TNI Standard

EL-V1M4 Sections 1.7.1 and 1.7.2

April 2015

Description

This TNI Standard has been taken through all of the voting stages and has received consensus approval by the TNI membership.

It will be incorporated into the next revision cycle of ELV1, scheduled for 2015.

1.7   Technical Requirements

1.7.1   Calibration

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

Calibrations may be performed at the instrumental level (analytical step only) or the method level (analytical plus preparation steps).

1.7.1.1   Initial Calibration

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

The following items are essential elements of initial calibration:

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

b)   sufficient raw data records shall be retained to permit reconstruction of the initial calibration (e.g., calibration date, method, instrument, analysis date, each analyte name, 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)   the laboratory shall use the most recent initial calibration analyzed prior to the analytical batch, unless otherwise specified by the method;

d)   Standards used for calibration shall be traceable to a national standard, when commercially available.

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

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

  ii. The laboratory may remove an entire single standard calibration level from the interior of the calibration curve when the instrument response demonstrates that the standard was not properly introduced to the instrument, or an incorrect standard was analyzed. A laboratory that chooses to remove a calibration standard from the interior of the calibration must remove that particular standard calibration level for all analytes. Removal

of calibration points from the interior of the curve is not to be used to compensate for lack of maintenance or repair to the instrument.

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

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

v. The laboratory may replace a calibration standard provided that

    a. the laboratory analyzes the replacement standard within 24 hours 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 concentration.

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

e) for regression or average response/calibration factor calibrations the minimum number of non-zero calibration standards shall be as specified in the table below. For calibrations not listed below, the number of initial calibration standards must result in at least three statistical degrees of freedom.

Type of Calibration Curve	Minimum number of calibration standards[b]
Threshold Testing[a]	1
Average Response	4
Linear Fit	5
Quadratic Fit	6

[a]The initial one point calibration must be at the project specified threshold level.
[b]Fewer calibration standards and degrees of freedom 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.

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

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

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

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

j)   the laboratory shall use and document a measure of relative error in the calibration.

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

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

   a.   measurement of the Relative Error (%RE)

   Relative error is calculated using the following equation:

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

x_i = True value for the calibration standard
x'_i = Measured concentration of the calibration standard

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

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

or:

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

   Relative Standard Error is calculated using the following equation:

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

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 Relative Standard Error must meet the criterion specified in the method. If no criterion is specified in the method, the maximum allowable RSE shall be numerically identical to the

requirement for RSD in the method. If there is no specification for RSE or RSD in the method, then the RSE shall be specified in the laboratory SOP.

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

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

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

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

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

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 shall 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.

1.7.2 Continuing Calibration Verification (CCV)

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

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

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

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

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

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

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

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

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

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

   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 immediately and the result is within acceptance criteria. Samples analyzed previously shall be considered valid if bracketed by a passing calibration verification sample (refer to 1.7.2(d)). The cause for the failure of the first calibration verification result shall be documented;

   ii. if the cause for the calibration verification failure is not identifiable or has impacted other samples, then corrective action shall be performed and documented. Prior to analyzing samples, the laboratory shall demonstrate acceptable performance after corrective action with calibration verification or a new initial calibration shall be performed. Samples analyzed prior to the calibration verification failure shall be reanalyzed or the results qualified if calibration verification bracketing is required (refer to 1.7.2(d));

   iii. . Data associated with an unacceptable calibration verification may be reported with qualification unless prohibited by the client, a regulatory program or regulation. Data associated with calibration verifications that fail under the following special conditions shall still be qualified, but may use a different qualifier

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

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