All Your Lab Questions...

...Answered!*

DNR Certification Services

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to the best of my ability

What are we talking about today

- We've collected questions received regarding wastewater testing and we have the answers!
- Whether it be BOD, cBOD, TSS, ammonia, or phosphorus, we have answers.
- And we can take your questions during the session as well

Who has a question?

…or should I start?

General Questions

Do I really need a 2nd refrigerator for samples & standards?

NR 149.46(6) (d) (d) Samples shall be stored separately from all standards reagents, food and other potentially contaminating sources. Samples shall be stored in areas that prevent or minimize cross–contamination

Do I really need to buy a new edition of (or online methods) Standard Methods?

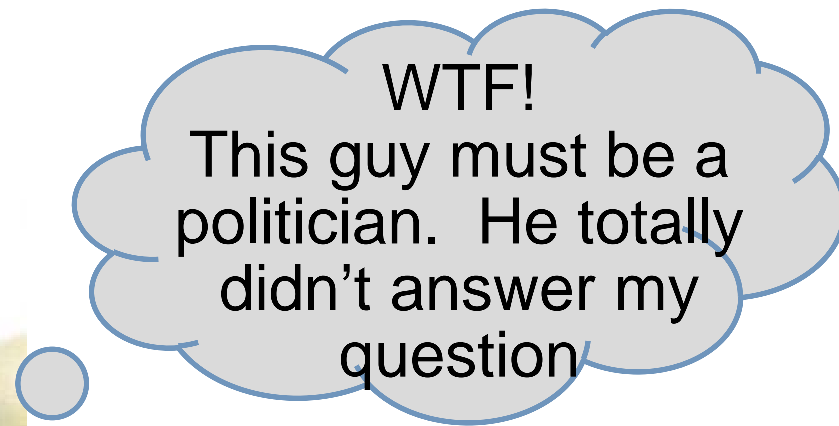
- The laboratory does not own a copy of the only approved BOD method for wastewater reporting in Wisconsin and does not use the correct format for the TSS method.

NR 149.41 (1), NR 219.01 and 04 (1) Table B, Parameters 9 and 55, Wis. Adm. Code.

General Questions

It seems like what every corrective action I take, it's never enough [to satisfy my auditor]?

- Corrective Action is a tricky subject. There are those labs that fail something routinely and do nothing.
- And those that try one thing and it doesn't work so they give up.
- You might hear the words "chronic" and "acute" failures…but those words don't exist in code.



WISCONSIN DNR Department of Natural Resources

Anatomy of a problem solved

- Missing PT letters go out in mid-June.
- Lab X calls and says, “hey…we failed 2 straight ammonias”, should I just get another PT?
- Me: “NO! If you fail that one, the goose is cooked”
- Lab: “We replaced our calibration standard”
- We looked at PT results. January failed high, March failed low. *Uh oh…those are bad!*
- We looked at data. Noted that both the LCS and PT results were off by close to 20%. *[LCS acceptance criteria= + 20%]*
- Clearly standards were very variable. Lab made it’s own standards vs. buying them.
- Tightened everything up…

Anatomy of a problem solved

- Re-calibrated. Slope fine. But analysis of a 2 mg/L standard yield 1.47 mg/L.
- Time to get vendor involved. Eliminated probe as a potential problem.
- Finally connected probe to a different channel on the meter. Great slope. Analysis of a 2 mg/L LCS yielded 2.16 mg/L.
- Re-analyzed PTs (bought as QC standards) from January and March…and hit the middle of the range.
- NOW ready to run a 3rd PT….and it passed on 8/15/18.
- **Moral of the story: You cannot just go along like nothing happened!**

New LOD Procedure Questions

I didn't do my *new* LOD...what happens now?

- Now we have to get you into the Quick Initial LOD protocol.
- We need you to analyze at least 7 (do 8!) spikes on 3 separate calendar days.
- Then we need the same amount of method blanks.
- We can use this data, but you also MUST get going on the 2 spikes/QTR

How many blanks do I need?

- For the initial you need at least 7 (8!)..
- Ultimately you want to have 6 months worth of data.
- And you MUST have 6 months of data (or at least 50 points—whichever is more).

New LOD Procedure Questions

How do I figure out my new LOD?

- It's the LOD_B or LOD_S…whichever is greater.

On Year 2, how does that work? Does it replace my existing LOD?

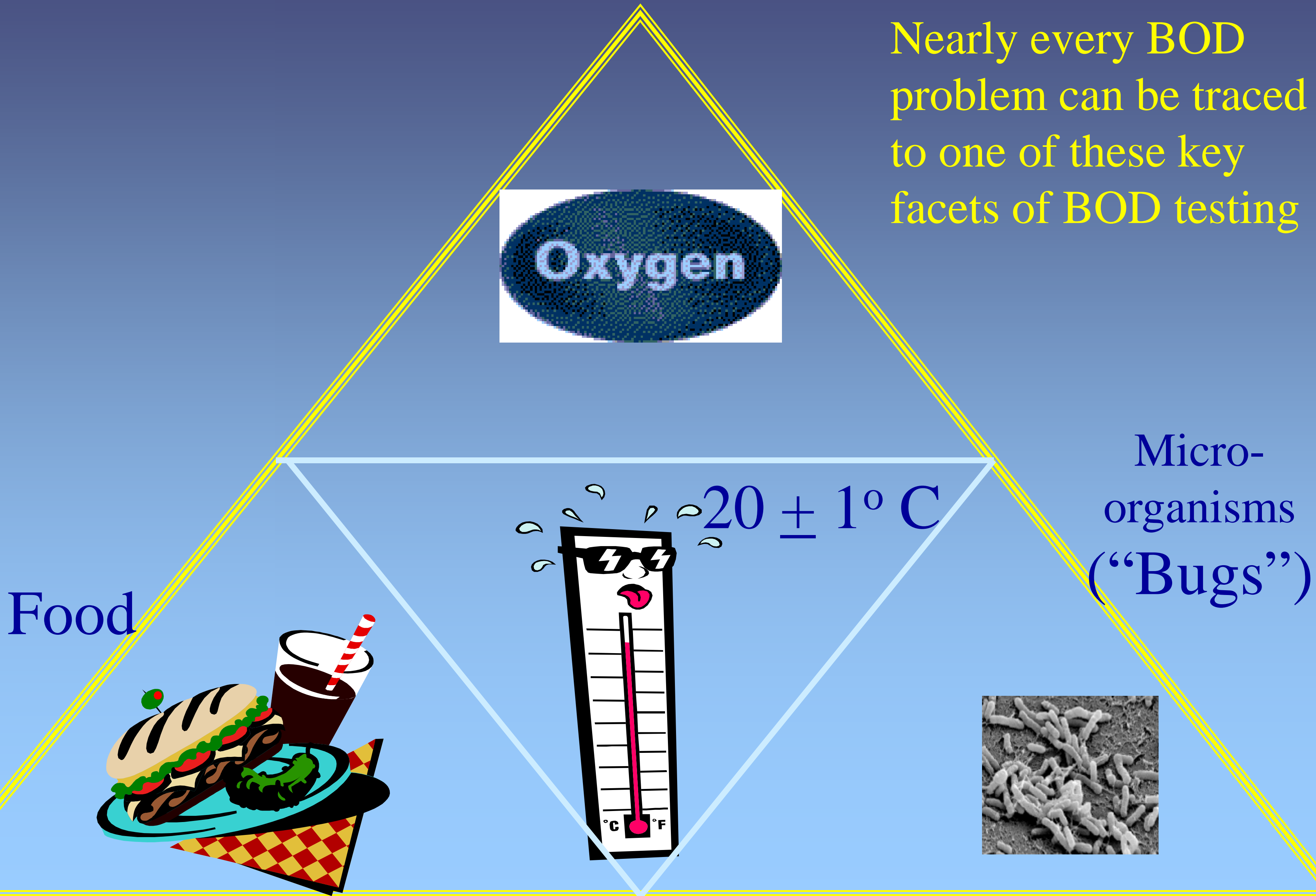
- It's the LOD_B or LOD_S…whichever is greater.
- But then you have to compare it to your existing LOD.
- If the Year 2 LOD is within 50% to 200% of the Year 1 LOD AND no more than 3% of the blanks exceeded the existing LOD, then you have the choice of keeping the Year 1 LOD or using Year 2.
- If the Year 2 LOD is < ½ or > 2X the Year 1 LOD OR more than 3% of blanks exceeded the LOD, then you MUST use the Year 2 LOD

BOD Questions

Why are my blanks failing?

- Need more input!
- Do they fail frequently? Or just occasionally?
- Do they fail by a lot (> 0.6 mg/L depletion)?
- Or just barely (depletion of 0.25-0.4 mg/L)?
- How many analysts do the testing?
- How consistent is the calibration?
- If they fail high, do not ASSUME it's contamination.

BOD Pyramid



Interpreting the Pyramid

- You need BOTH a food source (contamination) AND bugs (bacterial contamination for blanks to fail high.
- What's the likelihood that that is happening?
- Apply logic: if there is no food source but "bugs" present…what's keeping them alive for 5 days to use up oxygen?

BOD Questions

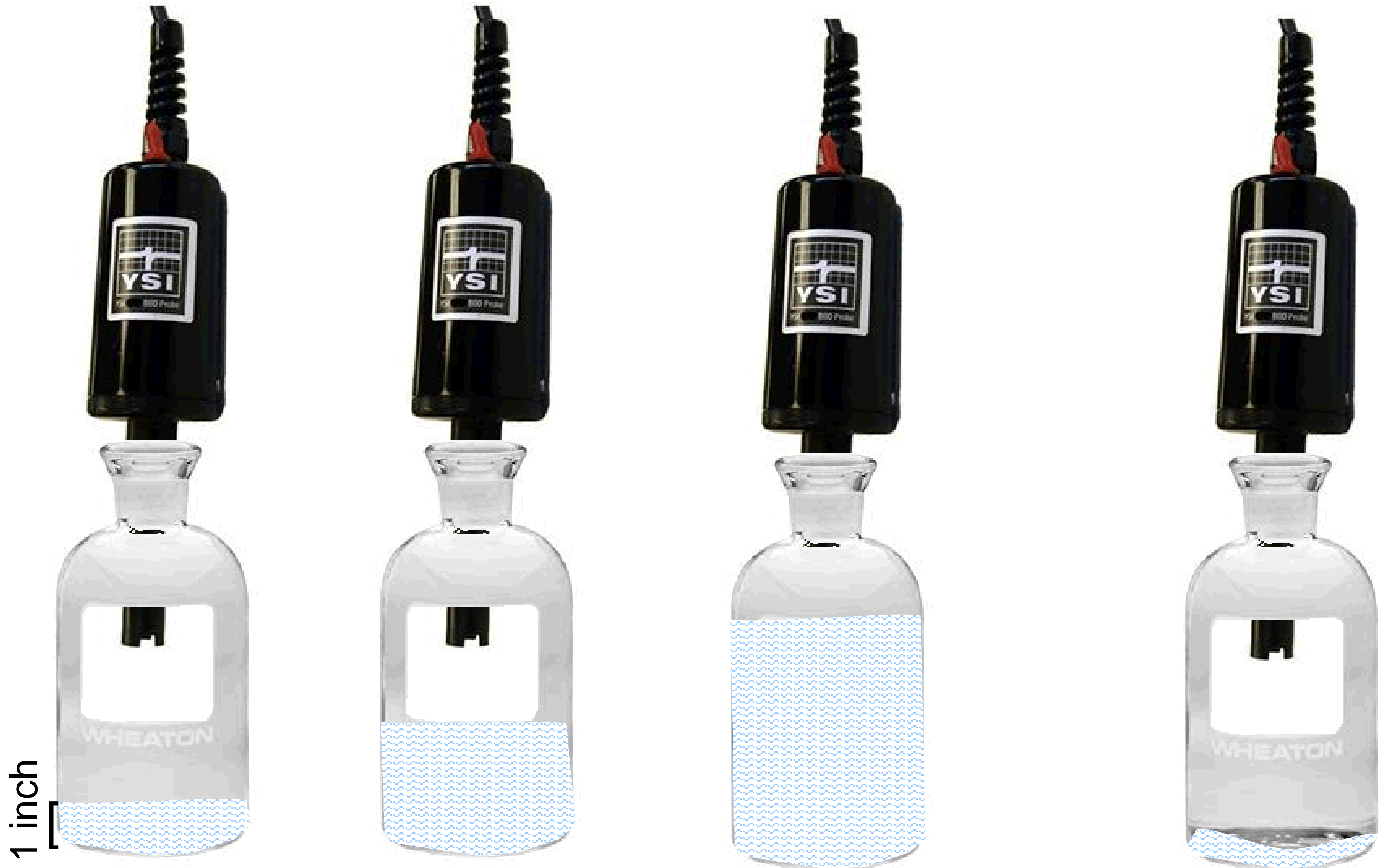
Why is my GGA [failing] low?

- What are you seeding with?
- Is it a variable source?
- What is the seed strength> (depletion/mL of seed)?
- How much seed is used?

Why is my GGA [failing] high?

- This is usually contamination.
- But COULD be nitrification
- Occasionally, if the seed is really active or too much seed is used, this can be the cause. Remember, GGA has a dilution factor of 24 (300/6). 0.3 mg/L of bias can result in GGA bias of 15 mg/L (0.3 x 50)

DO probe calibration consistency



…is CRITICAL!!!!

Every time you calibrate a DO probe inconsistently, a puppy dies.

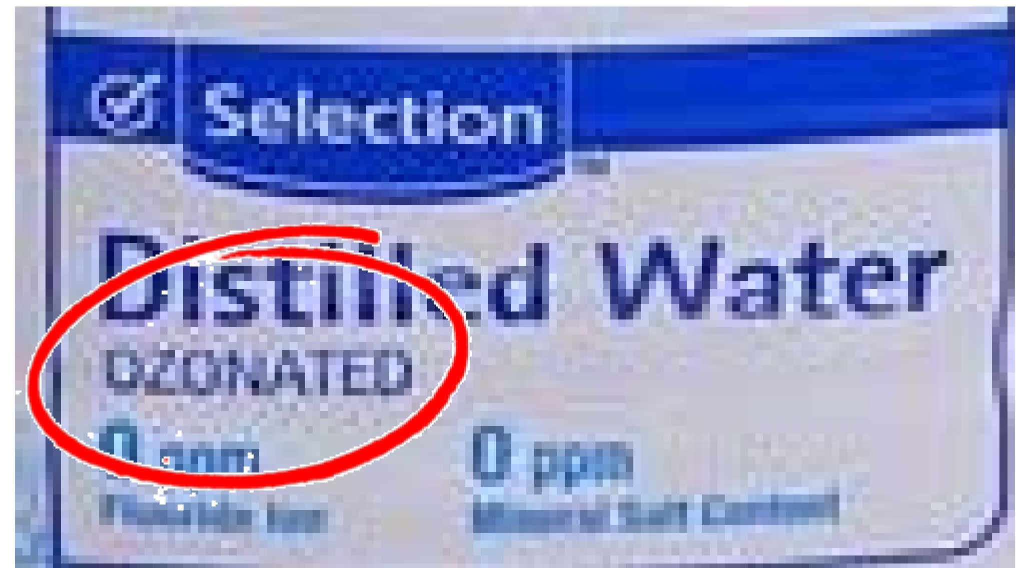
BOD Questions

Why do my BOD blanks have supersaturated initial DOs?

Any chance you are using bottled distilled or DI water?

Many of these now use ozonation for disinfection.

Ozone (O_3) breaks down to Oxygen (O_2)!



Ammonia questions

Do I raise the pH to 11 when using the TNT method?

- No. The pH requirement (>11) is ONLY for the probe method.
- The TNT method is a colorimetric, while the ISE method relies on converting all ammonia (NH_4^+) to the gaseous form (NH_3) which occurs above pH 9

Phosphorus questions

Why are my blanks so variable?

- Welcome to world of Quality Control (not!). This is why Hach says it's so important to zero on the method blank.

I follow the Hach method for digesting samples, but I got cited for the wrong temperature on my report. What's up with that?

- HACH says cook TPs in their block digestor at 100°C for 60 mins. but my auditor says it must be 150 °C for at least 30 min

Let’s look at this more closely!

- Hard boiled eggs usually take about 8 minutes in boiling water.
- HACH’s suggestion is that by dropping the temperature by 1/3, you simply double the cooking time.
- Hmmm. As an analogy….would you eat a “hard-boiled egg” that has cooked at 67 ° C for 16 minutes???

⬅8 min. in boiling water.

67°C for 16 min.➡

TSS questions

What’s the big deal about using crucibles?

- For one thing, crucible weigh a LOT…especially compared to the 1 mg/L residue requirement.
- Really? You want to try to determine a 1 mg weight change in something that weighs as much as 50 gm? (50,000 times!)
- Many of these we encounter take only a 10 or 20 mm filter.
- The volume that can be poured through is often limited. A 25 mL Gooch has a reporting limit of 40 mg/L.

Why can't you use Gooch crucibles

Typical TSS filter: 47 mm diameter
Peace Dollar: 38 mm diameter
Roosevelt Dime: 18 mm diameter
Jefferson Nickel: 21 mm diameter

Generally two sizes:

- 13 mL volume (15-16 mm)
- 25 mL volume (20-21 mm)

Labs using Gooch crucibles typically filter no more than 25 mLs, leading to an LOD of 40 mg/L or greater

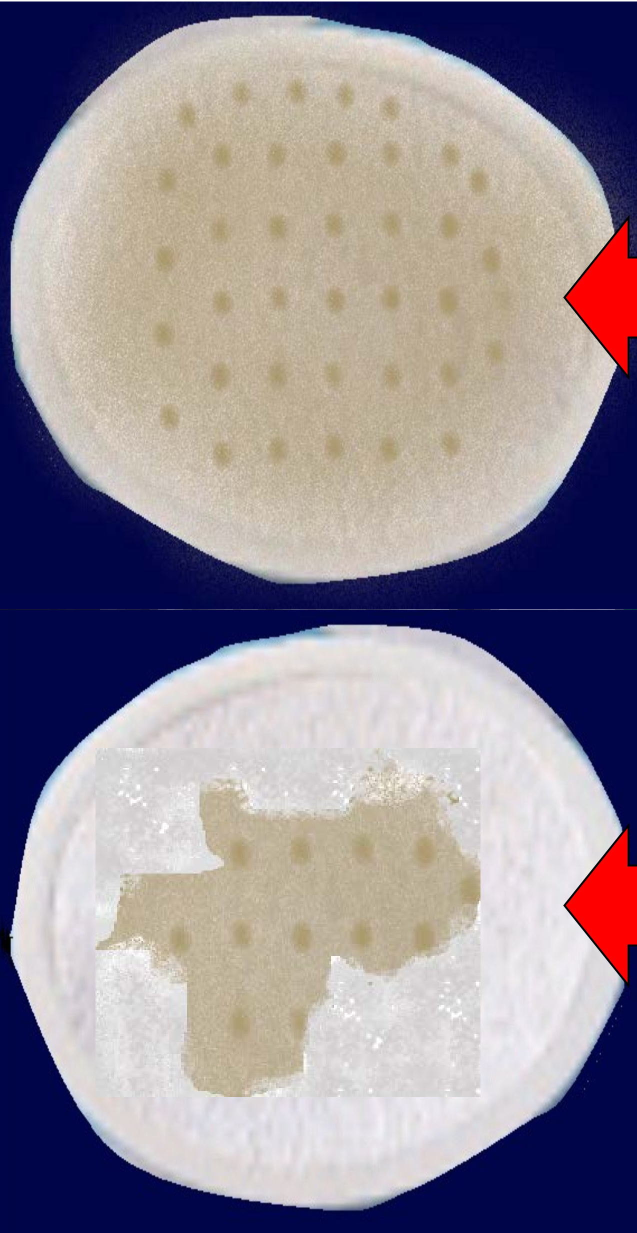
TSS questions

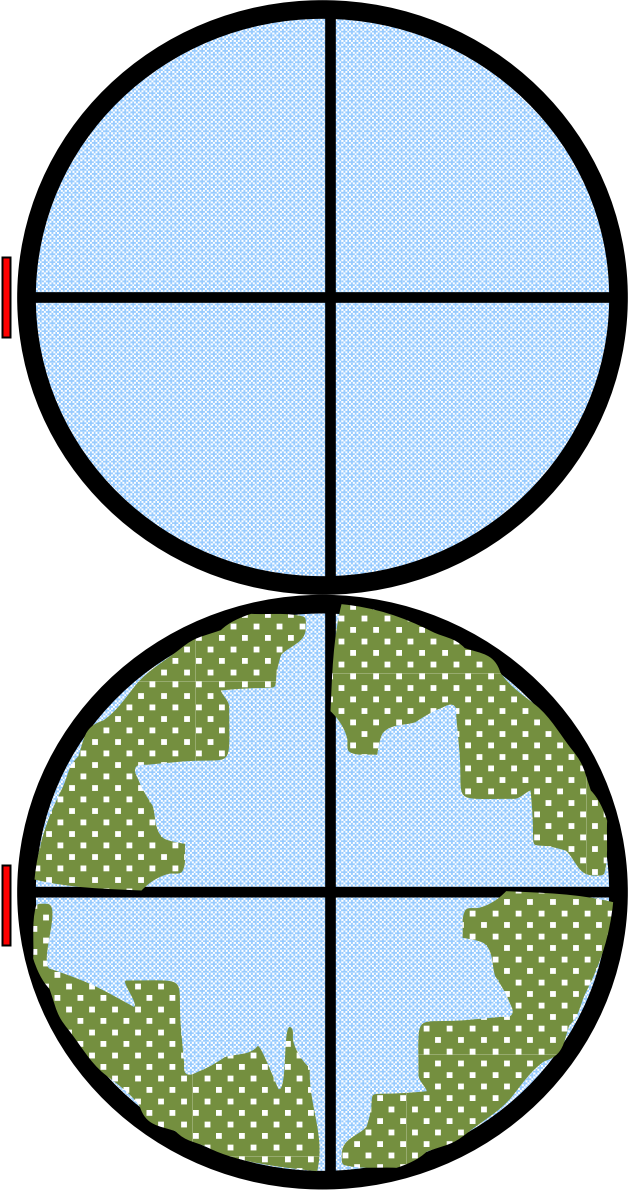
Why do I have to clean my filter screen?

- Technically, this "requirement" is…not.
- It is certainly a strong recommendation. But…

- If your showerhead is clogged with hardness deposits, don't you want to take some action?
- I might argue against it being a citation, but it is certainly a strong recommendation.

TSS - Filter Support screens





Summary

- There are a lot of nuances to lab testing.
- Some are in code (the law!) so you could be forced to make the change(s).
- But others are debatable.
- Never be afraid to politely ask your auditor to point out for you the specific code/method language that supports their citation.
- It's YOUR report, and reflects on YOUR facility. It's only fair that it be an accurate reflection.
- The big picture is that those that will see the report may not be able to distinguish between a recommendation and a deficiency.

Questions
Answers

Have YOU been cited for your QC Manual?

- **A quality manual that meets *all* the requirements [of NR149] , has not been completed. -- NR149.37**
  --The lab has an extremely brief and outdated quality manual from November 2001".
- A quality manual that addresses each of the nine elements listed in 2008 NR149.37 (3) must be completed. The laboratory could customize the quality manual that is available on our website

QA Manual – What NR 149 requires

- (3) CONTENT. **The quality manual shall include, address or refer to**, at a minimum, the following elements:
  - (a) Organization & management structure of the lab.
  - (b) Procedures for retention, control and maintenance of documents used in or associated with analyses.
  - (c) Procedures for achieving traceability of standards, reagents and reference materials used to derive any results or measurements.
  - (d) Procedures for handling samples.
  - (e) Lists of major analytical instruments and support equipment.

QA Manual – What NR 149 requires

- (f) Procedures for calibration, verification and maintenance of major analytical instruments and support equipment.
- (g) Procedures for evaluating QC samples, including, but not limited to, method blanks, and LCS...
- (h) Procedures for initiating, following up on and documenting corrective action addressing quality assurance and QC failures, discrepancies or nonconformance.
- (i) Procedures for reviewing analytical data and reporting analytical results.
- (4) **REVISIONS**. The quality manual shall be kept current... All editions or versions of the quality manual shall indicate the dates in which they were issued or revised.

Meeting the letter of the law?

- f) Procedures for calibration, verification and maintenance of major analytical instruments and support equipment.

- Calibrations require at least 3 standards.
- Calibrations for colorimetry are verified by analysis of a 2nd source ICV against 90-110% limits.
- Calibration linear regressions must have a correlation coefficient of $\geq$ 0.995.

Is that sufficient?