SUMMARY OF THE
TNI ENVIRONMENTAL MEASUREMENT METHODS EXPERT COMMITTEE MEETING

AUGUST 24, 2012

The Committee held a conference call on Friday, August 24, 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)	Absent
Ken Jackson, TNI administrative support staff	Present

Associate Committee members present: Arthur Denny; Dianna Shannon

2 – Minutes from August 7

Francoise recommended changes to 1.7.1.1 m) and n) under Item 3. In subsection m) she pointed out that the current language ("if the assumption of a linear model through the origin is appropriate") does not say what to do if you cannot verify it is linear through the origin. She asked for this to be stated, and that the committee will consider stating what to do if linearity though the origin is not met. In subsection n) Francoise asked for it to be stated that there was a lot of discussion regarding the second sentence ("Non- detected analytes may be reported without qualification in the event of calibration failures if the laboratory has performed a successful demonstration of adequate sensitivity".). Richard suggested adding that the committee agreed to do more work due to concerns that were raised at the meeting.

Anand pointed out that the adjournment time in Section 6 should be "EDT".

Ken agreed to draft language to address these changes and then circulate the amended draft minutes for approval.

3 – Definition and Procedure for the Determination of MDL

During discussions with EPA at the August Environmental Measurement Symposium in Washington DC, it was suggested EPA might be amenable to amendments to the MDL

procedure. Accordingly, Committee members had shared comments by e-mail on the EPA CFR document: "Appendix B to Part 136 – Definition and Procedure for the Determination of the Method Detection Limit". The version annotated with these comments and proposed changes is attached. The following discussion took place.

Definition. John had said it should be specified an analytical result must meet the method-specified qualitative identification criteria. Richard agreed that is important, but felt it does not belong in the definition. This was generally agreed, but Anand said it should be stated elsewhere. Richard added that the change from "concentration" to "analytical result" was to make it clear we are talking about a determined value rather than a true value.

Paragraph 4. Francoise had suggested, instead of subtracting the average of the blank measurements from the respective sample measurement, for the data to be statistically sound each blank/spike pair should be used instead. She added that statistically, it does not make sense to take an average of different blanks on different days and thhen use that average to perform some calculation on raw data. This was original language in the procedure, and it was agreed to delete the entire section (starting with "If a blank measurement is required..") it since it is doubtful if analysts have followed the directions for running a separate blank with each sample aliquot.

In the next two sentences, Lee had suggested that using a common MDL for multiple instruments should be demonstrated at the MDL verification point, not by trying to run the replicates over multiple instruments. By doing the latter you have still not shown if an individual instrument can hit the resulting MDL. Richard said spreading over multiple instruments is consistent with the DQFAC procedure, and Brooke suggested leaving it as it is since you need to get the maximum variability of all instruments up front and the way it is written may be the most efficient way of doing it. John had said the two replicates on each instrument must also be analyzed in different batches. The FACDQ V 2.4 procedure allows one to Verify the MDL on different instruments running the same method, but the highest MDL from all instruments is used if the lab is not going to treat the instruments separately (i.e. only one MDL for a given method). There was considerable discussion on re-wording the second sentence to make it clear how many replicates in how many batches would be needed. Brooke was concerned that most of the variability may arise in the preparation stage, and it was eventually agreed to change the sentence to read "A minimum of two replicates prepared and analyzed on different days is required on each instrument".

Paragraph 6. Francoise questioned the equation for the LCL and UCL, saying perhaps a table should be provided since people may have more than 7 replicates (there is a later table for the Student's T statistic). Richard added a comment that a table may be needed. Brooke pointed out an inconsistency. Since these two equations now refer to replicates and not aliquots, the same change needs to be made in the following sentence.

The sentence "Required procedure to determine if the MDL provides reasonable protection from false positives" was discussed. Richard confirmed this is performed right at the start when you are initiating your MDL. This sentence was made the start of a new

Paragraph 7. Dan had commented that several drinking water methods,(e.g. EPA 200.7, 524.2, 508 & 525.2) incorporate an RSD evaluation in the MDL procedure. The 200 series methods specify an RSD of the 7 replicates to be more than 10%. The 500 series methods specify the RSD to be less than 20- 30% depending on the method. There are also associated accuracy requirements for the replicates ranging from +/-20 to +/-30%. He asked if there would be a reasonable protection from false positives if an RSD requirement between 10% and 30% was added. It could provide a more global protection than the blank evaluation, since so many analytes return non-detect in the blanks. He added, in assessing a laboratory, they want to see that metals MDL replicates for instance are at least 10% RSD. There was a protracted discussion on this . Richard expressed reservation, saying this also must cover non-drinking water methods where there are some poor performing analytes where a laboratory may not get better than 20-30% RSD even at the LCS mid-level, so including that specification would be unrealistic for them. He added that finding no false positives in the blanks will mean none in the samples either, and false negative protection comes from an analysis of the distribution of results spiked at the QL, so those two things are covered without having to include RSD limits. There was general agreement to leave out RSD considerations at least for the time being.

John asked if it should be made clearer that all available blank data should be used, since we don't want analysts selecting which or how much blank data they want to use, without a statistically valid way of rejecting data. On Tim's suggestion and after some discussion the second sentence in (a) was modified to state "If data are not available a minimum of 7 method blanks prepared and analyzed on at least three different days are required; more should be made available up to a full year of method blank determinations." Brooke had commented this step could be eliminated if the method returns non-detects for method blanks. It was agreed to start subsection (a) with the statement "This section is only required for procedures that return numerical results for blanks". Dan asked in that case are we also saying if the procedure always returns blanks you have already demonstrated reasonable protection from false positives? Richard said that is so if it always returns no-detects for blanks. The following was added after the above opening statement of the subsection "(if all blanks are non-detects then protection from false positives has been demonstrated)" along with a note to consider later if it is necessary to state that. Francoise suggested that in (b) it should also be stated that the blanks must be collected over all instruments. It was agreed to insert the same sentence that is in (a).

Lee had commented "This concept of running 7 more runs over three days, following the 7 already done, needs some discussion. It seems burdensome only to prove protection from false positives. I'd like to explore the idea of an RSD requirement instead." Richard said it was not the intent to run 7+7, just the original 7.

4 – Adjournment

The meeting was adjourned at 3:30 pm EDT. The next conference call will be on September 7, 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

APPENDIX B TO PART 136 -DEFINITION AND PROCEDURE FOR THE DETERMINATION OF THE METHOD DETECTION LIMIT -REVISION 1.11

Definition

The method detection limit (MDL) is defined as the minimum ~~concentration of~~analytical result for a substance that can be measured and reported with 99% confidence that the analyte concentration ~~is greater than zero~~can be distinguished from a blank and is determined from analysis of a sample in a given matrix containing the analyte.

Scope and Application

This procedure is designed for applicability to a wide variety of sample types ranging from reagent (blank) water containing analyte to wastewater containing analyte. The MDL for an analytical procedure may vary as a function of sample type. The procedure requires a complete, specific, and well defined analytical method. It is essential that all sample processing steps of the analytical method be included in the determination of the method detection limit.

The MDL obtained by this procedure is used to judge the significance of a single measurement of a future sample.

The MDL procedure was designed for applicability to a broad variety of physical and chemical methods. To accomplish this, the procedure was made device- or instrument-independent.

The MDL is performed when the method is initiated, and then verification checks are performed approximately every quarter. The data from the verification check spikes and method blanks is assessed once per year to ensure that the MDL estimate is still reasonable.

Procedure

1. Make an estimate of the detection limit using one of the following:
    a. One to two times the standard deviation of a set of method blanks, plus the mean of the method blanks.
    ~~a.~~b. The concentration value that corresponds to an instrument signal/noise in the range of 2.5 to 5.
    ~~b.~~c. The concentration equivalent of three times the standard deviation of replicate instrumental measurements of the analyte in reagent water.
    ~~c.~~d. That region of the standard curve where there is a significant change in sensitivity, i.e., a break in the slope of the standard curve.
    ~~d.~~e. Instrumental limitations.

It is recognized that the experience of the analyst is important to this process. However, the analyst must include the above considerations in the initial estimate of the detection limit.

2. Prepare reagent (blank) water that is as free of analyte as possible. Reagent or interference free water is defined as a water sample in which analyte and interferent concentrations are not detected at the method detection limit of each analyte of interest. Interferences are defined as systematic errors in the measured analytical signal of an established procedure caused by the presence of interfering species (interferent). The interferent concentration is presupposed to be normally distributed in representative samples of a given matrix.
3. (a) If the MDL is to be determined in reagent (blank) water, prepare a laboratory standard (analyte in reagent water) at a concentration which is at least equal to or in the same concentration range as the estimated method detection limit. (Recommend between 1 and 5 times

the estimated method detection limit.). Sample preservatives must be added to these QCs. Proceed to Step 4.

(b) If the MDL is to be determined in another sample matrix, analyze the sample. If the measured level of the analyte is in the recommended range of one to five times the estimated detection limit, proceed to Step 4.

If the measured level of analyte is less than the estimated detection limit, add a known amount of analyte to bring the level of analyte between one and five times the estimated detection limit.

If the measured level of analyte is greater than five times the estimated detection limit, there are two options.

(1) Obtain another sample with a lower level of analyte in the same matrix if possible.

(2) The sample may be used as is for determining the method detection limit if the analyte level does not exceed 10 times the MDL of the analyte in reagent water. The variance of the analytical method changes as the analyte concentration increases from the MDL, hence the MDL determined under these circumstances may not truly reflect method variance at lower analyte concentrations.

4. (a) Take a minimum of seven aliquots of the sample to be used to calculate the method detection limit and process each through the entire analytical method. ~~The~~Processing and analysis of the replicates must be spread over at least three days. Make all computations according to the defined method with final results in the method reporting units. If a blank measurement is required to calculate the measured level of analyte, obtain a separate blank measurement for each sample aliquot analyzed. The average blank measurement is subtracted from the respective sample measurements.

If there are multiple instruments that will be assigned the same MDL, then the replicates must be evenly distributed across all of the instruments. A minimum of 2 replicates are required on each instrument.

(b) It may be economically and technically desirable to evaluate the estimated method detection limit before proceeding with 4a. This will: (1) Prevent repeating this entire procedure

Comment [CF1]: For the data to be statistically sound, shouldn't each blank/spike pair be used instead.

Comment [LW2]: I disagree with Brook on this. I think using a common MDL for multiple instruments should be demonstrated at the MDL verification point, not by trying to run the reps over multiple instruments. By doing the latter you still haven't shown if an individual instrument can hit the resulting MDL.

Comment [BFC3]: Move this up directly after the previous comment.

when the costs of analyses are high and (2) insure that the procedure is being conducted at the correct concentration. It is quite possible that an inflated MDL will be calculated from data obtained at many times the real MDL even though the level of analyte is less than five times the calculated method detection limit. To insure that the estimate of the method detection limit is a good estimate, it is necessary to determine that a lower concentration of analyte will not result in a significantly lower method detection limit. Take two aliquots of the sample to be used to calculate the method detection limit and process each through the entire method, including blank measurements as described above in 4a. Evaluate these data:

(1) If these measurements indicate the sample is in desirable range for determination of the MDL, take five additional aliquots and proceed. Use all seven measurements for calculation of the MDL.

(2) If these measurements indicate the sample is not in correct range, reestimate the MDL, obtain new sample as in 3 and repeat either 4a or 4b.

5. Calculate the variance (S^2) and standard deviation (S) of the replicate measurements, asfollows:

$$S^2 = \frac{1}{n-1}\left[\sum_{i=1}^{n} X_1^2 - \frac{(\sum_{i=1}^{n} X_1)^2}{n}\right] \quad S = (S^2)^{1/2}$$

Where:
Xi; I=1 to n, are the analytical results in the final method reporting units obtained from the n
sample aliquots and S refers to the sum of the X values from I=l to n.

6. (a) Compute the MDL as follows:

$$MDL = t_{(n-1,1-\alpha = 0.99)}(S)$$

where: MDL = the method detection limit $t_{(n-1,1-\alpha = .99)}$ = the students t value appropriate for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom. See Table. S = standard deviation of the replicate analyses.

(b) The 95% confidence interval estimates for the MDL derived in 6a are computed according to the following equations derived from percentiles of the chi square over degrees of freedom

2

distribution (/df).

x

LCL = 0.64 MDL for 7 ~~aliquots~~replicates
UCL = 2.20 MDL for 7 ~~aliquots~~replicates

where: LCL and UCL are the lower and upper 95% confidence limits respectively based on seven aliquots.

Required procedure to determine if the MDL provides reasonable protection from false positives

(a) Evaluate the mean and variance of a set of method blanks. A minimum of 7 method blanks prepared and analyzed on at least three different days are required; more should be used if available, up to a full year of method blank determinations.
(b) Calculate the upper confidence limit for the method blanks.

$$MDL_b = \overline{X} + st$$

$Where: MDL_b$ is the MDL estimate based on blanks

X is the mean of the method blank results

s is the standard deviation of the method blank results

t is the Student's t value for the 99% confidence interval

Set the MDL to the greater of the original MDL estimate from spiked samples and the MDL_b.

Verification

Once per quarter, analyze a single spike on each instrument. The spike level should be at 2-3 times the MDL for a single analyte method, and 2-5 times the MDL for multi analyte methods. All analytes should be detected, but up to 10% may have results below the calculated MDL.

Once per year, recalculate the MDL using the most recent quarterly spike results. At least 8 results must be used. If more than 8 results are available from the most recent year, use only the most recent year. Also, recalculate the MDL_b using the most recent year set of method blank results. If the calculated MDL / MDL_b is greater than 2X the existing MDL or less than 0.5X the existing MDL, reset the MDL to the new value.

~~7. Optional iterative procedure to verify the reasonableness of the estimate of the MDL and subsequent MDL determinations.~~

~~(a) If this is the initial attempt to compute MDL based on the estimate of MDL formulated in Step 1, take the MDL as calculated in Step 6, spike the matrix at this calculated MDL and proceed through the procedure starting with Step 4.~~[2]

~~(b) If this is the second or later iteration of the MDL calculation, use S from the current MDL calculation and S^2 from the previous MDL calculation to compute the F-ratio. The F-ratio is~~

Comment [d4]: Several drinking water methods,(e.g. EPA 200.7, 524.2, 508 & 525.2) incorporate an RSD evaluation in the method MDL procedure.

The 200 series methods specify an RSD of the 7 replicates to be more than 10%.

The 500 series methods specify the RSD to be less than 20- 30% depending on the method. There are also associated accuracy requirements for the replicates ranging from +/-20 to +/-30%.

Would there be a reasonable protection from false positives if we were to add an RSD requirement between 10% and 30% here?
It could provide a more global protection than the blank evaluation, since so may analytes return non-detect in the blanks.

Comment [CF5]: I believe we should retain the benefit of using the blank data for the methods that provide them. The data are available anyway.

Comment [BFC6]: If the method returns non-detects for method blanks, skip this step.

Comment [LW7]: This concept of running 7 more runs over three days, following the 7 already done, needs some discussion. It seems burdensome only to prove protection from false positives. I'd

Field Code Changed

Comment [CF8]: And immediately after the initial MDL determination (otherwise the MDL would be unverified for the first year)

Comment [BFC9]: So you may only have 4 spikes.

Comment [CF10]: We should discuss the accuracy requirement (Standard Methods requires recoveries between 50% and 150% for each of the replicates).

Comment [CF11]: Same assumption as Tim's

Comment [F12]: Assume 'detect' means satisfying all qualitative criteria defined in the method or SOP? What to do if this condition is n

Comment [d13]: This updated MDL value should fall within the confidence interval of the original value. This could be the verification for analytes with blank non-detects.

Comment [BFC14]: What do you do if you only had one instrument and therefore 4 results? Do you wait for 2 years to collect 8?

Comment [BFC15]: Change this to "If the calculated MDL or MDLb (whichever is larger) is greater…."

Comment [LW16]: I agree with Brooke on the 2x the prior MDL. It would happen the majority of the time, perhaps just due to rounding or depending on the magnitude of the value.

calculated by substituting the larger S into the numerator S_A^2 and the other into the denominator S_B^2. The computed F-ratio is then compared with the F-ratio found in the table which is 3.05 as follows: if S_A^2/S_B^2>3.05, then compute the pooled standard deviation by the following equation:

$$S_{pooled} = \left[\frac{6S_A^2 + 6S_B^2}{12}\right]^{\frac{1}{2}}$$

if S_A^2/S_B^2>3.05, respike at the most recent calculated MDL and process the samples through the procedure starting with Step 4. If the most recent calculated MDL does not permit qualitative identification when samples are spiked at that level, report the MDL as a concentration between the current and previous MDL which permits qualitative identification.

(c) Use the S_{pooled} as calculated in 7b to compute the final MDL according to the following equation:

$$MDL = 2.681 (S_{pooled})$$

where 2.681 is equal to $t_{(12,1-\alpha=.99)}$.

(d) The 95% confidence limits for MDL derived in 7c are computed according to the following equations derived from percentiles of the chi squared over degrees of freedom distribution.

LCL=0.72 MDL
UCL=1.65 MDL

where LCL and UCL are the lower and upper 95% confidence limits respectively based on 14 aliquots.

TABLES OF STUDENTS' T VALUES AT THE 99 PERCENT CONFIDENCE LEVEL

Number of replicates	Degrees of freedom (n-1)	$t_{(n-1,.99)}$
7	6	3.143
8	7	2.998
9	8	2.896
10	9	2.821
11	10	2.764
16	15	2.602

21	20	2.528
26	25	2.485
31	30	2.457
61	60	2.390
00	00	2.326

Reporting

The analytical method used must be specifically identified by number or title and the MDL for each analyte expressed in the appropriate method reporting units. If the analytical method permits options which affect the method detection limit, these conditions must be specified with the MDL value. The sample matrix used to determine the MDL must also be identified with MDL value. Report the mean analyte level with the MDL and indicate if the MDL procedure was iterated. If a laboratory standard or a sample that contained a known amount analyte was used for this determination, also report the mean recovery.

If the level of analyte in the sample was below the determined MDL or exceeds 10 times the MDL of the analyte in reagent water, do not report a value for the MDL.

[49 F.R. 43430, Oct. 26, 1984; 50 F.R. 694, 696, Jan. 4, 1985, as amended at 51 F.R. 23703, June 30, 1986]

200.7 & 200.8 & 200.9
Note: If additional confirmation is desired, reanalyze the seven replicate aliquots on two more nonconsecutive days and again calculate the MDL values for each day. An average of the three MDL values for each analyte may provide for a more appropriate MDL estimate. If the relative standard deviation (RSD) from the analyses of the seven aliquots is <10%, the concentration used to determine the analyte MDL may have been inappropriately high for the determination. If so, this could result in the calculation of an unrealistically low MDL. Concurrently, determination of MDL in reagent water represents a best case situation and does not reflect possible matrix effects of real world samples. However, successful analyses of LFMs (Section 9.4) and the analyte addition test described in Section 9.5.1 can give confidence to the MDL value determined in reagent water.

524.2
Calculate the MDL of each analyte using the equation described in Section 13.2[3].
9.3.3 For each analyte, the mean accuracy, expressed as a percentage of the true value, should be 80-120% and the RSD should be <20%. Some analytes,

Comment [CF17]: The statement "the level of analyte in the sample" should be made specific (measured or spiked level).

Also the statement "do not report a value for the MDL" should be revised. Though we are not obligated to report data down to the MDL, our auditors have interpreted this statement as "the MDL is not valid".

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particularly the early eluting gases and late eluting higher molecular weight compounds, are measured with less accuracy and precision than other analytes.

525.2
For each analyte and surrogate, the mean accuracy, expressed as a percentage of the true value, should be 70-130% and the RSD should be ≤30%.
9.3.4 Analyze seven replicate laboratory fortified blanks which have been fortified with all analytes of interest at approximately 0.5 µg/L. Calculate the MDL of each analyte using the procedure described in Section 13.1.2[1]. It is recommended that these analyses be performed over a period of three or four days to produce more realistic method detection limits.

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