

**SUMMARY OF THE
TNI ENVIRONMENTAL MEASUREMENT METHODS EXPERT COMMITTEE
MEETING**

DECEMBER 2, 2011

The Committee held a conference call on Friday, December 2, 2011, at 2:00 pm EDT.

1 – Roll call

Richard Burrows, Test America (Lab)	Present
Brooke Connor, USGS (Other)	Absent
Dan Dickinson, NYSDOH (Accreditation Body)	Present
Tim Fitzpatrick, Florida DEP (Lab)	Present
Nancy Grams, Advanced Earth Technologists, Inc. (Other)	Absent
Anand Mudambi, USEPA (Other)	Present
John Phillips, Ford Motor Co., (Other)	Present
Lee Wolf, Columbia Analytical Services (Lab)	Absent
Ken Jackson, TNI administrative support staff	Present

The following Associate Committee members were also present: Francoise Chauvin (NYC DOH), Arthur Denny (TCEQ)

2 – Minutes from November 4, 2011

It was moved by John and seconded by Anand to approve the minutes. All were in favor.

3 – Discussion of the Calibration Standard Approach

Richard presented a proposed draft standard (attachment 1) involving editing the existing Volume 1 Module 4 (Quality System requirements for Chemistry). This would limit new requirements to areas where there are clearly demonstrable weaknesses that are resulting in inaccurate quantitation. New requirements would be kept to a minimum. He said this would give the best chance of the new language being accepted and adopted into a TNI standard.

Nancy had suggested an alternate approach that would use a rigorous scientific basis for the language. This would require multi-replicate calibration levels (multiple standards at the same concentration), since in the absence of these data we cannot have a good understanding of the variance relationship to concentration, and therefore cannot know the most appropriate weighting for the data. Depending on the linearity, stability and variance of the instrument response, multi-replicate calibrations might be needed more or less often, and would control decisions regarding the number of calibration levels needed over a given concentration range.

John said both approaches have merit. He suggested when a method is developed the initial demonstration in the laboratory should require at least 3 replicates of each calibration point to decide the type of curve. After that, however, even for initial calibrations, Richard's approach would be appropriate. Tim suggested if the method is "straight out of the box", a laboratory shouldn't have to go through the initial rigorous validation. However, they should do so if they want to change the calibration method. Richard countered that in the few methods that define initial calibration there is no basis for the calibration type used. Anand asked about new method development, but Richard said the standard should not go into new methods.

Richard presented the scenario of a laboratory doing Method 8270, running 5 replicates of each point for initial calibration, finding some curvature, and putting that into its method SOP. Then if they find no curvature 2 weeks later, what do they do? John said they might adjust to a linear calibration because the instrument is now running better, but they need to make sure it stays that way. Tim said it might be because the detector sensitivity has changed and may keep changing. Richard asked, if the curve was initially linear and then becomes quadratic, should the laboratory make the linear curve fit or change the calibration type? Francoise said, since the quadratic curve could be because the instrument is no longer running optimally, the simplest model (linear) should continue to be used as long as it meets the criteria. Richard asked what should then be done if it meets an unweighted linear fit badly and a quadratic curve would be better. Anand suggested only going for a more complex curve if it really pays off, but requiring a minimum of (say) 5 points for a linear curve. He favored Richard's simpler approach by going for modest changes to the standard as long as there are data to support that approach.

At this point Richard suggested going through the discussion of which calibration issues currently are known to cause inaccurate quantitation, and therefore should be included in a revised standard (attachment 2). The attachment has Nancy's wording in black font and Richard's in red.

- a. Richard suggested these are valid points, but there may not be enough data to show this is the problem. Also, multiple points may cause more problems than we are trying to fix. John suggested fixing "d" and that might fix "a".
- b. It was said this causes unnecessary recalibration and there is less likelihood the analyst will focus on the analytes of real interest. Richard said single-point calibration should be suitable for non-detects.
- c. There was agreement on this point.
- d. It was agreed this is demonstrable.
- e. Unweighted calibration is always a bad choice and this is easy to demonstrate.

- f. Francoise reported that she has a lot of data to show the error on zero due to the intercept. She said a general rule is that the intercept on the concentration axis should be less than one third of the LOQ. She will circulate the data and show what action they take if it fails. Dan said some information should be provided to the laboratories stating how the intercept should behave under certain circumstances and whether it is acceptable to force it through zero.

Richard asked if the Committee members should vote on whether to include these points in the standard. Anand said it should only be done if there are data to show they result in inaccurate quantitation.

The following was moved by Tim and seconded by Anand:

"Include only things in the standard that are known to address issues that lead to inaccuracies and that are practical for implementation on a routine basis."

The motion was approved unanimously.

4 – Next Steps

Within a week Richard will circulate the list of items he thinks are important, and will ask participants by e-mail which they believe need to be addressed and discussed on the next call, which will then be scheduled as soon as convenient..

The meeting adjourned at 3:15 pm

Attachment 1

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 and be appropriate for a given regulation or decision. 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 test 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 test 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 test 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, test 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) A minimum of 6 calibration levels shall be used for any quadratic calibration.
- g) 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;
- h) a measure of relative error in the calibration shall be used. This evaluation may be performed by either:
- i. Measurement of the error at the mid-point (continuing calibration level) of the initial calibration and at the lowest point of the calibration. The error must be less than the maximum specified in the method. If no level is specified in the method, a level shall be specified in the laboratory SOP.
 - ii. Measurement of the Relative Standard Error (RSE). The RSE shall be less than or equal to the level specified in the method or laboratory SOP.
- i) 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;

the highest calibrant must be

Comment [bfc1]: This is in the existing standard, so we can't touch it, is that correct??

Comment [bfc2]: This should go after (i).

Comment [bfc3]: Are there no criteria for the high cal std? linearity? Skewing curve? Not more than x orders of magnitude??? Anything?

j) 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 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.

Comment [bfc4]: How do you establish linear range.

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.

Comment [bfc5]: So this makes it 3 stds for icp or icpms??

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

Comment [bfc6]: Where the method or manufacturer does not establish a frequency, then xxxx shall be used.

k) 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

l) 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.

m) Any analytes detected in samples associated with an initial calibration that does not meet the calibration criteria in the method or laboratory SOP shall be flagged as estimated.- Non-detected analytes may be reported without flagging if the laboratory has performed a demonstration of adequate sensitivity. This demonstration shall consist of analysis of a standard at or below the reporting limit with each analytical batch, and detection of all analytes.

Comment [bfc7]: Except if a CCV at the 40th injection fails low, because sensitivity is no longer being achieved, we aren't measuring that with a sensitivity check at the beginning of the run.... Is it possible to use a sensitivity check surrogate that can be part of the CCV throughout the run?

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 test 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) Calibration verification shall be performed at or below the mid-point of the calibration curve.
- d) 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.
- e) Sufficient raw data records shall be retained to permit reconstruction of the continuing instrument calibration verification (e.g., test 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 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.
 - iii. When analytes are not detected in the samples and a demonstration of adequate sensitivity has been performed within the number of samples between each CCV.

Attachment 2

Discussion of which calibration issues currently are known to cause inaccurate quantitation (and therefore should be included in a revised standard).

This is language from our old calibration guidance document

Some of the weaknesses listed below are well established and clearly have a negative impact on data quality. Others are more theoretical in nature and it is not always clear whether the additional work required to address the weakness would result in a sufficient return in improved data quality to be worthwhile.

- a. Most methods do not require replicate calibration points, ~~so there is no way of estimating the uncertainty of the calibration.~~ This prevents understanding the relationship of standard deviation to concentration and thus whether weighting is needed because standard deviation is not constant. Individual calibration points strongly affect the calibration. A single deviant point may result in the appearance of curvature in a calibration where replication would have identified the point as an outlier and the calibration as linear.
- b. In most methods no distinction is made between the calibration requirements for analytes that are not detected in the samples vs. analytes that are routinely detected in the samples and are present at concentrations throughout a calibration range. The calibration of analytes that are not routinely detected would be better focused on the range of calibration from detection to minimum quantitation.
- c. Highly regarded statisticians have pointed out that correlation coefficients and coefficients of determination are inappropriate measures for the quality of a calibration – yet they are required to be used in most methods. These statistics give a false sense of calibration quality, when highly problematic calibration points (especially at the lowest concentrations, and therefore for trace determinations) are present.
- d. Calibration verification is usually required to be performed based on the response of a mid-point standard. Therefore this verification quality control does not provide any indication of changes have taken place in the response at the top and bottom ends of the calibration (e.g., has the slope of a linear calibration shifted).
- e. In most EPA methods, unweighted linear regression is allowed and even sometimes preferred without basis for this assumption being required to be proven (i.e., that standard deviation is constant over the range of the calibration). Unweighted linear regression is prohibited in method 1631, an exception. Unweighted regression is appropriate only if both (a) analytical variance is constant along the length of the calibration and (b) the data user is interested in minimizing absolute rather than relative error. Typically neither of these is the case.

- f. In most EPA methods, the intercept is not a controlled parameter in the calibration, or the control is arbitrary (the intercept is required to pass through zero).
- g. Deletion of a calibrant from a curve is not allowed in some methods without the benefit of logical exceptions.

Comment [AM8]: NG - CALIBRANT IS A NEW TERM AND I WOULD SUGGEST NOT USING IT.

1. This is language from my e-mail 11/22/11
 - a. Current measures of calibration quality pass for curves that have very large relative error, especially at the low end of the calibration
 - b. There is little to no assessment of the quality of the calibration at the low end, which leads to highly inaccurate quantitation at levels that are often of critical environmental importance
 - c. Large amounts of effort are invested in demonstrating the ability to quantitate over a range of concentrations for analytes that are not present in the samples. This wasted effort results in a reluctance to calibrate as frequently as is desirable, and a willingness to accept compromised data for analytes that are present in the samples.
 - d. Ongoing calibration verification typically only evaluates one level.
2. Less critical issues, that probably do cause some data quality problems, but not to the extent of the issues above include the following – we may want to include these in a draft standard but should be willing to give on them during negotiation if necessary:
 - a. There is no or little specification for the spacing or number of calibration standards
 - b. There is no clarity regarding acceptance criteria for analytes that are part of a multi analyte method, but have poor performance