UNITED STATES DEPARTMENT OF DEFENSE

Data Validation Guidelines Module 1: Data Validation Procedure for Organic Analysis by GC/MS

Environmental Data Quality Workgroup

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Data Validation Guidelines Module 1

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Module 1: Data Validation Procedure for Organic Analysis by GC/MS (SW-846 8260, 8270)

1.0 Purpose

This document provides guidance on the validation of data generated by Gas Chromatograph/Mass Spectrometer (GC/MS) for Volatile Organic Compounds (VOCs) using method 8260, Semivolatile Organic Compounds (SVOCs) method 8270, or other applicable GC/MS methods. 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 and reporting for GC/MS data generated for Department of Defense (DoD) projects.

Project Specific requirements as identified in the Quality Assurance Project Plan (QAPP) should always supersede the requirements of this document.

This document assumes the user is familiar with data validation conventions and qualifiers used in the *DoD General Data Validation Guidelines* (2018). 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

2.1 Introduction

This document was written with primary consideration to SW-846 methods 8260B and 8270D with Quality Control (QC) criteria identified in the DoD Quality Systems Manual (QSM). However, some projects require other revisions such as method 8260A, 8260C, 8270C or 8270D selected ion monitoring (SIM). 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 methods 8260B, 8270D, 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
- Table of Contents
- 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
- 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*.

Stage 1 data validation consists of a review of sample results forms, 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 project 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 (can also be called Form I) and verify the following information, ensuring that:

- Holding times have been met, as applicable
- All sample identification labels are unique, and match the chain of custody
- All project GC/MS analytes have been analyzed and are reported
- 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 LODs have been met and are lower than the LOQs
- All project required LOQs have been met and those 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 that 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 all non-conformities with the data

For sample results (assuming no other qualifications due to data quality issues):

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

If the project QAPP changes reporting requirements from that specified in the QSM by reporting data down to the Detection Limit (DL), then any detects between the DL and LOQ are qualified as estimated **J.** Values below the DL are considered non-detects and are qualified as **U** at the stated DL.

If the project QAPP changes reporting requirements from that specified in the QSM by reporting data down to the Limit of Detection (LOD), then any detects between the LOD and below the LOQ are qualified as **J** estimated. Values below the LOD are considered non-detects and are qualified as **U** at the stated LOD.

If the project QAPP changes reporting requirements from that specified in the QSM by reporting data down to the Limit of Quantitation (LOQ), then any detects below the LOQ are considered non-detects and are qualified as **U** at the stated LOQ.

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/MS but were not requested should also be noted.

Analytes that have project action levels less than the laboratory's LOQ may reveal a severe deficiency in the data and a failure to meet project goals, and 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 validation report.

Errors in quantitation limits or missing and misidentified samples may require a higher than Stage 1 validation. Data validators are encouraged reach out to their point of contact identified in the project QAPP (such as the UFP-QAPP Worksheet #6) when preparing the 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/MS analyses requested on the CoC have been performed by the laboratory. Ensure that the CoC Sample Identification on the Laboratory Sample Results form 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 naming between the CoC and sample results form should be noted in the data validation report with the correct sample name being identified in the report and on the annotated Form I (if applicable), if the correct sample name 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 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 quality assurance project plan (such as UFP-QAPP Worksheet #19) should provide specific preservation requirements. The following are general guidance if project specifications were not stipulated.

Volatile Organics

- Concentrated waste samples are stored in containers with PTFE lined lids and cooled to ≤ 6°C.
- If acrolein or acrylonitrile are target analytes for aqueous samples, the sample pH should be adjusted to 4-5 and the samples cooled to ≤ 6°C.
- If vinyl chloride, styrene, or 2-chloroethyl vinyl ether were analytes of interest, a second set of samples without acid preservative should have been collected and analyzed.
- For biologically active soils, immediate chemical or freezing preservation is necessary due to the rapid loss of BTEX compounds within the first 48 hours of sample collection.

For further information, the following Table I from EPA Method 5035A may be used as a reference for volatile preservation and holding times.

TABLE I: Volatile Preservation & Hold Times

Sample Matrix	Preservative	Holding Time	Comment
Aqueous samples with NO residual chlorine present	Cool to ≤ 6°C	7 Days	If MTBE and other fuel oxygenate ethers are present and a high temperature sample preparative method is to be used, do not acid preserve the samples. If aromatic and biologically active compounds are analytes of interest, acid preservation is necessary, and the holding time is extended to 14 days.
	Cool to ≤ 6°C and adjust pH to < 2 with HCl or solid $NaHSO_4$	14 Days	Reactive compounds such as 2-chloroethylvinyl ether readily break down under acidic conditions. If these types of compounds are analytes of interest, collect a second set of samples without acid preservatives and analyze as soon as possible.
Aqueous samples with residual chlorine present	Cool to ≤ 6°C. Collect sample in a pre-preserved container containing either 25 mg ascorbic acid or 3 mg of sodium thiosulfate per 40-mL of chlorinated sample volume containing < 5 mg/L of residual chlorine.	7 Days	Samples containing > 5 mg/L of residual chlorine may require additional amounts of dechlorinating agents. If MTBE and other fuel oxygenate ethers are present and a high temperature sample preparative method is to be used, do not acid preserve the samples. If aromatic and biologically active compounds are analytes of interest, acid preservation is necessary, and the holding time is extended to 14 days.
	Collect sample in a pre-preserved container containing either 25 mg ascorbic acid or 3 mg of sodium thiosulfate per 40-	14 Days	Samples containing > 5 mg/L of residual chlorine may require additional amounts of dechlorinating agents. Reactive compounds such as 2-chloroethylvinyl ether readily break down under acidic conditions. If these types of compounds are

Sample Matrix	Preservative	Holding Time	Comment
	mL of chlorinated sample volume containing < 5 mg/L of residual chlorine. Cool to ≤ 6°C and adjust pH to < 2 with HCl or solid NaHSO4.		analytes of interest, collect a second set of samples without acid preservatives and analyze as soon as possible.
Solid samples	Sample is extruded into an empty sealed vial and cooled to ≤ 6°C for no more than 48 hours then frozen to < -7°C upon laboratory receipt.	14 Days	Analysis must be completed within 48 hours if samples are not frozen prior to the expiration of the 48-hour period. Sample vials should not be frozen below -20°C due to potential problems with vial seals and the loss of constituents upon sample thawing.
	Sample is extruded into an empty sealed vial and cooled to ≤ 6°C for no more than 48 hours then preserved with methanol upon laboratory receipt.	14 Days	Analysis must be completed within 48 hours if samples are not preserved with methanol prior to the expiration of the 48-hour period.
	Sample is extruded into an empty sealed vial and cooled to ≤ 6°C. Cool to ≤ 6°C; the coring tool used as a transport device.	48 Hours 48 Hours	The holding time may be extended to 14 days if the sample is extruded to a sealed vial and either frozen to < -7°C or chemically preserved. Coring tools should not be frozen below -20°C due to potential problems with tool seals and the loss of constituents upon sample thawing.
	Freeze to < -7°C; the coring tool used as a transport device.	48 Hours	The holding time may be extended to 14 days if the sample is extruded to a sealed vial and either frozen to < -7°C or chemically preserved. Coring tools should not be frozen below -20°C due to potential problems with tool seals and the

Sample Matrix	Preservative	Holding Time	Comment
			loss of constituents upon sample thawing.
	Sample is extruded into a vial containing reagent water and cooled to ≤ 6°C for 48 hours or less then frozen to < -7°C upon laboratory receipt.	14 Days	Analysis must be completed within 48 hours if samples are not frozen prior to the expiration of the 48 hour period. Sample vials should not be frozen below -20°C due to potential problems with vial seals and the loss of constituents upon sample thawing.
	Sample is extruded into a vial containing reagent water then frozen on-site to < -7°C.	14 Days	Sample vials should not be frozen below -20°C due to potential problems with vial seals and the loss of constituents upon sample thawing.
	Sample is extruded into a vial containing reagent water and 1 g $NaHSO_4$ and cooled to ≤ 6°C.	14 Days	Reactive compounds such as 2-chloroethylvinyl ether readily break down under acidic conditions. If these types of compounds are analytes of interest, collect a second set of samples without acid preservatives and analyze as soon as possible.
	Sample is extruded into a vial containing methanol and cooled to ≤ 6°C.	14 Days	

Semivolatile Organics

- Concentrated waste samples are stored in containers with PTFE lined lids. There is no preservative required.
- Aqueous samples with no residual chlorine and soil samples are stored in containers with PTFE lined lids and require only temperature preservation (≤ 6°C).
- Aqueous samples with residual chlorine present are stored in containers with PTFE lined lids and cooled to ≤ 6°C. The addition of sodium thiosulfate (0.008%) can be performed in the field or in the laboratory.
- Soil samples for SVOC analysis should be cooled to ≤ 6°C.

Evaluation of Preservation

If the analyzed aqueous VOA vial contains air bubbles (> 5-6 mm or roughly the size of a pea), headspace, is cracked, or has a cracked cap, detects should be qualified as **J-** and non-detects as estimated **UJ**. The sample data may be qualified **X** if the container damage is extensive or improper sealing is identified.

Both preserved and unpreserved samples must be cooled to ≤ 6°C. If the temperature is > 6°C, but is ≤ 10°C, note this in the data validation report, for resolution by the project team.

If the temperature of receipt is > 10°C, detects should be flagged as estimated **J-** and non-detects as estimated **UJ**.

If the temperature of receipt ≥ 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 on ice to the laboratory within a few hours (as defined in the QAPP or as specified by the project team) of collection and before the temperature of the cooler can 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 < 0°C, special note should be made but no qualification should be required with the exception of the following: If the sample is frozen or the container is broken then the sample may be qualified as **X**.

If the temperature upon receipt at the laboratory was not recorded, note this in the data validation report and assume that a temperature non-conformity may have occurred. Detects should be flagged as estimated **J-** and non-detects as estimated **UJ**. Review any log-in check sheets for indication that the samples were at least received on ice and note in the validation report.

If the receiving laboratory transferred the samples to another laboratory for analysis, apply the same temperature criteria to both laboratories.

If the sample was preserved incorrectly (e.g., a sample requesting 2-chloroethyl vinyl ether was acid-preserved), detects should be qualified **J-** and non-detects should be qualified **X**.

Chemical preservation of water samples is closely interrelated with holding time, therefore, actions and qualifications for chemical preservation other than those noted above are addressed below.

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 form (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 time-frame (i.e., hours, days, or months) of the requirement. The following examples give guidance on how hold time exceedances are measured:

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

- An exceedance of holding time for a sample with a 48-hour holding time will occur when the start of the 49th hour is reached. Therefore, a sample with a 48-hour holding time collected at 8:30 AM on April 4th must be analyzed or extracted before 9:00 AM (the start of the 49th hour) on April 6th, or an exceedance has occurred.

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.

Volatile Organics

The holding time for aqueous or solid samples preserved to a pH ≤ 2 and refrigerated to ≤ 6°C is 14 days from the collection date. If there is no indication of chemical preservation noted on the sample receipt checklist or instrument sequence log (if present), assume samples are unpreserved.

The holding time for unpreserved aqueous samples is 7 days from date collected and 14 days for solid samples (if frozen; refer to Table 1).

The holding time for unpreserved aqueous TCLP or SPLP is 14 days from field collection to leachate extraction and then 14 more days to analysis.

Semivolatile Organics

The holding time for aqueous samples is 7 days from the collection date to the beginning of solvent extraction, and 40 days from extraction to analysis. The holding time for concentrated waste and 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 semivolatile TCLP or SPLP is 14 days from the collection date to the leachate preparation, 7 days from leachate to solvent extraction, and then 40 more days to analysis.

Evaluation of Holding Times

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 by greater than a factor of 2 (e.g., a preserved volatile water sample has a holding time of more than 28 days), detects should be qualified as estimated **J-** and non-detects as **X**, exclusion of data recommended.

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.

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.

A **source 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.

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.

Evaluation of Field Blanks

Check that all coolers containing samples to be analyzed for volatile organics contained a trip blank that was also analyzed for volatile organics. 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 project point of contact (however named) 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 identified in the project QAPP 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.

Professional judgment should be applied to any equipment blank result that was associated with a contaminated trip blank. 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). For example, if both a source water blank and a trip blank were in the same cooler and the source water blank was also used as the trip blank water (and both were found contaminated), the sample results would be qualified based on the blank with the higher contaminant concentration.

The source blank water should be analyte free (undetected; less than Detection Limit) 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 II 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

1. Methylene chloride (VOC)
2. Acetone (VOC)
3. 2-Butanone (VOC)
4. phthalates (SVOC)

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)**	**None**
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**	**J+**
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 laboratory B qualifier is maintained and the validation qualifier is added in addition to the laboratory qualifier. The QAPP should specify reporting at either the DL or LOD.

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.

For field duplicate results, if the RPDs (Relative Percent Differences) or absolute differences are greater than those stated in the QAPP, qualification of the associated sample results is not necessary, but any non-conformities should be noted in the data validation summary.

If the sample results are below the LOQ, qualification based on RPD criteria is not necessary and should be noted in the validation report summary.

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/Reporting Limit (RL) and the other to be reported below the LOQ/RL or as a non-detect.

The equation for RPD calculations is given in Appendix B.

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

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 blank, duplicate, 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 identified in the project QAPP 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 (also called system monitoring compounds and deuterated monitoring compounds). 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 the criteria from Form II (or equivalent).

If any surrogate recovery is out of specification, then a reextraction (if applicable) and reanalysis should have been performed and reported. 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 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 identified in the project QAPP 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).

Volatile Organics

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.

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**.

Semivolatile Organics

If any surrogate percent recovery is < 10%, qualify all detects within that fraction (i.e., Acid or Base/ Neutral) as estimated **J-** and all non-detects as **X** for that fraction.

If any surrogate percent recovery is greater than the upper acceptance limit, qualify all detects in that fraction 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 detects within that fraction as estimated with a negative bias **J-** and non-detects as estimated **UJ**.

For semivolatile and medium level volatile analyses, surrogates may be reported as “diluted out”, if dilution is such that the surrogate can no longer be detected above the limit of detection (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 basic 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.

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

An LCS is an analyte free sample matrix spiked with known amounts of the analytes of interest 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 matrix spike duplicate 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 relative percent differences (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, relative percent differences (RPDs) (if applicable) and acceptance limits were reported for all target analytes and surrogates.

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 but the results remain within the DoD QSM limits, no qualification is necessary. If the laboratories 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.

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 is recommended.

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 detects for those analytes not spiked as **X** and non-detects for those analytes not spiked as **X**, exclusion of data is 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 summary. 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 relative percent difference (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 detects in the parent sample for those analytes in each batch not spiked as **X**, and non-detects in the parent sample for those analytes not spiked as **X**, exclusion of data is recommended.

If the MS or 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 or 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 is recommended.

If the MS/MSD relative percent differences (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.

Failure of MS/MSD due to the presence of target analyte(s) in the parent sample at > 4X the spike concentration or if semivolatile or medium level volatile matrix spikes are diluted to less than the LOQ, matrix spike 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.

Evaluation of Method Blanks

If no method blank was analyzed, qualify detects in samples with no associated method blank using an **X** flag. 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** due to interference in all affected samples and this should be noted in the data validation comments.

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 sample value should be reported as a non-detect and the reason should be documented in the data validation report. Qualification of the data should be performed as given in Table III.

Professional judgment should be applied to any field blank result that was associated with a contaminated method blank. Generally, if the blank result was qualified as a non-detect due to the method blank, it does not need to be applied to the associated sample results.

However, the fact that the field blank was qualified should be noted in the data validation report.

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 quality control 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 quality control 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 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 quality control 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 to include Instrument Blanks)
- Instrument Performance Check Summary (any equivalent to include Tuning)
- 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)

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) had been 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. The logs themselves do not require validation. However, 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 must be tuned and 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 GC/MS Tuning

GC/MS instrument performance checks (referred to as tune check) are performed to ensure mass resolution, identification, and to some degree, sensitivity are all within criteria. These checks are not sample specific. Conformance is determined using standard reference materials; therefore, the acceptance criteria should be met in all circumstances. Check that all sample analyses are associated with an acceptable tune check.

Make certain that a performance check is present for each 12-hour period samples are analyzed. Verify that all samples were injected within 12 hours after the performance check injection.

The mass spectrum should be acquired by the process outlined in the laboratory's procedure. One acceptable way is by averaging three scans (the peak apex scan and the scans immediately preceding and following the apex). Background subtraction may be accomplished using a single scan no more than 20 scans prior to the elution tune. It is unacceptable to background subtract part of the tune peak. Ideally, the mass range of the instrument performance check should be similar to that of the target analyte list and the ion abundance criteria should be comparable.

Method 8260(B) Volatile Organics

The analysis of the instrument performance check solution should be performed at the beginning of each 12-hour period during which samples or standards are analyzed. The instrument performance check, 4-bromofluorobenzene (BFB) for volatile analysis, should meet the ion abundance criteria given in Table IV below.

Table IV: Ion Abundance Criteria – BFB

m/z	Ion Abundance Criteria for 8260B
50	15–40% of m/z 95
75	30–60% of m/z 95
95	Base peak, 100% relative abundance
96	5–9% of m/z 95
173	< 2% of m/z 174
174	> 50% of m/z 95
175	5–9% of m/z 174
176	> 95% but < 101% of m/z 174
177	5–9% of m/z 176

%: percent m/z: mass-to-charge ratio

Alternative Tune criteria may be used if a volatile method other than 8260B is reviewed.

Method 8270(D) Semivolatile Organics

The analysis of the instrument performance check solution should be performed at the beginning of each 12-hour period during which samples or standards are analyzed. The instrument performance check, decafluorotriphenylphosphine (DFTPP) for semivolatile analysis, should meet the ion abundance criteria given in Table V below.

Table V: Ion Abundance Criteria – DFTPP

m/z	Ion Abundance Criteria for 8270(D)
51	10-80% of m/z Base Peak
68	< 2% of m/z 69
70	< 2% of m/z 69
127	10-80% of m/z Base Peak
197	< 2% of m/z 198
198	Base Peak, 100%, or > 50% of m/z 442
199	5–9% of m/z 198
275	10–60% of m/z Base Peak
365	> 1% of m/z 198
441	Present, but < 24% m/z 442
442	Base peak, 100%, or > 50% of m/z 198.
443	15-24% of m/z 442

%: percent m/z: mass-to-charge ratio

Alternative Tune criteria may be used if a semi-volatile method other than 8270(D) is reviewed.

For method 8270, the GC/MS tuning standard should also be used to assess GC column performance and injection port inertness. The degradation of DDT to DDE and DDD should be ≤ 20%. Benzidine and pentachlorophenol should be present at their normal responses and should not exceed a tailing factor of 2 (See Appendix B for formulas and calculations).

Evaluation of Tune Checks

Use professional judgment to qualify results when samples are injected beyond the 12-hour time limit.

Careful consideration should be given to any reported results that accompany a tune check that does not meet criteria. Based on QSM requirements, the samples should not have been analyzed. All associated data should be qualified as **X**, exclusion of data is recommended.

For method 8270, when DDT degradation is > 20% and ≤ 40%, qualify the data as estimated **J** (detects) or **UJ** (non-detects). When DDT degradation is > 40%, qualify as **X**. For peak tailing factors that exceed a factor of 2, qualify the data as estimated **J**. Qualify **X** the data if the peak tailing factor is 4 or greater.

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 instruments should be calibrated for all target analytes and surrogates or deuterated monitoring compounds (DMCs) with a minimum of five calibration standards depending on the type of curve. More standards are required for higher order regression curves.

Evaluation of Initial Calibration

If target analytes were not calibrated, qualify associated non-detects and detects as **X**. If surrogates or DMCs were not calibrated, or if a single point calibration was used for surrogates or DMCs, qualify associated data as X.

If less than the required minimum number of calibration standards were used, qualify all associated data as **X**.

If the laboratory has analyzed more than the required number of calibration standards and picked out the “best” set (e.g., analyzed 7 calibration standards and picked the 5 “best” to pass calibration criteria), make note of this in the data validation report and qualify the data as **X**.

Any other manipulation of calibration points (such as ‘dropping’ calibration levels at the ends of the calibration curve) should have a technical justification documented in the laboratory report. Use professional judgment to evaluate the data. If no technical justification is provided, then make note of this in the data validation report and qualify the data as **X**.

The lowest calibration standard should be at or below the LOQ. If the LOQ is below the lowest calibration standard, then the LOQ has been reported in a manner that is inconsistent with QSM requirements. Qualify all associated data as **X** and make note of this in the data validation report.

In order to produce acceptable sample results, the response of the instrument must be within the working range established by the initial calibration. Any sample detections above the working range of the calibration curve should be accompanied by a dilution that is within the working range. If dilutions were not performed, qualify all detections above the initial calibration working range as **X** and make note of the lack of dilution(s) in the data validation report.

If dilution(s) were performed that were within the working range of the initial calibration, then qualification of the data is not necessary. Make note in the data validation report that dilution(s) were performed.

5.3.1 Response Factors (RFs) and Relative Standard Deviation (%RSD)

VOC analysis

Evaluate the average RFs for all target analytes. RFs are an indicator of the sensitivity of the analyte to detection and quantitation by Mass Spectrometry (the higher the RF the more sensitive the analyte). For VOCs, the compounds in Table VI called the System Performance Check Compounds (SPCCs) should meet the listed minimum average RF values to be considered acceptable.

Calibration Check Compounds (CCCs) are indicators of overall system performance. Non-conformances represent a potential problem with the analytical system. All CCCs identified by method 8260B (listed in Table VII) should have an associated %RSD ≤ 30%.

SPCCs and CCCs should have been included in the calibration standards and reported, even if individual SPCCs and CCCs are not project target analytes.

Table VIII lists those VOCs that have poor sensitivity and are considered “poor performers”. The minimum average RF for the “poor performers” is 0.01. The minimum average RF for all other volatile target analytes should be ≥ 0.05.

An additional criterion is that all volatile target analytes should have a percent Relative Standard Deviation (%RSD) of ≤ 15%.

Table VI: SPCCs average RFs should meet the following criteria (Method 8260B):

Analyte	**Minimum Average RF (method uses the term “mean”)**
Chloromethane	0.1
1,1-Dichloroethane	0.1
Bromoform	0.1
Chlorobenzene	0.3
1,1,2,2-Tetrachloroethane	0.3

Table VII: CCCs (Method 8260B)

Analyte	
1,1-Dichloroethene	Toluene
Chloroform	Ethylbenzene
1,2-Dichloropropane	Vinyl Chloride

Table VIII: VOC Poor Performers (Method 8260B):

Analyte	
Acetone	1,2-Dibromo-3-chloropropane
2-Butanone	Isopropylbenzene
Carbon disulfide	Methyl acetate
Chloroethane	Methylene chloride
Cyclohexane	Methylcyclohexane
1,2-Dibromoethane	Methyl-tert-butyl ether
Dichlorodifluoromethane	trans-1,2-Dichloroethene
1,2-Dichloropropane	4-Methyl-2-pentanone
cis-1,2-Dichloroethene	2-Hexanone
1,4-Dioxane	Trichlorofluoroethane
1,2-Dibromo-3-chloropropane	1,1,2-Trichloro-1,2,2-triflouroethane

Evaluation of VOC RFs and %RSD

SPCCs are indicators of overall system performance. Non-conformities represent a problem with the overall analytical system. If the average RF for any SPCC does not meet the minimum average RF listed above, all detects in the associated samples should be qualified **J** and all non-detects in the associated samples should be qualified **X**.

For CCCs, make note of any CCCs that are above the maximum %RSD of 30%. No qualification is required, unless a CCC is also a specific target analyte identified in the QAPP. In that case, all associated detects are qualified as **J** and non-detects as **UJ**.

If the average RF for any poor performer is < 0.01, associated detects should be qualified **J** and associated non-detects should be qualified **X**.

If the average RF for a target analyte (that is not a poor performer) is < 0.05, associated detects should be qualified **J** and associated non-detects should be qualified **X**.

Evaluate the %RSD for all other target analytes. If any volatile target analyte has a %RSD > 15%, flag detects for the affected analytes as **J** and non-detects as **UJ** in the associated samples, unless a linear or higher order calibration curve met the criteria of section 5.3.2 or 5.3.3.

If the %RSD for any target analyte is excessively high (> 30%), qualify associated sample results as **X**, unless a linear or higher order calibration curve met the criteria of section 5.3.2 or 5.3.3.

SVOC Analysis

Evaluate the average RFs for all target analytes. Due to the wide range of SVOCs that can be analyzed by GC/MS systems, the minimum average RFs required by Method 8270D range from 0.01 to 0.9. Table IX lists those SVOCs and their minimum average RFs.

An additional criterion is that all semivolatile target analytes should have a percent Relative Standard Deviation (%RSD) of ≤ 15%.

Table IX: SVOC RF (Method 8270D)

Analyte	**Minimum Average RF (method uses the term "mean")**
Acenaphthylene	0.9
Acenaphthene	0.9
Fluorene	0.9
Phenol	0.8
2-Chlorophenol	0.8
2-Chloronaphthalene	0.8
Dibenzofuran	0.8
Benzo(a)anthracene	0.8
bis(2-Chloroethyl)ether	0.7
2-Methylphenol	0.7
Naphthalene	0.7
Phenanthrene	0.7
Anthracene	0.7
Chrysene	0.7
Benzo(b)fluoranthene	0.7
Benzo(k)fluoranthene	0.7

Analyte	**Minimum Average RF (method uses the term "mean")**
Benzo(a)pyrene	0.7
4-Methylphenol	0.6
Fluoranthene	0.6
Pyrene	0.6
N-nitroso-di-n-propylamine	0.5
Indeno(1,2,3-cd)pyrene	0.5
Benzo(ghi)peylene	0.5
Isophorone	0.4
2-Methylnaphthalene	0.4
4-Chlorophenylphenylether	0.4
Dibenz(a,h)anthracene	0.4
Hexachloroethane	0.3
bis(2-Chloroethoxy)methane	0.3
Nitrobenzene	0.2
2,4-Dimethylphenol	0.2
2,4-Dichlorophenol	0.2
4-Chloro-3-methylphenol	0.2
2,4,6-Trichlorophenol	0.2
2,4,5-Trichlorphenol	0.2
2,6-Dinitrotoluene	0.2
2,4-Dinitrotoluene	0.2
2-Nitrophenol	0.1
4-Bromophenylphenylether	0.1
Hexachlorobenzene	0.1
Hexachlorocyclopentadiene	0.05
Pentachlorophenol	0.05
Benzaldehyde	0.01
2,2'-Oxybis-(1-chloropropane)	0.01

Analyte	**Minimum Average RF (method uses the term "mean")**
Acetophenone	0.01
4-Chloroaniline	0.01
Hexachlorobutadiene	0.01
Caprolactam	0.01
1,1'-Biphenyl	0.01
2-Nitroaniline	0.01
Dimethyl phthalate	0.01
3-Nitroaniline	0.01
2,4-Dinitrophenol	0.01
4-Nitrophenol	0.01
Diethyl phthalate	0.01
1,2,4,5-Tetrachlorobenzene	0.01
4-Nitroaniline	0.01
4,6-Dinitro-2-methylphenol	0.01
N-Nitrosodiphenylamine	0.01
Atrazine	0.01
Carbazole	0.01
Di-n-butyl phthalate	0.01
Butyl benzyl phthalate	0.01
3,3'-Dichlorobenzidine	0.01
bis(2-ethylhexyl)phthalate	0.01
Di-n-octylphthalate	0.01
2,3,4,6-Tetrachlorophenol	0.01

Evaluation of SVOC RFs and %RSD

If any SVOC analyte listed above (except those with an average RF of 0.01) has an average RF less than that listed in the table, qualify detects **J** and non-detects **UJ**.

If the average RF for any target analyte is < 0.01, associated detects should be qualified **J** and associated non-detects should be qualified **X**.

Analytes not listed in the above table should have criteria listed in project planning documents (such as UFP-QAPP worksheet #24).

The response factors listed above should be met for the low calibration standard. If the low standard did not meet the minimum average RF, professional judgment should be applied when qualifying results for a low standard non-conformity.

Evaluate the %RSD for all target compounds. If any SVOC target analyte has a %RSD > 15%, flag detects for the affected compounds as **J** and non-detects as **UJ** in the associated samples, unless a linear or higher order calibration curve met the criteria of section 5.3.2 or 5.3.3.

If the %RSD is excessively high (> 30%) qualify all associated sample results as **X**, unless a linear or higher order calibration curve met the criteria of section 5.3.2 or 5.3.3.

5.3.2 Linear Least Squares Regression

The laboratory may employ a linear or weighted linear least squares regression. A minimum of five standards is required for a linear regression. 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.

Evaluation of Linear Least Squares Regression

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

5.3.3 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. It is a statistical requirement that the instrument response is the dependent variable (Y-axis). Verify that the instrument response is on the Y-axis.

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.

Evaluation of Non-Linear Regression

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 (< 0.95) or the r^2 value is excessively low (< 0.90), qualify all associated non-detects as **X** 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** all associated data based on third order (or higher) calibration curves.

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 VOC/SVOC 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 VOC/SVOC target compounds should be analyzed at the beginning of every twelve-hour period during which samples are analyzed, prior to sample analysis, and at the end of the analytical sequence. The end of the analytical sequence CCV should have an injection time prior to the end of the twelve-hour tune period. Continuing calibration checks satisfactory performance of the instrument on a day-to-day basis.

The twelve-hour tune injection time period is measured from the start of the injection of the tune until the start of the injection of the last sample or end of run CCV.

Verify the ICV was analyzed following the initial calibration and contained all VOC/SVOC target analytes. Verify the CCVs have been run prior to sample analysis, every twelve hours, and at the end of the analytical sequence. 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 VOC/SVOC target analyte and surrogate should be ≤ 20%. The CCV %D for each target analyte should be ≤ 20% for opening or continuing CCVs and ≤ 50% for closing CCVs.

Evaluating the ICV and CCV

Verify that the %Ds are within the acceptance criteria. If any target analytes do not meet the acceptance criteria, 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% for ICV/CCV and > 80% for closing CCV) qualify all associated data as **X**.

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

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

CCVs that have been analyzed beyond the 12-hour time limit criteria, qualify the associated sample detects as **J** and the non-detects as **UJ**. For gross exceedances of the 12-hour time limit (defined as > 16 hours), qualify all associated data as **X**.

5.5 Internal Standards

Internal standards (IS) performance criteria for Methods 8260B/8270D ensure that GC/MS sensitivity and response are stable during every analytical run. Internal standards should be added to all calibration standards, instrument QC checks, samples, and batch QC.

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 can be used.

The IS retention times for all field and QC samples should be within 30 seconds (or 10 seconds if QSM criteria is used) of the retention time of the midpoint standard in the ICAL, or on days when ICAL is not performed, the initial CCV is used.

Evaluation of Internal Standards

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

Analytes quantitated using an IS area count < 50% but ≥ 20% should be qualified estimated with a positive bias **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**.

If an IS retention time varies by more than 30 seconds (or 10 seconds if QSM criteria is used), non-detects should be qualified **X**.

6.0 Stage 3 Validation

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

The following documents are used for a Stage 3 validation

- Raw Data (including any laboratory forms, instrument outputs, spreadsheets, or handwritten calculations necessary for recalculation and re-quantification)
- Standards Traceability forms and worksheets
- Detection Limit 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, and field QC samples (blanks and duplicates). For method QC results, spiked recoveries and method blanks should be considered. For instrument QC, tune checks, calibrations (including response factors 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 Sample Delivery Group (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 reporting limits (such as limit of quantitation) are calculated correctly for the non-detects and reported accordingly. If a detection limit study was identified by the QAPP, recalculate one or more analyte detection limits.

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, field blanks, or equipment blanks). Field QC sample duplicate recalculations should include re-quantification of the same detected analyte sample/duplicate pair and verification of the percent difference (%D), or relative percent difference (RPD), as reported.

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 reporting limits (however defined) are calculated incorrectly, then continue to recalculate limits until it is determined that 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 as identified in the project QAPP 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 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 calibration factor, response factor, or slope; the preparation information; and percent moisture for solid samples to recreate the reported result.

6.2.1 Surrogate Spikes

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

6.2.2 LCS/LCSD

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.

6.2.3 MS/MSD

Re-quantitate 10% of the target analytes 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.

6.2.4 Method Blanks

Method blank analytical results are assessed to determine the existence and magnitude of contamination problems associated with sample extraction (if applicable) 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) from the reported average RF (or higher order regression, if used) per each batch of samples.

Evaluation of all Surrogate Spike, LCS, MS, and Method Blank 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 as identified in the UFP-QAPP 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 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 calculations qualify all affected analytes in associated samples as **X**, exclusion of data recommended.

For systemic problems with method blanks, surrogate spikes, or MS/MSD calculations qualify all affected analyte detects in associated samples as estimated **J** and non-detects as estimated **UJ**.

6.3 Instrument QC

6.3.1 Tune Check

Verify by re-calculating from the quantitation reports, that the mass assignment is correct and that the mass listing is normalized to the specified m/z for at least 10% of the abundance ratios in every tune. Verify by recalculation that the reported DDT degradation and tailing factor are accurate for SVOC performance checks.

6.3.2 Initial (Response 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 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 RFs, %RSDs, and regression function (if used) and r values reported for at least 10% of the target analytes per each internal standard, (preferably analytes of concern which were identified in the QAPP), per initial calibration curve type.

Re-quantitate and recalculate the Initial and Continuing Calibration Verification RF result and %D for at least 10% of the target analytes, proportionally per each internal standard and 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. RFs should not be evaluated for analytes with linear or higher order regression curves. If the ICAL included refitting of the data back to the model (RSE), the recalculate 10% of the target analytes for the RSE in each ICAL.

Recalculation of the low calibration standard is not required for higher order calibration curves.

6.3.3 Internal Standards

The analyte quantitation should be evaluated for all detects by evaluating the raw data. Analyte concentrations should be calculated based on the IS associated with that analyte. Quantitation should be based on the quantitation ion (m/z) specified in the analytical method (or laboratory SOP listed in the QAPP) for both the IS and target analytes. The analyte quantitation should be based on the RF or regression function from the appropriate ICAL.

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

Evaluation of Tune, ICAL, RF, Regression, ICV/CCV, and IS Recalculations

For the tune check, if the mass assignments are incorrect, or specific ion abundances were incorrect, qualify all data as **X**. The QSM states that no data should have been collected without a proper tune.

If SVOC degradation breakdown and tailing factors are calculated incorrectly, use professional judgment to qualify the data based on the actual correct calculations.

If the files provided do not match the quantitation report, the RFs 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 RFs or any other regression equations that cannot be corrected in a revised report, qualify all the data as **X**.

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** if the corresponding ICV/CCV %D has been calculated incorrectly by the laboratory and cannot be corrected in a revised laboratory report.

Qualify all data as **X** if the corresponding internal standard has been calculated incorrectly (or if the IS has been assigned to the wrong analyte) by the laboratory and cannot be corrected in a revised laboratory report.

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

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 Initial Calibration Verification (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 identified in the project QAPP (UFP-QAPP Worksheet #6) should be reached to get a revised (corrected) report from the laboratory. Minor issues (that does 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** all affected data. No samples should have been run without a valid second source standard (per QSM requirements).

For expired standards, per QSM requirements, a laboratory cannot use a standard beyond its expiration date. All associated data should be qualified as **X** 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 project QAPP may specify the review and validation of a detection/quantitation limit study. This could include studies such as Method Detection Limits (MDLs), quarterly Limit of Detection Verifications (LODVs), or Limit of Quantitation (LOQ) verifications. The project 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 project 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 as identified in the project 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 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 **X** the study.

7.0 Stage 4 Validation

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

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

Stage 4 is a qualitative review of non-detected, detected, and tentatively identified compounds (TICs) from instrument outputs. Chromatograms are checked for peak integration (10% of automated integration and 100% of manual integrations), baseline, and interferences; mass spectra are checked for minimum signal to noise, qualitative ion mass presence, ion abundances; retention times or relative retention times are within method requirements for analyte identification. Raw data quantitation reports, chromatograms, mass spectra, instrument background corrections, and interference corrections are required to perform review of the instrument outputs.

7.1 Target Compound Identification

The objective of the criteria for GC/MS 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 display all qualitative mass/ions at the correct retention times with passing mass/ion ratio calculated from the initial calibration standards. Qualitatively verify that the target analyte detects have valid spectra.

Relative Retention Times (RRTs) should be within ± 0.06 RRT units and updated with the latest daily CCV. Check a minimum of 10% of the reported target analyte detects for retention time. RRT performance in samples with only non-detects can be evaluated by reviewing the surrogate retention times.

Evaluation of Target Compound Identification

The application of qualitative criteria for GC/MS analysis of target analytes requires professional judgment. It is up to the reviewer's discretion to obtain additional information from their point of contact identified in the project QAPP, if qualitative identification problems are uncovered. The point of contact 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, and the laboratory cannot correct the problem, then all affected data should be qualified as **X**, exclusion of data recommended.

If it is determined that cross-contamination has occurred, all affected data should be qualified as **X.**-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, confer with the point of contact identified in the project QAPP to consider changing the reported detect to a non-detect for the affected analyte.

While retention time windows are less critical to mass spectrometry systems, there are certain occasions where retention times have a direct effect on GC/MS results. For example, retention time window drift on a Selected Ion Monitoring (SIM) system can have a direct impact on the reported results. Professional judgment should be used to qualify the data.

7.2 Tentatively Identified Compounds (TICs)

Verify all target analyte and TIC detects found in all samples against the raw data.

TIC mass spectra should present the following criteria:

- The peak for a TIC should have an area or height > 10% of the area or height of the nearest internal standard.
- All ions present in the standard mass spectrum at a relative intensity > 10% should be present in the sample spectrum.
- The relative intensities of these ions should agree within ± 20% between the standard and sample spectra. (Example: For an ion with an abundance of 50 percent in the standard spectrum, the corresponding sample ion abundance should be between 30% and 70%).
- Ions present at > 10% in the sample mass spectrum, but not present in the standard spectrum, should be considered and accounted for.

Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination, interference, or coelution of additional TIC or target analytes.

When the above criteria are not met, but in the technical judgment of the data reviewer or mass spectral interpretation specialist, the identification is correct, the data validator may report the identification.

Since TIC library searches often yield several candidate analytes having a close matching score, all reasonable choices should be considered. The reviewer may use judgment to change the reported tentative identity.

Evaluation of TICs

If the tentative identity for any sample is in error, confer with the point of contact identified in the project QAPP to consider changing the identity of the TIC.

All TIC results should be qualified **NJ** tentatively identified with approximated concentrations.

The reviewer should be aware of common laboratory artifacts and their sources such as siloxane analytes, which indicate capillary column degradation, and CO_2 which indicates a possible air leak in the system. These should be qualified **X**.

If a target analyte is identified as a TIC by non-target library search procedures, the reviewer should confer with the point of contact to request that the laboratory recalculate the result using the proper quantitation ion.

TIC results that are not above the 10X level in any blank should be qualified as **X**. Dilutions and sample size should be taken into account when comparing the amounts present in blanks and samples.

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 validation report. Instances of

incomplete information for manual integrations (such as failure to provide justification) should be reported to the point of contact identified in the project QAPP 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**.

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 Methods 8260B/8270D for comparison. The Table does not include all the QC elements from the methods or as listed in this guidance document.

QC Check	8260B Frequency and Acceptance Criteria	8270D Frequency and Acceptance Criteria	QSM Ver. 5.3 Frequency and Acceptance Criteria
Tune Check	Prior to ICAL and prior to each 12-hour period of sample analysis. **Mass Intensity Criteria**: m/z Required Intensity 50 15-40% of m/z 95 75 30-60% of m/z 95 95 Base Peak, 100% 96 5-9% of m/z 95 173 <2% of m/z 174 174 >50% of m/z 95 175 5-9% of m/z 174 176 >95% but <101% of m/z 174 177 5-9% of m/z 176	Prior to ICAL and prior to each 12-hour period of sample analysis. **Mass Intensity Criteria**: m/z Required Intensity 51 10-80%of base peak 68 <2% of m/z 69 70 <2% of m/z 69 127 10-80% of base peak 197 <2% of m/z 198 198 Base peak, 100%, or >50% of m/z 442 199 5-9% of m/z 198 275 10-60% of base peak 365 >1% of m/z 198 441 present but <24% of m/z 442 442 Base peak, 100%, or >50% of m/z 198 443 15-24% of m/z 442 DDT degradation ≤ 20%. Benzidine and pentachlorophenol tailing factor ≤ 2.	Same frequency and acceptance criteria as 8260B/8270D.

QC Check	8260B Frequency and Acceptance Criteria	8270D Frequency and Acceptance Criteria	QSM Ver. 5.3 Frequency and Acceptance Criteria
Initial calibration (ICAL) for all analytes (including surrogates)	At instrument set-up, prior to sample analysis. Each analyte should meet one of the options below: **Option 1:** Response Factor (RF) Minimum of 5 standards Minimum RFs for SPCCs: 0.10: Chloromethane; 1,1-dichloromethane; and bromoform. 0.30: Chlorobenzene and 1,1,2,2-tetrachloroethane. RSD for 1,1-dichloroethene; chloroform; toluene; 1,2-dichoropropane; ethylbenzene; vinyl chloride: < 30% RSD for each analyte ≤ 15%. **Option 2:** linear least squares regression or non-linear regression Minimum of 5 standards for linear and 6 standards for non-linear regression. $r^2 \geq 0.99$	At instrument set-up, prior to sample analysis. Each analyte should meet one of the options below: **Option 1:** Response Factor (RF) Minimum of 5 standards Minimum RFs: See table VII RSD for each analyte ≤20%. **Option 2:** linear least squares regression or non-linear regression Minimum of 5 standards for linear and 6 standards for non-linear regression. $r^2 \geq 0.99$ For linear least squares regression, re-quantification of low standard should be ± 30% the known value.	At instrument set-up, prior to sample analysis. Each analyte should meet one of the options below: **Option 1:** RSD for each analyte ≤ 15%; **Option 2:** linear least squares or non-linear regression for each analyte: $r^2 \geq 0.99$; If the specific version of a method requires additional evaluation (e.g., RFs or low calibration standard analysis and recovery criteria) these additional requirements should also be met.

QC Check	8260B Frequency and Acceptance Criteria	8270D Frequency and Acceptance Criteria	QSM Ver. 5.3 Frequency and Acceptance Criteria
Evaluation of Relative Retention Times (RRT)	With each sample. RRT of each reported analyte within ± 0.06 RRT units.	With each sample. RRT of each reported analyte within ± 0.06 RRT units.	Same frequency and acceptance criteria as 8260B/8270D. RRT of each reported analyte within ± 0.06 RRT units.
Initial Calibration Verification (ICV)	None specified.	Once after each ICAL, analysis of a second source standard prior to sample analysis. All reported analytes within ± 30% 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. If the specific version of a method requires additional evaluation (e.g., RFs or low calibration standard analysis and recovery criteria) these additional requirements should also be met.

QC Check	8260B Frequency and Acceptance Criteria	8270D Frequency and Acceptance Criteria	QSM Ver. 5.3 Frequency and Acceptance Criteria
Continuing Calibration Verification (CCV)	Daily before sample analysis; after every 12 hours of analysis time. SPCCs should meet minimum RF requirements in ICAL section above. Percent differences or percent drift ± 20%.	Daily before sample analysis; after every 12 hours of analysis time. Target analytes should meet minimum RF requirements in section above. Percent differences or percent drift ± 20%.	Daily before sample analysis; after every 12 hours of analysis time; and at the end of the analytical batch run. Minimum RFs per method version. All reported analytes and surrogates within ± 20% of true value for opening CCV. All reported analytes and surrogates within ± 50% for closing CCV. If the specific version of a method requires additional evaluation (e.g., RFs or low calibration standard analysis and recovery criteria) these additional requirements should also be met.

QC Check	8260B Frequency and Acceptance Criteria	8270D Frequency and Acceptance Criteria	QSM Ver. 5.3 Frequency and Acceptance Criteria
Internal standards (IS)	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.	Every field sample, standard, and QC sample. Retention time within ± 10 seconds from retention time of the midpoint standard in the ICAL; EICP area within - 50% to +100% of ICAL midpoint standard. On days when ICAL is not performed, the daily initial CCV can be used.
Method Blank (MB)	One per preparatory batch. No analytes detected. Detects in method blank should be ≤ 5% of sample concentration or regulatory limit.	One per preparatory batch. No analytes detected. Detects in method blank should be ≤ 5% of sample concentration or regulatory limit.	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. Common contaminants should not be detected > LOQ.

QC Check	8260B Frequency and Acceptance Criteria	8270D Frequency and Acceptance Criteria	QSM Ver. 5.3 Frequency and Acceptance Criteria
Laboratory Control Sample (LCS); **Matrix Spike (MS); Matrix Spike Duplicate (MSD)** **Relative per cent difference**	One per preparatory batch. Method specified control limits listed in method tables or in-house laboratory limits.	One per preparatory batch. Method specified control limits listed in method tables or in-house laboratory limits.	Same frequency as 8260B/8270D. A laboratory should use the QSM Appendix C Limits for batch control 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).
Surrogates	All field and QC samples. Recovery limits specified in method tables or in-house laboratory limits.	All field and QC samples. Recovery limits specified in method tables or in-house laboratory limits.	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.

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

Tune:

Ion abundance:

$$Ion\ Abundance = \frac{A_t}{A_b}\ x\ 100$$

Where:

A_t= Area of target m/z

A_b= Area of base m/z

(**8270 only) Percent Breakdown of DDT:**

$$DDT\ Percent\ Breakdown = \frac{A_{DDD} + A_{DDE}}{A_{DDT} + A_{DDD} + A_{DDE}} x\ 100$$

Where:

A_{DDD} = DDD peak area

A_{DDE} = DDD peak area

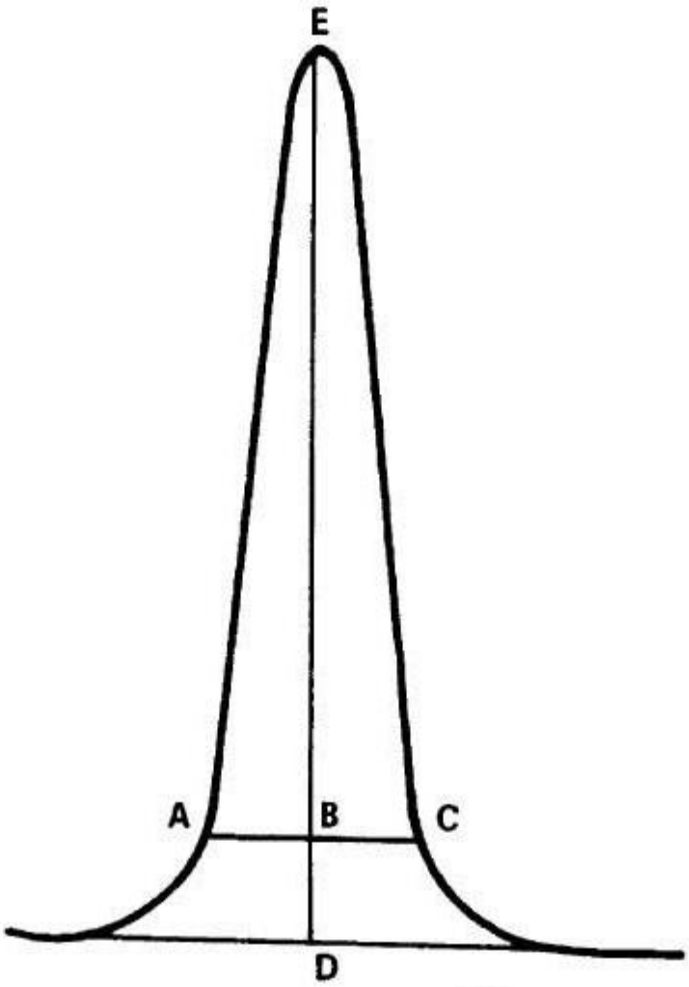
A_{DDT} = DDT peak area

Tailing Factor:

$$TailingFactor = \frac{BC}{AB}$$

Where:

AC = Width of peak at 10% height
DE = Height of Peak
B = Height at 10% of DE



Calibration:

Response Factor (RF):

$$RF = \frac{A_s \times C_{IS}}{A_{IS} \times C_s}$$

Where:

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

Average RF:

$$mean\ RF = \overline{RF} = \frac{\sum_{i=1}^{n} RF_i}{n}$$

$$SD = \frac{\sqrt{\sum_{i=1}^{n}(RF_i - \overline{RF})^2}}{n-1}$$

$$RSD = \frac{SD}{\overline{RF}} \times 100$$

Where:

RF_i = RF for each calibration standard
$\overline{RF}$ = mean RF for each compound from the initial calibration
N = number of calibration standards

SD = standard deviation
RSD = Relative standard deviation

Relative Retention time:

$$RRT = \frac{Retention\ time\ of\ the\ analyte}{Retention\ time\ of\ the\ internal\ standard}$$

Percent Difference:

$$\%D = \frac{C_s - C_k}{C_k} \times 100$$

Where:

C_s = Concentration, reported
C_k = Concentration, known

Sample Concentration:

Raw Values:

$$C_s = \frac{A_s * C_{IS}}{A_{IS} * \overline{RF}}$$

Where:

C_S= Concentration, sample
A_S=Area, Sample
C_{IS}= Concentration, Internal Standard
A_{IS}= Area, Internal Standard
$\overline{RF}$= Average RF

Linear Regression: y = mx + b

$$C_s = \frac{\left(\frac{A_s}{A_{IS}} - b\right) * C_{IS}}{m}$$

Where:

C_s =Concentration, Sample
A_s =Area, Sample
A_{IS} = Area, Internal standard
C_{IS} = Concentration, Internal Standard
b = Intercept
m = Slope

Quadratic Regression: $y = ax^2 + bx + c$

$$C_s = \frac{-b \pm \sqrt{b^2 - 4a\left(c - \frac{A_s}{A_{IS}}\right)}}{2a} \; x \; C_{IS}$$

Where:

C_s = Concentration, Sample
A_s = Area, Sample
A_{IS} = Area, Internal standard
C_{IS} = Concentration, Internal Standard
a = Quadratic Coefficient
b = Linear Coefficient
c = Constant Term

LCS or Surrogate Percent Recovery:

$$Percent\ Recovery = \frac{C_s}{C_K}\ x\ 100$$

Where:

C_s = Concentration, Reported
C_K = Concentration, Known

MS or MSD Percent Recovery:

$$Percent\ Recovery = \frac{C_M - C_s}{C_K}\ x\ 100$$

Where:

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

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

$$RPD = \frac{|C_s - C_d|}{(C_s + C_d)/2}\ x\ 100$$

Where:

C_s = Concentration, Sample
C_d = Concentration, Duplicate

Calculation of sample amounts:

$$x_s = \frac{A_s}{\overline{CF}}$$

$$x_s = \frac{A_s}{\overline{RF}}\ x\ \frac{C_{is}}{A_{is}}$$

where:

x_s = Calculated mass of the analyte or surrogate in the sample aliquot introduced into the instrument (in nanograms).
A_s = Peak area (or height) of the analyte or surrogate in the sample.
A_{is} = Peak area (or height) of the internal standard in the sample.
C_{is} = Mass of the internal standard in the sample aliquot introduced into the instrument (in nanograms).
$\overline{CF}$ = The average calibration factor from the most recent initial calibration.
$\overline{RF}$ = The average response factor from the most recent initial calibration.

Sample concentration by volume (µg/L), e.g., for aqueous samples:

$$Concentration\ (\mu g/L) = \frac{(x_s)(V_t)(D)}{(V_i)(V_s)}$$

where:

x_s = Calculated mass of the analyte (in nanograms) in the sample aliquot introduced into the instrument.

V_t = Total volume of the concentrated extract (in µL). For purge-and-trap analysis, V_t is the purge volume and will be equal to V_i. Thus, units other than µL may be used for purge-and-trap analyses.

D = Dilution factor, if the sample or extract was diluted prior to analysis. If no dilution was made, then D=1. The dilution factor is always dimensionless.

V_i = Volume of the extract injected (in µL). The nominal injection volume for samples and calibration must be the same. For purge-and-trap analysis, V_i is the purge volume and will be equal to Vt. Thus, units other than µL may be used for purge-and-trap analyses.

V_s = Volume of the aqueous sample extracted or purged, in milliliters (mL). If units of liters (L) are used for this term, then multiply the results by 1000 mL/L.

Sample concentration by weight (µg/kg), e.g., for solid samples and non-aqueous liquids:

$$Concentration\ (\mu g/kg) = \frac{(x_s)(V_t)(D)}{(V_i)(W_s)}$$

where:

x_s = Calculated mass of the analyte (in nanograms) in the sample aliquot introduced into the instrument. The type of calibration model used determines the derivation of x_s.

V_t = Total volume of the concentrated extract (in µL). For purge-and-trap analysis where an aliquot of a solvent (methanol, water, etc.) extract is added to reagent water and purged, V_t is the total volume of the solvent extract. This also includes any contribution from water present in samples prior to solvent extraction.

D = Dilution factor, if the sample or extract was diluted prior to analysis. If no dilution was made, then D=1. The dilution factor is always dimensionless.

V_i = Volume of the extract injected (in µL). The nominal injection volume for samples and calibration standards must be the same. For purge-and-trap analysis where an aliquot of a solvent (methanol, water, etc.) extract is added to reagent water and purged, V_i is the volume of the solvent extract that is added to the reagent water just prior to purging. Any dilutions made to the initial volume of the solvent extract are accounted for in the dilution factor.

W_s = Weight of sample extracted or purged (in grams). If units of kilograms (kg) are used for this term, multiply the results by 1000 g/kg.