

Interim Standard

EL-V1M4 Sections 1.7.1 and 1.7.2

April 2014

Description

The Voting Draft Standard (VDS), dated March 2013, was approved by the membership. It is now presented as an Interim Standard to allow stakeholders to review the changes made to the VDS as a result of persuasive comments received from the voting members. Stakeholders who may subsequently adopt, use, or be accredited to the standard are invited to discuss these changes with the TNI Chemistry Expert Committee and to submit any further comments on these changes.

The changes to the VDS are shown as tracking in this document.

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 such as 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). For certain methods, such as purge and trap or head space analyses, it is not possible to separate sample preparation from the analytical step. The elements presented in this Section may be applied to either instrument or method calibrations, including those where the calibration standards are processed through the sample 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 [instrument](#) calibration shall only be reported with appropriate data qualifiers.

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 [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 [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) the laboratory shall use the most recent initial calibration [standard\(s\)](#) analyzed prior to the analytical batch, unless otherwise specified by the method;

~~d) criteria shall be established by the laboratory for the rejection of any calibration standards analyzed but not used to generate an initial calibration. The reason for the rejection of any calibration standard shall be documented and no data below the lowest or above the highest remaining calibration standard shall be quantitatively reported (see also f and g). The calibration generated from the remaining calibration standards shall satisfy all the requirements specified for initial calibrations. The laboratory shall have a written procedure to address the rejection, removal or replacement of standards (i.e., concentration levels or~~

analyte points) from a calibration curve. Requirements for removal and replacement of standards differ. This procedure shall at a minimum address the following criteria:

i) Removal of standards

- a. At the low and/or high end of the calibration curve, entire concentration levels (i.e., all analytes), or individual analyte points with a poor response (e.g., particularly weak or strong), may be removed.
- b. Only one entire concentration level may be removed from the interior of the calibration curve.
- c. For multi-analyte methods, removal of individual analyte points from the interior of the curve is not permitted.
- d. The remaining points must be sufficient to meet all the requirements of this document (e.g., minimum number of required calibration concentration levels).
- e. When any individual analyte or concentration level is removed from the low or high end of the calibration curve, the working range of the calibration is changed accordingly, and any resulting changes to the LOQ or need for qualification of reported data shall be determined.

ii) Replacement of standards may only occur if:

- a. There is a documented and technically valid reason (e.g., leak in purge vessel, bad injection, all analytes show a significant bias in the same direction).
- b. The replacement level(s) are analyzed within 24 hours of the initial level(s) and prior to sample analysis.
- c. The number of replaced standards allowed is as follows:
 1. Only one level may be replaced from the low or high end of the calibration.
 2. Only one entire concentration level can be replaced from the interior of the calibration curve.

For multi-analyte methods, replacement of individual analyte points from any interior concentration levels of the calibration curve is not permitted.

- 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 be result in at least two statistical degrees of freedom.

Type of Calibration Curve	Minimum number of calibration standards ^b	Degrees of Freedom
Threshold Testing ^a	1	Not Applicable
Average Response	3	2
Linear Fit	4	2
Quadratic Fit	5	2

^aThe initial one point calibration must be at the project specified threshold level.

^bFewer 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 ~~instrument~~-calibration and may not be quantitated from any continuing ~~instrument~~-calibration verification unless otherwise required by regulation, method, or program;
- i) criteria for the acceptance of an initial ~~instrument~~-calibration shall be established (e.g., correlation coefficient or relative standard deviation). The criteria used shall be appropriate to the calibration technique employed;
- j) additionally a measure of relative error in the calibration shall be used and documented for calibrations evaluated using correlation coefficient or coefficient of determination. (the RSD from an average RF calibration is a sufficient measure of relative error). For calibrations using an average response factor, the relative standard deviation (RSD) may be used for the measure of relative error. This analysis may be performed by either:
 - i. measurement of the residual relative error at or near the mid-point of the initial calibration and at the lowest calibration standard. The error at these levels must be less than or equal to the maximum 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. Residual Relative error is calculated by quantitation of the calibration standards using the model (where re-quantitation is not possible, assessment may be performed by analyzing the standards at the lowest and mid-levels). Residual Relative error is calculated using the following equation:

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

x_i = True value for the calibration standard

x'_i = Measured result for concentration of the calibration standard

or:

- ii. measurement of the Relative Standard Error (RSE). The RSE shall be less than or equal to the maximum specified in the method. If no level criterion is specified in the method, the level 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. RSE is calculated by re-fitting the calibration data back to the model, 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 at of calibration level i.

p = Number of terms in the fitting equation.
(average = 1, linear = 2, quadratic = 3).
 n = Number of calibration points.

- 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. Prior to calibration, the laboratory desired linear calibration range of the instrument shall be established by analyzing a series of standards, one of which shall be at or below the LOQ. To establish linearity, the requirements for a linear fit multi-point calibration included in this section (specifically 1.7.1.1 i) and j)) shall be met. Linearity must be established annually and checked at least quarterly with a standard at the top of the linear calibration range, or at the frequency defined by the method.~~
 - iii. The zero point and single calibration standard within the linear ~~calibration~~ range shall be analyzed ~~with each analytical batch~~ at least daily and used to establish the slope of the calibration.
 - iiij. 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.
 - iviii. ~~Sample results within the established linear calibration range will not require data qualifiers. 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 upper reporting limit must be established 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. Linearity must be established annually and checked at least quarterly with a standard at the top of the linear working range, or at the frequency defined by the method.~~ Samples with results above the linear calibration range must be diluted, or the over-range results qualified as estimated values.
- l) for ~~multi-peak analytes (e.g., Arochlors, technical chlordane, toxaphene) using analysis of Arochlors which use~~ a linear through the origin model (or average response factor) it is acceptable to perform an initial multi-point calibration for a subset of ~~analytes (e.g., Arochlors (e.g., a mixture of 1016/1260 in PCB analysis))~~ and to use a one-point initial calibration to determine the calibration factor and pattern recognition for the remaining ~~analytes Arochlors~~;
- m) ~~initial calibration verification~~ Initial Calibration Verification (ICV): all initial ~~instrument~~ calibrations shall be verified with a standard obtained from a second independently prepared lot or from a second manufacturer or from a different lot. Traceability shall be to a national standard, when commercially available;
- 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. with more than 10 analytes where:
- ~~i. the calibration criteria and/or initial verification criteria fail marginally and;~~
 - ~~ii. a successful calibration sensitivity check determination has been performed;~~

~~non-detect sample results may be reported without qualification for initial calibration failure. The demonstration of sensitivity shall be the successful detection of the analyte(s) in the lowest calibration standard (at or below the LOQ) and meeting all identification criteria specified in the method or the SOP. Marginal failure is defined as:~~

Criterion	Allowed exceedance	Example
%RSD or RSE	10%	30% if the criterion is 20%
% Difference, Drift or Recovery	10%	30% if the criterion is 20%
Correlation coefficient or coefficient of determination	0.01	0.980 if the criterion is 0.990

1.7.2 Continuing Calibration Verification (CCV)

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, 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 ~~the mid-point of the calibration range (as determined by the average of the highest and lowest calibration standard)~~ 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 ~~and end~~ of each analytical batch, and at the frequency defined in the method;
 - ii. ~~when the defined time period for calibration or the most recent calibration verification has expired;~~
 - iii. ~~an instrument calibration verification (a second source calibration verification)~~ that passes the continuing calibration verification criteria may be used in place of a continuing calibration verification standard.
 - iv. a laboratory control sample (LCS) may be used in place of a continuing calibration verification for methods where the calibration goes through the same process as the LCS (using the continuing calibration verification ~~limits~~ 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 instrument 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, ~~corrective actions shall be performed. The laboratory shall demonstrate acceptable performance after corrective action with a calibration verification, 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 qualified. Data associated with an unacceptable calibration verification may be fully useable under the following special conditions~~the following steps shall be taken:
- i. if an obvious 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 obvious and/or has the potential to have 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. if samples are analyzed using a system on which the calibration has not been verified, the results shall be qualified. Data associated with an unacceptable calibration verification may be fully useable under the following special conditions:
 - i.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, without qualification for a continuing calibration verification failure; or 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.
 - i. ~~for methods with more than 10 analytes, non-detected analytes that marginally fail the continuing calibration verification low may be reported without qualification for a continuing calibration verification failure if a successful demonstration of~~

~~adequate sensitivity (see section n of the Initial Calibration section for criteria and reporting) has been performed within the same analytical batch. For methods that require bracketing continuing calibration verification standards, successful bracketing demonstrations of sensitivity are also required. Otherwise the samples affected by the unacceptable continuing calibration verification shall be qualified or re-analyzed.~~