Modified Working Draft Standard

EL-V1-M4 Sections 1.7.1 and 1.7.2 (Calibration)

December 2012

Description

A Working Draft Standard (WDS) was presented and discussed during the Environmental Measurement Symposium, Washington DC, on August 7, 2012. This Modified Working Draft Standard (MWDS) was prepared as a result of input received during and after that meeting.

Note. The tracking shows only the proposed changes that have been made to the WDS to create this MWDS. The TNI Chemistry Committee will limit discussion and further input to those marked changes.

1.7 Technical Requirements

1.7.1 Calibration

This module specifies the essential elements that shall define the procedures and documentation for initial calibration and continuing 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.

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

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) the laboratory shall use the most recent initial calibration standard(s) analyzed prior to the analytical batch, unless otherwise specified by ~~this standard~~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 ~~h~~ i) and ~~ii~~)). The calibration generated from the remaining calibration standards shall satisfy all the requirements specified for initial calibrations.

e) 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;

f) Initial calibration verification: 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;

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

h) a measure of relative error in the calibration shall be used and documented for calibrations evaluated using ~~(~~correlation coefficient or coefficient of determination ~~alone are not sufficient) for all calibrations created using a regression analysis~~ (The RSD from an average RF calibration is a sufficient measure of relative error). This analysis may be performed by either:

i. measurement of the residual error at or near the mid-point of the initial calibration and at the point closest to the LOQ. The error at these levels must be less than or equal to the maximum specified in the method. If no criterion for the LOQ level is specified in the method, ~~an appropriate level~~the criterion shall be specified in the laboratory SOP. Residual error is calculated by ~~re-fitting~~quantitation of the calibration ~~data back to~~standards using the model~~, using the following equation:~~ (where ~~re-fitting~~re-quantitation is not possible, assessment may be performed by analyzing the standards at the ~~appropriate~~ LOQ and mid-levels). Residual error is calculated using the following equation:

$$\%\ Residual\ Error = \frac{x_i - x_i'}{x_i} \times 100$$

x_i = True value for the calibration standard
~~x'_i~~ x'_j = Measured result for 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 is specified in the method, ~~an appropriate~~the level shall be specified in the laboratory SOP. RSE is calculated by re-fitting the calibration data back to the model, using the following equation:

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

x_i = True value of the calibration level i.
x'_i = Measured concentration at level i.
p = Number of terms in the fitting equation.
(average = 1, linear = 2, quadratic = 3).
n = Number of calibration points.

i) the lowest calibration standard shall be at or below the ~~LOQ. Any data reported below the LOQ shall be considered to have an increased measurement uncertainty and shall be reported using defined qualifiers or explained in the narrative;~~lowest concentration for which quantitative data are to be reported;

j) 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 measurement uncertainty and shall be reported using defined qualifiers or explained in the narrative;~~

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~~g) and ~~j~~h)) 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.

ii. The zero point and single calibration standard within the linear calibration range shall be analyzed with each analytical batch and used to establish the slope of the calibration.

iii. To verify adequate sensitivity a standard shall be analyzed at or below the ~~LOQ shall also be analyzed with each calibration and shall meet the criteria established by the method or laboratory. The calibration and sensitivity evaluation shall be performed prior to sample analysis~~lowest concentration for which quantitative data are to be reported. This standard shall be analyzed prior to sample analysis with each calibration and shall meet the criteria established by the method. If no criteria exist the laboratory shall specify criteria in the SOP.

iv. Sample results within the established linear calibration range will not require data qualifiers. Samples with results above the linear calibration range must be diluted, or the over-range results qualified as estimated values;~~.~~

l) ~~the minimum number of calibration standards for establishing the initial calibration shall be as specified in the reference or mandated method. If not specified in the method, the minimum number of calibration points shall be per the table below (for common calibration types).~~ 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 ~~regression type~~ calibrations not listed below, the number of initial calibration standards must be sufficient for at least two statistical degrees of freedom.

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

[a]The initial one point calibration must be at the project specified threshold level.

m) for multi-peak analytes (e.g., Arochlors, technical chlordane, toxaphene) using 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 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 ~~(if the assumprtion of a linear model through the origin is appropriate).~~;

n) ~~any analytes detected in samples associated with an initial calibration that does not meet the calibration criteria in the method or laboratory SOP shall, if reported, be qualified as estimated. Non-detected analytes may be reported without qualification in the event of calibration failures if the laboratory has performed a successful demonstration of adequate~~

~~sensitivity. This demonstration shall consist of analysis of a standard at or below the reporting limit with each analytical batch, with detection of all analytes in compliance with all applicable criteria for detection.~~non-detected analytes associated with an initial calibration failing %RSD/E criteria by <10%, or correlation coefficient/coefficient of determination criteria by <0.01, for that analyte may be reported without further qualification if the laboratory has performed a successful demonstration of adequate sensitivity. The demonstration of sensitivity shall be the successful detection (meeting all identification criteria specified in the method or the SOP) of the analyte in a sensitivity check standard. The sensitivity check standard shall be at or below the quantitation limit reported by the laboratory.

1.7.2 Continuing Calibration Verification

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).

d) Instrument continuing calibration verification shall be performed for methods that contain a calibration verification requirement:

   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. when the defined time period for calibration or the most recent calibration verification has expired;

   iii. a starting continuing calibration verification is not required for an analytical batch that contains an initial calibration and ~~an initial~~a second source calibration verification.

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 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 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 qualified. 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 without qualification; or

ii. when the acceptance criteria for the continuing calibration verification are exceeded low (i.e., low bias), ~~those~~ sample results of positively detected analytes may be reported as estimated values if they exceed a maximum regulatory limit/decision level; or~~.~~

iii. non-detected analytes that fail the continuing calibration verification low may be reported ~~without qualification~~ 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 re-analyzed after a new calibration curve has been established, evaluated and accepted.