EL-V1M4-2009

ENVIRONMENTAL LABORATORY SECTOR

VOLUME 1

MANAGEMENT AND TECHNICAL REQUIREMENTS FOR LABORATORIES PERFORMING ENVIRONMENTAL ANALYSIS

Module 4: Quality Systems for Chemical Testing

Working Draft Standard
July 2011

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PREFACE

This Standard is the result of many hours of effort by those volunteers on The NELAC Institute (TNI) Quality Systems Committee. 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 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

1.0 CHEMICAL TESTING

1.1 Introduction

This document contains detailed quality control 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 quality control procedures specified in this module are being followed.

1.2 Scope

The essential quality control procedures applicable to chemistry measurements are included in this module. Additional quality control 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

~~**Physical Parameter:** a measurement of a physical characteristic or property of a sample as distinguished from the concentrations of chemical or biological components.~~

Reserved

1.3.2 Exclusions and Exceptions

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1.4 Method Selection

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

~~A reference method is a method issued by an organization generally recognized as competent to do so. (When ISO refers to a standard method, that term is equivalent to reference method). When a laboratory is required to analyze a parameter by a specified method due to a regulatory requirement, the parameter/method combination is recognized as a reference method.~~

~~If there is not a regulatory requirement for the parameter/method combination, the parameter/ method combination need not be validated under 1.5.1b) as a non-reference method if it can be analyzed by another similar reference method of the same matrix and technology.~~ The inclusion of the ~~parameter~~analyte in the method shall meet all required calibration requirements and the quality control requirements of the method to which the ~~parameter~~analyte is being added. If no QC exists in the method, the laboratory shall adhere to the requirements outlined in ~~the~~ a similar reference method (when available). For example, when adding acetone to Method 624, the calibration and QC requirements shall follow Method 624. A method that meets the~~se above~~ requirements shall be identified in such a way so that there is no confusion that the method has been modified.

~~When it is necessary to use methods not covered by reference methods, these shall be subject to agreement with the client and shall include a clear specification of the client's requirements and the purpose of the environmental test. The method developed shall have been validated appropriately before use.~~

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.

~~a) The laboratory shall validate reference methods via the procedures specified in Sections 1.5.12 and 1.5.3Refer to Volume 1 Module 2, Section 5.4.5.~~

a) 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 1.6 can satisfy the requirements of 1.5.23.

b) 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.

~~The laboratory shall validate non-reference methods, laboratory-designed/developed methods, reference methods used outside their published scope, and amplifications and modifications of reference methods to confirm that the methods are fit for the intended use. The validation shall be as extensive as is necessary to meet the needs of the given application or field of application. The laboratory shall record the results obtained, the procedure used for the validation, and a statement as to whether the method is fit for the intended use. In the absence of other specifications, the minimum requirements for method validation are given in Sections 1.5.2, 1.5.3 and 1.5.4.~~

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 Limit of Detection (LOD)

If the laboratory is not reporting a value below the Limit of Quantitation, a Limit of Detection study is not required, unless specified by the method.

An LOD study is not required for physical parameters, for any component for which spiking solutions are not available or for any test that does not use a calibration curve (e.g., residues, specific conductance, chlorophyll, or titrimetric determinations~~,etc.~~).

The laboratory shall utilize a method that provides an LOD that is appropriate and relevant for the intended use of the data. If a mandated method or regulation includes ~~protocols~~ procedures for determining detection limits, these shall be followed. The laboratory shall document how LODs were derived from the determinations. If the protocol for determining the LOD is not specified, the selection of the procedure shall reflect instrument limitations and the intended application of the method.

All sample-processing and analysis steps of the analytical method shall be included in the determination or validation of the LOD.

a) When required, the laboratory shall determine or verify the LOD for the method for each target analyte of concern in the quality system matrices.

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b) The LOD shall be initially determined for the analytes of interest in each method in a quality system matrix in which there are neither target analytes nor interferences at a concentration that would impact the results or the LOD shall be performed in the quality system matrix of interest.

c) An LOD shall be performed each time there is a change in the method that affects how the test is performed, or when a change in instrumentation occurs that affects the sensitivity of the analysis.

d) The LOD, if required, shall be verified annually for each quality system matrix, technology, and analyte.

e) The validity of the LOD shall be verified by detection (a value above zero) of the analyte(s) in a QC sample in each quality system matrix. This QC sample shall contain the analyte at no more than 3X the LOD for single analyte tests and 4X the LOD for multiple analyte tests. This verification shall be performed on every instrument that is to be used for analysis of samples and reporting of data. The validity of the LOD shall be verified as part of the LOD determination process. This verification shall be done prior to the use of the LOD for the sample analysis.

~~c) An LOD study is not required for any component for which spiking solutions or quality control samples are not available such as temperature.~~

~~dc) The LOD shall be initially determined for the compound analytes of interest in each method in a quality system matrix in which there are neither target analytes nor interferences at a concentration that would impact the results or the LOD shall be performed in the quality system matrix of interest.~~

~~ed) An LOD shall be performed each time there is a change in the method that affects how the test is performed, or when a change in instrumentation occurs that affects the sensitivity of the analysis.~~

~~fe) The LOD, if required, shall be verified annually for each quality system matrix, technology, and analyte.~~

1.5.2.2 Limit of Quantitation (LOQ)

The LOQ must be established for each analyte in a reported test. A determination of an LOQ is not required for physical parameters, for any ~~component~~ analyte for which spiking solutions are not available or for any test that does not use a calibration curve (e.g., residues, specific conductance, chlorophyll, or titrimetric determinations ~~etc.~~). While an LOQ determination may not be required, some methods or regulations require reporting to a specific level or restrict reporting values below a certain level (e.g., BOD and residues).

~~When required, t~~The laboratory shall establish the LOQ by:

- using test conditions or instrument restrictions (e.g., sample volume, accuracy of balance, method QC requirements) or
- by a study using spiked samples (when required). ~~If spiking samples is not an option, or the laboratory shall determine an appropriate LOQ or as the basis~~

a) All sample-processing and analysis steps of the analytical method shall be included in the determination of the LOQ.

~~b) The LOQ study is not required for any component or property for which spiking solutions or quality control samples are not available or otherwise inappropriate (e.g., pH).~~

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~~e~~b) The LOQ shall be verified annually for each quality system matrix, technology, and analyte. Such verification shall be performed on every instrument that is to be used for analysis of samples and reporting of data unless~~However, the annual LOQ verification is not required~~ if the LOD was determined or verified annually on that instrument.

c) The validity of the LOQ shall be verified by successful analysis of a QC sample containing the analytes of concern in each quality system matrix at 1 to 2 times the claimed LOQ. A successful analysis is one where the recovery of each analyte is within the laboratory-established method acceptance criteria or client data quality objectives for accuracy.

d~~e~~) When an LOD is determined or verified by the laboratory, the LOQ shall be above the LOD.

~~e~~d) ~~The LOQ shall be verified annually for each quality system matrix, technology, and analyte. However, the annual LOQ verification is not required if the LOD was determined or verified annually on that instrument.~~

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 limit of quantitation, 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

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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) ~~Prior to~~ An individual who performs any activity involved with preparation and/or analysis of samples must have constant, close supervision until ~~acceptance and institution of any method for which data will be reported,~~ a satisfactory initial DOC is required (see Section 1.6.2).

b) Thereafter, ongoing DOC (Section 1.6.3), as per the quality control requirements in Section 1.7.3 (such as laboratory control samples) is required.

c) In cases where ~~a laboratory analyzes~~an individual has prepared and/or analyzed samples using a method that has been in use by the laboratory for at least one year prior to applying for accreditation, and there have been no significant changes in instrument type, ~~personnel~~ 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) For the initial DOC, appropriate records as discussed in Section 1.6.2 shall be completed.

e) An initial DOC shall be completed each time there is a change in instrument type, personnel, or method.

f) 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 A~~a~~n initial DOC ~~shall be conducted~~ prior to using any method (see 1.6.1 a) above), and at any time there is a change in instrument type, ~~personnel~~ or method or any time that a method has not been performed by the ~~laboratory or~~ 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)~~, or measured parameter(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.

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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 limit of quantitation.

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 ~~parameter~~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 ~~parameter~~analytes meet the acceptance criteria, the analysis of actual samples may begin. If any one of the ~~parameter~~analytes does not meet the acceptance criteria, the performance is unacceptable for that ~~parameter~~analyte.

e) When one or more of the tested ~~parameter~~analytes fail at least one 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 ~~parameter~~analytes of interest beginning with b) above.

ii. Beginning with b) above, repeat the test for all ~~parameter~~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 ~~compound~~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. The analyst(s) shall demonstrate on-going capability by routinely meeting the quality control 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 (1.6.2) shall be performed. It is the responsibility of the laboratory to document that other approaches to ongoing DOC are adequate.

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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);

Note: 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) would only require documentation for one of the tests.

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 for each method for each analyst each year;

d) a documented process of analyst review using QC samples. QC samples can be reviewed 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 predefined acceptance criteria (as defined by the laboratory or method) shall be performed.

1.7 Technical Requirements

1.7.1 Initial Calibration

1.7.1.1 Instrument Calibration

This module specifies the essential elements that shall define the procedures and documentation for initial instrument calibration and continuing instrument calibration verification to ensure that the data shall be of known quality for the intended use. 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.

The following items are essential elements of initial instrument calibration:

a) the details of the initial instrument calibration procedures including calculations, integrations, acceptance criteria and associated statistics shall be included or referenced in the method SOP. When initial instrument calibration procedures are referenced in the method, then the referenced material shall be retained by the laboratory and be available for review;

b) sufficient raw data records shall be retained to permit reconstruction of the initial instrument calibration (e.g., calibration date, method, instrument, analysis date, each analyte name, 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);

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

d) all initial instrument calibrations shall be verified with a standard obtained from a second manufacturer or from a different lot. Traceability shall be to a national standard, when commercially available;

e) criteria for the acceptance of an initial instrument calibration shall be established (e.g., correlation coefficient or relative percent difference). The criteria used shall be appropriate to the calibration technique employed;

f) the lowest calibration standard shall be at or below the LOQ. Any data reported below the LOQ shall be considered to have an increased quantitative uncertainty and shall be reported using defined qualifiers or explained in the narrative;

g) the highest calibration standard shall be at or above the highest concentration for which quantitative data are to be reported. Any data reported above the calibration range shall be considered to have an increased quantitative uncertainty and shall be reported using defined qualifiers or explained in the narrative;

h) the following shall occur for instrument technology (such as ICP or ICP/MS) with validated techniques from manufacturers or methods employing standardization with a zero point and a single point calibration standard:

i. Prior to the analysis of samples, the zero point and single point calibration standard shall be analyzed and the linear range of the instrument shall be established by analyzing a series of standards, one of which shall be at or below the LOQ. Sample results within the established linear range will not require data qualifiers.

ii. A zero point and single point calibration standard shall be analyzed with each analytical batch.

iii. A standard corresponding to the limit of quantitation shall be analyzed with each analytical batch and shall meet established acceptance criteria.

iv. The linearity is verified at a frequency established by the method and/or the manufacturer.

i) if the initial instrument calibration results are outside established acceptance criteria, 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 instrument calibration shall be reported with appropriate data qualifiers; and

j) if a reference or mandated method does not specify the number of calibration standards, the minimum number of points for establishing the initial instrument calibration shall be three.

1.7.2 Continuing Calibration

When an initial instrument calibration is not performed on the day of analysis, the validity of the initial calibration shall be verified prior to sample analyses by a continuing instrument calibration verification with each analytical batch. The following items are essential elements of continuing instrument calibration verification.

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

b) Calibration shall be verified for each ~~compound~~analyte, 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) Instrument calibration verification shall be performed:

i. at the beginning and end of each analytical batch. If an internal standard is used, only one verification needs to be performed at the beginning of the analytical batch;

ii. if the time period for calibration or the most recent calibration verification has expired; or

iii. for analytical systems that contain a calibration verification requirement.

d) 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 verification data to the initial instrument calibration.

e) 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 and analysis of a second consecutive (immediate) calibration verification fails to produce results within acceptance criteria, corrective actions shall be performed. The laboratory shall demonstrate acceptable performance after corrective action with two consecutive calibration verifications, or a new initial instrument calibration shall be performed. If the laboratory has not verified calibration, sample analyses may not occur until the analytical system is calibrated or calibration verified. If samples are analyzed using a system on which the calibration has not yet been verified the results shall be flagged. Data associated with an unacceptable calibration verification may be fully useable under the following special conditions:

i. 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

ii. 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.

1.7.3 Quality Control

The laboratory shall have quality control procedures for monitoring the validity of environmental tests undertaken as specified in this Section.

1.7.3.1 Negative Control – Method Performance: Method Blank

a) The method blank is used to assess the samples in the preparation batch for possible contamination during the preparation and processing steps. The method blank shall be processed along with and under the same conditions as the associated samples to include all steps of the analytical procedure. Procedures shall be in place to determine if a method blank is contaminated. Any affected samples associated with a contaminated method blank shall be reprocessed for analysis or the results reported with appropriate data qualifying codes.

b) The method blank shall be analyzed at a minimum of one (1) per preparation batch. In those instances for which no separate preparation method is used (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, not to exceed the analysis of twenty (20) environmental samples, not including method blanks, LCS, matrix spikes and matrix duplicates.

c) The method blank shall consist of a quality system matrix that is similar to the associated samples and is known to be free of the analytes of interest.

d) Method blanks are not applicable for certain analyses, such as pH, Conductivity, Flash Point and Temperature.

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

1.7.3.2.1 The LCS is used to evaluate the performance of the total analytical system, including all preparation and analysis steps. Results of the LCS are compared to established criteria and, if found to be outside of these criteria, indicates that the analytical system is "out of control." Any affected samples associated with an out of control LCS shall be reprocessed for re-analysis or the results reported with appropriate data qualifying codes.

1.7.3.2.2 The LCS shall be analyzed at a minimum of one (1) per preparation batch. Exceptions would be for those analytes for which no spiking solutions are available, such as total suspended solids, total dissolved solids, total volatile solids, total solids, pH, color, odor, temperature, dissolved oxygen or turbidity. In those instances for which no separate preparation method is used (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, not to exceed the analysis of twenty (20) environmental samples, not including method blanks, LCS, matrix spikes and matrix duplicates.

1.7.3.2.3 The LCS is a quality system matrix, known to be free of analytes of interest, spiked with known concentrations of analytes.

Note: The matrix spike may be used in place of this control as long as the acceptance criteria are as stringent as for the LCS.

Alternatively, the LCS may consist of a media containing known and verified concentrations of analytes or as Certified Reference Material (CRM). All analyte concentrations shall be within the calibration range of the methods. The following shall be used in choosing components for the spike mixtures:

The components to be spiked shall be as specified by the mandated method or regulation or as requested by the client. In the absence of specified spiking components, the laboratory shall spike per the following:

a) for those components that interfere with an accurate assessment, such as spiking simultaneously with technical chlordane, toxaphene and PCBs, the spike shall be chosen that represents the chemistries and elution patterns of the components to be reported; and

b) for those methods that have extremely long lists of analytes, a representative number 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:

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

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

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

1.7.3.3 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 Quality Control (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.

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.

1.7.3.3.1 Matrix Spike; Matrix Spike Duplicates

a) Matrix-specific QC samples indicate the effect of the sample matrix on the precision and accuracy of the results generated using the selected method. The information from these controls is sample/matrix specific and would not normally be used to determine the validity of the entire batch.

b) The frequency of the analysis of matrix spikes are as specified by the method or may be determined as part of the contract review process.

c) The components to be spiked shall be as specified by the mandated 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:

For those components that interfere with an accurate assessment such as spiking simultaneously with technical chlordane, toxaphene and PCBs, the spike shall be chosen that represents the chemistries and elution patterns of the components to be reported.

For those methods that have extremely long lists of analytes, a representative number 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.

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

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

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

1.7.3.3.2 Matrix Duplicates

a) Matrix duplicates are defined as replicate aliquots of the same sample taken through the entire analytical procedure. The results from this analysis indicate 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 may be determined as part of the contract review process.

c) Matrix duplicates are performed on replicate aliquots of actual samples. The composition is usually not known.

1.7.3.3.3 Surrogate Spikes

a) Surrogates, when required, are chosen to reflect the chemistries of the targeted components of the method and are added prior to sample preparation/extraction.

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

c) Surrogate compounds are chosen to represent the various chemistries of the target analytes in the method. They are often specified by the mandated method and are deliberately chosen for their being unlikely to occur as an environmental contaminant. Often this is accomplished by using deuterated analogs of select compounds.

1.7.3.4 Data Reduction

The procedures for data reduction, such as use of linear regression, shall be documented.

1.7.3.5 Reagent Quality, Water Quality and Checks

a) In methods where the purity of reagents is not specified, analytical reagent grade shall be used. Reagents of lesser purity than those specified by the method shall not be used. Documentation of purity shall be available.

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 written laboratory procedures.

1.7.3.6 Selectivity

The laboratory shall document selectivity by following the checks established within the method.

1.7.4 Data Acceptance/Rejection Criteria

1.7.4.1 Negative Control – Method Performance: Method Blank

While the goal is to have no detectable contaminants, each method blank shall be critically evaluated as to the nature of the interference and the effect on the analysis of each sample within the batch. The source of contamination shall be investigated and measures taken to minimize or eliminate the problem and affected samples reprocessed or data shall be appropriately qualified if:

a) the concentration of a targeted analyte in the blank is at or above the reporting limit as established by the method 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; and

c) a blank is determined to be contaminated. The cause shall be investigated and measures taken to minimize or eliminate the problem. Samples associated with a contaminated blank

shall be evaluated as to the best corrective action for the samples (e.g., reprocessing or data qualifying codes). In all cases the corrective action shall be documented.

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

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

The individual LCS is 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 or utilize client specified assessment criteria.

An LCS that is determined to be within the criteria effectively establishes that the analytical system is in control and validates system performance for the samples in the associated batch. Samples analyzed along with an LCS determined to be "out of control" shall be considered suspect and the samples reprocessed and re-analyzed or the data reported with appropriate data qualifying codes. 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) and there are associated samples that are non-detects, then those non-detects may be reported with data qualifying codes; or

ii. when the acceptance criteria for the positive control are exceeded low (i.e., low bias), those sample results 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 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 corrective action is necessary. This marginal exceedance approach is relevant for methods with long lists of analytes. It will not apply to target analyte lists with fewer than eleven analytes.

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 consecutively, it is an indication of a systemic problem. The source of the error shall be located and corrective action taken. Laboratories shall have a written procedure to monitor the application of marginal exceedance allowance to the LCS.

1.7.4.3 Sample Specific Controls

a) Matrix Spike; Matrix Spike Duplicates

The results from matrix spike/matrix spike duplicate are primarily designed to assess the precision and accuracy of analytical results in a given matrix and are expressed as percent recovery (%R), relative percent difference (RPD), or other appropriate statistical technique that allows comparison to established acceptance criteria. The laboratory shall document the calculation for %R, RPD or other statistical treatment 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 and document the method used to establish the limits. For matrix spike results outside established criteria, corrective action shall be documented or the data for that sample reported with appropriate data qualifying codes.

b) Matrix Duplicates

The results from matrix duplicates are primarily designed to assess the homogeneity of the particular sample chosen. If that sample is homogenous it may also describe the precision of analytical results in a given matrix. These may be expressed as relative percent difference (RPD) or another statistical treatment (e.g., absolute differences).

The laboratory shall document the calculation for relative percent difference or other statistical treatments.

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. For matrix duplicates results outside established criteria, corrective action shall be documented 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 corrective 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.

1.7.5 Sample Handling

a) All samples that require thermal preservation shall be considered acceptable if the arrival temperature of a representative sample container is either within 2°C of the required temperature or the method 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.

i. Samples that are delivered to the laboratory on the same day they are collected may not meet the requirements of Section 1.7.5.a. In these cases, the samples shall be considered acceptable if the samples were received on ice.

ii. If sample analysis is begun within fifteen (15) minutes of collection, thermal preservation is not required.

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

b) The laboratory shall implement procedures for checking sample preservation using readily available techniques, such as pH or chlorine, prior to or during sample preparation or analysis. An exception is allowed for volatile organic ~~compound~~analyte analyses; chemical preservation may be checked after analysis.