# XI. PERFORMANCE EVALUATION SAMPLES/ACCURACY CHECK

## A. OBJECTIVE

Performance Evaluation Samples (PESs) are analyzed to provide information on the overall accuracy and bias of the analytical method and on laboratory performance. PESs are evaluated for false negatives, false positives, and inaccurate target analyte quantitation. In general, the most serious problem a PES can expose is the failure of the laboratory to properly detect and identify a PES analyte. This failure is known as a false negative. False negatives significantly increase the "uncertainty" of any site decisions concerning the "cleanliness" or contamination level of a site. Also, the analysis of PE samples can reveal the laboratory's erroneous detection of unspiked analytes (false positives). False positives should always be evaluated in conjunction with blank data to determine the probable source(s) of contamination.

Finally, the PES provides information on the magnitude and direction of quantitative bias for the entire laboratory method, including sample preparation (extraction and cleanup) and analysis (chromatography and calibration). Sample data that are biased high or low can potentially impact site decisions, especially when sample data have target analyte concentrations at or near action levels.

Ideally, a PES is comprised of the same matrix as the field samples being evaluated. However, for some matrices (i.e., soil) PESs are not available. In these situations, a PES of another matrix (i.e., water) may be analyzed with the field samples to assess laboratory performance on the "analysis" portion, even though laboratory performance on the "sample preparation" portion cannot be assessed. The validator should use professional judgment when evaluating samples of one matrix using PES data from another matrix.

## B. CRITERIA

### 1. Zero Blind Performance Evaluation Samples

A Zero Blind PES is a quality control sample when the composition and concentration are known to the laboratory.

A Laboratory Control Sample (LCS) is a Zero Blind PES sample which is often used by the laboratory as an internal quality control check of analytical accuracy and method bias.

a. An LCS is required by some EPA methods and certain CLP SOWs. The frequency, concentration, acceptance criteria, and corrective actions for LCS analysis should be stated in the method, Sampling and Analysis Plan (SAP), or the Quality Assurance Project Plan (QAPP) and should support the DQOs of the project. The LCS should be prepared in the proper matrix for each parameter at the concentration level and frequency required in the EPA-approved project SAP, QAPP, and/or method. The LCS must contain one or more target analytes. The LCS must be prepared and analyzed concurrently with field samples contained in the sample delivery group (SDG).

b. The percent recoveries for LCS analytes must be within the method QC acceptance criteria.

c. Surrogate analytes for the LCS must meet validation criteria as per Section VI of this document.

**2. Single Blind Performance Evaluation Samples**

A Single Blind PES is a quality control sample whose composition and concentration is not known to the laboratory, but the sample is identified to the laboratory as a PES.

A Single Blind PES may be submitted with a sample delivery group to assess method bias, laboratory performance and to evaluate data quality. A Single Blind PES may also be submitted for analysis prior to sample shipment to prequalify a laboratory for a specific matrix and/or parameter.

a. EPA Region I Performance Evaluation Program Guidance, July 1996, Revision, requires that a Single Blind or Double Blind PES be sent with each sample delivery group (20 samples or less) that is sent to a laboratory. A PES is required for each matrix, parameter, and concentration level unless an EPA and/or non-EPA PES does not currently exist for that particular matrix, parameter, and concentration level.

The PE Program applies to the Superfund program including EPA Fund-lead and PRP/Federal Facility Oversight Projects. In addition, the PE Program applies to Fund-lead projects performed by States under Cooperative Agreements and other Federal Agencies under Interagency Agreements. The PE Program also applies to Non-Fund-lead Superfund projects undertaken by potentially responsible parties. The PE Program also applies to Non-Superfund Programs.

EPA-provided PE samples are available for certain categories of Superfund work as specified in the EPA Region I Performance Evaluation Program Guidance, July 1996, Revision. The EPA Performance Evaluation Chemist provides the current list of EPA-provided PE samples upon request. For those categories of Superfund work that do not have access to EPA-provided PE samples and for all Non-Superfund program work scientifically defensible PE samples should be obtained from commercial vendors.

b. Acceptance criteria for EPA PESs are statistically-derived by the Analytical Operations Center under the QATS contract. Tabulated report forms for EPA PESs must be submitted to the Region I OEME-QA Unit for scoring at the time of data validation, in accordance with the EPA Region I Performance Evaluation Program Guidance, July 1996, Revision. This guidance is found in Attachment H of the Part I - Data Validation Manual: The Data Quality System.

c. True values and QC acceptance criteria for all non-EPA PESs should be provided by the manufacturer and these acceptance criteria must be fully documented and must be scientifically defensible.

d. Surrogate analytes for EPA and non-EPA Single Blind PE samples must meet validation criteria as per Section VI of this document.

**3. Double Blind Performance Evaluation Samples**

A Double Blind PES is a quality control sample whose composition and concentration is not known to the laboratory and the sample is **not** identifiable as a PES nor is it identified to the laboratory as a PES.

A Double Blind PES may be submitted with a sample delivery group in lieu of a Single Blind PES, to assess method bias, laboratory performance and to evaluate data quality.

a. The use of Double Blind PESs is dictated by the project DQOs and should be documented in the EPA-approved SAP and/or QAPP.

b. True values and acceptance criteria for Double Blind PESs must be fully documented and must be scientifically defensible.

c. Surrogate analytes for EPA and non-EPA Double Blind PE samples must meet validation criteria as per Section VI of this document.

## C. EVALUATION/ D. ACTION

| C. EVALUATION | D. ACTION |
|---|---|
| | All potential impacts on the sample data resulting from performance evaluation sample anomalies should be noted in the Data Validation Memorandum. The validator should also document and justify all technical decisions made based on professional judgment in the Data Validation Memorandum. |
| **1. Zero Blind PES - LCS** | **1. Zero Blind PES - LCS** |
| a. Verify that an appropriate LCS sample (correct parameter, concentration level, target analytes, and matrix) was prepared and analyzed at the required frequency for each sample delivery group in accordance with the EPA approved project SAP, QAPP, and/or method. | a. If an appropriate LCS was not analyzed at the required frequency for the correct parameters, concentration levels, target analytes, or matrices, then the validator should use professional judgment to determine if the sample data should be qualified or rejected. |
| b. Verify that the required LCS results are provided for each sample delivery group. | b. If the required LCS results were not submitted for each sample delivery group, then the validator should contact the laboratory to obtain raw data and/or tabulated results. |

| C. EVALUATION | D. ACTION |
|---|---|
| 1. c. Verify that the reported recoveries for all LCS spike analytes are within the method QC acceptance criteria. | 1. c. Sample data should be qualified based on the number and type of analytes that recover outside the method QC acceptance criteria and based on the degree that analyte recoveries exceed the criteria.<br><br>i. If any of the LCS analyte recoveries are outside the method QC acceptance criteria, then the LCS results should be used to qualify sample data for the specific analytes that are included in the LCS solution. Professional judgment should be used to qualify sample data for non-LCS analytes, taking into account the analyte's chemical class, analyte recovery efficiency, and any analytical problems historically associated with the analyte or that were encountered by the laboratory.<br><br>ii. If an LCS analyte recovery is greater than the upper limit of the method QC acceptance criteria, then the validator should:<br><br>- Estimate (J) the affected analyte when detected in any sample associated with that LCS to indicate potential high bias.<br><br>- Accept the quantitation limit of the affected analyte in any sample associated with that LCS.<br><br>iii. If more than half of the LCS analyte recoveries are greater than the upper limit of the method QC acceptance criteria, then the validator should:<br><br>- Estimate (J) all positive detects in all samples associated with that LCS to indicate potential high bias.<br><br>- Accept all quantitation limits for non-detects in all samples associated with that LCS. |

| C. EVALUATION | D. ACTION |
|---|---|
| 1. c. Continued from above. | 1. c. iv. If an LCS analyte recovery is less than the lower limit of the method QC acceptance criteria but greater than or equal to 10%, then the validator should:<br><br>- Estimate (J) the affected analyte when detected in any sample associated with that LCS to indicate potential low bias.<br><br>- Estimate (UJ) the quantitation limit of the affected analyte in any sample associated with that LCS to indicate potential low bias.<br><br>v. If more than half of the LCS analyte recoveries are less than the lower limit of the method QC acceptance criteria but greater than or equal to 10%, then the validator should:<br><br>- Estimate (J) all positive detects in all samples associated with that LCS to indicate potential low bias.<br><br>- Estimate (UJ) all quantitation limits for non-detects in all samples associated with that LCS to indicate potential low bias.<br><br>vi. If an LCS analyte recovery is less than 10%, then the validator should:<br><br>- Estimate (J) the affected analyte when detected in any sample associated with that LCS to indicate potential low bias.<br><br>- Reject (R) the quantitation limit of the affected analyte in any samples associated with that LCS to indicate that the data are unusable due to the possibility of false negatives. |

| C. EVALUATION | D. ACTION |
|---|---|
| 1. c. Continued from above | 1. c. vii. If more than half of the LCS analyte recoveries are less than 10%, then the validator should:<br><br>- Estimate (J) all positive detects in all samples associated with that LCS to indicate potential low bias.<br><br>- Reject (R) quantitation limits for all non-detects in all samples associated with that LCS to indicate that the data are unusable due to the possibility of false negatives.<br><br>viii. If more than half of the LCS analyte recoveries are outside the method QC acceptance limits in one LCS, where some recoveries are low and some recoveries are high, then the validator should use professional judgment to qualify or reject a particular analyte, class of analytes, or the entire fraction for samples associated with that LCS.<br><br>ix. Based upon the number and type of analytes misquantified and a review of the project DQOs, the validator should use professional judgment to determine if the data set for an entire fraction or parameter is unusable and, therefore, should be rejected. Rejected data should be returned to the laboratory and payment denied. See Attachment I of Part I - Data Validation Manual: The Data Quality System. |
| d. Evaluate the surrogate analytes for the LCS. | d. Action on non-compliant surrogate recoveries should follow the guidance provided in Section VI. Professional judgment should be used to evaluate the impact that non-compliant LCS surrogate recoveries have on the sample data. |

| C. EVALUATION | D. ACTION |
|---|---|
| *1. e. Check and recalculate the percent recovery for at least one analyte per LCS fraction. Verify that the recalculated value agrees within ±10% of the reported result. | 1. e. If any transcription and/or calculation errors are detected, perform a more comprehensive review to determine the magnitude of the problem. If the problem is extensive, then the validator should have the laboratory requantitate and resubmit all corrected raw data and forms. If a discrepancy remains unresolved, the validator must use professional judgment to decide which value is more accurate. Under these circumstances, the validator may determine that the sample data should be qualified or rejected. A discussion of the rationale for data qualification and the qualifiers used should be documented in the Data Validation Memorandum. |
| **2. Single Blind <u>and</u> Double Blind PESs**<br><br>a. Verify that an appropriate Single Blind or Double Blind PES (correct parameter, concentration level, target analytes, and matrix) was analyzed at the required frequency for each sample delivery group in accordance with Region I PE policy and/or the EPA approved SAP and/or QAPP.<br><br>b. Verify that Single Blind PES results are provided for each sample delivery group in accordance with Region I PE policy. The PE policy is found in Attachment H of Part I - Data Validation Manual: The Data Quality System.<br><br>c. **EPA PESs**<br><br>If the PES was supplied and scored by Region I OEME-QA, then the Region I PES Score Report must be evaluated to determine how many of the analytes met or exceeded PES acceptance criteria. | **2. Single Blind <u>and</u> Double Blind PESs**<br><br>a. If a required Single Blind or Double Blind PES was not analyzed at the required frequency for the correct parameters, concentration levels, target analytes, or matrices, then the validator should use professional judgment to determine if the sample data should be qualified or rejected.<br><br>b. If the PES results were not submitted for each sample delivery group, then the validator should contact the laboratory to obtain raw data and/or tabulated results. If a PES was not submitted to the laboratory by the sampler, then the validator should contact the sampler to confirm the PES omission and document that fact on the worksheet and discuss the impact of the omission on the results in the Data Validation Memorandum.<br><br>c. **EPA PESs**<br><br>Note: PES results should not be qualified based on QC sample data and should not be reported on the Data Summary Table. Rather, PES results should be discussed in the Data Validation Memorandum or Tier I Validation Cover Letter and PES Score Reports should be attached as supporting documentation. |

| C. EVALUATION | D. ACTION |
|---|---|
| 2. c. Continued from above. | 2. c. Continued from above. |
| • Evaluate the "PES ANALYTES MISSED" to assess the potential for low bias and false negative sample results. | • Sample data should be qualified based on the number and type of "PES ANALYTES MISSED" identified on the PES Score Report.<br><br>i. If a PES analyte is not identified in the PES, then the validator should:<br><br>- Estimate (J) the affected analyte when detected in any sample associated with that PES to indicate potential low bias.<br><br>- Reject (R) the quantitation limit of the affected analyte in any sample associated with that PES to indicate that the data are unusable due to the possibility of false negatives.<br><br>ii. Based upon the chemical class, the number of analytes that were not identified, and a review of the project DQOs, the validator should use professional judgment to determine if the data set for an entire fraction or parameter is unusable and, therefore, should be rejected. Rejected data should be returned to the laboratory and payment denied. (See Attachment I of Part I - Data Validation Manual: The Data Quality System.) |
| • Evaluate "PES CONTAMINANTS" in conjunction with blank data to asses the potential for high bias and false positive sample results. | • Sample data should not be qualified based on the number and type of "PES CONTAMINANTS" identified on the PES Score Report <u>alone</u>.<br><br>i. If a TCL contaminant is detected in the PES and is also found in a blank, then the validator should evaluate and qualify sample data based upon blank contamination in accordance with Section V.<br><br>ii. If a TCL contaminant is detected in the PES but is not present in any blank, then that interference is specific to the PES and does not impact sample data. |

| C. EVALUATION | D. ACTION |
|---|---|
| 2. c. Continued from above.<br><br>● Evaluate "PES ANALYTES REPORTED" that were misquantified to assess the potential for high and/or low bias in sample data. | 2. c. Continued from above.<br><br>● Sample data should be qualified based on the number and type of misquantified (Action High/Action Low "PES ANALYTES REPORTED") identified on the PES Score Report. **Sample data should not be qualified based on "Warning Low/Warning High" scores for "PES ANALYTES REPORTED".**<br><br>i. If any of the PES analytes do not meet PES acceptance criteria, then the PES results should be used to qualify sample data for the specific analytes that are included in the PES sample. Professional judgment should be used to qualify sample data for non-PES analytes taking into account the analyte's chemical class, analyte recovery efficiency, and analytical problems historically associated with the analyte or that were encountered by the laboratory.<br><br>ii. If a PES analyte is scored in the "Action High" category, then the validator should:<br><br>- Estimate (J) the affected analyte when detected in any sample associated with that PES to indicate potential high bias.<br><br>- Accept the quantitation limit of the affected analyte in any sample associated with that PES.<br><br>iii. If more than half of the PES analytes are scored in the "Action High" category, then the validator should:<br><br>- Estimate (J) <u>all</u> positive detects in all samples associated with that PES to indicate potential high bias.<br><br>- Accept <u>all</u> quantitation limits for non-detects in all samples associated with that PES. |

| C. EVALUATION | D. ACTION |
|---|---|
| 2. c. Continued from above. | 2. c. iv. If a PES analyte is scored in the "Action Low" category, then the validator should:<br><br>- Estimate (J) the affected analyte when detected in any sample associated with that PES to indicate potential low bias.<br><br>- Reject (R) the quantitation limit of the affected analyte in any sample associated with that PES to indicate that data are unusable due to the possibility of false negatives.<br><br>v. If more than half of the PES analytes are scored in the "Action Low" category, then the validator should:<br><br>- Estimate (J) <u>all</u> positive detects in all samples associated with that PES to indicate potential low bias.<br><br>- Reject (R) <u>all</u> quantitation limits for non-detects in all samples associated with that PES to indicate that data are unusable due to the possibility of false negatives.<br><br>vi. If more than half of the PES analytes are scored in the "Action" levels in one PES, where some recoveries are low and some recoveries are high, then the validator should use professional judgment to qualify or reject a particular analyte, class of analytes, or the entire fraction for samples associated with that PES.<br><br>vii. Based upon the number and type of analytes misquantified, and a review of the project DQOs, the validator should use professional judgment to determine if the data set for an entire fraction or parameter is unusable and, therefore, should be rejected. Rejected data should be returned to the laboratory and payment denied. (See Attachment I of Part I - Data Validation Manual: The Data Quality System.) |

| C. EVALUATION | D. ACTION |
|---|---|
| 2. c. Continued from above. | 2. c. Continued from above. |
| • Evaluate the surrogate analytes for the EPA PES. | • Action on non-compliant surrogate recoveries should follow the guidance provided in Section VI. Professional judgment should be used to evaluate the impact that a non-compliant EPA PES surrogate recoveries would have on the sample data. |
| d. **Non-EPA PESs**<br><br>If the PES was obtained from a source other than Region I OEME-QA, then the validator should use the vendor's criteria to evaluate the PES results. Confirm that PES acceptance criteria are fully documented and scientifically defensible. | d. **Non-EPA PESs**<br><br>If the non-EPA PES acceptance criteria are not fully documented and/or scientifically defensible, then the validator should use professional judgment to qualify or reject the sample data. |
| • Evaluate the "PES ANALYTES MISSED" to assess the potential for low bias and false negative sample results. | • Sample data should be qualified based on the number and type of "PES ANALYTES MISSED" identified from the vendor's acceptance criteria.<br><br>i. If a PES analyte is not identified in the PES, then the validator should:<br><br>- Estimate (J) the affected analyte when detected in any sample associated with that PES to indicate potential low bias.<br><br>- Reject (R) the quantitation limit of the affected analyte in any sample associated with that PES to indicate that the data are unusable due to the possibility of false negatives.<br><br>ii. Based upon the chemical class, the number of analytes that were not identified, and a review of the project DQOs, the validator should use professional judgment to determine if the data set for an entire fraction or parameter is unusable and, therefore, should be rejected. Rejected data should be returned to the laboratory and payment denied. (See Attachment I of Part I - Data Validation Manual: The Data Quality System.) |

| C. EVALUATION | D. ACTION |
|---|---|
| 2. d. Continued from above. | 2. d. Continued from above. |
| • Evaluate "PES CONTAMINANTS" in conjunction with blank data to assess the potential for high bias and false positive sample results. | • Sample data should not be qualified based on the number and type of "PES CONTAMINANTS" identified from the vendor's acceptance criteria alone.<br><br>i. If PES CONTAMINANTS are detected in the PES and is also found in a blank, then the validator should evaluate and qualify sample data based upon blank contamination in accordance with Section V.<br><br>ii. If PES CONTAMINANTS are detected in the PES but is not present in any blank, then that interference is specific to the PES and does not impact sample data. |
| • Evaluate "PES ANALYTES REPORTED" that were misquantified to assess the potential for high and/or low bias in sample results. | • Sample data should be qualified based on the number and type of misquantified "PES ANALYTES REPORTED" identified from the vendor's acceptance criteria.<br><br>i. If any of the PES analytes do not meet acceptance criteria, then the validator should use the PES results to qualify sample data for the specific analytes that are included in the PES sample. Professional judgment should be used to qualify sample data for non-PES analytes, taking into account the analyte's chemical class, analyte recovery efficiency, and analytical problems associated with the analyte either historically or that were encountered by the laboratory. |

<table>
<tr><th>C. EVALUATION</th><th>D. ACTION</th></tr>
<tr><td>2. d. Continued from above.</td><td>2. d. Continued from above.<br><br>ii. If a PES analyte recovery is outside the upper limit of the vendor's documented acceptance limits, then the validator should:<br><br>- Estimate (J) the affected analyte when detected in any sample associated with that PES to indicate potential high bias.<br><br>- Accept the quantitation limit of the affected analyte in any sample associated with that PES.<br><br>(Note: The validator should confirm that the vendor's acceptance limits are calculated as plus and minus three standard deviations from the mean, similar to EPA-PES "Action Limits".)<br><br>iii. If more than half of the PES analyte recoveries are outside the upper limit of the vendor's documented acceptance limits (See note above, Section 2.d.ii), then the validator should:<br><br>- Estimate (J) <u>all</u> positive detects in all samples associated with that PES to indicate potential high bias.<br><br>- Accept <u>all</u> quantitation limits for non-detects in all samples associated with that PES.</td></tr>
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| C. EVALUATION | D. ACTION |
|---|---|
| 2. d. Continued from above. | 2. d. Continued from above.<br><br>iv. If a PES analyte recovery is outside the lower limit of the vendor's documented acceptance limits (See note above, Section 2.d.ii), then the validator should:<br><br>- Estimate (J) the affected analyte when detected in any sample associated with that PES to indicate potential low bias.<br><br>- Reject (R) the quantitation limit of the affected analyte in any sample associated with that PES to indicate that the data are unusable due to the possibility of false negatives.<br><br>v. If more than half of the PES analyte recoveries are outside the lower limit of the vendor's documented acceptance limits (See note above, Section 2.d.ii), then the validator should:<br><br>- Estimate (J) <u>all</u> positive detects in all samples associated with that PES to indicate potential low bias.<br><br>- Reject (R) the quantitation limits for <u>all</u> non-detects in all samples associated with that PES to indicate that the data are unusable due to the possibility of false negatives. |

| C. EVALUATION | D. ACTION |
|---|---|
| 2. d. Continued from above. | 2. d. Continued from above<br><br>vi. If more than half of the PES analyte recoveries are outside the vendor's documented acceptance limits in one PES (See note above, Section 2.d.ii), where some recoveries are low and some recoveries are high, then the validator should use professional judgment to qualify or reject a particular analyte, class of analytes or the entire fraction for samples associated with that PES.<br><br>vii. Based upon the number and type of analytes misquantified and a review of the project DQOs, the validator should use professional judgment to determine if the data set for an entire fraction or parameter is unusable and, therefore, should be rejected. Rejected data should be returned to the laboratory and payment denied. (See Attachment I of Part I - Data Validation Manual: The Data Quality System.) |
| • Evaluate surrogate analytes for the non-EPA PES. | • Action on non-compliant surrogate recoveries should follow the guidance provided in Section VI. Professional judgment should be used to evaluate the impact that non-compliant non-EPA PES surrogate recoveries would have on the sample data. |
| * e. Determine what percentage of PES analytes were below or above PES acceptance criteria. | e. If more than half of the PES analytes are high or low, then the validator should check the raw data and/or contact the laboratory to verify that the PE sample was prepared according to the PE instructions (if applicable). Check also that the appropriate PE instructions (for the PE concentration) were sent to the laboratory. |

| C. EVALUATION | D. ACTION |
|---|---|
| *2 f. Check and recalculate the analytical concentrations of at least one analyte per PES fraction. Verify that the recalculated value agrees within ± 10% of the reported result. | 2. f. If any transcription and/or calculation errors are detected, perform a more comprehensive review to determine the magnitude of the problem. If the problem is extensive, then the validator should have the laboratory requantitate and resubmit all corrected raw data and forms. If a discrepancy remains unresolved, the validator must use professional judgment to decide which value is more accurate. Under these circumstances, the validator may determine that the sample data should be qualified or rejected. A discussion of the rationale for data qualification and the qualifiers used should be documented in the Data Validation Memorandum.<br><br>i. If corrected data reports affect the original results reported on the initial EPA PES score report, then the validator should resubmit the corrected PES results to Region I OEME-QA for a PES rescore. Sample data should be reevaluated and requalified based on the corrected PES data.<br><br>ii. If corrected data reports affect the original results reported for the initial non-EPA PES, then the validator should reevaluate and requalify sample data based on the corrected PES data. |

*** Note: The following subsections are applicable only to a Tier III data validation:**

**C.1.e, C.2.e, C.2.f**

**Table Pest/PCB-XI-1:**

**QUALIFICATION OF INDIVIDUAL ORGANIC ANALYTES BASED ON LCS* RECOVERIES WHERE: ≤ ONE-HALF OF LCS ANALYTES OUTSIDE UPPER OR LOWER ACCEPTANCE LIMITS**

| Sample Results | % Recovery | | | |
|---|---|---|---|---|
| | %Rec < 10% | 10% ≤ %Rec < LL | LL ≤ %Rec ≤ UL | %Rec > UL |
| Detects | J | J | A | J |
| Non-detects | R | UJ | A | A |

* LCS = Laboratory Control Sample (LCS) is an internal laboratory quality control sample designed to assess analytical accuracy and method bias. The LCS is spiked with several or all of the method target analytes and/or Aroclors.

LL - Lower limit of method QC acceptance criteria
UL - Upper limit of method QC acceptance criteria

**Table Pest/PCB-XI-2:**

**QUALIFICATION OF ORGANIC ANALYTES BASED ON LCS* RECOVERIES WHERE: > ONE-HALF OF LCS ANALYTES OUTSIDE UPPER OR LOWER ACCEPTANCE LIMITS****

| Sample Results | % Recovery | | | |
|---|---|---|---|---|
| | %Rec < 10% | 10% ≤ %Rec < LL | LL ≤ %Rec ≤ UL | %Rec > UL |
| All Detects | J | J | A | J |
| All Non-detects | R | UJ | A | A |

* LCS = Laboratory Control Sample (LCS) is an internal laboratory quality control sample designed to assess analytical accuracy and method bias. The LCS is spiked with several or all of the method target analytes and/or Aroclors.

** Professional judgment should be used when a combination of low recoveries and high recoveries are obtained.

LL - Lower limit of method QC acceptance criteria
UL - Upper limit of method QC acceptance criteria

**Table Pest/PCB-XI-3:**

**QUALIFICATION OF INDIVIDUAL ORGANIC ANALYTES BASED ON PES RESULTS WHERE:**
**≤ ONE-HALF OF PES ANALYTES OUTSIDE UPPER OR LOWER ACCEPTANCE LIMITS**

| **Sample Results** | ● **Single Blind**<br>● **Double Blind**<br>**PES < Lower Limit**<br>**"Action Low"** | ● **Single Blind**<br>● **Double Blind**<br>**PES "Within Warning Limits"**<br>**"Warning High/Warning Low"** | ● **Single Blind**<br>● **Double Blind**<br>**PES > Upper Limit**<br>**"Action High"** |
|---|---|---|---|
| Detects | J | A | J |
| Non-Detects | R | A | A |

**Table Pest/PCB-XI-4:**

**QUALIFICATION OF ORGANIC ANALYTES BASED ON PES RESULTS WHERE:**
**> ONE-HALF OF PES ANALYTES OUTSIDE UPPER OR LOWER ACCEPTANCE LIMITS ***

| **Sample Results** | ● **Single Blind**<br>● **Double Blind**<br>**PES < Lower Limit**<br>**"Action Low"** | ● **Single Blind**<br>● **Double Blind**<br>**PES "Within Warning Limits"**<br>**"Warning High/Warning Low"** | ● **Single Blind**<br>● **Double Blind**<br>**PES > Upper Limit**<br>**"Action High"** |
|---|---|---|---|
| All Detects | J | A | J |
| All Non-Detects | R | A | A |

* Professional judgment should be used when a combination of low recoveries and high recoveries are obtained.

## E. EXAMPLES

Example #1: (One LCS analyte < lower limit; One LCS analyte > upper limit)

A Laboratory Control Sample (LCS) containing six pesticides spiked at three times the quantitation limit is found to have 4,4'-DDT with a % recovery of 45% and 4,4'-DDE with a % recovery of 165%. Less than one-half of the spiked LCS analytes were outside the LCS acceptance criteria (60-140%). The validator notes that the PEM preceding the LCS analysis had a DDT breakdown of 35.0%. The validator estimates (J) positive detects for 4,4'-DDT and 4,4'-DDE in all field samples associated with that LCS. The validator accepts the 4,4'-DDE non-detects and estimates (UJ) the 4,4'-DDT non-detects in all field samples associated with that LCS. The validator reports qualified data on the Data Summary Table and notes in the Data Validation Memorandum that DDT results are biased low and DDE results are biased high in all field samples associated with that LCS.

Example #2: (One Single Blind PES analyte < lower PES acceptance limit)

A Single Blind Performance Evaluation Sample (PES) is found to have an endrin ketone result that scored below the PES acceptance criteria. The validator determines that less than one-half of the spike PES analytes are outside the PES acceptance criteria. Therefore, the validator estimates (J) positive endrin ketone detects and rejects (R) the quantitation limits for endrin ketone non-detects in all field samples associated with that PES. The validator reports qualified data on the Data Summary Table and notes the positive endrin ketone detects are biased low and the non-detects are rejected due to the possibility of false negatives in the Data Validation Memorandum.

Example #3: (More than one-half of the PES analytes greater than the upper acceptance limits)

A Single Blind PES is found to have more than one-half of the spike pesticide PES analytes with % recoveries above the upper acceptance limits. The validator estimates (J) all positive detects in all field samples associated with that PES and accepts (A) all the quantitation limits for non-detects in all field samples associated with that PES. The validator reports qualified data on the Data Summary Table and notes the positive pesticide results are biased high in the Data Validation Memorandum.

Example #4: (More than one-half of PES analytes "Action High" or "Action Low")

A Single Blind PES is found to have more than one-half of the spike pesticide PES analytes with results that do not meet PES acceptance criteria. Some of the PES analytes are flagged "Action Low" and some flagged "Action High". The site DQOs are to determine whether or not cleanup levels were achieved. The validator determines that analytical error yields uncertainty in quantitative accuracy which may adversely affect site decisions. Therefore, the validator uses professional judgment to estimate (J) all positive detects in all field samples associated with that PES and reject (R) all quantitation limits in all field samples associated with that PES. The validator reports qualified data on the Data Summary Table and discusses the limited use of the data in the Data Validation Memorandum.

Example #5: (One "PES ANALYTES MISSED")

A Single Blind PES is found to have one "PES ANALYTES MISSED" for aldrin which is a contaminant of concern at the site. The validator estimates (J) all positive aldrin detects and rejects (R) all aldrin quantitation limits in all field samples associated with that PES. The validator reports qualified data on the Data Summary Table and discusses this in the Data Validation Memorandum.

E. EXAMPLES

Example #6: (One "PES CONTAMINANTS", also in blank)

A Single Blind PES is found to have one "PES CONTAMINANTS", gamma-BHC, at 1.2 ppb. The method blank contained 0.20 ppb of gamma-BHC, resulting in a Blank Action Level of 1.0 ppb. The validator uses the gamma-BHC Blank Action Level to evaluate the sample data and reports qualified data on the Data Summary Table. The validator suspects that the gamma-BHC false positive PES analyte is a result of laboratory contamination and discusses this in the Data Validation Memorandum. PES results are not reported on the Data Summary Table.

Example #7: (One "PES CONTAMINANTS", not in blank)

A Single Blind PES is found to have one "PES CONTAMINANTS", 4,4'-DDE, which is not detected in any of the blanks but is detected in two samples. The validator determines that the 4,4'-DDE is an interference specific to the PES because it was not detected in any of the method blanks or instrument blanks. The validator notes that 4,4'-DDD and 4,4'-DDT are present in each of the two samples in addition to 4,4'-DDE, therefore, the validator uses professional judgment to accept the positive 4,4'-DDE detects in the field samples and reports the data unqualified on the Data Summary Table and discusses this in the Data Validation Memorandum.

# XII. TARGET ANALYTE IDENTIFICATION

## A. OBJECTIVE

Qualitative criteria for analyte identification have been established to minimize the number of erroneous analyte identifications. An erroneous identification can be either a false positive (reporting an analyte that it is not present) or a false negative (not reporting an analyte that is present).

The identification criteria can be applied more easily in detecting false positives than false negatives (non-detects) since each positively identified analyte must be labeled on the chromatogram or on the printout of retention times from the data system. False negatives represent an absence of data and therefore, are more difficult to assess.

## B. CRITERIA

The Region I, EPA-NE Data Validation Functional Guidelines for Evaluating Environmental Analyses should be used to validate all Region I Organic data. The CLP - Pesticide/PCB method QC acceptance criteria listed in Appendix F should be used as the default criteria when none exist for the pesticide/PCB analytical method utilized and when similar QC parameters are required by the non-CLP method and acceptance criteria have not been specified. Deviations, modifications, or non-CLP method specific QC acceptance criteria may be used but must be explicitly defined in tabular format in the site-specific EPA approved QAPP/SAP or amendment to the QAPP/SAP.

1. **Retention Times:** Initially, a target analyte is identified when its retention time falls within the established retention time window for that analyte on a particular column. Analyte identification is confirmed when the sample is analyzed on a dissimilar GC column and the analyte falls within the retention time window established for that analyte on the second column. Occasionally, when a sample matrix interferes with positive analyte identification, or analyte coelution occurs on one or both columns, a third alternate GC column is used to provide necessary confirmation data.

    a. Retention times of all surrogates and target analytes reported in the samples must fall within the standard retention time windows established for all GC columns used for sample analyses.

2. **Analyte Chromatographic Criteria:** Analyte chromatographic criteria are critical to ensure that coelution does not interfere with analyte identification and quantitation.

    a. Target analytes should display symmetrical peak shapes.

    b. Target analytes should be adequately resolved. Analyte resolution should be evaluated using professional judgement.

    c. Target analyte peaks should return to baseline after elution.

    d. For multicomponent analytes: When more than one multicomponent analyte is observed in a sample, none of the peaks chosen to quantitate either analyte should be peaks common to both analytes.

3. **Chromatographic Plotting Criteria:** Criteria for chromatographic plotting are critical to ensure that chromatographic peaks can be visually and electronically evaluated to correctly identify and accurately quantitate target analytes.

a. The same scaling factor must be used for the field samples and the calibration standards. It is critical that the chromatograms for the initial calibration low point standard and the field sample with no target analytes reported can be compared by using the same scaling factor.

b. Chromatograms must display single component pesticides detected in the sample at less than full scale, and the largest peak of any multicomponent analyte detected in the sample at less than full scale.

c. If an extract must be diluted, chromatograms must display single component pesticides between 10 and 100 percent of full scale, and multicomponent analytes between 25 and 100 percent of full scale.

d. For any sample, the baseline of the chromatogram must return to below 50 percent of full scale before the elution time of alpha-BHC.

e. For any sample, the baseline of the chromatogram must return to below 25 percent of full scale after the elution time of alpha-BHC and before the elution time of decachlorobiphenyl.

f. If a chromatogram is replotted electronically to meet any of the above requirements, the scaling factor must be displayed on the chromatogram, and both the initial chromatogram and the replotted chromatogram must be submitted in the data package.

**4. GC/MS Confirmation:** GC/MS confirmation is required if the concentration of a target analyte exceeds 10 ng/uL in the final pesticide/PCB sample extract. **Note: A standard GC/quadrupole mass spectrometer can achieve 10 ng/uL single component pesticide confirmation.** Alternate GC/MS technology may achieve analyte identifications at less than 10 ng/uL. Mass spectra of the analyte in the sample and a current laboratory generated reference standard (10 ng/uL single component pesticides, 50 ng/uL Aroclors, and 125 ng/uL Toxaphene) must match according to the following criteria:

a. All ions present in the standard mass spectrum at a relative intensity greater than 10 percent must be present in the sample spectrum.

b. The relative intensities of these ions must agree within ± 20 percent 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 must be between 30 percent and 70 percent.)

c. Ions greater than 10 percent of the sample mass spectrum but not present in the standard spectrum must be considered and accounted for.

C. EVALUATION/ D. ACTION

| C. EVALUATION | D. ACTION |
|---|---|
| | All potential impacts on the sample data resulting from target analyte identification anomalies should be noted in the Data Validation Memorandum. The validator should also document and justify all technical decisions made based on professional judgment in the Data Validation Memorandum. |
| 1. a. Compare Form Is and the Pesticide/PCB Identification Summary (Form X, PEST-1, and PEST-2) and verify that reported retention times for all positive detects are within the calculated retention time windows reported on Pesticide Initial Calibration Forms (Form VI PEST-1 and -3). | 1. a. If sample results have been reported on the Form Is for target analytes (single or multicomponent) with retention times which are not within the calculated retention time windows, then the validator should review the raw data to determine whether or not the laboratory has made any analytical and/or transcription errors. The validator should have the laboratory resubmit all corrected forms. |
| * b. Verify that all analytes reported on Forms I and X display chromatographic peaks within the calculated retention time windows on two or more analytical columns. | b. If the retention time criteria for two (or more) column confirmations are not achieved, then affected target analytes that are reported as positive detects should be considered non-detects. The reported value is considered a false positive and it should be replaced on the Data Summary Table with the target pesticide/PCB sample quantitation limit. The validator should have the laboratory resubmit all corrected forms and raw data if necessary.<br><br>For multicomponent analytes, if the retention time criteria for one or more peaks chosen for quantitation are not met, then the validator should review the raw data to determine whether or not the laboratory has made any analytical, identification, and/or transcription errors. The validator should have the laboratory resubmit all corrected forms and raw data if necessary. |

| C. EVALUATION | D. ACTION |
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| *1. c. Verify that all analytes reported on Form Is as "not detected" show no chromatographic peaks within the calculated retention time windows on two or more analytical columns. Review the sample chromatograms to determine whether or not false negatives have been reported. | 1. c. If interferences obscure a target analyte's retention time window, then the validator should use professional judgment to elevate the target analyte's quantitation limit to the concentration of the interferent or reject (R) the sample data, in accordance with D.2.a.i. All technical decisions should be justified and documented in the Data Validation Memorandum.<br><br>A peak that meets retention time criteria on both analytical columns but was reported as a non-detect may be a false negative. The validator should review the relevant sample chromatograms for false negatives. If false negatives are found, the laboratory should be contacted and asked to re-evaluate the false negative peak and report it, if necessary.<br><br>The validator must evaluate whether significant matrix interference and/or coelution exists, and evaluate retention time data in conjunction with the sample chromatograms. The validator should use professional judgment when deciding if an analyte should be reported. All conclusions made regarding target analyte identification should be documented and justified in the Data Validation Memorandum. |
| * d. While reviewing the raw data, the validator should check for analyte retention time shifts which could lead to the reporting of false positives and/or false negatives. | d. If analyte retention times have shifted, then the validator should follow the chromatographic and resolution check guidance in Section II C and D 2.a-c. to ensure that false negatives and/or false positives have not been reported. |

| C. EVALUATION | D. ACTION |
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| After a validator has confirmed that all reported pesticides/PCBs meet analyte retention time criteria, one must next confirm that the chromatographic criteria are achieved in order to ensure positive analyte identification. | |
| *2. a. Confirm that analyte chromatographic criteria are achieved for each positive detect. Failure to meet chromatographic criteria may indicate the presence of target and/or non-target interferences, or analytical system issues (i.e. column degradation) that prohibit the positive identification and accurate quantitation of target analytes. | 2. a. Review raw chromatographic data to evaluate peak shape, resolution, and baseline. |
| * i. Evaluate peak shape. | i. The validator should evaluate whether or not symmetrical peaks were used for quantitating the results. If the peaks were not symmetrical, the validator should evaluate all confirmatory data, including GC/MS results, and use professional judgement to assess the impact of the unsymmetrical peaks on the report results and should justify all technical decisions in the Data Validation Memorandum.<br><br>For aqueous samples, the validator should determine if an appropriate cleanup procedure was performed on the extracts. If the required cleanup procedure was not performed, then the validator should request reextraction and reanalysis by the laboratory with appropriate cleanup procedures. If cleanup procedures do not reduce interferences, the validator should note this in the Data Validation Memorandum and recommend that a more selective and/or analyte-specific analytical procedure be employed. |

| C. EVALUATION | D. ACTION |
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| *2. a. ii. Evaluate chromatographic resolution. | 2. a. ii. If the chromatographic peak for a positive detect is not adequately resolved on both columns, then the validator should use estimate (J) the reported result and document it in the Data Validation Memorandum. If the interfering peak is a target analyte, evaluate target analyte resolution and refer to Section II GC/ECD Instrument Performance Check. |
| * iii. Evaluate chromatographic baseline. | iii. If the sample chromatogram does not return to baseline after the elution of a target analyte peak or if a peak elutes as a part of a "humpogram" or coelutes with a multicomponent analyte, then interference may impede positive analyte identification and/or quantitation. The validator should use professional judgment to assess the impact of baseline rise, humpograms, and the presence of other multicomponent analytes on the positive identification of target analytes and qualify the sample data, if appropriate, and justify all technical decisions in the Data Validation Memorandum. |
| * b. For multicomponent analytes, in addition to the above retention time and chromatographic evaluations, the validator should evaluate the overall similarity of chromatographic patterns between the samples and the standards, while also evaluating the relative peak height ratios. | b. If the chromatographic pattern of the multicomponent analyte in the sample does not match that of the standard, then professional judgment should be used to establish whether the differences are due to environmental "weathering" (i.e., degradation of the earlier eluting peaks relative to the later eluting peaks). |

| C. EVALUATION | D. ACTION |
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| *2. c. Ascertain if samples contain any combination of single component, multicomponent analytes and/or non-target analytes. | 2. c. If samples containing single component analytes, multicomponent analytes, and/or non-target analytes have complex chromatograms, then the validator must evaluate the sample data carefully for false positives and/or false negatives as described above in C.1.a-c. |
| * i. Determine if target and/or non-target interferences have caused a multicomponent analyte to be incorrectly identified as another multicomponent analyte. | i. If a multicomponent analyte has been misidentified, then the validator should have the laboratory resubmit all corrected raw data and forms. If a discrepancy remains unresolved, the validator must use professional judgment to decide which identification is more accurate. The validator may qualify or reject the data. A discussion of the reasons for data qualification and the qualifiers used must be documented in the Data Validation Memorandum. |
| * ii. Determine if multiple multicomponent analytes are present. | ii. If an observed pattern closely matches more than one Aroclor or other multicomponent analyte, then professional judgment should be used to decide whether the other possible Aroclor is a better match, or if multiple Aroclors (multicomponent analytes) are present.<br>If discrepancies between the raw data and reported data are found, then the validator should have the laboratory resubmit all corrected raw data and forms. If a discrepancy remains unresolved, the validator must use professional judgment to decide which identification is more accurate. The validator may qualify or reject the data. A discussion of the reasons for data qualification and the qualifiers used must be documented in the Data Validation Memorandum. |

| C. EVALUATION | D. ACTION |
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| *2. d. Review the PES data, refer to Section XI to assess the laboratory's ability to accurately identify and quantitate target analytes. | 2. d. If the laboratory failed to accurately identify and/or quantitate PE samples, then sample data are suspect and sample results should be qualified according to section XI. |
| * e. Review the sample chromatograms to determine if any analyses showed saturated peaks. If an instrument blank was not analyzed after a high concentration sample and the instrument is not proven to be free of contamination, then the possibility of sample carryover exists. | e. If carryover is a possibility, then the validator should use professional judgment to determine whether or not a reported target analyte is a native contaminant in the sample analyzed or an interferent from a previously analyzed sample. Refer to Section V for additional guidance. |
| * f. Review the continuing calibration analyses of the Standard Mixtures A and B and the Performance Evaluation Mixture to identify any potential analytical problems such as decreased column resolution or compromised instrument sensitivity that could affect the interpretation of sample chromatograms. | f. If analytical problems including decreased column resolution abilities or compromised instrument sensitivity are detected in the continuing calibration analyses of the Standard Mixtures A and B and/or the Performance Evaluation Mixtures, then the validator should use professional judgment to qualify or reject sample data. |
| * g. Review MS/MSD data to evaluate the effect of sample matrix on analyte identification and quantitation. | g. If matrix interferences exist that either suppress or enhance the signal of spiked matrix analytes, then the validator should consider the direction of the bias and use professional judgment to qualify the sample data. |
| *3. Review the sample chromatograms to verify that all chromatographic plotting criteria are achieved and that sample chromatograms are properly scaled to allow the validator to evaluate the presence/absence of pesticide/PCB peaks. | 3. If sample chromatograms do not demonstrate acceptable chromatographic separation and resolution, then the validator may not be able to adequately assess the presence/absence of pesticide/PCBs. In this situation the validator should contact the laboratory to replot and rescale the affected sample chromatograms. |

| C. EVALUATION | D. ACTION |
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| 4. a. Verify from the Form Is that GC/MS confirmation was performed for pesticide/PCB concentrations in the final sample extract which exceeded 10 ng/uL. | 4. a. If GC/MS confirmation was required but not performed, then the validator should request sample analysis by GC/MS. If GC/MS sample analysis data is not provided by the laboratory, then the validator should note this non-compliance in the Data Validation Memorandum. |
| * b. Review the GC/MS raw data. Compare the confirmatory sample analyte spectrum to the laboratory standard spectrum and verify the mass spectral match using the VOA/SV Target Analyte Identification criteria in Section XII. | b. The application of qualitative criteria for GC/MS analysis of target analytes requires professional judgment. It is left to the validator's discretion to obtain additional information from the laboratory if it is deemed necessary. If it is determined that the presence of a pesticide/PCB was not confirmed by GC/MS, then the validator should qualify all affected data as non-detected (U) or should reject (R) the sample data indicating unusable data and document the justification for this decision in the Data Validation Memorandum. |

*** Note: The following subsections are applicable only to a Tier III data validation:**

**C.1.b, C.1.c, C.1.d, C.2.a, C.2.a.i, C.2.a.ii, C.2.a.iii, C.2.b, C.2.c, C.2.c.i, C.2.c.ii, C.2.d, C.2.e, C.2.f, C.2.g, C.3, C.4.b**

## E. EXAMPLES

Example #1 (False negative)

The validator reviewed the sample chromatograms for pesticide/PCB soil sample SAA12 and noted that both GC column analyses had a chromatographic peak within the calculated retention time window for heptachlor. Heptachlor was reported as not detected in sample SAA12. The laboratory correctly identified heptachlor in the PE sample. No sample matrix interferences were noted in the MS/MSD analyzed for soil sample SAA11. Since no explanation was given in the SDG narrative for reporting heptachlor as a non-detect in sample SAA12, the laboratory was contacted and requested to justify their decision or requantitate the false negative result and report heptachlor as a positive detect. The laboratory requantitated the false negative result and reported heptachlor on the Form I. As a result of the heptachlor false negative, all field sample chromatograms were carefully reviewed for potentially positive results. The validator discusses all these actions in the Data Validation Memorandum.

Example #2 (Coeluting peaks)

Dieldrin is reported on the two GC columns at concentrations of 3.5 ug/kg and 4.3 ug/kg, respectively for pesticide/PCB soil sample SAA13. The validator reviews the sample chromatograms and determines that the peak identified as dieldrin was poorly resolved and emerged as a shoulder with its peak apex coeluting with another peak (non-target analyte) on the second column. Since this peak did not meet the required chromatographic criteria, it could not be positively identified as dieldrin. The validator determined that the laboratory correctly identified dieldrin in the PE sample. The validator also determined that dieldrin was well resolved in the standards and had a symmetrical peak shape. No other sample matrix interferences were noted in the MS/MSD analyzed for soil sample SAA10. Since the coeluting peak obscured the dieldrin peak apex on the second column, the presence/absence of dieldrin is unknown below a certain concentration (4.3 ug/kg). The validator reviewed the DQOs and determined that a higher detection limit provided usable data since the action limit for dieldrin is 10.0 ug/kg and the detection limit for dieldrin in sample SAA13 was elevated to 4.3 ug/kg, the highest potential concentration of dieldrin in that sample. The validator reports the value as an estimated non-detect at the level of the interferent concentration, 4.3 (UJ), on the Data Summary Table and notes this in the Data Validation Memorandum.

Example #3 (Coeluting peaks)

Aroclor 1260 and 4,4'-DDT were reported in aqueous sample SAA14. Aroclor 1260 concentrations were 9.8 and 9.3 ug/L and 4,4'-DDT concentrations were 5.6 and 5.8 ug/L on the two GC columns, respectively. The validator examines the chromatograms and determines that 4,4'-DDT elutes at the same retention time as one of the non-quantifying Aroclor 1260 peaks on both columns. The validator confirms that no retention time shifts have occurred in either the bracketing calibration standards or the sample surrogates. The validator concludes that the reported presence of 4,4'-DDT is suspect. However, the site DQOs have an action limit for 4,4'-DDT of 4 ug/L. The validator determines that the maximum concentration of 4,4'-DDT that could be present in sample SAA14 is 5.8 ug/L. Therefore, the validator elevates the quantitation limit for the non-detected 4,4'-DDT in sample SAA14 to 5.8 ug/L. The validator reports the SAA14 4,4'-DDT value at 5.8 (UJ) and Aroclor 1260 as 9.3 ug/L on the Data Summary Table and notes in the Data Validation Memorandum that the detection limits for 4,4'-DDT were not achieved and, therefore, the site DQOs were not achieved.

## E. EXAMPLES

Example #4 (False positive due to cross-contamination)

A large peak for endrin was noted in the initial analysis of sample SAX357. A 5X dilution was required to bring the peak into the linear calibration range. Sample SAX358, which was analyzed immediately following SAX357, reported endrin only slightly above the detection limit. The validator suspects that the endrin concentration reported in sample SAX358 is a false positive result due to carryover from the original SAX357 sample analysis. The laboratory did not report the analysis of an instrument blank following the high concentration sample in the analytical sequence. The validator reviews the site DQOs and endrin is not a contaminant of concern and, therefore, uses professional judgment to reject the positive endrin detect in sample SAX358 due to possible cross-contamination from the previously analyzed sample, SAX357. The validator reports endrin as rejected (R) in sample SAX358 on the Data Summary Table and notes this in the Data Validation Memorandum.

Example #5 (Incorrect chromatographic plotting scale)

Sample SAE632 was analyzed undiluted. Review of the chromatograms for both columns indicated that the 4,4'-DDE peak was off scale although the concentration was within the linear calibration range. The apex of the peak was not visible on the chromatograms which prevents evaluation of retention times, peak shape, and peak resolution. Since 4,4'-DDE is a contaminant of concern at the site, the validator requested the laboratory to rescale the chromatograms or reanalyze the sample in order to plot the 4,4'-DDE peak on scale. The laboratory reanalyzed and rescaled the sample to get the 4,4'-DDE peak on scale. The validator reports the reanalysis 4,4'-DDE positive detect on the Data Summary Table without qualification.

Example #6 (Missing GC/MS Confirmation Data)

Toxaphene was reported in aqueous sample SET069 at 300 ug/L in the pesticide/PCB data package. The validator notes that GC/MS confirmation was not provided but was required under the method used for analysis since the Toxaphene concentration exceeds 125 ng/uL in the final sample extract. The validator contacts the laboratory to obtain the GC/MS confirmation data. The laboratory complies and sends the required GC/MS confirmation data which meet GC/MS confirmatory criteria; therefore, the validator reports Toxaphene at 300 ug/L in sample SET069 and notes this in the Data Validation Memorandum.

## XIII. COMPOUND QUANTITATION AND REPORTED QUANTITATION LIMITS

### A. OBJECTIVE

The objective for the evaluation of analyte quantitation and reported quantitation limits is to ensure that reported quantitative results and quantitation limits are accurate. To this end, laboratory calculations proceeding from raw data to the final reported concentrations are evaluated for accuracy.

### B. CRITERIA

The Region I, EPA-NE Data Validation Functional Guidelines for Evaluating Environmental Analyses should be used to validate all Region I Organic data. The CLP-Pesticide/PCB method QC acceptance criteria listed in Appendix F should be used as the default criteria when none exist for the Pesticide/PCB analytical method utilized and when similar QC parameters are required by the non-CLP method and acceptance criteria have been not specified. Deviations, modifications, or non-CLP method specific QC acceptance criteria may be used but must be explicitly defined in tabular format in the site specific EPA approved QAPP/SAP or amendment to the QAPP/SAP.

1. a. Reported quantitation limits must meet projected-required DQOs.

   b. Reported concentrations for positive detects and analyte quantitation limits for non-detects and adjustments of those concentrations/analyte quantitation limits must be calculated according to the appropriate method requirements.

   c. Reported concentrations for positive detects and analyte quantitation limits for non-detects must be adjusted for percent solid results, sample dilutions, and concentrations and cleanup procedures that are not accounted for in the method.

2. a. Analyte Calibration Factors (CFs) for pesticides must be calculated based on the midpoint standard established during the initial three point calibration.

   b. Analyte Calibration Factors for multicomponent analytes must be calculated based on the single-point standard established during the initial calibration.

   c. Analyte quantitation must be calculated using the CF from the appropriate initial calibration.

3. a. The lower of the two concentrations obtained on the two dissimilar GC columns is reported as the sample result.

   b. The percent difference between the concentrations reported on the dissimilar columns must not exceed 25 percent.

4. All soil/sediment sample results must be adjusted for percent solid results, and must have percent solids greater than 30 percent.[1]

**[1]U.S. EPA office of Water Regulations and Standards Industrial Technology Division - Method 1620, p.29, Section 14.16 Draft, September 1989.**

Sediment samples are collected at CERCLA sites to establish whether or not the presence of hazardous chemicals has impacted the resident organisms and their natural environment. The data quality objectives for ecological risk assessment generally require that the analytical method used for sediment analysis achieve, at a minimum, the dry weight CLP SOW quantitation limits.

Most analytical methods established for soil-type matrices are applicable to both soils and sediments with no difference in how those two matrices are prepared and analyzed. Since a definition for soil and sediment matrices is not provided in the analytical methodology, Region I has adopted the definition for soil samples used by the Office of Water Regulations and Standards Industrial Technology Division (ITD). This definition states that soil samples are "soils, sediments, and sludge samples containing more than 30% solids".

High moisture sediments cannot be successfully analyzed by routine CLP analytical methods. Additional sampling and analytical preparation steps which are outside of the scope of a CLP method should be employed. For example, standing water may first be decanted, and then the sample may be centrifuged or filtered to remove excess water. To achieve the dry weight quantitation limits, the laboratory must perform a percent solids analysis prior to sample extraction and the initial weight of sample extracted must be increased accordingly. This presumes that the samplers have collected sufficient sample volume, above and beyond the normal volume requirements, so that additional sample can be extracted. As a last resort, the laboratory can decrease the final extract volume to a minimum of 0.5 milliliters.

Certain solid matrices, such as peat, are unusual in their reactive chemistry. Peat is a natural sink for organic analytes. It is composed of both a solid spongy matrix (which tightly binds organic analytes) and the interstitial pore water present therein.

Routine analytical methods underestimate the concentrations of organic analytes in peat matrices because the typical organic preparation and extraction techniques do not breach the matrix. In order for peat to successfully be analyzed, the matrix itself must be "sheared" into small pieces to increase surface area so that the extraction solvent can interact with the interstitial pore water and the spongy matrix to partition the target organic analytes into the solvent.

Sampling and analytical methodologies must be determined during project scoping processes and must be based on the project data quality objectives. For more information, see Attachment A of the Data Validation Manual.

**C. EVALUATION/ D. ACTION**

| C. EVALUATION | D. ACTION |
| --- | --- |
| | All potential impacts on the sample data resulting from analyte quantitation anomalies should be noted in the Data Validation Memorandum. The validator should also document and justify all technical decisions made based on professional judgment in the Data Validation Memorandum. |
| 1. Verify that the reported quantitation limits meet method requirements and support project DQOs. | 1. If reported quantitation limits do not meet the method requirements and/or support project DQOs, then the validator must investigate the cause of the deficiency and use professional judgment to assess the impact on the sample data. The validator must discuss this in the Data Validation Memorandum. |
| *2. a. Verify that sample results reported by the laboratory were accurately calculated according to the method. Recalculate, from the raw data, the concentration for at least one positive detect and one sample quantitation limit (for a diluted sample or a soil sample) for a pesticide and an Aroclor, in every field sample. | 2. a. If incorrect values, equations, or factors have been used to calculate sample results and/or sample quantitation limits, then the validator should have the laboratory requantitate and resubmit all corrected raw data and forms. If a discrepancy remains unresolved, the validator must use professional judgment to decide which value is more accurate. Under these circumstances, the validator may determine that the sample data should be qualified or rejected. A discussion of the rationale for data qualification and the qualifiers used should be documented in the Data Validation Memorandum. |
| * b. Verify that the concentration for positive detects and sample quantitation limits have been adjusted to reflect sample dilutions, concentration procedures, cleanup methods, and dry weight factors that are not accounted for in the method. | b. If the concentration for positive detects and/or sample quantitation limits were not correctly adjusted for sample dilutions, concentration procedures, cleanup methods, or dry weight factors, then the validator should have the laboratory requantitate and resubmit all corrected raw data and forms. If a discrepancy remains unresolved, the validator must use professional judgment to decide which value is more accurate. Under these circumstances, the validator may determine that the sample data should be qualified or rejected. A discussion of the rationale for data qualification and the qualifiers used should be documented in the Data Validation Memorandum. |

| C. EVALUATION | D. ACTION |
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| *2. c. Compare the raw data including quantitation reports, chromatograms, and sample preparation logs to the reported positive sample results and quantitation limits on Form I PEST and Form X PEST-1 and -2. | 2. c. If discrepancies between the raw and reported data are found, then the validator should have the laboratory requantitate and resubmit all corrected raw data and forms. If a discrepancy remains unresolved, the validator must use professional judgment to decide which value is more accurate. Under these circumstances, the validator may determine that the sample data should be qualified or rejected. A discussion of the rationale for data qualification and the qualifiers used should be documented in the Data Validation Memorandum. |
| *3. Verify that the correct standard CFs from the analysis of the calibration standards were used to quantitate sample results. | 3. If the laboratory utilized an incorrect CF to quantitate the value for any analyte, then the validator should have the laboratory requantitate and resubmit all corrected forms and quantitation reports. If a discrepancy remains unresolved, the validator must use professional judgment to decide which value is more accurate. Under these circumstances, the validator may determine that the sample data should be qualified or rejected. A discussion of the rationale for data qualification and the qualifiers used should be documented in the Data Validation Memorandum. |
| 4. a. Verify that the lowest of the two reported sample concentrations from Form X PEST was reported on Form I PEST. | 4. a. If the validator determines that the higher sample concentration is more accurate than the lower concentration, then the validator should report the higher value on the Data Summary Table and clearly justify the technical decision in the Data Validation Memorandum. |

| C. EVALUATION | D. ACTION |
|---|---|
| 4. b. Evaluate the percent difference (%D) obtained for positive results on the two GC columns. Verify that the percent difference between the calculated concentrations is less than or equal to 25.0 %. | 4. b. If the % D for sample results on the two GC columns is > 25.0%, then the chromatograms should be reviewed for chromatography, resolution, and interferences etc. (See Section XII Target Analyte Identification) and use professional judgment to qualify the results based on the following:<br><br>i. For **Single Component Pesticides**, if the %D for the sample results on the two columns is greater than 25.0% but less than 100%, then the validator should estimate (J) the positive detects for that analyte in the sample.<br><br>ii. For **Single Component Pesticides**, if the %D for the sample results on the two columns exceeds 100%, then the validator should reject (R) positive detects for that analyte in the sample. However, professional judgement should be used to evaluate the chromatography before rejecting positive results.<br><br>iii. For **Multicomponent Analytes**, if the %D for the sample results on the two columns is greater than 25.0% but less than 500%, then the validator should estimate (J) positive detects for that analyte in the sample.<br><br>iv. For **Multicomponent Analytes**, if the %D for the sample results on the two columns exceeds 500%, then the validator should reject (R) positive detects for that analyte in the sample.<br><br>v. If one sample concentration of either single component pesticides or multicomponent analytes is less than the quantitation limit and the other sample concentration is greater than or equal to the quantitation limit, then the validator should use professional judgment to determine which value to report and should qualify the reported positive value as estimated (J) or the reported quantitation limit as estimated (UJ). |

| C. EVALUATION | D. ACTION |
| --- | --- |
| 5. Determine if any soil/sediment/solid sample has less than or equal to 30 percent solids. | 5. a. If a soil/sediment/solid sample has greater than 30 percent solid results, then the validator should accept all sample data.<br><br>b. If a soil/sediment/solid sample has percent solids of greater than or equal to 10 percent but less than or equal to 30 percent, then the validator should:<br><br>● Estimate (J) positive detects.<br><br>● Reject (R) non-detects.<br><br>c. If a soil/sediment/solid sample has less than 10 percent solids, then the validator should reject (R) positive and non-detect sample results as unusable.<br><br>d. The validator should include a discussion of the sample matrices having low percent solids in the Data Validation Memorandum. The validator may need to contact the field sampler to determine whether sampling techniques were appropriate for the sample matrix. |
| 6. Determine whether or not the laboratory performed procedures to remove the aqueous medium and increased the sample size to account for low percent solids. | 6. If the laboratory performed procedures to decrease the aqueous medium and increased the sample size, then the validator should check the chromatograms for interferences and possible false negatives and use professional judgement to accept, qualify, and/or reject data. The validator must also verify that the sample-specific quantitation limits were adjusted and that the adjusted levels meet the project DQOs. |

**Note: The following subsections are applicable only to a Tier III data validation:**

**C.2.a, C.2.b, C.2.c, C.3**

**Table Pest/PCB-XIII-1:**

**QUALIFICATION OF PESTICIDE/PCB ORGANIC ANALYTES BASED ON SAMPLE PERCENT SOLIDS**

| Sample Result | % Solids > 30% | 10% ≤ % Solids ≤ 30% | % Solids < 10% |
|---|---|---|---|
| Detects | A | J | R |
| Non-detects | A | R | R |

**Table Pest/PCB-XIII-2:**

**QUALIFICATION OF PESTICIDE/PCB ANALYTES BASED ON %D OF ANALYTES BETWEEN TWO QUANTITATION COLUMNS.**

| %D Between the Two Quantitation Columns | Sample Results | |
|---|---|---|
| | Detects | Non-Detects |
| 25.0% < %D < 100%<br>(single component pesticides) | J | N/A* |
| %D > 100% (single component pesticides) | R | N/A |
| 25.0% < %D < 500% (Multicomponents) | J | N/A |
| %D > 500% (Multicomponents) | R | N/A |
| One Value < QL & One Value ≥ QL | J | UJ |

* N/A - Not Applicable

## E. EXAMPLES

Example #1: (25% < %D ≤ 100%)

The laboratory detected endosulfan sulfate in soil sample SAA12 on column 1 at 5.6 ug/kg and on column 2 at 8.2 ug/kg. The %D between the two quantitated endosulfan sulfate results is 46.4%. Since the %D is greater than 25% but less than 100%, the validator estimates (J) the positive detect for endosulfan sulfate on the Data Summary Table and reports this in the Data Validation Memorandum.

Example #2: (%D > 500%)

The laboratory detected Aroclor 1262 in soil sample SAA56 on column 1 at 110 ug/kg and on column 2 at 15 ug/kg. The %D between the two columns for this analyte is 630%. Since the %D is greater than 500%, the validator rejects (R) the positive detect for Aroclor 1262 as unusable in sample SAA56. The validator reports Aroclor 1262 as rejected (R) on the Data Summary Table and discusses this in the Data Validation Memorandum.

Example #3: (%D > 25%)

A positive result for dieldrin was reported in sample SAA13. The analyte concentrations were 1.8 and 3.0 ug/L on the first and second column (66 %D), respectively. The percent difference is great enough that the validator suspects a potential interference on one of the columns. The validator reviews the sample chromatograms and determines that chromatographic resolution criteria on the second column for the dieldrin peak have not been met. Dieldrin is not resolved from an interferant, resulting in an elevated concentration quantitated from the second column. The validator uses professional judgment to estimate the lower concentration and reports it on the Data Summary Table as 1.8J and discusses this in the Data Validation Memorandum.

Example #4: (10% ≤ % Solids < 30%)

DQOs for the Maple Street Site call for low PCB detection limits to assess human health risk posed by the site contamination. Soil sample SAA100 had 15% solids and a positive detect for Aroclor 1254. Due to low percent solids, the Aroclor 1254 positive detect in sample SAA100 is estimated (J) and all PCB non-detects are rejected (R) in sample SAA100 due to percent solids less than 30%. The validator reports the qualified data on the Data Summary Table and notes that the non-detected data are unusable and do not meet project DQOs in the Data Validation Memorandum.

Example #5: (% Solids < 10%)

Sediment sample SAA90 had 8% solids and positive detects for 4,4'-DDT and 4,4'-DDE. As a result of the extremely low percent solids (< 10%), the validator rejects (R) all positive detects and non-detects for this sample as unusable. The validator contacts the sampler to determine if the sampling techniques which were used accommodated the high moisture samples. The validator reports the data as rejected (R) on the Data Summary Table and discusses the high moisture content of the sample and the need to perform sampling techniques specific to samples with high moisture content with analytical method alternatives to accommodate the high moisture samples in the Data Validation Memorandum.

# XIV. SYSTEM PERFORMANCE

## A. OBJECTIVE

The objective of assessing overall system performance is to determine if any method preparatory and/or analytical procedures result in qualitative and/or quantitative system error or bias. All sample, QC sample, and blank results are reviewed for accuracy, chromatography, precision, sensitivity, and contamination to ascertain if there are any general trends in data quality.

## B. CRITERIA

Since there are no specific criteria for system performance, professional judgment should be used to assess the overall performance.

## C. EVALUATION/ D. ACTION

| C. EVALUATION | D. ACTION |
|---|---|
| *1. The results of Zero, Single, and Double Blind PESs, MDL Study, LFB, Performance Evaluation Mixture (PEM), calibration standards, MS/MSD, surrogate spike analytes, GPC calibration verification, and Florisil cartridge check analyses may be used to assess the overall system accuracy including extraction efficiency and instrument response.<br><br>* a. Evaluate all PES and other relevant QC data to determine if any analytical trends exist over the sample analysis period.<br><br>* b. The validator should ascertain from the PES and other relevant QC data if there is a high or low quantitative bias for a particular analyte or group of analytes.<br><br>* c. The validator should also determine from the PES and other relevant QC data if there is a potential for false negatives and/or false positives to be reported.<br><br>* d. The validator should ascertain from the MS/MSD and surrogate spike analyte analyses if the sample matrix effects impact analyte recovery, thus indicating a method bias outside the control of the laboratory.<br><br>* e. The validator should ascertain from the GPC calibration verifications and Florisil cartridge check analyses whether sample cleanup techniques impact analyte recovery. | 1. The validator should refer to the previous sections for specific guidance in evaluating accuracy using PES, MDL study, LFB, PEM, calibration standard, MS/MSD, surrogate data, GPC calibration verification, and Florisil cartridge check. If the validator determines that analytical trends indicate a qualitative and/or quantitative systematic bias, then the validator should use professional judgment to determine whether or not to qualify or reject the sample data based on the extent of the impact. The validator should discuss and justify all technical decisions in the Data Validation Memorandum. The validator should differentiate between sample matrix-related preparatory and analysis problems that are outside the laboratory's control and those within the laboratory's control. |

| C. EVALUATION | D. ACTION |
|---|---|
| *2. The results of the Resolution Check Mixture (RCM), PEM, PES, LFB, and calibration standard analyses as well as field samples may be used to assess the overall performance of the chromatographic system.<br><br>* a. Evaluate sample and QC sample chromatograms analyzed on all columns to determine if the column chromatography, peak shape, resolution, and baseline drift has either deteriorated or improved over the sample analysis period.<br><br>* b. The validator should determine from the raw data if unacceptable chromatography, e.g., baseline drift, high background noise, loss of resolution, peak tailing, or peak splitting, may contribute to a high or a low quantitative bias for a particular analyte or group of analytes.<br><br>* c. The validator should also determine from the raw data if unacceptable chromatography, e.g., baseline drift, high background noise, loss of resolution, peak tailing, or peak splitting, may result in a potential for false negative and/or false positive identifications. | 2. The validator should refer to the previous sections for specific guidance on evaluating analyte identification and quantitation. If the validator determines that chromatographic trends indicate a qualitative and/or quantitative systematic bias, then professional judgment should be used to determine whether or not to qualify or reject the sample data based on the extent of the impact. The validator should discuss and justify all technical decisions in the Data Validation Memorandum. The validator should especially note when chromatography problems and column degradations are caused by severe matrix interferences. The validator should recommend additional cleanup procedures and/or alternate analytical methods for future site work. |

| C. EVALUATION | D. ACTION |
|---|---|
| *3. The results of the PEM, calibration standard, MDL Study, surrogate spike analyte, MS/MSD, and field duplicate analyses may be used to assess overall system precision.<br><br>* a. Compare all of the the daily standard calibrations and PEMs area counts throughout analytical sequence to ascertain if the instrument had consistent detector response over the sample analysis period.<br><br>* b. Review the size of the solvent peak and the area counts of the surrogate analytes for each sample to ascertain if there is a change in detector response.<br><br>* c. The validator should evaluate the MS/MSD RPDs in conjunction with field duplicate RPDs to identify any analytical trends, ascertain if sample matrices were homogeneous or heterogeneous, and determine if sampling error may have contributed to field imprecision.<br><br>* d. Verify that samples were analyzed on the same instrument and under the same conditions as were used for the MDL Study analyses. | 3. The validator should refer to the previous sections for specific guidance on evaluating laboratory and field precision and surrogate analyte analyses. If the validator determines that an instrument produces erratic detector responses, then the validator should use professional judgment to qualify or reject sample data. If MS/MSD RPDs indicate laboratory imprecision, then the validator should suspect laboratory technique and take into consideration the results of the field duplicate RPDs when using professional judgment to qualify sample data. If field duplicate RPDs indicate field imprecision resulting from heterogeneous sample matrices or field sampling error, then the validator should use professional judgment to qualify sample data based on the extent of impact. The validator should differentiate between lack of precision due to instrument performance problems and ones caused by matrix effects or sampling error. |

| C. EVALUATION | D. ACTION |
|---|---|
| *4. The results of the LFB, PES, calibration standards, and PEM analyses may be used to assess the overall system sensitivity.<br><br>* a. Review all daily LFBs, low level calibration standards, and PES data to evaluate sensitivity for each instrument to verify that the target analytes can be identified and accurately quantitated at the quantitation limit over the sample analysis period. These problems could potentially result in false negatives and low biased results.<br><br>* b. Check the area counts of the daily PEM and calibration standards to monitor changes in instrument sensitivity.<br><br>* c. Compare the area counts of surrogates in each sample throughout the analytical sequence to determine if any samples show unacceptably low counts.<br><br>* d. Review the sample chromatograms for abrupt, discrete shifts in the chromatographic baseline which may indicate a change in the instrument's sensitivity or the zero setting. A baseline "decline" could indicate a decrease in sensitivity in the instrument or an increase in the instrument zero, possibly causing target analytes, at or near the detection limit, to be missed (false negatives). Additionally, a decline in the baseline may result in incorrect peak integration and produce inaccurate quantitation.<br><br>A sudden baseline shift could indicate problems such as a change in the instrument zero, a leak, degradation of the column, or the formation of matrix degradation products. The validator should check for any abrupt shift in the zero setting which may cause a false positive to be reported. Additionally, a rise in the baseline may result in incorrect peak integration and subsequent misquantitation.<br><br>* e. The validator may determine that instrument sensitivity is adequate but sample matrix effects may preclude the project required detection limits from being obtained while using the current analytical methods. | 4. The validator should refer to the previous sections for specific guidance on evaluating sensitivity, accuracy, analyte identification, and quantitation. If the validator determines that instrument sensitivity is unacceptable, then the validator should use professional judgment to qualify or reject the affected sample data. The validator should discuss and justify all technical decisions in the Data Validation Memorandum. The validator should also note if sample matrix interferences prohibited the quantitation limits from being achieved and should recommend additional cleanup procedures and/or alternate analytical methods for future site work. |

| C. EVALUATION | D. ACTION |
|---|---|
| *5. The results of the PES method, instrument, equipment/rinsate, trip, and bottle blank analyses may be used to assess overall system contamination.<br><br>* a. Review all blank and sample results to evaluate the possibility that sample contamination was introduced via cross-contamination from either a previously analyzed sample, or from field or laboratory general contamination.<br><br>* b. Compare blank analysis on two different instruments to determine if the contamination is instrument related or the interferents are present in the blank as a result of sample processing activities. | 5. The validator should refer to the previous sections for specific guidance on evaluating blank contamination. If the validator determines that there is a systematic blank error introduced during sample collection or processing (extraction or analysis), then the data should be qualified according to Section V. However, if the validator suspects intermittent or sporadic introduction of interferents during analysis, then the validator should use professional judgment to qualify or reject sample data and document and justify all technical decisions in the Data Validation Memorandum. |

* **Note:** **This section is only applicable to a Tier III data validation - If a validator suspects system performance has degraded to the degree that data are affected and only a Tier II validation has been requested, then the validator should contact the Site Manager to approve the necessary Tier III validation.**

## E. EXAMPLES

Example #1: (Low LFB recoveries; Decreasing counts of surrogate analytes)

During the review of pesticide/PCB data, the validator notices a trend of decreasing external standard areas over a discrete analytical time period on the instrument. The validator notes that the majority of LFB analyte recoveries are below 60%. The validator also notes that surrogate analyte area counts show a decreasing trend throughout the analytical sequence. The validator uses professional judgment to estimate (J) all positive detects and estimate (UJ) the quantitation limits of all non-detects for all samples analyzed during the analytical sequence. The validator reports the qualified data on the Data Summary Table and discusses this in the Data Validation Memorandum.

Example #2: (Abrupt decreasing baseline)

The validator notices an abrupt decrease in the baseline the instrument during the analysis of sample SAP01. The validator notes that the area of the last eluting surrogate analyte in sample SAP01 differs significantly from the areas of the same surrogate from the previous sample runs. The validator inspects the chromatogram and observes abrupt decrease baseline in the middle of sample SAP01 run. The validator suspects that target analytes eluting after the abrupt baseline shift which are at or near the detection limit may not be detected. Therefore, the validator estimates (J) the positive detects and rejects (R) the non-detects that elute after the abrupt baseline shift. The validator reports the qualified data on the Data Summary Table and discusses this in the Data Validation Memorandum.

Example #3: (Several PES analytes show low bias; %D of continuing calibration unacceptable; Several LCS analytes show low bias)

The validator reviews the results of the Region I EPA PES sample analyzed by the laboratory and discovers that over half of the PES analytes were scored "Action Low". The validator determines that a low bias for the detected analytes in all samples has occurred. In addition to the low bias problem, the validator discovers that several of the same analytes in the PEM standards had greater than 25% Difference in the continuing calibration. The validator also notices that the LCS analyte recoveries for over half of the analytes were less than 60% indicating a potentially low bias for all positive detects. As a result of the analytical trend identified above, the validator estimates (J) the positive detects and rejects (R) the non-detects in all field samples. The validator reports the qualified data on the Data Summary Table and discusses this in the Data Validation Memorandum.

Example #4: (Corruption of analytical system by oily sample)

The validator reviews the PEM analyzed during the continuing calibration and discovers that the 4,4'-DDT and Endrin breakdown criteria were not met for either chromatographic column after the analysis of sample SAA746. However, the sample results for sample SAA746 were acceptable as all QC criteria were met. The validator noted several other problems which occurred after the analysis of sample SAA746, e.g., dissimilar column %Ds for field samples did not meet criteria, peak tailing, and an upward drift in the baseline. The validator proceeded to check the preparatory log sheets and notes that the sample has a thick and oily consistency which would contribute to the unacceptable chromatography in the samples and standards analyzed after SAA746. The validator uses professional judgment to qualify sample data resulting from poor chromatography caused by the analysis of an oily matrix. The validator reports the qualified data on the Data Summary Table and discusses this in the Data Validation Memorandum.

# XV. OVERALL EVALUATION OF DATA

## A. OBJECTIVE

The objective of the final evaluation of a data package is to identify the "analytical error" and any "sampling error" associated with the data. The sum of the "analytical error" and the "sampling error" equals the "measurement error". "Measurement error" will then be used by the end user in conjunction with sampling variability (spatial variations in pollutant concentrations) to determine "total error" (total uncertainty) associated with the data. Ultimately, the end data user will assess data usability in the context of the pre-determined Data Quality Objectives (DQOs) and resultant "total error" of the data.

## B. CRITERIA

The Sampling and Analysis Plan (SAP) or Quality Assurance Project Plan (QAPP) and DQO Summary Form should specify the site specific DQOs and acceptable levels of uncertainty or "total error".

## C. EVALUATION/ D. ACTION

| C. EVALUATION | D. ACTION |
|---|---|
| 1. Obtain the SAP, QAPP, or DQO Summary Form for the project. Thoroughly review and understand the DQOs for the sampling event. | 1. In the first section of the Data Validation Memorandum, entitled Overall Evaluation of Data, summarize the appropriate project DQOs. The summary should be in a bulleted format. |
| 2. Evaluate the appropriateness of the analytical method chosen by reviewing all the discussions in the previous sections. For example, was the method capable of achieving quantitation limits sufficiently low to meet DQOs for risk assessment? Was the method capable of successfully analyzing each particular matrix sampled? Was a “low” method chosen when the samples were likely to contain concentrations well above the upper calibration range? | 2. If an inappropriate method was chosen for sample analysis, then the validator should discuss the method deficiencies and identify more appropriate methods or modifications for use in subsequent sampling rounds. The validator should include this discussion in the Overall Evaluation of Data section of the Data Validation Memorandum. |
| 3. Evaluate any analytical problems that were identified by reviewing all the discussions in the previous sections. | 3. Estimate and describe the "analytical error" that contributes to the "measurement error" associated with the data package in the Overall Evaluation of Data section of the Data Validation Memorandum.<br>a. If "analytical error" results in unusable data, then the validator should reject the data and return it to the laboratory and deny payment as per Attachment I.<br>b. If "analytical error" results in data of reduced worth to the Region, then the validator should recommend a reduction in the laboratory’s payment. See Attachment I. |

| C. EVALUATION | D. ACTION |
|---|---|
| 4. Evaluate any sampling issues that were identified in the previous sections.<br><br>Note: The validator is only responsible for evaluating those "sampling errors" that are identified during the routine data validation process. Other "sampling errors" may have occurred and they should be assessed by the end user prior to data use. | 4. Estimate and describe the "sampling error" that contributes to the "measurement error" associated with the data package in the Overall Evaluation of Data section of the Data Validation Memorandum. Examples of "sampling error" for which the validator would have information include highly contaminated equipment blanks as well as delayed sample shipment that caused holding time violations; elevated moisture content, etc.<br><br>a. If "sampling error" severely impacts potential data usability, then the validator should note this in the Data Validation Memorandum and contact the EPA project manager.<br><br>b. The end user should review the results of the sampler's field notes/trip report to determine additional "sampling error" issues with which to fully assess "measurement error". |
| 5. Evaluate data quality in terms of "measurement error" as a combination of "analytical error" and "sampling error". | 5. Discuss data quality in terms of "measurement error" as the sum of "analytical error" and "sampling error". All discussions should be included in the Overall Evaluation of Data section of the Data Validation Memorandum. |
| 6. Identify potential usability issues raised by an unacceptable degree of "measurement error". | 6. If data usability is potentially compromised by a high degree of "measurement error", then the validator should note this in the Overall Evaluation of Data section of the Data Validation Memorandum. If data quality impacts the use of those data by the end user, then the validator should detail in the Overall Evaluation of Data section of the Data Validation Memorandum how data use will be limited and for which end user, i.e., risk assessor, hydrogeologist, etc. |
| 7. Sampling variability is not assessed during data validation, and therefore, should be assessed by the end user prior to data use. | 7. The end user should review the results of the Data Validation Memorandum in conjunction with the sampler's field notes/trip report to assess the impact of sampling variability issues on data usability. |