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**ENVIRONMENTAL LABORATORY SECTOR**

**VOLUME 1**

**MANAGEMENT AND TECHNICAL REQUIREMENTS FOR LABORATORIES PERFORMING ENVIRONMENTAL ANALYSIS**

**Module 4: Quality Systems for Chemical Testing**

**TNI Standard**

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This page intentionally left blank.**PREFACE**

This Standard is the result of many hours of effort by those volunteers on The NELAC Institute (TNI) Chemistry and Quality Systems Committees. The TNI Board of Directors wishes to thank these committee members for their efforts in preparing this Standard as well as those TNI members who offered comments during the voting process.

This Standard supersedes and replaces preceding documents in whole or in part. It supplements Module 2, Quality Systems General Requirements, and may be used by any organization that wishes to implement a program for the accreditation of environmental laboratories.

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**VOLUME 1, MODULE 4**

Quality Systems for Chemical Testing

1.0 Chemical Testing

1.1 Introduction

 This document contains detailed quality control (QC) requirements for environmental testing activities involving chemical measurements. The evaluation of laboratories for this discipline is in conjunction with a quality system as specified in the general requirements module. Adherence to quality systems requirements will ensure that all QC procedures specified in this module are being followed.

1.2 Scope

 The essential QC procedures applicable to chemistry measurements are included in this module. Additional QC requirements that are either specified by method, regulation or project shall be met by laboratories.

1.3 Terms and Definitions

 The relevant definitions from TNI, Volume 1, Module 2, Section 3.0 are the preferred references. Definitions related to this document, which are used differently or do not exist in the above references are defined below.

1.3.1 Additional Terms and Definitions

 Reserved

1.3.2 Exclusions and Exceptions

 Reserved

1.4 Method Selection

 Refer to Volume 1, Module 2, Sections 5.4.2, 5.4.3, and 5.4.4.

 When adding a new analyte to a reference method, the inclusion of the analyte in the method shall meet all required calibration requirements and the QC requirements of the method to which the analyte is being added. If no QC exists in the method, the laboratory shall adhere to the requirements outlined in a reference method of the same technology (when available). For example, when adding acetone to EPA Method 624, the calibration and QC requirements shall follow EPA Method 624. A method that meets these requirements shall be identified in such a way so that there is no confusion that the analyte list has been modified.

1.5 Method Validation

1.5.1 Validation of Methods

Prior to acceptance and institution of any method for which data will be reported, all methods shall be validated.

1. The laboratory shall validate reference methods via the procedures specified in Sections 1.5.2 and 1.5.3. For reference methods, the procedures outlined in Section 1.6 can satisfy the requirements of Section 1.5.3.
2. For all methods, except reference methods, the validation must comply with Volume 1, Module 2, Sections 5.4.5.1, 5.4.5.2, and 5.4.5.3. This validation must include the minimum requirements outlined in Sections 1.5.2, 1.5.3, and 1.5.4 of this module.
3. For both reference and non-standard methods, laboratories shall participate in proficiency testing programs. The results of these analyses shall be used to evaluate the ability of the laboratory to produce acceptable data.

1.5.2 Limit of Detection and Limit of Quantitation (however named)

 Procedures used for determining limits of detection and quantitation shall be documented. Documentation shall include the quality system matrix type. All supporting data shall be retained.

1.5.2.1 Detection Limit (DL)

 If a mandated test method or applicable regulation includes protocols for determining detection limits, they shall be followed. The laboratory shall document the procedure used for determining the DL. If the method or regulation does not contain specific directions for determination of the detection limit, the following requirements shall apply. DL determinations are not required for methods/analytes for which a detection limit is not applicable such as pH, color, odor, temperature, or dissolved oxygen. DL determinations based on low level spikes are not required for analytes for which no spiking solutions are available. If results are not reported below the limit of quantitation (LOQ), an initial DL determination is required, but ongoing verification is not.

1.5.2.1.1 Initial determination of the DL

The laboratory DL procedure, unless following a mandated test method or procedure, at a minimum, shall incorporate language addressing the following requirements:

1. the DL shall reflect current operating conditions;
2. the DL determination shall incorporate the entire analytical process;
3. the DL determination shall include data from low level spikes and routine method blanks prepared and analyzed over multiple days; at least one low level spike and routine method blank must be analyzed on each applicable instrument; a minimum of seven (7) replicates is required for both low level spikes and routine method blanks;
4. results from low level spikes used in the DL determination shall meet qualitative identification criteria in the method, and shall be above zero;
5. the DL procedure shall include criteria for and evaluation of false positive rates in routine method blanks;
6. the DL shall be determined for the analytes of interest in each test method in the quality system matrix of interest in which there are neither target analytes nor interferences at a concentration that would impact the results, or the DL shall be performed in the sample matrix of interest.

NOTE: One option is to follow the United States Environmental Protection Agency Method Detection Limit (MDL) procedure, effective September 27, 2017.

1.5.2.1.2 Ongoing verification of the DL

At a minimum, ongoing verification of the DL shall include assessments of spikes at or below the LOQ and of method blanks. A minimum of one (1) verification spike and one (1) blank shall be analyzed on each instrument during each quarter in which samples are being analyzed and results are being reported below the LOQ. The criteria listed in Section 1.5.2.1.1 shall be met for ongoing verification over the course of a year.

If the method is altered in a way other than routine maintenance and the change can be expected to elevate the detection limit, then a spike at or below the LOQ concentration and a blank shall be prepared and analyzed. If the spike at the LOQ concentration gives a result meeting qualitative identification criteria above zero, and the blank gives a result below the DL, then the DL is verified. If not, the DL shall be re-determined.

In the event that verification fails, the laboratory shall perform a new DL study within thirty (30) calendar days.

1.5.2.1.3 When a new DL is determined, the laboratory shall verify that the LOQ value is greater than the DL. If it is not, the laboratory shall raise the LOQ value to greater than the DL.

1.5.2.2 Limit of Quantitation (LOQ)

If a mandated test method or applicable regulation includes protocols for determining quantitation limits, they shall be followed. The procedure used for determining the LOQ shall be documented by the laboratory. The laboratory shall select an LOQ for each analyte, consistent with the needs of its clients, and greater than the DL. An LOQ is required for each quality system matrix of interest, technology, method, and analyte, except for any component or property for which spiking solutions are not available or a quantitation limit is not appropriate, such as pH, color, odor, temperature, dissolved oxygen, or turbidity.

1. Each selected LOQ shall be verified through analysis of initial verification samples. An initial verification sample consists of a spiked matrix blank at or below the selected LOQ.
2. All sample processing and analysis steps performed for routine sample analysis shall be included in the LOQ verification testing.
3. The LOQ must be at or above the lowest corresponding calibration standard concentration with the exception of methods using a single point calibration.

d) The laboratory shall establish acceptance criteria for accuracy for the LOQ verification spikes.

1.5.2.2.1 Initial verification of the LOQ

When first establishing an LOQ, or when an LOQ concentration has been selected that is lower than the concentration of the LOQ verification spikes previously performed, an initial verification shall be performed as follows:

a) A minimum of seven (7) low level spikes at or below the LOQ concentration shall be processed through all steps of the method. Both preparation and analysis of these low level spikes shall include at least three (3) batches on three (3) separate days.

NOTE 1: Spiking slightly below the LOQ may help ensure that the results are also suitable for DL determination.

NOTE 2: If low level spikes have been analyzed in order to generate a DL, the results may be used to perform the initial verification of the LOQ.

i. If there are multiple instruments that will be assigned the same LOQ, then these low level spikes shall be distributed across all of the instruments.

ii. A minimum of two (2) low level spikes prepared and analyzed on different days shall be tested on each instrument.

b) Existing data may be used if compliant with the requirements for at least three (3) batches, generated within the last two (2) years and representative of current operations.

c) The LOQ is verified if the following criteria are met:

i. All results are quantitative (above zero and meet the qualitative identification criteria of the method; e.g., recognizable spectra, signal to noise requirements, and presence of qualifier ions).

If a result from an LOQ verification sample is not above zero and/or does not meet the qualitative identification criteria in the method, the problem shall be corrected and the verification repeated, or the LOQ verification shall be repeated at a higher concentration.

ii. The mean recovery of each analyte is within the laboratory established accuracy acceptance criteria.

iii. The LOQ is greater than the established DL and at or above the spiking concentration.

If the LOQ is less than or equal to the DL, the LOQ shall be raised to greater than the DL.

NOTE: It is **not** necessary to repeat the LOQ verification at a higher concentration when it is necessary to raise the LOQ to greater than the DL.

d) The laboratory shall document the results of the initial LOQ verification as described in Section 1.5.2.4.

1.5.2.2.2 Ongoing verification of the LOQ

The laboratory shall prepare and analyze a minimum of one (1) LOQ verification sample spiked at the same concentration as the initial LOQ verification on each instrument during each quarter in which samples are being analyzed for each quality system matrix, method, and analyte.

1. Results of each LOQ verification sample analysis shall be evaluated at the time of the testing and shall meet the qualitative identification criteria in the method and laboratory Standard Operating Procedure (SOP) and the quantitated result shall be greater than the DL and meet the laboratory established accuracy criteria as established by Section 1.5.2.2 d).
2. If a continuing LOQ verification test does not meet this requirement, the laboratory shall take corrective action and document a technically valid reason for the corrective action. Corrective action shall be one of the following: (i) correcting method or instrument performance and repeating the verification test; (ii) evaluating the laboratory established control limits to ensure they reflect current performance; or (iii) raising the spiking level (and the quantitation limit if the spiking level is above it) and repeating the initial verification study within thirty (30) calendar days of the initial failure. Any samples analyzed in a batch associated with a failing LOQ verification shall be reanalyzed or reported with qualifiers.

1.5.2.3 Verification of DL/LOQ

If no analysis was performed in a given year, the verification of the DL/LOQ is not required, but a new initial DL/LOQ verification shall be performed prior to analysis of client samples.

1.5.2.4 Documentation

 At least once per year, the laboratory shall tabulate all results of the ongoing verification sample testing. All data representative of the current operations shall be used, if generated within the last two (2) years. A minimum of seven (7) samples is required.

1. The laboratory shall record the analytical and preparation methods used, dates of preparation and testing, the batch identifiers, the testing instrument, quality system matrix, technology, analyte, concentration in the spiked sample with units, and the test result (if any) for each LOQ and/or DL verification test.
2. For each analyte, the laboratory shall record the percent recovery, the number of results (n), the mean and standard deviation of the percent recovery, and the spiking concentration of the spiked samples with units. These data shall be provided to clients upon request.

1.5.3 Evaluation of Precision and Bias

 a) Reference Methods. The laboratory shall evaluate the precision and bias of a reference method for each analyte of concern for each quality system matrix according to Section 1.6 or alternate documented procedure when the analyte cannot be spiked into the sample matrix and QC samples are not commercially available.

 b) Non-Reference Methods. For laboratory-developed methods or non-reference methods that were not in use by the laboratory before July 2003, the laboratory shall have a documented procedure to evaluate precision and bias. The laboratory shall also compare results of the precision and bias measurements with criteria established by the client, by criteria given in the reference method or criteria established by the laboratory.

 Precision and bias measurements shall evaluate the method across the analytical calibration range of the method. The laboratory shall also evaluate precision and bias in the relevant quality system matrices and shall process the samples through the entire measurement system for each analyte of interest.

 Examples of a systematic approach to evaluate precision and bias could be the following:

i. Analyze QC samples in triplicate containing the analytes of concern at or near the LOQ, at the upper-range of the calibration (upper 20%), and at a mid-range concentration. Process these samples on different days as three (3) sets of samples through the entire measurement system for each analyte of interest. Each day, one (1) QC sample at each concentration is analyzed. A separate method blank shall be subjected to the analytical method along with the QC samples on each of the three (3) days. (Note that the three (3) samples at the LOQ concentration can demonstrate sensitivity as well.) For each analyte, calculate the mean recovery for each day, for each level over each day, and for all nine (9) samples. Calculate the relative standard deviation for each of the separate means obtained. Compare the standard deviations for the different days and the standard deviations for the different concentrations. If the different standard deviations are all statistically insignificant (e.g., F-test), then compare the overall mean and standard deviation with the established criteria from above.

ii. A validation protocol, such as the Tier I, Tier II, and Tier III requirements in US EPA Office of Water’s Alternate Test Procedure (ATP) approval process.

1.5.4 Evaluation of Selectivity

 The laboratory shall evaluate selectivity by following the checks established within the method, which may include mass spectral tuning, second column confirmation, ICP inter-element interference checks, chromatography retention time windows, sample blanks, spectrochemical absorption or fluorescence profiles, co-precipitation evaluations, and electrode response factors.

1.6 Demonstration of Capability (DOC)

1.6.1 General

a) An individual who performs any activity involved with preparation and/or analysis of samples must have constant, close supervision (as defined in the laboratory's training procedure) until a satisfactory initial DOC is completed (see Section 1.6.2).

b) Thereafter, ongoing DOC (Section 1.6.3), as per the QC requirements in Section 1.7.2 (such as laboratory control samples), is required.

c) In cases where an individual has prepared and/or analyzed samples using a method that has been in use by the laboratory for at least one (1) year prior to applying for accreditation, and there have been no significant changes in instrument type or method, the ongoing DOC shall be acceptable as an initial DOC. The laboratory shall have records on file to demonstrate that an initial DOC is not required.

d) All demonstrations shall be documented. All data applicable to the demonstration shall be retained and readily available at the laboratory.

1.6.2 Initial DOC

 An individual must successfully perform an initial DOC prior to using any method (see Section 1.6.1.a above), and any time there is a change in instrument type, method, or any time that a method has not been performed by the analyst in a twelve (12) month period.

1.6.2.1 The laboratory shall document each initial DOC in a manner such that the following information is readily available for each affected employee:

 a) analyst(s) involved in preparation and/or analysis;

 b) matrix;

 c) analyte(s), class of analyte(s);

 d) identification of method(s) performed;

 e) identification of laboratory-specific SOP used for analysis, including revision number;

 f) date(s) of analysis; and

 g) summary of analyses, including information outlined in Section 1.6.2.2.c.

1.6.2.2 If the method or regulation does not specify an initial DOC, the following procedure is acceptable. It is the responsibility of the laboratory to document that other approaches to initial DOC are adequate.

a) The analyte(s) shall be diluted in a volume of clean quality system matrix (a sample in which no target analytes or interferences are present at concentrations that will impact the results of a specific method) sufficient to prepare four (4) aliquots at the concentration specified, or if unspecified, to a concentration of one (1) to four (4) times the LOQ.

 b) At least four (4) aliquots shall be prepared and analyzed according to the method(s) either concurrently or over a period of days.

 c) Using all of the results, calculate the mean recovery in the appropriate reporting units and the standard deviations of the sample (in the same units) for each analyte of interest. When it is not possible to determine mean and standard deviations, such as for presence/absence and logarithmic values, the laboratory shall assess performance against established and documented criteria.

 d) Compare the information from (c) above to the corresponding acceptance criteria for precision and accuracy in the method (if applicable) or in laboratory-generated acceptance criteria (if there are not established mandatory criteria). If all analytes meet the acceptance criteria, the analysis of actual samples may begin. If any one of the analytes does not meet the acceptance criteria, the performance is unacceptable for that analyte.

 e) When one or more of the tested analytes fail at least one (1) of the acceptance criteria, the analyst shall proceed according to i) or ii) below.

i. Locate and correct the source of the problem and repeat the test for all analytes of interest beginning with b) above.

ii. Beginning with b) above, repeat the test for all analytes that failed to meet criteria.

 f) Repeated failure, however, confirms a general problem with the measurement system. If this occurs, locate and correct the source of the problem and repeat the test for all analytes of interest beginning with b).

g) When an analyte not currently found on the laboratory’s list of accredited analytes is added to an existing accredited method, an initial demonstration shall be performed for that analyte.

1.6.3 Ongoing DOC

1.6.3.1 The laboratory shall have a documented procedure describing ongoing DOC that includes procedures for how the laboratory will identify data associated with ongoing DOCs. The analyst(s) shall demonstrate on-going capability by routinely meeting the QC requirements of the method, laboratory SOP, client specifications, and/or this Standard. If the method has not been performed by the analyst in a twelve (12) month period, an initial DOC (Section 1.6.2) shall be performed. It is the responsibility of the laboratory to document that other approaches to ongoing DOC are adequate.

1.6.3.2 This on-going demonstration may be one of the following:

a) acceptable performance of a blind sample (single blind to the analyst) or successful analysis of a blind performance sample on a similar method using the same technology (e.g., GC/MS volatiles by purge and trap for Methods 524.2, 624 or 5030/8260);

b) another initial DOC;

c) at least four (4) consecutive laboratory control samples with acceptable levels of precision and accuracy. The laboratory shall determine the acceptable limits for precision and accuracy prior to analysis. The laboratory shall tabulate or be able to readily retrieve four (4) consecutive passing LCSs or reference sample(s) for each method for each analyst each year;

d) a documented process of reviewing QC samples performed by an analyst or groups of analysts relative to the QC requirements of the method, laboratory SOP, client specifications, and/or this Standard. This review can be used to identify patterns for individuals or groups of analysts and determine if corrective action or retraining is necessary;

e) if a) through d) are not technically feasible, then analysis of real-world samples with results within a pre-defined acceptance criterion (as defined by the laboratory or method) shall be performed.

1.7 Technical Requirements

1.7.1 Calibration

 This module specifies the essential elements that shall define the procedures and documentation for initial calibration with second source verification and continuing calibration verification for methods that use calibration models including, but not limited to, average response factor or linear or quadratic regression, to ensure that the data shall be of known quality for the intended use. Calibration requirements for analytical support equipment are specified in Module 2. This Standard does not specify detailed procedural steps (“how to”) for calibration, but establishes the essential elements for selection of the appropriate technique(s). This approach allows flexibility and permits the employment of a wide variety of analytical procedures and statistical approaches currently applicable for calibration. If more stringent standards or requirements are included in a mandated method or by regulation, the laboratory shall demonstrate that such requirements are met. If it is not apparent which Standard is more stringent, then the requirements of the regulation or mandated method are to be followed.

1.7.1.1 Initial Calibration

 Samples shall be associated with an acceptable initial calibration. If the initial calibration is not acceptable, corrective actions shall be performed and all associated samples re-analyzed. If re-analysis of the samples is not possible, data associated with an unacceptable initial calibration shall only be reported with appropriate data qualifiers.

 The following items are essential elements of initial calibration:

1. the details of the initial calibration procedures including calculations, integrations, acceptance criteria, and associated statistics shall be included or referenced in the method SOP. When initial calibration procedures are referenced in the test method, then the referenced material shall be retained by the laboratory and be available for review;
2. sufficient raw data records shall be retained to permit reconstruction of the initial calibration (e.g., calibration date, method, instrument, analysis date, each analyte name, and analyst’s initials or signature; concentration and response, calibration curve or response factor; or unique equation or coefficient used to reduce instrument responses to concentration);
3. the laboratory shall use the most recent initial calibration analyzed prior to the analytical batch, unless otherwise specified by the method;
4. standards used for calibration shall be traceable to a national standard, when commercially available;

e) the laboratory shall have a written procedure addressing removal and replacement of calibration standards. The procedure shall comply with the following requirements:

i The laboratory may remove individual analyte calibration levels from the lowest and/or highest levels of the curve. Multiple levels may be removed, but removal of interior levels is not permitted.

ii. The laboratory may remove an entire single standard calibration level from the interior of the calibration curve when the instrument response demonstrates that the standard was not properly introduced to the instrument, or an incorrect standard was analyzed. A laboratory that chooses to remove a calibration standard from the interior of the calibration shall remove that particular standard calibration level for all analytes. Removal of calibration points from the interior of the curve is not to be used to compensate for lack of maintenance or repair to the instrument.

iii. The laboratory shall adjust the LOQ/reporting limit and quantitation range of the calibration based on the concentration of the remaining high and low calibration standards.

iv. The laboratory shall ensure that the remaining initial calibration standards are sufficient to meet the minimum requirements for number of initial calibration points as mandated by this Standard, the method, or regulatory requirements.

v. The laboratory may replace a calibration standard provided that:

a. the laboratory analyzes the replacement standard within twenty-four (24) hours of the original calibration standard analysis for that particular calibration level;

1. the laboratory replaces all analytes of the replacement calibration standard if a standard within the interior of the calibration is replaced; and

c. the laboratory limits the replacement of calibration standards to one calibration standard concentration.

vi. The laboratory shall document a technically valid reason for either removal or replacement of any interior calibration point;

f) for regression or average response/calibration factor calibrations, the minimum number of non-zero calibration standards shall be as specified in the table below;

|  |  |
| --- | --- |
| **Type of Calibration Curve** | **Minimum Number of Calibration Standardsb** |
| Threshold Testinga | 1 |
| Average Response | 4 |
| Linear Fit | 5 |
| Quadratic Fit | 6 |

a*The initial one-point calibration shall be at the project-specified threshold level.*

b*Fewer calibration standards may be used only if equipment firmware
or software cannot accommodate the specified number of standards. Documentation detailing that limitation shall be maintained by the laboratory.*

g) the lowest calibration standard shall be at or below the lowest concentration for which quantitative data are to be reported without qualification;

h) the highest calibration standard shall be at or above the highest concentration for which quantitative data are to be reported without qualification;

i) sample results shall be quantitated from the initial calibration and may not be quantitated from any continuing calibration verification unless otherwise required by regulation, method, or program;

j) criteria for the acceptance of an initial calibration shall be established (e.g., correlation coefficient or relative standard deviation);

k) the laboratory shall use and document a measure of relative error in the calibration;

 i. for calibrations evaluated using an average response factor, the determination of the relative standard deviation (RSD) is the measure of the relative error;

 ii. for calibrations evaluated using correlation coefficient or coefficient of determination, the laboratory shall evaluate relative error by either:

 a. measurement of the Relative Error (%RE)

$\% Relative Error= \frac{x'\_{i}-x\_{i}^{}}{x\_{i}}×100$ Relative error is calculated using the following equation:

*xi* = True value for the calibration standard
*x’i* = Measured concentration of the calibration standard

This calculation shall be performed for two (2) calibration levels: the standard at or near the mid-point of the initial calibration and the standard at the lowest level.

The Relative Error at both of these levels shall meet the criteria specified in the method. If no criterion for the lowest calibration level is specified in the method, the criterion and the procedure for deriving the criterion shall be specified in the laboratory SOP.

or,

b. measurement of the relative Standard Error (%RSE)

 Relative Standard Error is calculated using the following equation:

$$\% RSE=100×\sqrt{{\sum\_{i=1}^{n}\left[\frac{x\_{i}^{'}-x\_{i}}{x\_{i}}\right]^{2}}/{(n-p)}}$$

*xi*= True value of the calibration level i

*x’i*= Measured concentration of calibration level i

*p* = Number of terms in the fitting equation

 (average = 1, linear = 2, quadratic = 3)

*n* = Number of calibration points

The RSE shall meet the criterion specified in the method. If no criterion is specified in the method, the maximum allowable RSE shall be numerically identical to the requirement for RSD in the method. If there is no specification for RSE or RSD in the method, then the RSE shall be specified in the laboratory SOP.

 l) when test procedures are employed that specify calibration with a single calibration standard and a zero point (blank or zero, however specified by the method), the following shall occur:

i. The zero point and single calibration standard within the linear range shall be analyzed at least daily and used to establish the slope of the calibration.

ii. To verify adequate sensitivity a standard shall be analyzed at or below the lowest concentration for which quantitative data are to be reported without qualification. This standard shall be analyzed prior to sample analysis with each calibration and shall meet the quantitation limit criteria established by the method. If no criteria exist the laboratory shall specify criteria in the SOP;

m) for analysis of Aroclors which use a linear through origin model (or average response factor) the minimum requirement is to perform an initial multi-point calibration for a subset of Aroclors (e.g., a mixture of 1016/1260) and to use a one-point initial calibration to determine the calibration factor and pattern recognition for the remaining Aroclors;

n) Initial Calibration Verification (ICV): All initial calibrations shall be verified with a standard obtained from a second manufacturer or a separate lot prepared independently by the same manufacturer;

o) for those methods where reporting non-detected analytes based on successful completion of a sensitivity check is allowed (similar to threshold testing but only for non-detects) the requirements of this Standard shall not prohibit the practice;

p) some methods allow data within the linear range of the instrument, but above the daily calibration, to be reported without qualification. For these methods, the laboratory shall establish the upper reporting limit through analysis of a series of standards. The upper reporting limit is equal to the concentration of the highest standard meeting the method limits for accuracy. The laboratory shall establish linearity annually and check it at least quarterly with a standard at the top of the linear working range, or at the frequency defined by the method. The laboratory shall dilute samples with results above the linear calibration range, or qualify the over-range results as estimated values.

1.7.1.2 Continuing Calibration Verification (CCV)

 The validity of the initial calibration shall be verified prior to sample analyses by a continuing calibration verification with each analytical batch. The following items are essential elements of continuing calibration verification.

 a) The details of the continuing calibration procedure, calculations and associated statistics shall be included or referenced in the method SOP.

 b) Calibration shall be verified for each compound, element, or other discrete chemical species, except for multi-component analytes such as Aroclors, chlordane, total petroleum hydrocarbons, or toxaphene, where a representative chemical, related substance or mixture can be used.

 c) The concentration of the calibration verification standard shall be equal to or less than half the highest level in the calibration.

 d) Instrument continuing calibration verification shall be performed at the beginning and end of each analytical batch, and at the frequency defined in the method except:

i. if an internal standard is used, calibration verification shall be performed at the beginning of each analytical batch, and at the frequency defined in the method;

ii. a second source initial calibration verification that passes the continuing calibration verification criteria may be used in place of a continuing calibration verification standard;

iii. a laboratory control sample (LCS) may be used in place of a continuing calibration verification (but not as a replacement for a failing CCV) for methods where the calibration goes through the same process as the LCS (using the continuing calibration verification acceptance criteria).

 e) Sufficient raw data records shall be retained to permit reconstruction of the continuing instrument calibration verification (e.g., method, instrument, analysis date, each analyte name, concentration and response, calibration curve or response factor, or unique equations or coefficients used to convert instrument responses into concentrations). Continuing calibration verification records shall explicitly connect the continuing calibration verification data to the initial calibration.

 f) Criteria for the acceptance of a continuing instrument calibration verification shall be established. If the continuing instrument calibration verification results obtained are outside the established acceptance criteria, the following steps shall be taken:

1. if a cause for the calibration verification failure is identified *that impacts only the calibration verification sample* (e.g. a missed autosampler injection), then analysis may proceed if a second calibration verification sample is analyzed immediately and the result is within acceptance criteria. Samples analyzed previously shall be considered valid if bracketed by a passing calibration verification sample (refer to 1.7.1.2.d). The cause for the failure of the first calibration verification result shall be documented;
2. if the cause for the calibration verification failure is not identifiable or has impacted other samples, then corrective action shall be performed and documented. Prior to analyzing samples, the laboratory shall demonstrate acceptable performance after corrective action with calibration verification or a new initial calibration shall be performed. Samples analyzed prior to the calibration verification failure shall be reanalyzed or the results qualified if calibration verification bracketing is required (refer to 1.7.1.2.d);
3. Data associated with an unacceptable calibration verification shall be qualified if reported, and shall not be reported if prohibited by the client, a regulatory program or regulation. Data associated with calibration verifications that fail under the following special conditions shall still be qualified, but may use a different qualifier:

a. when the acceptance criteria for the continuing calibration verification are exceeded high (i.e., high bias) and there are associated samples that are non-detects, then those non-detects may be reported. Otherwise, the samples affected by the unacceptable calibration verification shall be re-analyzed after a new calibration curve has been established, evaluated and accepted; or

b. when the acceptance criteria for the continuing calibration verification are exceeded low (i.e., low bias), those sample results may be reported if they exceed a maximum regulatory limit/decision level. Otherwise the samples affected by the unacceptable verification shall be re-analyzed after a new calibration curve has been established, evaluated and accepted.

1.7.2 Quality Control (QC)

 The laboratory shall have QC procedures for monitoring method performance and the validity of environmental testing data as specified in this Section.

1.7.2.1 Negative Control – Method Performance: Method Blank

a) The method blank shall be analyzed at a minimum of one (1) per preparation batch. In those instances where no separate preparation method is required (for example, volatiles in water), the batch shall be defined as environmental samples that are analyzed together with the same method and personnel, using the same lots of reagents and spiking standards,, not to exceed the analysis of twenty (20) environmental samples; not including laboratory QC (method blanks, LCS, matrix spikes and matrix duplicates).

b) Method blanks are not applicable for certain analyses, such as, but not limited to, pH, Conductivity, Flash Point, and Temperature.

c) The method blank shall be prepared and analyzed using all of the same types of glassware, reagents, equipment, and analytical steps used for the associated samples. A blank material representing a quality system matrix that is similar to the associated samples and is known to be free of the analytes of interest may be used to ensure proper functioning of equipment, but should not be used if it is not also used for samples

d) Procedures shall be in place to determine if a method blank is contaminated. See section 1.7.3.1.

1.7.2.2 Positive Control – Method Performance: Laboratory Control Sample (LCS)

1. The LCS shall be analyzed at a minimum of one (1) per preparation batch. In those instances where no separate preparation method is required (example: volatiles in water), the batch shall be defined as environmental samples that are analyzed together with the same method and personnel, using the same lots of reagents and spiking standards, not to exceed the analysis of twenty (20) environmental samples, not including laboratory QC.
2. b) The LCS is used to evaluate the performance of the total analytical system, including all preparation, handling, and analysis steps.
3. The LCS is applicable for all analyses where a material which provides a known and verified analytical result can be obtained.

a)

1. All analyte concentrations shall be within the calibration range of the method being performed.

ii) The LCS is not required for analyses where spiking solutions or CRMs are not available. If a spiking solution or reference material becomes available for an analysis which historically has not required an LCS, the laboratory shall incorporate that material into the QC requirements for the method as an LCS.

1. Regardless of whether a spike or reference material is used, the components in the LCS shall be selected as specified by the mandated method or regulation or as requested by the client. In the absence of specified spiking or reference components, the laboratory shall use the following rules:
2. for methods that include one (1) to ten (10) target analytes, spike all analytes;

a) For those components that interfere with an accurate assessment the spike shall be chosen that represents the chemistries and elution patterns of the components to be reported; and

1. for those methods that have more than 10 analytes, a representative subset may be chosen. The analytes selected shall be representative of all analytes reported. The following criteria shall be used for determining the minimum number of analytes to be spiked. However, the laboratory shall insure that all targeted components are included in the spike mixture over a two (2) year period:
2. for methods that include eleven (11) to twenty (20) target analytes, spike at least ten (10) analytes or 80%, whichever is greater;
3. for methods with more than twenty (20) target analytes, spike at least sixteen (16) analytes or 80%, whichever is greater.
4. For those components that interfere with an accurate assessment the spike shall be chosen that represents the chemistries and elution patterns of the components to be reported.

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1.7.2.3 Sample Specific Controls

 The laboratory shall document procedures for determining the effect of the sample matrix on method performance. These procedures relate to the analyses of quality system matrix specific QC samples and are designed as data quality indicators for a specific sample using the designated method. These controls alone are not used to judge laboratory performance, unless specified by the method, regulation, program, or client.

 Examples of matrix-specific QC include: Matrix Spike (MS), Matrix Spike Duplicate (MSD), sample duplicates, and surrogate spikes. The laboratory shall have procedures in place for tracking, managing, and handling matrix-specific QC criteria, including spiking appropriate components at appropriate concentrations, calculating recoveries and relative percent difference, and evaluating and reporting results based on performance of the QC samples.

1.7.2.3.1 Matrix spike; matrix spike duplicates

1. The frequency of the analysis of matrix spikes is as specified by the method or when the method does not specify, as specified by the client, project, or program.
2. The components to be spiked shall be as specified by the method. Any permit- specified analytes, as specified by regulation or client requested analytes, shall also be included. If there are no specified components, the laboratory shall spike per the following:
3. For those components that interfere with an accurate assessment the spike shall be chosen that represents the chemistries and elution patterns of the components to be reported.
4. For those methods that have long lists of analytes, a representative subset may be chosen using the following criteria for choosing the number of analytes to be spiked. However, the laboratory shall insure that all targeted components are included in the spike mixture over a two (2) year period.

a. For methods that include one (1) to ten (10) targets, spike all components.

b. For methods that include eleven (11) to twenty (20) targets, spike at least ten (10) components or 80%, whichever is greater.

c. For methods with more than twenty (20) targets, spike at least sixteen (16) components.

1.7.2.3.2 Matrix duplicates

a) Matrix duplicates are replicate aliquots of the same sample taken through the entire analytical procedure. The results from this replicate sample(s) provide a measure of the precision of the results for the specific sample using the selected method. The matrix duplicate may provide a usable measure of sample homogeneity. It may also provide a measure of precision when target analytes are present.

b) The frequency of the analysis of matrix duplicates are as specified by the method or when the method does not specify, at the same frequency as the LCS. The frequency may also be specified by project, client, or program.

1.7.2.3.3 Surrogate spikes

a) As specified in certain test methods, s Surrogates are spiked into environmental samples prior to preparation and analysis. They are used to evaluate extraction efficiency and matrix interference on a sample-specific basis.

b) Except where the matrix precludes its use or when not commercially available, surrogate compounds shall be added to all samples, standards, and QC for all appropriate methods.

1.7.2.4 Reagent Quality, Water Quality, and Checks

 a) The quality of reagents shall be defined in the laboratory’s analytical methods, and shall meet the requirements in the appropriate reference method. In methods where the purity of reagents is not specified, the grade of reagents shall be suitable for its application and meet corresponding quality control objectives. Documentation of reagent purity shall be maintained.

 b) The quality of water sources shall be monitored and documented and shall meet method specified requirements.

 c) The laboratory shall verify the concentration of titrants in accordance with method requirements and written laboratory procedures.

1.7.2.5 Selectivity

 The laboratory shall document selectivity by following the checks established within each applicable method, or based on regulation, program, or project requirements.

1.7.3 Data Acceptance/Rejection Criteria

1.7.3.1 Negative Control – Method Performance: Method Blank

 Each method blank shall be critically evaluated as to the nature of any interference and the effect on the analysis of each sample within the batch. If contamination is present, as described in a) and b) below, the source of contamination shall be investigated and measures taken to minimize or eliminate the problem. Any affected samples associated with a contaminated method blank shall be reprocessed for analysis or the results reported with appropriate data qualifiers if:

 a) the concentration of a targeted analyte in the blank is at or above the specified level as established by the LOQ, method, project, or by regulation;

 b) the blank contamination otherwise affects the sample results as per the method requirements or the individual project data quality objectives; and

 c) if a blank is determined to be contaminated the laboratory shall take appropriate action. In all cases, the action taken shall be recorded.

1.7.3.2 Positive Control – Method Performance: Laboratory Control Sample (LCS)

 a) The results of the LCS shall be calculated in percent recovery or other appropriate statistical technique that allows comparison to established acceptance criteria. The laboratory shall document the calculation.

 Results of the LCS shall be compared to established acceptance criteria and, if found to be outside of these criteria, all affected samples shall be reprocessed for re-analysis, or the results reported with appropriate data qualifiers. This includes any allowable marginal exceedance as described in b) below.

 i. when the acceptance criteria for the positive control are exceeded high (i.e., high bias) associated, non-detect samples may be reported with data qualifying codes; or

 ii. when the acceptance criteria for the positive control are exceeded low (i.e., low bias), associated samples may be reported if they exceed a maximum regulatory limit/decision level with data qualifying codes.

 b) Allowable Marginal Exceedances. If a large number of analytes are in the LCS, it becomes statistically likely that a few will be outside control limits. This may not indicate that the system is out of control, therefore corrective action may not be necessary. Upper and lower marginal exceedance (ME) limits can be established to determine when corrective action is necessary. A ME is defined as being beyond the LCS control limit (three (3) standard deviations), but within the ME limits. ME limits are between three (3) and four (4) standard deviations around the mean. The number of allowable marginal exceedances is based on the number of analytes in the LCS. If more analytes exceed the LCS control limits than is allowed, or if any one analyte exceeds the ME limits, the LCS fails and non-conforming work procedures are necessary.

 The number of allowable marginal exceedances is as follows:

|  |  |
| --- | --- |
| **Number of Analytes in LCS** | **Number Allowed as****Marginal Exceedances** |
| > 90 | 5 |
| 71 – 90 | 4 |
| 51 – 70 | 3 |
| 31 – 50 | 2 |
| 11 – 30 | 1 |
| < 11 | 0 |

 If the same analyte exceeds the LCS control limit in consecutive batches, the source of the issue shall be located and action by the laboratory is required. Laboratories shall have a written procedure to monitor the application of marginal exceedance allowance to the LCS.

1.7.3.3 Sample Specific Controls

 a) Matrix Spike; Matrix Spike Duplicates

 The results from matrix spike/matrix spike duplicate shall be expressed as percent recovery (%R), relative percent difference (RPD), or other appropriate statistical technique that allows comparison to established acceptance criteria. The laboratory shall document the calculation for the statistical technique used.

 The results are compared to the acceptance criteria as published in the mandated method. Where there are no established criteria, the laboratory shall determine internal criteria or client-specified criteria and document the method used to establish the limits. For matrix spike results outside established criteria, laboratory action shall be recorded or the data for that sample reported with appropriate data qualifying codes.

 b) Matrix Duplicates

 The results from matrix duplicates may be expressed as RPD or another statistical technique (e.g., absolute differences).

 The laboratory shall document the calculation used.

 Results are compared to the acceptance criteria as published in the mandated method. Where there are no established criteria, the laboratory shall determine internal criteria or client-specified criteria and document the method used to establish the limits. For matrix duplicates results outside established criteria, laboratory action shall be recorded or the data for that sample reported with appropriate data qualifying codes.

 c) Surrogate Spikes

 The results are compared to the acceptance criteria as published in the mandated method. Where there are no established criteria, the laboratory shall determine internal criteria and document the method used to establish the limits. Surrogates outside the acceptance criteria shall be evaluated for the effect indicated for the individual sample results. The appropriate action may be guided by the data quality objectives or other site-specific requirements. Results reported from analyses with surrogate recoveries outside the acceptance criteria shall include appropriate data qualifiers.

1.7.4 Sample Handling

 a) All samples that require thermal preservation shall be considered acceptable if the temperature upon receipt of a representative sample container is within the method or program specified range. For samples with a specified temperature of 4°C, samples with a temperature ranging from just above the freezing temperature of water to 6°C shall be acceptable. The following exceptions are allowed:

i. Samples that are delivered to the laboratory on the same day they are collected may not meet the requirements of Section 1.7.4.a. In these cases, the samples shall be considered acceptable if received with evidence of cooling. If applicable, such evidence shall be recorded by the laboratory.

ii. Thermal preservation is not required in the field if the laboratory receives and refrigerates the sample or begins sample analysis within fifteen (15) minutes of collection.

 b) The laboratory shall implement procedures for checking sample preservation prior to or during sample preparation or analysis. An exception is allowed for volatile organic analyte analyses; chemical preservation may be checked after analysis.