The EPA has changed the LOD procedure...
Are YOU up to speed?

WISCONSIN
DEPT. OF NATURAL RESOURCES

WISCONSIN DNR
Department of Natural Resources

Nope...it wasn't us.

Federal Register /Vol. 82, No. 165 /Monday, August 28, 2017
ACTION: Final rule.
DATES: This regulation is effective on September 27, 2017.

- It's still based on precision (standard deviation).

- You still need to analyze spiked blanks to determine the LOD.

- You still have to do something annually (*the something has changed*).

- It remains in your best interest to perform a "reasonableness" check.
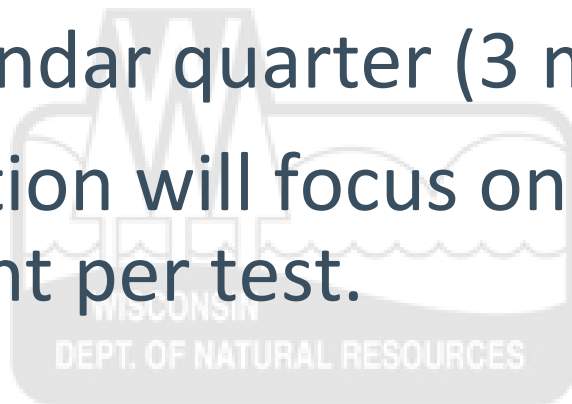
- One prepared spiked blank may be analyzed on multiple instruments so long as still have 7 spikes from at least 3 separate batches.

- Compare routine method blank results to the MDL.

- No more "validation" of the MDL.
    i.e. **Spike level > MDL > 10% spike level**
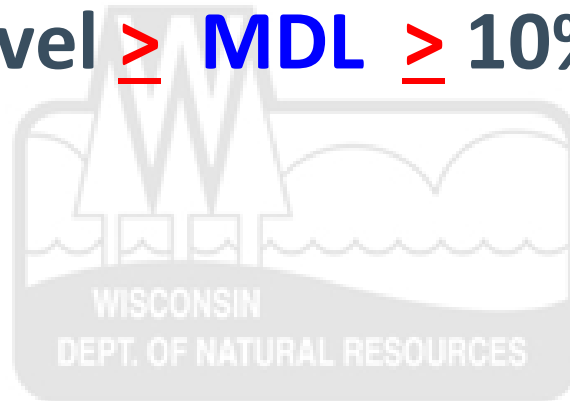
- WI uses "LOD." 40 CFR uses "MDL." We consider **MDL equivalent to LOD**.

- Regulation discusses "**spiked blanks**;" you known better as **LOD replicates**, standards, or spiked blanks (LCS).

- Method blank here is designated as "**MB**"

- Creates terms:
  MDL$_B$ (LOD$_B$) for LOD based on [method] blanks
  MDL$_S$ (LOD$_S$) for LOD based on spiked blanks.

- QTR means calendar quarter (3 months)

- This is presentation will focus on WWTP labs using only 1 instrument per test.

The Spreadsheet

Wisconsin DNR — Department of Natural Resources

File | Home | Insert | Draw | Page Layout | Formulas | Data | Review | View | Developer | ACROBAT | Tell me what you want to do

A2 — Estimating Initial LOD Worksheet (Single Instrument)

Wisconsin Department of Natural Resources

Spreadsheet for Use in Determining LOD per 40 CFR 136 Appendix B, Revision 2

Created: Feb. 14, 2018

Estimating Initial LOD Worksheet (Single Instrument)

Use this form if:	a new method is implemented

Use any of the six options to estimate the initial LOD. Fill in the green cells. Cells in yellow have the estimated LOD.

Previously Determined LOD:	Instrument limitations or vendor claims:	Point at which there is a significant change in sensitivity of the calibration curve:	Concentration where Signal to Noise Ratio is 3 - 5:

Spiked Blanks				Method Blanks		
	Date Analyzed	Result			Date Analyzed	Result
1				1		
2				2		
3				3		

Tabs: Estimate Initial LOD | Initial LOD (8 MB) | Initial LOD (>8 MB) | Ongoing LOD | Add or Change Instrument | NOTES | St …

The Spreadsheet

Wisconsin Department of Natural Resources — Spreadsheet for Use in Determining LOD per 40 CFR 136 Appendix B, Revision 2 — Created: Feb. 14, 2018

Estimating Initial LOD Worksheet (Single Instrument)

Use this form if:	a new method is implemented

Use any of the six options to estimate the initial LOD. Fill in the green cells. Cells in yellow have the estimated LOD.

Previously Determined LOD:	Instrument limitations or vendor claims:	Point at which there is a significant change in sensitivity of the calibration curve:	Concentration where Signal to Noise Ratio is 3 - 5:

Spiked Blanks

	Date Analyzed	Result
1		
2		
3		
4		
5		
6		
7		
8		

Standard Deviation:	

Estimated LOD_s:		mg/L

Method Blanks

	Date Analyzed	Result
1		
2		
3		
4		
5		
6		
7		
8		

Average:	
Standard Deviation:	

Estimated LOD_b:		mg/L

Estimate Initial LOD | Initial LOD (8 MB) | Initial LOD (>8 MB) | Ongoing LOD | Add or Change

Nothing much changes here

a. Mean + 3 Std Dev of "a set of blanks"

b. Concentration producing S/N ratio of 3-5

c. Concentration 3 X Std Dev of spiked blanks

Since you already have a real LOD...

Skip THIS

▶|▶|▶|▶|▶|

Initial LOD/LOQ Calculation and Validation Worksheet (Single Instrument)

Use this form if:	a new method is implemented
	the method was rarely used in the last 2 years and 10 or less method blanks have been analyzed
	there are not enough data to perform the Ongoing Annual Verification

Analytical Method:		Calculation Date:	
Matrix:		Calculation Analyst:	

Spiked Blanks

	Date Prepped	Date Analyzed	Result	% Recovery
1				
2				
3				
4				
5				
6				
7				
8				

Spike Level:		mg/L
Average:	#DIV/0!	#DIV/0!
Standard Deviation:	#DIV/0!	
Student's t-value to use:	#NUM!	
Calculated LOD_s:	NA	mg/L

Method Blanks

	Date Prepped	Date Analyzed	Result
1			
2			
3			
4			
5			
6			
7			
8			

Average:	#DIV/0!
Standard Deviation:	#DIV/0!
Student's t-value to use:	#NUM!
Calculated LOD_b:	mg/L

Calculated LOD:	NA	mg/L	(calculated from the greater of LOD_s and LOD_b)
Calculated LOQ:	#VALUE!	mg/L	(= 10/3 x LOD)

Were outliers rejected?		(only gross failures may be excluded)
If so, explain:		

NOTES:

Include **spiked blank** data generated within the last 2 years as long as the data all used the same spike level (include initial results if within 2 years).

If the lab thinks the sensitivity of the method has changed significantly, then the most recent data may be used (min. of 7 reps, 3 batches, over 3 days).

Only use data associated with passing calibrations and passing batch QC (reported data).

The LOD_s and LOD_b will need to be recalculated at least every 13 months.

Estimate Initial LOD | **Initial LOD (8 MB)** | Initial LOD (>8 MB) | Ongoing LOD

a. Spiking level = 2-10 X estimated [LOD]

NOTE: start with what you used last time.

– If any result **is ≤ 0,** repeat at higher spike concentration.

b. Analyze a minimum of 7 spiked blanks PLUS a minimum of 7 method blanks

– *Make the spiked blank solution on at least 3 different calendar days*

– *Run the spiked blank solution on at least 3 separate calendar days*

– *should not use outlier rejection (except for gross & documented failures*

Only 1 instrument!

d. Calculations

- The spreadsheet will calculate the LOD_S as it used to be done:

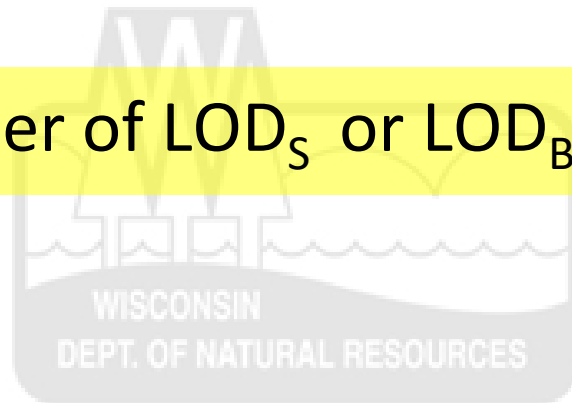 $LOD_S = t \times SD_s$

- The spreadsheet will calculate the LOD_B:

  $LOD_B = Mean_{MB} + (\, t \times SD_B)$

  if $Mean_{MB} < 0$, use "0"

- LOD = Greater of LOD_S or LOD_B

	Student's t value to dof.	#NUM.				Student's t value to dof.	#NUM.	
Calculated LOD$_s$:	NA	mg/L			Calculated LOD$_b$:		mg/L	

		Calculated LOD:	NA	mg/L	(calculated from the greater of LOD$_s$ and LOD$_b$)
		Calculated LOQ:	#VALUE!	mg/L	(= 10/3 x LOD)

Were outliers rejected?		(only gross failures may be excluded)
If so, explain:		

NOTES:

Include **spiked blank** data generated within the last 2 years as long as the data all used the same spike level (include initial results if within 2 years).

If the lab thinks the sensitivity of the method has changed significantly, then the most recent data may be used (min. of 7 reps, 3 batches, over 3 days).

Only use data associated with passing calibrations and passing batch QC (reported data).

The LOD$_s$ and LOD$_b$ will need to be recalculated at least every 13 months.

Optional LOD Checks (using outdated LOD regulations, but may give insight to LOD determination)					
	LOD	[spike]			
Low Spike Check - Did you spike too low? - - LOD < Spike Concentration -	NA	0.000	Not OK--Repeat LOD	If fails, you need to spike at higher concentration	Variability is too high, so the std deviation is too close to LOD
	[Spike]	LOD x 10			
High Spike Check - Did you spike too high? - - Spike Concentration < 10 x LOD -	0.000	#VALUE!	#VALUE!	If fails, you need to spike at lower concentration	LOD is unrealistically low
	LOD	Permit Limit			
Action Limit Check - LOD < Permit Limit? -	NA		Not OK--Repeat LOD	If fails, the method must be optimized to be able to meet permit limits.	
	Lower Limit	Upper Limit			
Is average recovery reasonable?	80%	120%	#DIV/0!	General guidelines, don't re-run study if outside	

◄ ▶ | Estimate Initial LOD | **Initial LOD (8 MB)** | Initial LOD (>8 MB) | Ongoing LOD

- **...is the LOD_B.**

- The LOD_S is simply the age-old calculation for LOD.

- With the new protocol, in addition to the familiar LOD calculation (now LOD_S), you calculate the LOD_B.

- The new LOD is set at the greater of LOD_B & LOD_S

The Spreadsheet

WISCONSIN DNR
Department of Natural Resources

Initial LOD/LOQ Calculation and Validation Worksheet (Single Instrument)

Use this form if:	a new method is implemented
	the method was rarely used in the last 2 years but more than 8 method blanks have been analyzed
	there are not enough data to perform the Ongoing Annual Verification

Analytical Method:	
Matrix:	

Calculation Date:	
Calculation by Analyst:	

Spiked Blanks

	Date Prepped	Date Analyzed	Result	% Recovery
Q1 A				
Q1 B				
Q2 A				
Q2 B				
Q3 A				
Q3 B				
Q4 A				
Q4 B				

Spike Level:		mg/L
Average:	#DIV/0!	#DIV/0!
Standard Deviation:	#DIV/0!	
Student's t-value to use:	#NUM!	
Calculated LOD$_s$:	NA	mg/L

Method Blanks (see data to the right)

>100 method blank results?	No
If yes, 99th percentile of blank results:	N/A
Average of all results:	#DIV/0!
Standard Deviation of all results:	#DIV/0!

LOD$_b$ if 99th percentile is used:	N/A	mg/L
LOD$_b$ if standard deviation is used:	#DIV/0!	mg/L

Which option will be used:	

(can only use 99th Percentile if more than 100 method blanks)

Student's t-value to use:	#NUM!	
Calculated LOD$_b$:		mg/L

Calculated LOD:	NA	mg/L	(calculated from the greater of LOD$_s$ and LOD$_b$)
Calculated LOQ:	#####	mg/L	(= 10/3 x LOD)

Were outliers rejected?	(only gross failures may be excluded)
If so, explain:	

Method Blank Data

Date	Result

Estimate Initial LOD | Initial LOD (8 MB) | **Initial LOD (>8 MB)** | Ongoing LOD | Add or Change Instrument | NOTES

e. Calculations with more than 8 method blanks

- **IF** $\geq$ *100 MB results,* then LOD$_B$ may use 99th %ile or standard deviation calculation

- *Spreadsheet will show both results—select the option that is best for your lab (may need a lower LOD or may not need to achieve a super-low LOD)*

The Spreadsheet

WISCONSIN DNR — Department of Natural Resources

Ongoing LOD/LOQ Calculation and Verification Worksheet (Single Instrument)

Analytical Method:		Calculation Date:
Matrix:		Calculation by Analyst:

Spiked Blanks (include data generated within the last 2 years)

	Date Prepped	Date Analyzed	Result	% Recovery
Initial LOD 1				
Initial LOD 2				
Initial LOD 3				
Initial LOD 4				
Initial LOD 5				
Initial LOD 6				
Initial LOD 7				
Initial LOD 8				
Q1 A				
Q1 B				
Q2 A				
Q2 B				
Q3 A				
Q3 B				
Q4 A				
Q4 B				
Q1 A				
Q1 B				
Q2 A				
Q2 B				
Q3 A				
Q3 B				
Q4 A				
Q4 B				

Spike Level (same as initial):		mg/L
Average:	#DIV/0!	#DIV/0!
Standard Deviation:	#DIV/0!	
Student's t-value to use:	#NUM!	
Calculated LOD$_s$:	NA	mg/L

Method Blanks (see data to the right)

>100 method blank results?	No
If yes, 99th percentile of blank results:	NA
Average of all results:	#DIV/0!
Standard Deviation of all results:	#DIV/0!

LOD$_b$ if 99th percentile is used:	NA	mg/L
LOD$_b$ if standard deviation is used:	#DIV/0!	mg/L

Which option will be used:
(can only use 99th Percentile if more than 100 method blanks)

Student's t-value to use:	#NUM!	
Calculated LOD$_b$:	NA	mg/L

Calculated LOD:	NA	mg/L	(calculated from the greater of LOD$_s$ and LOD$_b$)
Calculated LOQ:	######	mg/L	(= 10/3 × LOD)

Existing LOD:		mg/L	
Can the existing LOD be left unchanged?			Use the new calculated LOD.
Is spike level okay (<5% spiked blanks <0)?		#DIV/0!	#DIV/0!

Were outliers rejected?		(only gross failures may be excluded)
If so, explain:		

NOTES:
Recalculate LOD$_s$ and LOD$_b$ at least every 13 months.
Include **spiked blank** data generated within the last 2 years as long as the data all used the same spike level (include initial results if within 2 years).
If the lab thinks the sensitivity of the method has changed significantly, then the most recent data may be used (min. of 7 reps, 3 batches, over 3 days).

Method Blank Data

Date	Result

Tabs: Estimate Initial LOD | Initial LOD (8 MB) | Initial LOD (>8 MB) | **Ongoing LOD**

a. In a given quarter, prepare and analyze a minimum of 2 spiked samples in separate batches.

b. Need at *least* 7 spiked blanks *(by the end of the year)*

Can use up to 2 years of historical data:

Initial LOD: 8 replicates – *NO spiked replicate can be < 0*
Year 1: 16 total replicates – *NO spiked replicate can be < 0*
Year 2: 24 total replicates – *can have only 1 spiked replicate < 0*

c. Need at *least* 7 method blanks *(by the end of the year)*

d. Ideally use all MB data from last 24 months.

   OPTION (*use whichever provides more data*)
   – Use only the last 6 months of data, **OR**
   – Use the 50 most recent method blanks

e. At least every 13 months, re-calculate LOD_S and LOD_B from data collected.

f. Include data within the last 24 months, but only data at the same spike level. Only documented gross failures may be excluded.

BUT... *Must still have 7 spikes over 3 calendar days*

g. Include the initial LOD spikes if the data were generated within past 24 months.

h. Only use data with acceptable calibration and QC
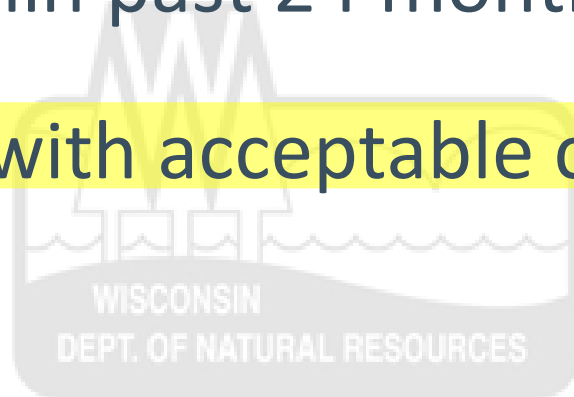
a. Verified LOD = the greater of: LOD_S or LOD_B

IF verified LOD is within 0.5x – 2x existing LOD **AND**
< 3% MB are numerical results > existing LOD,

THEN you may CHOOSE to keep existing LOD **OR** replace existing LOD with the verified LOD

IF verification does not meet the criteria,
MUST replace existing LOD with the new LOD

b. At least annually, re-evaluate <u>spike level</u>

– If > 5% of spiked blanks are not > 0, must increase spike concentration and re-determine Initial LOD.

c. If method is changed in any way *that can reasonably be expected to affect sensitivity* (e.g., LOD) must re-determine initial LOD and re-start ongoing data collection.

This is an important piece.

The key to the new protocol is that everything must be maintained the same:

- *Replicate spike concentration*
- *Instrument operating condition*
- *Reagent quality*

The Spreadsheet

Ongoing LOD/LOQ Calculation and Verification Worksheet (Single Instrument)

				Method Blank Data
Analytical Method:		Calculation Date:		Date	Result
Matrix:		Calculation by Analyst:			

Spiked Blanks (include data generated within the last 2 years)

	Date Prepped	Date Analyzed	Result	% Recovery
Initial LOD 1				
Initial LOD 2				
Initial LOD 3				
Initial LOD 4				
Initial LOD 5				
Initial LOD 6				
Initial LOD 7				
Initial LOD 8				
Q1 A				
Q1 B				
Q2 A				
Q2 B				
Q3 A				
Q3 B				
Q4 A				
Q4 B				
Q1 A				
Q1 B				
Q2 A				
Q2 B				
Q3 A				
Q3 B				
Q4 A				
Q4 B				

Method Blanks (see data to the right)

>100 method blank results?	No
If yes, 99th percentile of blank results:	NA
Average of all results:	#DIV/0!
Standard Deviation of all results:	#DIV/0!

LOD_b if 99th percentile is used:	NA
LOD_b if standard deviation is used:	#DIV/0!

Spiked Blanks summary

Spike Level (same as initial):		mg/L
Average:	#DIV/0!	#DIV/0!
Standard Deviation:	#DIV/0!	
Student's t-value to use:	#NUM!	
Calculated LOD_s:	NA	mg/L

Method Blanks summary

...ch option will be used:		
...can only use 99th Percentile if more than 100 method blanks)		
Student's t-value to use:	#NUM!	
Calculated LOD_b:	NA	mg/L

Calculated LOD:	mg/L	(calculated from the greater of LOD_s and LOD_b)
Calculated LOQ:	### mg/L	(= 10/3 x LOD)
Existing LOD:	mg/L	
Can the existing LOD be left unchanged?		Use the new calculated LOD.
Is spike level okay (<5% spiked blanks <0)?	#DIV/0!	#DIV/0!

...ere outliers rejected?		(only gross failures may be excluded)
If so, explain:		

NOTES:

Recalculate LOD_s and LOD_b at least every 13 months.

Include **spiked blank** data generated within the last 2 years as long as the data all used the same spike level (include initial results if within 2 years).

If the lab thinks the sensitivity of the method has changed significantly, then the most recent data may be used (min. of 7 reps, 3 batches, over 3 days)

The Spreadsheet

Add/Change Instrument LOD/LOQ Calculation and Verification Worksheet

Use this form if:	adding an instrument or changing to a new instrument.

Analytical Method:			Calculation Date:	
Matrix:			Calculation by Analyst:	

Spiked Blanks (include data generated within the last 2 years)

	Date Prepped	Date Analyzed	Result	% Recovery
Q1 A				
Q1 B				
Q2 A				
Q2 B				
Q3 A				
Q3 B				
Q4 A				
Q4 B				
Q1 A				
Q1 B				
Q2 A				
Q2 B				
Q3 A				
Q3 B				
Q4 A				
Q4 B				
New Inst 1				
New Inst 2				

Method Blanks

	Date Prepped	Date Analyzed	Result
New Inst 1			
New Inst 2			

Estimate Initial LOD	Initial LOD (8 MB)	Initial LOD (>8 MB)	Ongoing LOD	**Add or Change Instrument**

DEPT. OF NATURAL RESOURCES

- If a new instrument is added, analyze > 2 spiked blanks and > 2 MB. If both MB < existing LOD then the LOD_B is validated.

- Combine the new spiked blanks to existing data and re-calculate LOD_S .

- If re-calculated LOD is not less than 0.5x or more than 2x existing LOD, LOD_S is validated.

- Repeat initial LOD **if either** LOD_B **or** LOD_S not validated.

The Spreadsheet

- Some helpful hints are on the notes tab.

- The new rule has already taken effect (9/27/17)

- Currently already required to re-do or verify your LOD annually, so now is the time to begin.

- The rule breaks down to quarterly requirements

- Begin now to analyze 2 LOD spiked blanks (separate dates) per quarter
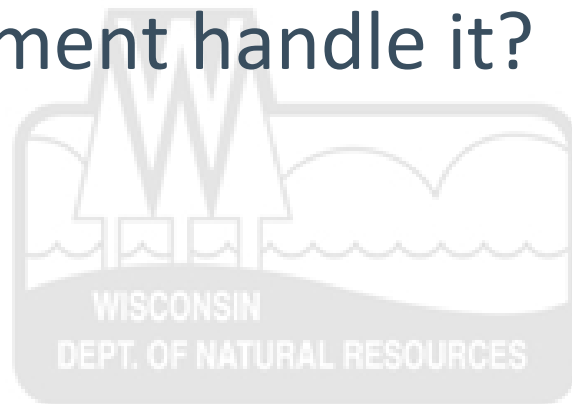
- Also record all your method blank results.

- Could be as simply as a handwritten list.

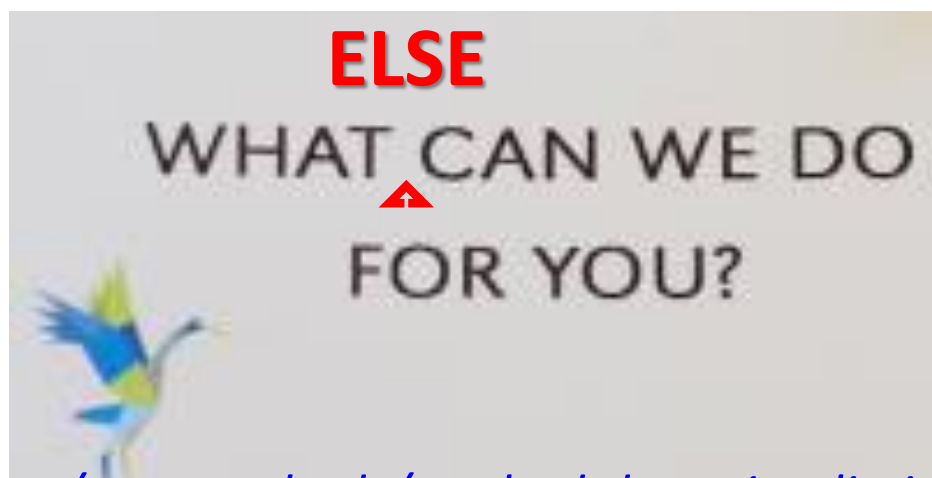- Could be the DNR Excel spreadsheet (or another spreadsheet or Google docs…or…)

- Can your instrument handle it? Hach WIMS?

- E-mail blasts of notification and links to resource materials.

- Develop spreadsheets and guidance for how to make (and document) this change.

- Offer to speak at regional WWOA meetings.

- Call your auditor for assistance.

ELSE
WHAT CAN WE DO
FOR YOU?

Thanks...Questions?

Autumn Farrell, DNR
Rick Mealy, DNR
George Bowman (ret.)