



VERIFICATION AND VALIDATION GUIDELINES

FOR

PCB/PESTICIDES

DA-SS03-v1

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1. PURPOSE AND INTRODUCTION

This procedure presents those data assessment steps which are unique to PSA Module SS03, PCB/Pesticides. This procedure is to be used in conjunction with the general guideline for data verification and validation, DA-GR01.

The purpose of this procedure is to provide guidance in the completion of Data Review Checklist (DRC) Examination, Data Verification, and Data Validation activities as part of the Rocky Flats Environmental Technology Site (RFETS) Analytical Services Division Data Assessment Program. The Data Assessment Program is described in the Kaiser-Hill Analytical Services Division Procedure ASD-001, Performance Assurance Data Assessment Program.

This version of DA-SS03, until replaced by a more recent version, is applicable to all versions of the PSA Module SS03-B.

This procedure for the data quality assessment of SS03 Sample Data Packages is organized into the following Sections:

- DRC Examination Instructions
- Verification and Validation Instructions
- Data Quality Assessment Report Preparation
- References
- Revision History
- Attachments

2. DATA REVIEW CHECKLIST (DRC) EXAMINATION INSTRUCTIONS

The instructions contained in this section are specific to PSA Module SS03 for PCB/Pesticides analyses. The instructions in this section are to be used in conjunction with the general instructions for DRC Examination found in Analytical Services Procedure DA-GR01.

2.1. Examination of NA Replies

Several items in the DRC Checklist may be marked as NA, indicating that the item was not applicable to the analysis performed or to the data package. For the following items, enter \surd in the \surd column of the DRC to indicate that the NA response is not verified but accepted:

Table 2-1 Non Applicable DRC Items

Section 1 Items	Section 3 Items	Section 4 Items	Section 5 Items	Section 6 Items
1-d	3-b	4-b	5-b	6-b-4
		4-e	5-c	6-b-5
			5-d	6-c-4
			5-e	6-c-5
			5-f	6-c-7
			5-g	6-d-1
				6-d-3
				6-d-5
				6-d-6
				6-d-7
				6-e-4

2.1.1. For all other items with marked NA in the Reply column, enter X in the \surd column to indicate that the verification is required for this item.

2.2. Examination of the Sample Narrative

Read the sample narrative for information which indicates additional items to be verified. Items to check include statements about data qualifiers, blank contamination, or sample handling problems.

2.2.1. If the narrative states that B or E flags are present, enter X in the $\sqrt{\quad}$ column of item 6-b-5 to indicate that verification is required for this item due to information provided in the Narrative.

3. VERIFICATION AND VALIDATION INSTRUCTIONS

The instructions contained in this section are specific to PSA Module SS03 for PCB/Pesticides analyses. The instructions in this section are to be used in conjunction with the general instructions for DRC Examination found in Analytical Services Procedure DA-GR01. The remainder of this section includes specific instructions for performing verification and validation activities for Sample Data Packages generated under PSA Module SS03. Each section corresponds to a DRC Checklist element that may contain multiple item numbers. These item numbers are referenced within each section of this procedure.

3.1. Chain of Custody, Holding Times, and Sample Preservation

DRC Items 4-a through 4-g

Review Items: Deliverable Section Number 4; Deliverable Section Number 6: Form 1D, COC record, sample preparation/extraction log.

Requirement Source: GR01 Exhibit B § 4.8 and SS03 Exhibit D § 3.

Objective: The objective is to ascertain the validity of results based on the holding time and preservation of the sample and to check that Sample COC documentation is included in the sample data package (SDP).

Note: The holding time is based on the date when collection was completed, rather than verified time of sample receipt (VTSR).

Evaluation: *The following items apply to both verification and validation:*

Items 4-a, b, c, and e:

Follow instructions in DA GR01

Item 4-d If samples were not maintained at 4°C prior to receipt by the laboratory, do not qualify the sample results. Comment and assign the following code to all applicable samples [703].

Item 4-f Technical requirements for sample holding times and sample preservation for SS03 are listed in the following table:

Table 3-1 Holding Time and Preservation Criteria

Matrix	Extraction Holding Time (maximum)	Analysis Holding Time (maximum)	Preservation
Water	7 days	40 days	Storage at 4°C
Soil	14 days	40 days	Storage at 4°C

Determine the actual analysis and preparation holding times by comparing the preparation and analysis dates on the raw data and the sample collection date on the

COC. If the actual holding time is greater than the maximum allowable holding time, record the appropriate qualification and reason codes on the electronic deliverable and in the Data Quality Assessment Report as determined from the following:

- Qualify all positive results as estimated (J) if the actual holding time was greater than the maximum holding time. Assign code [**J 101**] if the holding time violation is attributed to the laboratory. If the holding time violation is not attributed to the laboratory, assign code [**J 701**].
- Qualify all non-detected results as estimated (J) if the actual holding time was greater than the maximum holding time but less than two times the maximum holding time.. Assign code [**J 101**] if the holding time violation is attributed to the laboratory. If the holding time violation is not attributed to the laboratory, assign code [**J 701**].
- Qualify all non-detects as rejected (R) if the actual holding time was greater than two times the maximum holding time. Assign reason code [**R 102**] if the hold time violation is attributed to the lab. If the hold-time violation is not attributed to the laboratory, assign reason code [**R 702**].

Item 4-g If documentation indicates samples were not properly preserved after sample receipt, but prior to analysis, initiate a Non-Compliance Notification and qualify all results as estimated [**J 201**].

3.2. Sample Data Package Narrative

DRC Items 5-a through 5-g

Review Items: Deliverable Section Number 5: sample case narrative.

Objective: Review the narrative for compliance to requirements and for information useful for validation of data.

Requirement Source: GR01 Exhibit B § 4.9 and SS03 Exhibit B § 2.7

Evaluation: *The following items apply to both verification and validation:*

Check that the SDP Narrative is present and that each Item 5-a through Item 5-d are compliant.

- If any of the following items are non-compliant, do not qualify the results. Comment and include the reason code [**805**].

Item 5-a Method reference numbers and revisions.

Item 5-b Descriptions of matrix interferences.

Item 5-c Description of required dilutions.

Item 5-d Explanations of any QC deficiencies, missed holding times, or inability to achieve the required detection limits (RDLs).

Item 5-e Reasons for reanalysis, reanalysis Analytical Batch Identifications Numbers, and a synopsis of the reanalysis Analytical Batch QC Assessment.

Item 5-f Explanations and descriptions of all deviations from routine protocols, including deviations from approved standard operating procedures (SOPs), detection limit modifications, etc. If it was necessary to contact the CTR for instructions due to the nature of the deviation, the laboratory shall document those instructions in the narrative.

Item 5-g Explanations for each item marked “N” on the Data Review Checklist.

3.3. Surrogate Recovery

DRC Items 6-a-1, 6-b-3, and 6-c-3

Review Items: Deliverable Section Number 6: Forms 2E/2F, Form 6E, Form 8D, sample preparation/extraction log, sample chromatograms and integration reports.

Objective: Evaluate the results of the surrogate spikes. Laboratory performance on individual samples is established by means of spiking samples with surrogate compounds prior to extraction and analysis to determine surrogate spike recoveries

Note: The evaluation of the results of these surrogate spikes is not necessarily straightforward. The sample itself may produce effects due to such factors as interferences and high concentrations of analytes. Since 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 are frequently subjective and demand analytical experience and professional judgment.

Requirement Sources: SS03 Exhibit B § 2.8; SS03 Exhibit D § 2; GR01 Exhibit D.

Evaluation: *The following items apply to both verification and validation:*

Item 6-a-1 Check that Forms 2E/2F are present.

- If not provided, issue a Non-Compliance Notification to request the missing data. Do not qualify any data. Comment and assign reason code [801] to all applicable data.

Check that surrogate recoveries are reported for all sample, spike, and blank analyses.

- If not provided, issue a Non-Compliance Notification to request the missing data. Do not qualify any data. Comment and assign reason code [803] to all applicable data.

Check that the surrogate percent recoveries (%R) are within the following limits:

Table 3-2 Surrogate Control Limits

Method	Surrogate Compounds	Control Limits
CLP-SOW	Tetrachloro-m-xylene, Decachlorobiphenyl	30-150% (water & soil)
SW-846 8080A/8081	Tetrachloro-m-xylene, Decachlorobiphenyl	Laboratory-determined

- For SW-846, the laboratory may use the recovery from either surrogate to fulfill the %R requirement. Therefore, no qualification of the data is necessary if one of the two surrogates is inside the control limits.
- For CLP, both surrogates are necessary to fulfill the %R requirement. In general, take no action unless two of the four recoveries (%Rs) per sample are outside the control limits. However, comment and assign reason code [142] to all applicable data.

If two or more of the surrogates exceed the control limits for %R(s) as indicated above (SW-846 and CLP), qualify as follows:

- If the sample %R(s) is greater than the control limits, estimate [J 142] positive results.
- If the sample %R(s) is less than the control limits but greater than or equal to 10%, estimate [J 142] positive results and [UJ 142] non-detected results.
- If the sample %R(s) is greater than zero but less than 10%, estimate [J 142] positive results and reject [R 142] non-detected results.

- For CLP only, if one %R is greater than the control limits and another %R is less than the control limits but greater than or equal to 10%, estimate [J 142] positive results and [UJ 142] non-detected results.

Item 6-c-3 Check that surrogate retention times (Form 8D) are within the retention time limits provided by the laboratory.

- If surrogate retention times are outside of the retention time limits, use professional judgment to qualify the data. Consider how much the retention time varied, presence/absence of positive results, MS/MSD recoveries (demonstrates ability to identify positive results), etc.
- If a sample %R is not reported (e.g., D or DIL is reported instead of a percent recovery), estimate [J 142] positive results and reject [R 142] non-detected results.

Evaluation: *The following items apply to validation only:*

Item 6-b-3 Check chromatograms and quantitation reports to evaluate the recoveries. Verify at least one surrogate recovery per sample.

- If calculated recoveries are not within 5% of reported result, issue a Non-Compliance Notification and assign reason code [803] to all applicable data. Cease validation until a new data package is received. Inspect all other SDP deliverables for missing data, incorporate any deficiencies in the Non-Compliance Report, and return the SDP to ASD.

Item 6-a-1 If the %R values are not within the control limits, check the raw data for possible interferences or misidentification before qualifying the data.

- If the raw data confirms the surrogate recoveries, no further action is necessary.
- If the raw data indicates that a surrogate was misidentified, assign the reason code [804]. Use professional judgment to assign qualifiers based on the extent of the problems identified.

If no sample %R is reported (e.g., D or DIL is reported instead of a percent recovery), examine the sample data to determine if the surrogate may be present but slightly outside its retention time window.

- If the surrogate can be clearly identified, the surrogate recovery should be recalculated and the recalculated value used to qualify the data. If not, follow the guidance under “validation and verification” above.

3.4. MS/MSD Recovery

DRC Items 6-a-2 and 6-d-4

Review Items: Deliverable Section Number 6: Forms 3E/3F, Form 6E, MS/MSD chromatograms and integration reports.

Objective: Determine long-term precision and accuracy of the analytical method on various matrices.

Note: These data alone cannot be used to evaluate the precision and accuracy of individual samples.

Requirement Sources: SS03 Exhibit B § 2.8; SS03 Exhibit D § 2, 4; GR01 Exhibit D.

Evaluation: *The following items apply to both verification and validation:*

Item 6-a-2 Check that Forms 3E/3F are present and that MS/MSD analyses were performed at the required frequency.

- If forms are missing, issue a Non-Compliance Notification to request the missing data. Do

not qualify any data. Comment and assign reason code [801] to all applicable data.

- If MS/MSD analyses were not performed at the required frequency, comment and assign reason code [168] to all applicable data.

Check that the MS/MSD percent recoveries (%R) and relative percent differences (RPD) are within the following limits:

Table 3-3 MS/MSD Frequency and Control Limits

Spiking Compound	CLP-SOW %R Limits[RPD Limit]		SW-846 8080A* %R Limit	SW-846 8081 %R Limit
	Water	Soil	Water/Soil	
gamma-BHC (Lindane)	56-123[15]	46-127[50]	32-127 or lab limits	Not specified. Use lab limits.
Heptachlor	40-131[20]	35-130[31]	34-111 or lab limits	
Aldrin	40-120[22]	34-132[43]	42-122 or lab limits	
Dieldrin	52-126[18]	31-134[38]	36-146 or lab limits	
Endrin	56-121[21]	42-139[45]	30-147 or lab limits	
4,4'-DDT	38-127[27]	23-134[50]	25-160 or lab limits	
	Frequency: 1/20 samples		Frequency: 1/20 samples	Frequency: 1/20 samples

* SW-846 allows the laboratory to calculate their own recovery limits. Use laboratory limits if provided.

- No action is taken on MS/MSD or matrix duplicate data alone to qualify an entire batch. However, using informed professional judgment, the data Reviewer may use the MS/MSD results in conjunction with other QC criteria and determine the need for some qualification of data. At a minimum, comment and assign reason code [234] to all applicable data.

Evaluation: *The following item applies to validation only:*

Item 6-d-4 Calculate at least one %R and one RPD value in the MS/MSD data using the following calculations:

$$\% R = \frac{\text{Found_Value}}{\text{True_Value}} \times 100$$

$$RPD = \frac{|D_1 - D_2|}{\left(\frac{D_1 + D_2}{2}\right)} \times 100$$

where:

D_1 = MS Concentration.

D_2 = MSD Concentration.

- If the %R or % RPD values cannot be verified within 5%, cease validation until a new data package is received. Inspect all other SDP deliverables for other missing or incomplete information. Issue a Non-Conformance Notification for all noted deficiencies and assign reason code [803] to all applicable data. Return the SDP to ASD with the Non-Compliance Notification.

3.5. Sample Results

DRC Items 6-b-1 through 6-b-4, 6-c-6, 6-c-7, and 6-d-1 through 6-d-4

Review Items: Deliverable Section Number 6: Form 1D, Forms 6E/6F, Forms 7D/7E, Form 8D, Forms 10A/10B, COC record, extraction logs, sample chromatograms and integration reports, and GC/MS confirmation data (if applicable).

Objective: Evaluate qualitative criteria for compound identification to determine if false positives (reporting a compound present when it is not) or false negatives (not reporting a compound that is present) were reported.

Requirement Sources: SS03 Exhibit B § 2.8; SS03 Exhibit D § 1, 2; GR01 Exhibit D.

Evaluation: *The following items apply to both verification and validation:*

Item 6-b-1, 6-d-1, 6-d-2, 6-d-3, and 6-d-4:

Check that Form 1D is present for each sample including method QC.

- If not provided, issue a Non-Compliance Notification to request the missing data. Do not qualify any data. Comment and assign reason code [801] to all applicable data.

Check that significant figures and flagging protocol are as specified in CLP.

- If significant problems exist, issue a Non-Compliance Notification to request the missing data. Do not qualify the data. Comment and assign reason code [803] to all applicable data.

Evaluate Form 1D to ensure that no “B” qualifiers are present.

- If “B” qualifiers are present, proceed with the qualification specified under Blanks.

Ensure that blank contamination is addressed in the SDP Narrative.

- If not addressed, do not qualify the results. Comment and include the reason code [805].

Retention Time Windows

Item 6-c-6 and 6-c-7

Confirm positive results by reviewing Forms 10A/10B to ensure that all positive results were within the retention time windows (use initial calibration windows for CLP; daily calibration windows for SW-846).

- If the criteria for positive identification (i.e. peak within its window on both columns or any evident shifts explained) are met but the compound is reported as non-detected, the result may be a false negative. Use professional judgment either to quantitate and report the positive result or to reject [R 199] the non-detected result.
- If the criteria for positive identification (i.e. peak within its window on both columns or any evident shifts explained) are not met, use professional judgment to change the result to non-detected [U 199] at the MDL or reject [R 199] the positive result.

Evaluation: *The following items apply to validation only:*

Confirmation

Item 6-b-1 Verify the transcription of all results from the chromatogram and integration report to the Form 1D and Forms 10A/10B.

- If reviewed results are not transcribed accurately, issue a Non-Compliance Notification and assign reason code [803] to all applicable data.. Cease validation until a new data

package is received. Inspect all other SDP deliverables for missing data, incorporate any deficiencies in the Non-Compliance Report, and return the SDP to ASD.

Item 6-b-2 Verify that primary and secondary chromatograms are present for all samples analyzed by CLP and for those samples with positive results analyzed by SW-846.

- If confirmation data are not provided and a positive result (which may or may not have been reported) is evident in the primary data, reject **[R 145]** the result (which is either a reported positive result or a non-detected result).

Retention Time Windows

Items 6-b-2 and b-3:

Further review positive results by reviewing Forms 10A/10B against the sample chromatograms (6-b-2) and integration reports (6-b-3). For multi-component compounds, the retention times and relative peak height ratios or major peaks should be compared to the appropriate standard chromatograms.

- If the criteria for positive identification (i.e. peak within its window on both columns or any evident shifts explained) are met but the compound is reported as non-detected, the result may be a false negative. Use professional judgment either to quantitate and report the positive result or to reject **[R 199]** the non-detected result.
- If the criteria for positive identification (i.e. peak within its window on both columns or any evident shifts explained) are not met, use professional judgment to change the result to non-detected **[U 199]** at the MDL or reject **[R 199]** the positive result.

If retention time windows are not provided, evaluate the samples based upon the retention time shifts of the target compounds in the calibration standards, the retention time shifts of the surrogates in the calibration standards and samples, the abundance of peaks in the samples above the MDL, the number of target compounds under consideration, etc.

- Use professional judgment to qualify the data as valid or rejected **[R 199]**.

If multi-component target compounds exhibit marginal pattern-matching quality, professional judgment should be used to determine if this is due to environmental "weathering" (i.e., degradation of the earlier eluting peaks relative to the later eluting peaks).

- If the presence of a multi-component compound is strongly suggested, results should be reported as presumptively present **[NJ 199]**.

Cleanup

Verify that cleanup techniques were employed for samples with interferences present on the chromatography.

- If no cleanup techniques were employed do not qualify any data. Comment and assign reason code **[199]** to all applicable data.

Interference

The Reviewer should be aware of situations (e.g., high concentration samples preceding low concentration samples) when sample carry-over is a possibility and should use judgment to determine if carry-over has occurred.

- If interference/carry-over is causing identification problems of reported positive or non-detected target compounds, professional judgment should be used to evaluate the severity of the interference and to apply one of the following actions: estimate **[J 199]** the positive result, estimate **[UJ 199]** the non-detected result, reject **[R 199]** the positive result, or reject **[R 199]** the non-detected result.

- If the detection of a high level or multi-component target compound interferes with the detection of another target compound, use professional judgment to raise the MDL to the lower value of the two columns and report that MDL as either valid or estimated [**J 199**]. (This is most applicable when it is evident that the laboratory has performed similar action on other sample results.)

Gas Chromatography/Mass Spectrometry

Item 6-b-4 Verify that GC/MS confirmation was performed for pesticide concentrations exceeding 10 ng/uL (CLP only) in the sample extract.

- If not, comment and assign reason code [**199**] to all applicable data.

3.6. **Compound Quantitation and RDLs**

DRC Items 6-b-1, 6-b-3 and 6-b-5

Review Items: Deliverable Section Number 6: Form 1D, Forms 6E/6F, Form 8D, COC record, sample preparation/extraction logs, sample chromatograms and integration reports.

Objective: The objective is to ensure that the reported quantitation results and detection limits are accurate.

Requirement Sources: SS03 Exhibit B § 2.8; SS03 Exhibit C; SS03 Exhibit D § 2, 4; and GR01 Exhibit D.

Evaluation: *The following items apply to both verification and validation:*

Item 6-b-1 Using the Line Item Code from the COC record, ensure that the detection limits reported on Form 1D match the required detection limits (RDLs) listed in SSO3, Exhibit C.
Note: Dilutions, percent solids, and extraction steps will impact the final RDLs reported.

- If the detection limits are greater than the RDL, comment and qualify all non-detected results as rejected [**R 213**].

Item 6-b-5 Verify that B qualifiers are added to all positive sample results for compounds that are associated with contaminated blanks.

- If not, assign reason code [**803**] to all data that are missing the B qualifier. However, do not qualify the data.

Evaluate Form 1D to ensure that no “E” qualifiers are present. If “E” qualifiers are present, ensure that another Form 1D with a diluted sample analysis is present in the data package.

- If not, estimate [**J 148**] the positive “E” result. Ensure that required dilutions are addressed in the SDP Narrative. If not addressed, do not qualify the results. Comment and include the reason code [**805**].
- If the diluted sample analysis fails to keep the response of the major constituents in the upper half of the calibration range, use professional judgment to qualify the data. At a minimum, comment and assign reason code [**148**] to all applicable data.

Evaluation: *The following items apply to validation only:*

Item 6-b-3 Verify that responses for target compounds and standard peaks were measured consistently (i.e., all values were determined by either integrated areas or peak heights, not both).

- If the target compound and standard peaks were not measured consistently, issue a Non-Compliance Notification and assign reason code [**803**] to all applicable data.. Cease

validation until a new data package is received with consistently derived sample results. Inspect all other SDP deliverables for missing data, incorporate any deficiencies in the Non-Compliance Report, and return the SDP to ASD.

Calculations

Item 6-b-1 Compare integration reports, chromatograms, sample preparation/extraction logs, dilutions, and cleanups to the reported sample results.

- If significant problems exist, or if there are insufficient data to verify calculations, issue a Non-Compliance Notification to request clarification of the data or receipt of missing or additional data. Do not qualify the data. Comment and assign reason code [803] to all applicable data.

Examine the raw data to verify the correct calculation of one positive result per sample.

Note: If first-order linear regression was used for quantitation, sample concentration must be calculated from the equation of the line via a calculator. Follow the appropriate instructions for linear regression in the calculator literature.

Note: If second-order linear regression was used for quantitation, sample concentration must be calculated from the equation of the line provided by the laboratory.

- If the concentrations are not verified to within 5%, issue a Non-Compliance Notification and assign reason code [803] to all applicable data.. Cease validation until a new data package is received. Inspect all other SDP deliverables for missing data, incorporate any deficiencies in the Non-Compliance Report, and return the SDP to ASD.

Calculate using the following equations:

External Standard Technique

$$\frac{\text{ug}}{\text{Kg}} \text{ or } \frac{\text{ug}}{\text{L}} = \frac{A_x \times A \times V_t \times D}{A_s \times V_i \times ([V_s] \text{ or } [W \times P])}$$

where:

- A_x = Response for the analyte in the sample, using peak area or height
- A = Amount of standard injected, ng
- V_t = Volume of total extract, uL
- D = Dilution factor
- A_s = Response for external standard, using same units as A_x
- V_i = Volume of extract injected, uL
- V_s = Volume of water extracted or purged, mL
- W = Weight of soil extracted or purged, g
- P = Percent Solids/100

Internal Standard Technique

$$\frac{\text{ug}}{\text{Kg}} \text{ or } \frac{\text{ug}}{\text{L}} = \frac{A_x \times I_{is} \times D}{A_{is} \times RF \times ([V_s] \text{ or } [W \times P])}$$

where:

- A_x = Response for the analyte in the sample, using peak area or height
- I_{is} = Amount of internal standard added to volume purged or to extract, ng
- D = Dilution factor
- A_{is} = Response for the internal standard, using same units as A_x

RF = response factor for analyte, as determined below
 V_s = Volume of water extracted or purged, mL
 W = Weight of soil extracted or purged, g
 P = Percent Solids/100

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

where:

A_s = Response for the characteristic ion for the analyte to be measured, units area counts
 C_{is} = Concentration of the internal standard, ug/L
 A_{is} = Response for the characteristic ion for the internal standard, units area counts
 C_s = Concentration of the analyte to be measured, ug/L

3.7. Calibration

DRC Items 6-c-1, 6-c-2, and 6-c-8

Review Items: Deliverable Section Number 6: Forms 6D-J, Forms 7D/7E, sample and standard chromatograms and integration reports.

Objective: To ensure the instrument is capable of producing acceptable quantitative data.

Note: Initial calibration demonstrates that the instrument is capable of acceptable performance at the beginning of the analysis run. Continuing calibration verification documents satisfactory performance of the instrument over specific time periods during sample analysis.

Requirement Sources: SS03 Exhibit B § 2.8; SS03 Exhibit D § 2; GR01 Exhibit D.

Evaluation: *The following items apply to both verification and validation:*

Item 6-c-1

Resolution Check (CLP)

Use Form 6G to verify that the resolution criterion between two adjacent peaks for the required compounds in the Resolution Check Mixture is $\geq 60\%$.

- If not, quantitative and qualitative results may not be accurate. Estimate [J 170] detected target compounds that were not adequately resolved.
- Use professional judgment to reject [R 170] non-detects with retention times in the region of coelution, depending upon the extent of the problem.

Performance Evaluation Mixture (PEM)

Use Form 6H to verify that all peaks in all Performance Evaluation Mixture (PEM) analyses are $\geq 90\%$ resolved.

- If PEM resolution criteria are not met, quantitative and qualitative results may not be accurate. Estimate [J 170] detected target compounds that were not adequately resolved.
- Use professional judgment to reject [R 170] non-detects with retention times in the region of coelution, depending upon the extent of the problem.

Verify that the absolute retention times of each single component pesticide and surrogate in all PEM analyses are within the specific retention time windows.

- If not, use the guidance under Section 3.5, Item 6-c-6 to qualify the data.

Percent Breakdown

Verify that individual breakdowns for 4,4'-DDT and endrin meet the following criteria:

Table 3-4 Percent Breakdown Limits

Method	Compound	%Breakdown Limit
CLP	Endrin, 4,4'-DDT	20.0%
	Combined	30.0%
SW-846 8080A	Endrin, 4,4'-DDT	20.0%
SW-846 8081	Endrin, 4,4'-DDT	15.0%

If 4,4'-DDT breakdown exceeds criteria or is not performed qualify as follows:

- Estimate [J-147] positive results for 4,4'-DDT.
- If 4,4'-DDT was not detected but 4,4'-DDD and 4,4'-DDE were detected, reject [R-147] the non-detected result for 4,4'-DDT.
- Qualify as presumptively present at an estimated quantity [NJ-147] positive results for 4,4'-DDD and 4,4'-DDE.

If endrin breakdown exceeds criteria or is not performed qualify as follows:

- Estimate [J-147] positive results for endrin.
- If endrin was not detected but endrin aldehyde and endrin ketone were detected, reject [R-147] the non-detected result for endrin.
- Qualify as presumptively present at an estimated quantity [NJ-147] positive results for endrin aldehyde and endrin ketone.

If the combined 4,4'-DDT and endrin breakdown (CLP only) is >30.0%, consider the degree of individual breakdown of 4,4'-DDT and endrin and apply qualifiers as described above.

Initial Calibration

For SW-846, calibration factors (CFs) may be used for calculation of sample results if they meet the percent relative standard deviation (%RSD) limits in the table below. Otherwise, the laboratory may use a curve for calculation. For CLP, the CFs must be used for calculation and must meet the following limits (Form 6E):

Table 3-5 Initial Calibration Criteria

Method	Compound	# of Standards	Concentration	%RSD Limit
CLP	Alpha-BHC, delta-BHC	3	5.0 ng/mL	25.0%
	All other single-component compounds	3	5.0-50.0 ng/mL (depends on compound)	20.0%
SW-846 8080A	All target compounds	5	Low near but above established MDL; others should define the range of the detector used	20.0%
SW-846 8081	All target compounds (Aroclors 1016/1260 may be used to represent all Aroclors)	5	Low near but above established MDL; others should define the range of the detector used	20.0%

- If an inappropriate number of standards or inappropriate concentration levels are analyzed, use professional judgment to assess the impact on the data. At a minimum, comment and assign reason code [168] to all applicable data.

Percent Relative Standard Deviation

- Estimate [J 140] positive results and [UJ 140] non-detected results for those compounds whose %RSDs exceed the criteria in the associated initial calibration.

Calibration Curve

For the purposes of these guidelines, if a first-order linear regression is used rather than calibration factors, the correlation coefficient (r) for each compound should ≥ 0.995 .

- Estimate [J 140] positive results and [UJ 140] non-detected results for those compounds whose correlation coefficient was < 0.995 if first-order linear regression was used for quantitation.

For the purposes of these guidelines, if a second-order linear regression or a quadratic curve is used rather than calibration factors, verify that the required information is provided to accurately reproduce positive results.

- Estimate [J 140] positive results if the sample results cannot be reproduced using the second-order or quadratic equation provided for the initial calibration.

Item 6-c-2

Continuing Calibration

For SW-846, if CFs are used for calculation of sample results, they must be less than or equal to the percent difference (%D) limits in the table below. For CLP, the CFs must be used for calculation and must be less than or equal to the following limits (Forms 7D/7E):

Table 3-6 Continuing Calibration Criteria

Method	Standard	Frequency	Concentration	%D Limit
CLP	Alternate PEM/Individual Mix A and B	Every 12 hours and at the end of the analysis sequence	PEM has only one level; Individual A and B midpoint	25.0%
SW-846 8080A	All target compounds	Each working day, every 10 samples, and at the end of the analysis sequence	Mid-level	15.0%
SW-846 8081	All target compounds (Aroclors 1016/1260 may be used to represent all Aroclors; must inject others if found in samples)	Each working day, every 10 samples, and at the end of the analysis sequence	Low near but above established MDL; others should define the range of the detector used	15.0%

- If the continuing calibration frequency criteria are not met or if inappropriate concentration levels are analyzed, use professional judgment to assess the impact on the data. At a minimum, comment and assign reason code [168] to all applicable data.

Percent Difference

- Estimate [J 141] positive results and [UJ 141] non-detected results for those compounds whose %Ds exceed the criteria in the associated (bracketing) continuing calibrations.

Retention Time

Note: In addition to the criteria presented in Table 3-6 (above), the daily retention time windows must be met by each subsequent continuing calibration in a sequence.

Review Forms 7D/7E to ensure that the retention times of the associated continuing calibration fall within the established retention time windows.

- If they do not, use professional judgment to tentatively identify and estimate [NJ 199] the positive results for the affected compounds. (Further review of raw data precede action for validation. See below.)

Evaluation: *The following items apply to validation only:*

Item 6-c-8

Percent Breakdown

Verify at least one percent breakdown value:

$$4,4'\text{-DDT} = \frac{\text{Peak area (4,4'\text{-DDD} + 4,4'\text{-DDE})}}{\text{Peak area (4,4'\text{-DDD} + 4,4'\text{-DDE} + 4,4'\text{-DDT})}} \times 100$$

$$\text{Endrin} = \frac{\text{Peak area (endrin aldehyde + endrin ketone)}}{\text{Peak area (endrin aldehyde + endrin ketone + endrin)}} \times 100$$

$$\text{Combined \% Breakdown} = \% \text{ Breakdown } 4,4'\text{-DDT} + \% \text{ Breakdown Endrin}$$

Initial Calibration

Check the raw data and verify at least one CF per calibration standard. Recalculate at least one average CF and %RSD:

$$CF = \frac{\text{total area of peak}}{\text{nanograms injected}}$$

$$\% RSD = \frac{SD}{\bar{X}} \times 100$$

$$SD = \sqrt{\frac{\sum_{i=1}^n (X_i - \bar{X})^2}{(n-1)}}$$

where:

- X_i = Each individual value used to calculate the mean
- \bar{X} = The mean of initial calibration factors
- n = The total number of initial calibration factors

Calibration Curve

If first-order linear regression was used for quantitation, verify one correlation coefficient (r) following the appropriate instructions for linear regression in the calculator literature.

If second-order linear regression or quadratic curves were used for quantitation, verify that results are reproducible using the provided second-order equation.

Continuing Calibration

Recalculate at least one average CF and %D:

$$\% D = \frac{R_1 - R_2}{R_1} \times 100$$

where:

R_1 = Calibration factor from first analysis.

R_2 = Calibration factor from subsequent analysis.

- If the calculations for %D, CF, %RSD, or % Breakdown cannot be verified to within 5%, initiate a Non-Conformance Notification, cease validation until revised calculations are obtained. Inspect all other SDP deliverables for missing data, incorporate any deficiencies in the Non-Compliance Report, assign reason code [803] to all applicable data, and return the SDP to ASD.

Retention Time

- If continuing calibration retention times are not within their appropriate retention time windows, carefully examine the raw data for false positive or false negative results. Peaks outside the retention time window but shifted in the appropriate and magnitude (relative to that of the standard) may be considered acceptable. At a minimum, comment and assign reason code [804] to all applicable data. If definitive compound identification is not possible, qualify as addressed above under *Validation and Verification*.

3.8. Analytical Sequence (CLP)

DRC Item 6-c-3

Review Items: Deliverable Section 6: Form 8D.

Objective: Ensure calibration provides a sound, comparable analytical approach to initial calibration, continuing calibration, and instrument performance.

Requirement Sources: SS03 Exhibit B § 2.8; SS03 Exhibit D § 2; GR01 Exhibit D.

Evaluation: *The following items apply to both verification and validation:*

Item 6-c-3 The analytical calibration sequence for CLP must be as follows:

Table 3-7 Analytical Calibration Sequence For CLP

1	Resolution Check
2	PEM
3	Aroclor 1016/1260
4	Aroclor 1221
5	Aroclor 1232
6	Aroclor 1242
7	Aroclor 1248

	8	Aroclor 1254
	9	Toxaphene
	10	Low Point Standard A
	11	Low Point Standard B
	12	Midpoint Standard A
	13	Midpoint Standard B
	14	High Point Standard A
	15	High Point Standard B
	16	Instrument Blank
0 hour	17	PEM
	18	First sample
		Samples
12 hours		Last sample
		1st injection past 12 hours = Instrument Blank
		Individual Mix A
		Individual Mix B
12 hours		SAMPLES
		Last Sample
		1 st injection past 12 hours = Instrument Blank
		PEM
		etc.

Examine Form 8D to ensure that the analytical sequence is correct.

- If the sequence was not followed as required, determine the severity of the problem and its effect of the data using professional judgment. At a minimum, comment and assign reason code [168] to all applicable data.

3.9. Florisil Cartridge Check (CLP)

DRC Items 6-c-4 and 6-d-7

Review Items: Deliverable Section 6: Form 9A, Florisil data.

Objective: Ensure pesticide cleanup procedures remove matrix interferences from sample extracts prior to analysis.

Note: Florisil cartridge cleanup significantly reduces matrix interference caused by polar compounds. Pesticide cleanup procedures are checked by spiking the cleanup columns and cartridges and verifying the recoveries.

Requirement Sources: SS03 Exhibit B § 2.8; SS03 Exhibit D § 2; 4; GR01 Exhibit D.

Evaluation: *The following items apply to both verification and validation:*

Item 6-c-4 Ensure that all samples are accounted for on one of the Forms 9A

- If not all of the samples can be accounted for on one of the Forms 9A, comment and assign reason code [803].

Examine Form 9A to ensure that the recoveries are within the 80-120% recovery limits..

- If recoveries are outside the limits, determine the severity of the problem and its effect on the data using professional judgment. At a minimum, comment and assign reason code [211] to all applicable data.

Evaluation: *The following item applies to validation:*

Item 6-c-4 Examine Form 9A to ensure that the recoveries are within the 80-120% recovery limits.. If florisol recoveries are outside the limits, examine the raw data for the presence of polar interferences. Use their presence or absence for help in qualifying the data using professional judgment

- Low recoveries may result in the qualification of data as estimated [J 211]. High recoveries may result in the qualification of detected results [J 211].

Note: These items are used to assess the impact of low recoveries on the Form 9B. However, they are not solely used to qualify data.

Item 6-d-7 Recalculate 10% of the percent recoveries on Form 9A. Check transcription of the percent recoveries.

- If the recoveries are not calculated correctly assign reason code [803] to all associated data. However, do not qualify the data.

3.10. Gel Permeation Chromatography (GPC) [CLP]

DRC Items 6-c-5, and 6-d-5

Review Items: Deliverable Section Number 6: Form 9B, GPC data, GPC run logs.

Objective: Ensure pesticide cleanup procedures remove matrix interferences from sample extracts prior to analysis.

Note: GPC removes high molecular weight contaminants.

Requirement Sources: SS03 Exhibit B § 2.8; SS03 Exhibit D § 2; 4; GR01 Exhibit D.

Evaluation: *The following items apply to both verification and validation:*

Item 6-c-5 Ensure that all samples are accounted for on one of the Forms 9B.

- If not all of the samples can be accounted for on one of the Forms 9A, comment and assign reason code [804].

Examine Form 9B to ensure that the recoveries are within the 80-110% recovery limits.

- If high recovery is reported, estimate [J 199] associated positive results for that compound.
- If zero recovery is reported, [R 199] associated non-detected results for that compound.
- If low recoveries are reported, determine the severity of the problem and its effect of the data using professional judgment. At a minimum, comment and assign reason code [211] to all applicable data.

Evaluation: *The following item applies to validation only:*

Item 6-d-5 Recalculate 10% of the percent recoveries on Form 9B. Check transcription of the percent recoveries. In the raw data, check that the Aroclor patterns are similar to those of previous Aroclor standards.

- If the recoveries are not calculated correctly or if the Aroclor patterns are not similar to other Aroclor patterns, assign the reason code [804] to all applicable data points. However, do not qualify the data.
- If GPC recoveries are outside the limits, examine the UV traces, chromatograms, and

integration reports for the presence of high molecular weight compounds. Use their presence or absence for help in qualifying the data. Low recoveries may result in the qualification of data as estimated [J 211]. High recoveries may result in the qualification of detected results [J 211]. These items are used to assess the impact of low recoveries on the Form 9B. However, they are not solely used to qualify data.

Item 6-d-6 Verify that the absolute retention times of each single component pesticide and surrogate in all PEM analyses are within the specific retention time windows.

- If not, use the guidance under Compound Identification to qualify the data.

3.11. Blanks

DRC Items 6-a-3, 6-d-1, 6-d-2, and 6-d-3

Review Items: Deliverable Section Number 6: Form 4C, Instrument Blank, Method Blank, and Sulfur Cleanup Blank Forms 1D, chromatograms and integration reports.

Objective: Determine the existence and magnitude of blank contamination problems.

Note: The criteria for evaluation of laboratory blanks apply to method, instrument, and sulfur cleanup blanks associated with the samples. If problems with any blank exist, all data associated with the blank must be carefully evaluated to determine whether or not there is an inherent variability in the data or if the problem is an isolated occurrence not affecting other data.

Requirement Sources: SS03 Exhibit B § 2.8; SS03 Exhibit D § 2; 4; GR01 Exhibit D.

Evaluation: *The following items apply to both verification and validation:*

Item 6-a-3 Verify that Method Blank Summary Forms (4C) are present.

- If not provided, issue a Non-Compliance Notification to request the missing data. Do not qualify the data. Comment and assign reason code [801] to all applicable data.

Items 6-d-1, 6-d-2 and 6-d-3:

The following table summarizes blank criteria:

Table 3-8 Blank Criteria

Method	Types	Frequency	Criteria
CLP	Method	1/20 samples of similar matrix in each sample delivery group or whenever a sample extraction procedure is performed.	No contaminants should be present in the blanks. Method blanks should be analyzed on each GC system used to analyze that set of associated samples.
	Instrument	Once at least every 12 hours and immediately prior to the analysis of each continuing calibration (either the PEM or Ind. A/B). Following sample analysis which contain an analyte at a high concentration.	The concentration of each target compound in the instrument blank must be less than 0.5 times the RDL for that compound. (For comparing the results, assume that the material in the instrument blank resulted from the extraction of 1 L of water.)
	Sulfur Cleanup	Modified form of a method blank which has undergone sulfur cleanup. One per SDG (if all underwent sulfur cleanup, the method blank	The concentration of each target compound in the instrument blank must be less the RDL for that compound. The method blanks should be analyzed on each GC

Table 3-8 Blank Criteria (continued)

Method	Types	Frequency	Criteria
		satisfies the sulfur blank requirement) or subset of an SDG which has undergone sulfur cleanup.	system used to analyze that set of associated samples.
SW-846 8080A	Method	A method blank should be extracted with each extraction batch, when there is a change in reagents, and following any concentrated sample that has saturated ions from a compound.	The blank samples should be carried through all stages of the sample preparation and measurement steps (i.e., the method blank should be analyzed on the same instrument as the samples).
SW-846 8081	Method	A method blank should be extracted with each extraction batch, when there is a change in reagents, and following any concentrated sample that has saturated ions from a compound.	The blank samples should be carried through all stages of the sample preparation and measurement steps (i.e., the method blank should be analyzed on the same instrument as the samples).

Determine if blanks were analyzed at the appropriate frequency.

- If the proper blanks were not analyzed at the appropriate frequency, determine the severity of the problem and its effect of the data using professional judgment. At a minimum, comment and assign reason code [168] to all applicable data.

Determine if target compounds were found in the blanks. If more than one blank is associated with a sample, qualification should be based upon comparison of the blank with the highest level of contamination.

- If a target compound is found at any concentration in the blanks but not in the samples, no action is taken.

When a target compound is found in the blanks at any concentration and is also found in the sample, apply qualification using the following criteria:

- If the sample concentration is less than 5 times the blank concentration and less than or equal to the MDL: Report the RDL followed by [U]. Assign reason code [149].
- If the sample concentration is less than or equal to 5 times the blank concentration and greater than the RDL: Report the value followed by [U]. Assign reason code [149].
- If the sample concentration is greater than 5 times the blank concentration and greater than the RDL: Report the value unqualified.
- If an associated method blank exhibits gross contamination, reject [R 149] positive results for the affected compounds. The Functional Guidelines define gross contamination as saturated peaks. Professional judgment must be used to assess the impact the contamination has on the associated samples and which compounds are considered affected.
- If an associated method blank was not analyzed for the samples, estimate [J 149] positive results.

Evaluation: *The following item applies to validation only:*

Items 6-d-2 and 6-d-3:

Recalculate one positive result per blank. Review the chromatograms and integration reports to evaluate blank results.

Note: The Reviewer must consider the weights, volumes, percent solids, and dilution factors when applying the 5x rule. These factors must be accounted for so that an actual comparison of the contamination is made. The Reviewer should be particularly aware of sample results which undiluted exceed the action level, but fall within the action level as a result of the subsequent dilution.

3.12. **Sample Preparation Raw Data**

DRC Items 6-e-1 through 6-e-3

Review Items: Deliverable Section Number 6-e.

Objective: To check that sample preparation raw data deliverable requirements have been met and that raw data are present in a form suitable for validation and retention.

Requirement Sources: GR01 Exhibit B § 4.11, GR01 Exhibit F § 4, SS03 Exhibit B Section 2, and requirements of base methods cited in SS03 Exhibit D Section 2.

Evaluation: *The following items apply to validation activities only:*

Item 6-e-1 Check that preparation raw data (benchsheets and/or preparation logs) are included for all analyses performed and include the following:

- ◇ Analytical Batch identifier
- ◇ Date of preparation
- ◇ Identifiers for all samples, sample duplicates, and spikes
- ◇ Identifiers for at least one preparation blank and lab control sample
- ◇ For aqueous samples initial and final volumes for all samples and QC samples
- ◇ For solids and non-aqueous liquids reported by weight, initial weights and final volumes for all samples and QC samples
- ◇ For samples reported by weight, balance identifiers with dates of use.
- ◇ Dated signatures for at least one analyst and one reviewer

Check this item as complete if raw data were sufficient to perform calculations for all previous items.

- Omissions or errors which do not affect your ability to review the data shall be documented and with reason code [804].
- Other omissions or errors shall be documented for inclusion in a Non-Compliance Notification. Inspect all other SDP deliverables for any other missing or revised information needed for data assessment and return the SDP

to ASD with Non-Compliance Notification. Assign reason code [803] to all applicable data.

Item 6-e-2 and 6-e-3:

Verify that instrument run logs are available for all analytical sequences.

- Omissions or errors which do not affect your ability to review the data shall be documented and with reason code [804].
- Other omissions or errors shall be documented for inclusion in a Non-Compliance Notification. Inspect all other SDP deliverables for any other missing or revised information needed for data assessment and return the SDP to ASD with Non-Compliance Notification. Assign reason code [803] to all applicable data.

3.13. **Electronic Data Deliverable (EDD)**

DRC Items 7-a through 7-c

Review Items: Deliverable Section Number 10.

Objective: To ensure that electronically-reported data are accurate.

Requirement Sources: GR01 Exhibit B 4, and SS05 Exhibit B §2.12.

Evaluation: *The following items apply to both verification and validation:*

Items 7-a through 7-c:

See DA-GR01 for evaluation.

4. DATA QUALITY ASSESSMENT REPORT PREPARATION

Prepare a Data Quality Assessment Report in accordance with the criteria established in the General Data Assessment guidelines presented in GR01. A Data Quality Assessment Report template for DA-SS03 is presented as Attachment 1.

5. REFERENCES

- *USEPA Contract Laboratory Program National Functional Guidelines for Organic Data Review*, February 1994.
- *Reason Codes for Data Assessment*, Analytical Services Document
- *Statement of Work for Analytical Measurements, General Laboratory Requirements, Module GR01-B.1*, June 2, 1997.
- *Statement of Work for Analytical Measurements, PCB/Pesticides, Module SS03-B*, March 28, 1997.

6. REVISION HISTORY

- The first draft of DA-SS03 was prepared by QuantaLex Inc.
- Final drafting of DA-SS03-v1 was completed by Ed Brovsky of Kaiser-Hill Analytical Services on January 14, 1998. This revision included: formatting for consistency with DA-GR01-v1, formatting to separate evaluation and action criteria, inclusion of new and revised reason codes, corrections and additions of evaluation and action criteria, and general editing.

**Attachment 1: Data Quality Assessment Report Template
SS03**

**Data Quality Assessment Report
Rocky Flats Environmental Technology Site**

RIN Number	Analytical Method/PSA Line Item	Validation Level
Analytical Laboratory	Assessment Performed by	Number of Samples/ Matrix.

Sample Numbers: _____

Quality Control Element	Reviewed	Non-Compliance Identified
General (Cover Page, Table of Contents, DRC Checklist, Narrative)		
Chain of Custody		
Holding Times		
Sample Preservation		
Surrogate Recovery		
MS/MSD Recovery		
Sample Results		
Calibration		
Analytical Sequence (CLP)		
Florisil Cartridge Check (CLP)		
Gel Permeation Chromatography (CLP)		
Blanks		
Preparation Standards		
Other QC		

- Y Item was reviewed or non-compliance was identified
- N Item was not reviewed or non-compliance was not identified
- N/A Item is not applicable to the Line Item

Action Items:

Comments:

Verification/Validation Signature _____
Reviewer Signature _____
(*Validation Only*)

Date: _____
Date: _____