



# **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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## 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

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## VOLUME 1, MODULE 4

### Quality Systems for Chemical Testing

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#### 1.0 Introduction

This document contains essential quality control (QC) requirements for environmental testing activities involving chemical measurements. Additional QC requirements specified by method, regulation or project must be met by laboratories. 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.

#### 2.0 Normative References

Reserved

#### 3.0 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.

##### 3.1 Additional Terms and Definitions

**Calibration Standard:** A substance or reference material used for calibration.

**Internal Standard:** A known amount of standard added to a test portion of a sample as a reference for evaluating and controlling the precision and bias of the applied analytical method.

**Limit(s) of Quantitation (LOQ):** The minimum levels, concentrations, or quantities of a target variable (e.g., target analyte) that can be reported with a specified degree of confidence.

**Verification:** Confirmation by examination and objective evidence that specified requirements have been met. In connection with the management of measuring equipment, verification provides a means for checking that the deviations between values indicated by a measuring instrument and corresponding known values of a measured quantity are consistently smaller than the maximum allowable error defined in a standard, regulation or specification particular to the management of the measuring equipment.

**Matrix Spike:** Additional aliquot of a sample to which known concentration(s) of target analyte(s) is added. The spiked sample must then be handled exactly the same as the original sample through all analytical preparatory and analysis processes. The matrix spike is used to assess the effect of the sample's matrix has on a method's recovery efficiency.

**Matrix Spike Duplicate:** A replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte.

**Limit of Detection (LOD):** The minimum result which can be reliably discriminated from a blank with a predetermined confidence level.

**Measurement System:** A method, as implemented at a particular laboratory, and which includes the equipment used to perform the test and the operator(s).

### 3.2 Exclusions and Exceptions

Reserved

## 4.0 Technical Specialist

Reserved

## 5.0 Selection, Verification and Validation of Methods

Refer to Volume 1, Module 2, Section 7.2 for general requirements.

In cases where the laboratory has been performing a method for at least one (1) year prior to applying for accreditation, previously generated method data may be used to meet the requirements for verification in Section 5.1 or validation in Section 5.2 as long as there have been no significant changes in instrument type or method since the data was generated.

### 5.1 Initial Verification of Methods

Prior to implementation of a published reference method, the laboratory's capability and competency to perform the method must be verified for each analyte of interest in each quality system matrix for which accreditation is sought.

- a) The laboratory must verify the performance of a reference method using the procedures in the reference method and, at a minimum, must include an initial determination of detection limits (Section 6.1.1), an initial selection and verification of limits of quantitation (Sections 6.2 and 6.2.1), an initial and continuing calibration (Section 8.1), and the required quality controls (Sections 8.2 and 8.3).
- b) The laboratory must have an analyst with a successful demonstration of capability per Section 7.0.
- c) The laboratory must obtain acceptable performance of proficiency testing samples as required in Volume 1 Module 1.

### 5.2 Initial Validation of Methods

Prior to implementation of a non-reference method, laboratory-developed method, or a reference method used outside its intended scope, the laboratory must validate the method for each analyte of interest in each quality system matrix for which accreditation is sought.

- a) The method validation, at a minimum, must include all items in Sections 5.1.1 a) – c) and an evaluation of precision and bias (Section 5.3), an evaluation of selectivity (Section 5.4), the selection of appropriate method quality controls (Section 8.2), and the selection and determination of acceptance criteria (Section 8.3).
- b) When a reference method is used outside of its intended scope, such as the addition of a new target analyte or the addition of a new quality system matrix, the scope change(s) and/or modification(s) must be clearly identified.



### 5.3 Evaluation of Precision and Bias

- a) For non-reference methods, laboratory-developed methods, and reference methods used outside their intended scope, the laboratory must have a documented procedure to evaluate precision and bias.
- b) Precision and bias must be evaluated across the analytical calibration range of the method. At a minimum the evaluation must include the low, middle and upper segments of the calibration range.
- c) Samples used to generate precision and bias results must be processed through the entire measurement system for each analyte of interest in each quality system matrix.
- d) The laboratory must compare the results of the precision and bias measurements with criteria established by the client, criteria given in the reference method or a comparable reference method, or criteria established by the laboratory.

### 5.4 Evaluation of Selectivity

For non-reference methods, laboratory-developed methods, and reference methods used outside their intended scope, the laboratory must evaluate the method for selectivity of each analyte of interest in each quality system matrix.

### 5.5 Ongoing Method/Matrix/Analyte Verification

- a) Laboratories must perform ongoing verification for each method/matrix/analyte combination annually for all methods, including reference, non-reference and laboratory developed methods. The results of these ongoing verifications must be used to evaluate the ability of the laboratory to produce acceptable data. The requirement for ongoing verification may be achieved by performing one or more of the following actions, where applicable, for each method/matrix/analyte combination:
  - i. Completion of ongoing verification of the DL or LOQ (Sections 6.1.2 or 6.2.2).
  - ii. Acceptable performance of a blind sample (single blind to the analyst) or successful analysis of a proficiency testing sample where the analyte has an assigned value above the DL.
  - iii. Completion of an Initial DOC -(Section 7.2).
  - iv. Completion of an ongoing DOC -(Section 7.3).
- b) When a single action does not provide ongoing verification for each method/matrix/analyte combination (e.g., non-detects in PT samples), actions from above may be combined until a record of verification is available for each method/matrix/analyte combination.

## 6.0 Detection Limit and Limit of Quantitation (however named)

Procedures used for determining limits of detection and quantitation must be documented. Records must include the quality system matrix type. All supporting data must be retained. If a mandated test method or applicable regulation includes protocols for determining detection limits or limits of quantitation, they must be followed. If the method or regulation does not contain specific directions for

determination of the detection limit or limit of quantitation, the requirements below in 6.4.1 and 6.4.2 apply.

## 6.1 Detection Limit (DL)

### 6.1.1 Initial determination of the DL

Initial determination of the DL is required and must follow the United States Environmental Protection Agency Method Detection Limit (MDL) procedure, effective September 27, 2017, 40 CFR 136 Appendix B.

### 6.1.2 Ongoing verification of the DL

Ongoing verification of the DL is only required when the laboratory reports results below their limit of quantitation (LOQ). If required, ongoing data collection and ongoing verification of the DL must follow the United States Environmental Protection Agency Method Detection Limit (MDL) procedure, 40 CFR 136 Appendix B effective September 27, 2017.

a) When a new DL study is required per the USEPA MDL procedure, it must be completed within thirty (30) calendar ~~days~~days, and the laboratory must not report to the DL until a new DL is ~~established~~bestablished.

b) If a new instrument is added to a group of instruments sharing a single DL, analyze a minimum of two spiked replicates at the same concentration as the original spikes and 2 method ~~blank~~blanks, and proceed as described in the USEPA MDL procedure.

a)c) When a new DL is determined, the laboratory must confirm that the LOQ remains greater than the DL. If it is not, the laboratory must raise the LOQe to be greater than the DL.

## 6.2 Limit of Quantitation (LOQ)

The laboratory must select an LOQ for each method/matrix/analyte combination, consistent with the needs of its clients, and that is greater than the DL, except for any component or property for which spiking solutions are not available or a quantitation limit is not appropriate.

- a) Each selected LOQ must be verified through analysis of initial verification samples. An initial verification sample consists of a quality system matrix blank spiked with the analytes of interest at or below the selected LOQ.
- b) All sample processing and analysis steps performed for routine sample analysis must be included in the LOQ verification testing.
- c) 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 must establish acceptance criteria for accuracy of the LOQ verification spikes.

### 6.2.1 Initial verification of the LOQ

When establishing a new LOQ that is below the concentration of the previous initial LOQ verification samples, an initial verification must be performed as follows:

- a) A minimum of seven (7) initial verification samples at or below the LOQ concentration must be processed through all steps of the method. The initial verification samples must be prepared in at least three batches on three separate calendar dates and analyzed on three separate calendar dates.

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

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

- b) If there are multiple instruments that will be assigned the same LOQ, then these initial verification samples must be distributed across all of the instruments. A minimum of two (2) initial verification samples prepared and analyzed on different days must be tested on each instrument.

- c) 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.

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

- e) All results are quantitative (above zero and meet the qualitative identification criteria of the method; method, e.g., recognizable spectra, signal to noise requirements, and presence of qualifier ions).
- i. 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 must be corrected and the verification repeated, or the LOQ verification must 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 must 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.

- f) The laboratory must record the results of the initial LOQ verification as described in Section 6.5.

### 6.2.2 Ongoing verification of the LOQ

The laboratory must 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 method/matrix/analyte.

- a) Results of each LOQ verification sample analysis must be evaluated at the time of the testing and must meet the qualitative identification criteria in the method and laboratory Standard Operating Procedure (SOP). The quantitated result must be greater than the DL and meet the laboratory established accuracy criteria as established by Section 6.5.d).

If a continuing LOQ verification test does not meet this requirement, ~~the laboratory~~ an action must be ~~taken and~~ taken and record a technically valid reason for the action. The laboratory must also evaluate the impact to analyses on previously reported data back to the last passing LOQ verification. (See section V1M2 XXXX for nonconforming work).

- b) Action must 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.

- c) Any samples analyzed in a batch associated with a failing LOQ verification must be reanalyzed or reported with appropriate qualifiers.

- d) If no analysis was performed in a given year, the verification of the DL and LOQ is not required, but a new initial DL and LOQ verification must be performed prior to analysis of client samples.

### 6.3 Ongoing verification of the LOQ documentation

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

- a) The laboratory must record the analytical and preparation methods used, dates of preparation and testing, the batch identifiers, the testing instrument, quality system matrix, analyte, concentration in the spiked sample with units, and the test result (if any) for each LOQ and/or DL verification test.
- b) For each analyte, the laboratory must 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~~ This data must be provided to clients upon request.

## 7.0 Analyst Demonstration of Capability (DOC)

### 7.1 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 7.2). All reported data must be generated by or under the supervision of an individual who has current DOCs as defined in Sections 7.2 and 7.3.
- b) The laboratory must have documented procedures describing DOC requirements. The laboratory must identify and retain data associated with DOCs.
- c) For methods in which the laboratory routinely separates sample preparation (such as digestions, distillations, or extractions) and sample analysis into distinct processes performed by separate individuals, the Initial and/or ongoing DOC for sample preparation and analysis processes must be separated. In cases where the preparation and analysis processes are performed by separate individuals, each must demonstrate capability of their assigned process.
- d) 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 initial laboratory accreditation, and there have been no significant changes in instrument type or method, and the individual has performed the method within the past twelve (12) months, the ongoing DOC will be acceptable as an initial DOC. The laboratory must have records on file to demonstrate that an initial DOC is not required.
- e) All demonstrations must be recorded.

## 7.2 Initial DOC

An analyst new to a method must successfully perform an initial DOC for each method/matrix/analyte prior to independently generating reportable data for said method/matrix/analyte (see Section 7.1.a above). ~~Additionally~~Additionally, an initial DOC must be performed 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.

7.2.1 The laboratory must record each initial DOC in ~~a manner such~~such a manner that the following information is readily available for each affected employee:

- a) analyst(s) involved in preparation and/or analysis;
- b) quality system 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 7.2.2.c.

7.2.2 If the method or regulation does not specify an initial DOC, complete the following procedure. If this is not applicable it is the responsibility of the laboratory to select and document another approach to the initial DOC which incorporates criteria for precision, accuracy and acceptance.

- a) The analyte(s) must be diluted in a volume of clean matrix appropriate for use (a sample in which no target analytes or interferences are present at concentrations that will impact the results of a specific method) to a concentration of one (1) to four (4) times the LOQ.
- b) At least four independently prepared LCSs must be analyzed according to the method(s) either concurrently or over a period of days and meet LCS acceptance criteria.
- c) Using ~~all of all~~ the results, calculate the mean recovery in the appropriate reporting units and the relative 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 must assess performance against established and documented criteria.
- d) Compare the information from (b) 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, locate and correct the source of the problem and proceed according to i) or ii) below.
  - i. Beginning with a) above repeat the test for all analytes of interest
  - ii. Beginning with a) above, repeat the test for only analytes of interest that failed to meet criteria.
- f) When an analyte not currently found on the laboratory's list of accredited analytes is added to an existing accredited method, an initial demonstration must be performed for that analyte.

### 7.3 Ongoing DOC

- 7.3.1 An analyst must continue to demonstrate ongoing competence through completion of an ongoing DOC to continue to generate reportable data for said method. The laboratory must have a documented procedure describing ongoing DOC that includes procedures for how the laboratory will identify data associated with ongoing DOCs. The analyst(s) must demonstrate on-going capability by routinely meeting the QC requirements of the method, laboratory SOP, client specifications, and/or this Standard. If an ongoing DOC has not been completed by the analyst annually, an initial DOC (Section 7.2) must be performed. It is the responsibility of the laboratory to ~~document that document~~ their approaches to ongoing ~~DOCs which~~ DOCs which comply with their procedures for monitoring the competence of personnel (see V1M2 6.2.5.f).

## 8.0 Technical Requirements

### 8.1 Calibration

This section of the module specifies the essential elements that must define the procedures and documentation for initial calibration with second source verification and continuing calibration

verification for methods that use calibration to ensure that the data is of known quality for the intended use. Calibration requirements for support equipment are specified in Module 2.

#### 8.1.1 Initial Calibration

Sample results must be determined using an acceptable initial calibration, except as noted in 8.1.1.a below.

The following items are essential elements of initial calibration:

- a) The most recent initial calibration analyzed from the instrument utilized, prior to the analytical batch must be used. If the most recent initial calibration is not acceptable, any affected samples must be reanalyzed once a compliant initial calibration is achieved. If re-analysis of the samples cannot be performed, data associated with an unacceptable initial calibration must only be reported with appropriate data qualifiers.
- b) ~~the~~The details of the initial calibration procedures including calculations, integrations, acceptance criteria, and associated statistics must be included or referenced in the method SOP. When initial calibration procedures are referenced in the test method, then the referenced material must be retained by the laboratory and be available for ~~review~~review.
- c) ~~raw~~Raw data records must be retained to permit reconstruction of the initial calibration. In cases where ~~the raw~~raw data is unavailable due to a factory provided ~~calibration~~the calibration the laboratory must use a documented procedure to verify the factory calibration.
- d) ~~d)~~——If removal and replacement of calibration standards is necessary, the laboratory must comply with the following requirements:
  - i. ~~i)~~——The laboratory may remove individual analyte calibration levels from the lowest and/or highest levels of the calibration. Multiple levels may be removed, but removal of interior levels is not permitted except as noted below in 8.1.1.d.ii.
  - ii. ~~ii)~~——The laboratory may remove an entire single standard calibration level from the interior of the ~~calibration when~~calibration 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 must remove that particular standard calibration level for all analytes. Removal of calibration points from the interior of the calibration is not to be used to compensate for poor or erratic instrument response.
  - iii. ~~iii)~~——The laboratory must adjust the LOQ and quantitation range of the calibration based on the concentration of the remaining high and low calibration standards.
  - iv. ~~iv)~~——~~The~~The laboratory must ensure that the remaining initial calibration standards are sufficient to meet the minimum requirements for ~~number~~the number of initial calibration points as mandated by this Standard, the method, or regulatory requirements.
  - v. The laboratory may replace an initial calibration standard provided that:

- a. The laboratory analyzes the replacement standard by the end of the next working day of the original calibration standard analysis for that particular calibration level.
- b. 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.
- vi. The laboratory must record a technically valid reason for either removal or replacement of any interior calibration point.
- vii. The laboratory must recalculate all data associated with the calibration after the calibration point has been removed or replaced.
- e) for regression or average response/calibration factor calibrations, the minimum number of non-zero calibration standards must be as specified in the table below:

Type of Calibration	Minimum Number of Calibration Standards <sup>a, b, c</sup>
Threshold Testing <sup>a</sup>	1
Average Response	4
Linear Fit	5
Quadratic Fit	6

<sup>a</sup> The initial one-point calibration must be at the project-specified threshold level.

<sup>b</sup> Fewer calibration standards may be used only if equipment firmware or software cannot accommodate the specified number of standards. Documentation detailing that limitation must be maintained by the laboratory.

<sup>c</sup> Fewer calibration standards for ISE technologies are allowed based on manufacturer's instructions.

- f) ~~f)~~ the lowest calibration standard must be at or below the lowest concentration for which quantitative data are to be reported without qualification;
- g) ~~g)~~ the highest calibration standard must be at or above the highest concentration for which quantitative data are to be reported without qualification except as addressed in o below;
- h) sample results must be quantitated from the initial calibration and may not be quantitated from any continuing calibration verification unless otherwise required by regulation, method, or program;
- i) criteria for the acceptance of an initial calibration must be established and met;
- j) the laboratory must 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 must evaluate relative error by either:
    - a. measurement of the Relative Error (%RE)



$$\% \text{ Relative Error} = \frac{x'_i - x_i}{x_i} \times 100$$

following equation:

Relative error is calculated using the

$x_i$  = True value for the calibration standard

$x'_i$  = Measured concentration of the calibration standard

Unless the method specifies more points to be evaluated, this calculation must be performed for two calibration levels: the standard at or near the middle of the initial calibration range and the standard at the lowest level.

The Relative Error at both of these levels must 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 must be specified in the laboratory SOP.

or,

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

Relative Standard Error is calculated using the following equation:

$$\% RSE = 100 \times \sqrt{\sum_{i=1}^n \left[ \frac{x'_i - x_i}{x_i} \right]^2 / (n - p)}$$

$x_i$  = 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 must meet the criterion specified in the method. If no criterion is specified in the method, the maximum allowable RSE must 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 must be specified in the laboratory SOP.

iii. ISE calibrations and/or other point-to-point calibrations do not require a calculation of the measure of relative error.

k) when test methods are employed that allow calibration with a single calibration standard and a zero point (blank or zero, however specified by the method), the following must occur:

- i. The zero point and single calibration standard within the linear range must be analyzed at least daily and used to establish the slope of the calibration.
- ii. To verify adequate sensitivity a standard must be analyzed at or below the lowest concentration for which quantitative data are to be reported without qualification. This standard must be analyzed prior to sample analysis with each calibration and must meet the quantitation limit

criteria established by the method. If no criteria exist, the laboratory must specify criteria in the SOP.

- l) for analysis of Aroclors follow method requirements for calibration.
- m) Initial Calibration Verification (ICV): All initial calibrations must be verified with a standard obtained from a second manufacturer or a separate lot prepared independently by the same manufacturer when available. If the method does not specify acceptance criteria the laboratory must develop acceptance criteria.
- n) 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 must not prohibit the practice;
- o) 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 must 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 must 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 must dilute samples with results above the linear calibration range or qualify the over-range results as estimated values.

#### 8.1.2 Continuing Calibration Verification (CCV)

The validity of the initial calibration must 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 must be included or referenced in the method SOP.
- b) Calibration must be verified for each analyte, except for multi-component analytes such as Aroclors, chlordane, or total petroleum hydrocarbons, where a representative chemical, related substance or mixture can be used if the method allows.
- c) The concentration of at least one calibration verification standard per analytical batch must be equal to or less than half the highest level in the calibration.
- d) Instrument continuing calibration verification must 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 must 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 must be retained to permit reconstruction of the continuing instrument calibration verification. Continuing calibration verification records must explicitly connect the continuing calibration verification data to the initial calibration.

- f) Criteria for the acceptance of a continuing instrument calibration verification must be established. If the continuing instrument calibration verification results obtained are outside the established acceptance criteria, the following steps must be taken:
- i. 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 prior to analyzing additional samples and the result is within acceptance criteria. Samples analyzed previously are 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 must be recorded;
  - ii. if the cause for the calibration verification failure is not identifiable or has impacted other samples, then action must be taken and recorded to address the issue. Prior to analyzing samples, the laboratory must demonstrate acceptable performance after action with calibration verification or a new initial calibration must be performed. Samples analyzed prior to the calibration verification failure must be reanalyzed or the results qualified if calibration verification bracketing is required (refer to 8.1.2.d);
  - iii. Data associated with an unacceptable calibration verification must be qualified if reported, and must 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 must still be qualified, but may use a different qualifier:
- g) 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 must be re-analyzed after a new initial calibration has been established, evaluated and accepted; or
- h) 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 must be re-analyzed after a new initial calibration has been established, evaluated and accepted.

## 8.2 Quality Control (QC)

The laboratory must have QC procedures for monitoring method performance and evaluating the validity of environmental testing data. These procedures must include the quality control types as specified in this Section. If a method, regulation, program or client specify quality control requirements, those must be followed.

### 8.2.1 Negative Control – Method Performance: Method Blank

- a) The method blank must 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 must 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). Or at the frequency as described within a reference method.

- b) Method blanks are not applicable for certain analyses, such as pH, Conductivity, Flash Point, and Temperature.
- c) The method blank must be prepared and analyzed using all of the same lots of reagents, equipment, and analytical steps used for the associated samples.
- d) Procedures must be in place to determine if a method blank is contaminated. See section 8.3.1.

#### 8.2.2 Positive Control – Method Performance: Laboratory Control Sample (LCS)

- a) The LCS must be prepared and 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 must be defined as environmental samples that are analyzed together with the same method -, using the same lots of reagents and spiking standards, not to exceed the analysis of twenty (20) environmental samples, not including laboratory QC.
- b) The LCS is used to evaluate the performance of the total analytical system, including all preparation, handling and analysis steps.
- c) The LCS is applicable for all analyses where a material which provides known and verified analytical results is available. If a material becomes available for an analysis which historically has not required an LCS, the laboratory must incorporate that material into the QC requirements for the method as an LCS.
- d) All analyte concentrations of the LCS must be within the calibration range of the method being performed.
- e) Regardless of whether a spike or reference material is used, the components in the LCS must be selected as specified by the mandated method or regulation or as requested by the client. for those components that interfere with an accurate assessment, the spike must be chosen that represents the chemistries and elution patterns of the components to be reported
- f) In the absence of specified spiking or reference components, the laboratory must use the following rules
  - i. for methods that include one (1) to ten (10) targets, spike all analytes
  - ii. for those methods that have more than 10 analytes, a representative subset may be chosen. The components selected must be representative of all analytes reported. The following criteria must be used for determining the minimum number of analytes to be spiked. However, the laboratory must ensure that all targeted components are included in the spike mixture over a two (2) year period:
  - iii. for methods that include eleven (11) to twenty (20) ~~target~~, ~~target~~, spike at least ten (10) analytes or 80%, whichever is greater.

- iv. for methods with more than twenty (20) target analytes, spike at least sixteen (16) analytes or 60%, whichever is greater.

### 8.2.3 Sample Specific Controls

The laboratory must have procedures for determining the effect of sample matrix on method performance. These procedures must include:

- a) a description of the matrix-specific quality controls used (e.g., matrix spike, matrix spike duplicate, sample duplicate, surrogates),
- b) the design of the matrix-specific quality controls, including frequency, spiked components, and the spiked concentration of analytes,
- c) a mechanism for developing, tracking, updating, and implementing matrix-specific quality control criteria,
- d) the formulas used to measure matrix-specific quality control criteria, including percent recovery and relative percent difference, and
- e) a process for evaluating and reporting results based on the performance of the matrix-specific quality controls.

Matrix-specific quality controls alone are not used to evaluate laboratory performance unless specified by the method, regulation, program, or client.

#### 8.2.3.1 Matrix spike; matrix spike duplicates

- a) 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.
- b) The components to be spiked must be as specified by the mandated method. Any permit- specified analytes, as specified by regulation or client requested analytes, must also be included. If there are no specified components, the laboratory must spike per the following:
  - i. For those components that interfere with an accurate assessment the spike must be chosen that represents the chemistries and elution patterns of the components to be reported.
  - ii. The laboratory must ensure 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 analytes.
    - b. For methods that include eleven (11) to twenty (20) targets, spike at least ten (10) analytes or 80%, whichever is greater.
    - c. For methods with more than twenty (20) targets, spike at least sixteen (16) analytes, or 60%, whichever is greater.

#### 8.2.3.2 Matrix duplicates

- a) Matrix duplicates are replicate aliquots of the same sample taken through the entire analytical procedure. The results from 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 as specified by project, client or program.

#### 8.2.3.3 Surrogate spikes

- a) As specified in certain test methods, 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 must be added to all samples, standards, and QC for all appropriate methods.

#### 8.2.4 Reagent Quality, Water Quality, and Checks

- a) The quality of reagents must be defined in the laboratory's analytical methods and must meet the requirements in the appropriate reference method. In methods where the purity of reagents is not specified, the grade of reagents must be suitable for its application and meet corresponding quality control objectives. Records of reagent purity must be maintained.
- b) The quality of water sources must be monitored and recorded and must meet method specified requirements.
- c) The laboratory must verify the concentration of titrants in accordance with method requirements and written laboratory procedures.

#### 8.2.5 Selectivity

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

### 8.3 Data Acceptance/Rejection Criteria

The laboratory must have procedures for evaluating quality controls. This evaluation must be against the established acceptance criteria within the mandated methods. Where there are no established criteria, the laboratory must determine internal criteria or utilize client specified criteria and document the method used to establish the limits.

#### 8.3.1 Negative Control – Method Performance: Method Blank

Each method blank must be evaluated to determine 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 must be investigated and measures taken to minimize or eliminate the problem. Any affected samples associated with a contaminated method blank must be reprocessed for analysis or the results must be reported with appropriate data qualifiers:

- a) The concentration of a targeted analyte in the blank is at or above the specified LOQ or as established by the method, project or by regulation, and is greater than 1/10 of the amount measured in the sample.
- b) The blank contamination otherwise affects the sample results as per the method requirements or the individual project data quality objectives.

- c) If a blank is determined to be contaminated the laboratory must take appropriate action to address the ~~issue.~~issue. In all cases, the action must be recorded.

### 8.3.2 Positive Control – Method Performance: Laboratory Control Sample (LCS)

- a) The results of the LCS must be calculated in percent recovery or other appropriate statistical techniques that ~~allows~~allow comparison to established acceptance criteria. The laboratory must document the calculation.

If results are found to be outside of these criteria all affected samples must be reprocessed for reanalysis, 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 samples below the DL, may be reported with appropriate data qualifiers; 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 appropriate data qualifiers.
- 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 action may not be necessary. Upper and lower marginal exceedance (ME) limits can be established to determine when action to address the issue is necessary. ME defined as slightly exceeds the established control limits  $\pm 3$  standard deviations but within the ME limits which are between 3 and 4 standard deviations. 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 must be located and action taken by the laboratory. Laboratories must have a written procedure to monitor the application of marginal exceedance allowance to the LCS.

### 8.3.3 Sample Specific Controls

- a) Matrix Spike; Matrix Spike Duplicates

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

For matrix spike/matrix spike duplicate results outside established criteria, action to address the issue must be recorded or the data for that sample reported with appropriate data qualifiers.

b) Matrix Duplicates

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

The laboratory must document the calculation.

For matrix duplicates results outside established criteria, action to address the issue must be recorded or the data for that sample reported with appropriate data qualifiers.

c) Surrogate Spikes

Surrogates outside the acceptance criteria must be evaluated for the effect indicated for the individual sample results, action ~~to~~to address the issue must be recorded or the data for that sample or the data reported with appropriate data qualifiers.

8.4 Sample Handling

- a) All samples that require thermal preservation are acceptable if the temperature upon receipt of a representative sample container is within the regulation, method or project, specified range. 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 8.4.a. In these cases, the samples are considered acceptable if received with evidence of cooling. If applicable, evidence must 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 must 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 is checked after analysis.
- c) Samples that do not meet the above-mentioned criteria must include appropriate data qualifiers.