Validation of Metals and Cyanide Analytical Data

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Hazard Class: ☒ Low ☐ Moderate ☐ High/Complex

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The Responsible Manager has determined that the following organizations' review is required for initial procedure release as well as subsequent major revisions. Review documentation is contained in the Document History File.

Technical Leads Quality Assurance

Classification Review: ☒ Unclassified ☐ UCNI ☐ Classified

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Responsible Manager, Division and Title

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REVISION HISTORY

Document No./Revision No.	Issue Date	Action	Description
OIO-TP-5165	8/19/2015	Minor Revision	Periodic Review. Minor revision, changed document type and organization.
ER-AP-20313, R0	4/21/2017	Major Revision	Revised to reflect EPA method-specific data quality criteria and/or National Functional Guidelines for Inorganic Data Review and remove NNSA Model Validation.

TABLE OF CONTENTS

1. PURPOSE

This procedure establishes guidance for the qualification of metals inorganics analytical data. This document is intended to assist in the technical review of analytical data generated by environmental laboratories.

2. SCOPE

Qualification of data is the product of data validation, analytical laboratory analysis, and focused validation that describe validation anomalies and their consequences. Metals include parameters analyzed by inductively coupled plasma- (ICP-) optical emission spectroscopy (OES), ICP- mass spectroscopy (MS), and cold vapor atomic absorbance/fluorescence. Cyanide is analyzed using colorimetric spectrophotometry.

3. BACKGROUND

Data qualifiers and reason codes are assigned to analytical results from metals analyses according to the specifications in this method-specific procedure. These guidelines are developed using the EPA method-specific data quality criteria and/or National Functional Guidelines for Inorganic Data Review.

4. PRECAUTIONS AND LIMITATIONS

Nothing in this procedure precludes the data validator from going beyond the minimum requirements specified within this procedure. If additional directions are required, the data validator shall reference EPA method-specific guidelines and/or National Functional Guidelines for Organic Inorganic Data Review. Implementation of this procedure may be followed by a more focused and data use–specific evaluation of the data by the project chemist, especially if the implementation of this procedure indicates the data may contain technical deficiencies.

5. PREREQUISITE ACTIONS

Data Validators must:

- Possess a minimum of a Bachelor's degree in chemistry or one of the physical sciences and either two (2) years of experience in generating analytical data in an environmental analytical laboratory or two (2) years of experience in data validation.
- Complete Attachment 1, Data Validation Cover Sheet, and Attachment 2, Metals and Cyanide Analytical Data Validation Checklist, during data validation.

6. PERFORMANCE

6.1 Validation Process

EIM applies a subset of qualifiers described in this procedure to analytical data using auto-validation subroutines. EIM auto-validation applies qualification to analytical records using tests listed in Attachment 2 that have a Valid Reason Description containing "(AV)". When the project leader requests a focused validation the assigned data validator completes the following steps to assess all potential analytical data qualification:

[1] **REVIEW** the qualifiers assigned during EIM auto-validation to verify that qualifiers were assigned consistently with this procedure. If auto-validation qualification is found to be inconsistent with this procedure then the validator initiates a change request using ER-AP-20304, Change Control for Data in the Environmental Information Management (EIM) Database.

[2] **PRINT** Attachment 1 and **REVIEW** the data package for potential qualification using Attachment 2.

[3] **NOTE** conditions causing recommendation for qualification and options for qualification.

[4] **COMPLETE** Attachment 1 and **FORWARD** to the project leader with conditions and options.

The project leader is the responsible party for making the decision of record if validation qualifiers should be assigned and EIM validation records updated. This record of decision is added to comments section of Attachment 1.

Once the decision of record has been made, Attachment 1 is sent to the Sample Management Office (SMO) staff. The SMO staff re-print the data validation record from EIM and add Attachment 1 that includes the record of decision to the final records package.

6.2 Analyte Quantitation

The assignment of the detection status to analytical measurements is the first step of analytical data validation. Most validation qualifiers and validation reason codes are applied based on the measurement's initial detection status. Results that are less than the report method detection limit (RMDL) are qualified as nondetect with the U validation qualifier and U_LAB validation reason code. Results greater than or equal to the RMDL and less than the report detection limit (RDL) are qualified as detected and estimated with the J validation qualifier and J_LAB validation reason code. Results greater than or equal to the RDL are qualified as detected with the NQ validation qualifier.

Criteria	Validation Qualifier	Validation Reason Code
Target analyte result is < RMDL; a nondetect	U	U_LAB
Target analyte result is ≥ RMDL and < RDL; a detect	J	J_LAB
Target analyte result is ≥ RDL; a detect	NQ	NQ

Since a result can have only one validation qualifier and one validation reason code the sequencing of validation steps is important. Analyte quantitation occurs first, then analyte identification, because most other validation functions depend on the correct identification and quantitation of the analytical parameter. When two or more qualifiers can be applied to a record, the qualifier representing the more severe consequence to data usability supersedes the qualifier with less severe consequence. The R validation qualifier has the greatest impact on data usability and supersedes other validation qualifiers.

6.2 Analyte Quantitation (continued)

Order Of Severity	Validation Qualifier	Description
1	R	The reported sample result is classified as rejected due to serious noncompliances regarding quality control acceptance criteria. The presence or absence of the analyte cannot be verified.
2	UJ	The analyte is classified as not detected, with an expectation that the reported result is more uncertain than usual.
3	U	The analyte is classified as not detected.
4	J	The analyte is classified as detected but the reported concentration value is expected to be more uncertain than usual.
5	NQ	No validation qualifier flag is associated with this result, and the analyte is classified as detected.

LANL project chemists may identify quality deficiencies in analytical results affecting analyte quantitation. These deficiencies can include analytical results with detection limits elevated above project data-quality objectives, concentrations above the calibration range of the instrument or method, results exhibiting carryover or detector contamination, large relative percent difference between dual-column detects, chromatographic interference from another analyte, and other quality deficiencies. The reason code of I19 is applied to affected records by the project chemist to identify these quality deficiencies when they are identified.

6.3 Analyte Identification

Most inorganic methods do not have a separate validation for analyte identification.

6.4 Holding Times and Sample Preservation

Sample handling requirements are specified to ensure integrity and defensibility of analytical measurements. Samples are to be prepared and analyzed within specified time limits. Samples are also preserved chemically and physically by controlling temperature and light. When sample handling requirements are not met the I9 series of reason codes are applied to affected samples.

6.5 Initial and Continuing Calibration

Calibration is performed to set the operating range of the instrument and to ensure that the instrument is performing within specifications. The initial calibration and verification is performed prior to the start of analyses. Continuing calibration checks and instrument performance samples are performed periodically during analysis to ensure the instrument is providing accurate results. When initial calibration criteria are not met the I7 series of reason codes are applied to affected analytes in all samples analyzed after the unacceptable initial calibration to the next acceptable initial calibration for that instrument. When continuing calibration criteria or are not met the I7 series of reason codes are applied to affected analytes in all samples analyzed after the unacceptable continuing calibration to the next acceptable continuing calibration for that instrument. When instrument performance checks do not meet criteria the I16 series of qualifiers are applied to affected analytes in all samples analyzed after the unacceptable instrument performance check to the next acceptable instrument performance check for that instrument.

Two types of interference check samples (ICS) are analyzed during initial calibration and together determine the amount of interference. The ICSA contains only designated interferents (e.g., Al, Ca, Fe, Mg) at concentrations that are known to cause interferences while ISCAB contains the analytes of interest along with the interferents. When ICS checks do not meet performance criteria the I2 series of qualifiers are applied to affected analytes in all samples analyzed after a failed ICS until the next acceptable ICS.

6.6 Internal Standards

Internal standards are compounds not normally found in the environment, but which are easily measurable. They are added to samples, standards, and QC samples to compensate for fluctuations in the analytical system. Sample results are quantitated or adjusted by the relative response of associated internal standards. When internal standard criteria are not met the I1 series of reason codes are applied to the affected sample.

6.7 Blanks

The Method Blank is an analyte-free matrix that is prepared and analyzed in the laboratory with the samples. The method blank determines contamination from the analytical processes. Method blanks are prepared with every preparation batch. If more than one method blank is associated with a given sample, qualification is based upon a comparison with the associated blank having the highest concentration of the parameter. When method blank criteria are not met the I4 series of reason codes are applied affected samples.

6.7 Blanks (continued)

The Field Blank is an analyte-free matrix opened to the atmosphere at the time of sample collection. Field blanks are used to determine if atmospheric conditions resulted in contamination of samples during sample collection. Samples collected the same day as the field blank that does not meet blank criteria are qualified with the V4 series of reason codes.

The Equipment Blank is an analyte-free matrix poured over or through sample collection equipment. Equipment blanks are used to determine the cleaning effectiveness of sampling equipment between samples. Samples collected using the same tools as the equipment blank that does not meet blank criteria are qualified with the V4 series of reason codes.

6.8 Matrix Spike, Laboratory Control Sample, Serial Dilution

The laboratory control sample is created by adding known amounts of parameters of interest to an aliquot of a blank matrix. The laboratory control sample is used to evaluate the effect of the analytical process of the recovery of analytes. When laboratory control sample criteria are not met the I12 series of reason codes are applied to all associated samples.

The matrix spike is created by adding known amounts of parameters of interest to an aliquot of a sample matrix. The matrix spike is used to evaluate the effect of the sample matrix on the recovery of analytes. When matrix spike criteria are not met the I6 series of reason codes are applied to all associated samples.

The serial dilution is created by diluting a sample 5x and comparing the results to the original sample. The serial dilution is used to evaluate if significance physical or chemical interferences are inherent in the sample matrix. When serial dilution criteria are not met the I18 series of reason codes are applied to the affected analytes in the sample and any sample duplicates in the preparation batch.

7. RECORDS

Records generated by this procedure will be submitted to the Environmental Protection Records Management Office for document management in accordance with P1020-1, Laboratory Records Management and EP-AP-10003, Records Management.

- Completed Data Validation Cover Sheets (Attachment 1)
- Completed Metals and Cyanide Analytical Data Validation Checklists (Attachment 2)

8. REFERENCES

EP-AP-10003, Records Management

ER-AP-20304, Change Control for Data in the Environmental Information Management (EIM) Database

P1020-1, Laboratory Records Management

9. ATTACHMENTS

Attachment 1: Data Validation Cover Sheet
Attachment 2: Metals and Cyanide Analytical Data Validation Checklist

ATTACHMENT 1

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Data Validation Cover Sheet

Section I.

Request Number: _____ Validation Date: _____ Lab Code: _____

Contract Laboratory Name: _____

Validator: _____ Organization: _____

Analytical Suite (Check All That Apply):

☐ **TPH-GRO**	☐ **High Explosives**	☐ **Dioxin Furans**	☐ **LCMSMS Perchlorates**
☐ **TPH-DRO**	☐ **Metals & Cyanide**	☐ **PCB Congeners**	☐ **Organochlorine Pesticides/Polychlorinated Biphenyls**
☐ **General Chemistry**	☐ **Radiochemistry**	☐ **LCMSMS High Explosives**	

☐ **Other (Describe):** _____

_____

Section II. Completeness Check

YES	NO	N/A	(check one)	YES	NO	N/A	(check one)
☐	☐	☐	1. Chain-Of-Custody Form(S)	☐	☐	☐	6. Raw/BSS Data
☐	☐	☐	2. Case Narrative	☐	☐	☐	7. Quality Control Forms
☐	☐	☐	3. Sample Result Forms	☐	☐	☐	8. Quantitation Reports
☐	☐	☐	4. Sample Chromatograms	☐	☐	☐	9. TICS Forms
☐	☐	☐	5. Standard Chromatograms	☐	☐	☐	10. TICS Mass Spectra

Comments/problems noted (include information about requests for further information submitted to the contract laboratory and agreed-upon date of resolution and contract laboratory point of contact):

Validator's Signature: _____ Date: _____

ER-AP-20313, R0	Los Alamos Environmental Safety & Health
	(Attach additional comment sheets as necessary)

ATTACHMENT 2

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Metals and Cyanide Analytical Data Validation Checklist

Yes	No	N/A		Assign Qualifier Listed Below If Criterion = Yes	
(Check One)				Non-detected Analyte	Detected Analyte
Holding Time and Sample Preservation					
☐	☐	☐	1. The sample was analyzed > 180-day holding time. Mercury was analyzed > 28-day holding time. Cyanide was analyzed > 14-day holding time.	R, I9b	J-, I9b
☐	☐	☐	2. Non-aqueous sample or aqueous sample analyte is mercury or cyanide temperature > 10°C upon receipt at the laboratory.	UJ, I9c	J-, I9c
☐	☐	☐	3. Aqueous sample for cyanide analysis received with oxidizing agents, sulfides, or nitrate/nitrite present.	R, I9c	J, I9c
☐	☐	☐	4. Aqueous sample for mercury analysis is received with pH >2 and pH not adjusted.	R, I9c	J-, R9c
Calibration – Instrument Performance Check					
☐	☐	☐	5. The instrument performance sample did not pass method acceptance criteria.	R, I16	R, I16
☐	☐	☐	6. The mass calibration is not within 0.1 amu or percent relative standard deviation (%RSD) is >5% for any isotope (Be, Mg, Co, In, Pb).	UJ, I16a	J, I16a
☐	☐	☐	7. Samples were analyzed outside specific method tune time criteria.	N/A	J, I16b
☐	☐	☐	8. The required instrument performance sample information is missing. Contact the Sample Management Office (SMO) or external laboratory for information.	R, I16c	R, I16c

ATTACHMENT 2

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Yes	No	N/A		Assign Qualifier Listed Below If Criterion = Yes	
(Check One)				Non-detected Analyte	Detected Analyte
Calibration - Initial and Continuing Calibration					
☐	☐	☐	9. The affected results were not analyzed with a valid 5-point calibration curve and/or a standard at the reporting limit (RL).	UJ, R, I7	J, I7
☐	☐	☐	10. The affected analytes were analyzed with an initial calibration curve that exceeded the %RSD criteria and/or the associated multipoint calibration correlation coefficient is <0.995.	UJ, I7a	J, I7a
☐	☐	☐	11. The initial calibration verification (ICV) and/or continuing calibration verification (CCV) were recovered outside the method-specific limits.	UJ, I7c	J, I7c
☐	☐	☐	12. The initial calibration verification (ICV) and/or continuing calibration verification (CCV) were recovered less than 10%.	R, I16d	R, I16d
☐	☐	☐	13. The ICV and/or CCV were not analyzed at the appropriate method frequency.	UJ, I7d	J, I7d
☐	☐	☐	14. Required calibration information is missing or samples were analyzed on an expired calibration. Contact the SMO or external laboratory for information.	R, I7f	R, I7f
Calibration - Interference Check Sample					
☐	☐	☐	15. Metals interference check sample percent recover value is <50%.	R, I2	J-, I2
☐	☐	☐	16. Metals interference check sample percent recovery value is ≥50% and <80%	UJ, I2a	J-, I2a
☐	☐	☐	17. Metals interference check sample percent recovery value is >120%.	UJ, I2b	J+, I2b
☐	☐	☐	18. Metals interference check sample was not analyzed with the samples.	R, I2c	R, I2c

ATTACHMENT 2

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Yes	No	N/A		Assign Qualifier Listed Below If Criterion = Yes	
(Check One)				Non-detected Analyte	Detected Analyte
Blanks					
☐	☐	☐	19. The detected sample result is ≤5 times the concentration of the related analyte in the method blank.	NA	U, I4
☐	☐	☐	20. The affected analytes are considered estimated and biased high because this analyte was identified in the method blank but was >5 times.	NA	J+, I4a
☐	☐	☐	21. The detected sample result is ≤5 times the concentration of the related analyte in the instrument blank and continuing calibration blank.	N/A	U, I4b
☐	☐	☐	22. Continuing calibration blanks were not analyzed at the appropriate method frequency.	UF, I4c	J, I4c
☐	☐	☐	23. The detected sample result is ≤5 times the concentration of the related analyte in the trip blank, rinsate blank, or equipment blank.	N/A	U, I4d
☐	☐	☐	24. Required method blank information is missing. Data may not be acceptable for use. Contact the SMO or external laboratory for information.	R, I4e	R, I4e
Matrix Spike					
☐	☐	☐	25. The associated matrix spike (MS) recovery was <10%. Follow the external laboratory limits located within the associated data package.	R, I6	R, I6
☐	☐	☐	26. The associated matrix spike recovery was <the lower acceptance limit (LAL) but >10%. Follow the external laboratory limits located within the associated data package.	UJ, I6a	J-, I6a
☐	☐	☐	27. The associated matrix spike recovery was > the upper acceptance limit (UAL). Follow the external laboratory limits located within the associated data package.	UJ, I6b	J+, I6b

ATTACHMENT 2

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Yes	No	N/A (Check One)		Assign Qualifier Listed Below If Criterion = Yes	
				Non-detected Analyte	**Detected Analyte**
☐	☐	☐	28. Required matrix spike information is missing. Data may not be acceptable for use. Contact the SMO or external laboratory for information. If the laboratory control sample (LCS) information is present, do not reject. Qualify data based on the LCS information.	R, I6c	R, I6c
Duplicate Samples					
☐	☐	☐	29. The duplicate sample RPD is greater than the advisory limit and the sample result is detected. Manual review is suggested to determine the source of the difference between analyses.	UJ, I10	J, I10
☐	☐	☐	30. The sample and the duplicate sample results were ≥5 the RL and the duplicate relative percent difference (RPD) was >20% for water samples and >35% for soil samples.	UJ, I10a	J, I10a
☐	☐	☐	31. The duplicate sample was not prepared and/or analyzed with the samples for unspecified reasons. The duplicate information is missing. Data may not be acceptable for use. Contact the SMO or external laboratory for information.	UJ, I10d	J, I10d
Laboratory Control Samples					
☐	☐	☐	32. The LCS percent recovery was <10%. Follow the external laboratory limits located within the associated data package.	R, I12	R, I12
☐	☐	☐	33. The LCS percent recover was < the LAL but >10%. Follow the external laboratory limits located within the associated data package.	UJ, I12a	J-, I12a
☐	☐	☐	34. The LCS percent recovery was > the UAL. Follow the external laboratory limits located within the associated data package	N/A	J+, I12b

ATTACHMENT 2

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Yes	No	N/A		Assign Qualifier Listed Below If Criterion = Yes	
(Check One)				**Non-detected Analyte**	**Detected Analyte**
☐	☐	☐	35. The LCS documentation is missing. Data may not be acceptable for use. Contact the SMO or external laboratory for information. Do not reject if MS/MS duplicate (MSD) information is available. Qualify according to MS/MSD criteria.	R, I12c	R, I12c
Internal Standards					
☐	☐	☐	36. The quantitating internal standard (IS) area count is <10% for metals window in relation to the initial calibration blank. Follow the method-specific windows.	R, I1a	J, I1a
☐	☐	☐	37. The IS area count for the quantitating IS <60% but >10% for metals window in relation to the initial calibration blank. Follow the method-specific windows.	UJ, I1b	J, I1b
☐	☐	☐	38. The IS area count for the quantitating IS >125% in relation to the metals initial calibration blank. Follow method-specific windows.	UJ, I1c	J, I1c
□	□	☐	39. Required IS information is missing. Data may not be acceptable for use. Contact the SMO or external laboratory for information.	R, I1d	R, I1d
Serial Dilution					
☐	☐	☐	40. Serial dilution sample % difference (%D) was >10% and the sample result was >50 times the method detection limit (MDL) (>100 times the MDL for inductively coupled plasma mass spectrometry). Qualify ONLY the sample used for the serial dilution.	UJ, I18	J, I18
☐	☐	☐	41. Serial dilution sample was not analyzed with the samples.	UJ, I18a	J, I18a

ATTACHMENT 2

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Yes No N/A (Check One)				Assign Qualifier Listed Below If Criterion = Yes	
				Non-detected Analyte	**Detected Analyte**
Analyte Quantitation					
☐	☐	☐	42. The non-detected analytes have elevated detection limits and may not meet project data-quality objectives because the sample was diluted without any target analytes identified as a result of matrix interference. Reject non-detected results if the analytical laboratory cannot provide proof for matrix interference.	UJ, R_I15	NA
☐	☐	☐	43. The LANL project chemist identified quality deficiencies in the reported data that require further qualification. This code can ONLY be used under advisement of the LANL project chemist.	UJ, R, I19	J, R, I19
☐	☐	☐	44. Qualification of data via data validation did occur, however no data quality control requirements in this procedure were applicable. Adhere to the external laboratory qualifiers found within the Form 1 analytical data summary sheets generated by the external laboratory. (AV)	U, U_LAB	J, J_LAB NQ, NQ (No qualification)