STANDARD OPERATING PROCEDURES

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DATA VALIDATION PROCEDURE FOR ROUTINE INORGANIC ANALYSIS

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DATA VALIDATION PROCEDURE FOR ROUTINE INORGANIC ANALYSIS

1.0 OBJECTIVE

The objective of this Standard Operating Procedure (SOP) is to establish a protocol for evaluation and validation of the routine inorganic data generated in the Scientific, Engineering, Response and Analytical Services (SERAS) laboratory as well as data submitted to SERAS by subcontract laboratories in preparation for inclusion into an analytical report.

2.0 APPLICABILITY

This SOP is applicable to all samples submitted to SERAS for analyses for metals and cyanide whether samples are to be subcontracted or analysis is to be done in-house. See Appendices A, B and C for compound lists.

3.0 DESCRIPTION

3.1 Sample Holding Time

3.1.1 Objective

The objective is to ascertain the quality of results based on the holding time of the sample from time of collection to time of analysis including sample preparation, if appropriate.

3.1.2 Requirements

The analysis for metals must be performed within six months of collection for all samples (aqueous and non-aqueous) except mercury analysis which must be performed within 28 days. The cyanide analysis must be performed within 14 days.

3.1.3 Evaluation Procedure

Holding times are determined by comparing the date of collection on the chain of custody record with the date of sample digestion on the laboratory sample preparation log. The holding time for analysis is established by comparing the date of sample collection on the chain of custody form with the analysis date on the instrument's data printout.

3.1.4 Action

If holding times are exceeded, the reviewer must use professional judgment to determine the reliability of the data and the effects of additional storage on the sample results. Due to limited information concerning holding times for soil samples, it is left to the discretion of the data reviewer whether to apply water holding time criteria to soil samples. If the data are qualified when water holding time criteria are applied to soil samples, it must be clearly documented in the review.

If holding times and preservation are not met, qualify all results above the Instrument Detection Limit (IDL) as estimated (J) and results less than IDL as estimated (UJ).

3.2 Calibration and Calibration Verification

3.2.1 Objective

The objective in establishing compliance requirements for satisfactory instrument calibration is to ensure that the instrument is capable of producing acceptable quantitative data. Initial calibration demonstrates that the instrument is capable of acceptable performance at the beginning of the sample analysis runs. Continuing calibration verification documents satisfactory instrument performance (calibration accuracy) over specific time periods.

3.2.2 Requirements

3.2.2.1 Initial Calibration

Instrument must be calibrated daily and each time the instrument is set up.

1. Inductively Coupled Plasma (ICP) Analysis

   Calibration blank and at least one standard must be used in establishing the analytical curve.

2. Atomic Absorption (AA) Analysis

   Calibration blank and at least three standards must be used in establishing the analytical curve.

3. Cyanide (CN)

   Calibration blank and at least three standards must be used in establishing the analytical curve.

3.2.2.2 Calibration Verification

Continuing calibration checks and calibration blank analysis must be performed after every tenth sample and after the last sample is analyzed. Continuing calibration checks must be performed from a different source than that used for the initial calibration standards.

1. Inductively Coupled Plasma

   Calibration verification results must fall within the control limits of 90-110% of the true value.

2. Atomic Absorption

Calibration verification results must fall within the control limits of 90-110% for all AA analytes with the exception of tin and mercury for which the limits of 85-115% apply.

3. Cyanide

Calibration verification results must fall within the control limits of 90-110% of the true value.

3.2.3 Evaluation Procedure

- Verify that the instrument was calibrated at the proper frequency using the correct number of standards and a calibration blank.
- Verify that the calibration verification source used met requirements.
- Spot check calibration verification checks for each case/batch by recalculation of the percent recovery (%R) from the same data; verify that the recalculated value agrees with the laboratory reported values.

$$\%R = \frac{Actual\,Concentration}{Known\,Concentration}\ x\ 100$$

3.2.4 Action

The inability of a laboratory to perform acceptably on the calibration criteria indicates severe problems exist in the analytical system. These problems must be resolved. Any data generated under such conditions should be considered suspect. If improper calibration procedures were used, all data associated with that calibration should be re-analyzed. If the data in question are needed on a priority basis, professional judgment may be applied to determine to what extent the data may be utilized.

- If the minimum number of standards as defined above were not used for initial calibration, or if the instrument was not calibrated daily and each time the instrument was set up, qualify the data as unusable (R).
- If an analyte is not detected in a sample and the initial calibration verification result is greater than 110% then the usability of that analytical sample determination is acceptable.
- If an analyte is not detected in a sample and the initial calibration verification result is less than 90%, then the detection limit may be biased low.

3.3 Blanks

3.3.1 Objective

The results of blank analyses are assessed to determine the existence and magnitude of contamination problems. If problems with any blank exist, all data associated with the case must be carefully evaluated to determine whether or not there is an inherent variability in the data for the case, or the problem is an isolated occurrence not affecting other data.

3.3.2 Requirements

The laboratory preparation blank (reagent blank) is the only in-house blank the laboratory is responsible for reporting.

- At least one preparation blank must be prepared and analyzed for every 20 samples received, or for each batch of samples digested, whichever is more frequent.
- If the concentration of the blank is less than the detection limit, no corrective action is required to be taken by the laboratory.
- If the concentration of the blank is above the detection limit for any group of samples associated with a particular blank, the concentration of the sample with the least concentrated analyte must be 10X the blank concentration, or all samples associated with the blank and less than 10 times the blank concentration must be redigested and reanalyzed, with the exception of an identified aqueous soil field blank. The sample value is not to be corrected for the blank value.

No criteria apply to the levels of contaminant in field blanks.

3.3.3 Evaluation Procedures

Review all blanks reported on the results summary and blanks raw data (ICP printout, strip charts, printer tapes, bench sheets) and verify that the results were accurately reported.

If any blank contaminants were identified at levels greater than the detection limit, determine if redigestion/reanalysis was necessary by comparing blank levels with the reported sample results.

3.3.4 Action

If contaminant analytes are detected in samples at a concentration of less than 5 times the concentration found in the highest associated blank (preparation, field), these results should be considered suspect. Code the reported results as estimated (J). In this instance, a statement should be included in the narrative that indicates that it is not possible to verify whether the level of analyte detected in the sample was due to contamination.

3.4 ICP Interference Check Sample Analysis

3.4.1 Objectives

The ICP interference check sample analysis is performed to verify the laboratory's interelement and background correction factors.

3.4.2 Requirements

ICP check samples must be analyzed at the beginning and end of each sample analysis sequence. A control limit of ± 20% of the true value should be performed.

3.4.3 Evaluation Procedure

Review the ICP interference check and verify that results meet the criteria. Spot check raw data to verify the accuracy of the recoveries reported.

3.4.4 Action

Professional judgment may be applied to determine to what extent the data may be utilized in the event that the ICP interference check sample results exceed the control limit.

3.5 Duplicate Sample Analysis

3.5.1 Objective

The data reviewer can use the results of the duplicate analyses as an indicator of the bias of the sample results.

3.5.2 Requirements

At least one duplicate sample must be analyzed from each group of samples of a similar matrix type. A control limit of ± 20% for Relative Percent Difference (RPD) shall be used for sample values >5 times the detection limit.

3.5.3 Evaluation Procedures

Review data and verify that results fall within the control limits. Spot check the raw data to verify that results have been correctly reported.

3.5.4 Action

Actions taken as a result of duplicate sample analysis must be weighed carefully since it may be difficult to determine if poor replication is a result of the non-homogeneous nature of soil samples which often makes it more difficult to achieve good duplicate results compared to aqueous samples. Aqueous samples containing high levels of solids can also produce erratic duplicate results. In general, the results of duplicate sample analysis should be used to support

conclusions drawn about the quality of the data rather than as a basis for these conclusions. Since only one duplicate is generally performed per matrix type the bias results should be applied to all other samples of the same matrix type. An exception to this can be made when it appears evident that the duplicated sample was of a different chemical and physical nature than other samples given the same matrix classification. Unfortunately, descriptive information regarding certain aspects of the sample nature (i.e., appearance) is currently limited and not readily available to the reviewer.

3.6 Spiked Sample Analysis

3.6.1 Objectives

The spiked sample analysis is designed to provide information about the effect of the sample matrix on the digestion and measurement methodology.

3.6.2 Requirements

At least one spiked sample analysis must be performed on each group of samples of a similar matrix type. The analyte spike must be added prior to digestion.

3.6.3 Evaluation Procedures

Review the data and verify that the results fall within the specified limits. Spot check raw data to verify results were correctly reported. Spot check the raw data and recalculate the %R and RPD.

$$\%R = \frac{SSR - SR}{SA} \times 100$$

where,

SSR = Spiked sample result
SR = Sample result
SA = Spike added

$$\% RPD = \frac{|SR - SDR|}{(SR + SDR)/2} \times 100$$

where,

SR = First sample value
SDR = Duplicate sample value

3.6.4 Action

If the spike recovery is not within the limits of 75-125%, the data of all the samples associated with that spiked sample must be addressed to the case narrative.

3.7 Furnace Atomic Absorption QC Analysis

3.7.1 Objective

Duplicate injections and analytical spikes are incorporated into the QC scheme to establish a mechanism for reviewers to better estimate the precision and accuracy of individual analytical determinations relative to the overall method precision and accuracy.

3.7.2 Requirements

Duplicate injections are required for all furnace analyses. The average result is to be reported, raw data must contain all readings. All analyses must fall within the calibration range. The spike is required to be at a concentration twice the detection limit. The percent recovery of the spike determines how the sample must be quantitated.

3.7.3 Evaluation Procedures

Review Furnace AA raw data and standard addition results to verify that all analyses requirements have been met. Verify reported results by recalculating at least 10% of the data for each parameter.

3.7.4 Action

- If duplicate injections are outside the $\pm$ 20% Relative Standard Deviation (RSD) limits and a third injection has not been made as required, flag the data as estimated, "J".

- If the third injection does not agree with either of the first two injections ($\pm$20% RSD), flag the data as estimated (J).

3.8 ICP QC Analysis

3.8.1 Objectives

Serial dilution analysis is required so that the reviewer can ascertain whether significant physical or chemical interferences exist due to sample matrix.

3.8.2 Requirements

One sample from each group of samples of a similar matrix type and concentration, for each case of samples, or for each 20 samples received, must undergo at least one serial dilution.

3.8.3 Evaluation Procedures

Review raw data to insure the serial dilution analysis was performed at the proper frequency for each matrix type. Spot check the raw data and verify by calculation that the dilution analysis results compare within 10%.

$$Percent\ Difference\ (\%D) = \frac{|I - S|}{I} x\ 100$$

where,

I = Initial Sample Result
S = Serial Dilution Result

3.8.4 Action

If the 10% criteria is not met, flag the associated data as estimated (J).

3.9 Sample Result Verification

3.9.1 Objectives

The sample result verification process checks the concentration of the data computation and transcription, the quality of the calibration and the correct use of the codes described on the cover page of the data report.

3.9.2 Requirements

All required data reduction, reporting and documentation must be performed and presented in such a manner as to ensure the data package is both complete as well as free of computational and/or transcription errors.

3.9.3 Evaluation Procedures

All required data reduction and documentation must be examined to ensure the data package is complete (see appendices D and E -- Deliverable Checklist for Metals and Cyanide Analyses). The raw data should be examined to verify the correct calculation of sample result reported by the laboratories. Digestion and distillation logs, instrument parameters, strip charts, etc. should be compared to the reported sample results. A record of the result verification should be made using copies of raw data sheets as "check records". Note any anomalies on these sheets.

Furnace AA Parameters

All raw data from the instrument must be validated. Choose at least two furnace AA parameters for complete validation. If any errors are identified in the review of these parameters it will be necessary to evaluate all the project associated furnace data.

ICP Parameters

All raw data from instrument must be validated. Choose at least two ICP parameters for complete validation. If any errors are identified in this review then evaluate an additional two parameters. If errors are still encountered then all remaining ICP parameters must be evaluated.

Flame AA Parameters

All raw data from the instrument must be validated. If errors are identified review additional parameters as required under the previous section.

Mercury and Cyanide

All data for these parameters must be validated.

3.9.4 Action

If differences are identified between the reported result and the reviewer calculated result and the reported result is within 10% of the reviewer calculated result and the difference could be attributed to rounding, then no action is required; if it is greater than 10% different from the reviewer calculated result, or less than 10% but not attributable to rounding, contact the laboratory for verification. If an error is confirmed, request resubmission of corrected data sheets. Include a summary of all contacts with the laboratory in the check records.

4.0 RESPONSIBILITIES

4.1 QA/QC Data Reviewer

The Data Reviewer must have a working knowledge of the method used to obtain the data and must ensure that all documents are included and complete, that the lab is in compliance with the method and that all requested analysis were performed.

The Data Reviewer will provide completed checklists and a written report of anomalies.

The Data Reviewer is responsible for informing the Data Validation and Report Writing Group Leader of any major noncompliance of the method that may affect the usability of the data.

The Data Reviewer will prepare written communication to the laboratories detailing anomalies of the method, as necessary.

4.2 Data Validation and Report Writing Group Leader

The Data Validation and Report Writing Group Leader is responsible for the accurate updating of data validation SOP as requirements change.

The Data Validation and Report Writing Group Leader audits the review process to ensure compliance with review requirements.

The Data Validation and Report Writing Group Leader is responsible for communication of any major noncompliance of the method that may affect the usability of the data to the Task Leader of the project and to the Analytical Section Chief.

The Data Validation and Report Writing Group Leader initials the checklists, data assessment forms and anomaly reports.

4.3 QA Officer

The QA Officer is responsible for ensuring adherence to this SOP.

APPENDIX A
Compound List for PP/Metals with Detection Limits
SOP #1017
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DATA VALIDATION PROCEDURE FOR ROUTINE INORGANIC ANALYSIS

ANALYSIS: PP/METALS

SAMPLE PREPARATION METHOD:	SW-846, Method 3015, 3010, 3020 (Instrument and Sample Dependent)/SW-846, Method 3050
ATOMIC ABSORPTION METHOD:	SW-846 /Method 7000

COMPOUND LIST	DL H_2O (µg/L)	DL SOIL (mg/kg)
Antimony	5 - 10	0.5 - 1.0
Arsenic	5 - 10	0.5 - 1.0
Beryllium	5 - 10	1.0 - 2.5
Cadmium	5 - 10	0.5 - 1.0
Chromium	0 - 50	5
Copper	25	2.5 - 5.0
Lead	5 - 50	5
Mercury	0.2 - 0.4	0.04
Nickel	25 - 50	2.5 - 5.0
Selenium	5 - 10	0.5 - 1.0
Silver	10 - 25	1.0 - 2.5
Thallium	5 - 10	0.5 - 1.0
Zinc	10 - 25	1.0 - 2.5

APPENDIX B
Compound List for TCLP/Metals with Detection Limits
SOP #1017
November 1994

DATA VALIDATION PROCEDURE FOR ROUTINE INORGANIC ANALYSIS

ANALYSIS: TCLP/METALS

SAMPLE PREPARATION METHOD:	SW-846, Method 3015, 3010, 3020 (Instrument and Sample Dependent)
ATOMIC ABSORPTION METHOD:	SW-846, Method 7000

COMPOUND LIST	DL H_2O (µg/L)
Arsenic	5.0 - 10.0
Barium	5.0 - 10.0
Cadmium	5.0 - 10.0
Chromium	5.0 - 10.0
Lead	5.0 - 10.0
Mercury	0.2
Selenium	5
Silver	10

APPENDIX C
Compound List for TAL/Metals with Detection Limits
SOP #1017
November 1994

DATA VALIDATION PROCEDURE FOR ROUTINE INORGANIC ANALYSIS

ANALYSIS: TAL/METALS

SAMPLE PREPARATION METHOD:	SW-846, Method 3015, 3010, 3020 (Instrument and Sample Dependent)/SW-846, Method 3050
ATOMIC ABSORPTION METHOD:	SW-846, Method 7000

COMPOUND LIST	DL H_20 (µg/L)	DL SOIL (mg/kg)
Aluminum	50 - 100	500
Antimony	0.5 - 1.0	5 - 10
Arsenic	0.5 - 1.0	5 - 10
Barium	1.0 - 2.5	5 - 25
Berylium	1.0 - 2.5	5 - 10
Cadmium	0.5 - 1.0	5 - 10
Calcium	2.5 - 5.0	25 - 50
Chromium	5	10 - 50
Cobalt	2.5 - 5.0	25 - 50
Copper	2.5 - 5.0	25
Iron	5 - 10	50 -100
Lead	5	5 - 50
Magnesium	2.5 - 5.0	25 - 50
Manganese	2.5 - 5.0	25 - 50
Mercury	0.04	0.2 - 0.4
Nickel	2.5 - 5.0	25 - 50
Potassium	2.5 - 5.0	25 - 50
Selenium	0.5 - 1.0	5 - 10
Silver	1.0 - 2.5	10 - 25
Sodium	5 - 10	25 -100
Thallium	0.5 - 1.0	5 - 10
Vanadium	1.0 - 2.5	10 - 25
Zinc	1.0 - 5.0	10 - 25

APPENDIX D
Deliverable Checklist for Metal Analyses
SOP #1017
November 1994

DATA VALIDATION PROCEDURE FOR ROUTINE INORGANIC ANALYSIS

FOR LOCKHEED\ SERAS ONLY			
Assignment Name:	WA#	Report#:	Date:

Deliverable Checklist for Metal Analyses

All the following information must be included in the data package.
(Please check all blanks and submit the list together with the report.)

_____ Case narrative

_____ Chain of custody (signed with date of receipt)

_____ All sample preparation logs (include all re-extractions)

_____ Compositions of matrix spike solution and the volume used

_____ Worksheet of % solid or % moisture

_____ Analysis logs, if applicable

_____ Tabulated sample results (including the duplicate anlysis results)

_____ Tabulated spike recovery results

_____ Summary of the calibration curves for all specified elements

_____ Method numbers for all analyses

Raw Data (Instrument Printouts) for:

_____ Each initial calibration standards

_____ ICV

_____ CCVs

_____ ICB

_____ CCBs

_____ Method blank

_____ MS/MSDs

_____ Sample analyses

_____ Sample dilution analyses

_____ Instrument detection limit

_____
Signature

_____
Date

APPENDIX E
Deliverable Checklist for Cyanide Analyses
SOP #1017
November 1994

DATA VALIDATION PROCEDURE FOR ROUTINE INORGANIC ANALYSIS

FOR LOCKHEED\ SERAS ONLY			
Assignment Name:	WA#	Report#:	Date:

Deliverable Checklist for Cyanide Analyses

All the following information must be included in the data package.
(Please check all blanks and submit the list together with the report).

_____ Case narrative

_____ Chain of custody (signed with date of receipt)

_____ All sample preparation logs (include all re-extractions)

_____ Compositions of matrix spike solution and the volume used

_____ Worksheet of % solid or % moisture

_____ Analysis logs

_____ Tabulated sample results (including the duplicate analysis results)

_____ Tabulated spike recovery results

_____ Summary of the calibration curves

_____ Calculation sheet

_____ Method numbers for all analysis

Raw Data (Instrument Printouts) for:

_____ Each initial calibration standards
_____ Calibration check
_____ Method blank
_____ MS/MSDs
_____ Duplicates
_____ Sample analyses
_____ Sample dilution analyses
_____ Instrument detection limit

_____ _____
Signature Date