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STATE OF CONNECTICUT
DEPARTMENT OF PUBLIC HEALTH

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Environmental Health and Drinking Water Branch

EHDW Circular Letter # 2024-14

TO: All Connecticut Certified Environmental Laboratories
Local Health Directors

FROM: Lori Mathieu, Public Health Branch Chief

DATE: March 13, 2024

SUBJECT: **Method Detection Limit (MDL) Guidance**

To assist laboratories with implementing the newer method detection limit (MDL) requirements, the Connecticut Department of Public Health Environmental Laboratory Certification Program (ELCP) has developed two spreadsheets: a single analyte spreadsheet and a multi-analyte spreadsheet. Both spreadsheets will capture the initial MDL, compile the ongoing data, and perform the annual recalculation of the MDL. The spreadsheets are optional if the laboratory wishes to utilize them and can be found on the ELCP website: Environmental Laboratory Certification (ct.gov).

Circular letter #2021-05 was issued on January 8, 2021, requiring all Connecticut certified laboratories to implement the updated MDL procedure and be fully compliant by July 31, 2021. A guidance document from the NH Environmental Laboratory Accreditation Program is also attached to this circular letter along with some helpful links:

Revised MDL Procedure: eCFR :: 40 CFR Part 136 -- Guidelines Establishing Test Procedures for the Analysis of Pollutants

Frequently Asked Questions (FAQ): Method Detection Limit - Frequent Questions | US EPA

Please feel free to contact Dawn Shaban and Nicole Paradise at DPH.ELCP@ct.gov with any questions or for additional guidance.

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How to Calculate an MDL Following the Procedure in 40 CFR Part 136 Appendix B (Rev. 2)[1]

New Hampshire Environmental Laboratory Accreditation Program

This procedure is not intended for the following: [2]

Non-continuous distribution methods	Color
Whole effluent toxicity	pH
Presence/absence	Specific conductance
Microbiology colony counting methods	Many titration methods
BOD	Gravimetric methods*

*For some gravimetric methods an MDL based on method blanks can be determined.

Initial MDL

1. Estimate the initial MDL by either using the mean concentration plus 3X the SD in a set of method blanks, a concentration 3-5 times the S:N ratio, a concentration 3X the SD of replicate spikes, a region where instrument sensitivity significantly changes, the instrument limitations, or a previously determined MDL. [3]
2. Determine the initial MDL.
    - 2.1 Select a spiking level typically 2-10 times that of step 1.[4]
    - 2.2 Process at least 7 spiked samples and 7 method blanks following the analytical method.[5]
        - 2.2.1 The spikes and blanks must be prepared in at least 3 different batches on 3 different days and analyzed on separate days.
        - 2.2.2 Existing data may be used if generated in the last 24 months but the most recent spikes and method blanks within that data must be used.
        - 2.2.3 Do not remove statistical outliers. Gross failures such as instrument malfunctions, mislabeled samples, or cracked vials may be excluded. The reason for removing the gross failures must be documented as part of the MDL study.
        - 2.2.4 Distribute the spikes and method blanks across all instruments used for the analysis.
            - 2.2.4.1 At least 2 spikes and 2 method blanks prepared and analyzed on different days must be run on each instrument.
            - 2.2.4.2 The same extract may be used on multiple instruments provided there are at least 7 unique spikes and method blanks for the study.
    - 2.3 Verify all spikes are qualitatively identified (based on rules, guidelines, reference methods) and are greater than 0. If any are not then start over using a higher spiking level.[6]
    - 2.4 Calculate the concentrations of the spikes and method blanks as described in the method using the method-specified reporting units.[7]
    - 2.5 Calculate the standard deviation of the replicate spikes and the standard deviation of the method blanks.[7]
    - 2.6 Calculate the MDL_s based on the spikes using the formula in 40 CFR 136 App. B: II.(2)(d)(ii).

2.7 Calculate the MDL_b according to the following:[8]

2.7.1 If none of the method blanks contain either a positive or negative numerical value then the MDL_b does not apply.

2.7.2 If some of the method blanks contain either a positive or negative numerical value set the MDL_b equal to the highest method blank result.

2.7.2.1 If >100 method blanks were used set the MDL_b no less than the 99% percentile, rounding to the nearest whole number.

2.7.3 If all method blanks for an analyte give numerical results then calculate the MDL_b using the formula in 40 CFR 136 App. B: II(2)(d)(iii)(C).

2.8 Select the greater of MDL_s or MDL_b as the initial MDL.[9]

Ongoing Data Collection

1. For each quarter where samples are being analyzed prepare and analyze at least 2 spiked samples, at the same spike concentration used in the initial MDL, on each instrument in separate batches.[10]

1.1 If any of the analytes in the spike samples are not detected or do not qualitatively meet criteria repeatedly (more than once) the initial MDL should be performed at a higher spiking level.

2. Re-evaluate the spiking level at least once a year by ensuring at least 7 spiked samples and 7 method blanks are completed within the last year (if there is only one instrument then method blanks spanning the last 2 years may be used) and confirm that at least 95% of the spike samples have positive results which meet the qualitative identification criteria.[11]

2.1 If there are insufficient spiked samples (7) and/or method blanks (7) perform another Initial MDL.

2.2 If more than 5% of the spike samples do not have positive results increase the spiking level and perform another Initial MDL.

2.3 If the method blanks are altered where the sensitivity has changed, perform another Initial MDL.

2.4 If a new instrument has been added to a group of instruments analyze at least 2 spikes and 2 method blanks on the instrument.[12]

2.4.1 Verify these method blanks are below the existing MDL. If so, the current MDL_b value is validated.

2.4.2 Combine these spikes with the existing spiked sample results and recalculate the MDL_s. If the new MDL_s is within 0.5 to 2.0 times the existing MDL, the current MDL_s is validated.

2.4.3 If either the MDL_b or the MDL_s is invalid, perform another Initial MDL.

Ongoing Annual Verification

1. At least every 13 months recalculate the MDL_s and MDL_b using the data obtained from the last 24 months.[13]

1.1 Only use data from spikes at the same concentrations.

1.2 Spikes and method blanks can be omitted only if they are documented as a gross failure (instrument malfunction, mislabeled samples, cracked vials…). A rationale for all omissions must be documented.

1.3 If instrument sensitivity is suspected to have changed then the most recent data may be used provided there are at least 7 spikes and 7 method blanks prepared and analyzed on at least 3 separate days.

1.4 Include the initial MDL spiked samples if they were generated in the last 24 months.

1.5 Only use data associated with valid analytical batches.

1.6 At least all method blanks from the last 6 months or the 50 most recent method blanks must be used, whichever is greater. It is ideal to use all method blanks in the last 24 months, but is not necessary.

2. Consider the greater of the recalculated MDL_s or MDL_b as the verified MDL.[14]

2.1 If the verified MDL is within 0.5 to 2.0 times the existing MDL, and fewer than 3% of the method blanks have values above the existing MDL then the existing MDL may be left unchanged.

2.2 If the verified MDL exceeds 0.5 to 2.0 times the existing MDL, and more than 3% of the method blanks have values above the existing MDL then change the existing MDL to the new verification MDL.

Documentation[15]

1. Identify the analytical method by number or title with the data.
2. Use the method reporting units for all MDL values.
3. Document the MDL in a manner the calculations and data can be reconstructed by request.
4. Identify the sample matrix.
5. Document the spike concentrations and the mean recovery of each analyte.
6. Document the rationale for the removal of any outlier results.

MDL Determination based on a Specific Sample Matrix (Optional)[16]

1. Analyze the sample matrix to determine the native concentration of target analytes.

1.1 If the response of a target analyte has a S:N ration between 5 and 20, calculate the MDL using the Initial MDL procedure.

1.2 If the response of a target analyte has a S:N ratio <5, spike the target analyte(s) into the sample matrix to achieve a S:N ratio of approximately 10 to 20, then calculate the MDL using the Initial MDL procedure.

1.3 If the response of the target analyte(s) has a S:N ratio >20 an MDL calculated with the high value will most likely be bias high.

2. Use only method blanks for calculating the MDL_b.

NH ELAP Comments

1. Units of measure must be present for each numerical value within the support documents and spreadsheets. Identification of the unit of measure used for a column of data is acceptable, or if all numerical values within a document page are the same a single reference to the unit of measure may be made somewhere on the page.
2. The MDL_s, MDL_b, and MDL values for each analyte must be present in the laboratory's documentation of the MDL study. If the MDL_b does not apply according to the procedure then the method blanks which were used to make such conclusion must be documented.
3. Each spike or method blank used, including method blanks with no numerical values for the MDL study, must be traceable to a preparation batch and an analytical batch. If there is no sample preparation for the analytical method then traceability must be made to the analytical batch.
4. Perform the MDL procedure on an analyte by analyte basis when an analytical method contains more than one analyte. Meaning, if an MDL_b must be calculated for one analyte using the formula in 40 CFR 136 App. B: II(2)(d)(iii)(C) and an MDL_b does not apply to a second analyte, do not calculate an MDL_b value for the second analyte using the invalid values.
5. NH ELAP may accept another Initial MDL being performed in lieu of a laboratory performing the Ongoing Annual Verification. However, the Ongoing Data Collection must be performed.

Table of Endnotes

1 – https://www.ecfr.gov/current/title-40/chapter-I/subchapter-D/part-136
2 - 40 CFR 136 Appendix B: I(2)
3 - 40 CFR 136 Appendix B: II(1)(a-f)
4 - 40 CFR 136 Appendix B: II(2)(a)
5 - 40 CFR 136 Appendix B: II(2)(b)
6 - 40 CFR 136 Appendix B: II(2)(c)
7 - 40 CFR 136 Appendix B: II(2)(d)
8 - 40 CFR 136 Appendix B: II(2)(d)(iii)
9 - 40 CFR 136 Appendix B: II(2)(e)
10 - 40 CFR 136 Appendix B: II(3)(a)
11 - 40 CFR 136 Appendix B: II(3)(b-d)
12 - 40 CFR 136 Appendix B: II(3)(e)
13 - 40 CFR 136 Appendix B: II(4)(a-e)
14 - 40 CFR 136 Appendix B: II(4)(f)
15 - 40 CFR 136 Appendix B: III
16 - 40 CFR 136 Appendix B: Addendum to Section II