

**XI. ICP SERIAL DILUTIONS****A. OBJECTIVE**

Serial dilution sample results are generated to assess physical and chemical interferences caused by the sample matrix in ICP analysis. These interferences can cause suppression or enhancement of the analyte signal. If the analyte concentration in the sample is sufficiently high, an analysis of the diluted sample should agree within some acceptable QC criteria that have been established for that matrix and method. If not, a physical or chemical interference effect should be suspected.

**B. CRITERIA**

The Region-I, EPA-NE Data Validation Functional Guidelines for Evaluating Environmental Analyses should be used to validate all Region I Inorganic data. The CLP-Inorganic method QC acceptance criteria listed in Appendix I should be used as the default criteria when none exist for the Inorganic 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. In accordance with the SAP, QAPP and/or method, a field sample of each matrix is diluted, typically five-fold, to generate a serial dilution sample.
2. Field samples (not equipment or bottle blanks and not PE samples) must be diluted and analyzed to assess matrix interference effects.
3. The percent difference (% D) between the serial dilution sample result (after correction for the dilution) and the original determination (undiluted sample result) must be within the QC acceptance criteria specified in the method, SAP or QAPP. The analyte concentration must be sufficiently high, in accordance with method requirements, in order to apply the % D criteria.

## C. EVALUATION/D. ACTION

C. EVALUATION	D. ACTION
<p>1. Verify that a serial dilution sample was prepared and analyzed at the proper dilution and frequency, and that serial dilution sample results are provided for each sample matrix and for each ICP-AES and ICP-MS method used to report sample results. If the sample used for the serial dilution was diluted in order to bring the analyte's result within the initial calibration or linear range of the instrument, then the serial dilution must be performed on the diluted sample (from which the sample result was reported) for evaluating matrix interferences for that particular analyte.</p>	<p>All potential impacts on the sample data resulting from ICP serial dilution 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.</p> <p>1. If the laboratory did not prepare and analyze a serial dilution sample at the required dilution and frequency specified in the method for each sample matrix and ICP method, then the validator must use professional judgment to determine whether or not the associated sample data should be qualified.</p>
<p>2. Verify that a field sample was chosen for the serial dilution sample.</p>	<p>2. If an equipment blank, a bottle blank, or a PE sample was used for the serial dilution sample, then the validator should note this information in the Data Validation Memorandum and discuss the impact on assessing sample matrix effects and, ultimately, data usability</p>

C. EVALUATION	D. ACTION
<p>3. Verify that serial dilution percent differences are within the QC acceptance criteria specified in the method. If the analyte concentration in either the original (undiluted) sample or the diluted sample is sufficiently high, as specified in the method, then evaluate whether the serial dilution sample result (corrected for dilution) is greater than or less than the undiluted sample result to assess the potential for bias.</p> <ul style="list-style-type: none"> <li>- A serial dilution sample result that is greater than the undiluted sample result may indicate possible suppression of the analyte signal due to matrix interferences and potential low bias in sample results.</li> <li>- A serial dilution sample result that is less than the undiluted sample result may indicate possible enhancement of the analyte signal due to matrix interferences and potential high bias.</li> </ul>	<p>Note: Action applies to the affected analytes in <u>all</u> samples of the same matrix prepared and analyzed by the same method.</p> <p>3. a. If any serial dilution percent difference is greater than the method QC acceptance criteria and the serial dilution sample result is greater than the undiluted sample result, then the validator should:</p> <ul style="list-style-type: none"> <li>i. Estimate (J) positive detects for the affected analyte in all samples of the same matrix prepared and analyzed by the same method.</li> <li>ii. Estimate (UJ) non-detects for the affected analyte in all samples of the same matrix prepared and analyzed by the same method.</li> </ul> <p>b. If any serial dilution percent difference is greater than the method QC acceptance criteria and the serial dilution sample result is less than the undiluted sample result, then the validator should:</p> <ul style="list-style-type: none"> <li>i. Estimate (J) positive detects for the affected analyte in all samples of the same matrix prepared and analyzed by the same method.</li> <li>ii. Accept non-detects for the affected analyte in all samples of the same matrix prepared and analyzed by the same method. Professional judgment may be used to estimate non-detects if the direction of the bias cannot be determined.</li> </ul> <p>c. If the majority of analyte percent differences for a method are outside the QC acceptance criteria, then the validator may use professional judgment to estimate (J) all positive detects and estimate (UJ) all non-detects in all samples of the same matrix analyzed by the same method.</p>

C. EVALUATION	D. ACTION
<p>4. Evaluate the appropriateness of qualifying only the results of the sample used for the serial dilution analysis or a subset of the samples of the same matrix for the affected analyte.</p>	<p>4. Generally, action based on the serial dilution sample results is applied to the affected analyte across <u>all</u> samples of the same matrix prepared and analyzed by the same method in a sample delivery group. However, professional judgment may be used to determine sample matrix similarity and to apply the action only to the field sample used for the serial dilution analysis, or to a select group of samples in the SDG, if there is information to support such an action. All justifications for not qualifying all samples of the same matrix and limiting the qualification to specific samples should be documented in the Data Validation Memorandum and the potential impact on data usability in meeting the project DQOs should be discussed.</p>
<p>*5. Check and recalculate the analytical concentrations and percent differences for at least one analyte per analytical method. Verify that the recalculated values and % differences agree within <math>\pm 10\%</math> of the reported values. Confirm that the laboratory used the appropriate method criteria.</p>	<p>5. 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 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.</p>

\* **Note:** The following subsection is applicable only to a Tier III data validation:

**C.5**

Table INORG-XI-1:

**QUALIFICATION OF INORGANIC ANALYTES BASED ON SERIAL DILUTION  
PERCENT DIFFERENCES**

Sample Results	% D ≤ QC Limit	% D > QC Limit	
		Serial Dilution Sample Result > Undiluted Sample Result	Serial Dilution Sample Result < Undiluted Sample Result
Detects	A	J	J
Non-detects	A	UJ	A*

Note: Qualification is applied to the affected analyte in all samples of the same matrix prepared and analyzed by the same method. However, the validator may use professional judgment to qualify all positive detects and non-detects if the majority of the serial dilution analyte percent differences are outside the method QC acceptance criteria.

- \* Professional judgment may be used to estimate (UJ) non-detects if the direction of the bias cannot be determined.

#### E. EXAMPLES

Example #1: (Serial dilution % D > QC limit, Serial dilution sample result > undiluted sample result)

Aqueous sample MAEF47, analyzed by CLP SOW ILM05.4, has a high % D of 21% for lead in the five-fold serial dilution sample analysis by ICP-AES. The lead result of 175.1 ug/L in the original (undiluted) sample was greater than 50x the MDL of 3 ug/L, sufficiently high to apply the % D criteria. The lead result of 211.8 ug/L from the diluted sample analysis was greater than the original (undiluted) sample concentration of 175.1 ug/L.

Sample No.	Lead MDL (ug/L)	50x MDL (ug/L)	Undiluted Sample Result (ug/L)	Diluted Sample Result (corrected for dilution) (ug/L)	% D	% D QC Acceptance Criteria
MAEF47	3	150	175.1	211.8	21	10

As a result, the validator estimates (J) positive detects and estimates (UJ) non-detects for lead in all aqueous samples analyzed by ICP-AES on the Data Summary Table and notes in the Data Validation Memorandum the possibility of biased low results.

**E. EXAMPLES (continued)**

Example #2: (Serial Dilution % D > QC limit; Serial dilution sample result < undiluted sample result)

Soil sample MA7D14, analyzed by CLP SOW ILM05.4, has a high % D of 22% for chromium in the five-fold serial dilution sample analysis by ICP-AES. The serial dilution form, which reports the soil sample results as ug/L in the final digestate, shows a chromium result of 1331.26 ug/L in the original (undiluted) sample. This is greater than 50x the chromium MDL of 5 ug/L and sufficiently high to apply the % D criteria. The chromium result of 1037.42 ug/L from the five-fold diluted sample, reported on the serial dilution form, was less than the original (undiluted) sample concentration of 1331.26 ug/L.

Sample No.	Chromium MDL (ug/L)	50x MDL (ug/L)	Undiluted Sample Result (ug/L)	Diluted Sample Result (corrected for dilution) (ug/L)	% D	% D QC Acceptance Criteria
MA7D14	5	250	1331.26	1037.42	22	10

As a result, the validator estimates (J) positive detects and accepts non-detects for chromium in all soil samples analyzed by ICP-AES on the Data Summary Table and notes in the Data Validation Memorandum the possibility of biased high results.

**XII. SENSITIVITY CHECK****A. OBJECTIVE**

Many EPA methods including the CLP SOWs incorporate the analysis of sensitivity checks by requiring that a Method Detection Limit (MDL) study be performed prior to sample analysis and/or that a Laboratory Fortified Blank (LFB) be analyzed at the time of sample analysis. The MDL study generates statistically-based detection limits and can be used to assess method sensitivity, laboratory precision, and method bias for specific analytes within an analytical method on a specific instrument. An LFB, a type of Laboratory Control Sample, is a reagent blank which is spiked with the target analytes at their quantitation limits and is processed along with the samples. LFB data can be used to assess laboratory sensitivity and bias for specific analytes at the quantitation limit within an analytical method on a specific instrument at the time of sample preparation and analysis.

Region I routinely uses MDL studies as a pre-qualification check to verify the laboratory's ability to meet the technical specification/method requirements prior to contract award and field sample receipt. LFB analyses document the method sensitivity and bias associated with the day-to-day preparation and analysis of field samples.

**B. CRITERIA**

The Region I, EPA-NE Data Validation Functional Guidelines for Evaluating Environmental Analyses should be used to validate all Region I Inorganic data. The CLP-Inorganic method QC acceptance criteria listed in Appendix I should be used as the default criteria when none exist for the Inorganic 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. Method Detection Limit (MDL) Study**

- a. The method detection limit (MDL) for each analyte of interest must be established in accordance with the specified method and the Code of Federal Regulations (40 CFR Part 136, App. B). A minimum of seven replicates must be analyzed for each matrix of interest.
- b. Samples must be analyzed on the same instrument, under the same conditions, as was used for the MDL study.
- c. The MDL study must be performed within one year prior to the start of the preparation and/or analysis of the samples.
- d. The MDL for each target analyte must be less than or equal to that analyte's method-required quantitation limit.

**2. Laboratory Fortified Blank (LFB)**

- a. Verification of laboratory accuracy at the quantitation limit requires the routine analysis of an LFB spiked with target analytes at the quantitation limit.
- b. An LFB containing all of the target analytes at their respective quantitation limits must be prepared and analyzed along with the samples at the method-required frequency and analyzed at least once immediately prior to sample analysis but after instrument calibration.
- c. Method QC acceptance criteria must be met for target analytes and internal standards (if applicable).

**C. EVALUATION/ D. ACTION**

<b>C. EVALUATION</b>	<b>D. ACTION</b>
<p>Qualification of data should be based on a combined evaluation of both the MDL study and LFB results. To determine appropriate sample qualification, the MDL study should be evaluated first and then the LFB results.</p> <p><b>1. Method Detection Limit (MDL) Study</b></p> <ol style="list-style-type: none"> <li>a. Verify that the samples were analyzed on the same instruments as those used for the MDL study.</li> </ol>	<p>All potential impacts on the sample data resulting from MDL and/or LFB study 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.</p> <p><b>1. Method Detection Limit (MDL) Study</b></p> <ol style="list-style-type: none"> <li>a. If the samples were not analyzed on the same instruments as the MDL study, then the validator should contact the laboratory to obtain a correct MDL study. If an acceptable MDL study is unavailable, then the validator should evaluate the LFB data. If no LFB data are available, then the validator should use professional judgment to assess the impact of analytical sensitivity on data quality, taking into consideration the results of other low level standards analyzed.</li> </ol>

C. EVALUATION	D. ACTION
<p>1. b. Compare the date of the MDL study to the dates of all associated sample analyses to verify that the MDL study was performed within one year prior to the start of the first sample prepared and/or analyzed in the sample delivery group.</p> <p>c. Verify that all MDLs are less than or equal to the method-required quantitation limits.</p>	<p>1. b. If the MDL study was not submitted or was not performed within one year of the start of preparation and/or analysis of the first sample in the SDG, then the validator should contact the laboratory to obtain a current MDL study. If an acceptable MDL study is unavailable, then the validator should evaluate the LFB data. If no LFB data are available, then the validator should evaluate the instrument's response to the lowest standard of the initial calibration or other low level standard (e.g., Quantitation Limit Check Standard) and use professional judgment to assess the impact of analytical sensitivity on data quality.</p> <p>c. If the MDL study reveals that a target analyte has a detection limit greater than the method-required quantitation limit, then the validator should evaluate the LFB data. If no LFB data are available, then the validator should:</p> <ul style="list-style-type: none"> <li>i. Elevate the quantitation limit for that target analyte in all samples associated with that MDL study to the lowest concentration calibration standard, other low level standard (e.g., Quantitation Limit Check Standard) analyzed, or to the laboratory-reported MDL, whichever is higher.</li> <li>ii. Estimate (J) positive detects which were below the elevated quantitation limit for that target analyte in all samples associated with that MDL study.</li> <li>iii. The validator should evaluate the elevated quantitation limits in relation to the method-required quantitation limits and project DQOs. The validator should discuss any impact of the elevated quantitation limits on project objectives and data usability in the Data Validation Memorandum.</li> </ul>

C. EVALUATION	D. ACTION
<p>*1. d. Verify that the MDL study was generated in accordance with the method and 40 CFR Part 136, App. B. Verify that a minimum of seven replicates for each matrix of interest was prepared and analyzed.</p> <p>* e. For applicable methods (e.g., ICP-MS), verify that internal standard responses meet QC acceptance criteria.</p> <p>* f. Check and recalculate the MDL value for at least one analyte per MDL study per method. Verify that the recalculated values agree within <math>\pm 10\%</math> of the reported results. (Note: The MDL study raw data may not be provided with the data packages and may not be readily available to allow for verification or recalculation, as in the case of the CLP SOWs.)</p>	<p>1. d. If the required MDL study was not performed at all or was not performed according to the method or the CFR criteria, then the validator should evaluate the LFB data, if available, to determine the action to be taken. See Table INORG-XII-1. If no LFB data are available, then the validator should use professional judgment to assess the impact of analytical sensitivity on data quality. The results of other low level standards (e.g., Quantitation Limit Check Standard) should be evaluated and appropriate action taken. (See Section III, Calibrations.)</p> <p>e. If the MDL study reveals that a target analyte has a detection limit greater than the method-required quantitation limit, then the validator should evaluate the LFB data. If no LFB data are available, then the validator should:</p> <p>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, 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 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.</p>

C. EVALUATION	D. ACTION
<p><b>2. Laboratory Fortified Blank (LFB)</b></p> <p>a. Verify that an LFB was prepared (digested/distilled) and analyzed at the proper frequency and that it was spiked with the correct analytes at their quantitation limits.</p> <p>b. Verify that the reported recoveries for all LFB spike analytes are within the method QC acceptance criteria. If the LFB criteria are not met, then laboratory performance related to method bias and method/instrument sensitivity is questionable.</p>	<p><b>2. Laboratory Fortified Blank (LFB)</b></p> <p>a. If an LFB analysis was not performed or if the LFB was not analyzed for the correct analytes at the proper frequency and concentration, then the validator should use professional judgment to assess the impact of analytical sensitivity on data quality. Professional judgment should be used to qualify sample quantitation limits.</p> <p>b. If any of the LFB analyte recoveries are outside the method QC acceptance criteria, then the LFB results should be used to qualify sample data for the affected analytes that are included in the LFB solution. The validator should use professional judgment to qualify sample data for non-LFB analytes, taking into account information that may exist in the Sample Delivery Group for other low level standards.</p> <p>i. If an LFB analyte recovery is greater than the upper method QC limit, then the validator should:</p> <ul style="list-style-type: none"> <li>- Estimate (J) positive detects less than 2x the LFB true value for the affected analyte in all samples associated with that LFB to indicate potential high bias. The validator may use professional judgment to reject data based on the project DQOs.</li> <li>- Accept the non-detects for the affected analyte in all samples associated with that LFB.</li> </ul>

C. EVALUATION	D. ACTION
<p>2. b. Continued from above.</p>	<p>2. b. ii. If an LFB analyte recovery is less than the lower method QC limit but greater than or equal to 40%, then the validator should:</p> <ul style="list-style-type: none"> <li>- Estimate (J) positive detects less than 2x the LFB true value for the affected analyte in all samples associated with that LFB to indicate potential low bias.</li> <li>- Estimate (UJ) the non-detects at the quantitation limits for the affected analyte in all samples associated with that LFB to indicate potential low bias.</li> </ul> <p>iii. If an LFB analyte recovery is less than 40%, then the validator should:</p> <ul style="list-style-type: none"> <li>- Estimate (J) positive detects less than 2x the LFB true value for the affected analyte in all samples associated with that LFB. Professional judgment should be used to reject data taking into account project DQOs.</li> <li>- Reject (R) the non-detects at the quantitation limits for the affected analyte in all samples associated with that LFB to indicate that the data are unusable due to the possibility of false negatives.</li> </ul> <p>iv. For multi-analyte analysis, if more than half of the LFB analyte recoveries are outside the method QC acceptance criteria, then the validator may use professional judgment to apply validation actions to all positive detects and all non-detects at the quantitation limits associated with that LFB. A discussion of the rationale for data qualification and the qualifiers used should be documented in the Data Validation Memorandum.</p>

C. EVALUATION	D. ACTION
<p>2. b. Continued from above.</p>	<p>2. b. v. The validator should evaluate the LFB recoveries to determine whether project DQOs were achieved. Professional judgment should be used to determine whether the associated sample data should be qualified or rejected, taking into consideration the extent of deviation, the potential bias, and project DQOs. In some cases, it may be necessary to reject data. The Data Validation Memorandum should include a discussion of the rationale for data qualification and/or rejection.</p> <p>vi. The validator may use professional judgment to further apply data validation qualifiers to positive detects greater than 2x the LFB true value for the affected analyte, taking into account the extent of deviation from the LFB method QC acceptance criteria and the project DQOs. The validator should evaluate all relevant QC data which may provide information regarding the bias at the time of sample preparation and analysis and the laboratory's ability to accurately quantitate target analytes at concentration ranges greater than 2x the LFB true value. Qualification of results greater than 2x the LFB true value but less than the value of the next highest concentration QC sample, such as the laboratory control sample or PE sample, may be warranted. A discussion of the rationale for data qualification and the qualifiers used should be documented in the Data Validation Memorandum.</p>

C. EVALUATION	D. ACTION
<p>2. b. Continued from above.</p> <p>* c. Check and recalculate the % recovery for at least one target analyte per method and LFB. Verify that the recalculated value agrees within <math>\pm 10\%</math> of the reported result.</p>	<p>2. b. vii. If data quality objectives allow for greater variability of data at levels near the quantitation limit, then expanded LFB validation criteria should be documented in the EPA-approved site-specific QAPP or amendment to the QAPP.</p> <p>c. 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 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.</p>

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

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

Table INORG-XII-1:

**QUALIFICATION OF INORGANIC ANALYTES BASED ON LFB RECOVERIES**

Sample Results	% Recovery			
	% R < 40%	40% ≤ % R < LL	LL ≤ % R ≤ UL	% R > UL
Detects*	J (< 2x TV)**	J (< 2x TV)	A	J (< 2x TV)**
Non-detects	R	UJ	A	A

LFB = Laboratory fortified blank spiked with target analytes at their quantitation limits.

LL = Lower Limit of method QC acceptance criteria.

UL = Upper Limit of method QC acceptance criteria.

\* Action is applied to positive detects less than 2x the LFB true value.

\*\* Professional judgment may be used to reject positive results less than 2x the true value taking into account project DQOs. Professional judgment may be used to estimate positive detects greater than or equal to 2x the LFB true value but less than the value of the next highest concentration QC sample.

**E. EXAMPLES****Example #1:** (Low LFB recoveries for several analytes)

Water samples were analyzed by ICP-AES. Only the MDL values were reported with the data; the MDL study raw data were not available. The validator compares all MDL values to the method-required quantitation limits and determines that all MDLs were less than the required QLs. The LFB analytes chromium, nickel, and zinc recovered at 65%, 60%, and 53%, respectively, below the method QC acceptance criteria. The validator estimates (J) positive detects less than 2x the LFB true value for chromium, nickel, and zinc in all the samples associated with that LFB to indicate potential low bias and estimates (UJ) the non-detects at the quantitation limit for the chromium, nickel, and zinc non-detects in all samples associated with that LFB to indicate a decrease in sensitivity and the possibility of false negatives. The validator reports the qualified results on the Data Summary Table and notes this in the Data Validation Memorandum.

**Example #2:** (High LFB recoveries)

Water samples were analyzed by ICP-MS. Only the MDL values were reported with the data; the MDL study raw data were not available. The validator compares all MDL values to the method-required quantitation limits and determines that all MDLs were less than the required QLs. The LFB for selenium and thallium recovered above the method QC acceptance criteria. The validator estimates (J) positive detects less than 2x the LFB true value for selenium and thallium and accepts all non-detects. The validator reports the qualified results on the Data Summary Table and notes this in the Data Validation Memorandum.

Example #3: (Low LFB recovery < 40%)

Soil samples were analyzed by ICP-AES. Only the MDL values were reported with the data; the MDL study raw data were not available. The validator compares all MDL values to the method-required quantitation limits and determines that all MDLs were less than the required QLs. The cadmium LFB recovered below the method QC acceptance criteria and below 40%. Therefore, the validator rejects (R) all non-detects for cadmium and estimates (J) all positive cadmium detects less than 2x the true value of the LFB. Since the laboratory control sample and PE sample results at higher spike concentrations showed acceptable recoveries, and the QL Check Standard was within the method QC criteria, the validator uses professional judgment to take no further action on sample results greater than 2x the LFB true value. The validator reports the qualified results on the Data Summary Table and notes this in the Data Validation Memorandum.

**XIII. PERFORMANCE EVALUATION SAMPLES/ACCURACY CHECK****A. OBJECTIVE**

Data for Performance Evaluation Samples (PESs) are generated 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" surrounding any site decisions made concerning the "cleanliness" or contamination present at a site. A second problem revealed by PES analysis is the laboratory's erroneous detection of target and non-target analytes that were not spiked into the PES, otherwise known as false positives. False positives should always be evaluated in conjunction with blank data to ascertain 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 (digestion/distillation) and analysis (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 project action levels.

Ideally, a PES is comprised of the same matrix as the field samples being evaluated. However, for some matrices PESs may not be available. In these situations, a PES of another matrix 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 that is of a composition and concentration known to the laboratory.

A Laboratory Control Sample (LCS) is a Zero Blind PES which is often used by the laboratory as an internal quality control check of analytical accuracy and method bias, including the efficiency of the digestion/distillation procedure.

An LCS containing several or all of the target analytes spiked at concentrations at or near their quantitation limits is called a Laboratory Fortified Blank (LFB). Refer to Section XII (Sensitivity Check) for additional LFB guidance.

- a. An LCS is required by some EPA methods and 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 the target analytes and must be prepared and analyzed concurrently with field samples contained in the sample delivery group.

**B. CRITERIA (continued)**

1.
  - b. The percent recoveries for LCS analytes must be within the method QC acceptance criteria.
  - c. Internal standards, if applicable, for the LCS must meet validation criteria as per Section VII (ICP-MS Internal Standards) of this document.

**2. Single Blind Performance Evaluation Samples**

A Single Blind PES is a quality control sample that is of a composition and concentration 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 pre-qualify a laboratory for a specific matrix and/or parameter.

- a. The latest revision of the EPA Region I Performance Evaluation Program Guidance 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 or non-EPA PES does not currently exist for that particular matrix, parameter, or 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 latest revision of the EPA Region I Performance Evaluation Program Guidance. 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 Services Branch 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 latest revision of the EPA Region I Performance Evaluation Program Guidance.
- 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. Internal standards, if applicable, for the PES must meet validation criteria as per Section VII (ICP-MS Internal Standards) of this document.

**B. CRITERIA (continued)**

**3. Double Blind Performance Evaluation Samples**

A Double Blind PES is a quality control sample that is of a composition and concentration 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. Internal standards, if applicable, for the PES must meet validation criteria as per Section VII (ICP-MS Internal Standards) of this document.

**C. EVALUATION/ D. ACTION**

C. EVALUATION	D. ACTION
<p><b>1. Zero Blind PES - LCS</b></p> <ul style="list-style-type: none"> <li>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 and for each batch of samples prepared (digested/distilled) in accordance with the EPA approved project SAP, QAPP and/or method.</li> </ul> <p>Note: In the CLP SOW ILM05.4, the digested ICV serves as the aqueous LCS for mercury, and the distilled ICV serves as the aqueous LCS for cyanide. See Section III, Calibrations.</p>	<p>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.</p> <p><b>1. Zero Blind PES - LCS</b></p> <ul style="list-style-type: none"> <li>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.</li> </ul>

C. EVALUATION	D. ACTION
<p>1. b. Verify that the required LCS results are provided for each sample delivery group and for each batch of samples prepared (digested/distilled).</p> <p>c. Verify that the reported recoveries for all LCS spike analytes are within the method QC acceptance criteria.</p> <p>Note: The CLP SOW ILM05.4 aqueous LCS method acceptance criteria of 80-120% recovery does not apply to antimony and silver, which have no control limits. For data validation purposes, the 80-120% recovery method QC acceptance criteria shall be applied to both antimony and silver. If data quality objectives allow for greater variability of data, then an expanded LCS validation criterion should be documented in the EPA-approved site-specific QAPP or amendment to the QAPP.</p> <p>Note: Non-aqueous LCSs obtained from EPA as well as certified materials obtained from other sources typically provide upper and lower concentration control limits specific to that LCS. In this case, the validator should use the criteria established for that specific material to evaluate the non-aqueous LCS results. Confirm that LCS acceptance criteria are fully documented and scientifically defensible.</p>	<p>1. b. If the required LCS results were not submitted for each sample delivery group and for each batch of samples prepared, then the validator should contact the laboratory to obtain raw data and tabulated results.</p> <p>c. Sample data should be qualified based on the analytes that recover outside the method QC acceptance criteria and on the degree that analyte recoveries exceed the criteria.</p> <p>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 any analytical problems historically associated with the analyte or that were encountered by the laboratory.</p> <p>ii. If an aqueous LCS analyte recovery is greater than the upper limit of the method QC acceptance criteria, but less than or equal to 150%, or if the non-aqueous LCS analyte result is greater than the upper control limit, then the validator should:</p> <ul style="list-style-type: none"> <li>- Estimate (J) positive detects for the affected analyte in all samples associated with that LCS to indicate potential high bias.</li> <li>- Accept the non-detects for the affected analyte in all samples associated with that LCS.</li> </ul>

C. EVALUATION	D. ACTION
<p>1. c. Continued from above.</p>	<p>1. c. iii. If an analyte recovery for an aqueous LCS is greater than 150%, then the validator should:</p> <ul style="list-style-type: none"> <li>- Reject (R) positive detects for the affected analyte in all samples associated with that LCS.</li> <li>- Accept non-detects for the affected analyte in all samples associated with that LCS.</li> </ul> <p>iv. If an aqueous LCS analyte recovery is less than the lower limit of the method QC acceptance criteria but greater than or equal to 50%, or if a non-aqueous LCS analyte result is less than the lower control limit, then the validator should:</p> <ul style="list-style-type: none"> <li>- Estimate (J) positive detects for the affected analyte in all samples associated with that LCS to indicate potential low bias.</li> <li>- Estimate (UJ) non-detects for the affected analyte in all samples associated with that LCS to indicate potential low bias.</li> </ul> <p>v. If an analyte recovery for an aqueous LCS is less than 50%, then the validator should:</p> <ul style="list-style-type: none"> <li>- Reject (R) positive detects and non-detects for the affected analyte in all samples associated with that LCS.</li> </ul>

C. EVALUATION	D. ACTION
<p>1. c. Continued from above.</p>	<p>1. c. vi. If more than half of the LCS analyte recoveries for one LCS analyzed by a particular method are greater than the upper method QC acceptance criteria, or if more than half of the LCS analyte recoveries for a particular method are less than the lower method QC criteria, then the validator should use professional judgment to apply the above validation actions to all positive detects and non-detects in all samples associated with that LCS.</p> <p>vii. If more than half of the LCS analyte recoveries for a particular method 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, or all of the analytes, for samples associated with that LCS.</p> <p>viii. Based upon the number 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 method is unusable and, therefore, should be rejected. Rejected data should be returned to the laboratory and payment denied.</p>

C. EVALUATION	D. ACTION
<p>*1. d. Check and recalculate the percent recovery for at least one analyte per method per LCS. Verify that the recalculated value agrees within <math>\pm 10\%</math> of the reported result.</p>	<p>1. d. 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 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.</p>
<p><b>2. Single Blind <u>and</u> Double Blind PESs</b></p> <p>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.</p> <p>b. Verify that Single Blind PES results are provided for each sample delivery group in accordance with Region I PE policy.</p>	<p><b>2. Single Blind <u>and</u> Double Blind PESs</b></p> <p>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.</p> <p>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 omission of a PES and document that fact on the worksheet and in the Data Validation Memorandum.</p>

C. EVALUATION	D. ACTION
<p>2. c. <b>Region I EPA PESs</b></p> <p>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.</p> <p>i. Evaluate each PES "Analyte Missed" to assess the potential for low bias and false negative sample results.</p>	<p>2. c. <b>Region I EPA PESs</b></p> <p>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.</p> <p>i. Sample data should be qualified based on the PES "Analytes Missed" identified on the Region I PES Score Report. If a PES analyte is not identified in the PES, then the validator should:</p> <ul style="list-style-type: none"> <li>- Estimate (J) positive detects for the affected analyte in all samples associated with that PES to indicate potential low bias.</li> <li>- Reject (R) non-detects for the affected analyte in all samples associated with that PES to indicate that the data are unusable due to the possibility of false negatives.</li> <li>- Based upon the number of analytes that were not identified and a review of the project DQOs, the validator should use professional judgment to determine if all data generated by a particular method are unusable and, therefore, should be rejected. Rejected data should be returned to the laboratory and payment denied.</li> </ul>

C. EVALUATION	D. ACTION
<p>2. c. ii. Evaluate each PES “Contaminant” in conjunction with blank data to assess the potential for high bias and false positive sample results.</p> <p>iii. Evaluate the PES analytes that were misquantified (“Action High”/ “Action Low”) to assess the potential for high and/or low bias in sample data.</p>	<p>2. c. ii. Sample data should not be qualified based on the number of PES “Contaminants” identified on the Region I PES Score Report <u>alone</u>.</p> <ul style="list-style-type: none"> <li>- If a PES “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 III (Blanks).</li> <li>- If a PES “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.</li> </ul> <p>iii. Sample data should be qualified based on the number and type of misquantified PES analytes (“Action High”/ “Action Low”) identified on the Region I PES Score Report. <b>Sample data should not be qualified based on “Warning Low”/ “Warning High” scores for PES analytes.</b></p> <ul style="list-style-type: none"> <li>• 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. Professional judgment should be used to qualify sample data for non-PES analytes taking into account the analytical problems historically associated with the analyte or that were encountered by the laboratory.</li> </ul>

C. EVALUATION	D. ACTION
<p>2. c. iii. Continued from above.</p>	<p>2. c. iii. Continued from above.</p> <ul style="list-style-type: none"> <li>• If a PES analyte is scored in the “Action High” category, then the validator should:                             <ul style="list-style-type: none"> <li>- Estimate (J) positive detects for the affected analyte in all samples associated with that PES to indicate potential high bias.</li> <li>- Accept the quantitation limits of the affected analyte in all samples associated with that PES.</li> </ul> </li> <li>• If a PES analyte is scored in the “Action Low” category, then the validator should:                             <ul style="list-style-type: none"> <li>- Estimate (J) positive detects for the affected analyte in all samples associated with that PES to indicate potential low bias.</li> <li>- Reject (R) the quantitation limits of the affected analyte in all samples associated with that PES to indicate that the data are unusable due to the possibility of false negatives.</li> </ul> </li> <li>• If more than half of the PES analytes for one PES analyzed by a particular method are scored in the “Action High” category, or if more than half of the PES analytes for a particular method are scored in the “Action Low” category, then the validator should use professional judgment to apply the above validation actions to all positive detects and non-detects in all samples associated with that PES.</li> </ul>



C. EVALUATION	D. ACTION
<p>2. d. <b>Non-EPA PESs</b></p> <p>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.</p> <p>i. Evaluate the PES analytes missed to assess the potential for low bias and false negative sample results.</p> <p>ii. Evaluate the PES contaminants in conjunction with blank data to assess the potential for high bias and false positive sample results.</p>	<p>2. d. <b>Non-EPA PESs</b></p> <p>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.</p> <p>i. Sample data should be qualified based on the PES analytes missed identified from the vendor's acceptance criteria. If a PES analyte is not identified in the PES, then the validator should:</p> <ul style="list-style-type: none"> <li>- Estimate (J) positive detects for the affected analyte in all samples associated with that PES to indicate potential low bias.</li> <li>- Reject (R) the non-detects for the affected analyte in all samples associated with that PES to indicate that the data are unusable due to the possibility of false negatives.</li> <li>- Based upon the number of analytes that were not identified for a particular method and PES, and a review of the project DQOs, the validator should use professional judgment to determine if the data set for an entire method is unusable and, therefore, should be rejected. Rejected data should be returned to the laboratory and payment denied.</li> </ul> <p>ii. Sample data should not be qualified based on the number of PES contaminants identified from the vendor's acceptance criteria <u>alone</u>.</p>



C. EVALUATION	D. ACTION
<p>2. d. iii. Continued from above.</p>	<p>2. d. iii. Continued from above.</p> <ul style="list-style-type: none"> <li>- Accept non-detects for the affected analyte in all samples associated with that PES.</li> <li>• If a PES analyte recovery is outside the lower limit of the vendor's documented acceptance limits (see note above, Section 2.d.iii), then the validator should:             <ul style="list-style-type: none"> <li>- Estimate (J) positive detects for the affected analyte in all samples associated with that PES to indicate potential low bias.</li> <li>- Reject (R) non-detects for the affected analyte in all samples associated with that PES to indicate that the data are unusable due to the possibility of false negatives.</li> </ul> </li> <li>• If more than half of the PES analyte recoveries for one PES analyzed by a particular method are outside the upper limit of the vendor's documented acceptance limits, or if more than half of the PES analyte recoveries for a particular method are outside the lower limit of the vendor's documented acceptance limits, then the validator should use professional judgment to apply the above validation actions to all positive detects and non-detects in all samples associated with that PES.</li> </ul>



C. EVALUATION	D. ACTION
<p>*2. f. Check and recalculate the analytical concentrations for at least one analyte per method per PES. Verify that the recalculated value agrees within <math>\pm 10\%</math> of the reported result.</p>	<p>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 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.</p> <p>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.</p> <p>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.</p>

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

C.1.d, C.2.e, C.2.f

Table INORG-XIII-1:

**QUALIFICATION OF INORGANIC ANALYTES BASED ON LCS RESULTS\***

Sample Results	Aqueous LCS % Recovery				
	%R < 50%	50% ≤ %R < LL	LL ≤ %R ≤ UL	UL < %R ≤ 150%	%R > 150%
Detects	R	J	A	J	R
Non-detects	R	UJ	A	A	A

Sample Results	Non-aqueous LCS Result		
	Result < LL	LL ≤ Result ≤ UL	Result > UL
Detects	J	A	J
Non-detects	UJ	A	A

LL - Lower Limit of method QC acceptance criteria

UL - Upper Limit of method QC acceptance criteria

\* If more than half of the LCS analyte recoveries for a particular method fall within one of the above categories, then professional judgment may be used to apply the action to all analytes in all samples associated with that LCS. Professional judgment should be used when a combination of low recoveries and high recoveries are obtained.

Table INORG-XIII-2:

**QUALIFICATION OF INORGANIC ANALYTES BASED ON PES RESULTS\***

Sample Results	<ul style="list-style-type: none"> <li>● Single Blind</li> <li>● Double Blind</li> </ul> PES < Lower Limit "Action Low" or "Analyte Missed"	<ul style="list-style-type: none"> <li>● Single Blind</li> <li>● Double Blind</li> </ul> PES "Within Warning Limits" "Warning High/Warning Low"	<ul style="list-style-type: none"> <li>● Single Blind</li> <li>● Double Blind</li> </ul> PES > Upper Limit "Action High"
Detects	J	A	J
Non-Detects	R	A	A

LL - Lower Limit of method QC acceptance criteria

UL - Upper Limit of method QC acceptance criteria

\* If more than half of the PES analytes fall within one of the above categories, then professional judgment may be used to apply the action to all analytes in all samples associated with that PES. Professional judgment should be used when a combination of low recoveries and high recoveries are obtained.

## E. EXAMPLES

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

An aqueous Laboratory Control Sample (LCS) containing 22 analytes is found to have silver with a percent recovery of 60% and zinc with a percent recovery of 130%. The method QC acceptance criteria for aqueous LCS recoveries are 80-120% (exception: there are no method QC acceptance criteria for silver). The validator estimates (J) positive detects for zinc and silver in all field samples associated with that LCS. The validator accepts the zinc non-detects and estimates (UJ) the silver 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 the zinc positive detects are biased high, the silver positive detects are biased low, and the silver non-detects contain possible false negatives.

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

A Single Blind Performance Evaluation Sample (PES) is found to have a selenium positive result that scored below the lower PES acceptance limit. Therefore, the validator estimates (J) positive selenium detects and rejects (R) the non-detects for selenium in all field samples associated with that PES. The validator reports the qualified data on the Data Summary Table and notes in the Data Validation Memorandum that the positive selenium detects are biased low and selenium non-detects are rejected due to the possibility of false negatives.

Example #3: (More than one-half of PES analytes analyzed by ICP-AES > upper PES acceptance limits)

A Single Blind PES containing 22 analytes analyzed by ICP-AES is found to have more than one-half of the spiked PES analytes analyzed with % recoveries above the upper PES acceptance limits. The validator uses professional judgment to estimate (J) all positive detects identified by ICP-AES in all field samples associated with that PES and accept all ICP-AES non-detects in all field samples associated with that PES. The validator reports qualified data on the Data Summary Table and notes that the positive ICP-AES 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 22 spiked PES analytes analyzed by ICP-AES with results that do not meet PES acceptance criteria. Some of the PES analytes are flagged "Action Low" and some are flagged "Action High". 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 non-detects 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.

**E. EXAMPLES (continued)**Example #5: (One PES “Analyte Missed”)

A Single Blind PES is found to have one PES “Analyte Missed” for antimony which is a contaminant of concern at the site. The validator estimates (J) all positive antimony detects and rejects (R) all antimony non-detects 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.

Example #6: (One PES “Contaminant”, also in blank)

A Single Blind PES is found to have one PES “Contaminant”, sodium, at 450 ppb. The preparation blank contained 80 ppb of sodium, resulting in a Blank Action Level of 400 ppb. The validator uses the sodium Blank Action Level to evaluate the sample data and reports qualified data on the Data Summary Table. The validator suspects that the sodium 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 “Contaminant”, not in blank)

A Single Blind PES is found to have one PES “Contaminant”, barium, which is not detected in any of the blanks but is detected in two samples. The validator determines that the barium is an interference specific to the PES because it was not detected in any of the preparation or instrument blanks. The validator uses professional judgment to accept the positive barium detects in the field samples. The validator reports the data unqualified on the Data Summary Table and discusses this in the Data Validation Memorandum.

**XIV. ANALYTE 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 from raw data to the final reported concentrations are checked 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 Inorganic data. The CLP-Inorganic method QC acceptance criteria listed in Appendix I should be used as the default criteria when none exist for the Inorganic 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. Reported quantitation limits must meet project-required DQOs.
2.
  - a. 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.
  - b. Reported concentrations for positive detects and analyte quantitation limits for non-detects must be adjusted for percent solids, dilutions, concentrations, and sample preparation procedures that are not accounted for in the method.
3. Target analyte quantitation must be based on the masses and internal standards (ISs) specified in the method, if applicable.
4. Target analyte quantitation must be within the initial calibration range or within the established linear range of the ICP, if applicable.
5. All soil/sediment sample results must be adjusted for percent solids and must have percent solids greater than 30 percent.<sup>1</sup>

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.

<sup>1</sup>U.S. EPA Office of Water Regulations and Standards Industrial Technology Division - Method 1620, p. 29, Section 14.16, Draft September 1989.

5. (Continued)

Most analytical methods that deal with 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 may or may not be successfully analyzed by routine CLP analytical methods. Additional sampling and analytical preparation steps may need to 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 preparation and the initial volume of sample digested/distilled must be increased accordingly. This presumes that the samplers have collected sufficient volume, above and beyond normal volume requirements, so that additional sample can be digested/distilled. As a last resort, the laboratory can decrease the final prepared volume.

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
<p>1. Verify that the reported quantitation limits meet project-required DQOs.</p>	<p>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.</p> <p>1. If reported quantitation limits do not meet the project-required DQOs, then the validator must investigate and document the cause of the deficiency and use professional judgment to assess sample data.</p>

C. EVALUATION	D. ACTION
<p>*2. a. Recalculate from the raw data the concentrations for at least one positive detect and one sample quantitation limit (for a diluted sample or a soil sample) for each method, in every field sample to verify that laboratory-reported sample results were accurately calculated according to the method.</p> <p>* b. Verify that the concentrations for positive detects and sample quantitation limits have been adjusted to reflect sample dilutions, concentrations, sample preparation factors, and dry weight factors that are not accounted for in the method.</p>	<p>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 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.</p> <p>b. If the concentrations for positive detects and/or sample quantitation limits were not correctly adjusted for sample dilutions, concentrations, preparation 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 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.</p>

C. EVALUATION	D. ACTION
<p>3. Verify that the concentrations for positive detects are within the initial calibration range of the instrument or within the established linear range of the ICP, if applicable.</p>	<p>3. a. If the concentrations for positive detects exceed the upper limit of the initial calibration range or exceed the linear range of the ICP, if applicable, and no dilutions were reported, then the validator should estimate (J) those positive detects that exceed the initial calibration range or linear range.</p> <p>b. If the concentrations for positive detects fall below the lower limit of the initial calibration range (or below the lowest concentration standard), then the validator should estimate (J) those positive detects.</p>
<p>4. Ascertain if any soil/sediment/solid sample has less than or equal to 30 percent solids. Determine if appropriate sampling and/or analytical preparation steps were employed for high moisture content samples.</p>	<p>4. a. If a soil/sediment/solid sample has greater than 30 percent solids, then the validator should accept all sample data.</p> <p>b. If a soil/sediment/solid sample has percent solids of less than or equal to 30% but greater than or equal to 10%, then the validator should:</p> <ul style="list-style-type: none"> <li>• Estimate (J) positive detects.</li> <li>• Reject (R) non-detects.</li> </ul> <p>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.</p>

C. EVALUATION	D. ACTION
<p>4. Continued from above.</p>	<p>4. 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.</p> <p>e. If any sampling and/or analytical preparation steps were employed to address high moisture soil/sediment/solid samples, such as removing the aqueous medium or increasing the sample size to account for low percent solids, then the validator should use professional judgment to determine whether the associated sample data should be qualified or accepted and whether project DQOs were achieved. The validator must take into consideration the dry weight quantitation limits, whether the sampling and analytical methods were appropriate for the sample matrix, and the project DQOs. The Data Validation Memorandum should include a discussion of the rationale for data qualification and/or data acceptance.</p>

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

C.2.a, C.2.b

Table INORG-XIV-1:

**QUALIFICATION OF INORGANIC ANALYTES BASED ON SAMPLE PERCENT SOLIDS\***

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

\* Professional judgment should be used to accept, qualify or reject the associated sample data when sampling and/or analytical preparation steps were employed to address high moisture soil/sediment samples.

**E. EXAMPLES**Example #1: ( $10\% \leq \% \text{ Solids} \leq 30\%$ )

DQOs for the Maple Street site specify that soil samples be analyzed for low level metals to assess human health risk posed by the site contamination. Metals soil sample MAAH72 had 20% solids. Due to the low percent solids, all positive results are estimated (J) and all non-detects are rejected (R) as unusable because the elevated sample quantitation limits do not meet project DQOs. The validator reports the qualified data on the Data Summary Table and notes this problem in the Data Validation Memorandum.

Example #2: ( $\% \text{ Solids} < 10\%$ )

Sediment sample MAGH11 had 9% solids. As a result of the extremely low percent solids ( $< 10\%$ ), the validator rejects (R) as unusable all positive detects and non-detects for this sample. The validator contacts the field sampler to determine if sampling techniques were inappropriate for the sample matrix resulting in high moisture content. The validator reports the qualified data on the Data Summary Table and discusses the high moisture content of the sample and the inappropriateness of the sampling and/or analytical methods in the Data Validation Memorandum.

Example #3: ( $10\% \leq \% \text{ Solids} \leq 30\%$ ; Sample weight increased)

Soil sample MACH50 had 20% solids. The validator reviews the SDG narrative and preparation log which indicate that a higher sample weight was employed for sample digestion to address the sample's high moisture content. The validator determines that the dry weight CRQLs and project DQOs were achieved by the increased sample weight. Therefore, the validator uses professional judgment to accept the sample results. The validator reports the data unqualified on the Data Summary Table and discusses the high moisture content, the preparatory method, and the rationale used to accept the data in the Data Validation Memorandum.

## XV. 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, 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
<p>*1. The results of Zero (LCS), Single and Double Blind PESs, MDL studies, LFBs, QL Check Standards, calibration standards, calibration verifications, ICP interference check samples, and matrix spike analyses may be used to assess the overall system accuracy including sample digestion/distillation efficiency and instrument response.</p> <p>* a. Evaluate all PES and other relevant QC data to determine if any analytical trends exist over the sample analysis period.</p> <p>* 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.</p> <p>* c. The validator should also ascertain from the PES and other relevant QC data if there is a potential for false negatives and/or false positives to be reported.</p> <p>* d. The validator should ascertain from the matrix spike analyses if the sample matrix effects impact analyte recovery, thus indicating a method bias outside the control of the laboratory.</p>	<p>1. The validator should refer to the previous sections for specific guidance in evaluating accuracy using PES/LCS, MDL study, LFB, QL Check Standard, calibration standard, calibration verification, ICP interference check sample, and matrix spike data. 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 preparatory and analysis problems that are within the laboratory's control.</p>

C. EVALUATION	D. ACTION
<p>*2. The results of the calibration verification, internal standard (ICP-MS), analytical replicate (e.g., replicate integrations), laboratory duplicate, and field duplicate analyses may be used to assess overall system precision.</p> <p>* a. Compare the calibration verification results to ascertain if the instrument generated consistent responses over the sample analysis period.</p> <p>* b. Review the responses of the ICP-MS internal standards for each sample to ascertain if there is a change in instrument response.</p> <p>* c. Review the results of the analytical replicates to evaluate the precision of the individual determinations and to ascertain if there are any trends in precision over the entire analytical run.</p> <p>* d. The validator should evaluate the laboratory duplicate results in conjunction with the field duplicate results to identify any analytical trends, ascertain if sample matrices were homogeneous or heterogeneous, and determine if sampling error may have contributed to field imprecision.</p>	<p>2. The validator should refer to the previous sections for specific guidance on evaluating laboratory and field precision and analytical replicate and internal standard analyses. If the validator determines that an instrument produces erratic responses, then they should use professional judgment to qualify or reject sample data. If laboratory duplicate results indicate laboratory imprecision, then the validator should suspect laboratory technique and take into consideration the field duplicate results when using professional judgment to qualify sample data. If field duplicate results 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 that caused by matrix effects or sampling error.</p>

C. EVALUATION	D. ACTION
<p>*3. The results of the LFB, QL Check Standard, PES, calibration and internal standard (ICP-MS) analyses may be used to assess the overall system sensitivity.</p> <p>* a. Review all low level calibration standards, LFBs, QL Check Standards, and PES data to evaluate sensitivity for each instrument to verify that no instrument has lost its ability to accurately quantitate and identify analytes at the quantitation limit over the sample analysis period, which could potentially result in false negatives and low biased results.</p> <p>* b. Check the responses of the individual sample, QC sample, calibration verification, and blank internal standards (ICP-MS) as well as calibration verification results to monitor instrument sensitivity changes.</p> <p>* c. For instrument printouts which produce a baseline, review the raw data for abrupt shifts in the baseline which may indicate a change in the instrument's sensitivity or zero setting. Evaluate negative values which could indicate a decrease in the instrument's sensitivity caused by instrument or baseline drift, possibly resulting in target analytes at or near the detection limit to miss detection (false negatives). Similarly, the validator should also check for any abrupt shift which may cause a false positive to be reported. A decrease or increase in the baseline may result in incorrect integration and subsequent misquantitation.</p> <p>* d. The validator may determine that instrument sensitivity is adequate but sample matrix effects may preclude obtaining the quantitation limits required by the project DQOs using the analytical method employed.</p>	<p>3. The validator should refer to the previous sections for specific guidance on evaluating sensitivity, accuracy, and 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 did not allow quantitation limits to be achieved and should recommend additional and/or alternate preparatory or analytical methods for future site work.</p>

C. EVALUATION	D. ACTION
<p>*4. The results of the PES and preparation blank, calibration blank, equipment/rinsate blank, and bottle blank analyses may be used to assess overall system contamination.</p> <p>* a. Review all blank and sample results to evaluate the possibility of sample contamination introduced via either cross-contamination from a previously run sample or from general lab contamination.</p> <p>* b. Compare blank analyses to determine if the contamination is instrument related or if the interferences are present in the blank from sample processing activities.</p> <p>* c. Assess whether problematic blank results are reproducible when replicate aliquots are analyzed or are sporadic interferences. Sporadic interferences may indicate that the interferent is introduced from the laboratory environment. The validator should review the raw data for suspected outlier interferences.</p>	<p>4. 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 (digestion/distillation or analysis), then the data should be qualified according to Section IV (Blanks). However, if the validator suspects intermittent or sporadic introduction of interferences 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.</p>

- \* **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 a Tier II validation has been requested, then the validator should contact the Site Manager to approve the necessary Tier III validation.

#### E. EXAMPLE

##### Example #1: (Abrupt decrease in baseline)

The validator examines the instrument printout for the mercury analysis and observes a significant abrupt decrease in the baseline during the analysis of the last two samples, MAXN25 and MAXN26, as well as an erratic baseline: The instrument printout shows a steady baseline prior to the analysis of these two samples. The PE samples associated with these samples were acceptable; however, the PE samples were analyzed at the beginning of the run when the baseline was steady. The validator uses professional judgment to estimate (J) the positive detect and reject (R) the non-detect for mercury associated with these two samples. The validator reports the qualified data on the Data Summary Table. The validator notes the sensitivity loss of the mercury analyzer and justifies the decision to qualify sample data in the Data Validation Memorandum.

## XVI. 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 predetermined 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 to review the DQOs of the sampling event.	1. Synopsise in the first section of the Data Validation Memorandum, Overall Evaluation of Data, in bullet format, the appropriate project DQOs for the data package.
2. Evaluate the appropriateness of the analytical method chosen. 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?	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.

C. EVALUATION	D. ACTION
<p>3. Evaluate any analytical problems that were identified.</p>	<p>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.</p> <ul style="list-style-type: none"> <li>a. If "analytical error" causes the data to be unusable, then the validator should reject the data and return it to the laboratory and deny payment.</li> <li>b. If "analytical error" causes the data to be of reduced worth to the Region, then the validator should recommend that the laboratory's payment be reduced.</li> </ul>
<p>4. Evaluate any sampling issues that were identified.</p> <p>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.</p>	<p>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.</p> <ul style="list-style-type: none"> <li>a. If "sampling error" severely impacts potential data usability, then the validator should note this in the Data Validation Memorandum.</li> <li>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."</li> </ul>
<p>5. Evaluate data quality in terms of "measurement error" as a combination of "analytical error" and "sampling error."</p>	<p>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.</p>

C. EVALUATION	D. ACTION
<p>6. Identify potential usability issues raised by an unacceptable degree of "measurement error."</p>	<p>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.</p>
<p>7. Sampling variability is not assessed during data validation and, therefore, should be assessed by the end user prior to data use.</p>	<p>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.</p>