SUMMARY OF THE
TNI ENVIRONMENTAL MEASUREMENT METHODS EXPERT COMMITTEE MEETING

AUGUST 7, 2012

The Committee met at the Environmental Measurement Symposium, Washington DC, on Tuesday, August 7, 2012, at 9:00 am EDT.

1 – Roll call

Richard Burrows, Test America (Lab)	Present
Francoise Chauvin, NYC DEP (Lab)	Present
Brooke Connor, USGS (Other)	Present
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)	Present
Ken Jackson, TNI administrative support staff	Present

2 – Minutes from July 20

Action item 20 was changed to "complete". There was some confusion over the wording of the last sentence of Item 3, #4. Ken agreed to re-write the sentence with clearer syntax. It was moved by Anand and seconded by Tim to approve the minutes as amended. All were in favor except John and Brooke who abstained.

3 – Discussion of the Working Draft Standard on Calibration

Those present were provided with the attached draft copy of the Working Draft Standard (WDS), tracked to show proposed changes from the 2009 TNI standard sections on calibration (V1M4). Richard also presented slides (available on the TNI website) to aid in the discussion. Each proposed change to the standard was discussed and input was requested.

The committee agreed on a global change of "instrument calibration" to "calibration".

1.7.1.1 c). The last clause was questioned, and it was determined that it should be "unless otherwise specified by the method" and not by the standard. This was corrected.

1.7.1.1 d). No further changes were proposed, but John suggested reasons for rejection should be included in the guidance document.

1.7.1.1 h). It was suggested that measurement of relative error (first sentence) should be required to be documented. This change was made. In response to a question on whether this is limited to regression analysis, or whether it also includes average response factor, "average response/calibration factor" was added to the end of the first sentence.

In Option (i), it was suggested "re-fitting" should be changed to "re-quantitation". In the last sentence before the equation for % Residual Error, "the appropriate levels" was changed to the more specific "LOQ and mid-levels". Some additional word-smithing for clarification was also agreed.

In Option (ii) it was suggested "appropriate level" is subjective and could lead to auditing difficulties. It was changed to "the level". The use of "re-fitting" was removed.

1.7.1.1 i). A commenter felt the second sentence could be interpreted that measurement uncertainty shall be reported. It was agreed this sentence can be removed. Extended discussion followed on the first sentence requiring the lowest calibration standard to be at or above the LOQ. It was questioned, if a laboratory is working in a range above the LOQ, why it has to calibrate down to the LOQ. A suggestion was to replace LOQ with "reporting limit". Another suggestion was to change the definition of LOQ to the lowest level the laboratory has demonstrated to be quantitative. However, there was concern this could impact other areas of the standard where LOQ is used. It was finally agreed to change the sentence to read "the lowest calibration standard shall be at or below the lowest concentration for which quantitative data are to be reported."

1.7.1.1 j). There was discussion on whether the second sentence really belongs in the reporting section. The sentence was tentatively removed, pending a check on whether the language is already in the reporting section.

1.7.1.1 k). In (i), the reference in parentheses was corrected to read "specifically 1.7.1.1 h) and j)". In (iii) the text was modified to match the new wording in the previous section; i.e., "To verify adequate sensitivity a standard shall be analyzed at or below the lowest concentration for which quantitative data are to be reported". The second sentence was modified to specify that the standard must be analyzed prior to sample analysis. The sentence ending " .. and shall meet the criteria established by the method or laboratory" was considered insufficient to require the laboratory to document the criteria. It was amended to require the laboratory to specify criteria in its SOP.

1.7.1.1 l). It was suggested this section should make it clear that, if the standard is more stringent than the method on the number of calibration points, then the standard requirement must be met. However, it was argued this is a requirement throughout the TNI standard and should not need to be re-stated. It was clarified by stating "the minimum number of non-zero calibration standards shall be as specified in the table below". It was agreed to state at the beginning of the first sentence that this refers to regression or average response/calibration factor calibrations.

1.7.1.1 m). It was pointed out that the current language ("if the assumption of a linear model through the origin is appropriate") does not say what to do if you cannot verify it is linear through the origin. There was a suggestion to add "if allowed by the method". The committee agreed to consider stating what to do if linearity though the origin is not met. It was agreed the use of the word "appropriate" in parentheses was too subjective. The clause in parentheses was therefore removed, and the first sentence was modified to specify use of a linear through the origin model or response factor. It was noted that the method needs to be checked for this terminology. "Pattern recognition" was changed to "chromatographic pattern".

1.7.1.1 n). Tim suggested, and several others concurred, this has nothing to do with calibration and belongs in the reporting section of the standard. Richard suggested leaving it here, since it tells you the initial calibration needs to be run again. He said it could also be repeated in the reporting section. There was a lot of discussion regarding the second sentence ("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".). Some re-wording was suggested, and the committee agreed to do more work due to concerns that were raised at the meeting.

1.7.2. The header was changed to "Continuing Calibration Verification". In 1.7.2 d) iii, "initial calibration verification" was changed to "second source calibration verification". It was noted that 1.7.2 f) iii will need to be revised for consistency with the Initial Calibration section.

4 – Discussion of the Guidance Document

John summarized the main items the committee has identified for the guidance document that will be made available to back up the calibration standard

5 – Next Steps

The Committee will finalize its WDS during the next conference call on August 24. Definitions of calibration and response factor will be added to the glossary.

6 – Adjournment

The meeting was adjourned at 4:45 pm EDT.

LIST OF ACTION ITEMS TO BE COMPLETED

Item No.	Date Proposed	Action	Assigned to:	To be Completed by:
1	1/31/12	Add a definition of Reporting Limit or Quantitation limit to the standard.	Committee	Defer to quantitation sections
2	1/31/12	Continue to consider the concept of routine low-level QC in the standard.	Committee	Ongoing
3	1/31/12	Review Sections 1.5 and 1.6 of the 2009 standard's chemistry module to determine if current calibration requirements are adequate.	Committee	Not determined
4	1/31/12	Spacing of calibration standards will be considered for the guidance document.	Committee	Ongoing
5	2/17/12	Draft language for items in the calibration standard	Richard (Items 1 and 2) Anand (Item 3) Nancy (Item 5) Anand and Francoise (Item 6) Tim (Item 11)	Ongoing
6	2/17/12	Review Volume 1 Module 4 of the 2009 standard to identify any inconsistencies with the new language	All Committee Members	Not determined
7	3/2/12	Add 1-2 sentences under the header 1.7.1 to explain that method is also included in calibration.	John	Complete
8	3/2/12	Clean up the parts of Section 1.7.1 referring to initial calibration and the parts referring to continuing calibration.	Committee	Complete
9	3/2/12	Add criteria for rejection	Committee	Not

Item No.	Date Proposed	Action	Assigned to:	To be Completed by:
		of calibration standards to the guidance document.		determined
10	3/2/12	Add to the guidance document discussion of analysts using the most recent calibration rather than choosing which of 2 or more curves to use.	Committee	Complete (done in the standard)
11	3/2/12	Include a paragraph in the standard that addresses a single-point calibration for P/A testing.	Committee	Complete
12	3/30/12	Check the language does not contradict the existing standard regarding meeting method requirements vs. standard requirements for calibration.	Committee	Not determined
13	3/30/12	Sections 1.7.1.1 j and k will be modified further as a result of the March 30 discussions.	Anand and Francoise	Complete
14	3/30/12	Have the guidance document consider orders of magnitude in deciding the minimum number of standards, and keep a placeholder in Section 1.7.1 to refer to it.	Committee	Not determined
15	3/30/12	Add a definition for threshold testing	Committee	Not determined
16	3/30/12	Richard's, John's and Anand's March 30 changes will be incorporated into a single document.	Ken	Complete
17	5/4/12	Add to the guidance document that Section 1.7.1.1 (g) requirements should also be applicable for average response,	Committee	Not determined

Item No.	Date Proposed	Action	Assigned to:	To be Completed by:
		when you evaluate with the RSD, and that is numerically the same value as the RSE.		
18	5/4/12	Discuss in the guidance document how to check quarterly (ref. Section 1.7.1.1 (j) (i).	Committee	Not determined
19	6/1/12	Bullet points will be drafted for a proposed PowerPoint presentation	Brooke, Richard, Tim, Francoise, Anand	6/18/12
20	6/1/12	Bullet points will be drafted for a slide that will describe the items to be discussed in the guidance document.	John	Complete
21	7/20/12	Explain in the guidance document the difference between MDL and the true detection limit.	Committee	Not determined
21	8/7/12	Reasons for rejection of calibration standards should be included in the guidance document.	Committee	Not determined
22	8/7/12	Add definitions of calibration and response factor to the glossary.	Committee	Not determined

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 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.

1.7.1.1 Initial Calibration

The following items are essential elements of initial instrument calibration:

~~1.~~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;

~~2.~~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;

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 and i). The calibration generated from the remaining calibration standards shall satisfy all the requirements specified for initial calibrations.

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~~c)~~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;

~~d~~f) 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~~g) 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;

h) a measure of relative error in the calibration shall be used (correlation coefficient or coefficient of determination alone are not sufficient) for all calibrations created using a regression analysis. 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 the maximum specified in the method. If no criterion for the LOQ level is specified in the method, an appropriate level shall be specified in the laboratory SOP. Residual error is calculated by re-fitting the calibration data back to the model, using the following equation: (where re-fitting is not possible, assessment may be performed by analyzing the standards at the appropriate levels).

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

x_i = True value for the calibration standard
x'_i = 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 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.

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

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

~~h~~k) ~~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:~~ 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 the analysis of samples, the zero point and single point calibration standard 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.~~ 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.

ii. ~~A zero point and single point calibration standard shall be analyzed with each analytical batch~~ . 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. ~~A standard corresponding to the limit of quantitation shall be analyzed with each analytical batch and shall meet the established acceptance criteria.~~ To verify adequate sensitivity a standard 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.

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

~~i) 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~~

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~~j) 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.~~

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 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) 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).

~~j~~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.

1.7.2 Continuing Calibration

~~When an initial instrument calibration is not performed on the day of analysis, t~~The validity of the initial calibration shall be verified prior to sample analyses by a continuing

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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).

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

iii. ~~for analytical systems that contain a calibration verification requirement.~~ a starting continuing calibration verification is not required for an analytical batch that contains an initial calibration and an initial calibration verification.

~~d~~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.

~~e~~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 ~~flagged~~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~~. 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

~~1.~~ii. when the acceptance criteria for the continuing calibration verification are exceeded low (i.e., low bias), those sample results may be reported as estimated values 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. Non-detected analytes that fail the continuing calibration verification low may be reported without qualification if a demonstration of adequate sensititvity (see section n of the Initial Calibration section) has been performed within the same analytical batch. For methods that require bracketing continuing calibration verification standards, 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.

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