LODS

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October 23, 2024

LODs The Whats, The Whys, and The Hows!

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WISCONSIN DEPARTMENT OF NATURAL RESOURCES | DNR.WI.GOV

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This presentation is to try to help you understand LODs.

Exact definitions and technical jargon have been avoided.

There is a lot more to the LOD determination that likely does not apply to this audience's testing, so it will not be covered here.

What is an LOD?

The department considers the LOD to be equivalent to the method detection limit (MDL).

The limit of detection (LOD) is the lowest concentration that the analyte is **detectable** with a certain degree of confidence.

The limit of quantitation (**LOQ**) is the lowest concentration that the analyte is quantifiable (detected and countable) with a certain degree of confidence.





Why do we need an LOD?

- It is always possible that the analyte is present in the sample at a concentration below your LOD, so it's important that your LOD is low enough for the intended use of the data.
 - For example, if your permit limit is 0.075 mg/L for phosphorus, and your LOD for is 0.1 mg/L, then you know that your analysis is inadequate. You could have a "<LOD" result and the sample result would still not meet permit limits.
 - If your LOD is 0.05 mg/L, then a "<LOD" result indicates that the sample result is in compliance with your permit.





Do NOT redo the initial LOD unless needed. Only do the initial LOD when:

- you change methods.
 - For example: the lab changed from ammonia by ISE to Hach Test N Tube.
- a significant change has occurred that could affect sensitivity.
 - For example: the lamp was replaced in the spectrophotometer which may cause a significant change in sensitivity.
- the spiked blank concentration is changed.
 - For example: the lab changed the quarterly spiked blanks from 0.5 mg/L to 0.1 mg/L



"Initial" LOD



Prepare and analyze at least:



"Ongoing" LOD

2 spiked blanks every quarter in separate batches

and

Usual method blanks Have some system to remind yourself to do these each quarter.

Be sure the spiked blanks are in separate batches or different days each quarter.

You don't need to do any special LOD method blanks.





"Ongoing" LOD

Which data?

Always use the last 24 months of spiked blanks.

ONLY include the initial LOD data if it is was done within the last 24 months.

Ideally, use all method blank (MB) data from last 24 months.

If you have a LOT of MB data, you also have the option to use whichever of these that <u>provides more data</u>: at least the last 6 months of MBs or at least the 50 most recent MBs.

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



"Ongoing" LOD



6



"Ongoing" LOD

Year 1 (Initial+Year1)

Ideally, use all MB data from last 24 months.

"Ongoing" LOD

Year 2 (and beyond)

"Ongoing" LOD

Year 2 (and beyond)

Ideally, use all MB data from last 24 months.

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"Ongoing" LOD

Every analysis:

Report results to LOD

Every quarter:

Run 2 spiked blanks

Every year:

Calculate LOD and update if needed

2 years of spiked blanks

2 years of method blanks

Sniker	d Blanks (include	all I OD data den	erated within	the last 2 years)			Method Blanks (see d	ata to the right)	
Spiket	Date Prepped	Date Analyzed	Result	% Recovery		About h	ow often do vou normally rur	this method?	,
Q1 A	1/10/25	1/10/25	0.09400	94%		Select	1/week		
Q1 B	1/17/25	1/17/25	0.09000	90%		Use at least the 50 most recent method blanks.			
Q2 A	4/12/25	4/12/25	0.11200	112%		Use onl	/ the last 2 years of data.		
Q2 B	4/19/25	4/19/25	0.09600	96%		Enter the	e method blank data in the colum	ins to the right.	
Q3 A	7/7/25	7/7/25	0.09100	91%				•	
Q3 B	7/16/25	7/16/25	0.09000	90%					
Q4 A	10/2/25	10/2/25	0.08800	88%					
Q4 B	10/9/25	10/9/25	0.11000	110%					
Q1 A	1/13/22	1/13/24	0.10200	102%					
Q1 B	1/20/24	1/20/24	0.09000	90%					
Q2 A	4/1/24	4/1/24	0.08100	81%					
Q2 B	4/8/24	4/8/24	0.09100	91%		Nun	ber of method blanks entered:	50	
Q3 A	7/8/24	7/8/24	0.10400	104%					
Q3 B	7/15/24	7/15/24	0.11000	110%		LOD	b if standard deviation is used:	0.012	mg/L
Q4 A	10/10/24	10/10/24	0.09600	96%		l	OD _b if 99th percentile is used:	NA	mg/L
Q4 B	10/17/24	10/17/24	0.09600	96%		(can only use 99th Percentile if more than 100 method			hod blanks
	Spike Level (same as initial):	0.10000	mg/L			Select which option to use:	Standard	Deviation
		Average:	0.09631	96%			Average:	-0.00538	
Standard Deviation:			0.00893				Standard Deviation:	0.00513	1
Student's t-value to use:		2.602				Student's t-value :	2.405]	
Calculated LOD _s :		0.0232	mg/L			Calculated LOD _{b:}	0.0123	mg/L	
	Use only the las	st 2 years of data							
				Calculated LOD:	0.023	mg/L	(calculated from the greater of	LOD _s and LOD	»)
				Calculated LOQ*:	0.077	ma/l	$(= 10/3 \times 100)$		

"Ongoing" LOD

Tips

Watch for red alerts. If you're sure

2/1/2 2/8/2 2/15/2 2/22/2 3/1/2

3/8/2 3/15/2 3/22/2

3/29/2 4/5/2 4/12/2

4/19/2 4/26/2

5/3/2 5/10/2

5/17/2 5/24/2

5/31/2

6/7/2

6/14/2

6/21/2

6/28/2 7/5/2 7/12/2 7/19/2

7/26/2 8/2/2

8/9/2 8/16/2

you are just using the last 2 years of data, check for typos.

When you do the annual LOD calculation, fill in that date:

Ongoing LOD/LOQ Calculation and Verification Worksheet (Single Instrument) [Version 8/21/23]							
Facility: Acme Labs							
Analytical Method: SM 4500-P E	Calculation Date (Annual LOD): 12/15/2024						
Matrix: Wastewater	Calculation by Analyst: ARF						

Even though you do parts of the LOD determination each quarter, you only need to do the calculation and verification once per year. That is an important date to record.

If you set up a spreadsheet for the next year, you may put a reminder here:

"Ongoing" LOD

Tips

Ongoing LOD/LOQ Calculation and Verification Worksheet (Single Instrument) [Version 8/21/23]						
Facility: Acme Labs						
Analytical Method: SM 4500-P E		Calculation Date (Annual LOD): (D	UE Dec 2025)			
Matrix: Wastewater		Calculation by Analyst:				

If you set up a spreadsheet for the next year, also be sure to update (if needed) or enter the existing LOD:

"Ongoing" LOD Tips How do we determine the LOD?

When getting ready to enter data for the next year...

Before you delete any data, be sure to save a copy. You need to keep the data used to calculate the annual LOD.

- When you're done doing the annual calculation, enter the date on the spreadsheet.
- File, "Save" the current LOD spreadsheet (e.g., "Phos 2024").
- File, "Save As..." and rename the LOD spreadsheet for the next year (e.g., "Phos 2025").
- In the new spreadsheet (e.g., "Phos 2025,") delete the data that will be more than 2 years old (e.g., from 2023). Delete all spiked blanks and method blanks that will be more than 2 years old.

 To copy cells and move them in Excel, select the cells you want to move (click and drag), select Home > Copy (or Ctrl + C).

"Ongoing" LOD

Tips

This method will keep the formatting the same. There are other ways of doing the same thing.

- 2. Then select the upper left cell where you want to paste the date.
- 3. Then, Home > Paste > drop down arrow, and > Values (V).
- 4. Delete the duplicate data.

 To copy a tab in Excel, right-click on the "Ongoing Year 2 (and beyond)" tab. Select "Move or Copy..."

"Ongoing" LOD

Tips

/25	4/12/25	0.11200	1120/		USC at 1	cust the
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/25	4/19/25	0.09600	96%			method
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/25	7/16/25	0.09000	90%	m	Delete	-
/25	10/2/25	0.08800	88%	×	<u>D</u> elete	
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2. Then select "(move to end)," check the box to "Create a copy," then "OK."

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3800	LOD-LOQ Calculations Basic 3-Tab for WWOA.xls
000	Before sheet:
200	Initial LOD
9000	Ongoing Year 1 (Initial+Year1)
3100	Ongoing Year 2 (and beyond)
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ar1)	Ongoing Year 2 (and beyond) NOTES +

3. Then, right-click on the "Ongoing Year 2 (and beyond) (2) tab, and rename. Type a name, and press "enter."

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Questions

CONNECT WITH US

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