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Determination of Method Detection Limit

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1. Purpose:

1.1. This SOP describes the Georgia Environmental Protection Division Laboratory's procedure and documentation for the requirements of performing Method Detection Limit (MDL) studies.

1.2. This SOP also provides guidance for completing the appropriate forms for documentation of MDLs.

2. Scope and Application:

2.1. This procedure details the requirements for conducting, interpreting and reporting MDL studies. The procedure is based on guidance provided in 40CFR, Part 136, Appendix B, Revision 2.

2.2. With few exceptions, MDL studies should be performed on all analytical methods performed in the Laboratory.

3. Summary:

3.1. MDL studies are based on either the Ongoing (Continuous) MDL study procedure based on the criteria in 3.1.1 or the Initial MDL study based on the criteria in 3.1.2.

3.1.1. The Ongoing MDL study procedure consists of preparing and analyzing at least one MDL level spike and one corresponding MDL blank for each analytical batch of samples analyzed.

3.1.2. Seven or more replicates for each appropriate analytical method and matrix are prepared and analyzed. Each replicate is spiked with analytes of interest near but above the estimated detection limit(s) of the method/matrix.

3.2. Only analysts with valid Initial Demonstrations of Capability (IDC) or Continuing Demonstrations of Capability Form (CDF) on file should perform MDL studies. During method development, an experienced analyst should perform an MDL study necessary for validation of that method. In this case, there will be no IDC or CDF on file for that analyst.

3.3. The population standard deviation of the replicate true value concentration results is calculated. This value is multiplied by the appropriate *Student's t* value for the number of degrees of freedom (number of replicates (n) – 1) to determine the MDL with 99 percent confidence.

4. Definitions:

4.1. Method Detection Limit (MDL) - is 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 is specific for the sample matrix. Both the method blanks and the MDL level spiked samples are used to calculate an MDL.

The Ongoing MDL procedure will be used for all MDL studies except where the lab does not have adequate data to perform this procedure. Such occurrences would include significant maintenance to an instrument that would cause changes in response, a method that is rarely used within the last 24 month period, or a new method is implemented.

4.2. Initial MDL - Seven or more replicates for each appropriate analytical method and matrix are prepared and analyzed. Each replicate is spiked with analytes of interest either near but above the estimated detection limit(s) of the method/matrix or spiked based upon previous MDL studies.

4.3. Ongoing MDL (Continuous) – Data collected from a MDL level spike sample and the method blank prepared and analyzed with each analytical batch will be used to calculate the MDL for each appropriate analytical method and matrix.

4.4. Ongoing MDL Verification – A least every six months the MDLb and the MDLs must be recalculated to determine the new MDL based upon data collected during the previous six months of operation. An Ongoing MDL takes into account preparation and instrumentation variances that occur over the six month period.

4.5. Method Detection Limit Blank (MDLb) – The method blank that is prepared and analyzed with each analytical batch of samples.

4.6. Method Detection Limit Spike (MDLs) – A MDL level spiked sample that is prepared and analyzed with each analytical batch of samples. The level of the spike is the lowest calibration standard for all programs except NATTS Air which is below the lowest calibration standard.

4.7. Accuracy - is a combination of bias and precision of an analytical procedure, which reflects the closeness of a measured value to the true value.

4.8. Bias - provides a measure of systematic error in an analytical method. Bias is the difference between the mean of a set of values and the true value.

4.9. Instrument Detection Limit (IDL) - is the concentration equivalent to a signal, due to the analyte, equal to 3 times the standard deviation of a series of 10 replicate measurements of a reagent blank. The IDL is the smallest signal that can be distinguished from background noise.

4.10. Linear Calibration Range (LCR) - is the region of a linear regression calibration curve within which a plot of the concentration of an analyte verses response of that analyte remains linear. The correlation of the calibration curve line should be as close to 1 as possible.

4.11. Practical Quantitation Limit (PQL) - is a quantitation limit that is usually defined as 2 to 10 times the MDL. The PQL represents the routinely achievable quantitation limit with a high degree of certainty. The factor varies based upon the analytical method or program for which the samples are collected.

4.12. Precision - is a measure of the random error associated with a series of repeated measurements of the same analyte in a sample. Precision is reported as relative percent difference (RPD) between 2 values or as percent relative standard deviation (%RSD) for more than 2 values within the laboratory.

4.13. Reporting Limit (RL) - is an arbitrary number based on the experience and judgment of the analyst. The RL or PQL is the reporting limit within the laboratory.

4.14. Standard Deviation (σ) - is the most common measure of the spread of a distribution about the mean. The EPA standard is the population standard deviation or σ_{n-1}. Unless otherwise noted, both σ and σ_{n-1} represent the population standard deviation at the Laboratory.

4.15. Signal to Noise Ratio (S/N) - is the measure of the relative strength of an analytical signal to the average strength of the background instrument noise.

4.16. Statistical Outlier - is an observation or data point that appears to deviate markedly from other members of the population in which it occurs. Outliers are verified using a statistical method.

4.17. $t_{(n-1,\ 1-\alpha=0.99)}$ - the *Student's t* value appropriate for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom. See Table 4.18.

4.18. Student's t-values table

Table 4.18 - *Student's t* Values at the 99 Percent Confidence Level

Number of replicates	Degrees of Freedom (n-1)	$t_{(n-1,\ 1-\alpha=0.99)}$
7	6	3.143
8	7	2.998
9	8	2.896
10	9	2.821
11	10	2.764
12	11	2.718
13	12	2.681
14	13	2.650
15	14	2.624

5. Personnel Qualifications and Responsibilities:

5.1. With the exception of method development, analysts performing MDL studies must have a valid IDC or CDF for the method/matrix of interest on file.

6. Procedure:

Note: The Ongoing (Continuous) MDL study will be discussed before the Initial MDL study because the EPD Laboratory chooses to use the Ongoing MDL study wherever possible for all methods.

6.1. Ongoing (Continuous) MDL study:

6.1.1. For each analytical batch of samples at least one MDLb and one MDLs must be prepared and analyzed. All MDLb and MDLs samples must incorporate all aspects of collection parameters such as collection bottle and preservatives used for the appropriate analytical method.

6.1.2. The spike level used for the MDLs should be equal to the lowest calibration standard for all programs except Air NATTs. **Note: For NATTs (Air) methods: the spiking level must be less than the lowest calibration standard.**

6.1.3. After preparing the MDLb and the MDLs samples by following all preparation steps incorporated into the appropriate analytical method, they are analyzed using the appropriate instrumentation. These MDLb and MDLs samples may be analyzed on all instrumentation available for use for each analytical method. It is not necessary to prepare additional MDLb and MDLs samples for instrumentation that is not currently being used for samples. But it is necessary to verify all instrumentation every six months for a new calculated MDL.

6.1.4. For methods that do not generate a significant amount of data, there must be a minimum of at least seven MDLb and MDLs samples prepped and analyzed over at least three analytical batches or at least two MDLb and two MDLs samples analyzed on each

instrument per calendar quarter for the determination of a MDL for each analyte. A six month verification must be performed using the available data from the previous 24 month period. If there is still an insufficient amount of available data available, an Initial MDL study must be performed.

6.1.5. Batch QC acceptance criteria must be met for use of each batch MDLb and MDLs data. See Section 14 of each method SOP for specific criteria. If batch QC fails, the analytical run should be re-analyzed on the same instrument after the source of the problem has be diagnosed and corrected or the batch must be run on another instrument. In some cases, the entire batch may need to be re-prepped and re-run.

6.2. Labworks entry of the MDLb and MDLs for each analytical batch:

6.2.1. The test codes for the MDLb (B_ or $B_), the MDLs (ML or $ML), the amount spiked for the MDLs (MA or $MA) and the individual instrument (INSTR-) are assigned to the QC batch sample for each analytical batch. If additional MDLb and MDLs samples are analyzed they are assigned to other samples within the analytical batch or they may be assigned Labworks sample numbers using Labworks sample login procedure using MultiSample Login. The Source ID is MDLS, the Collection Date is the prep date, and the Collection Time is the prep time. Add the required test codes by using Edit, then Edit Analysis List.

6.2.2. The results for the MDLb are entered into either the B_ or $B_ test codes for the appropriate method. The response can either be a positive or a negative response. If neither a positive or negative response is generated by the instrument software, enter ND (Not Detected) into Labworks.

6.2.3. The results for the MDLs are entered into either the ML or $ML test codes for the appropriate method.

6.2.3.1. Positive identification of each compound is required following the guidance specified within individual analytical methods. But a predetermined acceptable percent recovery of each compound is not a determination for the use of a MDLs sample. However, gross failures such as instrument malfunctions, mislabeled samples, and cracked vials may be cause to exclude a MDLs sample from the MDL calculations. The rationale for the removal of specific outliers must be documented and maintained on file with the results of the MDL determination. A copy of corrective actions for the removal or exclusion of any MDLs that was initiated during the MDL verification period should be kept in a folder by the Supervisor for inclusion in the Ongoing MDL data set. Please consult with your Supervisor or Manager for determining a MDLs sample as an outlier.

6.3. Ongoing Verification procedure:

6.3.1. Every six months a verification of the MDL must be performed using the data from the previous two-year period. This verification is performed by running the Access program located at S:\MDLS\MDLS. Follow the prompt for Lab, MDL test code, INSTR- and Study period start and end dates, then SEARCH. Print the generated summary and data plots reports. The higher of the two values, MDLs or MDLb, is the new calculated MDL. Highlight the higher value for each analyte on the summary report. Note: If some, but not all, of the method blanks give numerical results for an individual analyte, set the MDLb to the highest method blank result. The NATTS Air program requires that the nominal spike level must be greater than the calculated MDL and less than 10-fold the calculated MDL. The 10-fold rule does not apply to the MDLb. These

reports are reviewed by the Scientist that generated the reports, reviewed by both the Supervisor and Manager assigned to the method, and then turned into the QA Manager for approval.

6.4. Initial MDL Study:
Note: This MDL study should only be used when validating a new method, maintenance on an instrument has caused a significant change in the response of the instrument or an individual method is not used often enough to generated sufficient data for the Ongoing MDL study.

6.4.1. Determining the Estimated Detection Limit: Make an estimate of the detection limit using one of the following:

6.4.1.1. The concentration value that corresponds to an instrument signal to noise ratio in the range of 2 to 10 times. Note: **For NATTS (Air) methods: signal to noise ratio of 3 to 5 for each analyte is used to estimate the detection limit.**

6.4.1.2. The concentration equivalent to three times the standard deviation of replicate instrument measurements of the analyte in reagent water.

6.4.1.3. The region of the calibration curve with a significant change in sensitivity, where identification criteria for the analyte is lost.

6.4.1.4. The lowest standard on the routine calibration curve. **Note: For NATTS (Air) methods: the spiking level should be less than the lowest calibration standard.**

6.4.1.5. Instrument limitations based on analyst experience using some of the above considerations.

6.4.1.6. Previously determined MDL.

6.4.2. Preparation and Analysis of MDL samples for an Initial MDL Study:

6.4.2.1. A minimum of seven MDLb and MDLs samples must be prepared and analyzed through the entire analytical method. All MDLb and MDLs samples must incorporate all aspects of collection parameters such as collection bottle and preservatives used for the appropriate analytical method over a minimum of three days. **Note: for NATTS (Air) methods: the prep and analysis must be over a minimum of three non-consecutive days.**

6.4.2.2. All MDLs samples must be spiked at a spike level of 2 – 10 times the estimated MDL determined in Section 6.4.1. **Note: For NATTS (Air) methods: the spiking level should be less than the lowest calibration standard.**

6.4.2.3. The MDLb samples are not spiked.

6.4.2.4. After preparing the MDLb and the MDLs samples by following all preparation steps incorporated into the appropriate analytical method, they are analyzed using the using the appropriate instrumentation.

6.4.2.5 Labworks entry of the MDLb and MDLs for each analytical batch: Follow the instructions in Section 6.2 of this SOP.

6.4.2.6 Ongoing Verification procedure: Follow the instructions in Section 6.3 of this SOP.

6.5. For gravimetric residue and titrimetic analyses report to the method recommended reporting limit. Laboratory apparatus for these analyses should have sufficient sensitivity to meet the method requirements; typically, the smallest measure the system is capable of determining the MDL.

6.6. The following analyses do not require MDL studies: BOD5 and CBOD5, use the method required depletion of 2 mg/L; Chlorophyll a; Color; Ignitability; Reactivity; Corrosivity; Conductivity; Turbidity; and Waste Fingerprinting.

6.7. MDL must be calculated on individual instruments. EPD laboratory chooses to calculate

MDLs on individual instruments even where there are multiple instruments in use for the same analytical method.

6.8. Only MDL Blanks that meet the specified qualitative criteria for identification (signal to noise, qualifier ion presence, etc.) are to be given a numerical result and used for MDL calculation.

6.9. Calculated MDLs must be below the current RLs or PQLs to be acceptable. EPD laboratory does not adjust PQLs for our Drinking Water program because they are based upon the regulations of the Federal Register. To make an adjustment to RLs for any other EPD programs the Lab Manager must consult with the Lab Director and Lab QA Manager to ensure that federal regulations are able to be met.
For all programs, if the new calculated MDLs or MDLb for any analyte is above the current PQL or RL, an initial MDL study must be repeated for that particular analyte on the instrument used to generate this data.

6.10. After performing an initial MDL study after major instrument maintenance, review the results with your supervisor and manager. The results of this initial MDL study must be submitted to the QA office for approval. If the results of the initial MDL study are comparable to the previous ongoing verification results, the new study results will be included in the current evaluation period. If they are not comparable they will not be included with previous results but will begin a new ongoing verification period from the time of the initial study.

6.11 The TO-15 Volatile standard is replaced approximately yearly. At the time a new standard is acquired an Initial MDL study will be necessary because the nominal value for the compounds will be slightly varied from the previous standard. An ongoing verification based on the previous standard will be performed, reviewed and submitted to the QA office. MDLs and RLs will not be updated in Labworks based upon this ongoing verification. An Initial MDL study will be performed using the new volatile standard nominal values. Labworks will be updated based upon this Initial MDL study. After six months an ongoing verification will be performed and Labworks will be updated.

7. Records Management:

7.1. MDL studies are maintained as part of the permanent data record for the laboratory. MDL study results and data are to be disposed of only after the appropriate program required archiving period has expired.

7.2. For Initial MDL studies: Identify the analytical method used by the standard method identifier ("EPA 507", "SM9050", etc.).

7.2.1. Report the MDL for each analyte in the appropriate reporting units for the method.

7.2.2. The sample matrix must be identified.

7.2.3. Report the analyst name, date of MDL study, spike concentration, average spike recovery, standard deviation, *Student's t* value used, and calculated MDL.

8. Quality Control/Quality Assurance:

8.1. For all methods requiring MDL studies, these studies must be performed every six months or more often if so specified by specific methods or programs.

8.2. MDL studies must be reviewed and approved by the analyst's Supervisor, the Laboratory

Manager and the QA Manager. MDL studies are not complete until approved by the QA Manager.

8.3. Instrument MDL studies must be performed on an instrument any time major maintenance is performed that has the potential to affect sensitivity unless the specific method provides for sensitivity testing after particular types of maintenance procedures. Routine maintenance procedures do not trigger the need for new MDL studies.

8.4. Calculations:

8.4.1. MDL studies are calculated by finding the standard deviation of seven or more analyte replicates. The standard deviation is multiplied by the *Student's t* value appropriate for the 99% confidence level and a standard deviation estimate, both with n-1 degrees of freedom. See Table 4.18.

8.4.2. The population standard deviation is calculated as follows:

8.4.2.1.
$$\sigma_{(n-1)} = \sqrt{\left[\frac{\sum_{i=1}^{n}\left(x_i - \bar{x}\right)^2}{n-1}\right]}$$

8.4.2.2. Where:

8.4.2.3. $\sigma_{(n-1)}$ = population standard deviation

8.4.2.4. x_i = individual results

8.4.2.5. $\bar{x}$ = mean of individual results

8.4.2.6. n = number of replicates

8.4.3. The MDL is calculated as follows:

8.4.3.1. $MDL = t_{(n-1,1-\alpha=0.99)} * \sigma_{(n-1)}$

8.4.3.2. Where:

8.4.3.3. $t_{(n-1,\ 1-\alpha=0.99)}$ = See definition Section 4.17 and Table 4.18.

9. References:

9.1. Definition and Procedure for the Determination of the Method Detection Limit, Revision 2, 40 CFR, Part 136, Appendix B, December 2016, EPA 821-R16-006.

9.2. Technical Assistance Document for the National Air Toxics Trends Stations Program, Revision 3, October 2016, US EPA Office of Air Quality Planning and Standards (C304-06) Research Triangle Park, NC 27711.

9.3. Standard Methods for the Examination of Water and Wastewater, On-line Edition.

9.4. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW846, 3rd Ed.

9.5. Analytical Detection Limit Guidance, Wisconsin Dept. of Natural Resources, Office of Technical Services, April 1995 Public Hearing.

Updates: Online revision statement added.