot be determined, communicate with the point of contact (QAPP Worksheet #6) to inquire if applicability can be determined.

Note: SDGs can be called by different names such as SEDD Lab Reporting Batch, depending on the project.

Ensure that units are correct when applying field blank qualifications.

Note: it may not be appropriate to make a direct quantitative comparison for aqueous field blanks (such as equipment blanks reported as µg/mL) to a solid parent sample (such as a soil sample reported as mg/kg). At best, only a qualitative comparison can be made.

Generally, when multiple blank type contaminations are present, the evaluation should not involve a ‘hierarchy’ of one blank type over another. Each blank is evaluated separately and independently. The final validated result should be assessed on the blank with the highest value (i.e., greatest effect on sample analyte concentration).

The source blank water should be analyte free (undetected or as defined by QAPP) and provided with the sample bottle kit by the contracted laboratory performing the analysis. To ensure the origin of the water used, consult with the field sampling team leader via appropriate channels identified in the QAPP (such as UFP-QAPP Worksheet #6). If source blank water is used as equipment blank water and both are contaminated, the affected samples are qualified by either the source blank or equipment blank results, whichever has the higher contaminant concentration.

If analytes (as appropriate) are detected in the field blanks, the procedure for the qualification of associated sample results is summarized below.

Compare the results of each type of field blank with the associated sample results. The reviewer should note that the blank analyses may not involve the same units, volumes, or dilution factors as the associated samples. These factors should be taken into consideration when applying the 5X and 10X criteria discussed below, such that a comparison of the total amount of contamination is actually made. Care should be taken to factor in any dilution factors when doing comparisons between detects in the sample and the blank.

- If an analyte is detected in the field blank, but not in the associated samples, no action is taken.
- If field blank contamination includes those analytes listed in Table I as common lab contaminants, then 10X (in lieu of 5X) should be used to determine the qualification of the sample.
- If field blanks were not collected at the proper frequency required by the QAPP, then use professional judgment to qualify the data, and make note of this in the data validation report.
- If an analyte is detected in the field blank (at any concentration) and in the associated samples, the action taken depends on both the blank and sample concentrations (Table III).

Table II: Common Lab Contaminants

Methylene chloride
Acetone
2-Butanone (MEK)
Phthalate Esters
Toluene
Hexane
2-Propanol

Table III: Blank Qualifications

	Blank	Sample		
Row Number	**Result**	**Result**	**Validated Result**	**Validation Qualifier**
1	**≤ DL or LOD**	**≤ DL or LOD**	**Report as required by QAPP (at DL or LOD)**	**U**
2	**> DL or LOD**	**≤ DL or LOD**	**Report at DL or LOD**	**U**
3	**> DL or LOD**	**> DL or LOD but ≤ LOQ**	**Report at LOQ**	**U**
4	**> DL or LOD**	**> LOQ but ≤ 5x blank**	**Report at Sample Result**	**U**
5	**> DL or LOD**	**> LOQ and > 5x blank**	**Report at Sample Result**	**None**

LOD = Limit of Detection **LOQ** = Limit of Quantitation **DL** = Detection Limit
Note: The QAPP should specify reporting at either the DL, LOD or both

3.3.2 Field Duplicates (can also be called replicates)

Field duplicates consist of either collocated or subsampled (split) samples. Field duplicates for groundwater and surface water samples are generally considered to be collocated samples. Soil duplicate samples may be split samples or collocated, as specified in the QAPP. Field duplicate results are an indication of both field and laboratory precision; the results may be used to evaluate the consistency of sampling practices.

Evaluation of Field Duplicates

Check to ensure that field duplicates were collected and analyzed as specified in the QAPP. If the sampling frequency is less than the frequency stated in the QAPP, no qualification of the associated sample results is necessary, but the incident should be discussed in the data validation report.

Relative Percent Differences (RPDs) should be calculated when detected results are reported for the duplicate(s) and at least one of those results is greater than or equal to the LOQ. For field duplicate results, if the RPDs or absolute differences are greater than those stated in the QAPP, qualify the associated sample results as estimated **J,** and any non-conformities should be noted in the data validation summary.

Professional judgment may be required in instances where the sample and field duplicate results are less than the LOQ or project Reporting Limits (RLs). RPD results can be elevated when low (e.g., <5x the LOQ) or estimated concentrations in the samples and duplicates are reported. If one or both results in a duplicate pair are <5x the LOQ, the absolute difference

between the two results can be used as an alternative acceptance criterion, if approved by the QAPP or project point of contact (QAPP Worksheet #6).

Some sampling schemes, such as Incremental Sampling Methodology (ISM) require specific replicate calculations, which should be specified in the QAPP.

It should be noted that RPDs or absolute differences for field duplicates are generally not calculated or reported by the laboratory and should be calculated by the validator.

There are instances where an RPD is not calculable (for example, when one result is a non-detect and the other is greater than the LOQ). In those cases, the RPDs are not calculated but the non-conformity should be noted in the data validation report. The reported concentrations should be carefully examined to determine what conditions would permit one result to be reported at or above the LOQ/RL and the other to be reported below the LOQ/RL or as a non-detect.

4.0 Stage 2A Validation

Note: Stage 2A includes all of Stage 1

Stage 2A requires the review and qualification of the following summary documents.

- Surrogate Recovery Summary
- Laboratory Control Sample/Laboratory Control Sample Duplicate
- Matrix Spike/Matrix Spike Duplicate Recovery Summary
- Method Blank Summary Form
- Sample Dilution/Reanalysis Summaries

Stage 2A is the validation of preparation batch specific QC data in addition to any sample specific parameters included in Stage 1.

Generally, a “preparation batch” of samples consists of up to twenty field samples (maximum) along with duplicate/replicate (laboratory or field), method blank, and control/matrix type QC samples. They are meant to be analyzed together on a single instrument. However, laboratories may choose to split up a batch over multiple instruments to save time. In this case, if the use of multiple instruments is uncovered in a Stage 2A validation, the validator should request from their point of contact (QAPP Worksheet #6) a Stage 2B validation to review sequence logs. The use of multiple instrumentation should be noted in the data validation report.

4.1 Surrogate Spikes

Extraction efficiency on individual samples is established by means of surrogate spikes. All samples are spiked with surrogates prior to sample extraction. The evaluation of the results of these surrogate spikes is not necessarily straightforward. The sample itself may produce effects due to such factors as interference and high concentrations of analytes. Because the effects of the sample matrix are frequently outside the control of the laboratory and may present relatively unique problems, the review and validation of data based on specific sample results is frequently subjective and demands analytical experience and professional judgment.

Verify that surrogate percent recoveries and acceptance limits were reported for all field and batch QC samples.

Sample and batch QC surrogate recoveries should be within control limits established in the QAPP or the QSM. Verify that no samples or batch QC have surrogate percent recoveries outside their criteria.

If any surrogate recovery is out of specification, then a re-extraction (if applicable) and reanalysis should have been performed and reported. Re-extraction is not required for surrogates with high bias associated with non-detect sample results. The laboratory should have reported both runs if the first was unsuccessful.

The laboratory does not have to reanalyze a sample if a matrix spike/matrix spike duplicate (MS/MSD) was performed on the sample with out-of-control surrogate results showing the same matrix effects, as long as the batch QC display acceptable surrogate percent recoveries.

Evaluation of Surrogates

If surrogate percent recoveries are out of specification with no evidence of re-extraction (if applicable) and reanalysis, justification should be noted in the laboratory case narrative (e.g., limited sample volume prevented reanalysis). If justification is not noted, the point of contact (QAPP Worksheet #6) should be reached for further guidance.

If the surrogate percent recovery control criteria displayed in the deliverable are not the same ranges stipulated in the QAPP or the DoD QSM, reference the required control ranges for evaluation instead of the summarized ranges in the deliverable. The project team should be informed to implement changes to the current deliverables or those to be created in the future. Please follow the notification protocols outlined in the QAPP (such as the UFP-QAPP Worksheet #6).

GC Organic Contaminants

If any surrogate percent recovery is < 10%, qualify detects as estimated **J-**, and non-detects as **X,** exclusion of data recommended for all associated target analytes in the sample.

If any surrogate percent recovery is greater than the upper acceptance limit, qualify associated detects in the sample as estimated with a positive bias **J+** and non-detects should not be qualified.

If any surrogate percent recovery is less than the lower acceptance limit but ≥ 10%, qualify all associated detects as estimated with a negative bias **J-** and non-detects as estimated **UJ**.

For samples that require dilution, surrogates may be reported as "diluted out", if dilution is such that the surrogate can no longer be detected above the LOD. If this is the case, note in the data validation report that surrogate evaluation could not be performed due to a high dilution factor. A full evaluation (Stage 4 validation) of the sample chromatogram and quantitation report may be necessary to determine that surrogates are truly "diluted out."

In the special case of blank analysis with surrogates out of specification, the reviewer should give special consideration to the validity of associated sample data. The primary concern is whether the blank failures represent an isolated incident with the blank alone, or whether there is a systemic problem with the analytical process. For example, if the samples in the batch show acceptable surrogate recoveries, the reviewer may determine the blank failure to be an isolated occurrence for which no qualification of the data is required. However, if surrogate failures occur throughout the field and QC samples, then consideration should be given to communicate with the QAPP point of contact (QAPP Worksheet #6) to receive a

revised report. If this cannot be done, then consideration should be given to qualifying all associated data as **X**, exclusion of data recommended.

4.2 Laboratory Control Sample/Laboratory Control Sample Duplicate (LCS/LCSD)

An LCS is a sample matrix free from the analytes of interest, spiked with known amounts of the analytes and taken through all sample preparation, cleanup and analytical steps. LCSs establish the method precision and bias for a specific batch of samples. Analysis of LCSDs may be required by the QAPP or may be used as an indication of batch precision in instances where MSD analysis is not possible (e.g., a limited volume of sample).

LCS (sometimes called a "Blank Spike") and, if analyzed, LCSD recoveries should be within the QC limits specified in the QAPP or as listed in the QSM. If an LCSD was analyzed, the RPDs should be within the QC limits specified in the QAPP or as listed in the QSM.

Evaluation of LCS/LCSD

Verify that results (from appropriate summary form), percent recoveries, RPDs (if applicable) and acceptance limits were reported for all target analytes and surrogates.

If the LCS/LCSD was not spiked with all target analytes, notify the project team by following the notification protocols outlined in the QAPP (such as UFP-QAPP Worksheet #6) and qualify all detects and non-detects for those analytes not spiked as **X**, exclusion of data recommended.

If the spike percent recovery control criteria displayed in the deliverable are not the same range (i.e., outside or wider than) as those stipulated in the QAPP or the DoD QSM, reference the required control ranges for evaluation instead of the summarized ranges in the deliverable. The project team should be informed to implement changes to the current deliverables or those to be created in the future.

In-house control limits are acceptable for any analytes not specified in the QAPP or DoD QSM. No qualification is necessary for any reported in-house control limit that is within (i.e., same or less than) those specified in the QAPP or DoD QSM. If the laboratory's in-house control limits are wider than those in the QSM and the results are outside of the DoD QSM limits, qualify the appropriate data as **X,** exclusion of data recommended.

If the LCS percent recoveries were greater than the upper control limit, qualify detects for the analyte in associated samples as estimated with a positive bias **J+**. Non-detects should not be qualified.

If the LCS percent recoveries were less than the lower control limit, qualify detects for the analyte in associated samples as estimated with a negative bias **J-** and non-detects as **X**, exclusion of data recommended.

If the LCS/LCSD RPDs were greater than the acceptance limits, qualify detects for the analyte in the associated sample(s) as estimated **J**. Non-detects should not be qualified.

Professional judgment should be utilized in qualifying data for circumstances other than those listed above.

4.3 Matrix Spike/Matrix Spike Duplicate (MS/MSD)

MS/MSD data are used to determine the effect of the matrix on a method's recovery efficiency and precision for a specific sample matrix.

Generally, qualifying action is taken only on the parent sample based on MS/MSD non-conformities. In instances where it can be determined that the results of the MS/MSD affect only the sample spiked, then qualification should be limited to that sample alone. Using informed professional judgment, the data reviewer may use the MS/MSD results in conjunction with other QC criteria (i.e., surrogates and LCS) and determine the need for additional qualification beyond that applied to the parent sample when the laboratory is having a systemic problem in the analysis of one or more analytes, which affects all associated samples.

If a field blank was used for the MS/MSD, this fact should be included in the data validation report. Sample matrix effects may not be observed with field blanks; therefore, the recoveries and precision do not reflect the extraction or analytical impact of the site matrix.

The laboratory should spike and analyze an MS/MSD from the specific project site as required by the QAPP for each matrix type and analytical batch. The MS and MSD should be spiked per QSM requirements with all target analytes. If the parent sample for the MS/MSD was from another site or project (for example, not enough sample collected, or multiple site samples analyzed within a single batch), the reason should be documented in the data validation report, and sample results should not be qualified due to any non-conformities noted in non-site-specific matrices.

Evaluation of MS/MSD

MS/MSD data should be reported on a MS/MSD summary form (or equivalent). Verify that the MS/MSD were spiked with all target analytes, and that percent recoveries were reported for all target analytes.

Compare the percent recovery and RPD for each analyte with LCS control limits established by the QAPP. If the spike percent recovery control criteria displayed in the deliverable are not the same range (i.e., outside or wider than) as those or stipulated in the QAPP or the DoD QSM, reference the required control ranges for evaluation instead of the summarized ranges in the deliverable. The project team should be informed to implement changes to the current deliverables or those to be created in the future. Please follow the notification protocols outlined in the QAPP (such as UFP-QAPP Worksheet #6).

If the MS/MSD was not spiked with all target analytes, notify the project team by following the notification protocols and qualify all detects and non-detects in the parent sample for those analytes in each batch not spiked as **X**, exclusion of data recommended.

If the MS/ MSD percent recoveries were greater than the upper control limit, qualify detects for the analyte in the associated parent sample as estimated **J+**. Non-detects should not be qualified.

If the MS/MSD percent recoveries were less than the lower acceptance limit but ≥ 10%, qualify detects for the analyte in the associated parent sample as estimated **J-** and non-detects as estimated **UJ**. If the percent recoveries were < 10%, qualify detects for the analyte in the associated parent sample as estimated **J-** and non-detects as **X**, exclusion of data recommended.

If the MS/MSD RPDs were greater than the acceptance limits, qualify detects for the analyte in the associated sample(s) as **J**. Non-detects should not be qualified.

If the MS/MSD fail due to the presence of target analytes in the parent sample at > 4X the spike concentration or if matrix spikes are diluted to less than the LOQ, then MS non-

conformities should not result in any qualifications. Note the incident in the data validation report.

4.4 Method Blanks

A method blank is used to identify systemic contamination originating in the laboratory that may have a detrimental effect on project sample results. The validator should identify samples associated with each method blank using a method blank summary form (or equivalent). Verify that the method blank has been reported per batch.

Compare the results of each method blank with the associated sample results. The reviewer should note that the blank analyses may not involve the same weights, volumes, percent moistures, or dilution factors as the associated samples.

These factors should be taken into consideration when applying the 5X and 10X criteria (discussed in section 3.3.1), such that a comparison of the total amount of contamination is actually made. Care should be taken to factor in the percent moisture or dilution factor when doing comparisons between detects in the sample and the method blank. If available, raw data should be used for comparison and evaluation.

Evaluation of Method Blanks

If no method blank was analyzed, qualify detects in samples with no associated method blank **X,** exclusion of data recommended. Non-detects do not require qualification.

If gross contamination exists (defined as greater than a Project Action Limit) in the method blanks, all analytes affected should be qualified **X,** exclusion of data recommended. due to interference in all affected samples and this should be noted in the data validation report.

If target analytes other than common laboratory contaminants (see Table II) are found at low levels in the method blank(s), it may be indicative of a problem at the laboratory and should be noted in the data validation report.

If an analyte is detected in the method blank, but not in the associated samples, no action is taken.

If an analyte is detected in the method blank and in the associated samples, the action taken depends on both the blank and sample concentrations. Table III (Blank Qualifications) and section 3.3.1 discussions on evaluations of results from the DL/LOD to LOQ is also applicable to the method blank.

Additionally, there may be instances where little or no contamination was present in the associated method blanks, but qualification of the sample was deemed necessary. Contamination introduced through dilution water is one example. Although it is not always possible to determine instances of this occurring can be detected when contaminants are found in the diluted sample result but are absent in the undiluted sample result. It may be impossible to verify this source of contamination. However, if the reviewer determines that the contamination is from a source other than the sample, the data should be qualified. In this case, the 5X or 10X rule does not apply. The reason should be documented in the data validation report. Qualification of the data should be performed as given in Table III.

Multiple blank contaminations (such as a batch with field blanks and a method blank) does not establish a ‘hierarchy’ of one blank over another. Each blank must be evaluated individually. Blanks should not be qualified due to the results of other blanks.

4.5 Sample Dilutions and Reanalysis

Laboratories may dilute samples due to high analyte concentrations or reanalyze samples due to QC non-conformities, and document both sets of results. Generally, the laboratory will report the “best” value for a given analyte in the official laboratory report (or equivalent form). In these instances, the validator should evaluate both the reported and the initial analysis result. The validator should consider the application of appropriate qualifiers to the reported results within the scope of the project due to elevated LODs/LOQs or other QC non-conformities. Qualifiers apply only to the reported results in the official laboratory report.

Evaluation of Sample Dilutions and Reanalysis

When sample results are reported at more than one dilution due to analyte concentrations exceeding the calibration curve, the lowest LODs are generally used for the non-detects unless a QC criterion has been exceeded.

Results reported from dilutions leads to elevated LODs for non-detects. The data validation report should indicate the reason for all reported dilutions (including cases where the laboratory did not perform an undiluted analysis) resulting in elevated sensitivity limits for non-detected results.

When reanalysis has occurred due to QC non-conformities, the validator should ensure that the non-conformity was corrected during the reanalysis. If that is not the case, then the appropriate qualifier should be placed on the reported results.

In some cases, using professional judgment, the validator may determine that an alternate result was more appropriate than the one reported. In those cases, explain the rationale for accepting the alternate result in the data validation report.

In some cases, reanalysis may lead to exceedances of holding time. Use professional judgment to evaluate the results and apply the appropriate qualifiers (if required).

5.0 Stage 2B Validation

Note: Stage 2B includes all of Stage 1, and Stage 2A

Stage 2B requires the review and qualification of the following summary documents.

- Sequence and Preparation Logs (or equivalent)
- Instrument Performance Check Summary (any equivalent to include Degradation Checks)
- Initial Calibration Summary (any equivalent to include Initial Calibration, Average Response Factors, and Regression)
- Initial/Continuing Calibration Verification Summary (any equivalent to include Initial and Continuing Calibration Verifications)
- Internal Standard Summary (any equivalent to include Internal Standards)
- Cleanup Procedure Summary (any equivalent to include Cleanup Recovery Checks)
- Second Column Summary (or equivalent to show analysis by a Second Column)

Stage 2B is the validation of instrument specific QC data.

5.1 Sequence and Preparation Logs

Sequence logs are reviewed by the data validator to ensure all QC samples (both batch and instrument specific) were analyzed within a specific batch, in the correct order. Preparation

logs are reviewed by the data validator to ensure that samples had the proper extraction performed, within specified holding times. Non-conformities uncovered in the review of the logs may point the validator to specific samples that require further review. Non-conformities uncovered in preparation or sequence logs should be noted in the data validation report.

Sequence logs are helpful in identifying when multiple instrumentation is used to analyze a batch of samples. For example, it is not uncommon to analyze a single batch of twenty samples at the same time on two or more different instruments. At a minimum, each instrument should be calibrated independently. Batch QC should be reviewed on each instrument, as appropriate. Non-conformities involving the use of multiple instruments should be noted in the data validation report.

5.2 Instrument Performance Checks (Method 8081: Organochlorine Pesticides)

4,4′-Dichlorodiphenyltrichloroethane (DDT) and Endrin are prone to degradation in the injection port liner with the presence of high boiling residue from sample injection or when the injector contains metal fittings. Degradation problems are checked by injecting a standard containing only DDT and Endrin. Presence of DDE, DDD, Endrin Aldehyde, or Endrin Ketone indicates breakdown. Unless otherwise specified in an approved project plan, this test should be performed as a test of the inertness of the analytical system even when DDT and Endrin are not target analytes for a given project.

Evaluation of Performance Checks

The breakdown of DDT and Endrin should be measured before samples are analyzed at the beginning of each 12-hour shift. Professional judgment should be applied to qualify results for samples that were analyzed more than 12 hours after the breakdown standard was analyzed.

Verify that the degradation does not exceed 15% for either DDT or Endrin on both GC columns.

1. If DDT breakdown is > 15%:
    - Flag all associated detects for DDT, DDD, and DDE as **J**, estimated.
    - If DDT was not detected in the breakdown standard, then qualify all results for DDT as **X**, exclusion of data recommended. Qualify DDD and DDE detects as presumptively present at an estimated quantity **NJ**.
    - If DDT is present and passes on one column, but not confirmed on the other column that has > 15% breakdown, qualify the associated DDT data **X,** exclusion of data recommended. Qualify DDE and DDE detects as presumptively present at an estimated quantity **NJ**.
2. If Endrin breakdown is > 15%:
    - Flag all associated detects for Endrin, Endrin Aldehyde, and Endrin Ketone as **J**, estimated.
    - If Endrin was not detected, but Endrin Aldehyde or Endrin Ketone are detected in the breakdown standard, then qualify the Endrin result as **X**, exclusion of data recommended. Qualify Endrin Ketone or Endrin Aldehyde detects as presumptively present at an estimated quantity **NJ**.

- If Endrin is present on one column but not confirmed on the other column that has > 15% breakdown, qualify the associated data **X,** exclusion of data recommended. In this case, the reviewer may determine that the compound needs to be reported as a tentative identification **N**.

5.3 Initial Calibration

The objective of initial calibration is to ensure that the instrument is capable of producing acceptable qualitative and quantitative data. Initial calibration demonstrates that the instrument is capable of acceptable performance in the beginning of the analytical run and of producing an acceptable calibration curve. The GC system can be calibrated using the external standard technique or internal standard technique. Because of the difficulty in selecting suitable internal standards, the external standard technique will most often be the method of choice.

Evaluation of External Calibration

A minimum of five standards is required for a linear calibration. The lowest calibration standard concentration should be at or below the LOQ. If the laboratory used more than the minimum number of standards and must exclude calibration points, only exclusion of the high or low standard is allowed. The calibration points in between should not be excluded without sound technical justification.

If reported target analytes were not properly calibrated, make note of this in the data validation report and qualify the associated data as **X**, exclusion of data recommended.

If the concentration of the lowest standard in the initial calibration was greater than the LOQ, qualify all detects between the DL and the lowest standard as X, exclusion of data recommended. Detects above the low standard do not require qualification. Non-detects do not require qualification.

Inform the point of contact (QAPP Worksheet #6) for further instruction in those instances of unwarranted manipulation of calibration curves. As an example, calibration curves that were run with excessive calibration points that are misapplied to achieve passing criteria (without any technical justification) require prompt notification of the project team. If the issue cannot be resolved with the laboratory, make note of this in the data validation report and qualify all affected data as **X**, exclusion of data recommended.

Calibration Factor (CF): External standard calibration involves a comparison of instrument responses from the sample to the target compound responses in the calibration standards. The ratio of the detector response to the amount of analyte in the calibration standard is defined as the CF. The instrument should have been calibrated for all target analytes and surrogates.

Evaluate the percent relative standard deviation (%RSD) for all target compounds. If any analyte has a %RSD greater than 20%, qualify detects for the affected compounds as **J** and non-detects as **UJ** in the associated samples that correspond to that initial calibration.

If the %RSD is excessively high (defined as > 40%) qualify associated target analyte sample results as **X**, exclusion of data recommended.

Linear Regression: The laboratory may employ a linear or weighted linear least squares regression curve. Evaluate the Correlation Coefficients (r) for all applicable target analytes.

The r value should be ≥ 0.995. Some instrumentation reports Coefficient of Determination (r^2). If the instrument reports r^2, the value should be ≥ 0.99.

If the r value for any target analyte is < 0.995 (or the r^2 value is < 0.99), qualify detects for the affected analytes **J** and non-detects as **UJ** in the associated samples.

If the r value is excessively low (defined as < 0.95) or the r^2 value is excessively low (defined as < 0.90), qualify all associated non-detects as **X,** exclusion of data recommended and detects as estimated **J**.

Non-Linear Regression: The laboratory may also generate a higher order curve for the calibration. The calibration curve should not be more than second order (Quadratic) in accordance with QSM requirements.

A minimum of six standards is required for a second order (quadratic) curve.

Evaluate the correlation coefficients(r) for all applicable target analytes. The r value should be ≥ 0.995. Some instrumentation reports coefficient of determination (r^2). If the instrument reports r^2, the value should be ≥ 0.99.

If the required number of calibration standards was not used, qualify detects **J**. Apply professional judgment to qualify non-detects based on the concentrations of the standards used.

If the r value for any target analyte is < 0.995 (or the r^2 value is < 0.99), qualify detects for the affected analytes **J** and non-detects **UJ** in the associated samples.

If the r value is excessively low (defined as < 0.95) or the r^2 value is excessively low (defined as < 0.90), qualify all associated non-detects as **X,** exclusion of data recommended and detects as estimated **J**.

Calibration curves that are higher than second order (such as a third order polynomial fit) are not allowed in accordance with QSM requirements. Qualify **X,** exclusion of data recommended all associated data based on third order (or higher) calibration curves.

5.3.1 Method 8081: Organochlorine Pesticides & Method 8082: Polychlorinated Biphenyls (Aroclors)

For Organochlorine Pesticides with multicomponent analytes such as Toxaphene and Chlordane, quantitation must be performed using a five-point calibration, in accordance with QSM requirements. Results may not be quantitated using a single point calibration. If Toxaphene and Chlordane results are reported without a multipoint calibration, then inform the QAPP point of contact (QAPP Worksheet #6). If the situation cannot be resolved with a revised laboratory report, then qualify all associated detects as **X**, exclusion of data recommended and make note in the data validation report.

For PCB Aroclors, a multipoint calibration employing a mixture of Aroclors 1016 and 1260 at five different concentrations is sufficient to demonstrate detector linearity because it will usually include many of the peaks of some of the other Aroclors. Although the method may be used to demonstrate that a sample does not contain peaks for some of the other Aroclors, the qualitative identification of the Aroclor is subject to the professional judgment of the analyst after comparison to standard(s) of that respective Aroclor. If any Aroclor other than 1016 or 1260 is detected, the result must be quantified against a multipoint calibration for the specific Aroclor mixture of interest prior to reporting a quantitative result for that Aroclor.

If any Aroclor other than 1016 or 1260 is detected in the associated sample and is not quantified against a multipoint curve of the identified Aroclor, then inform the QAPP point of contact (QAPP Worksheet #6). If the situation cannot be resolved with a revised laboratory report, then qualify all associated detects as **X**, exclusion of data recommended and make note in the data validation report.

5.3.2 Method 8151: Chlorinated Herbicides

Herbicide samples undergo a hydrolysis step during extraction and may undergo a derivatization step. If the calibration standards have undergone these steps as well, then the calibration curve is directly comparable to the samples. However, if the calibration standards did not undergo these steps, then then calculation of concentration (quantitation of the results) should have included a correction of the molecular weight of the methyl ester versus the acid herbicide.

This calculation may require a Stage 3 validation to determine if the correction factor was applied appropriately. Inform the point of contact (QAPP Worksheet #6) if sufficient information cannot be obtained for a Stage 2B validation.

5.4 Initial (Secondary Source) and Continuing Calibration Verification

The initial calibration curve should be verified with a standard that has been purchased or prepared from an independent source each time initial calibration is performed. This standard is called the secondary source or Initial Calibration Verification (ICV). The ICV should contain all of the GC target analytes. Note that multiple ICVs may be analyzed to encompass all of the target analytes.

After the initial calibration has been verified with a second source, samples may be run continuously until the initial calibration fails. To verify this, a Continuing Calibration Verification (CCV) containing all GC target compounds should be analyzed before sample analysis, after every 10 field samples, and at the end of the analysis sequence. Continuing calibration checks satisfactory performance of the instrument on a day-to-day basis.

The CCVs for Pesticide multicomponent mixtures Toxaphene and Chlordane by method 8081 and Aroclors other than 1016/1260 by Method 8082 are only required before sample analysis.

Evaluating the ICV and CCV

Verify the ICV was analyzed following the initial calibration and contained all target analytes. Verify the CCVs have been run at the proper frequency. When a new initial calibration is performed, the ICV can serve as the first CCV if samples are being run afterwards. The CCVs after the first ICV are not required to be a second source.

The ICV percent difference (%D) or percent drift for each target analyte and surrogate should be ≤ 20%. The CCV %D for each target analyte should also be ≤ 20%.

If the ICV (second source) has not been performed successfully after an initial calibration or if samples have been analyzed prior to a valid ICV, qualify **X**, exclusion of data recommended all associated data. No samples should have been analyzed in accordance with QSM requirements.

If the CCV has not been analyzed (either continuing or end-of-run), qualify **X,** exclusion of data recommended all associated data. No samples should have been analyzed without a valid CCV.

Verify that the %Ds are within the acceptance criteria. If any target analytes do not meet the acceptance criteria for the CCV, qualify detects for that analyte as estimated **J+** when the %D is higher than acceptance criteria and **J-** when below acceptance criteria. Non-detects are qualified as **UJ** in all associated samples for %D outside of acceptance criteria.

For gross exceedances of %D (defined as > 50%) qualify all associated data as **X,** exclusion of data recommended.

5.5 Internal Standards (Optional)

Internal standard (IS) calibration involves comparison of instrument responses from the target compounds in the sample to responses of internal standards added to the sample or extract before injection. A constant amount of the IS is added to all samples extracts and calibration standards. The peak response ratio of the target compound to the IS in the sample extract is compared with the same ratio for each calibration standard. This ratio indicates that the target compound response is calculated relative to that of the IS.

Evaluation of Internal Standards

Each IS area should be within 50-200% (same as QSM criteria of -50 to +100) of the area of the mid-point standard in the ICAL for associated standards. On days when ICAL is not performed, the daily initial CCV is used.

The IS retention times for all field and QC samples should be within 30 seconds of the retention time of the midpoint standard in the ICAL, or on days when ICAL is not performed, the initial CCV is used.

Detects for analytes quantitated using an IS area count > 200% should be qualified estimated with a **J**. Non-detects should not be qualified.

Analytes quantitated using an IS area count < 50% but ≥ 20% should be qualified estimated with a **J** for detects. Non-detects should be qualified estimated **UJ**.

If extremely low area counts are reported (< 20% of the area for associated standards), detects and non-detects should be qualified **X,** exclusion of data recommended.

Large retention time variations may call into question peak identifications. If an IS retention time varies by more than 30 seconds, detects and non-detects should be qualified **X**, exclusion of data recommended.

5.6 Cleanup Procedures for Methods 8081 (Organochlorine Pesticides), 8082 (PCBs), 8141 (Ortho phosphorous Compounds), and 8151 (Chlorinated Herbicides)

Cleanup techniques are used to eliminate or minimize chemical and chromatographic interferences arising from the samples themselves. Most environmental or waste samples may require one or more cleanup techniques after extraction and prior to analysis. The specific cleanup performed will be dependent on the nature of the samples.

A summary of recommended cleanup procedures can be found in Table IV. SW-846 method 3600 provides more in-depth guidance on cleanup method selection.

All associated batch QC samples must undergo the same cleanup procedure(s) as the samples.

A description of the different cleanup approaches follows:

- Adsorption Chromatography - Florisil (Method 3620), and Silica Gel (Method 3630) are useful for separating analytes of a relatively narrow polarity range away from extraneous, interfering peaks of a different polarity. These are primarily used for cleanup of a specific chemical group of relatively non-polar analytes such as pesticides and PCBs.
- Gel Permeation Chromatography (GPC) (Method 3640) - This cleanup technique applies to a broad range of pesticides and is capable of separating high molecular-weight, high boiling point material from the target analytes. GPC may not be applicable to elimination of extraneous peaks on a chromatogram which interfere with the analytes of interest. It is, however, useful for the removal of high boiling point materials which would contaminate injection ports and improve continuing calibration.
- Acid-base Partitioning (Method 3650) – This technique is useful for separating acidic or basic organics from neutral organics. It has been applied to analytes such as the Chlorinated Herbicides.
- Sulfur cleanup (Method 3660) – This technique is useful in eliminating known sulfur from sample extracts, which may cause chromatographic interference with analytes of interest.
- Sulfuric Acid/Permanganate Cleanup (Method 3665) – This technique improves elevated baselines for PCB sample extracts prior to analysis. This method cannot be used to cleanup extracts for other target analytes, as it will destroy most organic chemicals, including the pesticides.

Table IV: Cleanup Methods

Analyte Group	Analytical Method	Cleanup Methods
Organochlorine Pesticides	8081	3620, 3640, 3660
PCBs	8082	3620, 3630, 3665
Organophosphorus Pesticides	8141	3620
Chlorinated Herbicides	8151	3620, 3650

Evaluation of Cleanup Methods (Recovery Checks)

The analyst must demonstrate that the compounds of interest are quantitatively recovered before applying this method to actual samples. This test applies to both the column cleanup and cartridge cleanup procedures. A recovery check needs to be performed using standards of the target analytes at a known concentration near the LOQ for the target analyte. Only lots of cartridges/columns from which the spiked analytes are quantitatively recovered may be used to process the samples.

When using Florisil (3620) for pesticides, the lot of Florisil cartridges is acceptable if all pesticides are recovered at 80 to 110%, the recovery of Trichlorophenol is < 5%, and no peaks interfere with the target analytes. For Chlorophenoxy acid herbicides, the lot of Florisil is acceptable if the target analytes are quantitatively recovered, the recovery of trichlorophenol is < 5%, and no peaks interfere with the target analytes.

For Silica Gel (3630) the recovery of all analytes in the recovery check must be between 85-115%.

The GPC (3640) should be calibrated at least once per week. The retention time shift must be < 5% when compared to retention times in the last calibration UV trace. The UV trace requirements are as follows: corn oil and Phthalate peaks must exhibit > 85% resolution; Phthalate and Methoxychlor peaks must exhibit > 85% resolution; Methoxychlor and Perylene peaks must exhibit > 85% resolution; Perylene and Sulfur peaks must not be saturated and must exhibit > 90% baseline resolution. GPC elution should continue until after Perylene has eluted, or long enough to recover at least 85% of the analytes, whichever time is longer.

Acid-base Partition (3650), Sulfur Cleanup (3660), and Sulfuric acid/Permanganate (3665) requires only that the batch QC pass the QC limits outlined in the QAPP or the laboratory Standard Operating Procedure (SOP).

If it is determined that the QC samples were not treated with the same cleanup procedures as the field samples, inform the point of contact (QAPP Worksheet #6) to receive a revised laboratory report. If this is not possible, qualify all associated data as, exclusion of data recommended and make note of this in the data validation report.

If the recovery check standard fails high, qualify detects **J+** and no qualification is necessary for non-detects.

If the recovery check standard fails low, qualify associated positive field sample results as estimated **J** and non-detects as estimated **UJ**.

If the recovery standard fails unusually low (defined as < 10%), qualify positive field sample results as estimated **J** and non-detects as **X**, exclusion of data recommended.

If there is recovery for negative test analytes (Trichlorophenol > 5%) or peak resolution is less than required, inspect the field sample chromatograms and use professional judgment to qualify associated results.

5.7 Second Column Confirmation/Dissimilar Detector Confirmation

Second column confirmation of all detects above the QAPP stated DL must be performed for all GC work, unless an alternate detector was utilized for confirmation. The only exceptions are for single column methods such as Total Petroleum Hydrocarbon (TPH) by Method 8015 where confirmation is not required. For the purposes of reporting, both columns are considered equivalent, provided QC evaluations are within acceptance limits on both columns. Barring chromatographic problems (overlapping peaks, baseline shifts) or QC anomalies on one column or the other, the result from the column specified in the QAPP should be reported. Some projects may require the reporting of results from both columns.

Evaluation of Second Column Confirmation

The RPD between columns should be ≤ 40%. The concentrations of both analytical column peaks must be greater than the stated DL. If one column has a peak that corresponds to a concentration that is less than the associated DL, then the result must be reported as a non-detect, and the RPD is noted in the data validation report as “non-calculable”.

If the RPD between columns is > 40%, qualify the results as estimated **J.**

If second column confirmation is not performed, qualify any reported detect as presumptive and estimated, **NJ**. The validator should inform the QAPP point of contact (QAPP Worksheet #6) to obtain a revised laboratory report, if possible.

6.0 Stage 3 Validation

Note: Stage 3 validation includes all of Stage 1, Stage 2A and Stage 2B

Stage 3 requires the review of the following documents

- Raw Data (including any laboratory forms, instrument outputs, spreadsheets, or handwritten calculations necessary for recalculation and re-quantification)
- Standards Traceability forms and worksheets
- DL studies (optional)

Stage 3 validation includes the recalculation and re-quantification of selected samples, and method and instrument QC. The types of results that should be recalculated and re-quantified include target analytes, analytes with detects above the LOQ, second column results, and field QC samples (blanks and duplicates). For method QC results, spiked recoveries and method blanks should be considered. For instrument QC, calibrations (including CFs and regressions), calibration verifications, and internal standards should be recalculated and re-quantified. Some calculations may include the need to review standards preparation and serial dilutions.

6.1 Samples and Field QC

When choosing samples, field QC and analytes for re-quantification and recalculation, consideration should be given to the laboratory’s batching scheme to ensure a representative subsample of recalculations is performed. Additionally, if priority contaminants or contaminants of concern are identified in the QAPP, those analytes should be selected for re-quantification and recalculation. Other circumstances that should be prioritized for re-quantification and recalculation are diluted samples, manual integrations, re-runs of samples, and field QC blank failures.

Re-quantification and recalculation should be performed on the designated percentage of the samples per SDG (or however defined in the QAPP, such as percentage of total project samples) per analytical suite. As a minimum, it is recommended that 10% of the data should be re-quantified and recalculated unless specific instructions are given in the QAPP.

Sample recalculations should include the raw instrument result, re-quantified from the instrument response against the calibration function, and the final reported sample result, including any dilution, preparation factor, or percent moisture (if applicable). The equations in Appendix B can be used to calculate a sample result from the corresponding reported calibration or regression function, as appropriate.

Verify that one or more of the laboratory’s RLs (such as LOQ) are calculated correctly for the non-detects and reported accordingly. If a DL study was identified by the QAPP, recalculate one or more analyte DLs.

Re-quantitate all detected target analytes in the 10% sample data chosen. For some samples, all results may be non-detects, therefore recalculation would not be necessary. Verify that sample-specific results have been adjusted correctly to reflect percent solids, original sample mass/volume, and any applicable dilutions.

Re-quantitate all detects found in the field QC blanks (such as trip blanks, source blanks, or equipment blanks). Field QC sample replicate calculations should include re-quantification of the same detected sample/replicate sets and determination of RPD or RSD.

When recalculations require rounding of data, that rounding should be completed only once at the end of all calculations to minimize rounding errors. Calculations should be rounded to the significant figures of the underlying criteria. For example, an LCS criteria of 80-117% would still be considered acceptable if the recalculation was 117.4%.

Evaluation of Sample and field QC recalculations

If the laboratory's quantitation, or RLs (however defined) are calculated incorrectly, then continue to recalculate limits until it is determined whether the problem is systemic (such as incorrect equations used) or isolated (such as a transcription or rounding errors).

For systemic (defined as widespread and major in nature) issues that cannot be corrected through a revised laboratory report, qualify all results as **X**, exclusion of data recommended.

For isolated cases, use professional judgment. It may be necessary to engage the point of contact (QAPP Worksheet #6) to communicate with the laboratory, so they can provide revised (corrected) results. In all cases, if calculation errors affect project target analytes, the point of contact (QAPP Worksheet #6) should be notified, and all affected results noted in the data validation report, including listing the calculation errors.

6.2 Method QC

Re-quantification of batch QC sample results should use raw instrument response in tandem with the reported CF and regressions, the preparation information, and percent moisture for solid samples to recreate the reported result.

Verify the concentrations of surrogates from the raw data. Verify that the surrogate result and percent recovery were calculated and reported correctly by recalculating all surrogates in the 10% of chosen sample data and method QC that were originally selected.

To check that the spike percent recovery was calculated and reported correctly, using the equation in Appendix B, re-quantitate and then recalculate all contaminants of concern as outlined in the UFP-QAPP Worksheet #12 or #15. Use a random 10% of the analytes in the LCS/LCSD if contaminants of concern (target analytes) have not been specifically identified. Recalculate RPDs (if applicable) from LCS/LCSD pairs that would result in the qualification of a sample.

Re-quantitate 10% of the contaminants of concern as listed in the UFP-QAPP Worksheet #12 or #15 for both the MS and the MSD. Use a random 10% of the analytes in the MS and MSD if contaminates of concern have not been identified. The RPDs of the recalculated MS/MSD pairs should be calculated from the MS/MSD concentrations, not from the recoveries.

Method Blank (MB) analytical results are assessed to determine the existence and magnitude of contamination problems associated with sample extraction and analysis. If problems with any method blank exist, all associated data should be carefully evaluated to determine whether there is any bias associated with the data, or if the problem is an isolated occurrence not affecting other data. Results may not be corrected by subtracting any blank values.

Re-quantitate one or more detects found in the method blank (if applicable) per each batch of samples.

Evaluation of all Surrogate Spike, LCS, MS, and MB Recalculations

If transcription errors (or other minor issues such as rounding errors) are found in method QC results, use professional judgment to qualify the data. It may be necessary to engage the point of contact (QAPP Worksheet #6) to communicate with the laboratory, so they can provide revised (corrected) results. In all cases, if method QC calculation errors affect project target analytes, the point of contact (QAPP Worksheet #6) should be notified, and all affected results noted in the data validation report, including listing the calculation errors.

For systemic (defined as widespread and major in nature) problems with LCS/LCSD, method blanks, surrogate spikes, or MS/MSD calculations that cannot be corrected by the laboratory in a revised report, qualify all affected analytes in associated samples as **X**, exclusion of data recommended.

6.3 Instrument QC

6.3.1 Instrument Performance Checks

Verify by recalculation at least one of the reported DDT or Endrin breakdown degradation checks per SDG were calculated correctly, if Method 8081 was required by the QAPP.

6.3.2 Initial (Calibration Factors and Regressions) and Continuing Calibration Verifications

Initial calibration (ICAL) recalculations should use the raw instrument response for the target analytes and associated internal standards (if used) to recreate the calibration curve from the individual calibration standards. If multiple types of calibration curves are employed in an analytical suite, then one analyte per curve type should be recalculated.

Re-quantitate and recalculate the individual and average CFs, %RSDs, and regression function (if used) and r values reported for at least 10% of the target analytes per each IS, (preferably analytes of concern which were identified in the QAPP), per initial calibration curve type.

Re-quantitate and recalculate the ICV and CCV CF result and %D for at least 10% of the target analytes, proportionally selecting analytes based on each calibration curve type.

The laboratory may employ a linear or weighted linear least squares regression. The low standard should be recalculated using the calibration curve and evaluated. CFs should not be evaluated for analytes with linear or higher order regression curves. Recalculation of the low calibration standard is not required for higher order (Quadratic) calibration curves.

The analyte quantitation should be evaluated for all detects by evaluating the raw data (for example by visual inspection of chromatograms). The analyte quantitation should be based on the CF (%RSD) or regression function from the appropriate ICAL.

Verify all internal standards (if used) reported from the raw data for at least one sample per batch of samples and verify IS areas for samples that were qualified due to out-of-control IS areas.

For methods 8081 and 8082, re-quantitate and recalculate at least one multicomponent analyte (Toxaphene, Chlordane, or Aroclor) per SDG ensuring that a multipoint calibration was used for each.

For Method 8151, re-quantitate and recalculate at least 10% of the target analytes. Determine if the hydrolysis/derivatization steps were included in the calibration standards. If not, verify the quantitation included a molecular weight correction factor.

Evaluation of Instrument Performance Checks, ICAL, CF, Regressions, ICV/CCV, and IS Recalculations

If degradation breakdown checks are calculated incorrectly, use professional judgment to qualify the data based on the actual correct calculations. The QSM states that no data should have been collected without DDT and Endrin breakdown of ≤ 15%.

If the files provided do not match the quantitation report, the CFs reported are likely to be from another initial calibration and the laboratory report should be revised. The point of contact (UFP-QAPP Worksheet #6) should be reached to get a revised (corrected) report from the laboratory. For calculation errors for CFs or any other regression equations that cannot be corrected in a revised report, qualify all the data as **X,** exclusion of data recommended.

The reprocessed low standard of a regression curve should be within 30% of the true value. If the recalculated concentration is not within 30% of the true value, qualify detects (at the LOQ and above) for the affected analytes **J** and non-detects **UJ** in the associated samples.

Qualify all associated data as **X,** exclusion of data recommended if the corresponding ICV/CCV %D has been calculated incorrectly by the laboratory and cannot be corrected in a revised laboratory report.

If the issue cannot be corrected in a revised laboratory report, qualify all data as **X,** exclusion of data recommended when the corresponding IS (if used) has been calculated incorrectly by the laboratory or when more than one IS was used and the analyte has been assigned to the wrong IS.

For multicomponent analytes such as Aroclors, Toxaphene, and Chlordane with detects that were calculated with single point calibrations, if a multipoint curve cannot be obtained with a revised laboratory report, then qualify all associated detects as **X**, exclusion of data recommended and make note in the data validation report.

For Chlorinated Herbicides that were quantitated without the proper correction factor (if applicable) and cannot be corrected with a revised laboratory report, then qualify all associated detects as **X**, exclusion of data recommended and make note in the data validation report.

All instrument QC must be analyzed on both the primary and any secondary columns, such as the Instrument Performance Checks, ICAL, ICV/CCVs, and sample specific QC analyses such as surrogates. Consideration should be given to recalculating and re-quantifying target analyte detects on both the primary and secondary columns, to include the instrument QC of both as a minimum.

In all cases where instrument QC are calculated incorrectly, the UFP-QAPP point of contact (QAPP Worksheet #6) should be notified and noted in the data validation report.

6.3.3 Cleanup Recovery Checks

For samples that require a cleanup step, verify at least one recovery check per cleanup method has been calculated correctly. For some cleanup methods this may require review of the laboratory SOP. For samples with negative test analyte (Trichlorophenol < 5%) verify the absence of the analyte.

In all cases where cleanup recovery checks were not performed or calculated incorrectly, notify the UFP-QAPP point of contact (QAPP Worksheet #6) and make note in the data validation report. Use professional judgment to evaluate the effects on the associated samples and qualify accordingly.

6.3.4 Second Column Confirmation

Recalculate the RPD between at least one positive detect and the second column confirmation per each SDG if detects were found.

If the RPD was calculated incorrectly, notify the UFP-QAPP point of contact (QAPP Worksheet #6) and make note in the data validation report. Use professional judgment to evaluate the effects on the associated samples and qualify accordingly.

6.4 Standards Traceability

Evaluate the calibration standards used for the analytes of concern. From the Certificate of Analysis (however named), verify that the "true values" of each analyte of concern were correctly applied to create the calibration curve, and that all analytes of concern were in the calibration mix.

All initial instrument calibrations should be verified with a standard obtained from a second manufacturer prior to analyzing any samples. From the standard Certificate of Analysis verify that a second source was used for the ICV. The use of a standard from a second lot obtained from the same manufacturer (independently prepared from different source materials) is acceptable for use as a second source standard.

Check that the stock standards were diluted properly into working standards by recalculating the dilutions of one or more calibration standards. Recalculate one or more surrogate dilutions. Recalculate one or more method QC sample dilutions (such as LCS or MS/MSD) from the stock to the working standard.

Note: It is not the role of the data validator to evaluate the Certificate of Analysis for compliance with the *ISO-17034 Standard*, but to verify that stock and working standards were correctly applied in the creation of calibration curves.

Evaluation of Standards

Professional judgment should be used when evaluating errors in standards preparation. For minor issues, the point of contact (QAPP Worksheet #6) identified in the QAPP (UFP-QAPP Worksheet #6) should be reached to get a revised (corrected) report from the laboratory. Issues that do not affect the results of any target analytes should be noted in the data validation report.

For systemic (widespread) issues that cannot be corrected by the laboratory, or issues that affect the results of target analytes, the data should be qualified as **X**, exclusion of data recommended.

For ICV standards that were not verified to be from a second source, qualify **X,** exclusion of data recommended all affected data. No samples should have been run without a valid second source standard (per QSM requirements).

Per QSM requirements, a laboratory cannot use a standard beyond its expiration date. All associated data should be qualified as **X,** exclusion of data recommended if expired

standards were used. The expiration date of any working standard is based on the expiration date of the primary or stock standard.

6.5 Detection/Quantitation Limit Studies (Optional)

In some cases, a QAPP may specify the review and validation of a detection/quantitation limit study. This could include studies such as Detection Limit (DL) studies (for instance MDL), quarterly LOD verification, or LOQ verifications. The QAPP should specify the criteria for evaluating the study. As a minimum, at least 10% of the raw data in the study should be recalculated.

Evaluation of Detection Limit Studies

The criteria for evaluating a detection/quantitation limit study should be listed in the QAPP. The following guidance should be enacted if the QAPP does not specify the evaluation criteria.

If transcription errors (or other minor issues such as rounding errors) are found in detection/quantitation limit studies, use professional judgment to qualify the data. It may be necessary to engage the point of contact (QAPP Worksheet #6) as identified in the QAPP to communicate with the laboratory, so they can provide revised (corrected) results. In all cases, if calculation errors affect project detection or quantitation limits, the point of contact (QAPP Worksheet #6) should be notified, and all affected results noted in the data validation report, including listing the calculation errors.

When calculation errors are uncovered that cannot be corrected by the laboratory and that affect detection/quantitation results, consideration should be given to qualify the affected data as **X,** exclusion of data recommended. Points to consider are whether effects are limited to data below the LOQ or extend to data above the LOQ and whether calculation errors are limited to the detection limit study or if other calculation errors may be present.

7.0 Stage 4 Validation

Stage 4 requires the review of the following documents

Note: Stage 4 validation includes all of Stage 1, Stage 2A, Stage 2B and Stage 3

Raw Data (including any instrument outputs, spectra, or chromatograms)

Stage 4 is a qualitative review of all sample results from instrument outputs. Chromatograms are checked for peak integration (10% of automated integration and 100% of manual integrations), baseline, and interferences; chromatographic spectra are checked for minimum signal to noise; retention times or relative retention times (RRTs) are checked to ensure they are within method requirements for analyte identification. Raw data quantitation reports and chromatograms are required to perform review of the instrument outputs.

7.1 Target Compound Identification

The objective of the criteria for GC qualitative analysis is to minimize the number of erroneous identifications of target compounds. An erroneous identification can either be false positive (reporting a compound present when it is not) or a false negative (not reporting a compound that is present).

The identification criteria can be applied more easily in detecting false positives than false negatives. More information is available for false positives because of the requirement for submittal of data supporting positive identifications. Negatives, or non-detects, on the other hand represent an absence of data and are therefore more difficult to assess.

Target analyte detections should display a signal to noise of 3:1, have proper peak integration and have a stable baseline.

For internal standard calibration, Relative Retention Times (RRTs) should be within ± 0.06 RRT units of the midpoint standard of the ICAL curve or, on days when ICAL is not performed, the initial CCV. When not employing internal standard calibration, the Retention Time window width is determined at method set-up and is ± 3 times the standard deviation for each analyte RT from the 72-hour study or equal to 0.03 minutes, whichever is greater. The midpoint position is set using the midpoint standard of the ICAL curve or, on days when ICAL is not performed, the initial CCV.

Check a minimum of 10% of the reported target analyte detects for RRT or RT. RRT or RT performance in samples with only non-detects can be evaluated by reviewing the surrogate retention times. Both primary and secondary columns should be reviewed for target compound identification of target analyte detects.

Evaluation of Target Compound Identification

The application of qualitative criteria for GC analysis of target analytes requires professional judgment. It is up to the reviewer's discretion to obtain additional information from their point of contact (QAPP Worksheet #6) identified in the QAPP, if qualitative identification problems are uncovered. The point of contact (QAPP Worksheet #6) should arrange with the laboratory to obtain a revised (corrected) laboratory report. All qualitative identification problems should be discussed in the data validation report. If it is determined that incorrect identifications were made, or if a confirmed positive detect was made on one column but not found on the dissimilar column (without baseline or interference issues) and the laboratory cannot correct the problem, then all affected data should be qualified as **X**, exclusion of data recommended.

In all other cases it is understood that evaluation of the confirmation results can be subjective, and qualification requires professional judgment when the results do not meet the criteria.

Evaluate the chromatogram for signal to noise requirement for positive detections (3:1). Positive results require this minimum response above baseline. Verify that positive results are based on concentrations greater than the QAPP provided DL on both analytical columns from peaks that elute within their established retention times. Professional judgment should determine if reported results are usable.

Professional judgment should also be used to qualify the data if it is determined that cross-contamination has occurred, or if interferences found in one column conflicts with the result of the secondary column. Any changes made to the reported analytes or concerns regarding target analyte identifications should be clearly indicated in the data validation report.

If the spectra for a detected target analyte is considered invalid (such as interference or baseline issues), confer with the point of contact (QAPP Worksheet #6) identified in the QAPP to consider changing the reported detect to a non-detect for the affected analyte.

7.2 Retention Time Windows

Retention Time Windows (RTWs) are critical to GC systems, and can have a direct impact on compound identification. RTWs are established to compensate for minor shifts in absolute retention times as a result of variability in sample injections, gas flows, or normal chromatographic variability. The width of the RTW is carefully established to minimize the occurrence of both false positive and false negative results and improve reproducibility. RTWs are required to be established for both primary and secondary columns.

RTW width is required to be determined at method setup and after major maintenance. RTWs are established by analyzing a minimum of three standards over a 72- hour period and calculating the standard deviation (± 3 SD). As an alternative, the laboratory can establish a 0.03-minute retention time width, whichever is greater. RTW position is established once per initial calibration and at the beginning of each analytical sequence. Position should be set using the midpoint standard of the Initial Calibration curve when an Initial Calibration is performed. On days when the Initial Calibration is not performed, the retention times displayed in the initial CCV are used to set the position.

Multicomponent analytes such as Technical Chlordane, Toxaphene, Strobane, Aroclors and Fuels are distinguished based on the ranges of retention times for characteristic components. Separate calibration standards are necessary for each multi-component target analyte like Toxaphene. Typically, an alkane standard containing a homologous series of n-alkanes is used for establishing retention times for fuels like diesel. When the whole response (including the hump-o-gram) is used for quantitation, appropriate RTWs are established for the boiling point range or carbon number range used to define each multicomponent analyte. According to 8015, two specific gasoline components are used to establish the GRO range (2-methylpentane and 1,2,4-trimethylbenzene) or the DRO range (C10 and C 28 alkanes). Refer to the method or the QAPP for specific requirements. Retention time windows are established similarly as described above for the two components that bracket the multi-component analyte. The retention time range is then calculated based on the lower limit of the RTW for the first eluting component and the upper limit of the RTW for the last eluting component. When three to five unique peaks are used in the identification of Technical Chlordane, Toxaphene, Strobane, and/or Aroclors, these individual quantitation peaks shall have established RTWs as described above.

Evaluation of Retention Time Windows

Verify from the raw data that the RTWs were established and are calculated correctly. The CCV can be used to verify RTWs, and at least two analytes per calibration curve should be recalculated (if a standard deviation was used) to verify a correct window width and placement. If deviations are discovered, the laboratory should be contacted to correct and re-produce the report.

Verify that all reported analytes and surrogates are within their established RTWs for both the primary and secondary column. If positive results (detects) were reported from peaks outside of the established RTW, contact the laboratory to evaluate for false positives and re-issue a revised report.

Retention times of the peaks for detects must fall within the calculated window for both chromatographic columns, and the pattern of the peaks should match the pattern in the CCVs on both columns for multicomponent analytes. If the peaks fall outside of the RTW on

either analytical column, then the result must be reported as a non-detect, unless a known baseline shift has occurred.

When laboratory reports cannot be revised to correct retention time issues, use professional judgment to qualify the data. Since retention time is critical for analyte identification, strong consideration should be given to qualifying the data as **X**, exclusion of data recommended. Other qualifications should be explained within the data validation report. The RPD between the primary and secondary column and the chromatograms should be evaluated to determine if interference is indicated. Consideration should also be given to the magnitude of the detects on both columns (such as results less than the LOQ) and baseline shifts and interferences due to target or non-target analytes present in the sample when qualifying the data.

7.3 Manual Integrations

For Stage 4, the reviewer should examine and verify the validity of all manual integrations.

Performing improper manual integrations, including peak shaving, peak enhancing, or baseline manipulation to meet QC criteria or to avoid corrective actions is unwarranted manipulation and misrepresents the data. All manual integrations should be reviewed by the data validator. When manual integrations are performed, raw data records should include a complete audit trail for those manipulations (i.e., the chromatograms obtained before and after the manual integration should be retained to permit reconstruction of the results). This requirement applies to all analytical runs including calibration standards and QC samples. The person performing the manual integration should sign and date each manually integrated chromatogram and record the rationale for performing manual integration (electronic signature is acceptable). Any manual integration should be fully discussed in the case narrative, including the cause and justification.

Evaluation of Manual Integrations

Some level of manual integrations is considered necessary for the normal operation of chromatographic systems. Instances of properly integrated peaks do not require qualification but should be noted in the validation report. However, excessive manual integrations may show a lack of routine maintenance by the laboratory, a rush to complete samples, or the results of analyzing excessively ‘dirty’ samples. Excessive manual integrations may also be the result of faulty software peak/baseline integration.

The data validator should use professional judgment in the review of manual integrations. All instances of manual integrations should be noted in the data validation report. Instances of incomplete information for manual integrations (such as failure to provide justification) should be reported to the point of contact (QAPP Worksheet #6) to obtain a revised (corrected) laboratory report. Instances of excessive manual integrations that cannot be corrected by the laboratory (such as ‘dirty’ samples that cannot undergo further cleanup procedures) should be qualified as **X,** exclusion of data recommended.

If, in the professional judgment of the validator, there are instances of unwarranted manipulation of data (such as multiple manual integrations used to ‘pass’ QC criteria) then those cases should be reported to the project team as soon as practical (UFP-QAPP Worksheet #6).

Appendix A: Method QC Tables

Note: The following Table is based on the QSM Standard, with the Methods associated with 8000D for comparison. The Table does not include all the QC elements from the methods or as listed in this guidance document.

QC Check	QSM Ver. 5.3 Frequency & Acceptance Criteria	8000D Methods Frequency & Acceptance Criteria
Breakdown Check (Method 8081)	Before sample analysis and at the beginning of each 12-hour shift. Degradation of DDT and Endrin must be ≤ 15%.	Before sample analysis and at the beginning of each 12-hour shift. Degradation of DDT and Endrin must be ≤ 15%. Presence of 4,4'-DDE, 4,4'-DDD, or Endrin Ketone indicates breakdown.
Initial Calibration (ICAL)	For all analytes and surrogates At instrument set-up and after ICV or CCV failure, prior to sample analysis. **Each analyte should meet one of the options below:** **Option 1:** RSD for each analyte ≤ 20%; **Option 2:** linear least squares regression for each analyte: $r^2 \geq 0.99$; **Option 3:** non-linear least squares regression (quadratic) for each analyte: $r^2 \geq 0.99$. Minimum 5 levels for linear and 6 levels for quadratic. Quantitation for multipoint analytes such as Chlordane, Toxaphene, and Aroclors must be performed using a 5-point calibration.	At instrument set-up and after ICV or CCV failure, prior to sample analysis. **Each analyte should meet one of the options below:** **Option 1:** RSD for each analyte ≤ 20%; **Option 2:** linear least squares regression for each analyte: $r^2 \geq 0.990$ or $r \geq 0.995$; **Option 3:** non-linear least squares regression (quadratic) for each analyte: $r^2 \geq 0.99$ or $r \geq 0.995$; **Option 4:** Relative Standard Error (RSE) ≤ 20%. Minimum 5 levels for linear and 6 levels for quadratic. Single point calibration for multicomponent analytes.

QC Check	QSM Ver. 5.3 Frequency & Acceptance Criteria	8000D Methods Frequency & Acceptance Criteria
Retention Time Window Width Establishment	Once per ICAL, and at the beginning of the analytical sequence. Position shall be set using the midpoint standard of the ICAL curve when the ICAL is performed. Use initial CCV when ICAL not performed.	Once per ICAL, and at the beginning of the analytical sequence. Position shall be set using the midpoint standard of the ICAL curve when the ICAL is performed. Use initial CCV when ICAL not performed.
Retention Time (RT) Window Width	Method setup and after major maintenance RT width is ± 3 times standard deviation from 72-hour study or 0.03 minutes, whichever is greater.	Method setup and after major maintenance RT width is ± 3 times standard deviation from 72-hour study or 0.03 minutes, whichever is greater.
Initial Calibration Verification (ICV)	Once after each ICAL, analysis of a second source standard prior to sample analysis. All reported analytes within ± 20% of true value.	Once after each ICAL, analysis of a second source standard prior to sample analysis. All reported analytes within ± 20% of true value.
Continuing Calibration Verification (CCV)	Before sample analysis; after every 10 field samples; and at the end of the analytical batch run. Exception: Multicomponent analytes Toxaphene, Chlordane, Aroclors (other than 1016 and 1260) are only required before sample analysis. All reported analytes and surrogates within ± 20% of true value for opening CCV.	After every 10 field samples; more frequent verification of calibration (i.e., after every 10 samples) may be necessary for some types of detectors. Multicomponent analytes are only required before sample analysis. If ≤ 10% of the analytes exceed the calibration verification criteria, then the initial calibration may still be used, but any detected analytes exceeding the limit must be reported as estimated. All reported analytes and surrogates within ± 20% of true value for CCV.

QC Check	QSM Ver. 5.3 Frequency & Acceptance Criteria	8000D Methods Frequency & Acceptance Criteria
Internal Standards (if used)	Every field sample, standard, and QC sample. Retention time within ± 30 seconds from retention time of the midpoint standard in the ICAL; EICP area within - 50% to +100% of ICAL midpoint standard.	Every field sample, standard, and QC sample. Retention time within ± 30 seconds from retention time of the midpoint standard in the ICAL; EICP area within - 50% to +100% of ICAL midpoint standard. RRT range of each analyte within 0.80-1.20 units.
Method Blank (MB)	One per preparatory batch. No analytes detected > ½ LOQ or > 1/10 the amount measured in any sample or 1/10 the regulatory limit, whichever is greater.	Method blanks should be prepared at a frequency of at least 5%: one method blank for each group of up to 20 samples prepared at the same time. Results of the method blank should be less than the lower limit of quantitation (LLOQ) for the analyte or less than the level of acceptable blank contamination specified in the approved QAPP.
Laboratory Control Sample (LCS); **Matrix Spike (MS); Matrix Spike Duplicate (MSD)** **Relative percent difference (RPD)**	One each per preparatory batch. A laboratory should use the QSM Appendix C Limits for batch control and matrix spikes if project limits are not specified. If the analyte(s) are not listed, use in-house LCS limits if project limits are not specified. MSD or MD: RPD of all analytes ≤ 20% (between MS and MSD or sample and MD).	Should contain all of the target analytes. One each per batch of 20 samples. The laboratory should use 70 - 130% as interim acceptance criteria for recoveries of spiked analytes, until in-house LCS limits are developed. Duplicate RPD will be established for the field samples through the DQOs contained in a written QAPP.
Surrogate Spikes	All field and QC samples. QC acceptance criteria specified by the project if available; otherwise use QSM Appendix C limits or in-house LCS limits if analyte(s) are not listed.	All field and QC samples. Compared to developed in-house surrogate recovery limits. Data is reported as “estimated” if any re-analysis is not within limits.

QC Check	QSM Ver. 5.3 Frequency & Acceptance Criteria	8000D Methods Frequency & Acceptance Criteria
Confirmation of positive results (second column)	All results > the DL must be confirmed (except for single column methods such as TPH by method 8015). Results between primary and secondary column RPD ≤ 40%.	When confirmation is made on a second column, that analysis should meet all of the QC criteria (calibrations, retention times, and performance checks) of the first column. No RPD criteria given in 8000D.

Appendix B: Formulas used in Stage 3 and 4 Data Validation

Note: Not all formulas that may be necessary for validation are included herein.

Calibration:

Calibration Factor (CF): $\frac{A_s}{C_S}$

Note: A CF is calculated for each individual peak.

Response Factor (RF): $\frac{A_S * C_{IS}}{A_{IS} * C_S}$

A_S= Area, Standard
C_{IS}= Concentration, Internal Standard
A_{IS}= Area, Internal Standard
C_S= Concentration, Standard

Note: a RF is calculated if an internal standard is used.

Average CF or RF: $\frac{\sum RF}{n}$

$\sum RF$ = Sum of CFs or RFs for the standards
n= Number of standards

Percent Relative Standard Deviation: $\frac{S_{RF} * 100}{ARF}$

S_{RF}= Standard Deviation of CFs or RFs
ARF= Average CF or RF

Relative Retention time (RRT): $\frac{RT_A}{RT_{IS}}$

RT_A = Retention time of Analyte

RT_{IS} = Retention time of Internal Standard

Percent Difference: $\%D = \frac{C_S - C_K}{C_K} * 100$

C_s= Concentration, reported
C_K= Concentration, known

Sample Concentration (regression):

Raw Values

CF: $$C_p = \frac{A_p}{RF}$$

RF (IS): $$C_p = \frac{A_p * C_{IS}}{A_{IS} * ARF}$$

$$C_s = \frac{\sum C_p}{n}$$

C_p= Concentration of peak, sample
A_p=Area of peak, Sample
C_{IS}= Concentration, Internal Standard
A_{IS}= Area, Internal Standard
RF= CF or RF for each peak
C_s= Concentration, sample
n= number of peaks

Linear Regression (External calibration): y= mx + b

$$C_p = \frac{A_p - b}{m}$$

C_p= Concentration of peak, sample
A_p=Area of peak, Sample
b= Intercept
m= Slope

Linear Regression (Internal calibration): y= mx + b

$$C_p = \frac{[(A_p/A_{IS}) - b] * C_{IS}}{m}$$

C_p= Concentration of peak, sample
A_p=Area of peak, Sample
A_{IS}= Area, Internal standard
C_{IS}= Concentration, Internal Standard
b= Intercept
m= Slope

Quadratic Regression (External Calibration): y=ax2+bx+c

$$C_p = \frac{-b+\sqrt{[b^2-4a*(c-A_p)]}}{2a}$$

C_p= Concentration of peak, sample
A_p=Area of peak, Sample
a= Quadratic Coefficient
b= Linear Coefficient
c= Constant Term

Quadratic Regression (Internal Calibration): y=ax2+bx+c

$$C_p = \frac{-b+\sqrt{[b^2-4a*(c-A_p/A_{IS})]}}{2a*C_{IS}}$$

C_p= Concentration of peak, sample
A_p=Area of peak, Sample
A_{IS}= Area, Internal standard
C_{IS}= Concentration, Internal Standard
a= Quadratic Coefficient
b= Linear Coefficient
c= Constant Term

For linear and quadratic regressions:

$$C_s = \frac{\sum C_p}{n}$$

C_s= Concentration, sample
n= number of peaks

Reported Values:

Waters

Concentration µg/L = $R*V_f*D_f/V_i$

R= Raw value from above in micrograms per liter (ug/L)
V_f= Final Volume of extract in liters (L)
V_i= Initial Volume extracted in liters (L)
D_f= Dilution Factor

Solids

Concentration $\mu g/Kg$ (Dry weight basis) = $(R \times V_f \times 1{,}000 \times D_f) / (W_s \times D)$

R = Raw value from above in micrograms per liter (ug/L)
V_t = Final volume of extract in liters (L)
W_s = Weight of soil/sediment extracted, in grams (g)
D_f = Dilution factor.
$D = \frac{100 - \%\ moisture}{100}$

LCS or Surrogate Percent Recovery:

Percent Recovery: $\frac{C_s}{C_K} * 100$

C_s = Concentration, Reported
C_K = Concentration, Known

MS or MSD percent recovery:

Percent Recovery: $\frac{(C_M - C_S)}{C_K} * 100$

C_M = Concentration, MS or MSD
C_S = Concentration, Sample
C_K = Concentration, Known

MS/MSD or Duplicate Relative Percent Difference (RPD):

RPD: $\frac{|(C_S - C_d)|}{[(C_S + C_d)/2]} * 100$

C_s = Concentration, Sample

C_d = Concentration, Duplicate