SUMMARY OF THE
TNI CHEMISTRY EXPERT COMMITTEE MEETING

SEPTEMBER 21, 2012

The Committee held a conference call on Friday, September 21, 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)	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

Associate Committee member present: Dianna Shannon

2 – Minutes from August 24 and September 7

In the August 24 minutes, page 2 paragraph 4, Francoise said instead of subtracting each blank measurement, it should be the average blank measurement. It was moved by John and seconded by Francoise to approve the minutes with that one change. All were in favor

It was moved by Anand and seconded by Brooke to approve the September 7 minutes as presented. All were in favor except Francoise, John and Tim who abstained.

3 – Working Draft Standard on Calibration

There was a protracted discussion on Section 1.7.1.1 n). A commenter at the Washington DC meeting had asked what about the LCS when something is detected. Richard suggested two options. First, since LCS is a quantitative measure it is not important for samples where there is nothing to quantitate and does not need to be considered for non-detected analytes. Second, instead of a calibration standard providing a demonstration of qualitative identification capability, use a "reporting-level LCS". That would, however, be more difficult for a laboratory. John asked, if it is an analyte the laboratory expects to be a non-detect, if it would then run a reporting-level LCS instead of a typical LCS. Richard responded that the laboratory would probably run both. Brooke suggested you would then want to limit the reporting-level LCS to the end of your run because that is when you need to prove everything before it was present. There was some discussion on the frequency of the reporting-level LCS, and most agreed it need not be with every

batch. Lee spoke against this second option, with questions of how and when it is reported. He suggested looking at the language in 8270D. Anand said if it is called a reporting-level LCS, it would have to be treated as an LCS by running it with every preparation batch. Richard agree it creates something of a cross purpose since this is an instrument issue. Tim added that an LCS requires control limits. Although most methods define LCS control limits, they are not intended to be applied at the quantitation limit. Richard agreed it would have to be called something other than an LCS to avoid laboratories having to use control limits. Brooke suggested "sensitivity check". Francoise would be concerned about moving away from control limits, because there might be a problem with instrument sensitivity at that level. Richard agreed, but said it is going to be sensitive enough to detect at whatever your limit is. Tim said most laboratories would report a non-detect at their detection limit, which could be 1-2 orders of magnitude away from their reporting limit, so with a sensitivity check at their reporting limit they cannot say they didn't detect at their detection limit. Language is needed to prevent someone from doing that. John suggested adding after the second sentence ".. at the quantitation level". In the next sentence ("This demonstration shall consist of analysis of a standards at or below the reporting limit..") he suggested the intent is to be as close to the quantitation limit as reasonable. Richard said perhaps it should be within two times the quantitation limit. Tim stressed that all non-detect results must be censored at the level at which the sensitivity check was done, and John added that sensitivity check should be a spiked standard that has gone through the preparation process. Brooke suggested the following language: "A non-detected analyte may be reported as <xx without qualification in the event of calibration failures if the laboratory has performed a successful demonstration of adequate sensitivity at xx." She volunteered to work on the language before the next conference call. Lee suggested, after the second sentence ending with "..a successful demonstration of adequate sensitivity", stating that data may not be reported lower than the level at which the sensitivity check was run. There was some discussion on whether the next sentence should say the demonstration shall consist of the analysis of an extracted standard, but it was agreed an extracted standard should not be required as long as there is a section written on a sensitivity check with an extracted standard. Therefore, the sentence was changed to "This demonstration shall consist of analysis of a sensitivity check standard….". Richard suggested this may belong in a reporting section and can perhaps be removed from this section when reporting limit has been dealt with. The last sentence was removed, and based on Anand's recommendation, Richard added a new sentence: "The less than value for non-detected analytes may not be below the level of the sensitivity check standard".

Francoise said frequency of analysis has not been mentioned and perhaps the section should refer to section 1.7.2 f) iii. Richard said he would also move this language into the calibration verification part.

Francoise was concerned that TNI requires a second-source verification for the initial calibration, and in this case that requirement would not necessarily have been met; i.e, an incorrect standard may have been used for the sensitivity check. She suggested adding a reference to initial calibration verification to make it clear the second source must pass. There was disagreement on this, with Richard saying it is already stated it is an initial

calibration that does not meet the calibration criteria in the method, and it becomes too complicated putting in references to other paragraphs. Lee suggested moving Section 1.7.1.1 f) to immediately precede section 1.7.1.1 n), and then saying "see criteria above".

At Brooke's suggestion, she and Francoise will both propose alternative language for section 1.7.1.1 n) for the next call. Richard said whatever language is finally chosen, he will also put it in the continuing calibration verification section.

The short time remaining was used for a preliminary discussion of some of Nancy's suggestions on the WDS. She had suggested use of a non-parametric approach for blanks; i.e., in order to set the level at a concentration where it is exceeded by 1% of the blanks, simple counting is used to find the level at which 99 of 100 blanks are below it. Arguments were presented against replacing the statistical approach, including the difficulty of many laboratories (especially small utility laboratories) generating 100 blanks, the assumption that the blanks follow a normal distribution, and a cautionary note that it might be too big a change from the EPA procedure. It was suggested, however, that this could be added as an additional option. Nancy had also commented that verification should be more frequent than quarterly, and some commenters at the Washington DC meeting had said this, however both Richard and Tim felt it would entail running a lot of samples for multi-analyte methods.

Richard said the Committee will revisit Nancy's comments on the next call, besides finishing section 1.7.1.1 n).

4 – Adjournment

The meeting was adjourned at 3:25 pm EDT. The next conference call will be on October 5, 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)~~.

Comment [BR2]: Check terminology in the method

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.

Comment [BR3]: Needs work

~~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.

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

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).

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