USEPA REGION 4

Science and Ecosystems Support Division
Management & Technical Support Branch
Quality Assurance Section
980 College Station Road
Athens, Georgia 30605-2720

Data Validation Standard Operating Procedures for

CONTRACT LABORATORY PROGRAM CYANIDE DATA

BY

SPECTROPHOTOMETRIC / COLORIMETRIC TECHNIQUES

Review Process:	Print Name:	Organization:	Signature:	Date:
Prepared by:	Denise L. Goddard	SESD/QAS	Denise L. Goddard	9/2/11
Reviewed by:	Nancy Seabolt	SESD/QAS	Nancy Seabolt	9/2/11
Approved by:	Marilyn Maycock	SESD/QAS	Marilyn Maycock	9/2/11

Periodic Review

Reviewer:				
Date:				

Table of Contents

Tables

Attachments

A Data Review Summary Narrative
B Data Review-Time Tracker
C Data Review Summary Narrative (Manual Review)
D Data Review Assessment Report (Manual Review)
E Data Package/Archive Box Inventory Form

HISTORY OF REVISIONS

Revision Number	Issue Date	Action	Description
2.0	08/24/2011	Original	Original SOP for the Quality Assurance Section applicable to Data Review / Validation for Externally Generated Analytical Data Generated for Region 4

1.0 Purpose

The United States Environmental Protection Agency (USEPA), Contract Laboratory Program (CLP) is a key provider of analytical services to the Superfund Program. The Quality Assurance Section of the Science and Ecosystems Support Division (SESD), in conjunction with the Environmental Services Assistance Team (ESAT) contractor, is responsible for providing data review and validation services in support of Superfund data collection activities performed within Region 4.

2.0 Applicability

This Standard Operating Procedure is applicable to the review of water, soils and sediment cyanide data by spectrophotometric / colorimetric analysis at trace and low to medium concentrations. It is further based on the quality assurance/quality control (QA/QC) and technical requirements specified in Exhibit D of SOW ISM01.2, and revisions.

This document provides the criteria for performing technical and quality assurance reviews of data generated by contract laboratories under the CLP Statement of Work (SOW) - ISM01.2, Inorganic Superfund Methods, Multi-Media, Multi-Concentration, January 2010, and revisions. This SOP incorporates the content of the National Functional Guidelines for Inorganic Superfund Data Review (NFG) January 2010, and revisions. However, this SOP provides additional guidance to limit the use of professional judgment by taking into account region-specific data review and validation requirements and reporting formats, etc. This SOP does not contain the procedures for entering qualified data into the Region 4 LIMS system – this information is contained in a separate SOP. Contract compliance or data usability issues pertinent to risk assessment activities, are not addressed in this document.

This SOP shall be followed without deviation to ensure that a consistent data review product is provided to the Region 4 - CLP Inorganic Task Order/Project Officer (TO/PO). If the data reviewer(s), using professional judgment, decide to take exception to any of the criteria or actions specified in this SOP, he/she must consult the TO/PO prior to making any changes. No deviations from the specified criteria or actions stipulated in this SOP will be undertaken by the data reviewer(s) unless those changes are authorized, in writing, by the TO/PO.

Authorized deviations will be documented in the data review memorandum.

3.0 Personnel Qualifications

For EPA personnel a minimum of a four year degree from an accredited college or university in a scientific field is required. Experience in analyzing environmental samples, and in performing data review / validation is also recommended.

4.0 Procedural Steps: Data Processing

Samples are collected by EPA, contractor, or state personnel and then are submitted to an assigned contract laboratory for analysis. The laboratory analyzes the samples according to specified analytical protocols, assembles a data package and an electronic data file in accordance with specifications in the contract. The original data package is submitted to the Science and Ecosystem Support Division (SESD), Athens, Georgia, and a copy, along with the electronic data deliverable (EDD), are delivered to the Sample Management Office (SMO) / Data Assessment Support Services (DASS) contractor.

4.1 Contact Compliance Screening

At SMO/DASS, the data package and the EDD are checked for compliance with the contract. A Contract Compliance Screening (CCS) report is issued to the region and is posted on the WebDat web site. The EDD is then processed electronically to evaluate QC performance against the NFG and Region 4 data quality guidelines by the Electronic data eXchange and Evaluation System (EXES). Currently, for the routine inorganic contracts, a SEDD Stage 2a EDD is submitted by the laboratories.

4.1.1 Electronic Data Review - National Functional Guideline Report

A report of this electronic review (the NFG report) is submitted to the region, along with a text file containing the results, qualified in accordance with the Region 4 data qualifier hierarchy. The data package delivered to SESD is audited for evidentiary completeness. The report(s) of the electronic review (if available for all samples in the case) is examined to identify any issues that warrant further investigation. The results of Performance Evaluation Samples (PES) are scored and the data are appropriately qualified.

4.1.2 Manual Data Review

In the event that no electronic review was performed or the report(s) is not available, the data are manually reviewed for technical quality and for compliance with Region 4 data quality requirements, beginning with the case or SDG (Sample Delivery Group) narrative, the original unprocessed or raw data, the QC summary forms, and the sample tracking and processing information included in the package. Region 4 data qualifiers, intended to provide the customer with a more complete understanding of the factors affecting data quality, are added to the results. A report of this review is prepared to complete the documentation of data quality, and the data are electronically entered into the Region 4 laboratory information management system, *Element*. Review reports and project documents are maintained by the SESD Quality Assurance Section (QAS), and the data package is archived. Completed data validation reports should contain the following statement: A Stage 4 validation consisting of electronic and manual review was performed on the inorganic samples submitted as part of this case.

4.2 Procedural Steps: Review / Validation of Cyanide Data by Spectrophotometric / Colorimetric Techniques

4.2.1 Holding Times/Preservation (Forms IA-IN, IB-IN, XII-IN, XIII-IN, etc.)

Holding times are evaluated from the perspective of technical or actual holding times. These are determined as the age of the sample from date and time of sample collection to the date and time of sample preparation/distillation, and analysis. The contractual holding times are determined from the Validated Time of Sample Receipt (VTSR) and are used for contract compliance but will not be addressed in this SOP.

The following guidance is based on past practice in Region 4 and on the best available information on matrix holding times from 40CFR Part 136 requirements, as well as other USEPA guidance: The technical holding time is calculated from the time and date of sample collection to the date of analysis. The time and date of collection is located on the Traffic Report/Chain-of-Custody (TR/COC) form included in the analytical data package. The dates of sample preparation and analysis are located on the Form XIII-IN and the raw data. If holding times are exceeded or proper preservation has not occurred, describe this in the data review summary case narrative and take the appropriate actions.

Criteria:

- The technical holding time criteria for aqueous/water cyanide samples is 14 days; oxidizing agents removed, then preserved (with sodium hydroxide) to pH ≥ 12. The addition of sodium hydroxide to adjust the pH is only required for aqueous/water samples.

- The technical holding time criteria for soil/sediment cyanide samples is 14 days, based on the technical holding time criteria for aqueous/water samples.

- Cyanide samples (water and soil / sediment) shall be maintained at 4 ºC (± 2 °C) until preparation and analysis.

NOTE: Concentrations of cyanide detected between the MDL and the CRQL, shall be qualified as J, Q-2.

Table 1 Holding Time & Preservation for Cyanide Analysis

Holding Time	Preservation	Action for Samples
Aqueous/water cyanide samples received with oxidizing agents present.	Samples preserved with base at pH ≥ 12.	Non-Detects: R, custom flag Detects (> MDL but < CRQL): J, Q-2, custom flag Detects (≥ CRQL): J, custom flag
Aqueous/water cyanide samples received with sulfides present, and sulfides are not removed	Samples preserved with base at pH ≥ 12.	Non-Detects: R, custom flag Detects (> MDL but < CRQL): J, Q-2, custom flag Detects (≥ CRQL): J, custom flag

Table 1 Holding Time & Preservation for Cyanide Analysis - Continued

Holding Time	Preservation	Action for Samples
Samples prep/analyzed within 14 days of collection	Aqueous/water samples preserved in field with sodium hydroxide (base) to pH ≥ 12	No action required.
Samples prep/analyzed within 14 days of collection	Aqueous/water samples **were not** preserved in the field with base to pH ≥ 12. Lab **did not preserve** upon receipt.	Non-Detects are unusable: R, P-5 Detects (> MDL but < CRQL): J, P-5, Q-2 Detects (≥ CRQL): J, P-5
Samples prep/analyzed within 14 days of collection	Aqueous/water samples **were not** preserved in the field with base to pH ≥ 12. But Lab staff **preserved** sample with sodium hydroxide upon receipt	***Lab Allowed sample to sit for at least 24 hours prior to prep/analysis***. Non-Detects: No Qualification Detects: No Qualification
Samples prep/analyzed within 14 days of collection	Aqueous/water samples **were not** preserved in the field with base to pH ≥ 12. But Lab staff **preserved** sample with sodium hydroxide upon receipt	***Lab Did not allow the sample to sit for at least 24 hours prior to prep/analysis.*** Non-Detects: R, P-6 Detects (> MDL but < CRQL): J, Q-2, P-6 Detects (≥ CRQL) : J, P-6
Samples prep/analyzed after 14 days of collection	Aqueous/water samples preserved in field with base to pH ≥ 12.	Non-Detects: R, H-1 Detects (> MDL but < CRQL): J, Q-2. H-1 Detects (≥ CRQL): J, H-1
Samples prep/analyzed after 14 days of collection	Aqueous/water samples **were not preserved** in field or at laboratory with base to pH ≥ 12.	All Results: R, H-1, P-4
Samples prep/analyzed within 14 days of collection.	Samples not received at or stored at 4 ºC (± 2 ºC) Aqueous / water, soil / sediment	**Do Not Qualify Data. Document in Case Narrative.**
Samples prep/analyzed after 14 days from collection	Soil/sediment	Non-Detects: R, H-1 Detects (> MDL but < CRQL): J, Q-2, H-1 Detects (≥ CRQL): J, H-1

4.2.2 Initial and Continuing Calibrations (Form XVI-IN)

Method requirements for satisfactory instrument calibration are established to ensure that the instrument is capable of producing acceptable quantitative data for cyanide. Initial Calibration Verification (ICV) demonstrates that the instrument is capable of acceptable performance at the beginning of the analytical run. Continuing Calibration Verification (CCV) demonstrates that the initial calibration is still valid by checking the performance of the instrument on a continuing basis.

The instruments shall be successfully calibrated daily (or once every 24 hours), and each time the instrument is set up. The calibration date and time shall be included in the raw data.

A blank and at least five calibration standards shall be employed to establish the analytical curve. At least one of the calibration standards shall be at or below the Contract Required Quantitation Limit (CRQL). The calibration curve shall be fitted using linear regression or weighted linear regression. The curve may be forced through zero. The calibration curve for cyanide shall possess a correlation coefficient of ≥ 0.995 to ensure the linearity over the calibrated range. The percent differences calculated for all of the non-zero standards must be within ±30% of the true value of the standard. The y-intercept of the curve must be less than the CRQL.

All sample results shall be reported from an analysis within the calibrated range.

All standards shall be distilled. If the ICV or the CCV are not distilled, qualify the results that are ≥ MDL as estimated.

4.2.2.1 Initial and Continuing Calibration Verification (ICV and CCV) - Acceptance Criteria

The acceptance criteria for calibrations for cyanide analysis are:

Analytical Method	**Inorganic Analyte**	**ICV/CCV Low Limit (% of True Value)**	**ICV/CCV High Limit (% of True Value)**
Spec/Colorimetric	Cyanide	85	115

4.2.2.2 Initial Calibration Verification (Forms II-IN (Parts A & B), XI-IN, XIII-IN, and XVI-IN, etc.)

Criteria:

- Immediately after each cyanide colorimetric system has been calibrated, the accuracy of the initial calibration must be verified and documented for cyanide by the analysis of an ICV solution(s). If the ICV %R falls outside of the control limits, the analysis should be terminated, the problem corrected, the instrument recalibrated, and all affected samples reanalyzed.

- If the ICV is not available from USEPA, or where a certified solution of the analyte is not available from any source, analyses shall be conducted on an independent standard at a concentration level other than that used for instrument calibration, but within the calibrated range.

- For cyanide analysis, the ICV standard solution shall be distilled.

4.2.2.3 Continuing Calibration Verification

Criteria:

- To ensure accuracy during the course of each analytical run, the CCV shall be analyzed and reported.

- The CCV standard shall be analyzed at a frequency of every hour during an analytical run. The CCV standard shall also be analyzed at the beginning of the run, and again after the last analytical sample.

- The analyte concentration in the CCV standard shall be different from the concentration used for the ICV, and shall be at the mid level of the calibration curve.

- The same CCV standard solution shall be used throughout the analytical sequence for a Sample Delivery Group (SDG). The CCV shall be distilled.

- The CCV shall be processed and analyzed in the same fashion as an actual sample. If the %R of the CCV was outside of the control limits, the analysis should be terminated, the problem corrected, the instrument recalibrated, and all analytical samples analyzed since the last compliant CCV reanalyzed.

4.2.2.4 Preliminaries: Additional Guidance

Criteria:

- If the instrument was not calibrated daily and each time the instrument was set up, qualify the data as unusable (R). If the instrument was not calibrated with at least the minimum number of standards, or if the calibration curve does not include standards at required concentrations (e.g., a blank and a standard at or below the CRQL), use professional judgment to qualify results that are ≥ Method Detection Limit (MDL) as estimated (J) or unusable (R), and non-detects as estimated (UJ) or unusable (R). Refer to Table 2 below.

- If the correlation coefficient is < 0.995, the percent differences are outside the 70-130% acceptance limits, or y-intercept ≥ CRQL, qualify sample results that are ≥ MDL as estimated (J), and non-detects as estimated (J), [if other criteria are not met qualify as unusable (R)].

- If the standards, the ICV, or the CCVs are not distilled for cyanide, qualify sample results that are ≥ MDL as estimated (J).

- If the ICV or CCV %R falls outside the acceptance windows, use professional judgment to qualify all associated data. If possible, indicate the bias in the review. The following guidelines are recommended:

- If the ICV or CCV %R is < 70%, qualify non-detects as unusable (R). Use professional judgment to qualify all results that are ≥ MDL as estimated low (J) or unusable (R).

- If the ICV or CCV %R falls within the range of 70-84%, qualify sample results that are ≥ MDL as estimated low (J), qualify non-detects as estimated (UJ).

- If the ICV or CCV %R falls within the range of 116-130%, qualify sample results that are ≥ MDL as estimated high (J).

- If the ICV or CCV %R is within the range of 116-130%, non-detects should not be qualified.

- If the ICV or CCV %R is > 130%, use professional judgment to qualify results that are ≥ MDL as estimated high (J) or unusable (R). Non-detects should not be qualified.

- If the %R is > 160%, qualify all results that are ≥ MDL as unusable (R).

- If the laboratory failed to provide adequate calibration information, the Region's designated representative should contact the laboratory and request the necessary information. If the information is not available, the reviewer must use professional judgment to assess the data.

Note the potential effects on the reported data due to exceeding the calibration criteria in the Data Review Case Narrative. If calibration criteria are grossly exceeded, contact the CLP Inorganic TO/PO.

Table 2 ICV & CCV for Cyanide Analysis

Calibration Result	Action for Samples
Calibration not performed	All Results: R, Custom Flag
Calibration incomplete	Non-Detects: R, Custom Flag Detects (> MDL but <CRQL): R, Custom Flag Detects (≥ CRQL): J, Custom Flag
Correlation coefficient <0.995; residuals outside 70-130%; y intercept ≥ CRQL	Non-Detects: R, CLP16 Detects (> MDL): J, CLP16
ICV/CCV %R < 70%	Non-Detects: R, QC-5 Detects (> MDL but < CRQL): J, QC-5, Q-2 Detects (≥ CRQL): J, QC-5
ICV/CCV %R 70-84%	Non-Detects: J, QC-5 Detects (> MDL but < CRQL): J, QC-5, Q-2 Detects (≥ CRQL): J, QC-5
ICV/CCV %R 116-130%	Non-Detects: No Qualification Required Detects (> MDL but < CRQL): J, Q-2, QC-6 Detects (≥ CRQL): J, QC-6
ICV/CCV %R > 130%	Non-Detects: No Qualification Required Detects (> MDL but < CRQL): R, Q-2, QC-6 Detects (≥ CRQL): J, QC-6
ICV/CCV %R > 160%	Non-Detects: No Qualification Required Detects (> MDL but < CRQL): R, Q-2, QC-6 Detects (≥ CRQL): R, QC-6

4.2.3 Blanks (Forms I-IN, III-IN, XII-IN and XIII-IN, etc.)

The objective of evaluating blank analyses is to determine the existence and magnitude of contamination resulting from laboratory (or field) activities. The criteria for evaluation of blanks apply to any blank associated with the samples (e.g., method blanks, calibration blanks, etc.). However, it has been Region 4 data validation policy to exclude field blanks (equipment blanks and rinsates, etc.) as part of this evaluation. The case narrative will address field blank contamination if data quality is compromised. Contact the Region 4 CLP Inorganic TO/PO for further direction regarding the treatment of blank contamination.

If problems with any blank exist, all associated data must be carefully evaluated to determine whether or not there is an inherent variability in the data, or if the problem is an isolated occurrence not affecting other data. Contact the Region 4 CLP Inorganic TO/PO for further direction regarding the treatment of blank contamination.

Note: For non-CLP analyses, consult the CLP Inorganic TO/PO prior to data review to discuss how blank contamination will be treated.

Criteria:

- No contaminants should be found in the blank(s).

- The Initial Calibration Blank (ICB) shall be analyzed after the analytical standards, but not before analysis of the Initial Calibration Verification (ICV) during the initial calibration of the instrument.

- A Continuing Calibration Blank (CCB) shall be analyzed, immediately after every ICV and Continuing Calibration Verification (CCV). The CCB shall be analyzed at the beginning of the run, and again after the last CCV that was analyzed after the last analytical sample of the run. The CCB result (absolute value) shall not exceed the Contract Required Quantitation Limit (CRQL) for cyanide.

- At least one Preparation Blank shall be prepared and analyzed for each matrix, with every Sample Delivery Group (SDG), or with each batch of samples distilled, whichever is more frequent. The Preparation Blank consists of reagent water processed through the appropriate sample preparation and analysis procedure.

- If the cyanide concentration in the Preparation Blank is > CRQL, the lowest concentration of cyanide in the associated samples must be 10 times (10x) the Preparation Blank concentration. Otherwise, all samples associated with that Preparation Blank with a cyanide concentration < 10x the Preparation Blank concentration, and > CRQL, should be redistilled and reanalyzed (except for an identified field blank). The laboratory is not to correct the sample concentration for the blank value.

- If the concentration of the Preparation Blank for cyanide is < (-CRQL), all samples reported < 10x the CRQL (associated with that analyte in that blank), should be redistilled and reanalyzed.

Note: To avoid confusion, use the blank containing the highest concentration of analyte(s) as the basis for qualifying all the sample(s) in the analytical sequence.

- For ICBs that do not meet the technical criteria, apply the action to all samples reported from the analytical sequence.

- For CCBs that do not meet the technical criteria, apply the action to all samples in the analytical sequence.

- For Preparation Blanks that do not meet the technical criteria, apply the action to all samples prepared in the same preparation batch.

- The frequency and sequence of analysis for all of the required blanks should be consistent with requirements specified in ISM01.2. Exhibit D, Part D, Section 12.4.

Table 3 Blanks for Cyanide Analysis

Blank Type	Blank Result	Sample Result	Action for Samples
Preparation Blank ICB/CCB (No Field Blanks)[1]	Detects	Non-Detects	No Qualification Required
	< CRQL	< CRQL	Report CRQL value with a U.
	Detects	≥ CRQL and < 10 x Blank[1]	Report result with a U, B-4
	Detects	≥ CRQL and > 10 x Blank	No Qualification
Preparation Blank ICB/CCB (No Field Blanks)	≤ - MDL but ≥ - CRQL	Non-Detect: absolute value	Report CRQL value with a U.
		Detects: absolute value at ≥ CRQL and < 10 x Blank	Non-Detects: Raise to CRQL and qualify U, B-4 Detects **(> MDL but < CRQL & < 10x blank):** Raise to CRQL and qualify U, B-4 Detects **(≥ CRQL but < 10x blank):** Qualify result U, B-4. Detects **(≤ CRQL and ≥ 10x blank)**: No qualification Detects **(≥ CRQL and ≥ 10x blank):** No qualification
		Detects: absolute value at ≥ CRQL and > 10 x Blank	No Qualification

NOTE: **From the various blanks analyzed for a given SDG, select the blank containing the highest concentration of a detected analyte and use this blank to evaluate/qualify the associated samples/data**.

[1]If significant contamination of field blanks, and/or equipment/rinsate blanks occurs, the data user will be informed of this via the data validation memorandum. Do not qualify the data based on these blanks.

4.2.4 Duplicates (Forms VI-IN and XII-IN)

The objective of duplicate sample analysis is to demonstrate acceptable method precision by the laboratory at the time of analysis. Duplicate analyses are also performed to generate data that determines the long-term precision of the analytical method on various matrices.

Criteria:

- Samples identified as field blanks or Performance Evaluation (PE) samples cannot be used for duplicate sample analysis.

- At least one duplicate sample shall be prepared and analyzed from each group of samples of a similar matrix type (e.g., water or soil) or for each Sample Delivery Group (SDG). Duplicates cannot be averaged for reporting on Form I-IN. Additional duplicate sample analyses may be required by USEPA Regional request. Alternately, the Region may require that a specific sample be used for the duplicate sample analysis.

- A control limit of 20% for the Relative Percent Difference (RPD) shall be used for original and duplicate sample values ≥ five times (5x) the Contract Required Quantitation Limit (CRQL).

- A control limit of the CRQL shall be used if either the sample or duplicate value is < 5x the CRQL. The absolute value of the control limit (CRQL) shall be entered in the "Control Limit" column on Form VI-IN. If both samples are non-detects, the RPD is not calculated for Form VIIN. Qualify only the sample associated with the duplicate.

Table 4 Duplicate Samples for Cyanide Analysis

Duplicate Sample Results	Action for Samples
Both original water sample and water duplicate sample > 5x the CRQL and RPD > 20%.	Non-Detects: No qualification required Detects (> MDL but < CRQL): J, Q-2, QM-4 Detects (≥ CRQL): J, QM-4
Both original soil/sediment sample and soil/sediment duplicate sample > 5x the CRQL and RPD > 35%.	Non-Detects: No qualification required Detects (> MDL but < CRQL): J, Q-2, QM-4 Detects (≥ CRQL): J, QM-4
Original samples or duplicate samples ≤ 5x the CRQL (including non-detects) and absolute difference between sample and duplicate > CRQL.	Non-Detects: J, QM-4 Detects (> MDL but <CRQL): J, Q-2, QM-4 Detects (≥ CRQL): J, QM-4

4.2.5 Matrix Spike/Matrix Spike Duplicates [Forms V-IN (Part A & B) and XII-IN]

The spiked sample analysis is designed to provide information about the effect of each sample matrix on the sample preparation procedures and the measurement methodology. Non-homogenous samples can impact the apparent method recovery. However, aqueous/water samples are generally homogenous and most soil/sediment samples are homogenous within a factor of two or three. If the spike is added to the sample prior to any distillation steps (e.g., cyanide), it is referred to as a spiked sample, pre-distillation spike, or Matrix Spike. If the spike is added to the sample after the completion of the distillation procedures, it is referred to as a post-distillation spike, or analytical spike.

Criteria:

- Samples identified as field blanks or Performance Evaluation (PE) samples cannot be used for spiked sample analysis.

- At least one spiked sample (pre-distillation) shall be prepared and analyzed from each group of samples with a similar matrix type (e.g., water or soil), or for each Sample Delivery Group (SDG).

- When the pre-distillation spike recovery falls outside of the control limits and the sample result is < four times (4x) the spike added, a post-distillation spike shall be performed An aliquot of the remaining un-spiked sample shall be spiked at 2x the indigenous level or 2x the Contract Required Quantitation Limit (CRQL), whichever is greater.

- The spike Percent Recovery (%R) shall be within the established acceptance limits. However, spike recovery limits do not apply when the sample concentration is ≥ four times (4x) the spike added. In such an event, the data shall be reported un-flagged, even if the %R does not meet the acceptance criteria.

- If the spiked sample analysis was performed on the same sample that was chosen for the duplicate sample analysis, spike calculations shall be performed using the results of the sample designated as the "original sample". The average of the duplicate results cannot be used for the purpose of determining %R.

  Criteria:

- (See Criteria 3 above). Post distillation spike recoveries acceptance limits are 75 – 125%.

NOTES:

- Acceptance limits for cyanide spiked samples are 75 – 125%.

- Only the field sample associated with the non-performing MS/MSD should be qualified unless instructed otherwise by the EPA Inorganic TO/PO.

Table 5 Pre-Distillation & Post Distillation Spike Samples for Cyanide Analysis

Spike Sample Results	Action for Samples[2]
Matrix Spike %R ≤ 10% Post Distillation spike %R < 75%	**Reject non-detects** in the field sample associated with the MS/MSD. R, QM-6, CLP-34 Detect (>MDL but ≤ CRQL): J, Q-2, QM-6, CLP34 Detect (≥ CRQL): J, QM-6, CLP34
Matrix Spike %R is 10 % - 75% Post Distillation Spike %R < 75%	Non-Detects: R, QM-1, CLP-34 Detects (>MDL but < CRQL): J, Q-2, QM-1, CLP34 Detects (≥ CRQL): J, QM-1, CLP34
Matrix Spike %R is 10 % - 75% Post Distillation Spike %R 75% - 125%	Non-Detects: J, QM-1 Detects (>MDL but < CRQL): J, Q-2, QM-1 Detects (≥ CRQL: J, QM-1)
Matrix Spike %R > 125% Post Distillation spike < 75%	Non-Detects: No qualification required. Detects (>MDL but < CRQL): J, Q-2, QM-2, CLP34 Detects (≥ CRQL): J, QM-2, CLP34
Matrix Spike %R > 125% Post Distillation spike %R 75 – 125%	Non-Detects: No qualification required. Detects (>MDL but < CRQL): J, Q-2, QM-2 Detects (≥ CRQL): J, QM-2
Matrix Spike %R > 125% Post Distillation spike %R >125% but < 150%	Non-Detects: No Qualification Detects (> MDL but < CRQL): J, Q-2, QM-2, CLP35 Detects (≥ CRQL): J, QM-2, CLP35
Matrix Spike %R > 125% Post Distillation Spike ≥ 150%	Non-Detects: No qualification required. **Reject detects** for that analyte(s) in the field sample associated with the MS/MSD: R, QM-2, CLP35
Matrix Spike %R < 10% No Post Distillation Spike Performed	**Reject all data** only in the field sample associated with the MS/MSD. R, QM-1
Matrix Spike %R < 50% No Post Distillation Spike Performed	Non-Detects: R, QM-1 Detects (>MDL but < CRQL): J, Q-2, QM-1 Detects (≥ CRQL): J, QM-1
Matrix Spike %R 50% - 74% No Post Distillation Spike Performed	Non-Detects: J, QM-1 Detects (>MDL but < CRQL): J, Q-2, QM-1 Detects (≥ CRQL): J, QM-1
Matrix Spike %R > 125% No Post Distillation Spike Performed	**Reject detects** only in the field sample associated with the MS/MSD. R, QM-1

[2] Only the field sample associated with the matrix spike sample should be qualified.

4.2.6 Performance Evaluation Samples

A Performance Evaluation Sample (PES) or a set of PE samples are included as part of each project sample delivery group (SDG) submitted to the CLP Program for analysis. For larger projects, including sampling efforts extending for more than one week, multiple sets of PES may be used. The laboratories are required to prepare and analyze the PES with the field samples of the associated case/SDG. If the PES is not prepared, digested and/or analyzed concurrently with field samples for a particular project/SDG/case, the data reviewer shall contact the EPA Inorganic TO/PO for further instructions. The TO/PO may decide that it is not appropriate to use the PES for data qualification.

The table below summarizes data qualification required based on the PES scoring results. Under certain circumstances, the spiked analyte is not evaluated by scoring software. This may occur when either lower limits do not exist for a particular analyte or the analyte was not evaluated.

The reviewer may describe instances in the narrative when the laboratory failed to identify a spiked analyte for which lower limits did not exist but PES database statistics suggest that the analyte should still have been identified by the laboratory. Additionally, all analytes which are scored as PES contaminants, either less than or greater than the CRQL, are treated as method blank contaminants, applying standard blank rules described in Section 5 above.

If only one set of PES is included in a case, all samples will be qualified based on the PES scoring. If multiple sets of PES are included, all data for the associated sampling week will be qualified based on the PES scoring.

Table 6 Performance Evaluation Samples

PES Score	Actions for Samples
Within Limits	Non-Detects & Detects: No qualification required
Warning Low	Non-Detects: J, CLP25 Detects (> MDL but < CRQL): J, Q-2, CLP25 Detects (≥ CRQL): J, CLP25
Action Low	**Reject non-detects** : R, CLP27 Detects (>MDL but < CRQL): J, Q-2, CLP27 Detects (≥ CRQL): J, CLP27
Warning High	Non-Detects: No Qualification Detects (> MDL but < CRQL)): J, Q-2, CLP26 Detect (≥ CRQL): J, CLP26
Action High	Non-Detects: No qualification **Reject all detects**: R, CLP28

4.2.7 Data Qualifier Definitions

Region 4 applies qualifiers to the cyanide data as defined in the SOWs referenced above, and in the National Functional Guidelines with the exception of the qualifiers, B, E, and P, which are not used in Region 4 data reporting.

The following definitions provide brief explanations of the qualifiers assigned to results during the electronic data validation process. An additional set of data qualifiers is applied as needed to provide further information to the data user about data quality.

Data Qualifier	Data Qualifier Definition[3]
J	The analyte was positively identified in the sample, but the associated numerical value is an estimated concentration based on the associated quality control data/technical criteria.
R	The sample results are rejected due to serious deficiencies in the ability to analyze the sample and meet quality control criteria. The presence or absence of the analyte cannot be verified.
U	The analyte was included in the analysis, but was not detected above the method detection limit as defined in ISM01.2.

5.0 Data Review Documentation – Computer Aided Review

Use of the Electronic EXchange and Evaluation System (EXES) allows electronic validation of the CLP cyanide data.

The results of electronic data review are utilized to assist the data review process. If examination of the electronic review results and/or PES scoring results reveals discrepancies and/or serious data quality issues, the reviewer may investigate by going back to the hard copy data package.

Each EXES - NFG report is downloaded as a self expanding executable file and distributed to the data review team. The EXES - NFG report is organized by SDG.

Two (2) copies of the/EXES reports should be printed for each SDG for the data reviewer. A copy should be included in the data validation documentation to submit to the Quality Assurance Section (QAS) to be retained in the project file. The second copy should be archived with the actual data package.

A Data Review Document shall be prepared to document the inorganic data package validation. The document includes the Review Summary Narrative, Time Tracker, Performance Evaluation Sample (PES) Scores from the secure SPS-Web site, a copy of the spreadsheet used for data import into the *Element* data system, and the EXES - NFG. These reporting elements are described in greater detail below, and examples are included as attachments to this SOP.

[3]Current list of qualifier / definition flags are located at: http://www.epa.gov/region4/sesd/oqa/rassop.html

5.1 Document Contents:

5.1.1 Inorganic Data Review Summary Narrative - This narrative is in a letter format to summarize the information pertinent to the samples, analytical methods, highlights of findings, and a brief assessment of the overall data quality. Descriptions of major data quality issues and their impact on overall data quality should be presented.

5.1.2 Time tracker - This document is for recording the time line and efforts at different stages of the data review process. This form must be utilized and included in the data review documents for CLP data. Any unusual issues or factors affecting the level of effort required to complete the review in a timely manner, are discussed here and in the corresponding data validation memorandum. The time tracker should include the peer review information as part of the validation package requirements.

5.1.3 PE Score (SPS-Web) - This form is generated by the SPS-Web program to report the evaluation of the results of the performance evaluation samples (PES) associated with the data package. The "EPA" versions of this form should be included as attachments to the data validation memorandum whereas the "laboratory" version should be emailed to the EPA inorganic TO/PO.

5.1.4 Excel® Spreadsheet - The reviewed data with final assigned qualifiers attached, (if any) as they appear in Element, are included in the data review report as an Excel® spreadsheet.

5.2 Recording and Reporting of Data

Please refer to SOP "Data Processing and Final Production for Contract Laboratory Data in Element®.

5.3 Data Package Archives

The CLP data packages must be properly archived for future reference. For each data package, the form "Record Transfer Inventory" must be utilized to record the proper information pertinent to the content. All of the raw data, EXES reports, and any communication records must be included. Multiple data packages from different projects may be stored in one single box if sufficient space is available.

Data packages for one Case that are stored in multiple boxes must be clearly identified on the Record Transfer Inventory forms. An appropriate numbering system must be maintained to ensure that each box containing the data review supporting documentation has a unique archive number.

A copy of the inventory form should be kept within the box and an additional copy filed in a centralized system. The data package boxes shall be maintained under the custody of SESD as described in the Data Package Audit and Data Entry/Validation SOP. The Data Package Inventory Form is provided in Attachment E.

6.0 References

U.S. Environmental Protection Agency, Statement of Work for Inorganic Superfund Methods, Multi-Media, Multi-Concentration, ISM01.2, January 2010.

U.S. Environment Protection Agency, Contract Laboratory Program, National Functional Guidelines for Inorganic Superfund Data Review, January 2010.