Radionuclide Data Quality Evaluation Guidance – 9284

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ABSTRACT

A considerable amount of radioanalytical data is generated during various phases of the characterization and remediation of radiologically-contaminated sites and properties. It is critical that data generated from the analysis of collected samples be to a level of quality usable by the project and acceptable to stakeholders. In July 2004, the final version of a multi-agency guidance manual entitled *Multi-Agency Radiological Analytical Protocols Manual (MARLAP)* [1] was issued by the Environmental Protection Agency, Department of Energy, Department of Homeland Security, Nuclear Regulatory Commission, Department of Defense, National Institute of Standards and Technology, U. S. Geological Survey, Food and Drug Administration, and the States of Kentucky and California. The authors' purpose is to introduce readers to some key elements of MARLAP as it relates to radioanalytical lab quality control, and to demonstrate how these guidance elements can be effectively incorporated into mature radioanalytical lab operations and data validation regimes. Based upon the logic and statistical methodologies presented in MARLAP, the authors have revised existing project-specific Radioanalytical Data Evaluation Guidance (RadDEG) used at the FUSRAP Maywood Site in Maywood, NJ. The RadDEG allows users to qualify data in a meaningful way by tying the usability of the data to its activity and uncertainty relative to project action levels and QC results. This exercise may be useful to other projects looking to implement a MARLAP-based approach into their project/site-specific data evaluation methodologies.

INTRODUCTION

The Maywood Radioanalytical Data Evaluation Guidance (RadDEG) provides guidance in laboratory data quality evaluation of radiological data and is based, wherever possible, on MARLAP. MARLAP addresses the need for a nationally consistent approach to producing radioanalytical laboratory data that meet a project's or program's data requirements. MARLAP provides guidance for the planning, implementation, and assessment phases of those projects that require the laboratory analysis of radionuclides and is both scientifically rigorous and flexible enough to be applied to a diversity of projects and programs.

The scope of the RadDEG includes discussions of quality criteria, corrective actions, and data qualifications that should be used or applied during the data acquisition, verification, and validation data life-cycle phases. The RadDEG provides data quality guidelines to personnel involved in the testing of radiologically contaminated environmental media, including the interpretation and possible qualification of results. The RadDEG is also used at Maywood, by the Project Chemist to establish method quality objectives and perform oversight of laboratory operations. The RadDEG is used by Maywood lab personnel as guidance for establishing internal quality control (QC) criteria, establishing decision points

for implementing corrective actions, and applying initial data qualifiers. Finally, the RadDEG is provided to an independent third-party data validator to communicate criteria for the application/removal of data qualifiers consistent with projects DQOs.

One of the most important factors to consider when using the MARLAP approach is the issue of uncertainty, specifically establishing acceptable limits for the uncertainty of individual radioanalysis results. The term "uncertainty" refers to the degree of inaccuracy and imprecision associated with a measured quantity. The topic of measurement uncertainty goes into greater detail in MARLAP, Appendix C. The RadDEG establishes method quality objectives (MQO) for method uncertainty for every appropriate analyte/matrix combination. MARLAP also delves deeply into the concepts of hypotheses testing, of which uncertainty is an important component. Although it is outside of the intended scope of this document to discuss hypothesis testing, we define specific terms that are used when discussing radioanalysis measurement uncertainty:

- The upper bound of the gray region (UBGR) is usually the project action level (which is less than the regulatory action level) for a given analyte. The UBGR is also an activity level at which the probability of a Type I decision error is greater than the threshold established by stakeholders. In this application, a Type I error implies the likelihood that the action level is exceeded when lab results imply otherwise. The acceptable Type I error rate for radioanalysis results data produced for the project is currently set at 5%.

- The lower bound of the gray region (LBGR), or discrimination level, is that activity at which there is a finite probability of Type II decision error. In this application, a Type II error implies the likelihood that the action level is reported to be exceeded, as a result of analytical uncertainty, when the real world conditions are below action limits. The acceptable Type II error rate for radioanalysis results data produced for the project is currently set at 10%.

The required method uncertainty, μ_{MR}, at the upper bound of the gray region (UBGR) is defined as:

$$\mu_{MR} = \Delta / 10 \qquad \text{(Eq. 1)}$$

Where:
Δ is the width of the gray region (UBGR – LBGR).

For the Maywood Project, the UBGR is synonymous with the action level for those analytes that have an action level. For sample results that fall at or above the UBGR, the relative method uncertainty (φ_{MR}) is used to establish quality control parameter acceptance criteria. The quantity φ_{MR} is defined as:

$$\varphi_{MR} = \mu_{MR} / \text{UBGR} \qquad \text{(Eq. 2)}$$

The QC parameters described within the RadDEG and employed during sample batch testing at the Maywood Project help ensure that MQOs are met. The validation process involves three steps: criteria, verification, and validation.

Criteria are the qualitative and quantitative acceptance ranges for quality control parameter measurements. Criteria must be met so that the project is in compliance with established data quality objectives (DQO).

The data verification process is best summarized by the question: "Is this package of data correct, complete, and reliably obtained?" Verification assures that laboratory conditions, operations, and resultant data packages were compliant with established criteria, commonly communicated to both the

analytical lab and the third-party data validator via the contractual Scope of Work (SOW). The RadDEG can serve as an important supporting document in the preparation of SOW performance expectations. Depending on the relationship with the analytical lab, it is possible to incorporate RadDEG methodologies directly into internal lab QC processes. This is the case at the Maywood Project where the sole function of the lab is to support the project. When both the third-party validator and analysis lab work from a standard set of criteria and corrective actions, the frequency of data rejection after initial data delivery to the client, prior to final validation, is nearly eliminated.

Validation addresses the reliability of the data, and considers the degree of confidence in the reported analytical data. Data validation criteria and procedures should be established during the planning process and captured in the project plan documents including third-party data validator work scopes. Data validation qualifiers may be applied based upon QC results beyond tolerance (i.e., warning & control) limits. At Maywood, the RadDEG addresses the following radioanalysis QC criteria: *Radionuclide Quantitation and Detection Limits, Instrument Calibration, Blank Analysis, Tracer Recoveries, Laboratory Control Sample Analysis, Matrix Spike Sample Analysis, Laboratory Replicate/Field Duplicate Analysis, and Spectrometry Resolution*. Key facets of each QC criterion, as applicable to the radioanalysis techniques employed at Maywood, are addressed in the remainder of this paper.

An author's note: Throughout the remainder of this paper reference is made to a third-party validator who evaluates laboratory performance against established criteria. It is understood that laboratories must provide the validator, either as part of a data package or separately, QC and results documentation necessary to conduct a complete review. Standard practice for the Maywood Project third-party data validator is to withhold review pending receipt of the required documentation, or reject data when requested documentation cannot be provided.

RADIONUCLIDE QUANTITATION AND DETECTION LIMITS

Criteria

With this QC parameter, the objective is to ensure that the reported quantitation results are accurate and that the required detection limits have been met. When detection limit requirements are not met, the data quality objectives may not have been met. Therefore, all results should be evaluated relative to the uncertainty associated with the analysis and the sample reports shall report the uncertainty.

Radionuclide quantitation must be calculated according to the appropriate procedures specified in the contractual SOW. Detection limits specified in the specific procedures must be met unless other detection limits are specified in the SOW. It is important to assess lab method capabilities against method quality objectives, prior to the start of work, to ensure variable conditions (e.g., instrument efficiency, count times, sample dilutions, etc.) are evaluated and adjusted, where practicable, to maximize method sensitivity (i.e., lower minimum detectable activity (MDA)).

Analytical uncertainties must be reported with all results in order to qualify the data. Results and uncertainties must be reported for all required analyses regardless of the size or sign of the result. The reported uncertainty will typically include all uncertainties associated with the analysis (i.e., a total propagated uncertainty).

Verification & Validation

The raw data is examined by the validator to verify the correct calculation of sample results reported by the laboratory, as well as identify any anomalies (i.e., omissions, legibility, etc.). The validator verifies that all analytical uncertainties have been propagated and reported for all results. The validator typically

recalculates a few of the results if there is a suspicion the results have not been calculated properly. Qualifiers should be placed using professional judgment. Examples of primary data qualifiers communicated to both the Maywood Lab and data validator include the following:

Non-Detect "U" qualifier is applied when:

- result is negative with an uncertainty greater than the absolute value of the result;
- result is < critical level. The critical level is the upper 95% confidence interval of the background, essentially the background + 2σ;

Estimated "J" qualifier is applied when a result exceeds the MDA, but the result is less than its uncertainty.

Rejected "R" qualifier is applied when:

- significant or unresolvable errors are found in the calculations, necessary data are missing, or there are other major discrepancies in the data package. It is appropriate in this instance for the validator to confirm calculation methodologies and attempt to resolve discrepancies with the lab, via a designated Project representative (e.g., Chemist, QC Manager, Health Physicist, etc.) prior to rejecting the results. The validator uses professional judgment when assessing the significance of an error, omission, or discrepancy and determining if data rejection is appropriate.
- result is negative with an uncertainty smaller than the absolute value of the result. This is typically an indication of improper blank subtraction or background shift.

GAMMA SPECTROMETRY INITIAL ENERGIES & EFFICIENCIES CALIBRATION

Criteria

A *full energy and shape calibration*, *Peak-to-Compton Ratio calibration*, and *efficiency calibration*, collectively referred to as the *initial calibration*, is performed annually and after hardware replacement or significant instrument repairs. The initial calibration is typically performed with a NIST-traceable mixed gamma standard; a radioactive source with 9 to 12 radionuclides having gamma ray emissions at energies from approximately 60 keV to 2000 keV.

For the *full energy & shape calibration*, a linear plot is constructed of the true energy versus the observed energy (expressed as channel number). The percent difference between the true energy and the observed energy of any radionuclide gamma emission line should be less than 1.0%. The Full Width Half Maximum (FWHM) value should be less than 3% of the observed energy.

The *Peak-to-Compton Ratio*, an important characteristic of the detector, is performed by dividing the counts in the full energy peak centroid channel for Cs-137 (661 keV) by the average counts in the Cs-137 Compton region (typically 440 keV to 490 keV), then comparing the calculated ratio to the manufacturer's specification.

After the efficiency calibration has been performed by the system software and the parameters for the equation of the line calculated, the Fit and Delta % values are observed. The Fit value is the efficiency value of the best fit line at a given energy. The actual efficiency (AE) is calculated by dividing the observed counts by the activity of the standard. The Delta % value is then determined as:

$$\text{Delta \% Value} = [(\text{Fit Value} - \text{AE})/\text{AE}] \times 100 \qquad \text{(Eq. 3)}$$

For the best fit polynomial, linear, or quadratic equation, the Delta values must each be less than 5%. The full width tenth maximum to full width half maximum (FWTM-FWHM) ratio will also be checked quarterly.

Verification & Validation

For the energy calibration, the validator verifies that a plot of the observed energies versus the channel number is a straight line. The difference between the observed energy and the true energy of any radionuclide should be less than 1.0%. If the difference is greater than 1% for two or more radionuclides, the validator then verifies that the instrument gain was adjusted and the instrument recalibrated. The validator then verifies that the FWHM value for an energy peak is less than 3% of the observed energy; and that the peak-to-Compton ratio falls within the manufacturer's specification. For the efficiency calibration, the validator verifies that it was performed and that the delta values are less than 5%.

Data associated with the calibration would typically be deemed unusable if one more of the following criteria are exceeded:

- The energy percent difference from the energy calibration plot is greater than 1% for two or more radionuclides (and the instrument was not recalibrated after gain adjustment);
- the efficiency calibration delta values are greater than 5% for any one radionuclide; or
- the FWHM for any one energy peak is > 3%. If only one calibration radionuclide (other than Cs-137) has an energy percent difference greater than 1%, that radionuclide can be removed and the instrument calibrated without it.

GAMMA SPECTROMETRY CONTINUING CALIBRATIONS

Criteria

Continuing calibrations are performed daily, or every day that a gamma spectrometry detector analyzes samples and/or standards. The same NIST-traceable mixed gamma standard employed for the initial calibration is used for continuing calibrations. The activity of each radioisotope in the calibration standard must be within 10% relative of the true, decay-corrected activity. The energy of each isotope must be within 2.0 keV. The FWHM values for three selected calibration radionuclides, distributed across the energy spectrum, are monitored and must be less than 3% of the observed energy.

Verification & Validation

The validator verifies that the continuing calibration standard was analyzed on each day for which field and batch QC samples were analyzed, and that the calibration standard was analyzed before analysis of any samples. Default control limits of ± 10% (relative) and default warning limits of ± 7% (relative) of the true activity of each radionuclide are established. If the control limits for one or more radionuclides, or if the warning limits for two or more radionuclides are exceeded, the validator verifies that the continuing calibration standard was reanalyzed before analysis of any samples or batch QC.

The validator verifies that the mixed gamma standard contains at least 7 (preferably 8 to 10) radionuclides with energies that span the energy spectrum (approximately 60 keV to 2000 keV). Sources should provide at least 10,000 counts at each energy calibration point to maintain counting uncertainty below 1%. The difference between the true energy and the observed energy of any radionuclide gamma

emission line must be less than 2.0 keV. The FWHM value will be monitored and must be less than 3% of the observed energy for one each of a low, medium, and high energy calibration radionuclide.

The validator checks all continuing calibration standard radionuclide activities to ensure they fall within ±10% relative to the true activity. If any control limits were exceeded and the continuing calibration standard was not reanalyzed or the reanalysis results were also unacceptable, all sample results associated with that standard (essentially all results generated on that day) would typically be rejected. The validator will typically reject all results associated with a calibration if one or more of the following occurs:

- the difference between the true energy and the observed energy of any radionuclide gamma emission line is > 2.0 keV;
- the FWHM value is greater than 3% of the observed energy for the reviewed calibration radionuclide, and the calibration was not repeated, or if it was repeated and there was still an exceedance.

ALPHA SPECTROMETRY INITIAL ENERGIES & EFFICIENCIES CALIBRATION

Criteria

For both initial and continuing calibrations, as well as on any day that a QC or field sample is analyzed, a pulser check is run on each detector before the calibration or sample analysis on the same day as the calibration or sample analysis is performed. For each pulser check, the FWHM and efficiency must be within the mean ± 3σ (based on a dataset of at least twenty pulser check values). The Pulser Energy Center must be within 50 keV of the expected value, typically 5500 keV.

The alpha spectrometer system at Maywood is calibrated with a NIST-traceable standard containing five (5) isotopes: U-238, U-234, Th-230, Pu-239, and Am-241. The detector response created by three of these radioisotopes, U-238, Pu-239, and Am-241, are used to calibrate the Maywood alpha spectrometer detectors. The calibration standard provides at least 10,000 cpm for each isotope of interest to maintain measurement uncertainties less than 1%. An initial energy and efficiency calibration is performed annually, or whenever significant equipment changes occur such as replacement of a detector. The following Table I QC acceptance criteria are established for the initial calibration for each detector at the Maywood Lab:

Table I. QC Acceptance Criteria Established for the Initial and Continuing Calibrations for each Detector

QC CRITERION	Calibration Radioisotope		
	U-238	Pu-239	Am-241
Combined % Efficiency (detector specific)	20.72 – 23.20		
Maximum Peak Energy (keV)	4199 ± 7	5158 ± 8	5490 ± 8
Activity (% relative of true value)	90-110	90-110	90-110

Verification & Validation

The validator verifies that an initial calibration has been performed within one year (± 30 days) of the last initial calibration, and that the efficiency, activity (with % relative values), and calibration isotope maximum peak energies have been provided in the data package. The pulser check resolution (FWHM), pulser energy center, and efficiency values must be within acceptance criteria.

If the initial calibration isotope efficiency, activity and maximum peak energy values and alpha resolution values do not fall within criteria, all data associated with the initial calibration is deemed unusable and would typically be rejected by the validator.

ALPHA SPECTROMETRY CONTINUING CALIBRATIONS

Criteria

An energy and efficiency calibration is performed monthly using the same isotopic mixture as that used for the initial calibration. For the calibration isotopes, the maximum peak energy, activity and efficiency must be within the limits provided in Table I. At no time should the maximum peak energy value vary by more than 10 keV from the theoretical peak energy.

Verification & Validation

The latest energy and efficiency calibrations should be included in the analytical data package and the average efficiency, maximum peak energies, and activities should fall within the limits specified within Table I. If the laboratory does not have a record of the continuing calibration, all data that would have been associated with the calibration is unusable, unless the lab can verify that the calibration has not shifted.

If required factors are missing, or if the QC parameter values exceed the Table I limits, the validator may elect to qualify affected data estimated (J) to signify an increased level of uncertainty in the measurement because of the inability to correct the measured value for efficiency. If the calibration was not supplied in the package, and the laboratory cannot verify that the calibration has not shifted, or if the results of a continuing calibration have indicated a shift has occurred, the validator would typically reject all data resulting from the last calibration check.

GAS-FLOW PROPORTIONAL COUNTER CALIBRATION CHECKS

Gross alpha and gross beta initial instrument calibration checks typically consist of 20 or more analyses each of a gross alpha standard containing Th-230 and a gross beta standard containing Sr/Y-90. Average activities and standard deviations are then calculated and used to establish control chart warning ($\pm 2\sigma$) and control ($\pm 3\sigma$) limits for each detector. Subsequent continuing calibration standard checks are made on days of instrument operation, and checked against the control chart to ensure acceptable instrument operability prior to measurement of samples. The charts are updated periodically to reflect the most recent calibration checks.

The gas proportional counting systems are also used to measure Ac-228 in the Ra-228 analysis. Ac-228 is the daughter of Ra-228. A separate dedicated calibration is generated annually for this analysis using Sr-89, whose beta decay energy is closer to the Ac-228 decay energy than the Sr/Y-90 standard. The Sr-89 calibration is different than the gross alpha (Th-230) and gross beta (Sr/Y-90) calibrations since it uses several replicate standards instead of one standard and each replicate has a mass of solid that replicates the mass of solid generated for the Ra-228 test method. A mean efficiency is determined by calculating the efficiency of each replicate (dividing the cpm response by the known dpm activity) and then calculating the average efficiency. It is this mean efficiency, in conjunction with a sample response, which is used to calculate the activity of a sample.

Similar to the Sr-89 calibration, a dedicated calibration is generated for gross alpha by Method 7110C, employed for water samples with high (>500 ppm) total solids. The solid used is a mixed precipitate of ferric hydroxide and barium sulfate, and the mass of the precipitate in each replicate approximates the mass of solid generated in the Method. The radionuclide standard spike is Th-230. All other aspects of the calibration are the same as the one generated with Sr-89.

Criteria

For the calibration control charts, the Th-230 or Sr/Y-90 activities which are checked on each day that a gas proportional detector will be used and are in units of cpm or percent recovery, must be within QC limits of the mean ± 3σ for a given detector.

Verification & Validation

The validator verifies that the daily calibration checks are within the mean ± 3σ for a given detector, and that daily calibration checks were performed on every day that a sample and/or standard was analyzed. If a daily calibration check result was outside of QC limits, the validator confirms that it was reanalyzed and that the reanalysis results were within QC limits prior to sample analysis. If the gas proportional gross alpha or gross beta calibration checks are not within the mean ± 3 sigma, and the daily calibration was not successfully reanalyzed, all data associated with that calibration check are typically rejected by the validator.

BLANK ANALYSIS

For all methods, blank analysis results are assessed to determine the existence and magnitude of contamination problems. The criteria for evaluation of blanks apply to any blank associated with the samples. If problems with <u>any</u> blank exist, all associated results must be carefully evaluated to determine whether or not there is an inherent variability affecting the entire result dataset, or if the problem is an isolated occurrence with limited impact to other data.

Criteria

A daily blank is analyzed on each detector on every day that samples shall be analyzed on that detector (gamma spectrometry and gas proportional detectors only) A daily blank consists of a detector count of the same length as that of a regular sample, performed with a blank container in the shielding cave (gamma) or counting chamber (gas proportional counter). Daily blanks are not measured for alpha spectrometry.

Long background counts, between 12 and 16 hours each, are conducted weekly for gamma spectrometer and gas proportional detectors and monthly for alpha spectrometer detectors. The relative counting uncertainty (1σ) must be <10% of the integrated count. The background count rate must fall within the mean background ± 3σ. The most recent background count rate is subtracted from each sample and batch QC sample count rate. Due to the very low background count rates for alpha spectrometer detectors, an absolute total count value of six counts is used as a control limit for each detector. Six counts in 12 hours, or 720 minutes, is a count rate of 0.0083 counts per minute (cpm), one to two orders of magnitude less than the not-to-exceed MDA values for all alpha spectrometry analytes.

In addition, at least one method blank is analyzed for every matrix, every batch, or for every 20 samples (5% of samples), whichever is more frequent. For solid samples (gamma spectrometry only), the method blank consists of Ottawa sand, or a material with equivalent physical and radiological properties, that has

been dried, ground, and stirred to homogenize in the same or similar manner as field samples. For water samples (alpha spectrometry and gas proportional detection only), a deionized water blank is chemically prepared or processed in the same manner as the field samples. A deionized water blank may also be used as the method blank for alpha spectrometry soil sample batches. For onsite laboratories, due to the nature of sample flow and the rapid turnaround time requirement (often less than 24 hours), a batch may be defined as the samples received by the lab during a given week. Thus the method blank frequency at onsite laboratories is typically weekly, unless more than 20 samples are received in a given week, in which case a new batch is started.

The results of all blanks and backgrounds are reported with the sample results and should be plotted on a QC chart to facilitate trend analysis. Acceptable tolerances are based on system performance and analytical requirements. Warning ($\pm 2\mu_{MR}$) and control limits ($\pm 3\mu_{MR}$), where μ_{MR} is the required method uncertainty, are established for each detector for daily blanks and backgrounds, and for all detectors for method blanks. The relative counting uncertainty (1σ) for daily blanks must be less than 3% of the integrated counts. The μ_{MR} values should be derived from historical analysis data, when available. As a first approximation, control limits may be based upon the median one sigma counting uncertainty for the analytes of concern for sample sets of approximately 40 to 800, the size of the set varying depending upon the analyte and detector. The $3\mu_{MR}$ and $2\mu_{MR}$ values must be added to and subtracted from the mean blank value to establish control limits and warning limits, respectively. The mean blank value is often established using at least 30 points from each detector in the case of daily blanks (gamma spectrometry and gas proportional detectors only), and at least 30 points from all detectors in the case of method blanks. These points are typically over a time period of two to six months operations following the initial calibration of each instrument at the beginning of each year. For method blanks that are generated less frequently, the median blank value may be established using data accumulated over a longer period of time, such as 12 to 24 months.

Verification & Validation

The validator reviews the blank results and evaluates blank control charts, if available, as well as the raw data for all blanks. The validator then verifies that the results were accurately reported and that tolerance limits were not exceeded. If the blank result does not comply with the established criteria (i.e., a result is outside of the control limits ($\pm 3\mu_{MR}$), a "B" data qualifier should be applied with a "+" or "-" (depending upon whether the result is above or below the control limits) to all samples in the batch (in the case of method blanks), and to all samples analyzed on a given detector on a given day (in the case of the daily blank).

SAMPLE SPECIFIC CHEMICAL RECOVERY (TRACER)

The following discussion applies to alpha spectrometry tracers and Ba-133 measured by gamma spectrometry. A tracer is either an isotope of the same element as the isotope of interest, or an isotope of an element different from the element of the isotope of interest, but one that behaves chemically very similar to the isotope of interest. Tracers are added to both field samples and batch QC samples prior to sample preparation. Because the tracer is chemically either identical or very similar to the isotope of interest, it provides an indication of any method anomalies such as sample losses (e.g., absorption, reactivity, spillage, etc.) or artifacts specific to the measurement step. Thus the percent recovery of the tracer is used to normalize the measured activity of the isotope of interest.

Criteria

Each sample chemical tracer percent recovery (%R) is recorded and should be plotted on a QC chart for each radionuclide and method and fall within the prescribed limits of ±3σ of the mean recovery. There should be at least 30 points used to establish a control chart for each radionuclide and both the ±2σ warning limits and ±3σ control limits should be displayed. Batch QC tracer data is typically not used to develop control charts. The quantity of tracer material used must be adequate to provide a maximum uncertainty at the 95% confidence level in the measured recovery using the following equation:

$$2\sigma uncertainty = \frac{1.96\sqrt{(C_s / t_s) + (C_b / t_b)}}{(E)(Vol)(R)(2.22)} \qquad \text{(Eq. 4)}$$

Where:

C_s and C_b is the sample count rate (cpm) and background count rate (cpm), respectively
t_s and t_b is the sample count time (mins) and background count time (mins), respectively
E is the counting efficiency
Vol is the volume of sample (liters)
R is the radiochemical recovery
2.22 is the conversion factor from dpm to pCi

Verification & Validation

The validator checks the raw data to verify that sample specific recoveries were accurately reported, and recalculates up to 10% of the sample specific recoveries (%R) by dividing the reported tracer result by the known tracer concentration. The validator will also check spike levels to verify that sufficient activities are used to provide adequate precision, as determined by Eq. 4, for recovery determination; and will also check recoveries to verify that they fall within the established warning/control limits.

The validator qualifies results as estimated (J) for tracer recovery between the warning and control limits. For recoveries outside of the control limit, the affected sample(s) are typically reanalyzed by the lab as a corrective action. If no corrective action is performed, the data is typically rejected by the validator. The validator also typically rejects results if significant errors are identified during verification of calculated values.

LABORATORY CONTROL SAMPLE (LCS) ANALYSIS

For any radioanalysis technique, the laboratory control sample (LCS) serves as a monitor of the overall accuracy and performance of all steps in the analytical process. At least one LCS is analyzed for every matrix, every batch, or for every 20 samples (5% of samples), whichever is more frequent. The LCS should contain greater than 10 times a given radionuclide's detection limit activity, and should contain activities that fall close to project action levels.

Criteria

The LCS for alpha spectrometry and gas-flow proportional counting is a standard of known activity spiked into an analyte-free matrix that simulates the field sample matrix as closely as possible. The LCS is then prepared and analyzed in the same manner as field samples. For the gamma spectrometry soils LCS, there is typically no sample preparation. The gamma spectrometry LCS is a known standard in the same geometry/matrix and containing the same isotopes of interest as the samples to be analyzed. LCS percent deviation values are calculated via the following equation:

$$\%D = \frac{|(SSR - SA)|}{SA} x100 \qquad \text{(Eq. 5)}$$

Where:
%D is the percent deviation
SSR is the measured spiked sample activity/concentration
SA is the spike activity/concentration added to the sample.

Warning and control limits may be laboratory-derived and are displayed as the mean and the $\pm 2\varphi_{MR}$ X 100 and $\pm 3\varphi_{MR}$ X 100 (warning and control) limits of the percent deviation. The mean %D is typically calculated from the 30 most recent LCS results. LCS results from each detector are used for establishing LCS control limits for gamma spectrometry. Multi-detector system LCS results are used to establish control charts for both alpha spectrometry and gas-flow proportional counting. The mean values are updated periodically depending upon batch analysis throughput. The φ_{MR} value for each analyte is the average relative standard deviation, where the relative standard deviation values may be calculated from historical project data with values near the analyte action level.

Verification & Validation

The validator verifies that LCS samples were analyzed at the proper frequency and that all LCS percent deviation values fall within the established control limits. The validator also checks the raw data (counter printout, strip charts, bench sheets, etc.) to verify the reported recoveries.

If any result falls outside control limits, the lab should have taken corrective action to ensure acceptable LCS results. The corrective action will typically be reprocessing of the LCS and all batch samples associated with the LCS. If reanalysis is unsuccessful, then adjustments to instrument settings, preparation of a new LCS standard, and/or method modifications may be performed. The LCS would then be reanalyzed along with any samples associated with the LCS that had already been analyzed. If an acceptable LCS result cannot be generated, all sample results associated with the faulty LCS are qualified by the laboratory with an S- or S+ indicating a high or low recovery. The third party validator may use professional judgment and/or other QC criteria and apply additional U, J, or R qualifiers to the regular samples associated with the LCS in the analytical batch. If an LCS was not analyzed with a batch, all data associated with the batch is typically rejected by the validator.

MATRIX SPIKE SAMPLE (MSS) ANALYSIS

The matrix spike sample (MSS) analysis provides information about the effect of each sample matrix on the method preparation and measurement. MSS are required when sample specific chemical recoveries (tracers) are not used and the samples undergo a chemical preparation process. At Maywood, MSS analysis is typically only performed for the gas-flow proportional gross counting methods. The accuracy of an alpha spectroscopic analysis is typically assessed using tracers, while the accuracy of Method 904.0 used to measure Ra-228 is determined by measuring the gravimetric yield of barium sulfate. For gamma spectrometry soils, there is no matrix spike employed due to the difficulty creating a homogenous matrix spike. Matrix spikes may also be used for water samples to be analyzed by gamma spectrometry, although water samples are not analyzed by gamma spectrometry on the Maywood project.

Criteria

The acceptance criteria for matrix spike sample results are more complicated than for LCS and method blanks due to the pre-existing activity in the unspiked sample, which must be measured and then subtracted from the activity measured after spiking. The %D warning and control limits are dependent only upon one measured value, either the spiked result for LCS, or blank result for the method blank, whereas the matrix spike limits are dependant upon two measured values (spiked sample result and sample result), therefore %D is not a good statistic to use for MSS. Instead, a "Z-Score" equation is employed:

$$\text{Z-Score} = \frac{SSR - SR - SA}{\phi_{MR}\sqrt{SSR^2 + \max(SR, UBGR)^2}} \qquad \text{(Eq. 6)}$$

Where:

max (x,y)	denotes the maximum of the two values SR and UBGR
φ_{MR}	is the maximum allowable (relative) standard deviation at the UBGR
SSR	is the spiked sample result
SR	is the sample result
SA	is the activity spiked into the sample
UBGR	is 15 pCi/L for GA and 50 pCi/L for GB

A control chart is typically prepared which contains a mean Z score, obtained from 20-30 matrix spike results, as well as warning and control limits. The warning and control limits for the calculated Z-Score statistic are set at ±2 and ±3, respectively. MSS results that fall outside the control limit are typically confirmed through repeat analysis.

Verification & Validation

The validator shall verify that at least one MSS was analyzed for every matrix, every batch, or for every 20 samples (5% of samples), whichever is more frequent. Samples identified as field blanks must not be used for spiked sample analysis. The calculated matrix spike Z-Score must be recorded and plotted on a QC chart and fall within the prescribed limits. The validator verifies that the MS and its associated unspiked sample were reprepared and reanalyzed if the MS result exceeds control limits. If the sample result is > 4 times the spike level, the MSS Z-Score evaluation is not employed.

A calculated Z-Score statistic that falls outside the control limits should be qualified by the laboratory with an "S-" or "S+" indicating a low or high recovery. The third party validator may also apply a U, J, or R qualifier to the MSS and associated regular samples in the analytical batch based on professional judgment and the use of other QC criteria. Generally, if the calculated Z-Score statistic is between the warning and control limits, the sample result is qualified estimated (J). If the Z-Score is outside of the control limit, the data is typically rejected by the validator. Rejection of data for MSS failures requires professional judgment. If a result falls outside of control limits, corrective action may be taken by repreparing and reanalyzing the sample and its matrix spike. If the reanalysis result falls outside control limits the sample result is typically rejected. If the reanalysis falls within control limits, the result is typically qualified as estimated.

LABORATORY REPLICATE / FIELD DUPLICATE ANALYSIS

Replicate analyses are indicators of laboratory precision based on each sample matrix. The variability of sample results due to analyte heterogeneity in the sample is also reflected in the replicate result. At least one replicate must be analyzed for every matrix, every batch or for every 20 samples (5% of samples)

whichever is more frequent The laboratory may not be in control of the precision, therefore, replicate results are used to evaluate reproducibility of the complete laboratory process that includes subsampling, preparation, and analytical processes.

Field duplicate samples should be collected and analyzed as an indication of overall precision. A field duplicate is a co-located sample that is sent "blind" to the lab by labeling it such that it cannot be determined with which sample it is associated.

Criteria

Acceptance criteria for lab replicate/field duplicate analysis results depend on the relationship between the upper bound of the gray region (UBGR), typically an action level, and the average sample concentration, which is estimated as follows:

$$\overline{X} = \frac{X_1 + X_2}{2} \qquad \text{(Eq. 7)}$$

Where:

$\overline{X}$ is the average sample concentration
X_1 is the regular sample concentration
X_2 is the replicate/duplicate sample concentration

When the $\overline{X}$ < UBGR, the concentration value for absolute difference ($|X_1 - X_2|$) of the two results is evaluated against the following limits:

$$\underline{\text{Warning Limit}} = 2\, u_{MR} \sqrt{2} \approx 2.83\, u_{MR} \qquad \text{(Eq. 8)}$$

$$\underline{\text{Control Limit}} = 3\, u_{MR} \sqrt{2} \approx 4.24\, u_{MR} \qquad \text{(Eq. 9)}$$

Where u_{MR} is the uncertainty at the UBGR.

When the $\overline{X} \geq$ UBGR, the value for the relative percent difference (RPD) ($|X_1 - X_2|/\overline{X}$) of the two results is evaluated against the following limits:

$$\underline{\text{Warning Limit}} = 2\, \varphi_{MR} \sqrt{2} \approx 2.83\, \varphi_{MR} \qquad \text{(Eq. 10)}$$

$$\underline{\text{Control Limit}} = 3\, \varphi_{MR} \sqrt{2} \approx 4.24\, \varphi_{MR} \qquad \text{(Eq. 11)}$$

Where φ_{MR} is the uncertainty at the UBGR. Note that each value used in the RPD calculation and limit evaluation is typically converted from a decimal to percentage by multiplying the each calculated value by 100.

Verification & Validation

If replicate/duplicate analyses are required but not performed, their absence should be noted in the data validation report because overall analytical precision may be impacted. The validator verifies that replicate/duplicate results fall within the control limits provided by the lab.

If the calculated replicate/duplicate statistical value falls between the warning and control limits, all samples of the same matrix in the batch are typically qualified estimated (J). If the calculated replicate/duplicate statistic is outside the control limits, the laboratory typically applies a "P" qualifier to all associated sample results. The validator then uses professional judgment to determine whether to qualify the results as estimated (J) or rejected (R). Data are typically not rejected based upon replicate/duplicate results alone.

GAMMA SPECTROMETRY RESOLUTION

Criteria

The target radionuclide energy should be within 2 keV of the observed peak. This criterion does not apply for isotopes present at a value less than the MDA.

Verification & Validation

The validator will typically verify that the peak search algorithm of the instrument is set at 2 keV of the standard library energy for the identified radionuclide. The validator will also compare isotope concentrations with equilibrium concentrations. Unless enrichment is suspected, these concentrations should be comparable.

For radionuclide peaks that are detected but fail to meet the positive identification criterion (i.e., the peak energy is > 2 keV from the theoretical peak energy) the data is typically rejected by the validator. The validator may contact the lab to resolve differences and request additional information in an effort to resolve discrepancies.

ALPHA SPECTROMETRY RESOLUTION

Chemical separation specificity is the ability to separate various radionuclides by chemical separation techniques. The chemical separation specificity can be verified for alpha spectrometry measurements by observation of the alpha energy spectrum.

Criteria

The energy of the radionuclide of interest must be within 40 keV of the theoretical peak energy. This criterion does not apply for isotopes present at values less than the MDA.

Verification & Validation

The validator randomly checks that the energy of the observed peak of interest is within 40 keV of the theoretical energy for the radionuclide of interest.

If the energy of the peak of interest is more than 40 keV from the theoretical energy of the radionuclide, the results are typically rejected by the validator. Corrective actions for this type of exceedance may include careful cleaning of the detector, or changing the amplifier settings. In either case, communication with the instrument manufacturer technical support group is recommended.

CONCLUSIONS

The MARLAP guidance provides statistical quantities for establishing method and data quality objectives. These quantities, in conjunction with FUSRAP Maywood Superfund project action levels and established or estimated project data uncertainties, have been employed by the authors in this paper to establish warning limits and control limits for various laboratory QC parameters. The RadDEG, which incorporated some key MARLAP methodologies, provides guidance to radioanalysis lab(s) as well as third-party data validator(s). The RadDEG establishes performance expectations and acceptable data evaluation methods for the lab. For the validator, the RadDEG provides guidance for the evaluation and qualification of lab output. It is the authors' hope that other radioanalysis labs and data end-users will strongly consider the adoption of MARLAP guidance in their work processes. This paper, and the RadDEG on which it is based, provides a window into the MARLAP adoption process as it unfolds daily for the Maywood Team.

REFERENCES

1. MARLAP. *Multi-Agency Radiological Laboratory Analytical Protocols Manual*, NUREG -1576, EPA 402-N-04-001A, NTIS PB2004-105421. July 2004.