SUMMARY OF THE
TNI CHEMISTRY EXPERT COMMITTEE MEETING

SEPTEMBER 7, 2012

The Committee held a conference call on Friday, September 7, 2012, at 2:00 pm EDT.

1 – Roll call

Richard Burrows, Test America (Lab)	Present
Francoise Chauvin, NYC DEP (Lab)	Absent
Brooke Connor, USGS (Other)	Present
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)	Absent
Lee Wolf, Columbia Analytical Services (Lab)	Absent
Ken Jackson, TNI administrative support staff	Present

Associate Committee members present: Arthur Denny; Dianna Shannon; Gale Warren

2 – Minutes from August 24

In the absence of a quorum, Ken was asked to send out the minutes again for e-mail approval.

3 – Working Draft Standard on Calibration

During the public meeting in Washington DC, the WDS had been tentatively modified (attached). The purpose of this conference call was to verify if these modifications would remain in place and to address written comments from Marlene Moore.

Marlene asked for the term "measurement uncertainty" to be removed from 1.7.1.1 j). She suggested the second sentence should be replaced with "Any data reported above the calibration range shall be reported using defined qualifiers or explained in the narrative". However, it had also been suggested to remove the reporting language and just leave the first sentence. Anand cautioned that if all reporting language is removed, perhaps it will be necessary to refer to the reporting section of the standard. Richard noted a similar suggestion was received for 1.7.1.1 i). At the Washington DC meeting, it had been decided to tentatively remove the reporting language provided it was already adequately covered in the reporting section of the standard. This is V1M2 Section 5.10.3.1, which is the ISO language. The TNI language is Section 5.10.11 d); "Clear identification of numerical results with values outside the calibration range". Brooke suggested this is the section that needs to be modified by incorporating the language under consideration in 1.7.1.1 i) and j). However, it will be some time before that section of the standard is

again presented as a WDS. After a protracted discussion it was decided to leave the language out of 1.7.1.1 i) and j).

It was tentatively decided in Washington DC to change "instrument calibration" to "calibration" throughout the document. The former term had been favored to differentiate from calibration of balances etc. However, it had been argued that "instrument calibration" might infer that method calibration was excluded. The last sentence of 1.7.1 does state that the elements presented in the section may apply to either instrument or method calibration (i.e., calibrations that are processed through the method steps as well as the instrumental measurement step). After some discussion it was decided to leave "instrument calibration", but to change the last sentence of 1.7.1 to read "The elements presented in this Section may be applied to instrument calibrations, including those where the calibration standards are processed through the sample preparation steps".

The tentative changes in 1.7.1.1 c), h), k), l), and m) were clarified as needed by Richard and agreed on without further discussion.

Section 1.7.1.1 n) was flagged in Washington DC as needing work. Richard suggested leaving this until the majority of Committee Members are present to discuss it.

The addition of "Verification" in the header to Section 1.7.2 was agreed. It was questioned whether second source calibration verification of initial calibration was adequately discussed elsewhere, and the language in 1.7.1.1 f) was considered to be adequate. Richard marked this for possible further discussion.

Section 1.7.2 f) iii on non-detected analytes was left for later discussion.

Written comments from the New York State DOH were considered. The following were seen to have not already been addressed. A comment of an incorrect reference in 1.7.1.1 d) was valid and the parenthetical phrase in the second sentence was corrected to "(see also i and j)". A comment on measure of relative error questioned if the measure of error should be done for all calibrations including response factor and not just those involving regression. The answer is that if it is an average response factor you are using the RSD so you are doing that measure, since it will be the same numerical value as the relative error. A typographical error in 1.7.1.1 h) (i) was fixed. The references in 1.7.1.1 k) were corrected to read "(specifically 1.7.1.1 g and h)". In Section 1.7.1.1 d) it had been suggested to add the condition "unless a method SOP allows extension above the highest standard or below the lowest standard by use of additional QC check standard". Dan commented this probably refers to ICP. Richard cautioned that, while this might be appropriate in certain cases, addition of this language could also allow inappropriate use. Dan agreed to discuss these concerns with the New York State DOH scientists who had made the comment, and to ask them if they could propose appropriate language that would limit this to legitimate use.

4 – Adjournment

The meeting was adjourned at 3:15 pm EDT. The next conference call will be on September 21, 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
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

ATTACHMENT

WDS as modified during the Washington DC meeting

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.

1.7.1.1 Initial Calibration

The following items are essential elements of initial ~~instrument calibration~~calibration:

a) the details of the initial ~~instrument calibration~~calibration procedures including calculations, integrations, acceptance criteria and associated statistics shall be included or referenced in the method SOP. When initial ~~instrument calibration~~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~~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~~is~~ ~~standard~~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 and i). 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~~calibration and may not be quantitated from any continuing ~~instrument calibration~~calibration verification unless otherwise required by regulation, method, or program;

f) all initial ~~instrument calibration~~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~~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 and documented (correlation coefficient or coefficient of determination alone are not sufficient) for all calibrations created using ~~a~~ regression analysis or average response / calibration factor. 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~~the criterion shall be specified in the laboratory SOP. Residual error is calculated by ~~re-fitting the~~quantitation of the calibration ~~data back to~~standards using the model~~., using the following equation:~~ (where ~~re-fitting~~requantitation is not possible, assessment may be performed by analyzing the standards at ~~the appropriate levels~~the 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 = 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.~~lowest concentration for which quantitative data are to be reported. ~~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;~~

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;~~

Comment [BR1]: Check this language in the reporting section

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)~~h and ~~j~~l)) 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 lowest concentration for which quantitative data are to be reported.~~LOQ~~ This standard shall be analyzed prior to sample analysis with each calibration ~~shall also be analyzed with each calibration~~ and shall meet the criteria established by the method. If no criteria exist the laboratory shall specify criteria in the SOP.~~or laboratory. The calibration and sensitivity evaluation shall be performed prior to sample analysis.~~

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) for regression or average response/calibration factor calibrations the minimum number of non-zero 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) 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~~chromatographic pattern for the remaining analytes ~~(if the assumprtion of a linear model through the origin is appropriate)~~.

n) any ~~analytes detected in samples~~results 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.

~~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. In this context a not-detected analyte means that there is no signal meeting qualitative identification criteria.

1.7.2 Continuing Calibration Verification

The validity of the initial calibration shall be verified prior to sample analyses by a continuing ~~instrument calibration~~calibration verification with each analytical batch. The following items are essential elements of continuing ~~instrument calibration~~calibration verification.

a) The details of the continuing ~~instrument calibration~~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).

Comment [BR2]: Check terminology in the method

Comment [BR3]: Needs work

Comment [BR4]: Review UCMR3 method criteria
Also not detected means not detected, not present but censored out due to the quant level

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 a~~n initial~~ second source calibration verification.

e) Sufficient raw data records shall be retained to permit reconstruction of the continuing ~~instrument calibration~~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~~calibration verification shall be established. If the continuing ~~instrument calibration~~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~~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 may be reported as estimated values if they exceed a maximum regulatory limit/decision level.

iii. Non-detected analytes that fail the continuing calibration verification low may be reported without qualification if a demonstration of adequate ~~sensititvity~~sensitivity (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.

Comment [BR5]: Fix language to match initial calibration section