2017 Revised Method Update Rule Information

MDL Examples and EPA Procedure
Years Past ... (since 2012)

- Past MDL requirements (guidance provided on FTC website)
  - 1020 B. 4
  
  - Ideally, prepare and analyze at least seven (7) portions of this solution over a 3-day period to ensure that the MDL determination is more representative of routine measurements as performed in the laboratory.
  
  - The replicate measurements should be in the range of one to five times the estimated MDL, and recoveries of the known addition should be between 50 and 150%, with %RSD (relative standard deviation) values ≤ 20%.
Years Past ... (since 2012)

• Past MDL requirements
  – 4020 B.1.b. – Verify MDL at least annually.
  – Ideally use pooled data from several analysts rather than data from one analyst. *(example provided)*

  • Real people language – have several operators, who run this test, analyze an NH3 Standard at a concentration of 0.15 mg/L over several days with a total of at least 7 samples
    – Joe analyzes 3 samples on Monday
    – Bob analyzes 3 samples on Tuesday
    – Mary analyzes 3 samples on Wednesday

• Run this once a year
... Now (since September 2017)

• The initial MDLs
  – Process a minimum of **seven spiked samples** and **seven method blank samples** through all steps of the method.
    • The samples used for the MDL must be prepared in at least **three batches** on three separate calendar dates and analyzed on three separate calendar dates. (Preparation and analysis may be on the same day.)
      – *Real people language – Sounds familiar, right?*
    • Existing data may be used, if compliant with the requirements for at least three batches, and generated within the last twenty four months.
... Now (since September 2017)

• Ongoing MDLs
  – MDLs must be re-evaluated at least once every 13 months using all data generated within the past 24 months. (If necessary change the reported MDL to the new value.)
    • Analyze at least 2 spikes (the same concentration as the initial MDL spikes) in separate batches per quarter.
    • Analyze method blanks as required by normal laboratory batch QC. (A minimum of 2 method blanks in separate batches are also required.)
... Now (since September 2017)

• Ongoing MDLs
  
  • Real people language – You are already doing the spikes and blanks in accordance with the MUR (method update rule) as your required QA/QC. (12 step 40 CFR 136.7)
  
  You are just logging the information into the MDL Calculator and it does the work for you.

  – Record all values in a log book or keep a running log in a spreadsheet (or MDL Calculator).
Layout of the Document

• The links provided in the guidance take you directly to the EPA procedure (*Click link*) – ammonia as nitrogen example.
  – *Click link* to navigate to EPA’s *Definition and Procedure for the Determination of the Method Detection Limit, Revision 2.*

• Procedure 1 (*Click link*) – Estimate initial MDL Determination
  
  Click “Blue-gray References” to launch to EPA Procedure. From Procedure press “Alt” + “Left Arrow” or “Right-Click” and choose “Previous View” to return to the example.
Layout of the Document

• Procedure 2 (*Click link*) – Initial MDL Determination

• Procedure (2) (c) (*Click link*) – Record and evaluate MDL spiking level

• Procedure (2) (d) (ii) (*Click link*) – Calculate the initial MDL spike ($MDL_s$).
  – Use a suitable statistical spreadsheet

• Procedure (2) (b) (*Click link*) – Prepare method blanks
Procedure (2) (d) (iii) *(Click link)* – Calculate the initial MDL blank (MDL\textsubscript{b}).

- Use a suitable statistical spreadsheet

Procedure (2) (e) *(Click link)* – Initial MDL Calculation

Procedure (3) *(Click link)* – Ongoing Data Collection

Procedure (4) *(Click link)* – Ongoing Annual Verification
MDLb only - Total Suspended Solids Example

- Procedure 2 (*Click link*) – Initial MDL Determination
- Procedure (2) (b) (*Click link*) – using reagent grade water
- Procedure (2) (d) (iii)(*Click link*) – Calculate Initial MDLb
  - Use a suitable statistical spreadsheet
Layout of the Document

• Procedure 3 *(Click link)* – Ongoing Data Collection

• Procedure 4 *(Click link)* – Ongoing Annual Verification

• Flow chart

• EPA procedure – *Definition and Procedure for the Determination of the Method Detection Limit, Revision 2*
Exercise for Spikes and Blanks

• Ammonia as Nitrogen
  – *Standard Methods for Water and Wastewater Analyses*, (2011 approval date)
    • **Ammonia** exists naturally in the **air** at **levels** between 1 and 5 parts in a billion parts of **air** (ppb).
    • Prepare method blanks using reagent water (ammonia free) 4500-NH₃ B. 3.
      – Strongly acidic cationic exchange resin
      – Distillation
    • Unable to store ammonia-free water for any length of time. Must be prepared fresh.
Exercise for Spikes and Blanks

• Ammonia as Nitrogen – Initial MDL
  – Prepare spike solutions using ammonia-free reagent water
    • Concentration range for ammonia as nitrogen is typically between 0.1 to 0.03 mg/L.
    • Use reagent grade water
    • Consider preparing 0.03 mg/L concentration into 1L using this formula $C_1 \times V_1 = C_2 \times V_2$
Exercise for Spikes and Blanks

• Ammonia as Nitrogen
  – For initial MDL - Prepare spike (standard) solutions
    • Consider preparing 0.03 mg/L concentration into 1L.

• Use or make a 100 mg/L ammonia as nitrogen standard.

\[ C_1 \times V_1 = C_2 \times V_2 \]

100 mg/L \times V_1 = 0.03 \text{ mg/L} \times 1000 \text{ mL/L}

\[ V_1 = 0.3 \text{ mL} \]
Exercise for Spikes and Blanks

• Ammonia as Nitrogen

Take 0.3 mL of the 100 mg/L standard and put into 1000 mL volumetric flask.

Note - You can prepare your 0.03 mg/L standard any way that you like

Using approved method analyze at least seven spike samples.
Exercise for Spikes and Blanks

<table>
<thead>
<tr>
<th>Date</th>
<th>Analyst</th>
<th>Number</th>
<th>Spike mg/L</th>
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<tbody>
<tr>
<td>04/12/18</td>
<td>BGL</td>
<td>1</td>
<td>0.027</td>
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<tr>
<td>04/12/18</td>
<td>BGL</td>
<td>2</td>
<td>0.028</td>
</tr>
<tr>
<td>04/13/18</td>
<td>BGL</td>
<td>3</td>
<td>0.025</td>
</tr>
<tr>
<td>04/13/18</td>
<td>BGL</td>
<td>4</td>
<td>0.028</td>
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<tr>
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<td>BGL</td>
<td>5</td>
<td>0.030</td>
</tr>
<tr>
<td>04/14/18</td>
<td>BGL</td>
<td>6</td>
<td>0.025</td>
</tr>
<tr>
<td>04/15/18</td>
<td>BGL</td>
<td>7</td>
<td>0.027</td>
</tr>
<tr>
<td>04/15/18</td>
<td>BGL</td>
<td>8</td>
<td>0.025</td>
</tr>
</tbody>
</table>
Statistical Spreadsheet

- Pull up MDL Calculator on FTC’s website (Excel spreadsheet)
Exercise for Spikes and Blanks

• Enter the analytical results into a statistical spreadsheet.
Exercise for Spikes and Blanks

- Ammonia as Nitrogen – Initial MDL
  - Prepare blanks using ammonia-free reagent water
    - Pour up at least 7 ammonia-free blanks on three different dates.

<table>
<thead>
<tr>
<th>Date</th>
<th>Analyst</th>
<th>Number</th>
<th>Method Blank, mg/L</th>
</tr>
</thead>
<tbody>
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<tr>
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<td>0.01</td>
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<tr>
<td>04/13/18</td>
<td>BGL</td>
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<tr>
<td>04/13/18</td>
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<tr>
<td>04/14/18</td>
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<tr>
<td>04/15/18</td>
<td>BGL</td>
<td>8</td>
<td>0.01</td>
</tr>
</tbody>
</table>
Exercise for Spikes and Blanks

- Enter the analytical results into a statistical spreadsheet.
State MDL Calculator

• When you enter the dates, analysts and the values (true values and readings obtained in the analyses) into the spreadsheet for MDLs (tab) or MDLb (tab), you generate:
  – Spike standard deviation,
  – Spike average,
  – Data points <24 months and
  – Student t value (calculated automatically) data will be generated.
State MDL Calculator

• If any result for any of the spiked samples does not provide a numerical result greater than zero, repeat the spiked sample analysis at a higher concentration.

• If you obtain an “nd” reading on a blank (or some other text output that is non-numeric) and enter that into the calculator, the MDL\textsubscript{b} will be set to the highest blank value. (MDL\textsubscript{b} tab)
State MDL Calculator

- However, “0”s and negative values are acceptable to enter into the calculator table.
- The *Click links* take you from the examples to the EPA procedure. It explains what considerations are made in the calculations.
- You must also enter the analyte name and the date so that the MDL will be re-evaluated based on the most recent 24 months’ data. (examples are provided)
State MDL Calculator

- The spreadsheet will also generate the following information:
  - Required # of Dates PASS/FAIL
  - Required # of replicates PASS/FAIL
  - Spike level evaluation PASS/FAIL
  - Spiked MDL (value)
  - Blank MDL (value)
  - Minimum level (value)
  - METHOD detection limit (incorporating both blanks and spikes) (value)
State MDL Calculator

• Once you’ve entered all this information into the MDL calculator, you have determined that
  – You have provided the required # of data points - PASSED
  – You have provided the required # of replicates - PASSED
  – You have provided the required # of replicates - PASSED
  – Your spike level was adequate – PASSED
State MDL Calculator

– Your spike MDL was calculated 0.0054 mg/L
– Your blank MDL was calculated as 0.0435 mg/L (from the MDLₐ tab)
– The minimum level was calculated for you as 0.1306 mg/L
– And, finally, the MDL that gave consideration to spikes and blanks was determined to be 0.0435 mg/L
Ongoing Data Collection for Spikes and Blanks

• Analyze at least 2 spikes (the same concentration as the initial MDL spikes) in separate batches per quarter.

• Analyze method blanks as required by normal laboratory batch QC. (A minimum of 2 method blanks in separate batches are also required.)

• Record all values in a log book or keep a running log in a spreadsheet (or MDL Calculator).
Ongoing Annual Verification for Spikes and Blanks

• At least once every 13 months re-calculate using all data generated within the past 24 months. (If necessary change the reported MDL to the new value.)
  
  – Be certain to save or print off the MDL data for the previous year before changing the date for calculating the next MDL.
Exercise for Blanks Only

• Total Suspended Solids – Initial MDL
  – Prepare blanks reagent grade water
    • pour up at least 7 reagent blanks on three different dates.
Exercise for Blanks Only
# Exercise for Blanks Only

<table>
<thead>
<tr>
<th>Date</th>
<th>Analyst</th>
<th>Number</th>
<th>Method Blank, mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>03/05/18</td>
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<tr>
<td>03/09/18</td>
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<tr>
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</tr>
<tr>
<td>03/14/18</td>
<td>SP</td>
<td>8</td>
<td>0.6</td>
</tr>
</tbody>
</table>
Exercise for Blanks Only

- Calculate the Initial MDL_b.
  - Use a suitable statistical spreadsheet
Exercise for Blanks Only

– If 100 or more method blanks are available, as an option, MDLₐ 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) of the EPA Procedure.
Exercise for Blanks Only

• **Initial MDL Calculation** –
  - The Initial MDL is equal to the MDL$_b$ value as calculated above.

• **Ongoing Data Collection** -
  - Analyze method blanks as required by normal laboratory batch QC. (A minimum of 2 method blanks in separate batches.) Record all values in a log book or keep a running log in a spreadsheet.
Exercise for Blanks Only

• **Ongoing Annual Verification** –
  
  – At least once every 13 months re-calculate using all data generated within the past 24 months. (If necessary change the reported MDL to the new value.) *Procedure (4) (a) and (4) (f)*
  
  – Ideally, use all method blank results from the last 24 months for the MDL\textsubscript{b} calculation.
    
    • The laboratory has the option to use only the last 6 months of method blank data or the 50 most recent method blanks, whichever criteria yields the greater number of method blanks. *Procedure (4) (e)*
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