# The New MDL Procedure, 40 CFR Part 136

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# Method Detection Limit (MDL) Procedure

- 2015 Method Update Rule, 40 CFR Part 136
  - Proposed on February 19, 2015 – Federal Register
  - Final Rule – August 28, 2017 – Federal Register
  - Effective September 27, 2017, Revision 2
    - EPA recognizes change cannot occur instantaneously
    - Labs should check and comply with requirements of control or permitting authority.

# Method Detection Limit (MDL) Procedure

### *DEFINITION OF MDL*

- *Previous*
  - *Defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero*

- *Current (Revision 2)*
  - *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*

# Method Detection Limit (MDL) Procedure

- Determination of MDL
  - *Determined from analysis of a sample in a given matrix containing the analyte.*
    - *Water*
    - *Soil*
  - *Analysis specific*
  - *Analytical Method Specific*
    - *Most analysis methods require an MDL Determination*

# Method Detection Limit (MDL) Procedure

- No MDL Determination Required For:
  - Whole Effluent Toxicity
  - Presence/Absence Methods (ex. MMO-MUG)
  - Microbiological Methods
    - Colony Counts (Membrane Filtration)
    - Most Probable Number (Colilert-QT)

# Method Detection Limit (MDL) Procedure

- No MDL Determination Required For:
  - BOD
  - pH, Conductivity
  - Color and Odor
  - Dissolved Oxygen
  - Other analyses that cannot Incorporate Spikes

# So Why the Need for a Change?

# MDL New Procedure

- ## Previous MDL Procedure – Limitations

  - Assumed that all instruments will perform the same and have the same responses
  - Narrowed the estimation of the variability of the method.
    - Limited Sample Set – 7 replicates
    - Measured over a short period of time
    - Measured only annually

# MDL New Procedure

- **Previous MDL Procedure – Limitations**
  - Instrument Sensitivity Increasing
    - Better precision in instruments
    - Calculated MDLs getting lower and lower
      - But can the MDL really be achieved in laboratory day to day operations?

# MDL New Procedure

- ## New MDL Procedure
  - Originally created by The NELAC Institute (TNI)
  - EPA Proposed New Revisions, February 19, 2015
    - Federal Register
  - Better representation of inter-laboratory variability
  - More representative of actual laboratory detection limits

# MDL New Procedure

- ## New MDL Procedure
  - Thought to produce a more reasonable MDL
    - Address blank contamination and false positive results.
      - Accounts for background levels and contamination
      - Reduces False positive detections
  - More representative of lab detection limits
  - On-going quarterly verification
    - At least two spiked samples on each instrument
      - Separate batches if possible.

# MDL New Procedure

## *PREVIOUS MDL PROCEDURE

- A low-level reference standard is prepared
  - 1-10 times the expected method detection limit

* 40 CFR Part 136, Appendix B, Promulgated in 1984

### Example MDL Study

| Method | Total Cyanide |
|---|---|
| Date: | 3/15/2016 |
| Expiration Date: | 3/15/2017 |
| Instrument ID | Lachat |
| Replicate | 5.0 ug/L |
| 1.00 | 6.475 |
| 2.00 | 6.943 |
| 3.00 | 6.760 |
| 4.00 | 6.884 |
| 5.00 | 6.741 |
| 6.00 | 7.179 |
| 7.00 | 7.779 |
| STD Conc. | 5.0 |
| Student T | 3.143 |
| % Recovery | 139.317 |
| Average | 6.966 |
| Stdev | 0.418 |
| %RSD | 5.999 |
| MDL | 1.313 |
| PQL | 5.000 |

# MDL New Procedure

## *PREVIOUS MDL PROCEDURE

- Seven (7) aliquots of standard analyzed
  - Taken through the entire analytical process
    - Using the approved SOP
    - Each applicable analysis

  \* 40 CFR Part 136, Appendix B, Promulgated in 1984

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## *PREVIOUS MDL PROCEDURE

### Example MDL Study

- The standard deviation is calculated using the 7 replicate results
- The MDL is calculated
  - Product of:
    - the standard deviation
    - the student's t value for 99% confidence level with n-1 degrees of freedom (3.14) for the seven replicates.

* 40 CFR Part 136, Appendix B, Promulgated in 1984

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# MDL New Procedure

- New MDL Procedure -
  - Estimation of an Initial MDL
  - Determination of the Initial MDL
  - On-Going Data Collection
  - Annual MDL Verification

# MDL New Procedure

- New MDL Procedure
  - Preparation of Spikes
  - A low-level reference standard  is prepared
    - 2-10 times the expected MDL
      - Previous MDL
      - No previous MDL information?  Initial MDL will need to be estimated.

# MDL New Procedure

- Estimation of Initial MDL
  - Mean Concentration plus 3 times the standard deviation of a set of method blanks
  - The concentration equivalent to 3 times the standard deviation of replicate Instrumental measurements of spiked blanks.
  - The concentration value that corresponds to an instrument signal to noise ratio in the range of 3 to 5
  - The region of the calibration where there is a significant change in sensitivity.

- **New MDL Procedure**
  - A <span style="color:red">minimum</span> of seven (7) blanks
  - A <span style="color:red">minimum</span> of seven (7) spiked samples analyzed
    - Taken through the entire analytical process
      - Includes any preservation processes
      - Preparation processes.

# MDL New Procedure

- # Spike and Blanks
  - Replicates analyzed across three (3) or more preparation and analytical batches

  - Batches prepared and analyzed on at least three (3) separate calendar dates

2 samples Monday

1 sample Tuesday

2 samples Thursday

2 samples Friday

- # Spikes and Blanks
  - ## Multiple Instruments, if necessary
    - ### Minimum of two spikes and two blanks per instrument.

1 spike/blank Wednesday
2 spikes/blanks Thursday

1 spike/blank Monday,
1 spike/blank Thursday

1 sample/blank Monday
1 spike/blank Wednesday

# MDL New Procedure

- Evaluation of Spiked Sample Results
  - If spiked samples do not produce a numerical result
    - Prepare spiked samples again at a higher concentration.

# MDL New Procedure

- Evaluation of Blank Results
  - If blanks give no numerical results, the blank MDL does not apply
    - Numerical result includes both positive and negative results
  - If some but not all blanks give numerical results
    - Set the blank MDL equal to the highest blank result

- **New MDL Procedure**
  - The MDL of the spikes is calculated
    - $MDL_s = tS_s$
      - S is the standard deviation of Spikes
      - t is the student's t value for 99% confidence level with n-1 degrees of freedom (3.14) for seven replicates.
        - Different if more than seven.

- The MDL of the blanks is calculated
  - $MDL_b = X_{avg} + tS_b$
    - X is the average of the results for the blanks
    - $S_b$ is the standard deviation of Blank Results
    - t is the student's t value for 99% confidence level with n-1 degrees of freedom (3.14) for the seven replicates.

# MDL New Procedure

- Student t Value will vary according to how many replicates are used in the determination

**Student's Value**

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

| 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 |
| 11 | 10 | 2.764 |
| 16 | 15 | 2.602 |
| 21 | 20 | 2.528 |
| 26 | 25 | 2.485 |
| 31 | 30 | 2.457 |
| 61 | 60 | 2.390 |
| 100 | 100 | 2.326 |

# MDL New Procedure

- New MDL Procedure
  - Higher value between $MDL_s$ and $MDL_b$ is the winner and gets to be the MDL!



| Analyst | Joe Analyst | |
|---|---|---|
| Date | 4/14/2015 | |
| Expires | 4/14/2016 | |
| strument ID | | |
| MDL Study | | |
| Replicate | STD CONC | Blank |
| Day 1 | 0.029 | 0.001 |
| Day 1 | 0.030 | 0.005 |
| Day 2 | 0.025 | 0.008 |
| Day 3 | 0.028 | 0.001 |
| Day 3 | 0.024 | 0.002 |
| Day 4 | 0.021 | 0.006 |
| Day 4 | 0.019 | 0.003 |
| ncentration | 0.030 | |
| t's t for n=7 | 3.143 | 3.143 |
| Average | 0.02514 | 0.00371 |
| % Recovery | 83.81 | |
| d Deviation | 0.00414 | 0.00269 |
| MDL | 0.01301 | 0.0121 |

Lachat-1 MDL Study

# MDL New Procedure

- **On-going Collection of Data/Annual Recalculation**
  - Analyze at least 2 spikes and 2 blanks every quarter in separate batches. (Exception: if no samples are analyzed in the quarter, this is not required).
    - Each Instrument
      - Total of at least 7 spikes annually
      - Total of at least 7 blanks annually
  - Make sure to analyze an initial MDL study
    - If method is altered in any way to changed sensitivity OR
    - Instrument is moved.

# MDL New Procedure

- Annual Recalculation of MDL
  - Recalculate $MDL_s$ and $MDL_b$ Every 13 Months
    - Use data from the quarterly spike and blank samples
    - Include Data from prior 24 months, if available
    - Use only data associated with acceptable QC

# MDL New Procedure

- Annual Recalculation of MDL
  - MDL is verified if it is between 0.5 to 2 times the existing MDL AND
  - Results for Less than 3 % of the method blanks analyzed were above the existing MDL
    - MDL can be updated if desired, or retained for the next year.

  - MDL Must be Updated if the above requirements are not met.

# MDL New Procedure

- **Previous  MDL vs New MDL**

  - Previous: 7 Replicates of Standard/Annually
  - New: 7 replicates of a standard and 7 replicates of a blank

  - Previous: All 7 replicates of Standard analyzed at the same time
  - New: At least 3 batches run on at least 3 separate days. Note:  Can use previous data also.

- **Previous MDL vs New MDL**

  - Previous: No Blanks Analyzed
  - New: At Least 7 replicates of a blank sample analyzed on at least 3 separate days. Note: Can use previous data.

# MDL New Procedure

- Previous  MDL vs New MDL

  - Previous:  Replicates analyzed on one instrument
  - New:  Replicates analyzed across multiple instruments, if lab has more than one

  - Previous: MDL Performed Annually
  - New: Quarterly Verification; Annual Recalculation.

# MDL New Procedure

- Previous MDL vs New MDL

  - Previous: Replicates analyzed on one instrument
  - New: Replicates analyzed across multiple instruments, if lab has more than one

  - Previous: MDL Performed Annually
  - New: Quarterly spike sample data and method blank sample data collected. Annual Recalculation

# MDL New Procedure

- ## New MDL Procedure – Effects

  - ### Laboratories seeing increased MDL values
    - Mostly seems to be due to the incorporation of blank analyses into the method.

      - Analyses where the target is not usually detected in the method blanks, or at low levels – Minimal Change

      - *Analyses where there are frequent detections in the method blanks -  Potentially A Lot.*

# MDL New Procedure

- New MDL Procedure – Effects

  - EPA Realizes This
    - Permittees will need to review permit limits
      - Ensure the most sensitive methods are used for compliance.
      - Might need to review and/or adjust regulatory limits???

# MDL New Procedure

- References
  - 40 CFR Part 136
  - *Definition and Procedure for the Determination of the Method Detection Limit, Revision 2*, EPA Office of Water, EPA 821-R-16-006

  https://www.epa.gov/sites/production/files/2016-12/documents/mdl-procedure_rev2_12-13-2016.pdf

# MDL New Procedure

QUESTIONS?