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DAQ-15-007.1 Standard Operating Procedure (SOP) Method Detection Limit Determination Electronics and Calibration Branch (ECB) Responsibilities

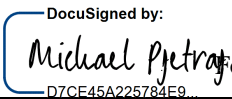


1.0 Approval Sign Off-Sheet

I certify that I have read and approve of the contents of the Method Detection Limit Determination, Electronics and Calibration Branch (ECB) Responsibilities Standard Operating Procedure with an effective date of May 7, 2021.

Director, Air Quality Division

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Signature:  For Michael Abraczinskas Date: 5/10/2021

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Signature:  Date: 5/10/2021

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This document, and any revision hereto, is intended solely as a reference guide to assist Electronics and Calibration Branch technicians in the setup, calibration, maintenance, operation, and the collection of data related to the North Carolina Division of Air Quality’s Ambient Monitoring Program. This document is intended as a supplement to, and not a substitute for, the education, training, and experience in addition to other North Carolina DAQ Reference Manuals, QAPPs and EPA Guidance. It is not a substitute for the extensive training and experience required for the efficient operation of ambient air monitoring equipment needed for scientifically valid data.

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2.0 Scope and Purpose

The method detection limit (MDL) as prescribed in 40 Code of Federal Regulation (CFR) Part 136, Appendix B was initially developed and applied to wastewater analyses. Since then, then this procedure has been applied to a variety of other matrices and analysis methods to approximate the lowest concentration (or amount) of analyte that can be reported with 99% confidence that the actual concentration (or amount) is greater than zero. MDLs are determined according to the updated MDL procedure described in 40 CFR Part 136, Appendix B, the [Method Update Rule](#).

The MDL refers to the lowest concentration of a substance that can be reliably determined by a given procedure. The MDL is typically not provided by the vendor. Based on the objectives of the Photochemical Assessment Monitoring Station (PAMS) and the Precursor Gas Program, it is expected that most sites will be measuring pollutant concentrations at lower ranges than the typical State and Local Monitoring Stations (SLAMS) network. Therefore, the ability to quantify concentrations at these lower levels is very important. As monitors are deployed into monitoring networks, where both environmental conditions, equipment (calibration, dilution devices, sampling lines, gaseous standards) and operator activities can vary, it is important to estimate what pollutant concentrations can truly be detected, above background noise (the potential conditions mentioned above). The site-specific MDL establishes an estimate based on the routine operation (and conditions) of that instrument in the network and provides a more meaningful evaluation of data as it is aggregated across the precursor gas network. By establishing site-specific MDLs, values less than the MDL can be flagged which would allow data users a more informed decision on the use of that data. MDLs should be determined for each instrument employed to measure PAMS Required Site parameters. PAMS monitoring sites are collocated at the national core (NCore) site within the core-based statistical area (CBSA) per the regulations promulgated in October 2015.

Currently, the Electronics and Calibration Branch (ECB) of the Ambient Monitoring Section (AMS) of the Division of Air Quality (DAQ) does not perform annual MDL studies at NCore sites but relies on manufacturer's specification of instrument detection limit (IDL) or something similar. The ECB is responsible for conducting MDL determination at PAMS (true NO₂) sites.

3.0 Equipment

The equipment used to conduct MDL determination should be what is currently in use at the site for each specific monitor and will include the following:

- Monitor
- Dynamic Gas Calibrator
- Zero Air Generator
- EPA Protocol gas cylinder: In some cases, with the NCore equipment, lower concentration cylinders might be necessary to develop the low MDL concentrations. If the cylinder is outside of EPA Protocol G1 parameter, it will not be a Protocol cylinder.
- Teflon™ Sampling Line
- Data Management System (e.g., Envidas/Envista)
- Dedicated Windows compatible Site Computer
- Ethernet / Modem connectivity
- Temperature Controlled Monitoring Shelter

4.0 Determining the MDL Zero-Blank (MDL_b)

Once the monitor and all supporting equipment have been installed at the site and the monitor has been calibrated and collecting data, the MDL zero-blank should be completed, ideally withing 30 days from the beginning of data

collection or as soon as practical. The short-term data (e.g., 5-minute or 1-minute data) should be reviewed to ensure the monitor background is stable and not continuing to decrease. To perform the MDL_b determination using DAS software:

1. Select the ZERO phase for the monitor being tested set the zero test to run for 4 hours. Allow time for the monitor to equilibrate and become stable.
2. Once the ZERO phase has run generate a report of 10-minute zero-air averages from a one-minute time base as shown below.

3. Record zero air blank data for minimally seven discrete 30-minute periods over the course of minimally three different dates, preferably non-consecutive days.
4. The averaged 10-minute values are computed for each of these seven measurement periods to generate seven concentration values. More than seven blanks can be included in the calculation, and, when included, will typically provide a better approximation of the background contribution. Zero blanks with technical problems (e.g., power surge detector spikes, missing minute data, or ambient air leaks) may be excluded from the subsequent calculations; however, a valid technical reason to exclude data should be documented and justified.
5. Repeat the ZERO phase from sequence on 3 non-consecutive days and enter the data into the MDL calculation spreadsheet.

The MDL_b is calculated as follows:

1. Calculate the average concentration of the zero-blank measurement concentrations, if the mean values are less than zero then let the mean value equal zero.
2. Calculate the standard deviation of the zero-blank measurement.
3. Multiply the standard deviation of the zero blank by the one-sided 99th percentile Student's t value corresponding to the number of blanks analyzed.
4. Calculate MDL_b as the sum of the mean zero-blank values and the product of the standard deviation and the associated Student's t value:

$$\text{MDL}_b = \text{mean blank-zero} + \text{standard deviation of blank zero} * t$$

5.0 Determining the MDL Sample (MDL_{sp})

The most difficult aspect of determining the MDL_{sp} portion of the MDL is generating suitable low concentration standards. Modern "trace" level analyzers are capable of detecting single-part-per-billion concentrations of gaseous criteria pollutants, and the ability to generate concentrations in this range is limited by the starting stock gas concentration and the effective dilution factor of the gas calibrator used to generate the standards. The first step in determining the MDL_{sp} is selecting a concentration at which to perform the MDL_{sp} procedure. To select a concentration, one should consider the following in decreasing order of importance:

1. The concentration at which the instrument response is approximately three to five-fold the baseline response
2. Analysis of a suite of zero blanks, such as the measurements recorded determining the MDL_b – (Section 4.0) - calculate the standard deviation of the measured concentration and multiply by 3.
3. Previously acceptable MDL studies and related experience.

As practical, the selected concentration would be generated to determine the MDL_{sp}. If the standard and dilution equipment cannot generate a concentration sufficiently low, then as low a concentration as possible should be used, given the system limitations. The absolute accuracy of the challenge concentration is not evaluated in the determination and is not as important as the ability to generate a stable concentration.

The MDL_{sp}, low level concentration standards should be generated in the similar manner as the MDL_b. Once the MDL_{sp} concentration has been selected a SPAN Phase (solely for MDL testing) should be created using DAS software to generate the target MDL_{sp} concentration.

To perform the MDL_{sp} determination using DAS software:

1. Select the SPAN phase specifically created for the monitor being tested and set the SPAN test to run for 4 hours. Allow time for the monitor to equilibrate and become stable.
2. Once the SPAN has run generate a report of 10-minute zero-air averages from a one-minute time base as shown below.

The screenshot shows the 'Station Report' dialog box with the following settings:

- Primary:** AQS
- Purpose:** All
- Region:** All
- City:** All
- Organization:** All
- Station:** All Stations, CSSRW
- On Monitors:** All, On Monitors
 - O3
 - CPS
 - SOL_RAD
 - TMP
 - NO2
 - PM25
 - T700_ACTCONC
 - T700U_ACTO3
 - T700_ACTCALFLOW
 - T700ACTDILFLOW
- Output:** Tabular, Graph, Excel
- Duration:** Daily, Weekly, Monthly, Period
- Date And Time:**
 - Start Date: 4/20/2021
 - Start Time: 00:00
 - Stop Date: 4/26/2021
 - Stop Time: 23:50
- Type:** Criteria, Status, Add Features
 - Average Type:** AVG, Partial
 - From Time Base:** 1 Minute, Use Raw
 - Time Base:** 10 Minutes, Accumulate
 - Seperate Monitors
 - Round Data
 - Summary Only
 - Display Monitor Unit As:** Default Units

- Record SPAN data for minimally seven discrete 10-minute periods over the course of minimally three different dates, preferably non-consecutive days.
- The averaged 10-minute values are computed for each of these seven measurement periods to generate seven concentration values. More than seven blanks can be included in the calculation, and, when included, will typically provide a better approximation of the sample analysis. Sample values with technical problems (e.g., power surge detector spikes, missing minute data, or ambient air leaks) may be excluded from the subsequent calculations; however, a valid technical reason to exclude data should be documented and justified.
- Repeat the SPAN phase from sequence on 3 non-consecutive days and enter the data into the MDL calculation spreadsheet.
- Reconfigure the monitor and auxiliary equipment once each SPAN phase is complete to resume sampling of ambient air until the next sample test is to be completed.

Calculate the MDL_{sp} as follows:

1. Calculate the standard deviation of the averaged concentration for the standard measurement periods.
2. Calculate the MDL_{sp} by multiplying the standard deviation by the one-sided 99th percentile Student's t value at 99% confidence corresponding to the number of measurement periods analyzed.

$$\text{MDL}_{\text{sp}} = \text{standard deviation} * t$$

1. The file for the MDL_b and MDL_{sp} should be saved Left click the "file" toolbar icon, scroll down to "save as" and left click.
2. Under file name (highlighted) change the MDL spreadsheet file name using the following format: Model ID Instrument ID MDL and YYYYMODA to YYYYMODA. For example, "T500 #2 MDL 20210301 to 20210312.xls" is an MDL completed using a T500U NO2 monitor between the dates of March 1 and March 12, 2021.

6.0 Student's t Test Distribution Table

For reference, the one-sided 99th percentile Student's t value corresponding to the number of blanks analyzed is provided below – see Appendix 12.3 for an Expanded Student's t Distribution Table.

t- Distribution Table			
v	99%	v	99%
1	31.8205	16	2.5835
2	6.9646	17	2.5669
3	4.5407	18	2.5524
4	3.7469	19	2.5395
5	3.3649	20	2.5280
6	3.1427	21	2.5176
7	2.9980	22	2.5083
8	2.8965	23	2.4999
9	2.8214	24	2.4922
10	2.7638	25	2.4851
11	2.7181	26	2.4786
12	2.6810	27	2.4727
13	2.6503	28	2.4671
14	2.6245	29	2.4620
15	2.6025	30	2.4573

7.0 On-Site Installation

There is no additional on-site installation needed.

8.0 Ongoing Determination of the MDL

Once the MDL has been initially established, the MDL should be re-determined when changes to the instrument would reasonably expect to affect the sensitivity. If changes have not been made to the instrument that affect sensitivity, the MDL should be updated annually.

9.0 Accuracy Audits

Not Applicable for MDL determination.

10.0 Revision History

This is a new SOP – there is no revision history.

11.0 References

1. 40 CFR Part 136, Appendix B ([https://www.law.cornell.edu/cfr/text/40/appendix-B to part 136](https://www.law.cornell.edu/cfr/text/40/appendix-B%20to%20part%20136))
2. Definition and Procedure for the Determination of the Method Detection Limit, Revision. EPA Office of Water, EPA 821-R-16-006, December 2016. Available at (accessed March 2018): https://www.epa.gov/sites/production/files/2016-12/documents/mdlprocedure_rev2_12-13-2016.pdf
3. PAMS Technical Assistance Document (TAD) ([PAMS TAD](#))
4. Technical Assistance Document (TAD) for Precursor Gas Measurements in the NCore Multi-pollutant Monitoring Network Version 4. ([NCore TAD](#))
5. Quality Assurance Handbook for Air Pollution Measurement Systems. Volume II – Ambient Air Quality Monitoring Program. EP454/B-08-002. U. S. Environmental Protection Agency. January 2017. ([QA Handbook](#))

12.0 Appendices

- | | |
|------|------------------------------------------------------------------|
| 12.1 | Example of MDL Determination steps to follow |
| 12.2 | Example of Data Collected during MDL _b Determination |
| 12.3 | Example of Data Collected during MDL _{sp} Determination |
| 12.4 | Expanded Student's t Distribution Table and Confidence Levels |

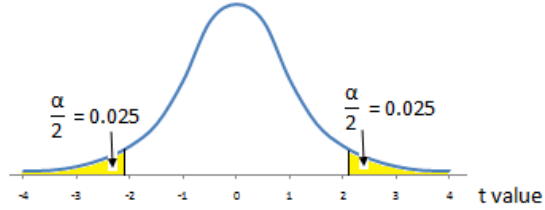
Appendix 12.1 Example of MDL Determination steps to follow

MDL TEST	
	Date: _____ thru _____
1	Run ZERO Point on 3 non-consecutive days for an adequate amount of time for the ZERO point to stabilize Using DAS software generate 10-minute average values from the minute data collected Enter the values into the MDL Blank min data tab to determine the target MDL sample test concentration Once completed proceed to the MDL Sample test
2	Connect cylinder used for sample point MDL to CYL 2 port on rear of calibrator, bleed cylinder Leak check and bleed the cylinder Enter cylinder type and concentration into calibrator menu Set the the air/gas flows to obtain MDL Sample point target concentration
3	Run MDL SPAN Point on 3 non-consecutive days for an adequate amount of time for the SPAN point to stabilize Using DAS software generate 10-minute average values from the minute data collected Enter the values into the MDL Sample min data tab
4	Disconnect the cylinder used for MDL sample test once procedure is completed
5	MDL Test Conducted by: _____
6	Save the file in the following format: Model Number Instrument Number MDL and Date range the test was completed (e.g. T500 #2 MDL 20210301 to 20210312)

Appendix 12.4 Expanded Student's t Distribution Table and Confidence Levels

Student's t Distribution Table

For example, the t value for
 18 degrees of freedom
 is 2.101 for 95% confidence
 interval (**2-Tail** $\alpha = 0.05$).



	90%	95%	97.5%	99%	99.5%	99.95%	1-Tail Confidence Level
	80%	90%	95%	98%	99%	99.9%	2-Tail Confidence Level
	0.100	0.050	0.025	0.010	0.005	0.0005	1-Tail Alpha
<i>df</i>	0.20	0.10	0.05	0.02	0.01	0.001	2-Tail Alpha
1	3.0777	6.3138	12.7062	31.8205	63.6567	636.6192	
2	1.8856	2.9200	4.3027	6.9646	9.9248	31.5991	
3	1.6377	2.3534	3.1824	4.5407	5.8409	12.9240	
4	1.5332	2.1318	2.7764	3.7469	4.6041	8.6103	
5	1.4759	2.0150	2.5706	3.3649	4.0321	6.8688	
6	1.4398	1.9432	2.4469	3.1427	3.7074	5.9588	
7	1.4149	1.8946	2.3646	2.9980	3.4995	5.4079	
8	1.3968	1.8595	2.3060	2.8965	3.3554	5.0413	
9	1.3830	1.8331	2.2622	2.8214	3.2498	4.7809	
10	1.3722	1.8125	2.2281	2.7638	3.1693	4.5869	
11	1.3634	1.7959	2.2010	2.7181	3.1058	4.4370	
12	1.3562	1.7823	2.1788	2.6810	3.0545	4.3178	
13	1.3502	1.7709	2.1604	2.6503	3.0123	4.2208	
14	1.3450	1.7613	2.1448	2.6245	2.9768	4.1405	
15	1.3406	1.7531	2.1314	2.6025	2.9467	4.0728	
16	1.3368	1.7459	2.1199	2.5835	2.9208	4.0150	
17	1.3334	1.7396	2.1098	2.5669	2.8982	3.9651	
18	1.3304	1.7341	2.1009	2.5524	2.8784	3.9216	
19	1.3277	1.7291	2.0930	2.5395	2.8609	3.8834	
20	1.3253	1.7247	2.0860	2.5280	2.8453	3.8495	
21	1.3232	1.7207	2.0796	2.5176	2.8314	3.8193	
22	1.3212	1.7171	2.0739	2.5083	2.8188	3.7921	
23	1.3195	1.7139	2.0687	2.4999	2.8073	3.7676	
24	1.3178	1.7109	2.0639	2.4922	2.7969	3.7454	
25	1.3163	1.7081	2.0595	2.4851	2.7874	3.7251	
26	1.3150	1.7056	2.0555	2.4786	2.7787	3.7066	
27	1.3137	1.7033	2.0518	2.4727	2.7707	3.6896	
28	1.3125	1.7011	2.0484	2.4671	2.7633	3.6739	
29	1.3114	1.6991	2.0452	2.4620	2.7564	3.6594	
30	1.3104	1.6973	2.0423	2.4573	2.7500	3.6460	