

Mealy comes

UnBIBI.
BaceR.

Mouthguards in...?

Helmets on?

...

Let's ride!

- This session will focus on the “big 4” wastewater parameters: BOD, TSS, ammonia, and total phosphorus. Discussion will center around key problems encountered in each of these tests, how to prepare for a lab audit, and how to resolve issues when they arise. How proposed changes to NR 149 affect these parameters will also be discussed.
- Attendees should come prepared with questions and data to help solve real life problems.
- The “unplugged” aspect offers an opportunity for attendees to direct the presentation to address their particular concerns or questions.

- What lab practices will get you



- What aspects of testing will drive you



- Do you feel requirements are



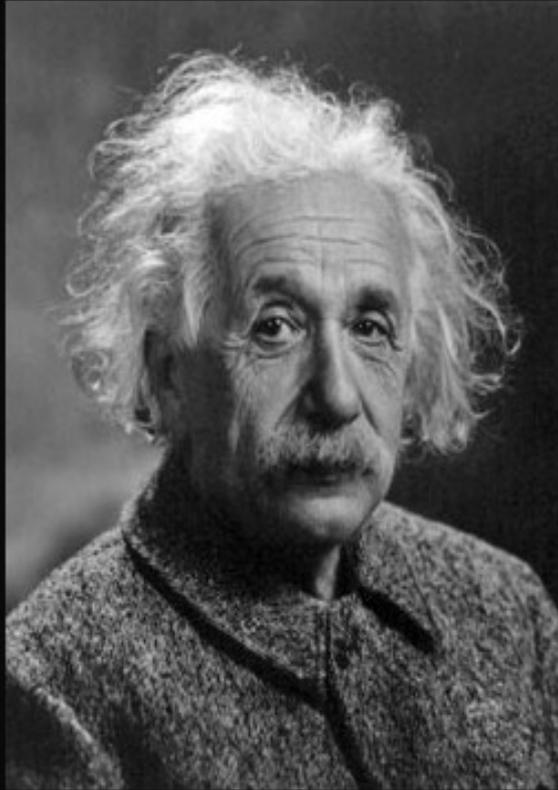
- But... I don't think that's what the code says...

Crossing
The Line

- "Gimmies" are those things that stare an auditor in the face...begging for a-busting.
- Don't get busted by the Thermometer Police!
- ...or the balance police.
- ...or the autopipette police.
- You get the idea.
- Take care of the housekeeping tasks!



- Is your QA Manual up to par?
- How about your SOPs?
- Have you done your new LOD?
- Do you have an IDC that meets your policy for EVERY facility member that does testing?
- Stay organized!
- The longer it takes to locate data, the longer the auditor will be there.



Unthinking respect for authority is the greatest enemy of truth.

(Albert Einstein)

izquotes.com

Auditors are human too. If you feel something is not right or goes too far, respectfully request them to show you where the requirement exists in code.

WheresYourAuthority.com

Rick Mealy, Sole Proprietor



- Respectfully challenging authority
- Making deficiencies disappear
- Just had an audit? Call me!

CALL BIGTROUBLE 800-BAD CITE 800 FUBARed
(244)876-8253 (800) 223-2483 (800) 382-2733

DEFICIENCY: The laboratory has not verified that the cleaning procedure **and cleaning frequency** used on the sample collection containers are not contributing to the contamination of samples.

Citation Reference NR 149.46 (1) (b)

- The sample collection containers need to be assessed on the day before normal routine cleaning is performed – in order to show that the cleaning frequency used is adequate.
- If the results are unacceptable the cleaning frequency will need to be shortened until acceptable results are obtained. The sample collection containers also need to be assessed after the normal routine cleaning is performed – in order to show that the cleaning procedure used is adequate. If the results are unacceptable the cleaning procedure will need to be corrected until acceptable results are obtained.
- This is a one-time requirement - as long as the containers used, the cleaning frequency, and the cleaning procedure does not change.

When the laboratory provides containers and preservatives for sample collection, including bulk sampling containers such as “carboys”, the laboratory shall have

standard operating procedures in place

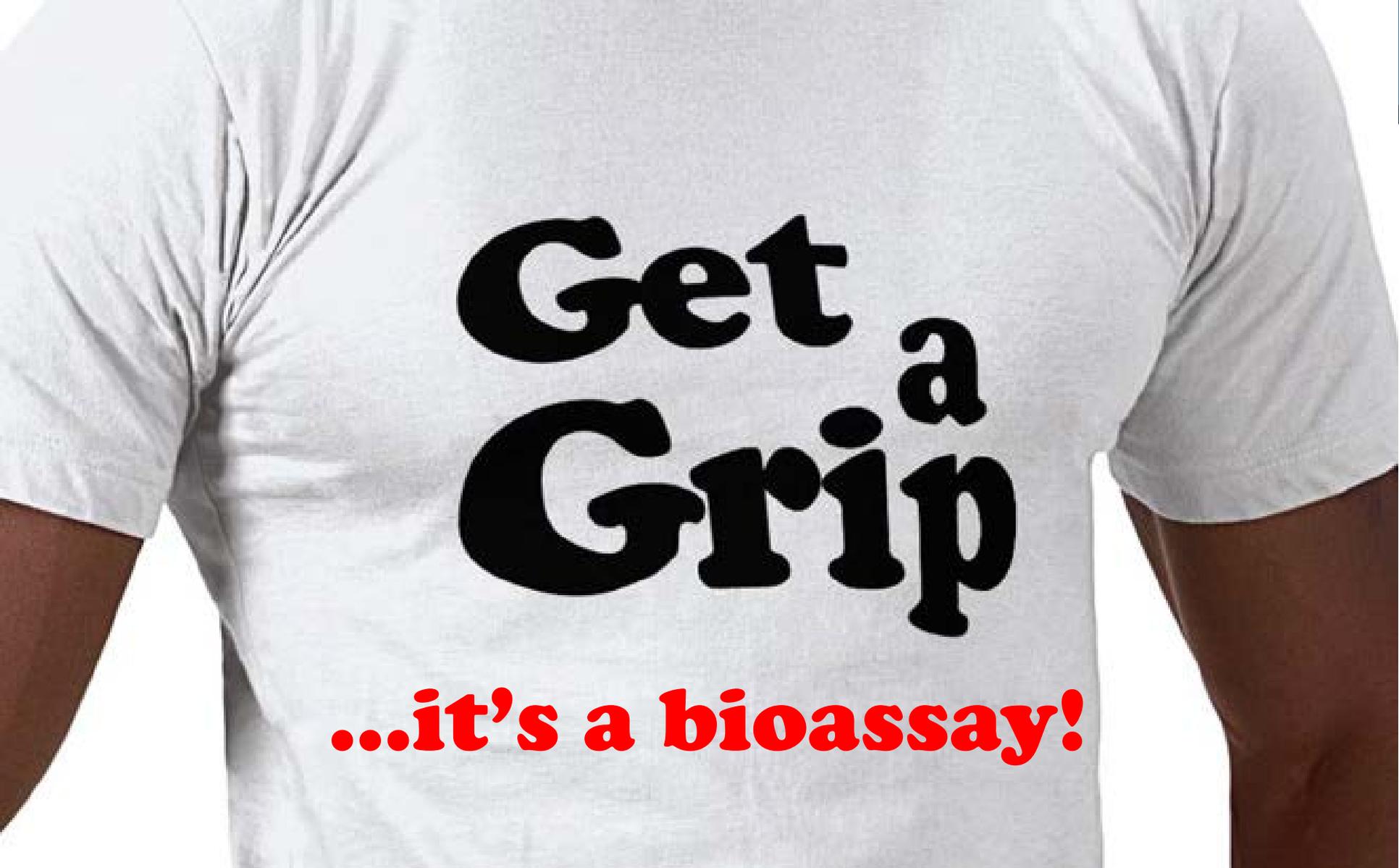
which address concerns that

1. the containers are adequately cleaned **and**
2. not contributing to contamination of samples, **and**
3. do not contain analytes of interest at levels which will affect sample determinations

- There is NO mention of frequency, before vs. after, or any corrective action!
- Besides...contamination = high bias. Who cares?
- This goes away 9-1-19

BOD...

unhinged

A white t-shirt is shown from the chest down to the waist. The text 'Get a Grip' is printed in a large, bold, black, sans-serif font. The word 'Get' is on the top line, 'a' is a smaller word on the second line, and 'Grip' is on the third line. The t-shirt is worn by a person whose arms are visible on the sides.

Get a Grip

...it's a bioassay!

We have to keep in mind that BOD is not like other tests we audit. It's not chemistry. It is not subject to laws of chemistry. It's about keeping a bunch of bugs in their happy place so they will munch on waste.

The room barometer is not verified for accuracy.

10

The thermometer used to monitor the laboratory's room temperature has not been verified against a NIST traceable thermometer, and the laboratory does not apply correction factors to all thermometers.

7

Critical sample pre-treatment [**super-saturation**] is not performed before BOD analysis.

7

Critical sample pre-treatment [**pH**] is not performed before BOD analysis.

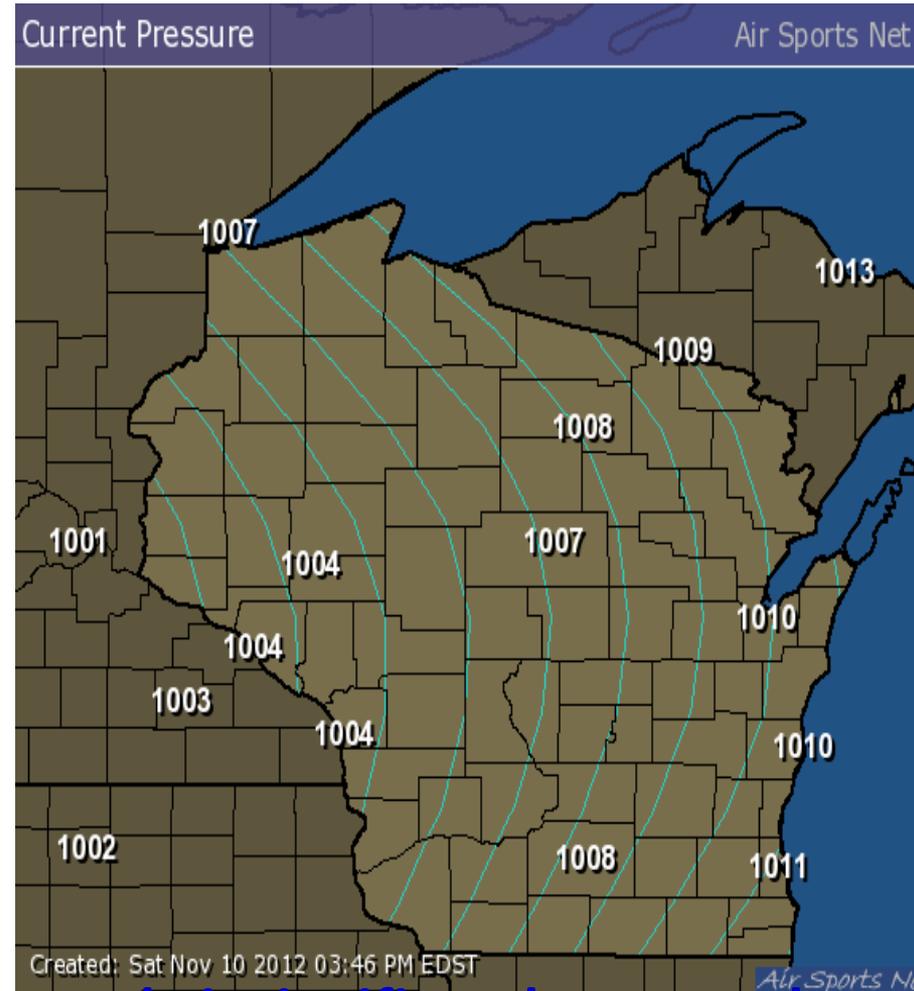
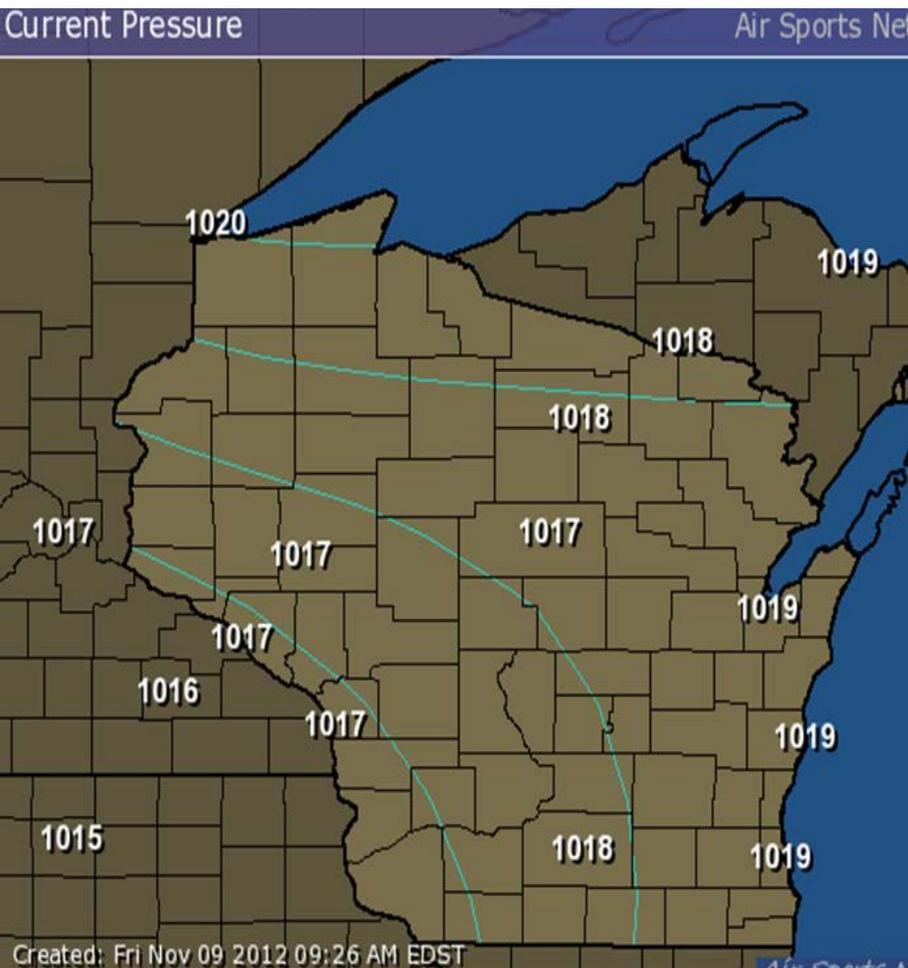
6

Critical sample pre-treatment [**sample temperature**] is not performed before BOD analysis.

5

Blank issues.

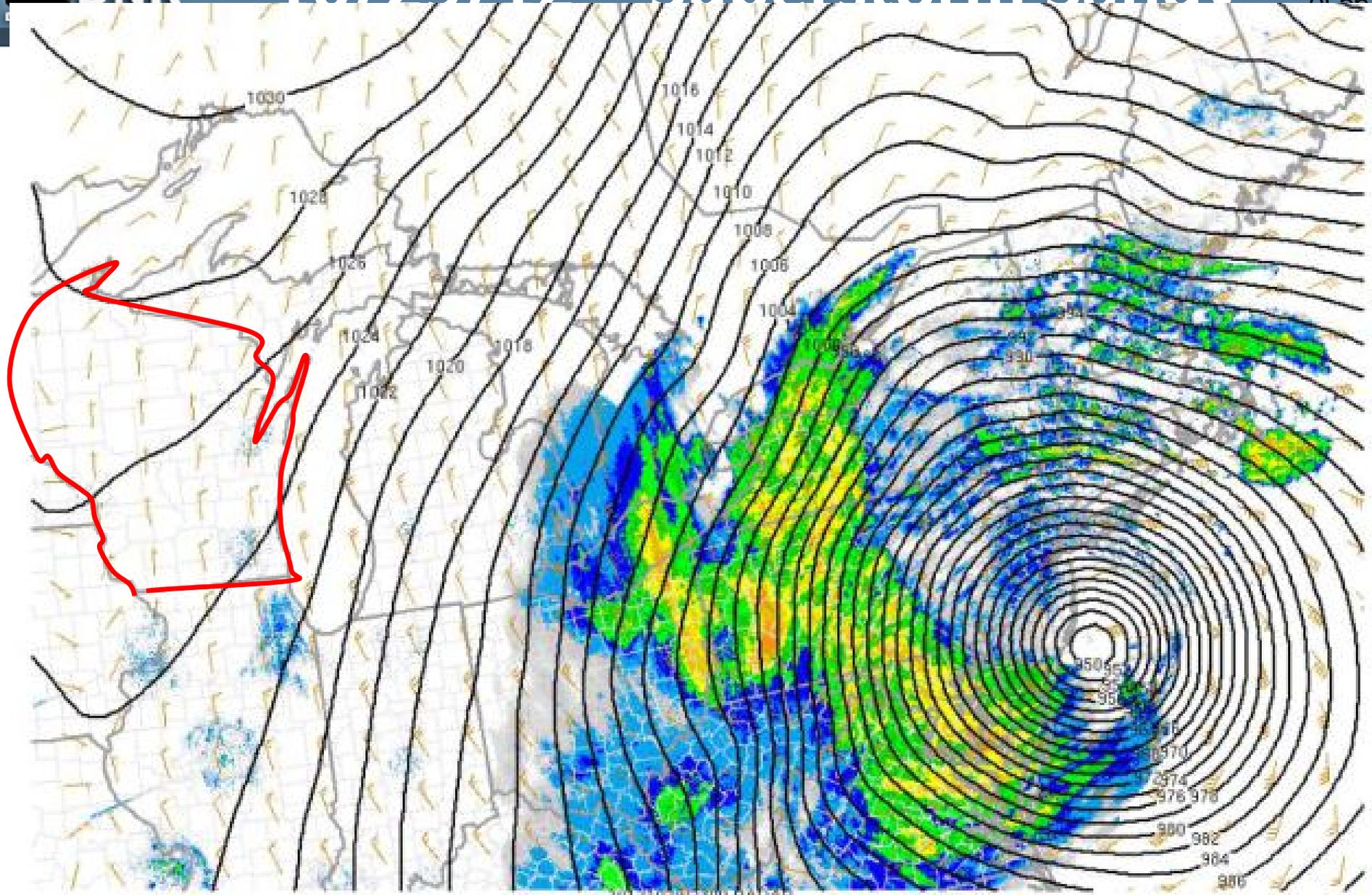
5



On a clear, calm day, pressure changes only insignificantly across the state. One could use pressure from several hundred miles away.

5 mm of mercury = 6.7 millibars = 0.06 mg/L

<http://www.usairnet.com/weather/maps/current/wisconsin/barometric-pressure/>



201210292200 MSL Pressure and surface wind

1 mb = 0.750062 mm Hg

Thus 5 mm of mercury = 6.7 millibars

What lab practices will get you

BUSTED

- Not using wide bore pipet tips
- Optical D.O. probes – calibrate each day
- Averaging multiple GGA
- Not seeding samples that have been disinfected or inhibited
- Barometric pressure – local, not adjusted to sea level
- Using chlorine strips that only test down to 1 mg/L

What aspects of testing will drive you



- **Super-saturation**

If your IDO's are supersaturated, samples will be biased high and blanks likely will fail.

- **Blank failures**

Face the facts...blanks WILL fail. It's a flaw in Standard Method's requirements.

- **GGA failures**

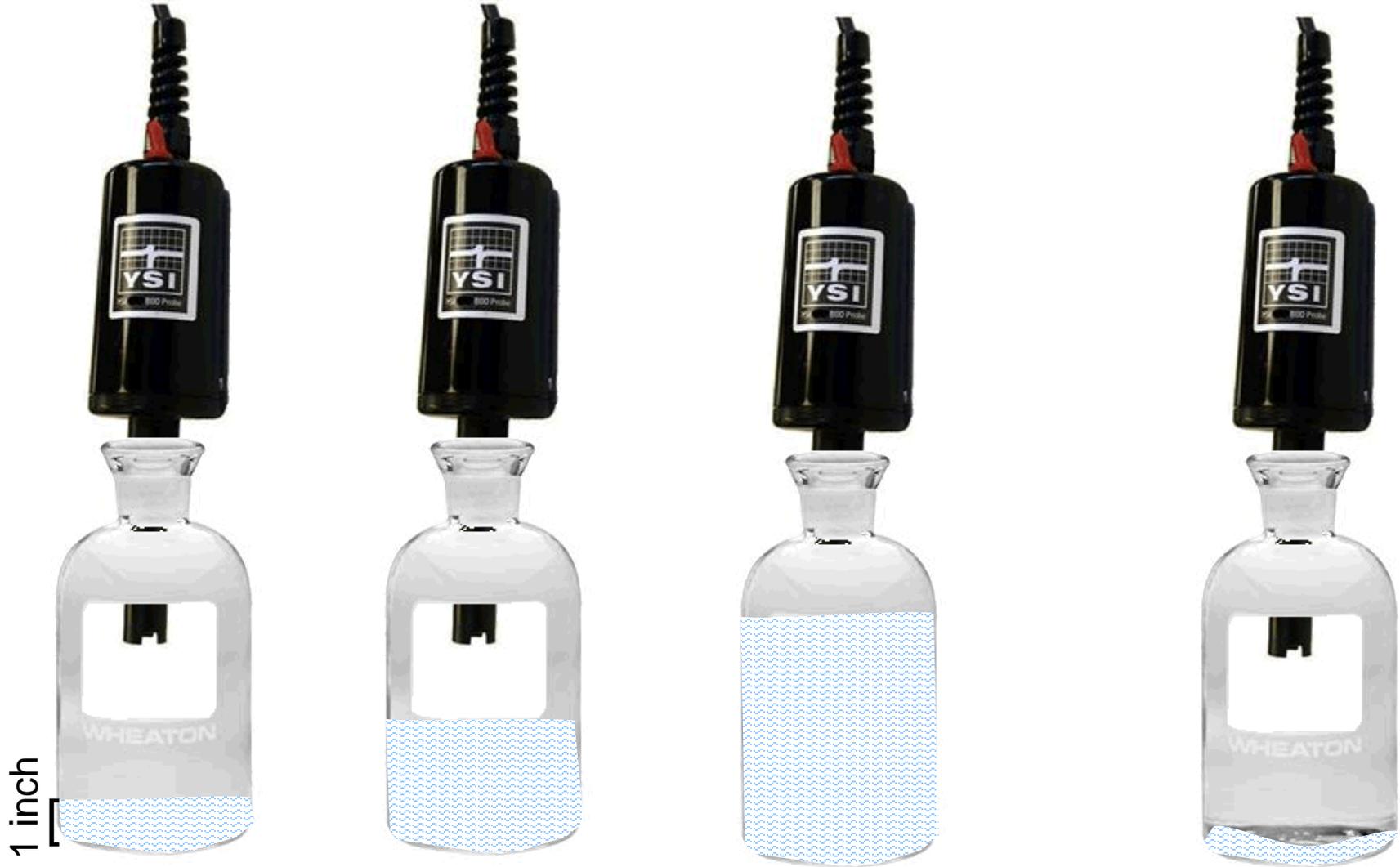
GGAs will fail low if you use a weak seed or insufficient (because it's weak) seed.

- **Calibration & consistency**

Whatever you do, BE VERY CONSISTENT!!!!!!

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





...is CRITICAL!!!!



What aspects of testing will drive you



- **Vendor claims vs. regulations**

Lots of claims are made every day...but are they accurate claims? How often does a vendor ultimately get whacked upside the head for such claims?



Activia yogurt

Dannon used actress Jamie Lee Curtis to tout “scientifically proven” claims that Activia helps regulate digestion and boost the immune system.

A judge said Dannon “simply hadn’t proven” its claim and ordered the company to pay \$45 million to settle a lawsuit.

Activia is a more than \$2B brand. \$45M (\$0.045B) is a very small price to pay to get name recognition. That fine is peanuts!

Who even heard about the judgement?



Which requirements are



- Dilutions made must be designed to expect at least 2 mg/L depletion
- Others????

But... I don't think that's what the code says...

Crossing
The Line

- The SOP for BOD does not describe the procedures in enough detail. -- NR149.40 (1) (c) -- With the exception of only the DO meter calibration for BOD, the laboratory must write an SOP for BOD that deals with blank setup, typical influent and effluent BOD sample volumes, GGA procedure, and seeding procedure for GGA.

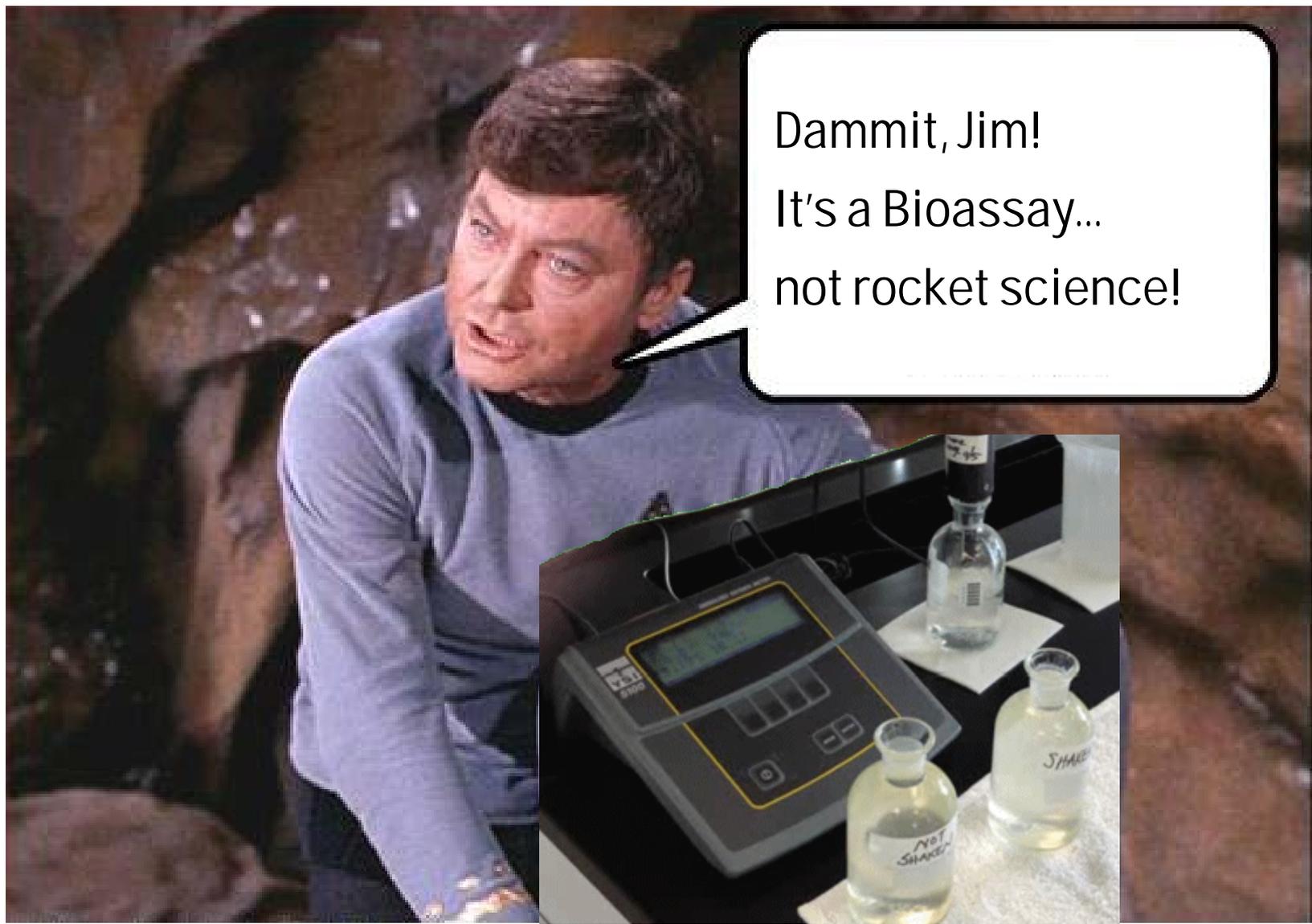
At what point does detail requested cross the line?

- Is that a valid deficiency?
- Part of it?
- None of it?
- Subjective?



- The laboratory does not maintain the exact record of raw data for generating results for the BOD test. --NR149.39 (3) (a)–

(3) ANALYTICAL AND TECHNICAL RECORDS. (a) The laboratory shall maintain all analytical and technical records containing raw and derived data, or original observations, necessary to allow historical reconstruction of all laboratory activities that contributed to generating reported results.



Dammit, Jim!
It's a Bioassay...
not rocket science!

Colorimetry . . .

unhinged

NH₃ and TP

What lab practices will get you

BUSTED

- Method blank subtraction (regardless of what vendor tells you)
- Diluting samples after adding color reagent
- Initial calibration – Entering a response of “0” instead of the actual measured response
- Performing “hot block” digestions at anything other than 150 ± 2 °C for at least 30 mins.

What aspects of testing will drive you



- (At least for TP TNT) variable blanks
- Variability in reagent packets
- Who is correct? The vendor? Or the DNR?
- Why CAN'T I use my pre-programmed calibration?

But... I don't think that's what the code says...

~~Crossing~~
The Line

- Samples and QC for Total Phosphorus (TP) are not prepared as required. -- SM 4500 P B (5)(c) --

What does SM 4500 P B (5)(c) say?

Boil gently on a preheated hot plate for 30 to 40 min or until a final volume of 10 mL is reached.

Organophosphorus compounds such as AMP may require as much as 1.5 to 2 h for complete digestion.

Alternatively, heat for 30 min in an autoclave or pressure cooker at 98 to 137 kPa.

ISE...

unhinged

NH₃

What lab practices will get you

BUSTED

- Slope acceptance criteria < 54 or > 60 mV
- Not doing a full calibration daily
- Samples and standards at different temperatures

What aspects of testing will drive you



- What's this about slope criteria between each segment (i.e. 0.2 -2 and 2-20 ppm)
- What if I have a High performance probe?
The mV acceptance criteria changes to > 54 and <=65 mV
- How is a “high performance” different than a “classic” probe?
Storage and Linearity

Which requirements are



As clear as mud

- ??????

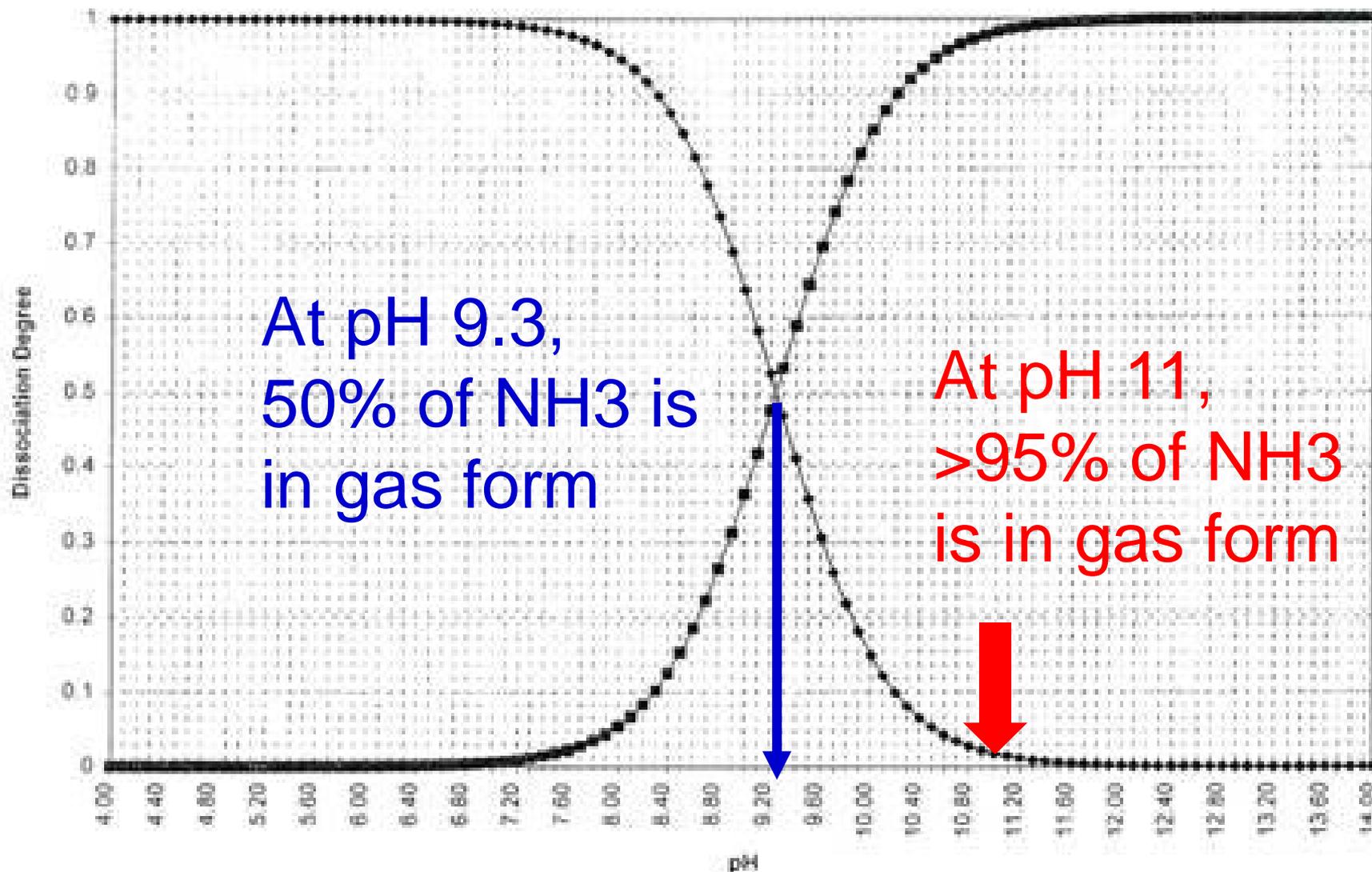
But... I don't think that's what the code says...

~~Crossing~~
The Line

Samples for NH₃-N are not analyzed as required.
--SM 4500 NH₃ D (4) (b) and (c) --

(b). Electrometer calibration: ...Add a sufficient volume of 10N NaOH solution (1 mL usually is sufficient) to raise pH above 11... Keep electrode in solution until a stable millivolt reading is obtained. Do not add NaOH solution before immersing electrode, because ammonia may be lost from a basic solution.

Ammonia Gas / Ammonium Ion Interconversion Dependence on pH



- Normal WWTP (non-lagoon systems) effluent NH₃ values are very low to < LOD...except during the cold months!
- So...if you have data from cold months for a WWTP that clearly shows ammonia levels, isn't that "proof" that the NaOH added is sufficient to raise the pH???
- Are you passing PTs and QC? Wouldn't that be unlikely if the pH wasn't appropriate?

TSS...

unhinged

What lab practices will get you



- Not using wide-bore pipets
- Using Buchner funnels or Gooch crucibles
- Failure to adhere to the 2 mg/L reporting limit

What aspects of testing will drive you

- Nothing????
- This is TSS!!! There should be nothing here to raise blood pressure even 1 point.



But... I don't think that's what the code says...

~~Crossing~~
The Line

TSS analysis does not comply with the method requirements. -- SM 2540D (2) and (3)

2540D.2. Apparatus

Apparatus listed in Sections 2540B.2 and 2540C.2 is required, except for evaporating dishes, steam bath, and 180°C drying oven. *In addition: Aluminum weighing dishes.*

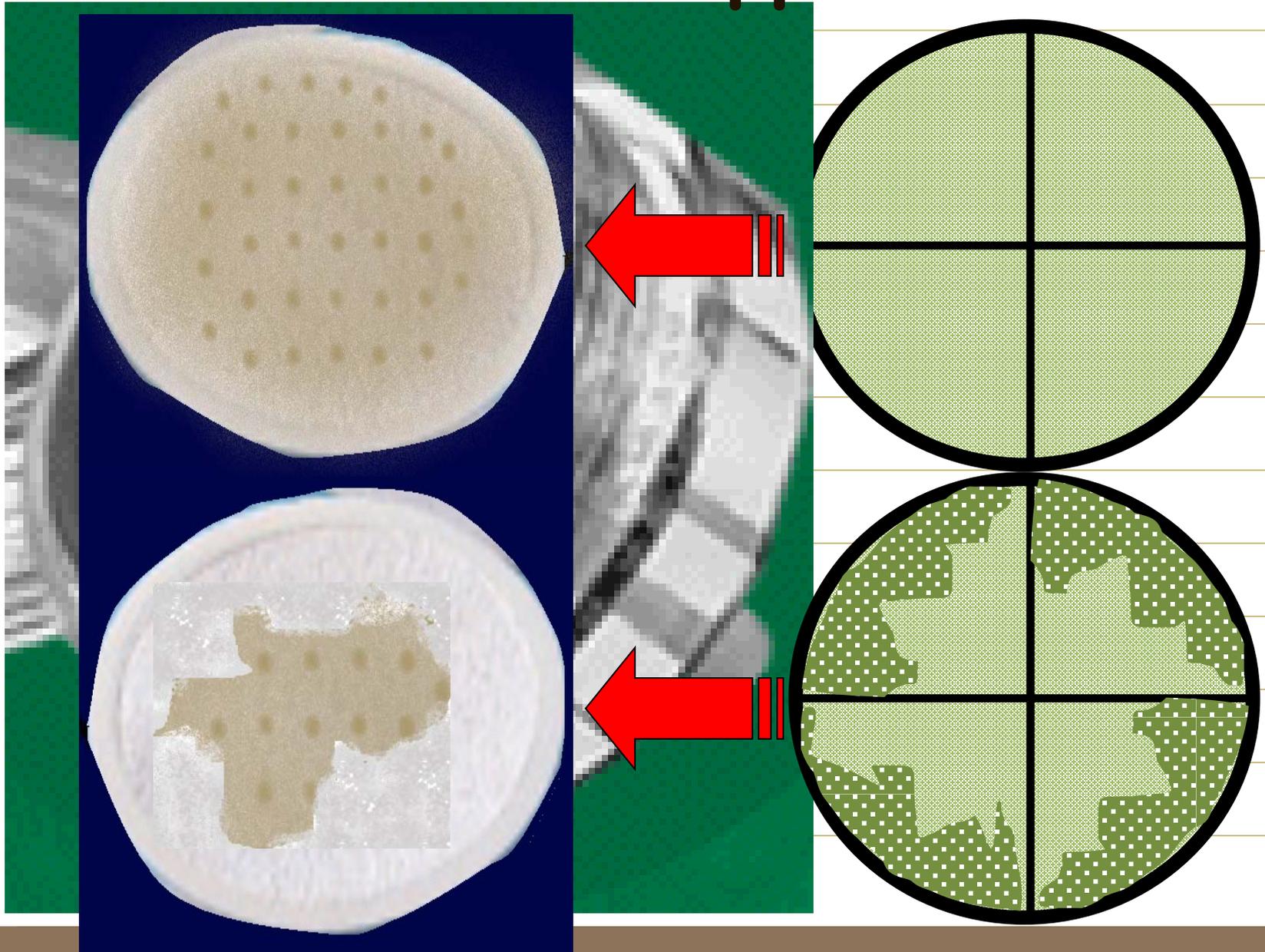
2540C.2

b. Filtration apparatus: One of the following, suitable for the filter disk selected:

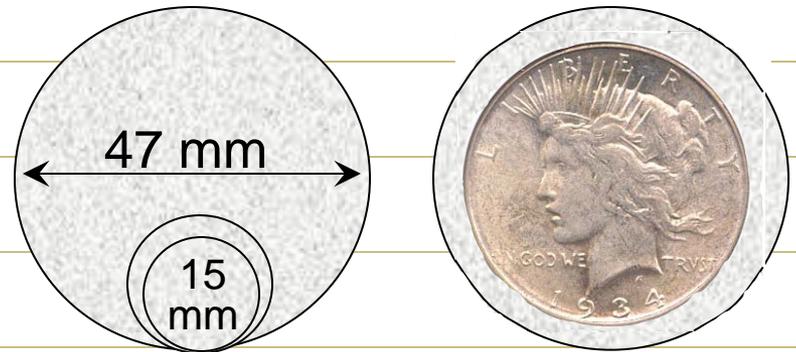
1) Membrane filter funnel.

3) Filtration apparatus with reservoir and coarse (40-60 μm) fritted disk as filter support.

TSS - Filter Support screens



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

Some other
things that
come up

Sent: Wednesday, August 22, 2018 10:14 AM

To: Mealy, Richard G - DNR <Richard.Mealy@wisconsin.gov>

Subject: Hello from NCL

Hi Rick,

I have been a Chemist for almost 50 years, but today I learned something new from one of your auditors: EDTA solutions must be stored in the dark. I never knew that. I have been selling EDTA solutions for over 30 years and have used them for over 50 years and never noticed any degradation from storing them in lighted areas.

Could you please cite the reference for that fact?

Thanks,

Mike Raynovic

**Very
respectfully
questioned**

- **SM 2340C (2)(d)**
- **Because the titrant extracts hardness producing cations from soft glass containers, store in polyethylene (preferable) or borosilicate glass bottles.**
 1. There is nothing about storing the titrant in the dark.
 2. Scientifically speaking, EDTA is not going to degrade in the presence of direct sunlight or UV.
 3. An internal LabCert policy was written some time ago regarding handling of titrants, but the focus there was on those that degrade, particularly silver nitrate titrant for chlorides

...and another issue
that pops up

- **Deficiency:** The laboratory is not storing samples and standards separately.
- Citation Reference NR 149.46 (6)(d)
- What does that code reference say?

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

They kinda gotcha

What are you being told to do?

- The laboratory must store samples and standards separately to minimize cross-contamination.
- Update the SOP or Quality Manual that the samples will be stored separately from the standards. One option is to store standards in a tightly-lidded plastic storage container within the sample refrigerator.

- Did the auditor go too far here?

Here is an example of an air tight container that you could use to store the ammonia samples in your chemical refrigerator.

This one is from Walmart but you could probably buy it at Target and maybe even from a grocery store.

You do not have to use a plastic box container. You can use a zip lock bag as long as it is air tight.



- Perhaps mis-interpreted as direction rather than suggestion?
- This shows what a fine line auditors have to walk. Only trying to be helpful, the issue became a “telephone” game with misinterpretations

...and another ...

SOPs

The SOPs in use do not contain the required information. -- NR 149.40 (2) --

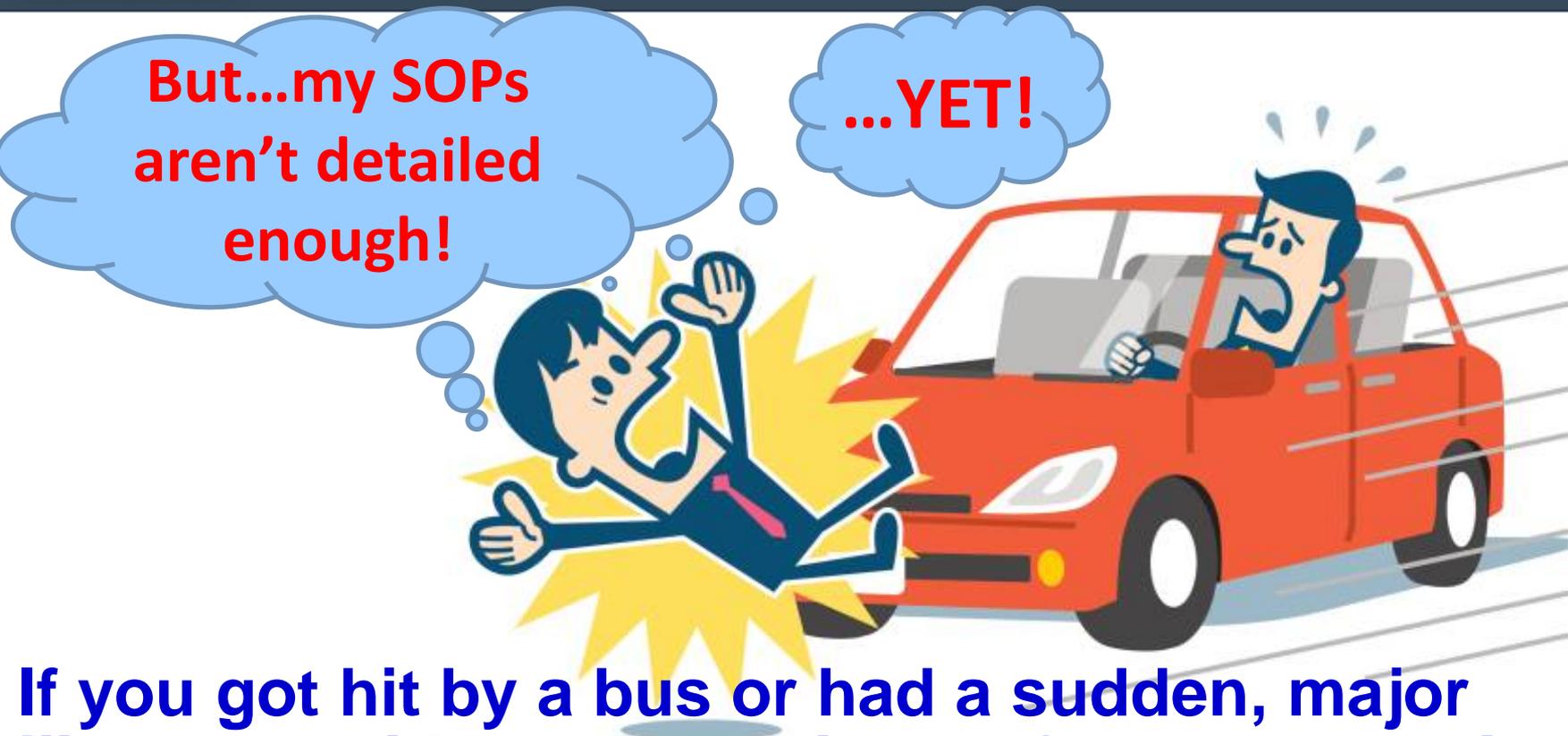
The TSS SOP needs to be revised for the following:

- Proper analysis method: SM 2540D – 1997
- The reporting limit should be based on the volume of sample used;
- Potential interferences
- Equipment, supplies, and reagents
- Corrective actions and contingencies for out of control data
- The lab is currently drying samples overnight, but the SOP only discusses the process for one-hour re-dry

- NR 149.40 Standard operating procedures.
- (1) GENERAL REQUIREMENTS.
- (b) SOPs **may** be documents written by laboratory personnel
- **OR** may consist entirely of copies of published documents, manuals or procedures **if** the laboratory follows the chosen source exactly.
- (c) SOPs **may** consist in part of copies of published documents, manuals or procedures **if**:
 - 1. Modifications to the published source are described in writing in additional documents.
 - 2. Clarifications, changes or choices are completely described in additional documents, when published sources offer multiple options, ambiguous directives **or insufficient detail to perform or reproduce an analysis**.
- (d) SOPs shall indicate their dates of issue or revision.

You have 3 options for SOPs

1. Write your own. **Downside:** *You have to have each section specified in code and may be the target of subjective review of what's "good enough".*
2. You can wave a copy of an approved method and bypass specific section requirements. **Downside:** *You MUST follow it to the letter!*
3. You may use a hybrid approach. An approved method plus an additional sheet that spells out differences from the method. . **Downside: ??**



If you got hit by a bus or had a sudden, major illness, could someone else perform your analyses to the same accuracy & precision simply by reading your SOPs?

Bottom Line: If the answer is “probably not”, then they need work.

...and another ...

QC Manuals

- **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”.
- **Supplemental Information:** 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.

- (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.

- (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.

Objective vs Subjective

An unmade bed!



Art!



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

My procedure is:

- 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 ≥ 0.995 .

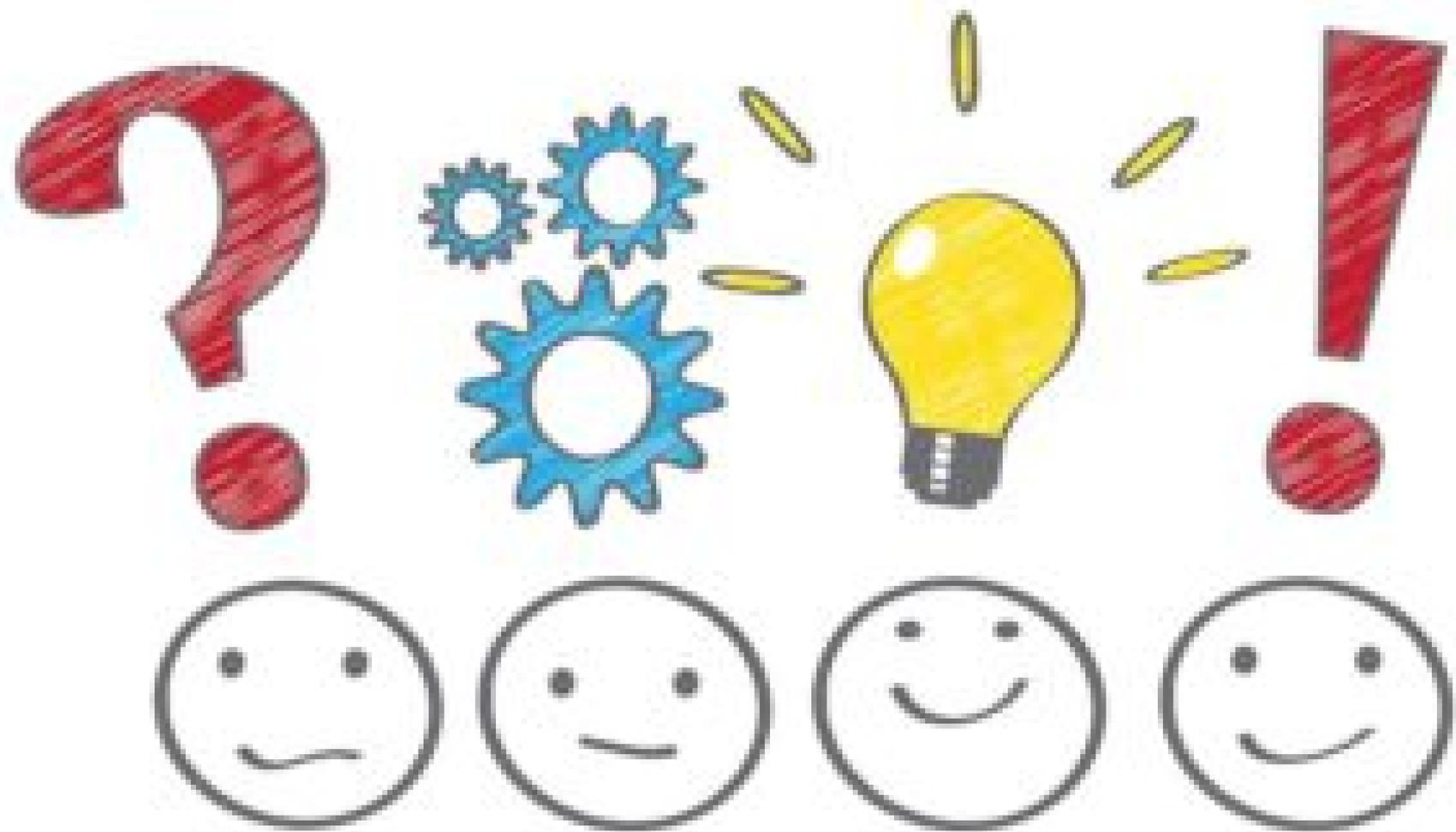
Is that sufficient?

- Unless there are any more bold souls with questions....
- That's all I have...

- T minus 3 weeks till retirement (officially 1/18/2019)
- My time with the DNR may be over, but I plan to still be around...I'd like to do some consulting work
- I plan to continue doing things but want to **work when I want to...**
- Because this girl needs a Grandpa to teach her things that will annoy her parents.



Insert gratuitous plea for votes for WWOA Board



Weighing heavily on my mind

The ASTM Class 1 weights used to verify the accuracy of the analytical balance do not have valid certificates. -- NR 149.44 (3)(g)(2) --

Currently, the laboratory checks their analytical balance daily with one ASTM Class 1 weight. The analysts are allowed to select any single weight from a full set for the daily check. Examination of the records show that at least one weight in the mg and one in g range was checked monthly.

However, the weights do not have valid certificates. Code requires that weights be certified for accuracy every 5 years by a metrology service outside the laboratory or new individual weights of suitable class or type traceable to NIST be purchased for use.

Code requires that at least one weight in the milligram range and one weight in the gram range be used to verify the analytical balance monthly. The lab does not have a policy of requiring the analysis of required weights on a monthly basis. They must institute a policy to measure one weight in the milligram range and one weight in the gram range monthly. A 100 mg and a 1 g weight are suggested.

- (3)(g) Analytical balances that have been used at least once in a month shall be checked monthly with at least 2 certified weights, one weight in the gram range and one weight in the milligram range. The weights used to perform these checks shall be:
 2. Certified for accuracy every 5 years by a metrology service outside the laboratory or new individual weights of suitable class or type traceable to NIST shall be purchased for use.

Speak up on this one!

- The citation is for failure to have current weight certifications.
- But then it take a left turn and discusses monthly balance checks...
- ...and cites (“shall/must”) the lack of a policy
- Yet the audit showed they met requirements!
- ...and where is the requirement for a policy?