QAM-Q-101

Laboratory Quality Control

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Texas Institute for Applied Environmental Research

1.0 Applicability and Purpose

1.1. This procedure applies to operations of the analytical laboratory at the Texas Institute for Applied Environmental Research (TIAER), Tarleton State University, Stephenville, Texas and the TIAER mobile laboratory. The purpose of this procedure is to establish guidelines for quality control (QC) of all data produced by the TIAER laboratory. This procedure is used in conjunction with other TIAER analytical Standard Operating Procedures (SOPs) for the laboratory, TIAER Quality Assurance Manual (QAM) chapters and, where applicable, Quality Assurance Project Plans (QAPPs) for which TIAER's laboratory provides environmental data.

1.2. This document includes additional quality control measures for radiochemistry. **Note: Not all TIAER staff will be trained on radiochemistry.** Other analyses are now classed as stable chemistry.

2.0 Definitions

2.1 Accuracy: the degree of agreement between an observed value and an accepted reference value. Accuracy includes a combination of random error (precision) and systematic error (bias) components that are due to sampling and analytical operations; a data quality indicator.

2.2 Ambient Water Reporting Level (AWRL) standard: a standard of very low concentration required for certain analytes on projects sponsored by the Texas Commission on Environmental Quality (TCEQ). The AWRL establishes the reporting specification at or below which data for a parameter must be reported to be compared with TCEQ criteria and screening levels.

2.3 Batch: environmental samples that are prepared and/or analyzed together with the same process and perso*nn*el, using the same lot(s) of reagents. Samples are normally assigned to a batch based on order of receipt by the laboratory, but use of professional judgment and knowledge of the sub-matrix of samples being received may also be used in assigning samples

to batches, in order to provide the best analytical and QC results.

2.3.1 An analytical run batch (ARB) is a set of environmental samples (extracts, digestates, or concentrates) analyzed as a group that share the same quality control samples for analysis (calibration standards, initial calibration verification standard, initial blank verification, and initial calibration blank). An ARB can consist of more than 20 samples, and can include prepared samples originating from various environmental matrices.

2.3.2 A preparation batch (PB) consists of a set of environmental samples of the same matrix prepared, filtered or preserved at the same time. A PB shares the same quality control samples for preparation (method blank, matrix spike, matrix spike duplicate, laboratory control sample (LCS), LCS or sample duplicate and, where required, limit of quantitation check standard), and normally consists of 20 or fewer environmental samples. A sample duplicate is included in the PB if required by QAPP, project, or analytical method; sample duplicates or spike duplicates may also be included for information purposes, even if not required. The maximum time between the start of process of the first and last samples in the preparation batch is 24 hours.

2.3.3 A quality control batch (QCB) is a part of an analytical run batch that shares QC samples requiring 10 or fewer environmental samples. These types of QC samples are typically continuing calibration verification standard, continuing calibration blank, and, when present, a field split. A sample duplicate is included in each QCB if required by QAPP, project, or analytical method; spikes or spike duplicates may also be included for information purposes, even if not required.

2.4 Bias: consistent deviation of measured values from the true value, caused by systematic errors in a procedure. Bias is assessed by percent recoveries of calibration verifications, laboratory control samples and laboratory control sample duplicates for TIAER projects involving the TCEQ and others.

2.5 Blank: a sample that has not been exposed to the analyzed sample stream in order to monitor contamination during sampling, transport, storage or analysis. The blank is subjected to the usual analytical and measurement process to establish a zero baseline or background value and is sometimes used to adjust or correct routine analytical results.

2.5.1 Initial calibration blank (ICB): type II ASTM deionized water used in the calibration curve to set the instrument reading at baseline. The ICB contains the same preservation, reagents, and treatment as calibration standards and environmental samples.

2.5.2 Initial blank verification (IBV): type II ASTM deionized water to which all reagents used in the procedure are added in the same manner as samples. An IBV is run at the beginning of each AR batch for verification of instrument stability.

2.5.3 Continuing calibration blank (CCB): type II ASTM deionized water to which all reagents used in the procedure are added in the same manner as samples. A CCB is run at the end of each QC batch for verification of instrument stability.

2.5.4 Method blank (MB; also known as reagent blank): a sample of a matrix similar to the batch of associated samples (when available) that is free from the analytes of interest and is processed simultaneously with and under the same conditions as samples through all steps of the analytical procedures, and in which no target analytes or interferences are present at concentrations that impact the analytical results for sample analyses. The MB indicates contamination during sample preparation processes and is prepared each day that samples are processed for any analysis, normally with each PB.

2.6 Blind sample: a sample of concentration unknown to the analyst, but for which there are documented values; used to test the laboratory's or analyst's proficiency in the execution of the measurement process. Concentrations in double blinds are also not known by the Laboratory Manager (LM) or Laboratory

Quality Assurance Officer (LQAO), such as in the case of Proficiency Testing (PT) samples.

2.7 Calibration: set of operations that establish, under specified conditions, the relationship between values of quantities indicated by a measuring instrument or measuring system, or values represented by a material measure or a reference material, and the corresponding values realized by standards.

2.8 Commands: older procedural directions for what is required and what is allowed within a method are no longer required. ***Commands in QAMs/SOPs such as "should" or "may" no longer have any special meaning. "Shall" is archaic and now removed from use.***

2.9 Contamination: the presence of an interfering substance, analyte of interest, or radioactive material in a place where it is not wanted.

2.10 Control chart: a means of demonstrating statistical control, monitoring a measurement process, or diagnosing measurement problems by calculating statistical control limits for the most recent 20 or more samples or measurements. Control charts may be mathematical rather than graphical representations. Control charts or limits may be calculated and maintained for tracking, trending, or statistical control of QC by the LM, Radiation Safety Officer (RSO) or LQAO, or by the ESDMS QC Module. An example of a graphical control chart is shown in Attachment 3.

2.11 Control limit: a value that equals 3 times the standard deviation above or below the mean. UCL = upper control limit; 3 standard deviations above the mean. LCL = lower control limit; 3 standard deviations below the mean. A Manager Set Control Limit (MSCL), UCL or LCL may be used to narrow, but not broaden, the acceptance range beyond the requirement limits of a project QAPP or an approved QAM/SOP that contains all required QC of the published method.

2.12 Controlled document: a paper or electronic form, file, method or other document that is maintained current and controlled for issuance. Controlled documents are maintained separately from controlled data logbooks. Any forms, logs, or other

documents not in the immediate control of TIAER personnel are considered uncontrolled documents.

2.13 Corrective action: the action taken to eliminate the causes of an existing nonconformity, defect or other undesirable situation in order to prevent recurrence.

2.14 Demonstration of Capability (DOC): A documented process to ensure that an analyst is trained well enough to produce acceptable data.

2.15 Demonstration of Performance (DOP): a documented process to ensure that any new method or instrument, or any instrument that has undergone major repairs, performs in an acceptable manner.

2.16 Duplicate (Dup, also known as laboratory sample duplicate): aliquot of an environmental sample or LCS taken from the same container under laboratory conditions and processed and analyzed independently with each PB, QCB, or method-specified frequency. The relative percent difference between the original sample or standard and its dup is calculated to determine precision. Dups may be produced in the laboratory during analytical runs or preparation. Laboratory control samples and other solutions may be duplicated. For radiochemistry, duplicates should have detectable amounts of activity. Matrix spike duplicates may be used, if necessary, to obtain detectable activity for precision determinations.

2.17 Electronic logbook (Elog): a computer spreadsheet or document file that can be appended for data entry, storage and/or calculation. The Laboratory Manager controls integrity and security of the Elog.

2.18 Environmental Sample Database Management System (ESDMS): An interface to a Microsoft® Access or SQL Server database created by TIAER and used to enter laboratory, field, and descriptive data into the database.

2.19 Field duplicate: an environmental sample collected in the field immediately after another environmental sample collected from the same location and submitted to the laboratory with its own sample identification number.

2.20 Field split (FS): a single sample subdivided by field staff immediately following collection and submitted to the laboratory as two separately identified samples. Split samples are preserved, handled, transported, and analyzed identically and are used to assess variability in all processes.

2.21 Holding time (maximum allowable hold time): the maximum time that a sample can be held from the time and date of collection to the time and date for determination of the analyte of interest and still be considered valid or not compromised. Attachment 1 lists holding times for many analytes measured by TIAER. Holding times for each analyte measured by TIAER are included in individual analytical QAMS/SOPs.

2.22 Instrument Detection Limit (IDL): the concentration of an analyte that produces a signal or detectability that is five times the signal/noise ratio of the instrument. IDL = 1.645 times σ (standard deviation) for seven calibration blank replicates. IDL is used for information only.

2.23 Laboratory Control Sample (LCS; also known as laboratory fortified blank, LFB): a sample matrix, free from the analytes of interest, spiked with verified known amounts of the analyte or a material containing known and verified amounts of analyte. The LCS is generally spiked at a level less than or near the mid-point of the calibration curve and is carried through the complete preparation and analytical process. The LCS is used to establish analyte specific precision and bias, assess the performance of all or a portion of the measurement system, or verify the ratio of instrument or method measurement response to analyte amount after the instrument or method is calibrated. The LCS is prepared from a standardized reference material source that may be different from the stock used to prepare calibration standards.

2.24 Laboratory Control Sample Duplicate (LCSD): a duplicate of the LCS; typically used to evaluate precision.

2.25 Limit of Detection (LOD): the minimum concentration of a substance (an analyte) that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte. For seven replicates of the

sample, the mean must be 3.14 times σ (standard deviation) above the blank. The concentration of the LOD standard is about 2 to 3 times the estimated IDL.

2.26 Limit of Quantitation (LOQ): the minimum level concentration, minimum reporting level (MRL), or quantity of a target variable (e.g., target analyte) that can be reported with a specified degree of confidence.

2.26.1 TIAER's most recent LOQs are listed in the annual Limit of Detection memo, which is issued and maintained by the LM.

2.26.2 Most LOQs at TIAER are set by the TCEQ (often at the AWRL) and are not necessarily compliant with the Standard Methods definition of LOQ, but certain projects require a lower LOQ. TIAER will, at client request, report at a lower LOQ, as long as the LOQ is greater than the TIAER LOD.

2.27 Matrix Spike (MS) (also known as laboratory fortified matrix, or LFM): a sample prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate of target analyte concentration is available. MSs are analyzed with each PB. Percent recoveries are calculated to indicate the effect of the particular sample matrix on the method's recovery efficiency.

2.28 Matrix Spike Duplicate (MSD) (also known as laboratory fortified matrix duplicate, or LFMD): a duplicate of the MS that may be used for accuracy within a matrix, determination of interference and/or precision. MSDs are normally analyzed with each PB immediately after the MS.

2.29 Mean (χ): the average of a set or distribution of numbers which is determined by the sum of all values (x_1, x_2, ..., x_i) divided by the number of values (n)

$$\chi = \sum_{i=1}^{n} x_i / n$$

2.30 Method Detection Limit (MDL): The *previous* term used for limit of detection (LOD). MDL is no longer used at TIAER.

2.31 Minimum Detectable Activity (MDA): Radiation measurement level similar to the LOQ for stable chemistry-an estimate of the smallest true activity (or activity concentration) of an analyte in a sample that ensures a 95% probability of detection, given a detection criterion that ensures only a 5% probability of detection in analyte-free samples.

2.32 Mobile Laboratory: a portable enclosed structure with necessary and appropriate accommodation and environmental conditions, within which testing is performed by trained TIAER staff using the same QAMS/SOPSs and quality system as the main lab.

2.33 National Environmental Laboratory Accreditation Conference (NELAC): a voluntary organization of State and Federal environmental officials and interest groups purposed primarily to establish mutually acceptable standards for accrediting environmental laboratories. NELAC has been succeeded by the NELAC Institute (TNI).

2.34 National Environmental Laboratory Accreditation Program (NELAP): the overall National Environmental Laboratory Accreditation Program administer by TNI. TIAER currently uses the promulgated 2016 TNI Standard.

2.35 National Institute of Standards and Technology (NIST): a non-regulatory federal agency within the U.S. Department of Commerce, whose mission is to promote U.S. innovation and industrial competitiveness by advancing measurement science, standards, and technology. Where possible, all laboratory reference check standards and radionuclide sources are NIST traceable.

2.36 Practical Quantitation Limit (PQL): the constituent concentration of an analyte that may be considered with statistical confidence for project use that the analyte is actually present at a level greater than the blank. The PQL is defined as five times the LOD. Though not used by TCEQ, TIAER uses this Standard Method tool for evaluation of Dup RPD significance. If both samples of a duplicate pair are below the PQL, the precision evaluation is insignificant unless specifically stated otherwise by project or client requirements.

2.37 Precision: the degree to which a set of measurements of the same property obtained under similar conditions conform to themselves; a data quality indicator. Precision is usually expressed as standard deviation, variance or range, in either absolute or relative terms. Precision is assessed by means of analysis of LCS/LCSD pair or duplicate/replicate sample analysis.

2.38 Proficiency Testing (PT) sample: double blind sample prepared by a NELAP-approved vendor that is analyzed by the TIAER laboratory staff to assess whether the analyst/laboratory can produce analytical results within specified acceptance criteria.

2.39 Quality Assurance (QA): an integrated system of activities involving planning, quality control, quality assessment, reporting and quality improvement to ensure that a product or service meets defined standards of quality with a stated level of confidence.

2.40 Quality Assurance Manual (QAM): a document stating the management policies, objectives, principles, organizational structure and authority, responsibilities, accountability, and implementation of the laboratory to ensure the quality of its product to its users. The TIAER Lab QAM is comprised of a main body (Q-100) with several attachments and chapters resembling procedures (QAMs). Specific Standard Operating Procedures are used for analyses only, per the Standard Methods definition of SOP.

2.41 Quality Assurance Project Plan (QAPP): a formal document prepared specifically for projects for which environmental data are collected, where required by the contracting agency. Required quality control and acceptance criteria are generally specified in each QAPP, resulting in requirements that can change over time and from project to project.

2.42 Quality Control (QC): the overall system of bench level technical activities whose purpose is to measure and control the quality of a product or service so that it meets the needs of users.

2.43 QC Module: a component of the Environmental Sample Data Management System that assigns samples to batches, documents and calculates values of QC samples, evaluates QC

sample values against established acceptance criteria and documents any deviations, and provides data integrity checks to verify that all required QC samples were analyzed.

2.44 Quality System: a structured and documented management system describing the policies, objectives, principles, organizational authority, responsibilities, accountability, and implementation plan of an organization for ensuring quality in its work processes, products (items), and services. The quality system, which includes the QAM, provides the framework for planning, implementing, and assessing work performed by the organization and for carrying out required QA and QC.

2.45 Quantitation Limits: levels, concentrations, or quantities of a target variable (e.g., target analyte) that can be reported at a specified degree of confidence.

2.46 Range: the difference between the minimum and the maximum of a set of values

2.47 Raw data: any original factual information from a measurement activity or study recorded in a laboratory notebook, Elog, worksheets, records, memoranda, notes, or exact copies thereof that are necessary for the reconstruction and evaluation of the report of the activity or study. Raw data may include constructed graphs, curves, charts, tables, photography, microfilm or microfiche copies, computer printouts, magnetic media, including dictated observations, and recorded data from automated instruments. If exact copies of raw data have been prepared (e.g., tapes which have been transcribed verbatim, dated and verified accurate by signature), the exact copy or exact transcript may be submitted.

2.48 Reagent grade: a chemical specification that conforms to requirements established by the American Chemical Society (also ACS grade). All reagents used by the TIAER Laboratory are of the highest grade appropriate for testing.

2.49 Relative Error: A measure of precision. A ratio of the absolute error of a measurement to the measurement being taken. Expressed in Relative Standard Deviation (RSD) for calibrations evaluated using an average response factor and as Relative Error (%RE) for calibrations evaluated using correlation coefficient or coefficient of determination.

2.50 Relative Percent Difference (RPD): a measure of the precision between duplicate sample values as determined by the absolute difference of the values divided by the mean of the values multiplied by 100 for percent.

$$RPD = [(x_1 - x_2) / ((x_1 + x_2) / 2)] \times 100$$

2.51 Standard: analyte-free water or other matrix spiked with the analyte of interest prepared from standardized reference material. Standards are carried through the complete analytical process, but not necessarily through the preparation process.

2.51.1 Calibration Standard: a substance or reference material used to calibrate an instrument. At least four standards are used when an analysis is first initiated and each day of sample analysis thereafter, where required. Calibration standards are used to create or verify the standard curve and bracket the range of reportable results. Certain instruments and methods may store calibration curves and factors that are not remade with each run, but the stored calibration or factor is verified with an ICV and CCV at a minimum.

2.51.2 Initial Calibration Verification (ICV): a standard used in the analytical run batch for the first verification of the ratio of instrument or method measurement response to analyte amount after the instrument or method is calibrated. It is normally a mid-range calibration standard on the curve and is made from a source other than that used to make calibration standards. A radiochemistry source check is used as an ICV and is analyzed at least daily when samples are analyzed.

2.51.3 Continuing Calibration Verification (CCV): a standard used for verification of instrument or method response on a continuing basis, normally performed before and after each QC batch analysis. CCVs may be made from a source other than that used to make calibration standards.

2.51.4 LOQ Check Standard: a standard prepared with verified and known amounts of target analytes in the sample matrix (e.g. DI water, sand, commercially available tissue); the amount is equal to or less than the analyte

LOQ. The LOQ check standard is carried through the complete preparation and analytical process. LOQ check standards are analyzed as specified by project QAPPs, which include program-defined measurement performance specifications. LOQ check standards are analyzed with PBs. LOQ check standards typically come from a different source than LOQ calibration standards.

2.51.5 LOQ Calibration Standard: a standard prepared with verified and known amounts of target analytes in the sample matrix (e.g. DI water, sand, commercially available tissue); the amount is equal to or less than the analyte LOQ. The laboratory will analyze a calibration standard (if applicable) at the LOQ on each day samples are analyzed, where required by the project. Calibrations including the standard at the LOQ will meet the calibration requirements of the analytical method before data in the batch are acceptable.

2.52 Standard curve: a calibration curve which plots concentrations of known analyte calibration standards versus the instrument response to the analyte.

2.53 Standard Operating Procedure (SOP): an approved and controlled document that describes the *analytical* method to be used in the laboratory in sufficient detail that a competent analyst unfamiliar with the method can conduct a reliable review and/or obtain acceptable results.

2.54 Standard deviation (σ or s): a measurement of precision among several data points as determined by the square root of the summation of the squares of differences between each measurement and the group mean divided by the number of measurements minus one.

$$\sigma = [\ \sum(x - \chi)^2 / (n - 1)\ ]^{½}$$

where $\sum$ = summation

x = each measurement

n = number of measurements

χ = mean of all measurements

2.55 The NELAC Institute (TNI): A national organization whose purpose is to foster the generation of environmental data of

known and documented quality through an open, inclusive, and transparent process that is responsive to the needs of the community. TNI is dedicated to the vision that all entities generating environmental data in the United States be accredited to a national standard. TNI has now taken over administration and oversight of NELAP.

2.56 Uncertainty: The combined standard uncertainty, when used, is the uncertainty of a measured value expressed as an estimated standard deviation. It is calculated by combining the standard uncertainties of the input estimates. The experimentally observed precision at each testing level is not statistically greater than the maximum combined standard uncertainty of the measurement results at that level, although it may be somewhat less. All radiochemical measurements shall provide the uncertainty of each quantitative measurement result, normally expressed as 2 standard deviations, with the measured result.

2.57 Validation: confirmation by examination and provision of objective evidence that the particular requirements for a specific intended use are fulfilled. Validation occurs after initial verification that the data meet project-specific criteria.

2.58 Verification: confirmation by examination and provision of evidence that specified requirements have been met.

2.59 Warning limit: a value which equals twice the standard deviation above or below the mean. UWL = upper warning limit; two standard deviations above the mean. LWL = lower warning limit; two standard deviations below the mean.

Definitions pertaining only to radiochemistry:

2.60 Background: the radioactivity level measured in a system or area without the presence of source standards or samples caused by electronic "noise" and from the detection of cosmic radiation and other natural radiation sources in the environment. The background counting rate for most detectors is usually between 10 and 100 counts per minute (cpm). Initial average background is performed by taking at least 20 measurements and constructing a control chart. Routine

background measurements outside 3 sigma require corrective action.

2.61 Counts per minute (cpm): The measure of radioactivity by which the number of nuclear disintegrations per minute (dpm) are detected and counted through detection of alpha, beta, or gamma radiation. Dpm is determined from cpm based on the detector's efficiency in measuring the radiation.

2.62 Disintegrations per minute (dpm): the actual radioactivity of a substance representing the number of atoms decaying per minute by alpha, beta, and/or gamma radiation. Dpm is a calculated value based on the detector's cpm and efficiency in measuring the radiation.

2.63 Efficiency: the ability of an instrument or detector to measure radioactivity as compared to the actual, known activity of a source standard. Refer to specific methods for how efficiency is used to determine data values. Efficiency may be affected by detector type or voltage, radionuclide, geometry of the sample, containers, matrix and other contributing factors.

2.64 Energy calibration: radionuclides measured under specific methods (i.e. gamma or alpha spectrometry) are identified by defined levels of energy. Reference sources containing known levels of the radionuclide are used to calibrate such instruments for those specific energy levels.

3.0 Equipment, Reagents and Standards

Though not used directly in this procedure, the use and traceability of all equipment, reagents, and standards are documented for all data collection activities with unique identifiers or codes. This does not include equipment, such as certain types of labware and magnetic stirrers, that is not calibrated or checked for calibration.

4.0 Procedure

4.1. The Quality Control program at the TIAER laboratory consists of seven primary elements: ***certification of operator competence, recovery of known additions, analysis of externally provided standards, analysis of various blanks, calibration with standards, analysis of duplicates, and maintenance of and adherence to the QC module in ESDMS.*** Project specific QAPPs may require other components and/or criteria.

4.2. Operator competence is certified by completion of an initial DOC. Before an analyst is permitted to produce reportable data, the analyst demonstrates competence in accordance with QAM-Q-107, "Laboratory Personnel Training" and is certified by the LM with a documented DOC. See QAM-Q-107 for DOC requirements. A Demonstration of Capability Certification Statement (Q-100-1) is then completed in accordance with the TIAER Quality Assurance Manual (QAM-Q-100) main document.

4.2.1. The DOC is performed upon initial training of an analyst in a chemical determination procedure where data is collected and reported, after a major change in an analytical SOP, and at least annually after that.

4.2.2. Criteria for completion of the DOC are detailed in QAM-Q-107.

4.2.3. For all analytes analyzed by the TIAER Laboratory for which standards are available, the LM and/or LQAO periodically submit to the analyst testing standards that are of unknown analyte quantity to the analyst (blinds), but of known analyte quantity to the LM, QAO, LQAO, and/or some outside authority or provider.

4.2.3.1. The blinds or PT standards may be from outside providers or interlaboratory cross checks.

4.2.4. For any new method or instrument used in the TIAER laboratory, a Demonstration of Performance (DOP) is completed. As part of the initial DOP for analysts, a Personnel Training Record (Q-107-1) is completed, following the same acceptance criteria described for DOC in QAM-Q-107. In addition, an entry is completed in the

DOP logbook (Q-103-4) for each new method or instrument. A DOP for an method or instrument may also serve as a DOC for the analyst, providing all requirements are met.

4.2.4.1. A DOP is completed for new methods and associated equipment or instruments prior to placing the method and equipment into service for quality data generation.

4.2.4.2. An approved SOP is issued and the LOD and PQL are determined in accordance with definitions specified in this SOP.

4.2.4.3. The DOP includes precision and accuracy data from analysis of a DOP standard obtained from a source other than the calibration standards.

4.2.4.3.1. The DOP standard, or alternate, is prepared in four separate aliquots at a level of one to four times the PQL or at the midrange of the calibration curve.

4.2.4.3.2. The mean and standard deviation of the four aliquots are calculated and compared to historical performance data for the analyte, method or equipment or to the precision and accuracy described in the reference method for a new SOP, if available. Otherwise, the mean and standard deviation are compared to project requirements.

4.2.4.3.3. **Relating only to Radiochemistry:** Where gamma-ray spectrometry is used to identify and quantify more than one analyte, the laboratory control sample shall contain gamma-emitting radionuclides that represent the low (e.g., 241Am), medium (e.g., 137Cs) and high (e.g., 60Co) energy range of the analyzed gamma-ray spectra. As indicated by these examples, the nuclides need not exactly bracket the calibrated energy range or the range over

which nuclides are identified and quantified. Alpha spectrometry may also have the same requirements with different isotopes to cover the energy range.

4.2.4.4. The LM and LQAO concur on the acceptability of the DOP, using the same acceptance criteria as the DOC or project-specific requirements. The LM and LQAO indicate approval in the DOP Logbook, Q-103-3 in accordance with QAM-Q-103, "Laboratory Equipment Maintenance.

4.3. Recovery of known additions is demonstrated by analysis of matrix spikes and laboratory control samples.

4.3.1. Matrix spikes and Matrix spike duplicates (MS/MSD) are generally required to determine any effects from the matrix for most analytes except solids and are generally analyzed at a rate of 20% or more of the samples processed. Spiking of sample matrices is performed on each QC batch, where applicable and/or required by the analysis SOP. Precision between MS & MSD is evaluated by some projects and methods.

4.3.2. Spiking is performed prior to sample digestion or processing. Spiking may also be performed after sample digestion or processing, just prior to analysis, but the spiked sample must be designated as a post-processing spike (PS). Post-processing spikes may be performed in addition to pre-processing spikes to show matrix interferences alone, but they are not used in lieu of pre-processing spikes.

4.3.3. Spiking levels

4.3.3.1. MSs & MSDs are added at the regulatory or required level for an analyte, if specified by the project or QAPP for which the data are collected.

4.3.3.2. If no specified MS requirement exists, the addition should result in a concentration between 2 and 300 times the LOQ or between 1 and 10 times the level estimated or known in the sample, whichever is greater.

4.3.3.3. Suggested spiking levels for most parameters analyzed by TIAER may be found in Attachment 4. Spiking levels for higher concentration samples are generally at the analyst's discretion.

4.3.3.4. If spiking a sample aliquot changes the volume more than 1%, the volume change is considered in the recovery calculation, otherwise it is negligible.

4.3.3.5. Some samples may be high in concentration and require dilution to obtain a value within calibration range. In such cases, the spike may be diluted to an inconsequential level. If the recovery does not pass, a CAR is completed. The project manager then decides if the sample needs to be reanalyzed or resampled.

4.3.4. The formula for determining percent recovery of matrix spikes is calculated using the following equation in which,:

$$\%R = (SSR - SR)/SA * 100$$

where %R is percent recovery,
SSR is the observed spiked sample concentration,
SR is the sample result, and
SA is the reference concentration of the spike added

Manager-set acceptance limits for matrix spikes are included in Attachment 2.

4.3.5. The choice of sample for spiking in the batch is done in a systematic and objective fashion (usually by position number as received sequentially) and is not biased due to sample color, cleanliness or assumed matrix interferences. Generally the first of every ten samples in the QC batch is chosen for duplication and spiking. Reasons for choosing another sample for spiking are recorded in the log in accordance with QAM-Q-102, "Document and Data Control". Spiking levels for each analyte for which matrix spikes are required can be found in individual analytical SOPs.

4.3.6. Laboratory control sample (LCS) is a sample matrix, free from the analyte of interest, which is spiked with a known amount of the analyte at or near the midpoint of the calibration range for the specified analyte.

4.3.6.1. An LCS and a duplicate of the LCS (LCSD), which have been carried though the complete preparation and analytical process, are run with every preparation batch for analytes that can be spiked.

4.3.6.2. Percent recovery, where SR is the measured result and SA is the true result, is calculated by the following formula:

$$\% R = SR/SA * 100$$

4.3.6.3. Performance limits in the QC module or QAPPs, or other project-specific limits are used to determine the acceptability of LCS analyses.

4.3.6.4. Batches for which the LCS does not meet the acceptance limit are reanalyzed. A corrective action report is written to document the excursion.

4.4. Analysis of externally supplied standards (Proficiency Testing samples)

4.4.1. At least two PT samples per year are purchased by the LM or LQAO from a NELAP-approved PT provider for all analytes analyzed by TIAER, where available. The LQAO, with assistance from the LM, submits PT samples for analysis in the same manner as environmental samples to TIAER analysts and submit results to the provider. The PT samples are unknown to all TIAER parties (double blinds). Corrective action is performed on any failed PT sample. Successful completion of two out of three PT samples is required to remain NELAP compliant.

4.4.2. The LQAO compares obtained results with true values and maintains records of these blind studies for tracking and trending of analytical accuracy.

4.4.2.1. The LQAO documents all dilutions and preparations of PT samples in the Standards Log.

4.4.2.2. These results may be submitted to outside agencies or companies for scrutiny of TIAER's laboratory program and quality control.

4.4.2.3. Passage of the analysis is defined by the provider using statistical means.

4.4.3. The laboratory is required to pass at least two out of the last three PT samples for each analyte measured by the laboratory, where PT samples are available.

4.4.4. QAM-Q-107, “Laboratory Personnel Training” describes demonstrations of capability for individual analysts.

4.5. Analysis of blanks is performed to establish a baseline value against which nondetected analytes can be compared. High blank results are indicators of possible contamination in the sampling or analytical process

4.5.1. Method blanks (MBs) are analyzed with each group of processed samples, at least once per preparation batch, if not otherwise specified by the QAPP for which the data are collected. Some procedures (e.g., pH determination) do not require blanks.

4.5.1.1. MBs are treated in the same manner as all samples and standards and carried throughout the entire preparation and analytical procedure.

4.5.2. Field blanks may be periodically submitted and analyzed with other samples.

4.5.3. Initial calibration blanks (ICBs) are used to establish an instrument baseline for the use of standards during an analytical run batch. ICBs are always part of a calibration curve and have a concentration of zero, though they may have an instrument response. Analyses without calibrations may not use ICBs, but have some method of establishing the baseline. ICB acceptable detection level is generally at or below ½ the LOQ.

4.5.4. Initial blank verification (IBV) is analyzed after each instrument calibration to demonstrate instrument stability.

4.5.5. Continuing calibration blanks (CCBs) are analyzed after each QC batch. CCBs values above the LOQ may result from high concentration samples that have carried over from one sample to the next. Each CCB is associated with the QC batch analyzed both before and after it in the analytical run.

4.5.6. Other blanks may be required for projects, including trip blanks or equipment blanks. These requirements are

documented in QAPPs or project contracts and documents.

4.5.7. Criteria for blanks

4.5.7.1. If blanks are detected at greater than the positive LOQ or less than the negative LOQ, a Corrective Action Report (CAR) is initiated to document the occurrence.

4.5.7.2. Where required by project specifications, blanks detected at greater than the positive LOQ or less than the negative LOQ are rerun to confirm the detected level. If the second blank exceeds the LOQ, all data associated with the batch are flagged.

4.5.7.2.1. For blanks outside the acceptance criteria, if the method blank concentration is less than 5 percent of the value of the lowest concentration measured for samples in the batch, the blank does not need to be rerun.

4.5.7.3. If the second analysis indicates a failed blank, the LM initiates an investigation into the root cause of the occurrence. Any results of the investigation are documented in the CAR. Should it not be possible to determine the root cause, the client is notified of any information in the investigation that might further qualify the flagged data.

4.6. Calibration with standards for instruments and methods

4.6.1. Standards are of known purity and NIST traceable whenever possible. If NIST traceability is not available, then standards are of ACS or reagent grade quality, or of the best attainable grade.

4.6.2. Establishing the calibration curve

4.6.2.1. The minimum number of non-zero calibration standards shall be as specified in the table below:

Type of Calibration	Minimum Number of Calibration Standards
Threshold Testing	1
Average Response	4

Linear Fit	5
Quadratic Fit	6

4.6.2.2. Calibrations have a correlation coefficient of 0.995 or better.

4.6.2.3. Each standard used in the curve is within 25% of the expected value when the response is put into the line formula. ***This is a modification of the 10% response recommendation in SM 4020 and follows the guidelines set by TCEQ AWRL methodology.***

4.6.2.4. In addition, the relative standard deviation (RSD) will be determined for calibrations evaluated using an average response factor. Acceptable calibrations will have an RSD that is >-10 and <10. See attachment 5, Relative Error E-log.

4.6.2.5. For calibrations evaluated using correlation coefficient or coefficient of determination, the %Relative Error (%RE) will be determined for the lowest calibration standard and a standard at or near the mid-point of the calibration. Acceptable calibrations will have a %RE that is >-25 and <25. See attachment 5, Relative Error E-log.

4.6.2.6. The highest standard does not exceed the linear range of the instrument or method, except as directed by certain methods. If any sample in an analytical run exceeds the highest calibration standard value, the sample is reanalyzed with dilution.

4.6.3. Projects may require the inclusion of a calibration standard at or below the limit of quantitation (LOQ) on each day samples are analyzed. The LOQ standard is normally the AWRL, but may be lower due to project requirements.

4.6.3.1. The LOQ standard may be analyzed as a calibration standard or as a QC sample (LOQ check standard), and is used to demonstrate ongoing ability to recover at the reporting limit.

4.6.3.1.1. If analyzed as a LOQ check standard, it is analyzed once per each batch of 20 or fewer environmental samples.

4.6.3.1.2. Calibrations including the LOQ as a calibration standard meets the calibration requirements of the analytical method, including a linear correlation coefficient of 0.995 or better.

4.6.3.1.3. The instrument response for the reporting limit standard is treated as a response for the sample by use of the calibration equation in calculating an apparent concentration of the standard.

4.6.3.2. The recovery criterion for LOQ check standards is 70-130% of the expected value, or as specified in project QAPPs. The recovery criterion for LOQ calibration standards is 75–125%, or as specified in contracting agency requirements.

4.6.3.2.1. Percent recovery at the LOQ is calculated using the following equation, where CR is the calculated concentration and SA is the reference concentration:

$$\%R = CR/SA * 100$$

4.6.3.2.2. If the LOQ calibration standard does not meet the recovery criterion, it is reanalyzed prior to analysis of the first batch of environmental samples, unless a standard lower than the LOQ meets the criterion.

4.6.3.2.3. For many TIAER projects, if the LOQ or lower standard does not meet the criterion upon reanalysis, the next highest standard in the calibration curve becomes the reporting limit for all samples analyzed by that method on that day.

4.6.3.2.4. In batches for which the LOQ standard does not meet the criterion, any samples that require a passing LOQ standard are qualified or excluded when the data are submitted. A CAR is written to document the excursion.

The Project Manager, in consultation with the QAO, LQAO and/or the LM, determines acceptability of the data for use in their project.

4.6.3.3. The current limits of quantitation for most parameters analyzed by the TIAER laboratory are included in Attachment 4.

4.6.4. Verification of instrument calibration and baseline by analysis of ICV, CCV, CCB, and IBV samples.

4.6.4.1. ICVs and IBVs are analyzed immediately after instrument calibration. CCVs and CCBs are analyzed after every QC batch throughout an analytical run, and at the end of an analytical run batch to ensure that the instrument or method has not drifted or changed since calibration.

4.6.4.2. ICVs, IBVs, CCVs, and CCBs are matched to the generated standard curve and screened for acceptability by recovery.

4.6.4.2.1. Acceptance criteria for CCBs are described above.

4.6.4.2.2. Acceptance criteria for ICVs and CCVs vary according to analyte and are presented in Attachment 2.

4.6.4.2.3. Suggested standards, spiking, ICV and CCV concentrations are listed in Attachment 4.

4.6.5. All standards made in the laboratory, and dilutions thereof, is documented in the Standards Logbook, Q-102-2, in accordance with QAM-Q-102, "Laboratory Material Acceptance Criteria". In this way, standards may be traced back to original lot numbers, manufacturer, specifications and receipt when compared to the Chemical Inventory Log, Q-102-1.

4.7. Analysis of duplicates. A duplicate aliquot of an LCS or a sample is prepared and analyzed in the same manner as other samples with each preparation batch for determination of precision.

4.7.1. The relative percent difference between the LCS or sample and its duplicate is calculated according to the following formula:

$$RPD = (X_1 – X_2) / \{(X_1 + X_2)/2\} * 100$$

where X_1 is the LCS or sample and X_2 is the duplicate. If a value is measured between zero and the LOD, the LOD is used as the concentration in the formula. If a value is measured between zero and the negative LOQ, use zero in the formula. If a value is measured below the negative LOQ, the equipment calibration is reviewed before proceeding.

4.7.2. Duplicate type and acceptance criteria conform to the published method, SOP, and QAPP requirements.

4.7.2.1. Refer to QAPPs for specific project requirements or SOPs for analyte specific requirements. General acceptance criteria for duplicates are presented in Attachment 2.

4.7.3. Corrective actions for failure of RPD to meet acceptance criteria for duplicates

4.7.3.1. If the concentration of either sample exceeds the PQL, the preparation or QC batch is reanalyzed.

4.7.3.2. If the concentration of one or both exceeds the LOQ but neither exceeds the PQL, a CAR is written to document the situation but the batch does not need to be reanalyzed.

4.7.3.3. If both the sample and duplicate concentrations are below the LOQ, no action or documentation is required.

4.7.4. Analysis of field splits (FS). Field splits are collected, if required by project QAPP, at a rate of 10% of samples collected.

4.7.4.1. Precision of field split results is calculated with the same formula used for laboratory duplicates.

4.7.4.2. Acceptance criteria for field splits are specified by the project QAPP and generally apply to samples whose concentration exceeds 5 * LOQ. Corrective actions for failure to meet the acceptance criteria for

field splits are evaluated outside the lab and do not require reanalyzing the batch or split samples.

4.7.4.3. The information derived from field splits is generally considered to be event or site specific and does not determine the validity of an entire batch.

4.8. Maintenance of control charts or tables

4.8.1. All QC standards pass project-specific acceptance criteria in order for the sample data to be valid. Project needs may determine acceptance limits, but charting of results or use of statistical tables to obtain more narrow limits is preferred.

4.8.1.1. All duplicate RPDs, recoveries for LOQs, ICVs, CCVs, CCBs, matrix spikes, and method blank results may be displayed mathematically or graphically on separate control charts for each analyte and updated, with mean, UCL, UWL, LWL and LCL calculated and displayed each time new data are added.

4.8.1.1.1. The mean and standard deviation is determined for the most recent twenty points or for a specific time frame. The UCL, UWL, LWL, and LCL may be drawn linearly about the mean on the graphical chart, clearly defined within a chart, or clearly displayed on a mathematical table. Longer range tracking and trending for more than 20 samples or readings may be used.

4.8.1.1.2. Results for generated data per each QC run or preparation batch may be deemed acceptable if the newly obtained point is between the UCL and LCL with exception for the following cases:

4.8.1.1.2.1. It is the seventh consecutive point on one side of the mean,

4.8.1.1.2.2. It is the third out of three successive points exceeding the UWL or LWL,

4.8.1.1.2.3. Four of five successive points exceed the standard deviation.

4.8.1.1.2.4. Other QC requirements are not met.

4.8.1.2. Out-of-control points are included in each set of points for control chart generation and are not discarded from the calculation due to failure alone.

4.8.1.3. A book or computer record of up-to-date control charts or tables will generally always be available to the analysts, LM, QAO, and LQAO for review and reference. Control limits do not necessarily constitute acceptance criteria, but are used as tools in evaluation of method performance.

4.8.1.4. Values above 100% of an upper range standard on a curve, including spikes, may be entered into the QC module, but is diluted and reanalyzed prior to reporting.

4.8.1.5. Any observed values within ±5 percent of the expected value may be deemed acceptable, even if the control chart limits indicate failure.

4.9. Limit of Detection (Method Detection Limit)

4.9.1. LODs (formerly MDLs) are determined annually for every method and instrument used for data collection or generation, where appropriate. New analysts prove ability to read at low levels with an LOQ standard. Generally, analytes that have spike or standards require LOD determination.

4.9.1.1. Where applicable, LODs are determined separately for various matrices.

4.9.1.2. LODs are determined by the analyst performing the test at the time.

4.9.1.3. LODs is determined separately for each analyte measured in TIAER's mobile laboratory, where applicable.

4.9.1.4. LODs are determined immediately prior to placing any instrument in service that is new or has had major repairs or modifications. The LM is responsible for determining the significance of the repairs and possible effects on the method. The DOP log is completed in such cases.

4.9.2. The TIAER LOQ is always at or below the AWRL. If it is not, corrective action is initiated and documented.

4.9.3. The TIAER laboratory demonstrates and documents on an ongoing basis the laboratory's ability to quantitate at its LOQ by analysis of a standard at the limit of quantitation as a verification standard for the calibration curve, and as a calibration standard within the curve, if required by a project.

4.10. Data Storage. All raw data is kept on file for a minimum of five years after the end of a project and remain accessible to auditors, analysts and contracted entities through the LM.

4.11. Personnel and Responsibilities. Responsibilities for TIAER laboratory technicians, analysts, manager and QA officers may be found in section 17.1 of the Quality Assurance Manual, QAM-Q-100.

4.12. Further consideration for radiochemistry **(Only specially trained analysts)**:

4.12.1. Given that radiation detection efficiency is essentially independent of sample activity at all but high activity levels (where dead time becomes significant), the requirements for calibration ranges of standards, of data reporting in calibration range, and the number of calibration standards are not applicable to radiochemical method calibrations except for mass attenuation in gas-proportional counting and sample quench in liquid scintillation counting. Nuclear counting instruments are subject to calibration prior to initial use, when the instrument is placed back into service after major repairs, when the instrument's response has changed as determined by a performance check, or when the instrument's response exceeds predetermined acceptance criteria for the instrument quality control. Instruments may also be recalibrated on a regular frequency even in the absence of these conditions. The frequency of calibration is described in the laboratory method SOP/QAM. A specific frequency (e.g., annually) or calibrations based on observations from the associated control or tolerance chart, is specified in the laboratory method SOP/QAM.

4.12.2. As with other analytes, radiochemistry instrument calibrations are performed with certified reference standards traceable to NIST. The standards have the same general characteristics (i.e., geometry, homogeneity, density, etc.) as

the associated samples. Calibration verification samples, LCSs, Matrix Spikes, Duplicates and blanks all meet the same criteria for acceptance as with stable chemistry isotopes.

4.12.3. For radiochemistry, control charting is important to monitor performance (see Attachment 3 for an example). Instrument calibration verification (ICV, CCV) are performed using appropriate check sources and monitored with control charts or tolerance charts to ensure that the instrument is operating properly, the detector response has not significantly changed, and therefore the instrument calibration has not changed. The same check source used in the preparation of the tolerance chart or control chart at the time of calibration is used in the calibration verification of the instrument. The check sources provide adequate counting statistics for a relatively short count time and the source is normally sealed or encapsulated to prevent loss of activity and contamination of the instrument and laboratory personnel.

4.12.3.1. For gamma-ray spectroscopy systems, performance checks for detection efficiency, energy calibration, and peak resolution is performed on a day-of-use basis.

4.12.3.2. For alpha-particle spectroscopy systems, the performance check for energy calibration is performed on a weekly basis and the performance check for detection efficiency is performed on at least a monthly basis.

4.12.3.3. For gas-proportional and liquid scintillation counters, the performance check for detection efficiency is performed on a day-of-use basis. For batches of samples that uninterruptedly count for more than a day, a performance check may be performed instead at the beginning and end of the batch as long as this time interval is no greater than one week. For scintillation counters the calibration verification for detection efficiency shall be performed on a day-of-use basis.

4.12.4. Background measurements are made on a regular basis and monitored using control charts or tolerance charts to ensure

that a laboratory maintains its capability to meet required measurement quality objectives. (This background measurement is not the short term check for contamination). These values must be subtracted from the total measured activity in the determination of the sample activity.

4.12.4.1. For gamma-ray spectroscopy systems, background measurements are performed on at least a monthly basis.

4.12.4.2. For alpha-particle spectroscopy systems, background measurements are performed on at least a monthly basis.

4.12.4.3. For gas-proportional counters background measurements are performed on at least a weekly basis.

4.12.4.4. For scintillation counters, background measurements are performed each day of use.

4.12.5. Instrument contamination monitoring is covered in QAM-S-101, “Laboratory Safety” and indicates the frequency of the monitoring and the criteria which initiates corrective action.

4.12.6. Any affected samples associated with a failed method blank are either reprocessed for analysis or the results reported with appropriate data qualifying codes. The method blank frequency of analysis is the same as for stable chemistry-analyzed at a minimum of one per preparation batch, which is a maximum of twenty (20) field samples, for all radiochemical methods ***except gross alpha/beta in solid matrices and gamma-ray spectrometry***. The method blank consists of a quality system matrix that is similar to the associated samples and is known to be as free of the analytes of interest as possible. There is no subtraction of the method blank result from the sample results in the associated preparation or analytical batch unless permitted or required by method or program. This requirement does not preclude corrections for background radiation (e.g., instrument background, analyte in the tracer or carrier, reagent impurities, peak overlap, etc.) to all analyzed samples, both program/project submitted and internal quality control samples. However, these corrections do not depend on the result of the method blank analysis,

whose purpose is to check for uncorrected contamination or other low-level bias. The method blank sample is prepared with aliquot size similar to that of the routine samples for analysis.

4.12.7. The activity of the **LCS** for radiochemistry is at least ten times the MDA, and at a level comparable to that of routine samples (when such information is available) and if the sample activities are expected to exceed ten times the MDA. Where a radiochemical method, other than gamma-ray spectroscopy, has more than one reportable analyte isotope (e.g. plutonium, ^{238}Pu and ^{239}Pu, using alpha-particle spectrometry), only one of the analyte isotopes need be included in the laboratory control sample at the indicated activity level. However, where more than one analyte is detectable, each is assessed against the specified acceptance criteria. Where gamma-ray spectrometry is used to identify and quantify more than one analyte, the laboratory control sample contains gamma-emitting radionuclides that represent the low (e.g., ^{241}Am), medium (e.g., ^{137}Cs) and high (e.g., ^{60}Co) energy range of the analyzed gamma-ray spectra. As indicated by these examples, the nuclides need not exactly bracket the calibrated energy range or the range over which nuclides are identified and quantified. The laboratory control sample is prepared with similar aliquot size to that of the routine samples for analyses. The **matrix spike** is prepared by adding a known activity of target analyte after sub-sampling, if required, but before any chemical treatment (e.g., chemical digestion, dissolution, separation, etc.). Again, where a radiochemical method, other than gamma-ray spectroscopy, has more than one reportable analyte isotope (e.g. plutonium, ^{238}Pu and ^{239}Pu, using alpha-particle spectrometry), only one of the analyte isotopes need be included in the matrix spike sample at the indicated activity level. However, where more than one analyte is detectable, each is be assessed against the specified acceptance criteria. For low-level samples (less than approximately three times the MDA) a laboratory control sample duplicate or a replicate matrix spike (matrix spike and a matrix spike duplicate) may be analyzed to determine reproducibility within

a preparation batch in place of a sample replicate. In addition based on project or program requirements, a laboratory control sample duplicate or a matrix spike duplicate may be analyzed in place of a sample replicate.

4.12.8. Tracers: For those methods that employ a tracer for yield determination, each sample result has an associated tracer yield calculated and reported. The tracer is added to the sample after subsampling, if required, but before any chemical treatment (e.g., chemical digestion, dissolution, separation, etc.) unless otherwise specified by the method. The tracer yield for each sample result is one of the quality control measures to be used to assess the associated sample result acceptance. The tracer yield is assessed against the specific acceptance criteria specified in the laboratory method SOP. When the specified tracer yield acceptance criteria are not met, the specified corrective action and contingencies are followed. The occurrence of a failed tracer yield and the actions taken are noted in the laboratory report to the client through flagged data. *Tracers and carriers are not currently used at the TIAER Lab*.

4.12.9. Measurement Uncertainties. Each result for radiochemistry is reported with its measurement uncertainty. The report should clearly explain the uncertainty. At a minimum the report indicates whether the uncertainty is the combined standard uncertainty ("**one sigma**") or an expanded uncertainty; and for expanded uncertainties, indicate the coverage factor (k) and optionally the approximate level of confidence. *Normally, the standard uncertainty is reported* (value ± 1 σ).

4.12.10. Radiological Control Program. QAM-S-101 and QAM-W-101 address the procedures for segregating samples with potentially widely varying levels of radioactivity. Low-level and high-level samples are identified, segregated and processed in order to prevent sample cross-contamination. The radiological control program under the RSO includes the measures taken to monitor and evaluate background activity or contamination on an ongoing basis.

4.12.11. Data Acceptance/Rejection Criteria and Method Performance

4.12.11.1. Negative Control- While the goal is to have no statistically significant difference from zero, each method blank is critically evaluated as to the nature of the interference and the effect on the analysis of each sample within the batch. The source of contamination or other bias is investigated and measures are taken to minimize or eliminate the problem. Affected samples are reprocessed or data are appropriately qualified if the absolute value of the activity of a targeted analyte in the blank exceeds three times its combined standard uncertainty (3 sigma), AND is greater than 1/10 of the activity measured in any sample; or the method blank result otherwise affects the sample results as per the method requirements or the project-specific measurement quality objectives. The acceptance criteria for samples associated with a failed method blank are calculated in a manner that compensates for sample results based on differing aliquot sizes. When a blank result is determined to be significantly different from zero, the cause is investigated and measures taken to minimize or eliminate the problem. Samples associated with a failed blank are evaluated as to the best corrective action for the samples (e.g., reprocessing or data qualifying codes). The occurrence of a failed method blank and any associated corrective action are noted in the laboratory report to the client with data flagging.

4.12.11.2. Positive Control- Laboratory Control Sample (LCS): The results of the individual batch LCS are calculated in percent recovery. The individual LCS is compared to the acceptance criteria as published in the approved method. An LCS that is determined to be within the criteria effectively establishes that the analytical system is in control and validates system performance for the samples in the associated preparation batch. Samples analyzed along with an LCS determined to be “out of control” are considered suspect and the samples reprocessed and re-analyzed or the data reported with appropriate data qualifying codes/flags. The occurrence of a failed LCS and any associated actions are noted in the laboratory report to the client.

4.12.11.3. Sample-Specific Control- Matrix Spike; Matrix Spike Duplicates: As with stable chemistry, the results from matrix spike/matrix spike duplicate are primarily designed to assess the precision and accuracy of analytical results in a given matrix and are expressed as percent recovery (%R), relative percent difference (RPD), or other appropriate statistical technique that allows comparison to established acceptance criteria. For matrix spike results outside established criteria, corrective action is documented and the data are reported with appropriate data qualifying codes/flags. The occurrence of a failed matrix spike and any associated actions are noted in the laboratory report to the client.

4.12.11.4. Sample-Specific Control- Replicates: The results from replicates are primarily designed to assess the precision of analytical results in a given matrix and are expressed as relative percent difference (RPD). For replicate results outside established criteria, corrective actions are documented or the data reported with appropriate data qualifying codes/flags. The occurrence of a failed replicate and any associated actions are noted in the laboratory report to the client in the same manner as stable chemistry results.

5.0 Quality Control and Safety Aspects

5.1. All procedures undertaken by the TIAER laboratory follow a Standard Operating Procedure (SOP) and/or Quality Assurance Manual chapter (QAM).

5.1.1. Each SOP/QAM is developed, implemented and adhered to in accordance with this procedure and QAM-S-101, "Laboratory Safety".

5.1.2. SOPs are used in conjunction with the general guidance document QAM and its chapters. These procedures are designed to allow change and improvement through proper protocols of generation and acceptance. SOPs/QAMs reflect improvements in technology and strive to increase quality and enhance safety.

5.1.3. SOPs are designed to be "stand alone" procedures referring only to other TIAER SOPs/QAMs. Generally, no other books or manuals are required to complete a procedure, but information and/or specific instrument manuals may be needed for troubleshooting.

5.1.4. Approved SOPs from another agency or entity may be used on occasion for specific purposes relating to a project for that agency or entity. TIAER QAMs are categorized according to general purposes.

5.1.4.1. "Q" series procedures designate quality functions.

5.1.4.2. "S" series indicate safety.

5.1.4.3. "A" series indicate administrative functions.

5.1.4.4. "W" series designate waste control or waste handling procedures.

5.1.4.5. "I" series indicate instrument operation and calibration.

5.1.4.6. SOPs are analytical methods and designated as “C" series procedures describe chemical analyses in step-by-step fashion.

5.1.4.7. QAMs and SOPs related to radiochemistry are also designated with “R”.

5.2. The LM may institute control limits for quality data acceptance if the tracking and trending data on control charts indicate expanding or shrinking limits or areas of concern. Managerial set control limits for acceptance are never less stringent than those delineated in project requirements or contractual obligations without prior, written approval from the Project Manager, Project Quality Assurance Officer(s), and/or client. Any cases of data acceptance outside QC limits are always documented with a CAR and qualified.

5.2.1. In the event of an out-of-control situation, a Corrective Action Report is initiated in accordance with QAM-Q-105, "Corrective Actions".

5.2.2. If a situation is not correctable after more than two attempts or re-analyses, the data is flagged or denoted as questionable with an appropriate qualifier such as “estimate only”, or is discarded entirely (at the discretion

of LM, project manager, client, and/or QAO). The reasons are described on any report that utilizes the data. Data qualifiers designated by the client is used where requested. General data qualifiers on client reports generated by the LM are described in QAM-A-103, “Data Reporting by the Laboratory Manager”.

5.3. All CARs, raw data and procedures are maintained in accordance with QAM-A-102, "Data and Document Control".

5.4. The LM maintains a list of analytes accredited under NELAP, or other authorized entity approving quality of data produced at TIAER.

5.5. Documented lab meeting notes may be used to clarify points not yet in the procedure or too minor to include in the SOP/QAM, if approved by the LM.

5.6. At the time of this revision, recoveries, background, efficiency and spiking limits for radiochemistry have not been established outside the approved individual methods. Refer to the approved SOP for specifications.

6.0 References

6.1. Good Laboratory Practice Standards, ed. by Willa Y. Garner, et al., American Chemical Society, Washington, D.C., 1992.

6.2. Standard Methods for the Examination of Water and Wastewater, Sections 1020, 2020, 4020, 7020, 9020, ed. by Arnold E. Greenberg, et al., APHA, AWWA, Washington, D.C., latest approved editions.

6.3. Code of Federal Regulations, Title 40, Parts 136, 141, 160.

6.4. Test Methods for Evaluating Solid Waste, Third Edition, United States Environmental Protection Agency, November 1986.

6.5. EPA Quality Management Tools-Best Practices for Laboratory Quality Systems, http://www.epa.gov/quality/bestlabs.html

6.6. National Environmental Laboratory Accreditation Program Standard, 2016, The NELAC Institute (TNI).

6.7. TIAER Quality Assurance Manual, most current revision.

6.8. TCEQ AWRL Methodology: http://www.tceq.state.tx.us/assets/public/policy/ta/crp/QA/AWRL-AnExplanation.pdf

7.0 Attachments

7.1. Attachment 1: EPA Holding Times, Preservations, Sample Requirements in Water

7.2. Attachment 2: Acceptance Limits for Duplicates, Spikes and Standard Recovery

7.3. Attachment 3: Control Chart Example

7.4. Attachment 4: Reporting Limits, LCS, ICV, CCV, Suggested Spiking Levels

7.5. Attachment 5: Example Relative Error E-log

Attachment 1: EPA Holding Times, Preservations, and Sample Requirements in Water

Analysis	Min. Volume	Container	Preservative	Holding Time
Alkalinity/acidity	100 ml	plastic	Cool >0-≤6°C	14 days
Ammonia, total or dissolved (filtered)	25 ml	plastic	pH <2 H_2SO_4; Cool >0-≤6°C,	28 days
Bacteria (*E. coli, Enterococcus*, total coliform)	250 ml	Sterile plastic	Cool >0-≤6°C	6 hours (+ 2 for TCEQ)
Biochemical Oxygen Demand, including carbonaceous; 5 or 20 day	1000 ml	plastic	Cool >0-≤6°C	48 hours
Chemical Oxygen Demand	50 ml	plastic	pH <2 H_2SO_4; Cool >0-≤6°C	28 days
Chloride	100 ml	plastic	Cool >0-≤6°C	28 days
Chlorine (total residual, free available, chloramines)	200 ml	plastic	None	Immediate
Chlorophyll-a/Pheophytin-a	1000 ml	amber plastic	Cool >0-≤6°C; dark; filter < 48 hours	28 days after filtration, if frozen
Cyanide (total, amenable)	500 ml	plastic	pH >12 NaOH; Cool >0-≤6°C	14 days
Fluoride	300 ml	plastic	None	28 days
Hardness	100 ml	plastic	pH < 2 HNO_3, H_2SO_4	6 months
Kjeldahl and Organic Nitrogen	100 ml	plastic	pH <2 H_2SO_4; Cool >0-≤6°C	28 days
Chromium VI	200 ml	plastic	Cool >0-≤6°C	24 hours
Mercury	100 ml	plastic	pH < 2 HNO_3	28 days
Metals other than mercury and chromium VI	400 ml	plastic	pH < 2 HNO_3	6 months
Solid metals other than mercury and chromium VI	200 g	plastic	Cool >0-≤6°C	6 months
Nitrate-Nitrite Nitrogen (cadmium reduction) total or dissolved (filtered)	25 ml	plastic	pH <2 H_2SO_4; Cool >0-≤6°C	28 days
Nitrate or Nitrite Nitrogen (other methods)	100 ml	plastic	Cool >0-≤6°C	48 hours
Oil and Grease	1000 ml	AJTLL	pH <2 H_2SO_4; Cool >0-≤6°C	28 days
Organic Carbon (TOC)	60 ml	plastic	pH <2 H_2SO_4; Cool >0-≤6°C	28 days
Petroleum Hydrocarbons (TRPH)	1000 ml	AJTLL	pH <2 H_2SO_4; Cool >0-≤6°C	28 days
Phenolics	500 ml	AJTLL	pH <2 H_2SO_4; Cool >0-≤6°C	28 days
Phosphorus hydrolyzable	50 ml	plastic	pH >12 NaOH; Cool >0-≤6°C	28 days
Phosphorus, orthophosphate, dissolved	25 ml	plastic	Cool >0-≤6°C; filter immediately or lab-filter	48 hours
Phosphorus, total	125 ml	plastic	pH <2 H_2SO_4; Cool >0-≤6°C	28 days

Analysis	Min. Volume	Container	Preservative	Holding Time
Radiochemistry (alpha, beta, gamma)	Depends on activity	Plastic	pH < 2 HNO_3	6 months
Residue, total (Total Solids-TS)	150 ml	plastic	Cool >0-≤6°C	7 days
Residue, filterable (Total Dissolved Solids-TDS)	400 ml	plastic	Cool >0-≤6°C	7 days
Residue, nonfilterable (Total Suspended Solids-TSS)	1000 ml	plastic	Cool >0-≤6°C	7 days
Residue, nonvolatile (fixed), volatile and volatile nonfilterable (Total Fixed Solids-TFS, Total Volatile Solids-TVS and Volatile Suspended Solids-VSS)	400 ml	plastic	Cool >0-≤6°C	7 days
Silica	50 ml	plastic	Cool >0-≤6°C	28 days
Specific Conductance	150 ml	plastic	Cool >0-≤6°C	28 days
Sulfate	50 ml	plastic	Cool >0-≤6°C	28 days
Sulfide	50 ml	plastic	pH > 9 NaOH, ZnAc; Cool >0-≤6°C	7 days
Sulfite	50 ml	plastic	None	Immediate
Surfactants (linear alkyl sulfonates, MBAS)	500 ml	plastic	Cool >0-≤6°C	48 hours
Turbidity	100 ml	plastic	Cool >0-≤6°C	48 hours
Purgeable Aromatic Hydrocarbons, Volatile Organics, Non-halogenated Volatile Organics	40 ml	VOA vial	pH < 2 HCl, 0.008% $Na_2S_2O_3$ Cool >0-≤6°C	14 days
Pesticides, chlorinated, organophosphorus, Herbicides, PCBs, Semivolatile Organics, Phthalate esters, and Acid/Base Extractables	1000 ml	AJTLL	See individual procedures	See individual procedures
Coliform, total and fecal; Enterococcus and *Escherichia coli* from chlorinated sources, includes presence/absence tests	250 ml	Sterile plastic	0.008% $Na_2S_2O_3$ for chlorine; Cool >0-≤6°C	6 hours (+2 hrs in lab per TCEQ)
Fecal Streptococci	100 ml	Sterile plastic	0.008% $Na_2S_2O_3$ for chlorine and Cool >0-≤6°C	6 hours
TCLP extraction	4000 ml	AJTLL	None	7 days
Hazardous Waste Corrosivity	2000 ml	AJTLL	None	7 days
Hazardous Waste Ignitability	100 ml	AJTLL	None	7 days
Hazardous Waste Reactivity (Cyanide/Sulfide)	250 ml each	plastic	Cool >0-≤6°C, dark	7 days

1. Information is for water and wastewater samples. Refer to individual procedures for solids matrix and soil sample handling, preservations and holding times.
2. AJTLL = amber jar with a Teflon™ lined lid

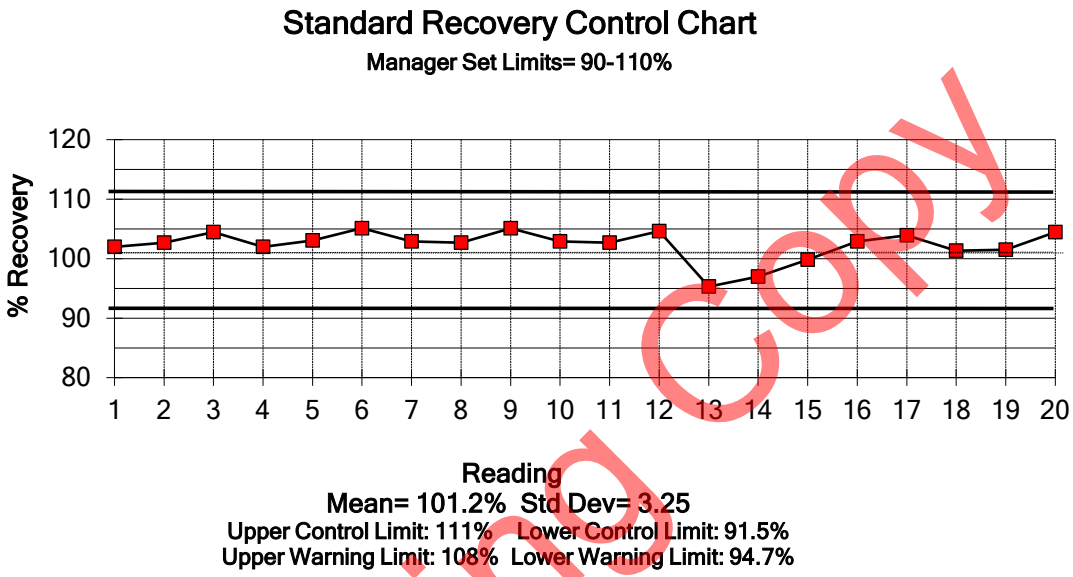
For analytes not listed here, refer to the specific SOP/QAM for minimum volume, bottle type, holding times & preservation. **Low level analyses often require more volume than listed.**

Attachment 2: Manager-Set Limits (MSL) for Acceptance of Duplicates, Spikes and Standard Recovery

TIAER SOP	Analysis	Accuracy Std Recovery % (ICV/CCV)	Accuracy MS/MSD Recovery %	Precision Duplicate % RPD
C-101	Biochemical Oxygen Demand	NA	NA	20
C-102	Chemical Oxygen Demand	90-110	75-125	20
C-103	TKN & Total Phosphorus	90-110	75-125	20
C-104	Ammonia as Nitrogen	90-110	75-125	20
C-105	Nitrate/Nitrite as Nitrogen	90-110	75-125	20
C-106	Orthophosphate as Phosphorus	90-110	75-125	20
C-107	Total Suspended Solids	NA	NA	*
C-108	TFS, TVS, VSS	NA	NA	*
C-109	Total Dissolved Solids	NA	NA	*
C-112	Chlorophyll-a & Pheophytin-a	NA	NA	20
C-113	Specific Conductance	NA	NA	20
C-120	pH	NA	NA	NA
C-121	Residual Chlorine	NA	NA	20
C-124, 114	*E. coli* and Enterococcus by IDEXX or mTEC	NA	NA	See QC Module
C-126	Temperature	NA	NA	NA
C-130	Total Solids	NA	NA	*
C-135	Tannin/Lignin	NA	NA	NA
RC-101	Gross Alpha/Beta	TBD	TBD	TBD
RC-102	Uranium, Radium	TBD	TBD	TBD
RC-103	Tritium	TBD	TBD	TBD

* RPD acceptance limits for solids are ± 10% for sample duplicates and ± 20% for LCS/LCSD.

Note: Project QAPPs may indicate different acceptance criteria for analyses, which take precedence for data collected for those projects. When new analytes or methods are added, the QC Module is revised to accommodate them. The acceptance criteria is documented in the QC Module. This attachment is updated at least annually to include new analytes information added throughout the year. Some items are **To Be Determined** at this time (TBD).



SOP-Q-101 Laboratory Quality Control
Attachment 4
Reporting Limits, LCS, ICV/CCV, and Suggested Spiking Levels
All values in mg/L except where otherwise denoted

Analyte	AWRL/LOQ	LCS	ICV/CCV	MS/MSD
BOD/CBOD	2*	200/160	NA	NA
Chlorophyll-a (µg/L)	3	3.0	NA	NA
E. coli and Enterococcus	1	NA	NA	NA
COD	5	75	75	50
Metals	**	**	**	**
NH_3-N	0.06	3.0	3.0	1.0
NO_2+NO_3-N	0.05	2.0	2.0	1.0
OPO_4-P	0.04 / 0.005	0.5	0.5	0.5
Oil and Grease	NA*	10	10	10
pH	NA*	NA	NA	NA
Pheophytin a (µg/L)	3	3.0	NA	NA
Soil Calcium Carbonate	NA*	NA	NA	NA
Soil Estimated Organic C	NA*	NA	NA	NA
Soil Extractable Nitrate N	NA*	2.0	2.0	0.50
Soil Extractable Phosphorus	NA*	0.5	0.5	0.25
Specific Conductance	NA*	NA	NA	NA
Total Dissolved Solids	10*	100	NA	NA
Total Fixed Solids	10*	166	NA	NA
Total Kjeldahl N	0.2	5.0	5.0	4.00
Total Phosphorus	0.06	5.0	5.0	4.0
Total Solids	10*	300	NA	NA
Total Suspended Solids	5*	100	NA	NA
Total Volatile Solids	10*	134	NA	NA
Volatile Suspended Solids	5*	0***	NA	NA
Radioisotopes	TBD	TBD	TBD	TBD

* AWRL/LOQ standards not required
** There are different criteria for the different types of metals. See QC Module for specific criteria.
***No residue left upon ignition.
Note: When new analytes or methods are added, the QC Module is revised to accommodate them. The limits and levels is documented in the QC Module. This attachment is updated at least annually to include new analytes information added throughout the year. TBD=To Be Determined

Attachment 5
Example Relative Error E-log

Average Response Relative Error Template

Approved: jrh 8/3/22 |RSE| < 10

Date: Analyst: Instrument: SOP:

Standard	Response	Conc.	Conc/Resp
Std 1			=C7/B7
Std 2			=C8/B8
Std 3			=C9/B9
Std 4			=C10/B10
Std 5			=C11/B11
Std 6			=C12/B12
Std 7			=C13/B13

Mean: =AVERAGE(D7:D13)

Std. Dev. =STDEV.P(D7:D13)

RSE: =F9/F7

Pass/Fail: =IF(F11<>0,IF(F11<-10,"FAIL",IF(F11>10,"FAIL","PASS")),"")

Linear Regression Relative Error Template

Approved: jrh 8/3/22 |%RE| <25

Date: Analyst: Instrument: SOP:

Slope: Intercept:

Standard	Response	Conc.	Cal. Conc.	% Relative Error	Pass/Fail
LOQ			=(B24*C21)+E21	=((D24-C24)/C24)*100	=IF(E24<>0,IF(E24<-25,"FAIL",IF(E24>25,"FAIL","PASS")),"")
Midpoint			=(B25*C21)+E21	=((D25-C25)/C25)*100	=IF(E25<>0,IF(E25<-25,"FAIL",IF(E25>25,"FAIL","PASS")),"")

Quadratic Regression Relative Error Template

Approved: jrh 8/3/22 |%RE| <25

Date: Analyst: Instrument: SOP:

X^2: X: Intercept:

Standard	Response	Conc.	Cal. Conc.	% Relative Error	Pass/Fail
LOQ			=(C33*(B36*B36))+(B36*E33)+G33	=((D36-C36)/C36)*100	=IF(E36<>0,IF(E36<-25,"FAIL",IF(E36>25,"FAIL","PASS")),"")
Midpoint			=(C33*(B37*B37))+(B37*E33)+G33	=((D37-C37)/C37)*100	=IF(E37<>0,IF(E37<-25,"FAIL",IF(E37>25,"FAIL","PASS")),"")