LABNOTES
News & Updates of the LabCert Program

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We're back...and with a whole new format and approach. Your audit exit survey feedback makes it clear that you want and value information provided via LabNotes and that you want a more regular and consistent product. So we are unveiling this new approach that offers a quick e-mail broadcast overview of current topics with links to get you to the entire edition or more complete information if only a specific topic or two is of interest.

2015 Registered Lab of the Year

…and the award goes to… Ripon WWTP

This is the Lab Cert program's 20th year recognizing a registered Laboratory of the Year. Looking back, we realized that the laboratory community has evolved during these past couple decades. The large majority of labs are now reliably producing good quality environmental data for the agency, so we decided we would look at our nomination process and kick things up a notch - to look for labs that go beyond compliance - to identify labs that really stand out.

Our new nomination form includes questions such as:

- Do they have any innovative solutions to common lab problems?
- Is the lab successful because of a single (or small number of) analyst(s), or is it because of a corporate/municipal culture and support system?
- How does the lab plan for staff transition?
- Does the lab proactively communicate with DNR staff when issues/questions arise?
- Does the lab deserve special consideration for its efforts to improve or overcome difficult circumstances?

Using these additional criteria, **Ripon stood out as the new gold standard for how to make a good laboratory great.** There are several great examples in their nomination papers, but I will highlight just one example here.

Like many facilities, Ripon is dealing with how to manage lower phosphorous limits. Ripon's limits are especially important since they discharge to a tributary to Green Lake, which is a critical natural resource for that community, and for Wisconsin. Here is an excerpt from Mark Stanek's nomination. Mark is the DNR's Wastewater Engineer for this region:

DNR Secretary Cathy Stepp with Jack Wendler (c) and Chris Liveris (R) of Ripon WWTP

"It was a pleasure working with Jack Wendler and the staff at the treatment facility as we dealt with very complicated issues related to the new phosphorus and thermal rules. The city is currently achieving extremely low phosphorus concentrations (without chemical addition), levels that are likely the lowest in the state for a municipal treatment plant. To achieve these low levels, quite a bit of extra lab analysis, experimentation, and quality control testing is required. The city has a very cooperative relationship with the Department, and they have always been receptive to trying new ways of doing things in the laboratory and at the treatment plant."

And another quote from one of our lab auditors, John Condron, who also nominated Ripon:

"*Ripon's wastewater laboratory is one of the few laboratories to fully understand the interconnectedness of the laboratory and running its own treatment plant."*

John's statement really gets to the intent of the Clean Water Act and the funding used to build all these laboratories in the 1970's – to provide real-time data

to effectively manage wastewater treatment operations.

Mark Stanek explains how Ripon does this so well: "At least half of the wastewater loading entering the facility comes from industrial users. The variability of the influent constantly challenges the operators. I cannot over emphasize how important of a role Ripon's laboratory is in providing quality data to its operators for process control. Of special note is the amount of nutrient analysis that is performed in order to maintain the proper nutrient ratio's for the biological treatment process."

Mark ends his nomination with this: "Jack Wendler is the most conscientious lab analyst I have worked with in my career at the Department and I strongly support the nomination of the city of Ripon for Laboratory of the Year."

Congratulations to the staff at the Ripon Wastewater Treatment Facility – WELL DONE!

LOD & LOQ Unplugged

The complex and confounding relationship between calibration, the LOD, and the LOQ

The list of acronyms associated with the conceptual detection and quantitation limits is a veritable alphabet soup with an overabundance of "D"s and "L"s.

The NELAC (TNI) program has its own list of concepts and definitions, as do the EPA, a number of federal programs, and even various states. To further complicate things, the EPA has recently proposed a wholesale change to the "MDL" protocol, the first in over 30 years. But at the end of the day, in this state, we are bound by our administrative code. So, while we can appreciate the difficulty in juggling this multitude of concepts, definitions, and protocols for labs that operate nationwide, our programs depend on us to follow our administrative rule. It's as unrealistic to request that the LabCert program accept the Department of Defense's procedures as it is for us to request that they accept ours. In the absence of a nation-wide consensual approach to these issues, satisfying multiple regulatory entities is simply the price of doing business in the national arena. LabCert's primary mission directive is to support the internal DNR programs. Our approaches to these issues serve as the foundation of each environmental programs' determination of whether or not an action level has been exceeded, or a trigger point has been tripped requiring additional monitoring.

Actually, the cart may have been placed before the horse (*or the chicken before the egg*) on this issue. While the issues of detection and quantitation are important, one could make a solid argument that they are both meaningless in the absence of a robust calibration. We focus intently on details of the LOD and LOQ, yet there are no equivalent detailed requirements of the calibration which is required to obtain these values. But that's a whole different article. We need to talk about two very basic concepts (detection and quantitation) and the very critical bridge —calibration— between them.

We first have to define our terms. Again, there are numerous definitions out there, but in this state, we are bound by our administrative code. It's also important to keep these definitions centered on your radar screen.

LOD

"Limit of detection" or "LOD" means 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. For department purposes, the LOD approximates the MDL and is determined per 40 CFR Part 136 Appendix B.

LOQ

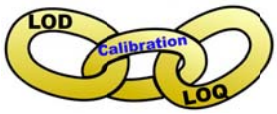
"Limit of quantitation" means the lowest concentration or amount of an analyte for which quantitative results can be obtained.

Stripped of its entourage of endless theories and opinions, the LOD is simply the point at which an analyte is present and that it is not a false positive; the LOQ is simply the point at which quantitative results are obtained. Note that there is no implied accuracy or precision associated with the LOQ (although many try to incorporate it). It's that simple. One is the point at which you can conclusively state that "X" is present, and the other is the point at which you can definitively state how much "X" there is.

While it could be interpreted that the LOD is not a measurable result, that would be an incorrect assertion. We recognize that values between the LOD and the LOQ represent a gray area where quantitation is uncertain. We get it; our programs get it. In fact, if one looks at the hierarchy of decision making process determining whether a particular action limit or standard has been exceeded, the LOD and LOQ are significant parts of the assessment process. That also explains why the LabCert program staff must remain focused on our administrative rule requirements, regardless of what other, external programs are doing.

What's this got to do with calibration points?

Quite frequently our auditors get an earful about LODs and how unrealistic they are. But just as frequently, upon encountering an what appears to be an unrealistic LOD and they subsequently review calibration data, auditors find that the questionable LOD or LOQ are directly related to how the calibration was constructed. Years ago when Flame AA (FLAA) was still in vogue we used to see LODs in the 1 to 10 ppb range and calibrations beginning at 500 or 1000 ppb. Then we'd find that the low calibration standard was associated with an almost imperceptible instrument response. Newsflash; those LODs were not realistic. Things have improved over the years (and FLAA has almost gone the way of the 8-track), but we can still trace a number of LOD problems to the calibration.



Bottom up – not top down

Our administrative rule tethers the LOD to the LOQ and then the LOQ to the calibration. Some programs have apparently adopted a top-down approach where the low calibration standard is established as the LOQ and then the LOD is derived as some fraction of the LOQ. While a top-down approach is often preferred over a bottom-up one, in this case we need to start from the bottom (the LOD) and work our way up, because the LOD is the piece of the puzzle that is developed via a strict formula. Everything else can be definitively related to the LOD.

A significant recurring deficiency that auditors encounter is that, instead of mathematically relating their LOQ to their LOD, labs simply establish their LOQ at the concentration of the lowest calibration standard and their LOD at one-half the concentration of the lowest calibration standard. This practice does not meet administrative code requirements and therefore is not acceptable.

The Lab Cert program does not allow labs to indiscriminately establish their LOQ based on any point in their calibration. Our program establishes the LOD and then states that the LOQ must be "related" to the LOD. While some may disagree, by "relate" our intent was that the relationship be mathematically defined (and stating that the LOQ must be greater than the LOD does not satisfy this requirement). One only needs to go back to the original treatise on LOD/LOQ ("Principles of Environmental Analysis" Analytical Chemistry, 1983, Vol. 55, pp. 2210-2218) to see that the most recognized relationship between the LOD and LOQ is that the LOQ is statistically 10/3 times the LOD. Then, where analyses are being performed down to the LOD (which is a requirement of most of the agency's environmental programs**), the lowest point in the calibration is required to be "near" the LOQ.**

Even Siri has trouble with "near"

Admittedly, that is a poor choice of terms, but it affords us some flexibility. The intent here is clearly "in close proximity to". If you're going to meet somebody "nearby", it certainly wouldn't involve a 30-minute drive. The underlying point here is that, with the exception of a few technologies (e.g., ICP), the further away from the LOQ the lowest calibration point, the more difficulty one will have in establishing a reasonable LOD.

LabCert Requirements

The LabCert program has recently developed a resource (2015LOD_LOQ_Clarity) which should help clarify the critical requirements for labs as it relates to LOD, LOQ, and calibration.

Method modifications?

Careful with that axe, Eugene

When all is said and done, a method is really a recipe. You can change the recipe a little bit and enhance certain flavors. Or you can make major eliminations or substitutions, in which case you risk ending up with something very different and potentially unpalatable. The same can be said for method modifications. Would you run the risk of

suffering Chef Gordon Ramsey's legendary wrath with the modification you have incorporated into your "recipes"?

Myths & Legends

This topic is the source of considerable angst in the LabCert Program. You know by now that our auditors are very familiar with the methods, and they quickly spot things that are out of the ordinary. The problem stems from the "flexibility inherent in SW-846 methods". That statement is constantly thrown back at the auditors who question your modifications. What we hear –quite frequently– is that SW-846 is a compendium of purely performance-based methods. It seems that the prevailing belief is that the methods merely serve as a starting point, and "anything goes" from there. In restaurant parlance, any and all substitutions would seem to be fair game. All you have to do is "demonstrate acceptable performance". **Hold on there; not so fast…**

> *"Glassware, reagents, supplies, equipment and settings other than those listed in this manual may be employed, provided that method performance appropriate for the intended RCRA application has been documented. Such performance includes consideration of precision, accuracy (or bias), recovery, representativeness, comparability, and sensitivity…"*
> **--SW-846 Chapter 2 (2.1)**

As the old adage goes, if you're not part of the solution, you're part of the problem. And the limited information about what constitutes one's demonstration of "acceptable performance" is absolutely part of the problem. What must be analyzed? How many of them? What are the acceptable criteria? Is a statistical analysis required? And if the criteria are broad enough that a Mack truck can slide through with ease, what does that really say about the data quality? In short, **who** gets to decide whether performance is acceptable?

Sure, it's clear that SW-846 methods have been designed with flexibility in mind appropriate for the wide range of samples and projects one might encounter. But let's stay tethered to earth. Nowhere in that disclaimer is there any suggestion that one may "modify these methods freely without limitation or fear of reprisal". SW-846 is a set of methods designed for the EPA's RCRA program. But there are other arms of the EPA. The Drinking Water program has established a position whereby method modifications are not allowed.

In the middle of the spectrum lies the Clean Water Act (Wastewater) program which has recently promulgated a healthy list of what it has established to be acceptable modifications. Goldilocks would say that the Clean Water Act's approach is just right.

A little logic goes a long way

First, let's separate compliance samples from screening type situations. If your "modification" is to do a 30 second hand-shaken micro-extraction instead of a 16-24 hr Soxhlet extraction, that may be enough to decide whether a particular investigation has removed the most heavily contaminated soils. But the intent, of course, would be to perform the "full" method" in order to demonstrate that further remediation is not required. Is it a short cut? Absolutely. But the results are not intended for compliance. Therefore, that would be a perfectly acceptable modification.

But what if the samples are for compliance testing? Shouldn't we take a longer look before we decide a particular modification is acceptable? When we encounter what appear to be major modifications, in response to questioning about how the modification was validated, the response is that, "…the method QC works fine". Good to know; but what's more important is knowing how the modification works in the face of a matrix. A prime example is the digestion for phosphorus or total Kjeldahl nitrogen (TKN). Making major changes to oxidants or digestion times and temperatures will likely have no impact on lab control standards (LCS), since the spike material is usually orthophosphate and ammonia respectively. In fact, you could eliminate the digestion entirely for these QC samples and still meet acceptance criteria! What we really need to know is whether the modification will stand up in the face of a matrix.

There's an app for that!

If the lab SOP contains critical procedural changes from the method, then the lab must have a study that validates that the change makes the data better - not worse. Non-critical procedural changes will be allowed. If the lab wants to change the method so that the chemistry of the method is different, however, then the lab may need to apply for an ATP (via the EPA).

Descending the slippery slope

Digestions (and extractions) can be tweaked to some extent (initial and final volumes), but the acid selection, ratios, and percentages as well as heating conditions (temperature and time) are what define the product. Change those and you change the final product. But, what if the lab has modified its digestion procedures to according to one of the following:?

- Hydrogen peroxide is not used for digestions and trace elements that require it,
- The digestion time is changed from what can be a couple of hours to a 30 minute process,
- Instead of a 2 hour digestion at 85-95 °C for, the lab digests samples overnight at 60 °C?

Objectively speaking, these changes all result in a lesser digestion. The recipe has been changed well beyond what might be viewed as an enhancement. Most would agree that adding a little vanilla extract and orange zest to a traditional recipe for French toast would not change the dish, but only enhance its flavor. But, would you bake a cake at 250° instead of 350°? Would you bake it for 8 minutes instead of 40 minutes? Not if you want to eat something with any resemblance to cake!

Warning: Excessive modifications can lead to an unacceptable product.

What is the LabCert Program's approach to method modification?

Generally speaking, the LabCert Program **will not allow modifications that appear to be strictly designed as shortcuts**.

If, however, there appears to be a legitimate rationale for a particular modification, *supported by sound chemistry or science*, the program may entertain a side-by-side comparison to demonstrate that the modification provides equal or better performance.

Elvis has left the building

Let's be honest; "*But we've been doing it this way for 20 years…"* is not documentation. And if you think we're singling out your lab, we're not – it's a common refrain. We rarely find documentation adequate to support the modifications we see. Like Elvis, documentation seems to have left the building.

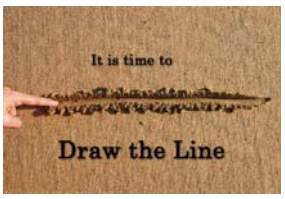
Here is another place where some of the programs, notably SW-846 methods, have left us high and dry. SW-846 indicates that modifications may be incorporated provided that, "*…method performance appropriate for the intended RCRA application has been documented. Such performance includes consideration of precision, accuracy (or bias), recovery, representativeness, comparability, and sensitivity…*".

There is no guidance provided as to what constitutes "method performance appropriate for the intended RCRA application. On the other hand, it does seem clear that the modification would not be allowed for purposes beyond a RCRA application. Unfortunately, most labs make modifications and then apply them across regulatory programs.

The side-by-side comparison that will be required by the LabCert program, should a lab wish to demonstrate that their particular modified method is acceptable, was modelled after guidance provided in the Clean Water Act itself for demonstrating that distillation is not required for ammonia samples (40 CFR Part 136.3 Table IB, footnote 6). The program will require a statistical analysis be performed in order to establish with statistical certainty that the modified method yields equivalent results to the referenced method on a wide array of sample matrices.

> Manual distillation is not required if comparability data on representative effluent samples are on file to show that this preliminary distillation step is not necessary: however, manual distillation will be required to resolve any controversies. In general, the analytical method should be consulted regarding the need for distillation. If the method is not clear, the laboratory may compare a minimum of 9 different sample matrices to evaluate the need for distillation. For each matrix, a matrix spike and matrix spike duplicate are analyzed both with and without the distillation step. (A total of 36 samples, assuming 9 matrices). If results are comparable, the laboratory may dispense with the distillation step for future analysis. Comparable is defined as < 20% RPD for all tested.

Certainly we can review/approve MINOR modifications but **when wholesale method change is involved, we have to draw a line in the sand**. If the recipe is changed to the point where the end result differs from the menu item, then we need to say "No". Do you think substituting cod for halibut would make it past Chef Ramsey running the pass?



CONCLUSIONS

The EPA is merely suggesting that depending on the intended use of the data and the potential to encounter challenging sample matrices, one size may not fit all. Some modifications may be allowable —or even necessary— to mitigate these concerns. If the plan was to throw caution to the wind and open the door to complete and total method anarchy, why bother writing any methods at all, let alone regularly revising them?

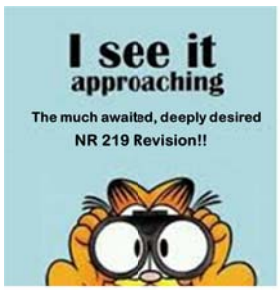
The final missing piece in all this is that at the end of the day, the analyses performed and methods (including modifications) employed must meet the needs of the end user of the data, and for compliance samples, that is the regulatory agency. The LabCert program serves as the gatekeeper for the agency's programs. The programs look to us to ensure that contractor labs are providing data that meets their program needs. And any primacy state can choose to be more stringent than the federal rules.

We would like to see labs consult with us when considering modifications so we can deal with this proactively before quality of data that has been generated comes into question. In addition, before selecting an alternative method other than SW-846 for RCRA related testing and monitoring activities, we recommend that you discuss your plans with your regulating authority and project planning committee.

Let's face it, the modifications we encounter do not involve "additions"; rather, the typical modified method involves cutting and slashing which all too often extends to critical aspects of the procedure. There may be a reason to do some pruning here and there, but cutting too much results in major structural damage to the foundation. The moral of the story is: careful with that axe, Eugene.

NR 219 revisions to take effect

Anticipated to take effect by June 1



Maybe it's less of a "long awaited" and more of "it's been so long we forgot about it" thing. It's like when that Christmas gift that was on a lengthy backorder finally arrives at your door. Yes, NR 219, the administrative code that governs the analytical test methods and procedures used for samples that are analyzed in compliance with the Wisconsin Pollution Discharge Elimination System (WPDES) is first and goal at the one yard line and rapidly approaching promulgation as this edition went to press. It has passed through the state Assembly and state Senate.

The major takeaways from the update are

- SW 846 methods are no longer allowed for testing wastewater samples (but may be used for biosolids).
- The multiple editions of approved standard methods have been removed and replaced with only a single approved standard method for each test.
- Standard methods are no longer referenced by edition – they are referenced by published year. The Standard Methods website has lists that cross-reference promulgated methods in wastewater and drinking water to the specific hard copy edition(s) in which you can find them.
- The first day of the first month after it appears in Wisconsin's Administrative Register, the rule will take effect. That is likely to be May 1 or June 1. At that time, only those methods listed in this update should be used for compliance testing on wastewater and biosolid samples.

There are new or revised provisions in some of standard methods updates that conflict with our program requirements. While this may be a source of confusion, NR 149 grants the LabCert program authority in determining which is more stringent when method and code requirements are in conflict. Largely, our approach will be to stick with the tried and true practices we have been teaching and enforcing for the last couple of decades. Below are a handful of the most popular methods we review, along with the approved year that will be in NR 219. Where there may be conflict between our program requirements and information provided in Standard Methods, we clarify what you will be held to.

TSS: SM 2540D – 1997 *[This appears in the 20th and 21st hard cover editions plus the online edition]*

- Our program requirements are that a minimum 1 milligram (mg) of residue be captured (method indicates 2.5 mg is required). We believe 2.5 mg is excessive. Our programs also allow for a maximum of 500 mL be filtered. If 1 mg of residue is not captured, then the lab may report "< 2 mg/L".

BOD: SM 5210B – 2001 *[This appears in the 21st hard cover edition plus the online edition]*

Our program requirements are…

- an undiluted sample pH range of 6.0 – 8.5 (method indicates 6.0 – 8.0).
- a method blank depletion limit maximum of 0.24 mg/L (method indicates 0.20 mg/L).
- (if pH adjustment is required) an adjusted sample pH range of 6.5 – 7.5 (method indicates 7.0 – 7.2).
- each GGA analyzed must meet depletion criteria
- results of multiple GGA standards may not be averaged to meet criteria (method indicates analysis of 3 GGA standards and using the average to assess control).

NH3-N (ISE): SM 4500-NH3 D- 1997 [*This appears in the 20th and 21st hard cover editions plus the online edition]*

NH3-N (Colorimetry): SM 4500-NH3 F- 1997 *[This appears in the 20th and 21st hard cover editions plus the online edition]*

TP (manual Color): SM 4500-P E- 1999 *[This appears in the 21st hard cover edition plus the online edition]*

TP (auto. Color): SM 4500-P F- 1999 *[This appears in the 21st hard cover edition plus the online edition]*

If you have any questions about NR 219 please contact someone in the Lab Cert Program.

Colorimetric NH3? There's an app for that

Switching from probe (ISE) to colorimetry for ammonia requires an application.

Have you switched recently to using the colorimetric "Test N Tube" method for ammonia? Or are you considering it? If so, please keep in mind that, since our accreditation is by technology, not just analyte, you cannot just "switch". You must apply or run the risk of receiving a Notice of Non-Compliance (NON) for performing testing without the proper accreditation.

Note that the scope of accreditation appearing on the right shows that ammonia certification for the colorimetry appears very differently on your certificate. Make sure you have the right accreditation!

Wisconsin Registration under NR 149
Matrix: Aqueous (Non-potable Water)

Class: General Chemistry
Ammonia as N *by Colorimetry* ←
Ammonia as N *by ISE* ←
Biochemical Oxygen Demand (BOD) *by 5-d Assay*
Carbonaceous Oxygen Demand (cBOD) *by 5-d Assay*
Phosphorus, Total *by Colorimetry*
Residue, Nonfilterable (TSS) *by Grav*

The LabCert program has developed a document which clearly outlines the steps you need to take to switch from using the probe (ISE) to the colorimetric method (Applying for accreditation to perform ammonia testing using the colorimetric procedure). Labs may wish to consider the colorimetric technology as it is less labor intensive than the ISE method. In addition, if you are already accredited to perform total phosphorus testing, which falls under the Colorimetry technology, you can save at least $65 on your annual lab accreditation fees because you won't need to carry the ISE technology.

Be sure to let us know that once the accreditation for the colorimetry is granted, you wish to withdraw your accreditation for the ISE.

Tackling low GGA issues

Poor seed source is the most likely suspect

Summary of problem

Many labs have recurring problems with low BOD results on their glucose-glutamic acid (GGA) controls. In most cases the likely source of the problem is a poor seed source. Often laboratories may observe reasonable DO depletion in their seed controls (e.g., seed correction in the 0.6 to 1.0 mg/L). However, the seed mixtures do not appear to have an adequate number of organisms or ones viable enough to oxidize the GGA.

History

In the past many laboratories used settled influent (raw) wastewater from their facility as a seed source for BODs. Some had problems using the raw as a seed source because their facility's influent characteristic varied greatly due to input from industrial customers or they experienced high levels of inflow and infiltration (I & I). Consequently, it was

difficult to predict how much seed to use from day to day. Many began using commercially prepared seeds because they offered hope of some consistency and predictability. Problems developed over time with the quality and consistency of these seeds. Most facilities using the commercial seeds have had problems from time to time.

If a laboratory has recurring problems with low or erratic GGA results (i.e., failing both high and low), the likely suspect may be the synthetic seed that laboratory is using. Bear in mind, however, that the cardinal rule is that low GGA results are invariably due to weak or poor quality seed. This has been typically what we have observed from synthetic seeds.

We encourage labs to try using either their raw, primary or mixed liquor as a seed source. Mixed liquor may be the best choice since it tends to be more uniform than raw, and it is less likely to be affected by I & I. The laboratory may wish to use the supernatant from the mixed liquor settleability test as a seed source. The volume used for the seed controls and for seeding individual bottles will depend on the BOD of the mixed liquor. Often the mixed liquor settles so well that a small amount of settled floc must be added to the supernatant to boost the solids (i.e., increase the number of bugs) a bit. Microorganisms cling to the solids so adding back some floc will often improve the seed characteristics.

A little trial and error may be required to determine the best ratio of supernatant-to-floc. Laboratories may have to set up a few extra dilutions for their seed controls than usual and try several volumes of seed to see what works best. Laboratories are encouraged to run several side-by-side tests with their synthetic seed until they can nail down the optimum volumes of mixed liquor to use.

Below is a suggested procedure that will act as a good starting point for most laboratories.

Suggested procedure

❶ Perform the mixed liquor settleability test.

❷ Pour off about 250 mL of the clear supernatant into a 400 to 500 mL beaker. DO NOT allow the mixed liquor to settle overnight. It must be used after the settleability test so the organisms are fresh and viable.

❸ Using a wide-tip serological pipet, transfer between 2 and 5 mL of the settled floc from the settleability test to the beaker containing the 250 mL of supernatant. This will fortify the supernatant with extra suspended solids (and thus bugs).

❹ Place a stir bar in the beaker containing the supernatant and floc. Place the beaker on a magnetic stir plate and stir at a moderate speed to insure the solids in the supernatant stay suspended. Use this mixture to prepare the seed controls and to seed the GGA samples.

***Note**: It is important to keep the beaker mixing while withdrawing portions for the seed controls and when seeding the individual BOD bottles. This ensures that a representative sample is taken every time.*

❺ Starting point for seed controls:

a. For many labs, seed controls of 10, 15 and 20 mL are good starting points. Some fine-tuning may be needed to obtain optimal seed control volumes. Strive to have a least 2 seed controls that have at least 2 mg/L DO depletion and no less than 1 mg/L residual DO at the end of the 5-day test period.

b. Prepare 2 to 3 GGA samples. Try seeding these with three different volumes. The laboratory may wish to try 1 mL, 2 mL and 3 mL of the seed mixture. One of these volumes will likely produce an acceptable GGA in the 198 ± 30.5 mg/L range.

c. Use the seed volume that produces the best GGA results for routine analysis. DO NOT be overly concerned if the seed correction factor is not in the **0.6 to 1.0 mg/L range. This range is intended as guidance only**. Use the seed volume that produces the best GGA results even if the seed correction is just under 0.6 mg/L.

d. Once the optimal volumes are determined, document the seeding process in the laboratory's BOD SOP and post instructions.

Contact the Laboratory Certification Staff if there are any questions regarding the use of mixed liquor as a seed source for BOD testing.

Using "pre-programmed" calibrations...

...is not allowed for compliance testing

This could really be the shortest article in program history:
They're not allowed. Period.

But some folks will likely need a bit more information, so let's start by defining our terms.

When we talk about pre-programmed calibrations, we are not talking about user-generated calibrations that can be stored on an instrument. We're talking about factory algorithms that are hard-coded onto instrument circuitry. These may be perfectly valid for in-plant process control measurements.

But for compliance testing? A laboratory must generate its own standard curve. A manufacturer's claim that its method is approved or acceptable does not mean that the approval extends to pre-programmed calibrations. When the EPA issues "approval" to one of these manufacturers that their particular technique is "equivalent" to a referenced EPA method, the approval is granted on the basis of no significant difference in the stoichiometry or chemistry of the procedure.

Factory "pre-programmed" calibrations establish a fixed relationship between concentration and instrument response. And that fixed relationship is identical for every instrument sold. The relationship is formed using new instruments under very controlled conditions by a single analyst. Such an approach does not take into account variables such as instrument maintenance, the lifespan and variability with an aging spectrophotometer lamp/bulb, quality and accuracy of reagents and standards, or analyst technique. We all recognize that these variables DO affect the analysis. Therefore a calibration must be performed using the laboratory's instrument, reagents, and personal under the conditions of that laboratory.

This doesn't even begin to address the violations of administrative code due to lack of calibration traceability. Where's the raw data? Administrative code requires a new calibration at least annually. Would the vendor do this and then flash update the BIOS to every lab that purchased their equipment?

So, how do we reject the use of pre-programmed calibrations? Let us count the ways.

1. **Pre-programmed calibrations are not allowed by administrative code.**

Using pre-programmed calibrations would result in violation of at least two sections of administrative code (NR 149) related to instrument calibration and measurement traceability.

> All analytical instruments shall be calibrated at least once in any year in which they have been used. [NR 149.44 (5)(a)] Will the vendor update its software annually?

> Laboratories shall quantitate sample results from an instrument response that is within the range of the initial calibration. [NR 149.44 (6)(L)] Does the lab even know what the range of response is?

> Except as allowed in s. NR 149.39 (3) (c) 12., laboratories shall retain all the raw data necessary to reconstruct or reproduce, independently of analytical instruments, all calibration functions associated with initial calibrations. [NR 149.44 (6)(o)] Does the vendor provide the raw data used to generate the pre-programmed functions?

> The laboratory shall ensure that results of analyses can be linked to all the standards and reagents used to derive results. [NR 149.45 (1)(a)] More data that is not available.

2. **Pre-programmed calibrations are not allowed by method.**

The approved reference methods themselves clearly direct the lab to generate a calibration function using standards purchased or prepared by the laboratory.

Standard Method 4500-P E, the most frequently cited method of analysis for total phosphorus instructs the user as follows:

> Preparation of calibration curve: Prepare individual calibration curves from a series of six standards within the phosphate ranges … Plot absorbance vs. phosphate concentration to give a straight line passing through the origin.

The EPA reference method (365.1) is even more definitive:

> 10.0 CALIBRATION AND STANDARDIZATION
> 10.1 Prepare a series of at least three standards, covering the desired range, and a blank by pipetting and diluting suitable volumes of working standard solutions (Section 7.12 or 7.13) into 100 mL volumetric flasks. Suggested ranges include 0.00-0.10 mg/L and 0.20-1.00 mg/L.
> 10.2 Process standards and blanks as described in Section 11.0, Procedure.

3. **If you give a mouse a cookie…**

In a popular film, Glenn Close's character portrayal of the Vice President of the United States explains that, "[*If you give a mouse a cookie,] its going to want a glass of milk.*" We'd add that further requests would likely include a napkin and a nice comfortable bed for a post-snack nap.

In our case, giving the mouse a cookie comes in the form of, "What's next?" Will we have vendors creating pre-programmed calibrations for trace elements by graphite furnace AA? ICP? ICP-MS? GC?

What about BOD? A quick review of PT study results for BOD indicates that if a lab reported a value of 56.6 mg/L, they would have passed in 16 of the most recent 20 PT studies. Will we soon be seeing a pre-programmed calibration for DO meters that just spits out the number "56.6" for BOD?

The age old argument is, "But we can show that it works". Sure you can. Initially, right out of the box. What happens when the lamp wears out? When reagents are used when they should be replaced? And what happened to basic quality control?

If we give this mouse a cookie, it won't stop at a glass of milk.

4. It just plain doesn't make sense.


We program calibrations 24/7

It's hard not to picture a plethora of PhDs in starched, blinding white lab coats, complete with heavily loaded pocket protectors, lined up along a warehouse-sized lab bench, each preparing hundreds of calibrations using brand new top-of-the-line instruments with brand new light sources, reagents and standards in a pristine lab. That's what you use in your lab…right?

What happens when the lamp performance starts to decline? What if the analyst doesn't clean the optics? Is the pre-programmed calibration still valid? We have more questions than answers. And that's not going to be acceptable for generating compliance data.

FY 2016 fee increase

3.4% fee increase effective 7/1/2015

Each December the Lab Certification Program works with the Certification Standards Review Council (Lab Cert Council) to prepare a budget for the following year. The Program is entirely funded through your laboratory fees; no GPR (public tax dollars) are used to fund lab certification. Fees are determined using a formula tied to the number of laboratories and the number of certifications for each laboratory. The Natural Resources Board approves our budget in February each year.

Fees will increase for FY 2016 (which begins July 2015) an average of $34 for municipal labs and an average of $150 for commercial labs. The budget increase is just 0.4%, but fees will increase more than that due to the overall tendency for the commercial labs to cut back on their certifications this past year. We keep a close eye on how we compare to other states' programs and we are still average or below the average for lab fees.

One noteworthy staffing plan within the budget - we have been increasing fees the last two years ($20,000 each year) to prepare for a future replacement for George Bowman, our contract auditor. Once George fully retires in a couple years, we plan to replace him with a full time employee, unless we can find another retired laboratory expert who is willing to work part-time, with lots of travel.

Tips from & for lab analysts

It never fails to amaze us how innovative wastewater operators and lab analysts can be, particularly when dealing with the limited resources. Over the last four years George Bowman has been capturing images of some of those innovations while visiting laboratories around the State of Wisconsin. Many of the novelties are simple yet effective solutions to challenges that arise in the lab. The following are just a few clever approaches that seem to rise to the top.

Interesting use of coffee filters

Like a good bottle of wine, water that is to be used to prepare BOD dilution water must breathe before it is used. Commercially prepared distilled water is typically sterilized by bubbling ozone through the water immediately before bottling. Some of that ozone can persist and raise havoc with the critters during BOD testing. Ozone will quickly dissipate if it is allowed to breathe for a day or so.

Water must also be saturated with DO before use. The Chilton Wastewater Treatment Plant folks have a simple solution to deal with both issues that would make Joe "Mr. Coffee" DiMaggio proud. They remove the caps from the gallon bottles of distilled water and cover them with a coffee filter secured with a rubber band. The coffee filters allow ozone to escape and the water to saturate with DO while keeping dirt and debris out Tim Keuler explained that the tip originated from Chris Groh, the Wastewater Trainer from Wisconsin Rural Water Association. The Chilton folks store enough distilled water in their BOD incubator to perform BODs for a full week.

BOD bottle drying rack

The folks from the Town of Beloit wastewater treatment plant built this unique drying rack by boring holes in PVC pipe and inserting and gluing PVC reducers into the tube. The end of the pipe is placed over a sink so as the water drips from the BOD bottles it drains directly to sink. According to Curt Carlson, the system works very well.

Water pump

Does your laboratory buy reagent water in five gallon polycarbonate bottles and struggle pouring from them? The folks at the Peshtigo wastewater treatment plant found a simple, inexpensive pump from Dolphin™ was the answer. According to Jeff Mayou, the Lead Operator, the pump works very well. It is chemical resistant, does not leach BOD into the water and it can be disassembled for easy cleaning.

Insufficient sample volume for MS/MSD?

There are times that commercial laboratories are not receiving sufficient sample back from samplers so there is enough sample for the required batch QC samples. This is very common for aqueous organic samples, which require 3 containers from at least one sample site for every 20 samples submitted for analysis.

Laboratories are expected to take an active role to obtain enough sample material. Labs should ensure that sufficient sample containers are supplied on a regular basis.

Now here's the TIP: Using samples received from previous sampling events for the matrix spike/matrix spike duplicate is the preferred alternative to having to split a sample into one-thirds in order to meet the requirement. In a pinch, one could also use well-mixed garden soil for a solid matrix, or water from a nearby source for an aqueous matrix.

Note: *the lab may not split Oil and Grease (HEM) samples to create the matrix spike, but do need to communicate with the samplers to ensure the required matrix spike can be processed and analyzed.*

LabNotes

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