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

The LOD Procedure has changed

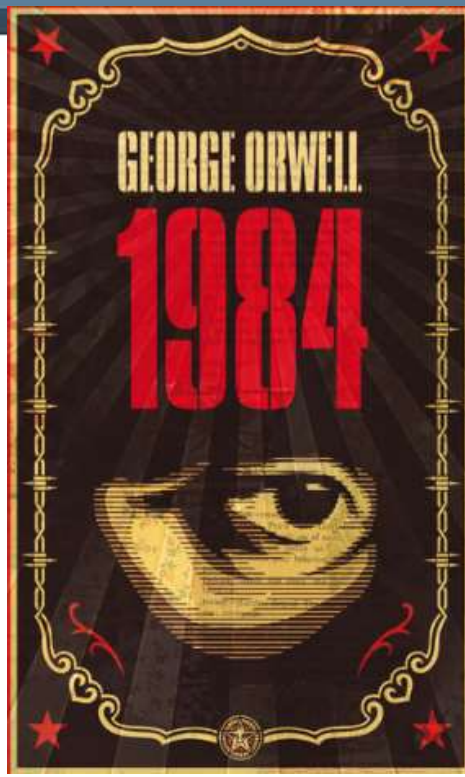
Federal Register /Vol. 82, No. 165 /Monday, August 28, 2017

ACTION: Final rule.

DATES: This regulation is effective on September 27, 2017.


WITH THEIR OWN

1984 historical perspective



- Michael Jackson's hair catches fire
- Barneveld WI F-5 tornado
- President Reagan: *"....I've signed legislation that will outlaw Russia forever. We begin bombing in five minutes."*
- Bank interest rates ~ 9% **(<0.1%)**
- Dow Jones 1211 pts **(> 22,300)**
- Median household income $21,100 **($53,000)**
- The first Apple Macintosh goes on sale
- Birth of the "minivan"
- 1st commercial CD Players (Sony and Philips)
- 1st 3 1/2" computer disk (Sony) aka "stiffies"
- Prince Harry is born

Oh yeah…and the EPA published the infamous MDL protocol (40 CFR Part 136 App B)

The Long Journey to revised LOD

- Feb. 19, 2015 – Proposed rule
- Comment period until Apr. 20,2015
- Apr. 20, 2015 FR: 30-day comments extension

  New comment period until May 20, 2015
- Dec. 2016 Pre-promulgation version appears
- Jan. 20, 2017 Inauguration; Trump Administration
- Jan. 20, 2017 Freeze on all new rules
- Feb. 17, 2017 new EPA Administrator confirmed
- Aug. 28 2017 FR – Final rule for promulgation
- Sept. 27, 2017 Effective date of new LOD procedure

After many years of talk....

...a Hail Mary of Flutie magnitude!

Proposal to Promulgation

EPA is revising the procedure for determination of the MDL primarily to address laboratory blank contamination and to better account for intra-laboratory variability. The suggestion for these revisions came first from The NELAC Institute. EPA proposed to adopt these revisions.

The **majority of commenters supported the revised MDL** procedure. All lab associations commented in favor. Comments not in favor of the MDL revision were received from individual laboratories, individuals, one utility, and two state government departments.

As a result of the comments, EPA has made minor clarifications to the MDL procedure.

WISCONSIN DNR
Department of Natural Resources

Select Wisconsin comments

- Incorporating “background contamination” into the LOD can be perceived as a license to ignore contamination. Why analyze method blanks?
- The proposed rule does not “make the MDL more representative” (multiple instruments)
- Proposed protocol lacks any mechanism to evaluate the MDL, other than comparing it to blanks.
- there is a need to establish a national standard for the LOQ.
- This proposal overlooks two critical considerations: calibration and assessment of laboratory blanks.
- The approach presented inappropriately alters the basic definition of a limit of detection.

WISCONSIN DNR
Department of Natural Resources

Why Change It?

What's wrong with precision?

- Precision is based on the instrument condition, analyst technique, reagent quality, and other issue such as background contamination.
- And with the LOD formula, the better the precision, the LOWER the LOD.
- So… if ONE analyst analyzes 7 replicates all in the same day, and even within the same hour, unless there is background contamination, variability is minimized and the LOD will be ⬇⬇⬇.
- How does that compare with "real life": analyst variability, instrument condition, reagents, etc.?

What's wrong with precision

If you analyze a 0.2 ppm standard and measure 0.021 (average).

Then if you measure a standard at the LOD (0.02 ppm), wouldn't you expect to measure 0.002?

The Good, The Bad, & the Ugly

- **Good:** **If you only do BOD and/or TSS** in your lab…you don't have to worry about this!

- **Bad:** Didn't fix the precision issue.

- **Ugly:** Allows LOD to be raised to the level of background contamination. **And that might have permit issues.**

What has NOT changed

- 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.

WISCONSIN DNR
Department of Natural Resources

WHAT'S NEW?

- Clearly specifies that MDL is inappropriate for (WET), Micro, BOD/cBOD), color, pH, specific conductance, and titration methods.
- Provides options/alternatives to determine the initial spiking level to determine the MDL.
- Requires assessment of routine blanks in addition to replicate spiked blanks.
- Requires MDL "spikes" be separated and analyzed over time. Over at least 3 separate calendar days.
- Discourages outlier rejection of replicate spikes. Exclusion ONLY if can document a valid reason.

WISCONSIN DNR
Department of Natural Resources

WHAT'S NEW?

- All instruments in use must be incorporated.
- If you add an instrument: Must prepare/analyze (on different calendar dates) at least 2 spikes and 2 blanks per instrument.
- One prep sample may be analyzed on multiple instruments so long as still have 7 spikes from at least 3 separate batches.
- MDL "spikes" must meet qualitative ID criteria (for each analyte) **AND** provide a numerical result > zero.
- No more "validation" of the MDL.

  i.e. **Spike level > MDL > 10% spike level**

Definition- What are we determining?

Proposed Feb 2015 (same as original 1984)

The MDL is 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** and is determined from analysis of a sample in a given matrix containing the analyte.

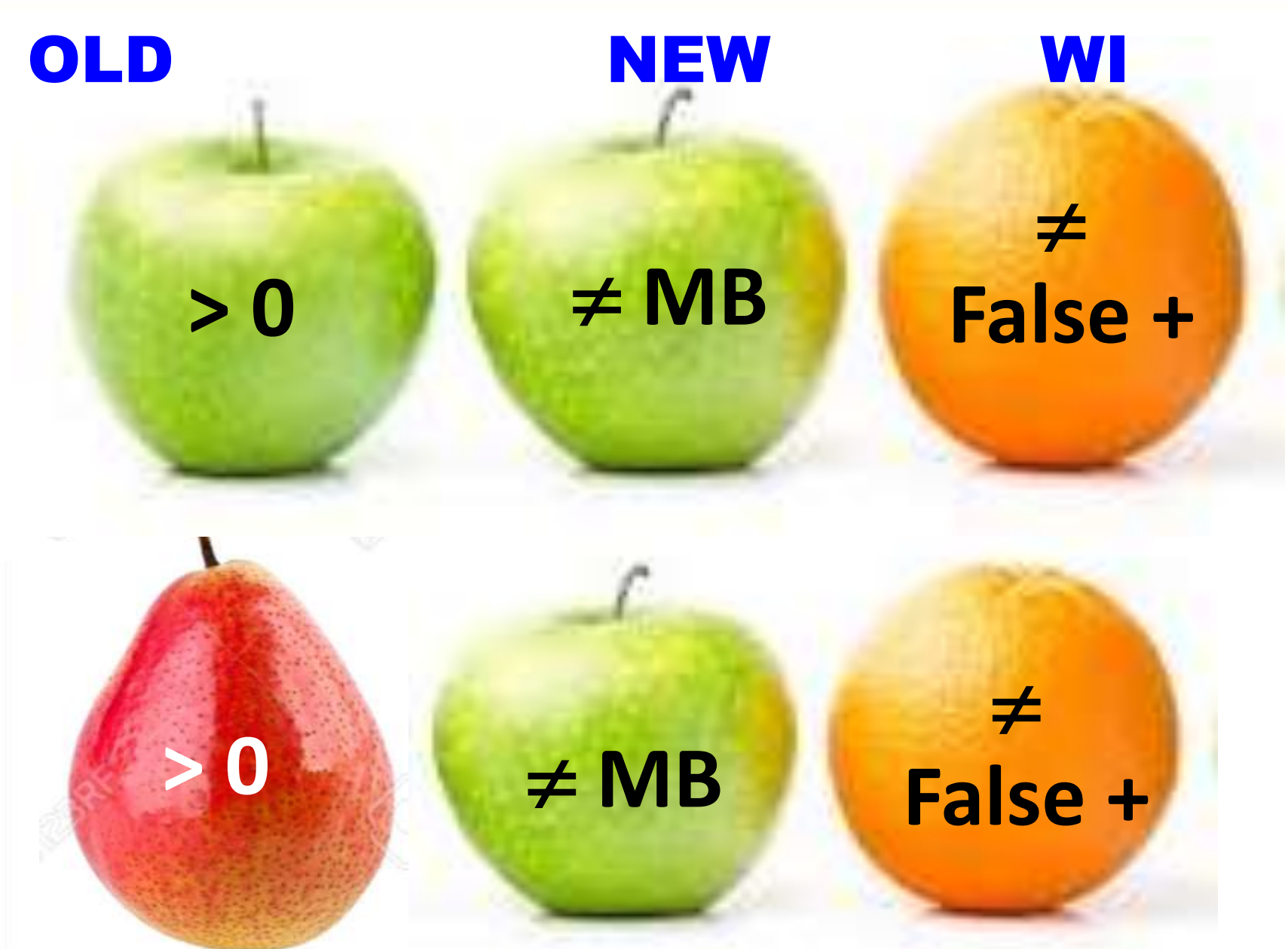
Soapbox time

Method blanks consider both contamination and normal background "noise". If higher LODs are desired and the LOD can be elevated simply by having more contamination, isn't that a conflict for the quality system? Why bother trying to control contamination? **Everything becomes "ND"!**

NR149 (existing and proposed revisions)

LOD = the lowest concentration or amount of analyte that can be identified, measured, and **reported with confidence** that **the concentration is not a false positive value**.

Or..Apples to pears to oranges?



Wait...WHY do we have to do this?

WISCONSIN DNR
Department of Natural Resources

Housekeeping: A few notes

WISCONSIN DNR
Department of Natural Resources

Time to get down to it

1. Estimate the [LOD]

Nothing much changes here

a. Mean + 3 SD of "a set of blanks"

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

c. Concentration= 3 X SD of spiked blanks

The idea is to come up with an appropriate level at which to prepare spiked blanks.

Since you already have a real LOD…

2. Determine Initial [LOD]

a. Spikin

NOT

low rec

quired if

b. Proce

minim

– *at le*

– *shou*

US

s

oss &

docu

If

!

2. Determine Initial [LOD]

c. If any analyte does not meet qualitative ID criteria or **has a result ≤ 0,** repeat at higher spike concentration.

d. Calculations

i. Calculate SD of spiked samples and blanks

ii. $LOD_S = t \times SD_S$

2. Determine Initial [LOD]

d. Calculations

i. LOD_B =

A. IF no blanks yield numeric result, THEN LOD_B = **N/A**

B. IF some, but not all, blanks yield numeric results

THEN LOD_B = highest *MB*

OR IF ≥ *100 MB results* **THEN** LOD_B = 99^{th} %ile MB

C. ELSE IF all blanks yield numeric results THEN

$LOD_B = Mean_{MB} + (t \times SD_B)$ if $Mean_{MB} < 0$, *use "0"*

OPTION: IF ≥ *100 MB* THEN LOD_B = 99^{th} %ile MB

If 100 < N ≤ 150, then $MB_{0.99}$ = 2nd highest blank

e. LOD = Greater of (LOD_S, LOD_B)

So…the only twist here

- **…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
- Let's go back and review how the LOD_B is calculated for common wastewater tests (NH3, TP, Chloride).

Breaking down the LOD_B

LOD_B for the WWTP =

- **N/A** *if no blanks yield numeric result*

  Ex. Chromatography: no peak detected

- ***If some (but not all) have numeric results…***

  IF < 100 MB results] ➔ **highest MB**

OR *IF ≥ 100 MB results]* ➔ **99th percentile MB**

- OTHERWISE ***if all blanks have numeric results…***

  $Mean_{MB} + (t \times SD_{MB})$ *[if* $Mean_{MB} < 0$, $Mean_{MB} = 0$*]*

NOTE: *IF ≥ 100 MB results]* ➔ **99th percentile MB**

3. ONGOING DATA COLLECTION

a. If any samples analyzed in a given QTR prep/analyze a minimum of 2 spiked samples, in separate batches, on each instrument.

b. Need at least 7 spiked samples (blanks) + 7 method blanks *(at the end of the year)*

If only 1 instrument, can use up to 2 yrs of historical data

c. At least annually, re-evaluate spike level

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

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

WISCONSIN DNR
Department of Natural Resources

So…is it 7 or 8 replicates?

INITIAL (2) (b) Process a minimum of **seven** spiked samples and **seven** method blank samples. 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.)

ONGOING DATA COLLECTION 3.a. If any samples analyzed **in a given QTR** prep/analyze a minimum of **2 spiked** samples**, in separate batches**, on each instrument.

ONGOING ANNUAL VERIFICATION (4) (a) At least once every thirteen months, recalculate MDLs and MDLb from the collected spiked samples and method blank results. (b) Include data generated within the last 24 months, but only data with the same spiking level.

7? Or 8? (Spikes) EPA FAQ

Samples Required	Revision 1.11	Revision 2
Spiked samples	7/year	8/year (2/quarter)
Methods blanks (MBs)	0	0 (use routine MBs)

How many blanks?

ONGOING (3) (a) the method blank population should include all of the routine method blanks analyzed with each batch during the course of sample analysis.

https://www.epa.gov/cwa-methods/method-detection-limit-frequent-questions

3. ONGOING DATA COLLECTION

d. 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

ONGOING DATA COLLECTION – ADDING A NEW INSTRUMENT

3.e.

- If a new instrument is added, analyze $\geq$ 2 spiked blanks and $\geq$ 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 new LOD_S $\geq$ 0.5X **AND** $\leq$ 2X existing LOD, LOD_S is validated.
- Repeat initial LOD **if either** LOD_B **or** LOD_S not validated.

WISCONSIN DNR Department of Natural Resources

Ex. Buying a new instrument

You purchase a Hach DR3900 to replace a Genesys 10.

Existing LOD_B = 0.015 ppm.

You analyze 2 blanks: 0.013 and 0.014 ppm

Both are <0.015, so

LOD_B is verified.

Existing LOD_S = 0.020 ppm.

You analyze 2 spikes:

Combined LOD= 0.039

LOD_S is verified.

Spike level	0.1 ppm
Spike	Result
Replicate 1	0.109
Replicate 2	0.102
Replicate 3	0.118
Replicate 4	0.113
Replicate 5	0.120
Replicate 6	0.112
Replicate 7	0.108
Replicate 8	0.102
MEAN	0.111
SD	0.007
t-value	2.998
LOD_S	0.020

Spike level	0.1 ppm
Spike	Result
Replicate 1	0.109
Replicate 2	0.102
Replicate 3	0.095
Replicate 4	0.113
Replicate 5	0.097
Replicate 6	0.091
Replicate 7	0.108
Replicate 8	0.102
New Inst 1	0.129
New Inst 2	0.128
MEAN	0.107
SD	0.013
t-value	2.998
LOD_S	0.039

4. ONGOING ANNUAL VERIFICATION

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

b. 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*

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

d. Only use data with acceptable calibration and QC

If method is changed in any way that can reasonably be expected to affect sensitivity use only data collected after the change.

4. ONGOING ANNUAL VERIFICATION

e. 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

Let's go thru some examples

WISCONSIN DNR
Department of Natural Resources

Pine Stump WWTP
TP "Initial" LOD spikes

Spike Level:	0.030
Units	mg/L

Determine LOD_S

Seems simple enough…

LOD_S = 0.006 ppm

MDL Study Sample Number	Result	% Recovery
Replicate 1	0.026	93%
Replicate 2	0.027	96%
Replicate 3	0.032	107%
Replicate 4	0.031	103%
Replicate 5	0.027	90%
Replicate 6	0.029	97%
Replicate 7	0.027	90%
Replicate 8	0.031	103%
Replicate 9		0%
Replicate 10		0%

Average:	0.029	96%
Standard Deviation:	0.002	

Student's t-value to use:	2.998	
Calculated LOD:	0.006	mg/L

WISCONSIN DNR
Department of Natural Resources

Pine Stump WWTP Lab Blanks

75 TP blanks (most recent 6 months) from a WWTP

0.0040	0.0010	0.0000	0.0000	-0.0010
0.0040	0.0010	0.0000	0.0000	-0.0010
0.0040	0.0010	0.0000	0.0000	-0.0010
0.0040	0.0010	0.0000	0.0000	-0.0010
0.0030	0.0010	0.0000	0.0000	-0.0010
0.0030	0.0010	0.0000	0.0000	-0.0010
0.0030	0.0010	0.0000	0.0000	-0.0010
0.0030	0.0010	0.0000	0.0000	-0.0010
0.0030	0.0010	0.0000	0.0000	-0.0010
0.0030	0.0010	0.0000	0.0000	-0.0010
0.0030	0.0010	0.0000	0.0000	-0.0010
0.0010	0.0010	0.0000	0.0000	-0.0010
0.0010	0.0010	0.0000	0.0000	-0.0030
0.0010	0.0010	0.0000	0.0000	-0.0030
0.0010	0.0000	0.0000	-0.0010	-0.0030

Mean: 0.00044

SD: 0.00152

Range: - 0.003-0.004

Pine Stump WWTP Initial LOD

Manual hotplate LOD spike level 0.03 ppm

blanks	spikes
75 blanks over most recent 6 months	0.028
	0.027
	0.032
	0.031
Range: -0.003 to 0.004	0.027
	0.029
	0.027
mean 0.00044	0.029
SD 0.00152	0.002

MDL_S =

2.998 x 0.029 = 0.006

MDL_B =

0.00044 + (2.378 x 0.00152)

= 0.004

If had > 100 blanks, could use the 99th percentile blank

$MDL_S > MDL_B$

$MDL = MDL_S$

MDL = 0.006

Pine Stump WWTP
Ongoing spike collection

Test: Phosphorus	
Spike Level:	0.030
Units	mg/L

8 batches **8 prep dates**

MDL Study Sample Number	Result	% Recovery	Prepped	Analyzed
QTR 1 A	0.034	113%	02/27/2017	02/27/2017
QTR 1 B	0.031	103%	03/20/2017	03/20/2017
QTR 2 A	0.026	87%	04/21/2017	04/21/2017
QTR 2 B	0.028	93%	05/28/2017	05/28/2017
QTR 3 A	0.037	123%	07/08/2017	07/08/2017
QTR 3 B	0.030	100%	09/11/2017	09/11/2017
QTR 4 A	0.036	120%	10/15/2017	10/15/2017
QTR 4 B	0.025	83%	12/04/2017	12/04/2017

Ongoing spike data collection records for a wastewater lab may look something like this

WISCONSIN DNR
Department of Natural Resources

Pine Stump WWTP Ongoing Blanks

150 TP blanks (1 calendar year) from a WWTP

0.007	0.003	0.002	0.001	0.000	0.000	-0.001	-0.001	-0.001	-0.002
0.007	0.003	0.002	0.001	0.000	0.000	-0.001	-0.001	-0.001	-0.002
0.006	0.003	0.001	0.001	0.000	0.000	-0.001	-0.001	-0.001	-0.002
0.006	0.003	0.001	0.001	0.000	0.000	-0.001	-0.001	-0.001	-0.002
0.006	0.003	0.001	0.001	0.000	0.000	-0.001	-0.001	-0.001	-0.002
0.006	0.003	0.001	0.001	0.000	0.000	-0.001	-0.001	-0.001	-0.002
0.004	0.003	0.001	[illegible]	0.000	[illegible]	-0.001	-0.001	-0.001	-0.002
0.004	0.003	0.001	0.000	0.000	0.000	-0.001	-0.001	-0.001	-0.002
0.004	0.003	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	-0.001	-0.001	-0.002
0.004	0.003	0.001	0.000	0.000	0.000	-0.001	-0.001	-0.001	-0.002
0.004	0.003	[illegible]	[illegible]	[illegible]	0.000	[illegible]	-0.001	-0.001	-0.002
0.004	0.003	0.001	0.000	0.000	0.000	-0.001	-0.001	-0.001	-0.003
0.004	0.002	0.001	0.000	0.000	0.000	-0.001	-0.001	-0.001	-0.003
0.003	0.002	0.001	0.000	0.000	0.000	-0.001	-0.001	-0.002	-0.003
0.003	0.002	0.001	0.000	0.000	-0.001	-0.001	-0.001	-0.002	-0.004

Mean: 0.0004

SD: 0.0021

Range: -0.004-0.007

99th %ile: 0.007

WISCONSIN DNR Department of Natural Resources

Pine Stump WWTP Annual Verification

MDL Sample ID	Result
QTR 1 A	0.034
QTR 1 B	0.031
QTR 2 A	0.026
QTR 2 B	0.028
QTR 3 A	0.037
QTR 3 B	0.030
QTR 4 A	0.036
QTR 4 B	0.025
Initial LOD 1	0.028
Initial LOD 2	0.027
Initial LOD 3	0.032
Initial LOD 4	0.031
Initial LOD 5	0.027
Initial LOD 6	0.029
Initial LOD 7	0.027
Initial LOD 8	0.031
Mean:	0.0299
SD:	0.0035

Current LOD = 0.006

- New LOD_S = 0.0091
  0.0035 2.602 = 0.0091*
- New LOD_B = 0.0053
  0.0004+ (2.3516 x 0.0021)
- New LOD = 0.009
  0.009 > 0.005
- Acceptable range = 0.003 to 0.012

LOD is verified

Can keep LOD at 0.006 OR switch to 0.009

Ex. 2 This Lab has a problem

TNT LOD spike level 0.1

	blanks	spikes
	0.0192	0.16
	0.0461	0.13
	0.002	0.11
	0.0461	0.10
	0.014	0.09
	0.0293	0.12
	0.069	0.09
mean	0.03224	0.11386
SD	0.02295	0.02435

MDL_S =

3.143 x 0.024 = 0.075

MDL_B =

0.032 + (3.143 x 0.023) = 0.104

$MDL_B > MDL_S$

$MDL = MDL_B$

MDL = 0.10

Ex. 3 This lab has serious issues

TNT LOD spike level 0.1 ppm

	blanks	spikes
	0.191	0.13
	0.265	0.13
	0.230	0.10
	0.200	0.12
	0.281	0.13
	0.246	0.11
	0.245	0.11
mean	0.237	0.118
SD	0.033	0.0122

LOD > spike level!

MDL_S =

$3.143 \times 0.0122 = 0.037$

MDL_B =

$0.237 + (3.143 \times 0.033) = 0.341$

$MDL_B > MDL_S$

$MDL = MDL_B$

$MDL = 0.34$

Ex. 4 High bias, but it works

Hotplate + Genesys 10 **spike level= 0.1 ppm**

blanks	spikes
0.01	0.116
0.0	0.128
0.01	0.144
0.01	0.132
0.01	0.128
0.0	0.136
0.01	0.142
mean 0.00714	0.1323
SD 0.0049	0.0096

MDL_S =

3.143 x 0.0096= **0.0302**

MDL_B =

0.00714 + (3.143 x 0.0049)

= **0.02254**

Ex. 5 The Perils of Precision

Autoclave + manual Spec Spike level= 0.05 ppm

	blanks	spikes
	0.009	0.056
	0.004	0.055
	0.007	0.057
	0.005	0.056
	0.02	0.056
	0.012	0.057
	0.018	0.057
mean	0.0117	0.0563
SD	0.0063	0.0008

MDL_S =

3.143 x 0.008= 0.00251

MDL_B =

0.0117 + (3.143 x 0.0063)

= 0.0315

WISCONSIN DNR
Department of Natural Resources

Example overload?

So…what do YOU have to do?

- The new rule has already taken effect!
- Effective date was 9/27/2017.
- 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
- We suggest Oct-Dec; Jan-Mar, Apr,-Jun., Jul-Sept
- Begin now to analyze 2 LOD replicates (separate dates) per quarter
- Also record all your method blank results.
- Goal: coincide with revisions to NR 149, which we are planning to take effect 9/1/2018.

It's not so bad…

…but remember that you will now have to catalog the following:

- Collect and retain all blank data
- Remember to add Quarterly LOD spikes to your "TO DO" list
- If your blanks run high and variable, your LOD_B may be your LOD and it may not be suitable for permit compliance
- Do a little more analysis annually to determine whether to keep or change the existing LOD

Capturing blank data

- Could be as simple as a handwritten list.

- Could be an Excel (or Google docs…or…) spreadsheet.

- Can your instrument handle it? Hach WIMS?

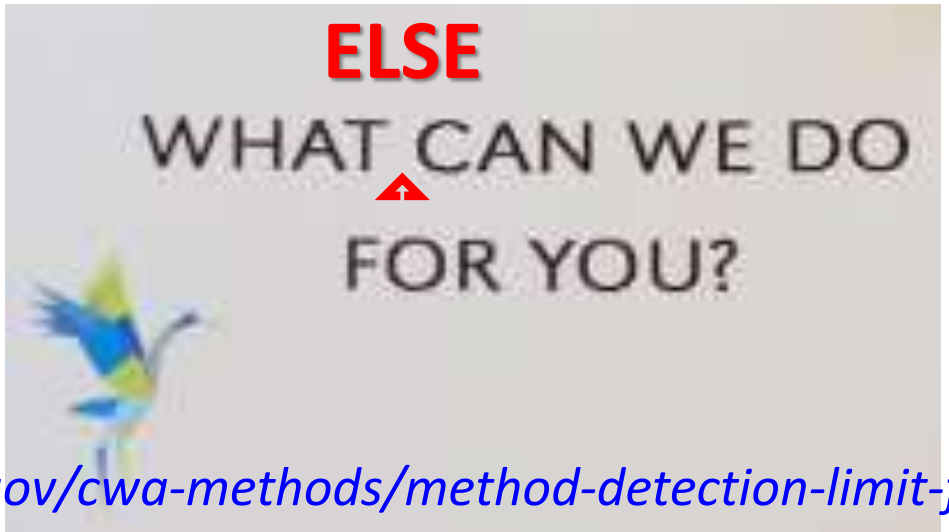
How many blanks do you need?

- A lab doing phosphorus 3 times/ week is going to generate 156 blanks.
- Even if an analysis is only performed once weekly, you would generate 52 blanks per year.
- Consequently, you should have at least 50 and many will have more than 100 blanks.
- The procedure allows you to use only the most recent 50 blanks or 6 months of blank data…whichever yields more data points.

If you run Total Phosphorus at least 3 times/weekly, 6 months = at least 72 blanks.
So unless you run < 3x/week, you will need 6 months data

Resources LabCert can provide

- 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 –or me – for assistance.



https://www.epa.gov/cwa-methods/method-detection-limit-frequent-questions

Thanks…Questions?

Rick Mealy, DNR
George Bowman (ret.)