DRAFT SUMMARY OF THE
TNI ENVIRONMENTAL MEASUREMENT METHODS EXPERT COMMITTEE MEETING

MARCH 2, 2012

The Committee held a conference call on Friday, March 2, 2012, at 2:00 pm EST.

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)	Present
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: Arthur Denny

2 – Minutes from February 17, 2012

It was moved by John and seconded by Anand to approve the minutes of February 17, as presented. All were in favor. The list of action items was updated.

3 – Discussion of Items to Include in the Calibration Section of the Standard

Prior to the meeting, Richard had circulated an edited Section 1.7 of V1M4 of the 2009 TNI standard (chemistry module; calibration). This is appended as Attachment 1. It included additions and changes proposed by Richard, Anand, Nancy, Francoise and Tim (as assigned in Action Item #5). The proposed amendments to the standard were then discussed.

Section 1.7.1.

Nancy questioned whether the standard should refer to method calibration rather than just instrument calibration, since some methods require calibration standards to be taken through the entire method. Richard added that what is put in the section should also specify when you put the method steps through the entire calibration. John volunteered to add 1-2 sentences under the header 1.7.1 to explain that method is also included in calibration.

It was agreed to change the 1.7.1 header to read "Calibration", and to change 1.7.1.1 to "Initial Calibration". The first paragraph under 1.7.1.1 would then be moved up to 1.7.1. It was pointed out this section includes some reference to continuing calibration, and Richard added an **action item** to clean up the parts referring to initial calibration and the parts referring to continuing calibration.

Section 1.7.1.1 b)

The proposed new paragraph "criteria shall be established…" was discussed. Nancy commented there is nothing stating you have to complete the initial calibration before testing; i.e., that you cannot reject a standard and then add another later. However, in determining PCBs, you might want to put in a calibration curve later if a PCB is suddenly detected. Anand said you should not put in a time restriction for running initial calibration standards. Nancy had added "any requirement for minimum number of calibrants must be met", but it was agreed this can be removed since it is already covered in the next sentence. The word "curve" will be deleted from the first sentence, and "calibration" will be deleted from the last sentence. It was questioned if specific language should be put in rather than just telling the analyst to "establish criteria"; however, it was considered there would be too many alternatives to list. Therefore, it was decided on an **action item** to add criteria for rejection of calibration standards to the guidance document. It could be moved to the standard later if it is seen there is a need. Francoise suggested that "substitution" may be better than "rejection", because analysts should be prevented from generating 2 calibration curves and then deciding which to use. Richard said perhaps it should state they must use the most recent calibration. Nancy suggested putting this is Johns' initial section (in 1.7.1 above). He agreed to do that, but proposed an **action item** to include more discussion of this in the guidance document.

Section 1.7.1.1 c), d), and e)

It was agreed to delete "instrument".

Section 1.7.1.1 e)

It was agreed to add Nancy's words "and documented" and "for all regression type calibrations".

Under "(i)" it was pointed out that error is not specified in most methods. Nancy said a better term then "the maximum specified" is needed, and asked how you measure the error. Perhaps "residual" should be used. It was questioned whether a specific equation should be used for RSE and for error, or if it should be in the terms and definitions. Richard will see if EPA uses it consistently in its methods. It was asked if Nancy's "within 10%" should be left in. There was discussion about defining the mid-point of the calibration, and perhaps it would be better to use the median of the curve. In response to a question, Richard said if there are only 2 calibration standards, you should run the curve and then run another standard at the mid-point. Not everyone agreed with this. Richard said you need clarify what you are measuring the error <u>of</u>. It was suggested specifying

the LOQ rather than the lowest point of the calibration. Richard will take the comments into account and will rewrite the section.

Section 1.7.1.1 f)

It was questioned, if the lowest standard is below the LOQ, whether you need to qualify the data at that level. Richard will edit this section.

Section 1.7.1.1 g)

Although there had been no changes to this section, Richard said he will edit it.

Section 1.7.1.1 h)

Anand questioned if this section is really needed, and if so whether it should refer to anything more than ICPAES and ICPMS. Tim remarked that pH and conductivity could also be included. Richard suggested adding a requirement to run check standards along various points of the calibration curve (this is already in the new 6010 method). Lee agreed to re-write this section.

Section 1.7.1.1 j)

There was discussion about the minimum number of points that should be specified. It was asked if it should be 5. Dan said 3 was specified because it allows one degree of freedom. He added you could say 3 is sufficient for a linear curve and 4 is needed for a second-order curve, but perhaps that much detail should not be in the standard. Lee agreed the standard should be kept simple, but with more detail in the guidance document. Nancy added that some methods may only need one calibration standard if just testing for excedance of a specific limit, so the standard should not specify a minimum of 3 points. Anand will add a table for the number of standards, and will decide if he should include the number of degrees of freedom allowed. Suggested language changes were to refer to average response factor or regression curve calibrations.

An **action item** is to include a paragraph in the standard that addresses a sinle-point calibration for P/A testing.

Section 1.7.1.1 k)

In the first paragraph, Brooke suggested changing “reanalyzed” to “quantitated” to remove the requirement to re-analyze. Nancy suggested this section could be used to include single-point quantitation.

In considering Nancy’s comments on “(iii) it was agreed this is a J-flag. There was inconclusive discussion on whether “at least one”, and “before and after’ (i.e., bracketing) are important. In response to Nancy’s question Richard confirmed a calibration standard

can be used; it doesn't need to be a QC sample or even an extracted standard. It was thought to be impractical to ask analysts to run a calibration check with each analytical batch. Tim suggested stating an LOQ could be run after the sample if you want to report it without qualification. Richard will edit this section.

5 – Adjournment

The meeting was adjourned at 3:45 pm EST. The next meeting will be March 30, 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	John	3/30/12

Item No.	Date Proposed	Action	Assigned to:	To be Completed by:
		explain that method is also included in calibration.		
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	Not determined
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 analysts using the most recent calibration rather than choosing which of 2 or more curves to use.	Committee	Not determined
11	3/2/12	Include a paragraph in the standard that addresses a single-point calibration for P/A testing.	Committee	Not determined

ATTACHMENT 1

1.7 Technical Requirements

1.7.1 Initial Calibration

METHOD CALIBRATION – SHOULD WE INDICATE IT IS ACCEPTABLE WHERE ALLOWED, MATERIALS BELOW ARE SPECIFIC TO INSTRUMENT CALIBRATION, BUT MAY ALSO APPLY TO METHOD?

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.

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);

criteria shall be established by the laboratory for the rejection of any calibration standards ANALYZED BUT NOT used to generate an initial calibration curve. 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 f and g) AND ANY REQUIREMENT FOR MINIMUM NUMBER OF CALIBRANTS MUST BE MET. The curve generated from the remaining calibration standards shall satisfy all the requirements specified for initial calibrations.

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c) sample results shall be quantitated from the initial ~~instrument~~ calibration and may not be quantitated from any continuing instrument calibration verification unless otherwise required by regulation, method, or program;

d) all initial instrument calibrations shall be verified with a standard obtained from a second manufacturer or from a different lot. Traceability shall be to a national standard, when commercially available;

e) criteria for the acceptance of an initial instrument calibration shall be established (e.g., correlation coefficient or relative percent difference) AND DOCUMENTED. 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 is not sufficient) FOR ALL REGRESSION-TYPE CALIBRATIONS. This evaluation may be performed by either:

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i. Measurement of the error at or near (within 10%) of the mid-point ~~(continuing calibration level)~~ of the initial calibration and at the lowest point of the calibration. The error must be less than the maximum specified in the method. If no level is specified in the method, a level shall be specified in the laboratory SOP. HOW DOES ONE MEASURE THE ERROR? %DIFF %RECOVERY CAN WE PUT A MAXIMUM VALUE ON THIS OR STRATEGICALLY WAIT UNTIL ANOTHER PASS.

ii. Measurement of the Relative Standard Error (RSE). The RSE shall be less than or equal to the level specified in the method or laboratory SOP. HOW DOES ONE DETERMINE THE RSE?

f) the lowest calibration standard shall be at or below the LOQ DOES TNI USE THE ROUTINE/STANDARD REPORTING LIMIT TERM OR IS THERE JUST LOQ?. Any data reported below the LOQ shall be considered to have an increased quantitative uncertainty and shall be reported using defined qualifiers or explained in the narrative; SHOULD THIS LAST STATEMENT BE BELOW THE LOWEST CALIBRATION STANDARD IN ORDER TO BE CONSISTENT WITH OTHER USES?? SEE G.

g) the highest calibration standard shall be at or above the highest concentration for which quantitative data are to be reported. Any data reported above the calibration range shall be considered to have an increased quantitative uncertainty and shall be reported using defined qualifiers or explained in the narrative;

h) the following shall occur for TESTING ~~instrument technology (such as ICP or ICP/MS) with validated techniques from manufacturers or methods~~ USING CALIBRATION ~~employing standardization~~ with a zero point and a single point calibration standard: WOULD IT NOT BE WORTH OUR CONSIDERING A PROCEDURE WHERE BY 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 – AND PERHAPS SLOPE.

i. ~~Prior to the analysis of samples, the zero point and single point calibration standard shall be analyzed and~~ ??NOT SURE WHY THE DISCUSSION OF SAMPLE ANALYSIS GOT MIXED INTO THIS ??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. HOW MANY STANDARDS, SHOULD THERE BE A MINIMUM PER ORDER OF MAGNITUDE? A TNI MINIMUM. HOW IS LINEARITY ESTABLISHED, WHAT ARE THE MINIMUM CRITERIA?

ii. A zero point and single point calibration standard shall be analyzed with each analytical batch. WHY IS IT ZERO POINT AND SOME POSITIVE

POINT. COULD IT NOT BE REPORTING LIMIT LEVEL OR LOWER RATHER THAN ZERO?

iii. THIS MATERIAL IS REALLY MATERIAL FOR THE CALIBRATION VERIFICATION. A standard corresponding to the limit of quantitation shall be analyzed with each analytical batch and shall meet established acceptance criteria. WHY EACH BATCH? IS THERE ANY MINIMUM CRITERIA FOR ACCEPTANCE?

iv. The linearity is verified at a frequency established by the method and/or the manufacturer. TNI SHOULD ESTABLISH A MINIMUM.

~~iv.~~v. WHAT ABOUT AT THE HIGH END? WE HAVE NOT INDICATED THAT THE POSITIVE STANDARD HAS TO BE 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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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

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. Additional calibration standards shall be used if the linear calibration range is greater than two orders of magnitude or when nonlinear calibrations are performed. ~~For linear regression techniques~~In all cases the number of initial calibration standards must be sufficient for at least one statistical degree of freedom. IS IT REASONABLE TO GO TO TWO DEGREES OF FREEDOM?

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Note; Guidance document to have a table with examples of calibration types, degrees of freedom, and minimum of standards.

k. For multi-peak analytes (e.g, PCBs, technical chlordane,toxaphene), analysis using an~~n~~ initial one point calibration is allowed, provided that this initial calibration shows that ~~which ensures that~~ all representative peaks can be detected. If not specified by the method the acceptance criteria shall be defined in the laboratory SOP. Samples with hits shall be reanalyzed on a multipoint curve.

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Comment [FC1]: I believe that, in the same manner as the allowed concentration range for MDL confirmation is specified in the TNI standard, the requirements to be met to show "detection" should be specified here, e.g. allowed concentration range.

Comment [FC2]: I believe the word "hits" should be changed (result above reporting limit?)

iii. 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 by qualified ~~be flagged~~ as estimated. WHAT DOES QUALIFIED AS ESTIMATED MEAN? IS THIS ANOTHER J FLAG OR IS THERE A SPECIFIC

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QUALIFIER FOR CALIBRATION FAILURE?? 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 AT LEAST ONE??~~a~~ standard (CALIBRATION, CALIBRATION CHECK, CONTINUING, ETC.) OR QUALITY CONTROL SAMPLE at or below the ~~reporting~~CENSORING LIMIT FOR THE SAMPLES IN QUESTION ~~limit~~ with each analytical batch BEFORE AND AFTER??, with~~and~~ detection of THE AFFECTED ~~all~~ analytes in compliance with all applicable criteria for detection. A BATCH OF 20 SAMPLES CAN BE A SHORT TIME IN SOME METHODS., AND THE REAL NEED IS NOT THAT IT BE IN THE SAME BATCH BUT THAT THE INSTRUMENT WAS SENSITIVE ENOUGH AT TO HAVE DETECTED IT AT THE TIME OF THE TESTING OF THE SAMPLES. I AM CONCERNED THAT THIS IS ADDING A BURDEN WHERE IT DOES NOT NEED TO BE ADDED

i)

~~i)~~j)

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;

iii. 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

iv. ~~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.~~v. 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. CAN THIS BE A BEFORE AND AFTER RATHER THAN THE SAME BATCH? A BATCH OF 20 SAMPLES CAN BE A SHORT TIME IN SOME METHODS., AND THE REAL NEED IS NOT THAT IT BE IN THE SAME BATCH BUT THAT THE INSTRUMENT WAS SENSITIVE ENOUGH AT TO HAVE DETECTED IT AT THE TIME OF THE TESTING OF THE SAMPLES.

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