

LLNL Environmental Restoration Division (ERD)
Standard Operating Procedure (SOP)

**ERD SOP 4.6: Validation and Verification of Radiological and
Nonradiological Data Generated by Analytical Laboratories**
Revision: 4



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1.0 PURPOSE

This procedure specifies the procedure used by the ERD QC chemists when reviewing analytical data to ensure consistent results of a known quality so that the data user may evaluate and make judgments based on the analytical results.

2.0 APPLICABILITY

This procedure applies to the radiological and chemical data generated by analytical laboratories from the analysis of ground and surface water and soil, rock, and sediment samples that are reviewed by the Environmental Restoration Division (ERD) for the Environmental Protection Department.

3.0 REFERENCES

- 3.1 U.S. Environmental Protection Agency (EPA) (1994), *Contract Laboratory Program (CLP) National Functional Guidelines for Organic Data Review*, U.S. Environmental Protection Agency, Washington, D.C. 20460 (EPA-540/R-94-012).

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- 3.2 EPA (1994), *CLP National Functional Guidelines for Inorganic Data Review*, U.S. Environmental Protection Agency, Washington, D.C. 20460 (EPA-540/R-94-013).
- 3.3 EPA (1987), *Data Quality Objectives For Remedial Response Activities*, Office of Emergency Response and Office of Waste Programs Enforcement, Washington, D.C., 20460.
- 3.4 LLNL Environmental Restoration Division (1999), *Livermore Site and Site 300 Quality Assurance Project Plan*.
- 3.5 Lawrence Livermore National Laboratory's (LLNL) Environmental Protection Department (EPD) and the Lawrence Berkeley National Laboratory's (LBNL) Analytical Statement of Work.

4.0 DEFINITIONS

SEE SOP Glossary.

5.0 RESPONSIBILITIES

5.1 Division Leader

The Division Leader's responsibility is to ensure that all activities performed by ERD at the Livermore Site and Site 300 are performed safely and comply with all pertinent regulations and procedures, and provide the necessary equipment and resources to accomplish the tasks described in this procedure.

5.2 Subproject Leader (SL)

The SL's responsibility is to review the analytical data from the areas that they are responsible for, against historical data for internal consistency and informing the QC Chemist of potential or suspect data.

5.3 Quality Control (QC) Chemists

The ERD QC Chemists are responsible for reviewing 100% of the analytical data for technical adequacy, internal consistency and quality, determining and flagging data quality and requesting additional information from the analytical laboratories if there are suspect data points or problematic QC results.

5.4 Data Management Team (DMT)

The DMT is responsible for decoding collocated sample identifications and electronically recording qualifier flags. Flags assigned by QC Chemists are hand entered and those flags that can be generated automatically (see Attachment B) are assigned by running a computer program.

6.0 PROCEDURE

6.1 QC Chemist Review

In order for the QC Chemist to perform data validation/verification, the analytical laboratory must provide sufficient information for the QC chemist to determine the status of the following:

- A. Integrity and stability of the samples(s) analyzed.
- B. Performance of the instrument(s) used for analyses.
- C. Results of Internal quality control checks.
- D. Identification and quantification of the analyte(s) in the sample(s) analyzed.

The information sent with the analytical results varies somewhat by laboratory. The contract analytical laboratories are contractually obligated to provide specific information as described in the ERD QAPP and analytical Statement of Work. The QC Chemists use this information to determine if the analytical results require qualification. Attachment A shows the typical flow of the QC Chemists review. Attachment B lists all the Data Qualifier Flags available including those automatically assigned by the electronic flagging program.

6.1.1 Integrity and Stability of Sample(s) Analyzed

- A. Review signed Chain-of-Custody (CoC) form for each sample received to determine if the chain of custody has been broken. Sample results may need qualification if defensibility or traceability of samples cannot be determined (i.e., S or R flag).
- B. Check date and time of both extraction and analysis of each sample to ensure the appropriate holding times (if applicable) are met. If the holding time has not been met (see SOP 4.3, "Sample Containers and Preservation," for holding times), the associated results should be qualified with the H flag. This is performed automatically by the electronic flagging program run by DMT. If the turn around times (TAT) specified on the CoC were not met, this information is documented on the sample invoice and in the Sampling Plan and Chain-of-Custody Tracking (SPACT) database.
- C. Review the condition of sample upon receipt form to determine if the samples were damaged or compromised during shipment. Samples should arrive at the laboratory at the proper preservation temperature (see SOP 4.3 for proper preservation temperatures). Sample results may need qualification based on this review (i.e., S or R flag).

6.1.2 Performance of the Instruments(s) Used for Analysis

Analytical methodology for analyzing the samples will determine the type of instrument(s) to be used by the laboratory. The following steps are performed to demonstrate the working condition of instrument(s) during analysis:

- A. Compare the reporting limits to the contract required reporting limits. If the reporting limits are elevated due to sample dilutions, the dilution factor should be checked against the concentration range for appropriateness. A Data Review Request (see Section 6.2.2) may be necessary if inappropriate reporting limits were reported. The D flag is automatically assigned by the electronic flagging program when dilutions are performed.
- B. Identification of each instrument used for analysis to determine if QC samples were analyzed on the same instrument.

6.1.3 Internal Quality Control Checks

- A. At least one method blank analyzed in every analytical batch of samples or whenever system contamination is suspected following a high level sample. If analytes are detected in the method blank above the minimum detectable activity or reporting limit, the detections of the analytes in the associated samples are qualified with the B flag. Non-detects (NDs) are not qualified.
- B. If surrogate or tracer yield recoveries are outside method specified control limits, the associated results are qualified. QC Chemists should use professional judgement when assigning flags based on surrogate results. For example, results may not need to be qualified if surrogates are slightly outside of control limits. The following should be considered as guidelines only:
1. If surrogate or tracer yield recoveries (%RCV) are greater than the upper control limit (UCL), then any sample detections should be flagged "IJ". NDs do not require flagging.
 2. If %RCVs are less than the lower control limit (LCL), but greater than 50%, then flag positive sample results "IJ" and flag NDs "IUJ" for estimated sample quantitation limit.
 3. If %RCVs are less than the LCL, and less than 50%, then flag positive sample results "IJ" and flag NDs "IR". In some cases, the acceptable control limit range will go lower than 50% (i.e., Semivolatiles), therefore best professional judgement should be used when %RCV is < LCL

Note: When QC sample surrogates are out of control, all supporting information (i.e., MS/MSD accuracy and precision, LCS accuracy, and sample location historical data) should be considered to determine if the associated samples were affected.

- C. Accuracy as percent recovery (%RCV) and precision as relative percent difference (RPD) should be determined with each batch of samples, when appropriate, as indicated by the analytical method. Accuracy is determined by the analysis of matrix spikes (MS). For nonradiological analyses, precision is determined by the analysis of matrix spike duplicates (MSDs) and expressed as RPD. For radiological analyses, precision is determined by the analysis of sample duplicates and expressed as RPD and/or relative error ratio (RER). Radiological laboratories are not required to perform MSDs due to waste disposal issues. When %RCVs, RPDs, and/or RERs are outside method specified control limits the data is qualified. The QC Chemist should try to determine if the %RCVs, RPDs, or RERs are outside acceptance limits due to matrix effects. If matrix effects are determined to have caused the failed QC, then the extent of the matrix effects should be determined. Instances where matrix effects have been determined to affect the sample spiked only (not the other samples in the batch), then qualification should be limited to this sample alone. However, it may be determined that a laboratory is having systematic problem in the analysis of one or more analytes which affects all associated samples. The reviewer must use professional judgment to determine the need

for qualification of unspiked analytes and samples. The following should be used as guidelines only:

1. If both the MS and MSD %RCV are out of control (either above the UCL or below the LCL), then flag sample results (both detections and NDs) "L". If only one %RCV is out of control, no flag is necessary unless no MSD exists, then flag "L".
2. If MS/MSD %RCV is less than 30%, use professional judgement to determine if matrix interference may affect the determination of the analyte in the samples and flag positives "J" and NDs with an "R".
3. If the RPD/RER is out of control (either above the UCL or below the LCL) for an analyte, then flag sample results (both positive and negative detections) "O". LCSs should be analyzed with every batch of samples. If the LCS %RCV is outside of control limits the associated results are qualified as described below:
4. If the LCS %RCV is greater than the UCL for an analyte, then flag positive sample results from the same batch "J". No flags are necessary for ND results.
5. If the LCS %RCV is less than the LCL for an analyte, then flag positive sample results from the same batch "J" and flag NDs with "R".

Note: If more than half of the compounds in the LCS are not within the required recovery criteria, then all associated data should be qualified "R".

6.1.4 Identification and Quantification of the Analyte(s) in the Sample(s) Analyzed

Field quality control samples (SOP 4.9, "Collection of Field QC Samples," describes the collection of field QC samples) may be submitted for analysis to support the determination by the QC Chemist that the detected constituents have been identified correctly.

- A. Detections of analytes in equipment blanks may indicate inadequate decontamination of sampling equipment potentially leading to cross-contamination of samples. Analytes detected in both the equipment blank and associated samples should be qualified with the F flag.
- B. Detections of analytes in field blanks may indicate contamination from the sampling container and/or the environment in which the primary sample was collected. Analytes detected in both the field blank and associated samples should be qualified with the F flag.
- C. Detections of analytes in trip blanks may indicate sample contamination through handling, preservation, and shipping. Analytes detected in the trip blank and associated samples should be qualified with the F flag.

Note 1: If there are detections in the blanks, but not in the associated samples, no qualification is necessary.

Note 2: When flagging detections in samples based on detections in the blanks, the blanks themselves do not require qualification.

Note 3: The QC Chemists should use professional judgement to determine whether trip, field, or equipment blanks need to be qualified when associated QC is outside acceptance limits. In many cases the blanks themselves do not require qualification. (i.e., when a MS/MSD %RCV is outside of limits).

- D. The QC Chemist should compare the results of decoded intralaboratory collocated samples. If the results are not comparable, a DRR (see Section 6.2.2) should be initiated. It is important to contact the individual(s) affected by the suspect results immediately incase resampling is necessary. Based on the results of the DRR sample results may need to be flagged suspect (S), estimated (J), or rejected (R).
- E. The QC Chemist may compare the analytical results to historical results when available. If the data is not consistent with the historical results, the QC Chemist may initiate a DRR (see Section 6.2.2) and request that the analytical laboratory review the supporting data or reanalyze the sample. The resolution to the DRR may result in data qualification.
- F. The QC Chemist periodically reviews the output of the Statistical Data Outliers computer program. This program identifies data points as outliers when they diverge from the historical data by 3 sigma. (see SOP 5.21, "Outlier Identification Program").

6.2 Data Validation/Verification Documentation

6.2.1 Data Qualifier Flag Form

During the QC Chemists data review, the data are qualified using the Data Qualifier Flag Form (Attachment C). The QC Chemist fills out the form, and places the qualification form in the analytical results, under the case narrative when one exists. For visibility, the form should be made on yellow paper.

6.2.2 Data Review Request (DRR)

A DRR is initiated when a problem or a question with analytical results occur that requires resolution. The DRR is logged into the DRR logbook. The laboratory is notified of the DRR by electronic mail. The telephone may be used; however, it should be followed up with an e-mail so there is a written record. The e-mail should be printed and filed with the resolution.

6.2.3 Quality Improvement Form

The Quality Improvement Form (QIF) may be necessary if an analytical error requiring a database change or a systematic laboratory problem is discovered (see Attachment A, SOP 4.12, "Quality Improvement Forms [QIFs]").

6.2.4 Analytical Results

The QC Chemists should separate the QC and place it behind the analytical results. The CoC should be placed at the back of the QC results. The front page upper right-hand corners of the results are marked with a “V” for validated, “N” when validation cannot be performed due to missing information, or “O” if a revision is reviewed that does not change the data quality. The reviewed date should be marked under the validation status (i.e., V, N, or O) and then the reviewers initials.

Example:

V
3/31/00
VRD

6.2.5 Sampling Plan and Chain of Custody Tracking (SPACT) Database

Once validation/verification is complete, the QC Chemist should document the review in SPACT per the following instructions:

- A. Log into the SPACT database and select “UV” (update submenu/verifications).
- B. Enter the data package CoC number. Once the existing information for that CoC is on-screen, enter initials, validation date, validation status (V or N), N or Y depending on whether flags are required, N or Y depending on whether the report met turnaround times, invoiced date, and any comments. If a revision is requested, then enter requestor initials, date, and reason.

6.2.6. Invoices

Invoices should accompany the reported results. The QC Chemist approves the invoice for payment by signing the invoice and indicating the date of payment in the SPACT database. Any missed holding or turnaround times or unusable data due to severe quality problems that are the fault of the laboratory, should be noted on the invoice so that the Technical Release Representative may apply any necessary penalties per the current Statement of Work requirements.

7.0 QA RECORDS

- 7.1 CoC forms
- 7.2 Original analytical results
- 7.3 DRRs and QIFs
- 7.4 Data Qualifier Flag form

8.0 ATTACHMENTS

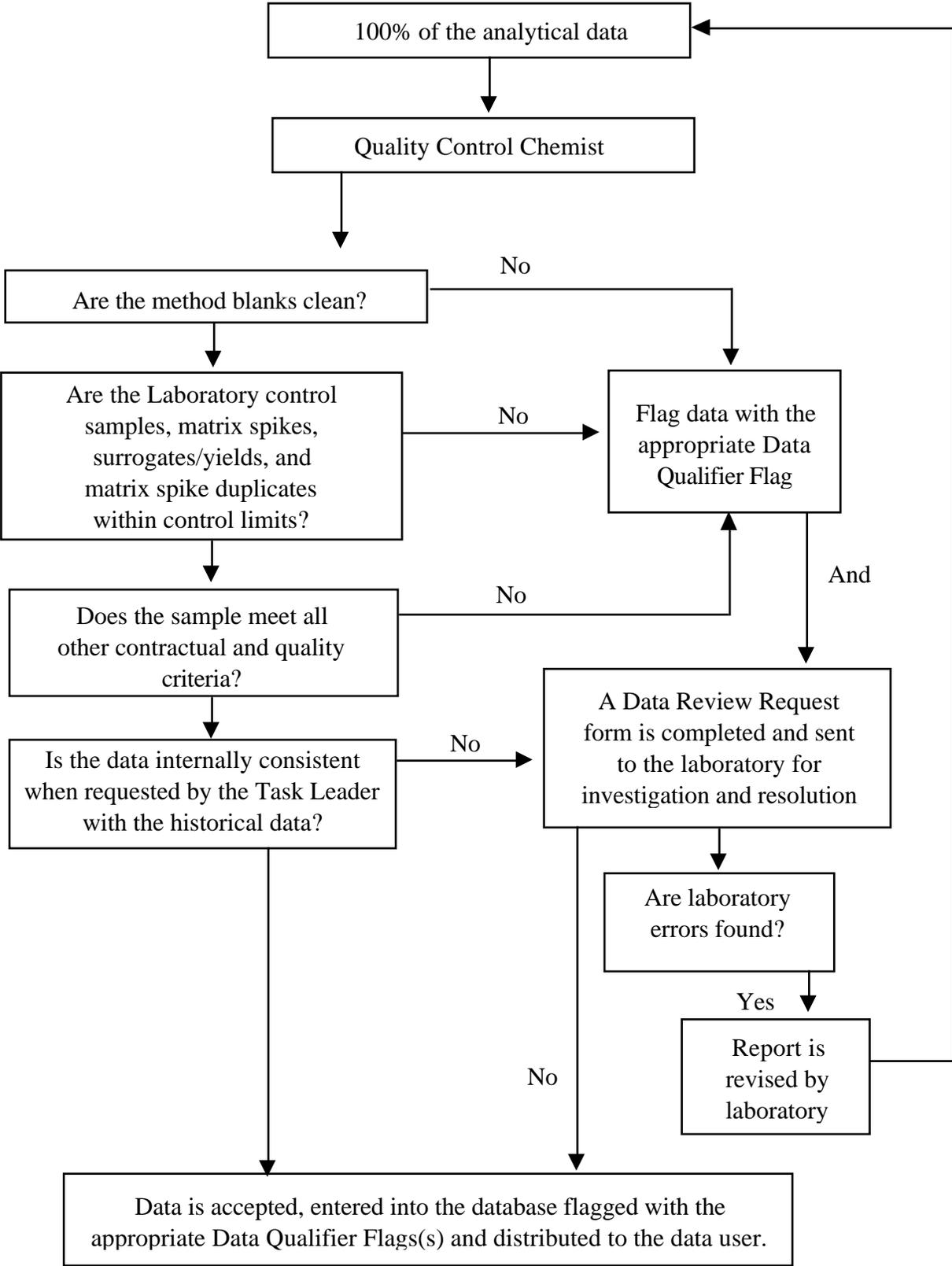
Attachment A—Flow of Analytical Data During Validation/Verification

Attachment B—Data Qualifier Flags

Attachment C—Data Qualifier Flag Form

Attachment A

Flow of Analytical Data During Validation/Verification



Attachment A. Flow of analytical data during validation/verification.

Attachment B

Data Qualifier Flags

List of Environmental Restoration Division Qualifier Flags

Flag	Definition
B	Analyte found in method blank, sample results should be evaluated.
D ^a	Analysis performed at a secondary dilution or concentration.
E ^a	The analyte was detected below the LLNL reporting limit, but above the analytical laboratory minimum detection limit or activity.
F	Analyte found in field blank, trip blank, or equipment blank, sample results should be evaluated.
G	Quantitated using fuel calibration, but does not match typical fuel fingerprint (fuel maybe gasoline, diesel, motor oil etc.).
H ^a	Sample analyzed outside of holding time, sample results should be evaluated.
I	Surrogate or tracer yield recoveries were outside of QC limits, sample results should be evaluated.
J	The analyte was positively identified; however, the associated numerical value is the approximate concentration or activity of the analyte in the sample.
L	Matrix spike recoveries not within control limits.
O	Matrix spike duplicate RPD, sample duplicate RPD, or RER not within control limits.
P	Indicates that the absence of a data qualifier flag does not mean that the data does not need qualification, but that the implementation of electronic data qualifier flags was not yet established.
R	Sample results are rejected due to serious deficiencies in the ability to analyze the sample and meet QC criteria. The presence or absence of the analyte cannot be verified.
S	The analytical results for this sample are suspect.
T ^a	Analyte is tentatively identified compound; result is approximate.
U ^a	Compound was analyzed for, but not detected above the detection limit.

^a Automatically flagged in the database by the electronic qualifier flag program.

RPD = Relative Percent Difference.

RER = Relative Error Ratio.

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Attachment C

Data Qualifier Flag Form

Today's Date: _____

DATA QUALIFIER FLAG FORM

Circle the appropriate qualifier flags and fill out information below.

Flag	Definition
B	Analyte found in method blank.
F	Analyte found in field blank, trip blank, or equipment blank (circle one).
G	Quantitated using fuel calibration, but does not match typical fuel fingerprint.
I	Surrogate or tracer yield recoveries were outside of QC limits (circle one).
J	The analyte was positively identified; the associated numerical value is the approximate concentration of the analyte in the sample. Explain circumstances below.
L	Matrix spike recoveries not within control limits.
O	Matrix spike duplicate RPD, sample duplicate RPD, or RER not within control limits. (circle one).
R	Sample results are rejected due to serious deficiencies in the ability to analyze the sample and meet QC criteria. The presence or absence of the analyte cannot be verified. Explain circumstances below.
S	The analytical results from this sample are suspect. Explain circumstances below.
T	Analyte is tentatively identified compound; result is approximate.

Laboratory Code: (circle one) BB, CN, TN, GE, QR or other: _____

QC Chemist Initials: _____ Requested Analysis: _____

Analyte(s)/Code: _____

Explanation (check one or fill in):

Insufficient sample for spike. _____ in method blank.

Matrix interference. LCS validates methodology.

High concentration of analyte in spiked sample.

Other/comments: _____

Log Number of Affected Samples: _____

<i>For Data Management Use Only:</i>	
Entered: Initials _____	Date: _____
Elect. Confirmed: Initials _____	Date: _____