August 2018

Subject: Appendix B to Part 136 Method Detection Limit – Revision 2

Dear Accredited Laboratory Manager:

General Timeline for Implementing the Revisions to Appendix B: Method Detection Limit – Revision 2

As a reminder the 2017 Clean Water Act Method Update Rule (MUR) became effective September 27, 2017 and includes a revision to the procedure, Method Detection Limit – Revision 2 (MDL – Rev 2), outlined in 40 CFR Part 136 Appendix B for determining the Method Detection Limit (MDL). MNELAP accredited laboratories were required to begin following the MDL – Rev 2 procedure in 2018 and have all MDL-Rev 2 studies completed by 2019. Beginning January 1, 2019, laboratories will be assessed for compliance with the MDL-Rev 2 procedure and non-conformances will be cited.

Please note a MDL- Rev 2is not applicable to methods that do not produce results with a continuous distribution, such as, but not limited to, methods for whole effluent toxicity, presence/absence methods, and microbiological methods that involve counting colonies. The MDL-Rev 2 also is not applicable to measurements such as, but not limited to, biochemical oxygen demand, color, pH, specific conductance, many titration methods, and any method where low-level spiked samples cannot be prepared.

Method Detections Limit – Revision 2 as Applied to Drinking Water

Per the EPA Region 5 and EPA Office of Water and Drinking Water, Technical Support Center (TSC) recommendations, MNELAP is allowing and encouraging the use of the revised 40 CFR Part 136, Appendix B Method Detection Limit - Revision 2 (MDL – Rev 2) procedure for laboratories that are accredited to analyze drinking water under the Safe Drinking Water Program (SDWP) **even if** the methods include the steps for the 'old' MDL procedure. However, if a drinking water regulation or the method specifically cites 40 Part 136, Appendix B than the laboratory **must** follow the MDL – Rev 2 procedure.

For initial MDL- Rev 2 studies involving multiple instruments, in accordance with EPA Region 5 and EPA Office of Water and Drinking Water TSC's recommendations, MNLEAP encourages laboratories to perform a full 7-point Initial Demonstration of Capability (IDC) on each instrument, but we will not

require it. The MDL – Rev 2 states that pooled initial MDL is acceptable provided it is performed according to 40 CFR 136 Appendix B.2.i – iii (at least 2 blank spikes and 2 blanks on each instrument, where the blank spikes are prepared and analyzed on different calendar dates from each other, and the blanks are also on different calendar dates from each other, which may be the same as the blank spike dates). If a new instrument is being added into a group of instruments with existing data, a pooled MDL-Rev 2 is acceptable provided it is performed according to App B.3.e (at least 2 blanks and 2 blank spikes on the new instrument, presumably inclusive of App B.2.i. through iii. requirements that these be from different dates).

Safe Drinking Water Act Program Detection Limits for Radionuclides

Radiochemistry detection limit calculations may be directed towards the following EPA publication, Safe Drinking Water Act Program Detection Limits for Radionuclides

Training, Tools, and FAQs

An on demand TNI training The New MDL Procedure is available for a fee. The webcast reviews the new procedure and provides examples of how to implement the procedure using real data.

A Method Detection Limit – Revision 2 checklist (attached)

Many questions and answers can be found on the EPA Method Detection Limit-Frequent Questions

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DEPARTMENT OF HEALTH

Method Detection Limit Revision 2
40 CFR 136 Appendix B

ENVIRONMENTAL LABORATORY ACCREDITATION PROGRAM (MNELAP)

Definition and Procedure for the Determination of the Method Detection Limit, Revision 2 [40 CFR 136 Appendix B] EPA 821-R-16-006, https://www.epa.gov/cwa-methods
The method detection limit (MDL-Revision 2) is defined as the minimum measured concentration of a substance that can be reported with 99% confidence that the measured concentration is distinguishable from method blank results. The MDL-Revision 2 will be referred to in this document as MDL for formatting purposes.

Laboratory:_____MNELAP ID_____

Assessor Name: _____Analyst Name:_____ Review Date_____

Records Examined: SOP Number/ Revision/ Date _____ Analyst:_____

Method: _____ Matrix: _____ Analyte: _____

Instrument(s): _____ MDL Date: _____

Relevant Aspect of Standards	Method Reference	Y	N	N/A	Comments
1. Were all sample processing steps used by the laboratory included in the determination of the MDL?	Scope and Application				
2. NOTE: The MDL is not applicable to methods where low-level spiked samples cannot be prepared and other measurements such as, but not limited to, whole effluent toxicity, presence/absence, pH, BOD, color, specific conductance and many titration methods. An MDL based on method blanks alone is acceptable for gravimetric methods when spiked samples are not appropriate.	Scope and Application				
3. Were samples prepared from a ____ a) clean reference matrix spiked with a known and consistent quantity of the analyte? ____ b) specific sample matrix with a signal to noise ratio of approximately 10 -20?	Scope and Application/Addendum				
ESTIMATION OF THE INITIAL MDL					

Thank you to the Commonwealth of Virginia, Division of Consolidated Laboratory Services for allowing MNELAP the use of their checklist framework

4. Was the INITIAL MDL estimated using one or more of the following (indicate the selection(s)) _____ a) The mean determined concentration plus 3x the standard deviation of a set of method blanks _____ b) The concentration value that corresponds to an instrument signal-to-noise ratio in the range of 3 to 5 _____ c) The concentration equivalent to three times the standard deviation of replicate instrumental measurements of spiked blanks _____ d) That region of the calibration where there is a significant change in sensitivity, i.e, a break in the slope of the calibration _____ e) Instrumental limitations _____ f) Previously determined MDL	1(a) through 1(f)				
DETERMINATION OF THE INITIAL MDL					
5. NOTE: The initial MDLis used when the laboratory does not have adequate data to perform the Ongoing Annual Verification specified in Section (4), typically when a new method is implemented or if a method was rarely used in the last 24 months	2				
6. Was a spiking level typically 2-10 times the estimated MDLselected? NOTE: Spiking levels in excess of 10x the estimated detection limit may be required for analytes with very poor recovery	2(a)				
7. Were a minimum of 7 spiked samples and 7 method blanks processed through all steps of the method?	2(b)				
8. Were samples used for the MDLprepared in at least 3 batches on three separate calendar dates?	2(b)				
9. Were samples used for the MDL analyzed on three separate calendar dates?	2(b)				
10. NOTES: o Preparation and analysis may be on the same day. o Existing data may be used, if compliant with the requirements for at least 3 batches and generated within the last 24 months. o The most recent available data for method blanks and spiked samples must be used. Only data associated with gross failures with documentation for rationale may be removed.	2(b), 2(b)(iii)				

MDL Revision 2 Checklist
MNELAP
Revision: 1: August 23, 2018
To obtain this information in a different format, call: 651-201-5324.

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***NOTE: This checklist is an interview and/or data review tool used by assessors and program staff and is not to be considered as a substitute for requirements of the published method of the Code of Federal Regulations. The checklists are subject to change and withdraw. Please notify MNELAP immediately of any errors or omissions.**

o The same prepared extract may be analyzed on multiple instruments.					
11. If multiple instruments will be assigned the same MDL, sample analyses must be distributed across all instruments. Was each instrument represented with a minimum of two spiked samples and two blank samples prepared / analyzed on different days?	2(b)(i), 2(b)(ii), 2(d)				
12. Spiking level evaluation: Did every result from spiked samples meet the method qualitative identification criteria? Did every result from spiked samples provide a numerical result greater than zero? If the answer to either question is NO, the spiked samples used for initial MDL determination must be repeated at a higher concentration.	2(c)				
13. Were all computations made as specified in the analytical method and expressed in the method-specified reporting units?	2(d)				
14. Was the MDL_s (the MDLbased on spiked samples) computed as follows? $MDL_s = t(n-1, 1-\alpha=0.99)*Ss$ Where MDL_s = MDL based on spiked samples $t(n-1, 1-\alpha=0.99)$ = the Student's t-value appropriate for a single-tailed 99th percentile t statistic and a standard deviation estimate with n-1 degrees of freedom. (See Table 1, below; 3.143 when n=7) Ss = sample standard deviation of the replicate spiked sample analyses	2(d)(ii)				
15. Was the MDL_b (the MDL based on method blanks) computed as follows? <u>If none of the method blanks give numerical results for an individual analyte</u>, the MDL_b does not apply. NOTE: A numerical result includes both positive and negative results, including results below the current MDL, but not results of "ND" [not detected] commonly observed when a peak is not present in chromatographic analysis. --- OR ---	2(d)(iii)(A)				

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If some (but not all) of the method blanks for an individual analyte give numerical results, set the MDL_b equal to the highest method blank result. If more than 100 method blanks are available, set MDL_b to the level that is no less than the 99th percentile of the method blank results. For "n" method blanks where n ≥ 100, sort the method blanks in rank order. The (n * 0.99) ranked method blank result (round to the nearest whole number) is the MDL_b. [Refer to published method for a mathematical example.] --- OR --- If all of the method blanks for an individual anayte give numerical results, then calculate the MDL_b as: $MDL_b = \bar{x} + t_{(n-1, 1-\alpha=0.99)} S_b$ Where MDL_b = MDL based on method blanks $\bar{x}$ = the mean of the method blank results $t_{(n-1, 1-\alpha=0.99)}$ = the Student's t-value appropriate for a single-tailed 99th percentile t statistic and a standard deviation estimate with n-1 degrees of freedom. (See Table 1, below; 3.143 when n=7) S_b = sample standard deviation of the replicate method blank analyses NOTE: If the mean of the blanks is <0 (i.e., a negative number), substitute 0 for the mean. NOTE: If 100 or more method blanks are available, as an option, MDL_b may be set to the concentration that is greater than or equal to the 99th percentile of the method blank results, as described in Section (2)(d)(iii)(B)	2(d)(iii)(B) 2(d)(iii)(C)				
16. Was the greater of MDL_s or MDL_b selected as the initial MDL?	2(e)				
ONGOING DATA COLLECTION					
17. Was ongoing data collected as follows?	3(a)				

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During any quarter in which samples are being analyzed, prepare and analyze a minimum of two spiked samples on each instrument, in separate batches, using the same spiking concentration used in Section 2 [initial MDL calculation]. NOTE: If any analytes are repeatedly not detected in the quarterly spiked sample analyses or do not meet the qualitative identification criteria of the method the spiking level should be adjusted upward. (See 3(c).) NOTE: It is not necessary to analyze additional method blanks together with spiked samples; include all of the routine method blanks analyzed with each batch during the course of sample analysis.					
18. Did ongoing data collection ensure that at least seven spiked samples and seven method blanks were completed for the annual verification? NOTE: If only one instrument is in use, a minimum of seven spikes are still required, but they may be drawn from the last two years of data collection.	3(b)				
19. At least once per year, was the spiking level re-evaluated? NOTE: If more than 5% of the spiked samples do not return positive numerical results that meet all method qualitative identification criteria, the spiking level must be increased and the initial MDL re-determined following the procedure in Section 2.	3(c)				
20. NOTE: If the method is altered in a way that can be reasonably expected to change its sensitivity, re-determine the initial MDL according to Section 2 and restart the ongoing data collection.	3(d)				
21. If applicable, was the following addressed if a new instrument was added? If a new instrument is added to a group of instruments whose data are being pooled to create a single MDL, analyze a minimum of two spiked replicates and two method blank replicates on the new instrument.	3(e)				

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• If both method blank results are below the existing MDL, then the existing MDL_b is validated. • Combine the new spiked sample results to the existing spiked sample results and recalculate the MDL, as in Section 4. • If the recalculated MDL_s does not vary more than the factor specified in Section 4(f) of this procedure, then the existing MDLs is validated. • If either of these two conditions is not met, then calculate a new MDL following instructions in Section 2.					
ONGOING ANNUAL VERIFICATION					
22. Was the MDL_s and MDL_b re-calculated at least once every thirteen months from the collected spiked samples and method blank results using the equations in Section 2?	4(a)				
23. For the MDL_s, was all data generated within the last 24 months, but only data with the same spiking level, included in the recalculation? NOTE: Include the initial MDL spiked samples, if the data were generated within 24 months. NOTE: Use only data associated with acceptable calibrations and batch QC. Include all routine data with the exception of batches that are rejected and the associated samples reanalyzed. NOTE: Only documented instances of gross failures may be excluded from the calculations. NOTE: If the laboratory believes the sensitivity of the method has changed significantly, then the most recent data available (i.e., data collected after the change) may be used, maintaining compliance with the requirement for at least 7 replicates in three batches on three separate days (per Section 2(b).)	4(b), 4(c), 4(d)				
24. For the MDL_b, were all method blank results from the last 24 months used?	4(e)				

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NOTE: The laboratory has the option to use only the last six months of method blank data or the 50 most recent method blanks, whichever criteria yields the greater number of method blanks. Indicate the option used by the laboratory: _____ _____					
25. Was the verified MDL the greater of the MDL_s or MDL_b?	4(f)				
26. Was the verified MDL within 0.5 to 2.0 times the existing MDL, and did fewer than 3% of the method blank results have numerical results above the existing MDL? _____ If so, the existing MDL may be left unchanged at the option of the laboratory. If not, adjust the MDL to the new verified MDL.	4(f)				
27. Were documentation requirements met? _____ The prep date, analysis date, and instrument for each analysis was available for evaluation of MDL compliance. _____ The analytical method used for MDL determination was specifically identified by number or title. _____ The MDL for each analyte was expressed in the method reporting units. _____ Data and calculations used to establish the MDL can be reconstructed upon request. _____ The sample matrix used to determine the MDL was identified with the MDL value. _____ The mean spiked and recovered analyte levels were documented with the MDL. _____ The rationale for removal of outlier results, if any, was documented and maintained on file with the results of the MDL determination.	Documentation and Procedure				

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Notes/ Comments:

Table 1: Single-Tailed 99th Percentile *t* Statistic (or, conduct a web search using the table title for a full table)

Number of replicates	Degrees of freedom (n-1)	$t_{(n-1, 0.99)}$
7	6	3.143
8	7	2.998
9	8	2.896
10	9	2.821
16	15	2.602
32	31	2.453
50	49	2.405
80	79	2.374
100	99	2.365

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