Volume 1 Module 4: Quality Systems for Chemical Testing

1.5.1 DoD/DOE (Requirement)

In addition to TNI 1.5.1.a) and 1.5.1.b), the following is required:

c) The laboratory must evaluate non-standard methods (including laboratory-developed methods) using quality control procedures and acceptance criteria that are consistent with those of similar standard methods or technology and must include the following:

i) Scope;

ii) Calibration;

iii) Interferences/contamination;

iv) Analyte identification;

v) Analyte quantitation;

vi) Selectivity;

vii) Sensitivity;

viii) Precision; and

ix) Bias.

d) The use of any non-standard method requires an approval by DoD/DOE personnel.

e) DoD/DOE consider method modifications that include a change of stoichiometry, technology, mass tuning acceptance criteria, and quantitation ions as modifications that require method validation.

1.5.1 DoD/DOE (Guidance)

DoD/DOE allows method modifications as described in the November 20, 2007 USEPA Memorandum on method flexibility.

Methods that are not published in Standard Methods for the Examination of Water and Wastewater or Multi-Agency Radiological Laboratory Analytical Protocols Manual, or by recognized entities such as USEPA, USDOE, ASTM, or NIOSH, are considered non-standard methods.

1.5.2.1. DoD/DOE (Requirement)

The following shall be implemented in lieu of TNI 1.5.2.1.b:

b) A laboratory shall establish a detection limit (DL) using a scientifically valid and documented procedure for each suite of analyte-matrix-method, including surrogates. The DL may be established based on historical data. The DL shall be used to determine the LOD for each analyte and matrix as well as for all preparatory and cleanup methods routinely used on samples.

As a minimum for DoD-ELAP accreditation, each preparation method listed on the scope of accreditation must have quarterly LOD/LOQ verifications. Not all possible combinations of preparation and cleanup techniques are required to have LOD/LOQ verifications. However, if LOD/LOQ verifications are not performed on all combinations, the laboratory must base the LOD/LOQ verifications on the worst case basis (preparation method with all applicable cleanup steps).

After each DL determination, the laboratory must immediately establish the LOD by spiking a quality system matrix at a concentration of equal to or greater than (≥) two times the DL. This spike concentration establishes the LOD and the concentration at which the LOD shall be verified. It is specific to each suite of analyte, matrix, and method (including sample preparation). The following requirements apply to the initial LOD establishment and to the LOD verifications.

i) The apparent signal to noise (S/N) ratio at the LOD must be at least three and the results must meet all method requirements for analyte identification (e.g., ion abundance, second column confirmation, or pattern recognition). For data systems that do not provide a measure of noise, the signal produced by the verification sample must produce a result that is at least three standard deviations greater than the mean method blank concentration. This is initially estimated based on a minimum of four method blank analyses and later established with a minimum of 20 method blank results.

ii) If the LOD verification fails, then the laboratory must repeat the DL determination and LOD verification or perform and pass two consecutive LOD verifications at a higher spike concentration and set the LOD at the higher concentration.

iii) The laboratory shall maintain documentation for all DL determinations and LOD verifications.

iv) The DL and LOD must be reported for all analyte-matrix-methods suites, unless it is not applicable to the test or specifically excluded by project requirements.

1.5.2.1. DoD/DOE (Requirement)

The following shall be implemented in lieu of TNI 1.5.2.1.f):

f) For DoD/DOE, the LOD shall be verified quarterly. In situations such as mobile labs or methods set up and used on an infrequent basis, the laboratory may choose to perform LOD verifications on a one per batch basis.

1.5.2.2. DoD/DOE (Requirement)

The following shall be implemented in lieu of TNI 1.5.2.2.c):

c) The laboratory procedure for establishing the LOQ must empirically demonstrate precision and bias at the LOQ for each suite of analyte-matrix-method, including surrogates. The LOQ and associated precision and bias must meet client requirements and must be reported. If the method is modified, precision and bias at the new LOQ must be demonstrated and reported. For DoD/DOE projects, the LOQ must be set within the calibration range, including the lowest calibration level.

1.5.2.2. DoD/DOE (Requirement)

The following shall be implemented in lieu of TNI 1.5.2.2.e:

e) For DoD/DOE, at a minimum, the LOQ shall be verified quarterly. In situations such as mobile labs or methods set up and used on an infrequent basis, the laboratory may perform LOQ verifications on a one per batch basis.

1.6.2. DoD/DOE (Requirement)

The following shall be implemented in addition to TNI 1.6.2

The laboratory shall have a documented procedure for performing the initial demonstration of capability (DOC) for methods used.

Changes in any condition that could potentially affect the precision and bias, sensitivity, or selectivity of the output (e.g., a change in the detector, column type, matrix, method revision, or other components of the sample analytical system) must result in a new initial DOC.

1.7.1.1. DoD/DOE Initial Calibration (Requirement)

The following shall be implemented in lieu of TNI 1.7.1.1.d):

d) All initial instrument calibrations shall be verified with a standard obtained from a second manufacturer prior to analyzing any samples.

The use of a standard from a second lot obtained from the same manufacturer (independently prepared from different source materials) is acceptable for use as a second source standard. The concentration of the second source standard shall be at or near the midpoint of the calibration range. The acceptance criteria for the initial calibration verification must be at least as stringent as those for the continuing calibration verification.

1.7.1.1. DoD/DOE Initial Calibration (Requirement)

The following shall be implemented in lieu of to TNI 1.7.1.1.j):

j) The initial calibration range shall consist of a minimum of five calibration points for organic analytes and three calibration points for inorganic analytes and Industrial Hygiene samples (except metals by ICP-AES or ICP-MS with a single-point calibration or otherwise stated in the method). All reported target analytes and surrogates (if applicable) shall be included in the initial calibration. Reported results for all target analytes and surrogates shall be quantified using a multipoint calibration curve (except as noted above). Exclusion of calibration points without documented scientifically valid technical justification is not permitted.

1.7.1.1. DoD/DOE Initial Calibration (Requirement)

The following shall be implemented in lieu of TNI 1.7.1.1.g):

g) The LOQ and the highest calibration standard of a multi-level calibration curve establish the quantitation range. For metals analysis with a single-point calibration, the LOQ and the calibration standard establish the quantitation range, which must lie withinin the linear dynamic range.

When sample results exceed the quantitation range, the laboratory shall dilute and reanalyze the sample (when sufficient sample volume and holding time permit) to bring results within the quantitation range. For metals analysis with a single-point calibration, the laboratory may report a sample result above the quantitation range if the laboratory runs and passes a CCV that exceeds the sample concentration but is within the linear dynamic range. Results outside the quantitation range shall be reported as estimated values and qualified using appropriate data qualifiers that are explained in the case narrative.

1.7.2. DoD/DOE (Requirement)

The following shall be implemented in addition to TNI 1.7.2.c) i) through iii):

iv) The concentration of the CCV standard shall be between the low calibration standard and the midpoint of the calibration range.

1.7.2. DoD/DOE (Requirement)

The following shall be implemented in addition to TNI 1.7.2.d):

d) All CCVs analyzed must be evaluated and reported. If a CCV fails, corrective actions must be taken.

1.7.2. DoD/DOE (Requirement)

The following shall be implemented in lieu of TNI 1.7.2.e):

i) If a CCV fails, the laboratory can immediately analyze two consecutive CCVs.

ii) Both of these CCVs must meet acceptance criteria in order for the samples to be reported without reanalysis.

iii) If either of these two CCVs fail or the if the laboratory cannot immediately analyze two CCVs, the associated samples cannot be reported and must be reanalyzed

iv) Take corrective action(s) if the above scenario fails until an acceptable CCV is obtained. All affected samples since the last acceptable CCV must be reanalyzed.

v) Flagging of data for a failed CCV is only appropriate when the affected samples cannot be re-analyzed. The laboratory must notify the client prior to reporting data associated with a failed CCV.

1.7.3.2.3. DoD/DOE (Requirement)

The following shall be implemented in lieu of TNI 1.7.3.2.3.b):

b) All target analytes must be spiked in the LCS (with the exception of Aroclor analysis, which is spiked per the method). Target analytes are identified by the project on a project-specific basis. This may require the preparation of multiple LCSs to avoid interferences.

The concentration of the spiked compounds shall be at or below the midpoint of the calibration.

c) A laboratory shall establish LCS in-house limits that:
   i) Are statistically-derived based on in-house historical data, using scientifically valid and documented procedures;
   ii) Meet the limits specified by the project or as stated in the method, if available;
   iii) Are updated on an at least an annual basis or as stated in the method, whichever is more frequent, and re-established after major changes in the analytical process (e.g., new instrumentation);
   iv) Are based on at least 30 data points generated under the same analytical process; and
   v) Do not exclude failed LCS recovery data and statistical outliers from the calculation, unless there is a scientifically valid and documented reason (e.g., bad LCS standard, leaking purging cell).
   vi) Control limits may not be greater than ± 3 times the standard deviation of the mean LCS recovery.

d) Control charts shall be maintained and used to detect trends and prevent out-of-control conditions. Control limits shall be continually monitored for shifts in mean recovery, changes in standard deviation, and development of trends. Laboratories may choose representative compounds for control charts for the purpose of trend analysis.

e) The QA Officer or designee shall review control charts at a specified frequency for out-of-control conditions and initiate appropriate corrective actions. Data analysis software may also be used for the statistical evaluation of data for trends and biases.

f) A laboratory must use its in-house statistically established LCS control limits for the purpose of batch control, and its in-house statistically established LCS control limits must be within project-specified LCS control limits (which may have been established based on DoD QSM or method LCS limits).

g) A laboratory with in-house statistically established LCS limits falling within the project-specified LCS limits may use project-specified LCS limits for data reporting. A laboratory may report sample results with batch LCS failing its more stringent in-house control limits, but passing the less stringent project-specified control limits.

1.7.3.3 DoD/DOE (Requirement)

The following shall be implemented in addition to TNI 1.7.3.3:

The results of all MS/MSDs must be evaluated using the same acceptance criteria used for the LCS.

1.7.3.3.1. DoD/DOE (Requirement)

The following shall be implemented in lieu of TNI 1.7.3.3.1.b):

b) Each preparation batch of samples must contain an associated MS and MSD (or matrix duplicate (MD)) using the same matrix collected for the specific project. The requirements for MS/MSD are not applicable to all methods (e.g., certain radiochemical samples, air-testing samples, classic chemistry, and industrial hygiene samples). If adequate sample material is not available, then the lack of MS/MSDs shall be noted in the case narrative. Additional MS/MSDs may be required on a project-specific basis.

1.7.3.3.1. DoD/DOE (Requirement)

The following shall be implemented in lieu of TNI 1.7.3.3.1.c):

c) The MS and MSD must be spiked with all target analytes (with the exception of PCB analysis, which is spiked per the method).

1.7.3.3.1.DoD/DOE (Guidance)

c) Multiple spiked samples may need to be prepared to avoid interferences.

If the known concentration of concern is greater than five times the LOQ, a matrix duplicate (MD) may be analyzed in place of the MSD. A matrix spike is still required. Duplicate analysis should be performed at a minimum frequency of once per preparatory batch per matrix type, and cannot be performed on a blank QC sample.

1.7.3.3.3 DoD/DOE (Requirement)

The following shall be implemented in addition to TNI 1.7.3.3.3 a) thru c)

d) Surrogate spike results shall be compared with project-specific acceptance criteria specified by the client. If project-specific criteria are not available, the laboratory shall compare the results with its in-house statistically established criteria.

1.7.3.5 DoD/DOE (Requirement)

The following shall be implemented in addition to TNI 1.7.3.5 a) through c):

d) The quality (e.g., purity) specifications for all standards and reagents (including water) shall be documented or referenced in SOPs.

1.7.3.6 DoD/DOE (Requirement)

The following shall be implemented in addition to TNI 1.7.3.6:

a) Tentative identification of an analyte occurs when a peak from a sample extract falls within the daily retention time window. Confirmation is necessary when the composition of samples is not well characterized. Confirmation techniques include further analysis using a second column with dissimilar stationary phase, GC/MS (full scan or SIM) or HPLC/MS (if concentration permits), GC or HPLC with two different types of detectors, or by other recognized confirmation techniques.

b) When reporting data for methods that require analyte confirmation using a secondary column or detector, project-specific reporting requirements shall be followed. If project-specific requirements have not been specified, follow the reporting requirements in the method. If the method does not include reporting requirements, then report the results from the primary column or detector, unless there is a scientifically valid and documented reason for not doing so and is concurred with by the client.

c) Results that are unconfirmed, or for which confirmation was not performed, shall be identified in the test report, using appropriate data qualifier flags, and explained in the case narrative.

1.7.4.1 DoD/DOE (Requirement)

The following shall be implemented in lieu of TNI 1.7.4.1 a)

a) The method blank will be considered to be contaminated if:

i) The concentration of any target analyte in the blank exceeds 1/2 the LOQ and is greater than 1/20 the amount measured in any associated sample, or 1/20 the regulatory limit, whichever is greater;

ii) The concentration of any common laboratory contaminant in the blank exceeds the LOQ, and is greater than 1/10 the amount measured in any sample, or 1/10 the regulatory limit, whichever is greater.

iii)

iv) If a method blank is contaminated as described above, then the laboratory shall reprocess affected samples in a subsequent preparation batch, except when sample results are below the LOD. If insufficient sample volume remains for reprocessing, the results shall be reported with appropriate data qualifiers.

1.7.4.2. DoD/DOE (Requirement)

The following shall be implemented in addition to TNI 1.7.4.2.b):

c) Sporadically Marginal Exceedances are not allowed for target analytes (as identified by a project) without project-specific approval.

d) DoD considers the same analyte exceeding the LCS control limit two (2) out of three (3) consecutive LCS to be indicative of non-random behavior, which requires re-analysis of the LCS.