SUMMARY OF THE
TNI ENVIRONMENTAL MEASUREMENT METHODS EXPERT COMMITTEE MEETING

MAY 18, 2012

The Committee held a conference call on Friday, May 18, 2012, at 2:00 pm EDT.

1 – Roll call

Richard Burrows, Test America (Lab)	Present
Francoise Chauvin, NYC DEP (Lab)	Present
Brooke Connor, USGS (Other)	Absent
Dan Dickinson, NYSDOH (Accreditation Body)	Present
Tim Fitzpatrick, Florida DEP (Lab)	Absent
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

Associate Committee member present: Arthur Denny

2 – Continued discussion of Items to Include in the Calibration Section of the Standard

A few typographical errors in section 1.7.1 were first cleaned up. In this call, Section 1.7.2 (Continuing Calibration) was to be discussed, and this is attached.

Paragraphs 1.7.2 (a) and (b) were not amended. John suggested 1.7.2 (c) (i) should become a stand-alone paragraph. There followed discussion of (ii), (iii) and (iv), and Dan suggested replacing "if" with "when" at the beginning of (iii), and Anand suggested "or" should be removed from the end. Richard suggested (iv) should be moved into the sentence at the beginning of (c). Anand felt that (c) (i) should be moved up after paragraph (b), and should be a new (c) with a blanket statement that the concentration of the calibration verification standard shall be equal or less than the mid-point of the calibration range. Then (c) becomes (d) and describes the frequency of the verification. Francoise suggested the first sentence of the introductory paragraph could lead to confusion, so it was decided to remove it. Richard agreed and said it would then be appropriate to have a new paragraph (iv) to state that a starting continuing calibration verification is not required for an analytical batch that contains an initial calibration. Dan said in the new (d) it should state it is a continuing calibration.

Paragraph 1.7.2 (d) becomes (e) and is unchanged.

In Paragraph 1.7.2 (e), which becomes (f), Arthur suggested it would be better under (i) and (ii) to say these are just estimations if the acceptance criteria are exceeded. Richard felt that the non-detects can still be reported without flagging, but for the low bias results it was added to the text that they may be reported as estimated values. Richard then proposed removing the sentence in (ii) beginning "Otherwise the samples affected..". In (iii) there was discussion over demonstration of adequate sensitivity. Dan was concerned that, if the continuing calibration verification fails after the demonstration of adequate sensitivity performed earlier, perhaps the sensitivity has changed in the meantime, so perhaps the sensitivity should be re-checked. Richard suggested adding a sentence that for methods requiring bracketing continuing calibration verification standards, there must also be bracketing of demonstrations of sensitivity. Returning to (i), Anand said it should be stated it is without qualification when the non-detects may be reported. Anand also pointed out the last sentence of (i), beginning "Otherwise…" also applies to (ii) and (iii), so it should be removed from (i) and should just be a separate sentence at the end of section (f).

3 – Next Steps

Richard said a proposed draft needs to be submitted for presentation at the August meeting. He suggested having a vote on the acceptability of the draft for presentation. It was agreed to do this and complete the vote by e-mail, since all members were not present on the call. The following was moved by Anand and seconded by John:

> "We will present the calibration language as it stands (subject to minor editorial and formatting cleanup) as a Working draft standard at the TMI meeting in Washington DC this August."

All present voted in favor. Richard will send this out for e-mail vote by the rest of the committee.

There was discussion on the format for presentation in August and it was agreed that the new version should be compared to the original, so it will be clear what changes have been made. Ken will prepare a cleaned up document showing the changes in a tracking form. It was agreed there should be Powerpoint slides to accompany the presentation at the August meeting. The slides would describe the reasoning behind the significant changes.

There was some inconclusive discussion on whether to complete the calibration guidance document next or proceed to the detection/quantitation standard.

4 – Adjournment

The meeting was adjourned at 3:30 pm EST. The next meeting will be June 1, 2012 at 2:00 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 of calibration standards to the guidance document.	Committee	Not determined
10	3/2/12	Add to the guidance document discussion of	Committee	Complete (done in the

Item No.	Date Proposed	Action	Assigned to:	To be Completed by:
		analysts using the most recent calibration rather than choosing which of 2 or more curves to use.		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, when you evaluate with the RSD, and that is numerically the same value as the RSE.	Committee	Not determined

Item No.	Date Proposed	Action	Assigned to:	To be Completed by:
18	5/4/12	Discuss in the guidance document how to check quarterly (ref. Section 1.7.1.1 (j) (i).	Committee	Not determined

ATTACHMENT

1.7 Technical Requirements

1.7.1 ~~Initial~~ Calibration

Comment [BR1]: Reviewed - OK

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 instrument level (analytical step only) or the method level (analytical plus preparation steps). For certain methods, such as purge & trap or head space analyses, it is not possible to not 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 ~~Instrument~~ Initial 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.~~

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;

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.

~~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;

a measure of relative error in the calibration shall be used (correlation coefficient or~~f~~ coefficient of determination alone are not sufficient) ~~FOR ALL REGRESSION-TYPE CALIBRATIONS~~for all calibrations created using a regression analysis. This evaluation may be performed by either:

Measurement of the residual error at or near ~~(within 10%) of~~ the mid-point ~~(continuing calibration level)~~ of the initial calibration and at the point closest to the LOQ. The error must be less than or equal ~~-~~the maximum specified in the method. If no 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:

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

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

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:
~~level specified in the method or laboratory SOP.~~

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

x_i = True value of the calibration level i.
x'_i = Measured concentration at level i.
p = Number of terms in the fitting equation.

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Comment [BR3]: Reviewed - OK
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Comment [BR4]: Needs review
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(average = 1, linear = 2, quadratic = 3).
n = Number of calibration points.

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

~~h~~j) When test procedures are employed that ~~use~~specify calibration with a single calibration standard and a zero point (blank or zero, however defined by the method), the following shall occur:~~the following shall occur for instrument technology (such as ICP or ICP/MS) with validated techniques from manufacturers or methods employing standardization testing using calibration with a zero point and a single point calibration standard~~:

~~i.~~ Prior to calibration, 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. To establish linearity, the requirements for a linear fit multi-point calibration included in this section (specifically 1.7.1.x.x) shall be met. Linearity must be established annually and checked at least quarterly, or at the frequency defined by the method. ~~Prior to the analysis of samples, the zero point and single point calibration standard shall be analyzed and Ithe 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.~~

i.

~~ii.A zero point and single point calibration standard shall be analyzed with each analytical batch.~~

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

iii. To verify adequate sensitivity a standard corresponding to the LOQ shall also be analyzed with each analytical batch and shall meet the criteria established by the method or laboratory. The calibration and sensitivity evaluation shall be performed prior to sample analysis.~~A standard corresponding to the limit of quantitation shall be analyzed with each analytical batch and shall meet established acceptance criteria~~.

iv. Sample results within the established linear range will not require data qualifiers. Samples with results above the linear range must be diluted, or the over-range results qualified as estimated values~~The linearity is verified at a frequency established by the method and/or the manufacturer~~.

Comment [BR5]: Needs review

Comment [O6]: Does TNI use the routine/standard reporting limit term or is there just LOQ?

Comment [O7]: Should this last statement be below the lowest calibration standard in order to be consistent with other uses? See i.

Comment [BR8]: Needs review

Comment [O9]: Would it not be worth considering a procedure whereby a lab could do a demonstration of linearity (e.g., once a year) and then for as ICP and ICPMS do if criteria for linearity are met? This would open up the potential for more methods with good calibration linearity to do two point calibrations. However, we should also have criteria for linearity – an dperhaps slop.

Comment [O10]: Not sure why the discussion of sample analysis got mixed into this.

Comment [BR11]: Needs review

Comment [O12]: How many standards/? Should there be a minimum per order of magnitude? A TNI minimum? How is linearity established? What are the minimum criteria?

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Comment [O13]: Why is it zero point and some positive point. Could it not be reporting limit level or lower than zero?

Comment [O14]: This material is really material for the calibration verification

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Comment [O15]: Why each batch? Is there any minimum criterion for acceptance?

Comment [O16]: TNI should establish a minimum

v.

~~j)~~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) ~~h~~i. ~~if a reference or mandated method does not specify~~ 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 ~~for establishing the initial instrument calibration for common calibration types shall be three is given~~shall be per ~~in~~ the table below (for common calibration types). ~~For linear regression techniques the number of initial calibration standards must be sufficient for at least one two statistical degrees of~~ For regression type calibrations not ~~included in the table~~listed below, the number of initial calibration standards must be sufficient for at least two statistical degrees of freedom.

~~d. freedom.~~

~~e.~~

Type of ~~Standard~~ Calibration ~~Curve~~	Minimum number of calibration standards	Degrees of Freedom
~~Pass/Fail~~ Threshold Testing [(a)]	1	Not Applicable
Average Response	3	~~Not Applicable~~2
Linear ~~Regression~~ fit	4	2
Quadratic fit	5	2

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

~~f.~~

~~g.~~

~~k~~m). ~~If~~Where ~~specifi~~allowed by~~in~~ the method and for ~~For~~ multi-peak analytes (e.g, ~~PCBs~~Aroclors, technical chlordane, toxaphene), it is acceptable to perform an initial multi point calibration for a subset of analytes (e.g. Aroclors 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 assumption of a linear model through the origin is appropriate)~~an initial one point calibration is allowed which ensures that all representative peaks can detected. In this case the working range is defined by the analyte(s) that do have multi-point calibrations~~.

~~h. Samples with hits shall be reanalyzed and quantitated on a valid multipoint curve. Exception: Samples analyzed for pass/fail testing (threshold testing) do not need to be reanalyzed if the initial one point calibration is at the project specified presence/absence (pass/fail or threshold) level. .~~

~~i.~~

Comment [O17]: What about at the high end? We have not indicated that the positive standard has to be at the top of the calibration range. Should there not be some control on reporting above the positive standard or a QC sample to confirm continued linearity to the highest level the lab reports data without diluting?

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Comment [BR18]: Reviewed – OK?

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Comment [BR19]: Consider adding reference to guidance document for range of calibration

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Comment [BR20]: Add definition for thresho ...

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Comment [BR21]: Reviewed, needs addition ...

Comment [BR22]: Maybe need to add ...

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Comment [CF23]: I believe this requires mor ...

Comment [BR24]: Add definition for thresho ...

~~j.~~

~~k.~~

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 by qualified ~~be flagged~~ as estimated. Non-detected analytes may be reported without qualification~~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, with~~and~~ detection of all analytes in compliance with all applicable criteria for detection.

~~j)~~i)

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Comment [BR25]: Reviewed, may need additional review

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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 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) Instrument calibration verification shall be performed:

i. at a concentration equal to or less than the mid-point of the calibration range (as determined by the average of the highest and lowest calibration standard).

ii 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

iv~~ii~~. for analytical systems that contain a calibration verification requirement.

d) 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) 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. 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~~ii ~~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 (except see following paragraph).

~~iv.~~ ~~iii~~iii. Non-detected analytes that fail the calibration verification low may be reported without flagging if a demonstration of adequate sensitivity (see section k of the Initial Calibration section) has been performed within the same analytical batch.

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Comment [d26]: Concerned about signal drift occurring after the "demonstration of adequate sensitivity" and prior to the CCV. As written, the use of the CCV to check drift is weakened. When a CCV is low, the "demonstration of adequate sensitivity" should be chronologically later in the sequence in order for this clause to be fully valid.