



LABNOTES

News & Updates of the LabCert Program



Volume 27 Number 1

Published September, 2016

It's time for another edition of LabNotes. As usual, once we sit down and toss ideas around, we end up having a surplus of potential articles that we can hold off for the next edition. Remember to check your e-mails because in order to be more environmentally friendly, we only distribute LabNotes via e-mail. You can find the most current as well as recent editions of LabNotes on our website at: <http://dnr.wi.gov/regulations/labcert/info.html#tabX3>.

2016 Registered Lab of the Year

...and the award goes to... City of Columbus' Wastewater Treatment Plant (WWTP)!

The laboratory staff were presented their award by DNR Secretary Cathy Stepp at the February 2016 meeting of the Natural Resources Board.

Lab Director John Nehmer says that their success has been a team effort from Day 1. He learned from previous operators and has passed that knowledge along. John is quick to share credit and thanks a supportive City Management for keeping them up to date with modern instruments. John also credits lab operators Kevin Neu and Ryan Hoffman who take ownership of the lab and do excellent work for the community. Kevin and Ryan take great pride in getting good results and resolving problems when they do come up.

Congratulations, Columbus!

Approved Methods for TOC in Solid Samples

... HammerTime: only ONE technology available

Analysis of total organic carbon (TOC) is often requested during site characterization work. TOC levels can be an important parameter as the relative concentration of TOC impacts how environmental toxics will be adsorbed or released into the environment.

As far as we can tell, it does not appear that TOC analysis requests will be going away anytime in the near future. Data users still find it practical to use TOC results as a means of normalizing organic pollutants so that toxicity and bioavailability estimates can be made.



DNR Secretary Cathy Stepp with (from left) Ryan Hoffman, John Nehmer, and Kevin Neu of the City of Columbus WWTP

The problem we have is that a wide array of modified methods and pseudo-methods have become available and are routinely used for these analyses. Unfortunately, several commonly used procedures do not mesh with available options for accreditation. Subsequently we find ourselves having to differentiate between client accreditation desires and what DNR programs actually require.

So let's take a look at which methods are widely used and whether or not they are acceptable for analysis of TOC in solid (sediment) samples in Wisconsin.

The Gold Standard - SW 846 method 9060A.

Method 9060A offers a combustion/oxidation technique followed by non-dispersive infrared (NDIR) or flame ionization measurement of carbon dioxide (CO₂) generated. This is the only TOC technology for which WI offers accreditation. Additionally, method

9060A also offers itself as a recognized authoritative method based on it being an EPA document and it being one of the authoritative sources listed in NR 149 Appendix iii. Note that SW 846 9060 has been retired by the EPA and 9060A is the version that is currently acceptable for use. Although this method may not explicitly be written for solids it can easily be adapted to solids by weighing out a certain portion of sample and placing it in a boat instead of aliquoting a certain volume of sample.

The Walkley-Black procedure.

We'd call this a procedure, rather than a method, because it has been modified extensively over the years, and includes correction factors. It is over 50 years old and was written as a soil agronomy method used to determine "organic matter" –not TOC– in soils.

The Walkley-Black method is a titrimetric procedure that changes from a dull green to a reddish brown color. Note that the endpoint can be very difficult to discern in samples that contain any natural color, particularly sediments laden with tannins or lignins.

Besides the multitude of different versions of this procedure being currently utilized (can you say inconsistent analysis) the main problem is that titrimetry is not a TOC technology for which WDNR offers accreditation. Further, Walkley-Black is not recognized as an authoritative method by the EPA and it is not one of the authoritative sources listed in NR 149 Appendix iii. It is well documented that the Walkley-Black method is subject to interferences (chlorides and iron) and does not oxidize all organic carbon and is particularly poor for digesting elemental carbon forms. To overcome the incomplete digestion the method was later modified to include an extensive heating step during the sample digestion which most labs do not utilize.

The "Lloyd Kahn" method.

This is a method written by a quality assurance chemist for EPA Region II. It has never been sanctioned by the EPA and does not have any official EPA document number. And, in fact, it was originally developed for the determination of TOC in ocean sediments!

Inorganic carbon from carbonates and bicarbonates is removed by acid treatment. The organic compounds are decomposed by pyrolysis in the presence of oxygen or air. The carbon dioxide that is formed is determined by direct non-dispersive infrared detection (NDIR),

flame ionization gas chromatography (GC-FID) after catalytic conversion of the carbon dioxide to methane; or thermal conductivity gas chromatography (GC-TCD), after removal of water.

Lloyd-Kahn's "procedure" offers several GC technique options for determination, which is not a TOC technology that WI offers accreditation for. It is not recognized as an authoritative method by the EPA or it would have been given an official method number and it is not one of the authoritative sources listed in NR 149 Appendix iii. On top of that, this "method" offers multiple versions or options of itself to users. There is no one official industry standard version of the Lloyd Kahn method recognized so it is hardly certain to even say that a single method exists.

The bottom line is that the only accreditation Wisconsin offers for TOC in solid samples is the combustion/oxidation technology.

There are many advantages to using this singular method for all TOC analyses in solids.

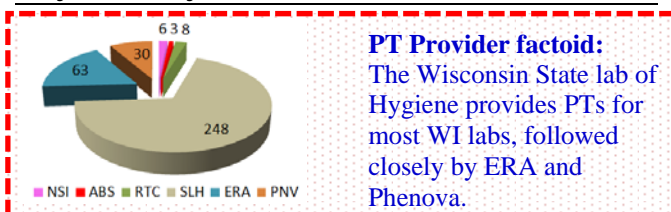
- It is EPA acceptable
- It is NR 149 acceptable

Finally, using one method to generate TOC results provides consistency to the data users when multiple labs are used. Wisconsin data users have noted TOC results with an order of magnitude of difference in results when different TOC methods are utilized.

CRITICAL CAVEAT: Keep in mind that just because our program does not certify TOC methods other than those using oxidation/combustion followed by IR – it does not mean that these alternate procedures cannot be used for agency projects. It just means that accreditation is not offered for them.



Certain project sites may prefer other TOC methods for historical purposes, site specific interference purposes, or special data use purposes. That is fine if there is a project specific quality assurance project plan (QAPP) that outlines exactly what method is being performed – version and source - and exactly what elements of the method must be followed if all of the method procedures are not required. NR 149 has an allowance where the QAPP can supersede the requirements of the administrative code as long as they are clearly documented in the QAPP.



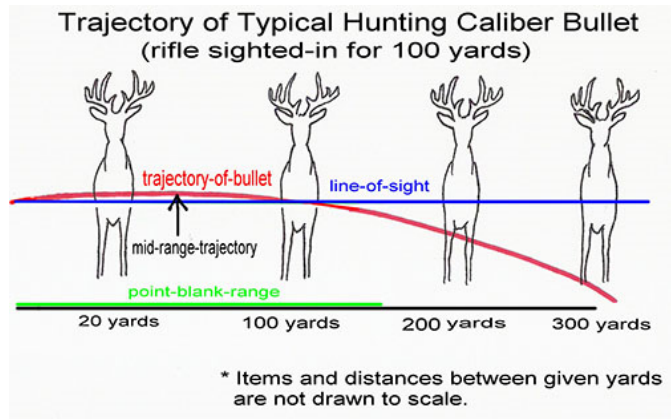
PT Provider factoid:
The Wisconsin State lab of Hygiene provides PTs for most WI labs, followed closely by ERA and Phenova.

Are You Calibrating Your Total Phosphorus Within Range?

...psst...it's only linear to about 1 ppm!

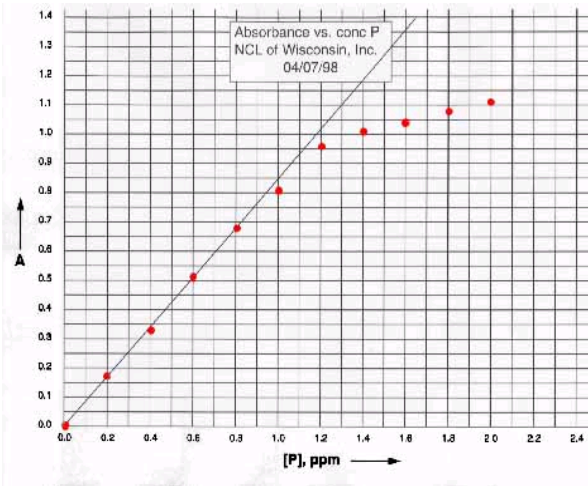
Each year, hunters sight-in (re-calibrate) their rifles prior to deer season. You might call this a 3-point calibration: zero, 25 or 50, and 100 yards. For most of us who hunt woodlots or northern Wisconsin cedar swamps, this calibration is just fine. But what if this year, you're taking that big trip out west to try your luck at elk or mule deer. Your calibration out to 100 yards isn't going to work out so well in Big Sky Country where 300-plus yard shots are common. Your 30-06, sighted in at 100 yards, will drop about 12 inches at 300 yards. Best know your calibration range before you take that shot!

While we don't have gravity working against us, the same concept applies to total phosphorus. Due to the nature of the chemistry of colorimetric phosphorus analysis, instrument response becomes non-linear past about 1 ppm. If you calibrate up to 1 ppm and the absorbance of your sample is greater than the absorbance of your 1 mg/L standard, then your total phosphorus result will be biased low.



Abs	Concentration as calculated from curve	Actual Concentration
0.17	0.2	0.2
0.38	0.4	0.4
0.53	0.6	0.6
0.69	0.8	0.8
0.9	1.0	1.0
0.96	1.1	1.2
1.01	1.1	1.4
1.04	1.2	1.6
1.08	1.2	1.8
1.11	1.2	2.0

Calculated versus actual phosphorus concentrations.



The relationship between phosphorus concentration and absorbance. Graphic courtesy of North Central Labs.

So, if you do not dilute your sample such that the absorbance is below that of your high standard (typically 1.0 ppm or less) you will under-report the actual concentration of phosphorus in your sample.

The more you go beyond the linear portion of the curve, the more inaccurate your results will become. This is important in reporting accurate and defensible compliance data. Many facilities measure the phosphorus in their influent to gauge the level of required phosphorus removal. If you do not sufficiently dilute your sample to within the linear range of the curve (as close to the middle as you can is the best for the most accurate results) you will be underestimating how much actual phosphorus is coming into your plant. This, in turn, could grossly underestimate the percent removal you are achieving.

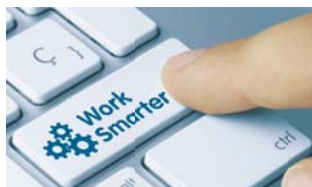
In summary, do not extend your calibration like you would for your rifle. Instead, bring your phosphorous target within range and DILUTE!

Top 5 inefficiencies in the WWTP Lab



It's pretty common knowledge that **a significant percentage of small WWTP operators are forced to wear many hats**. These folks are often the same people doing municipal lawn maintenance, snowplowing, street cleaning, and even such unimaginable tasks as lining sports fields in advance of games or tournaments. Subsequently, we can offer an array of options to improve the efficiency of your lab testing.

We've selected the top five for this article. The bottom line is to **work smarter, not harder**.



1. Purchase Reagents...don't make 'em!

The chemistry testing that you do requires reagents. One or more—often dry—reagents are measured out and diluted to a specified volume. Making these things from scratch can really create a bottle-neck for you. Let's look at just one example—the GGA reagent for BOD determinations. GGA (glucose + glutamic acid) requires purchase of dry chemicals of each of these two compounds. Let's make a deal, shall we?

Behind Door #1 we have the option making the reagents ourselves. Purchasing these two reagents alone costs about \$60/year. Then there's all the other things we need to do after that. But we'll get to that in a bit.

Behind Door #2, there is the option of purchasing individual sterile ampules containing exactly 6 mLs of the appropriate GGA solution. A pack of 20 vials costs a little over \$40. Assuming one GGA standard is required per week, that means the sterile ampule option costs under \$100/year.

And finally, behind Door #3, from a routine lab equipment vendor you can obtain individual 50-mL vials of ready-to-use GGA. Each vial can be used to prepare 7-8 GGA standards, at a cost of about \$45 for a pack of 12 vials. That's 84-96 GGA standards for \$45, more than enough for a year's worth of testing.

And now for the downside to Door # 1, making your own reagents. What's the cost (in materials & labor) of making up your own standards/reagents?

- Time & cost of replacing reagents.
- Time to dry & desiccate reagents.

- Time to weigh out reagents.
- Time to prepare in solution.
- Time to ensure that the solution is valid.
- Time to autoclave (best for GGA reagents).
- Reagent tracking time.
- Time to document each part of the process.
- Time to re-prepare before solutions expire.

Can you do all that for under \$40/year? Because that's the difference in cost between Doors #1 and #2. And Door #3 offers a pre-made option which costs 25% less than the reagents alone. We don't even need to consider what Jay has on his table or what's in **the box that Carol Merrill points to on the floor** →.



It just makes good sense to purchase quality prepared reagents whenever possible. Instead of making the four separate reagents used to prepare BOD dilution water, simply add one powder pillow or concentrate and dilute to the specified volume. And it works for all tests...not just BOD.

What are you waiting for?

2. Batch samples for nutrients

Batching samples decreases the number of QC samples you analyze, which cuts both your time and the chances of failing QC! This approach works really well for wastewater nutrients.

Simply acid preserve samples for ammonia (NH_3) and total phosphorus upon receipt back at the lab. The holding time is 28 days. Run ortho-phosphorus (o-PO_4) daily using a quick test kit instead of doing total P every day. o-PO_4 tracks really well with total P for a given plant and is quick & easy to perform. (*Note: just be sure you are looking at both o-PO_4 and total P in the same units—as P, not as PO_4 !*). Many facilities test for ammonia daily although the data is not critical for immediate process control. Check with your superintendent to see if they are actually using the daily NH_3 data. If not, why not suggest doing the testing weekly or every two weeks. Don't be afraid to ask questions.

Then you can analyze ammonia and Total P either once a week, once every other week, or even once a month. Analyzing total P or ammonia just once a month rather than 5 days a week results in a 20-fold reduction in QC samples analyzed! 40 QC samples means 40 chances of exceeding criteria, which will only lead to more time spent taking required corrective action.

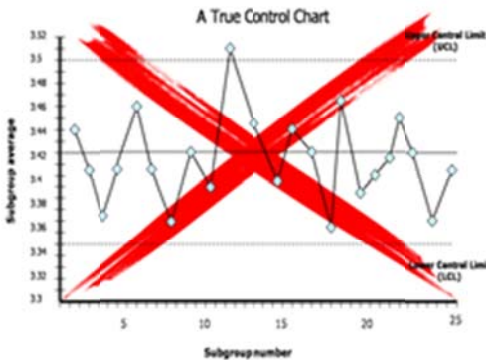
40 QC	8 QC	2 QC
DAILY	WEEKLY	MONTHLY
20 CCV/LCS	4 CCV/LCS	1 CCV/LCS
20 Blanks	4 Blank	1 Blank
20 samples	20 samples)	20 samples

200% QC	40% QC	10% QC
Time: prep/analyze 60 samples; 20 "runs"	Time: preserve 20 samples; 4 "runs"	Time: preserve 20 samples; 1 "run"

If you choose to use this approach and re-use bottles, remember NOT to "pre-dose" bottles with sulfuric acid. Sulfuric acid (H₂SO₄) is a powerful oxidant which can actually char "poly" sample bottles.

3. Stop control charting

Are you generating QC samples but not really using them? Just going through the motions to construct control charts but don't really know why?



Control charts were originally developed as an element of statistical process control. If one is manufacturing widgets, one desires those widgets to meet certain specifications. Widgets that are out of spec are excluded from the line. Well...we're not manufacturing widgets. We are producing data. The LabCert program has never required the use of quality control charts, although quality control limits must be employed to be certain our "widget"—QC samples—fall within requirements.

Yes...there is some value to Control Charts. But if you simply go through the paces to make them...but don't really use them....you are wasting time that could be better spent elsewhere.

You must analyze matrix spikes and replicates (or MS/MSD) if the methods require them. But if the method you use does not require matrix spikes (MS)/replicates (DUP), then consider not preparing or

analyzing them. While some might place value of doing "extra" QC, in most cases extra QC is going to require more effort (and cost) with very little benefit. MS and DUP samples can provide information about a matrix, but we are most interested in how your lab does when no matrix can be blamed. That is the role of the LCS.

Bottom line: You get paid to provide RESULTS...NOT produce a research project! Do NOT analyze extra QC unless you have the need, the time, and the energy to address issues raised by them. Because if you opt to perform optional QC we can cite the facility if there is not a set of control limits against which these QC samples are evaluated or if the facility is not properly responding to QC exceedances. The QC samples that you analyze should be suited for your operation and provide you with the feedback you –and we– need regarding performance.

4. Colorimetry for Ammonia

A number of labs have tossed out their annoying "probes" (ion selective electrodes, ISE) and traded them in for HACH's Ammonia Test'nTube (TNT) Plus colorimetric procedure, which has been approved for wastewater testing. But there are many other facilities that could also benefit from the time savings associated with this change and should consider switching to colorimetric ammonia (TNT method). We have estimated that making the switch reduces labor by about 40% over the ISE method.

As ISE probes age their response times decrease resulting in calibration issues (*how long does your probe take to obtain a stable reading for a 0.2 ppm standard?*). Be aware though, that, like electrodes, the colorimetric test is only suitable for domestic, municipal wastewater effluent unless the lab plans to distill. Also note that despite vendor claims, you cannot use "pre-programmed" calibrations; you must prepare your own calibrations.

If you are already accredited for the colorimetry technology (Total P) you will save some \$\$ too. That's because a lab could withdraw from the ISE technology accreditation.



**For ammonia
by colorimetry**

BUT...don't forget that **you MUST submit a revised application before switching** and doing testing. Since you would be switching technologies, a revised application and a new PT (by colorimetry) is required.

Please call and check in with us before making the switch; we can help.

5. Use Mechanical pipets

It's long past time to trade in your multitude of glass pipets for a couple of mechanical pipets. Not only is the accuracy and precision likely better than that of the "old school" approach, but you eliminate all of the pipet washing and drying time—knowing full well that, while drying (especially when many labs have the pipet drying rack right by a main sink), glass pipets can easily be contaminated.



Many WWTP labs are using Hach TestNTube™ kits, and these vials absolutely require accuracy when using very small volumes, which really requires the use of mechanical pipets. There's certainly a capital outlay required, although a lab can make do with only two variable volume pipets which come at a price tag of about \$280-\$400 each. A 0.1-1 mL and a 1-10 mL adjustable pipet are all most labs need.

Mechanical pipets are quick and easy to use, and make the preparation of calibration curve standards a breeze, as any microliter volume needed can be delivered accurately. In addition, single-use pipet tips eliminate or at least minimize contamination.

Bottom line: Purchasing a couple of mechanical pipets is a small price to pay for efficiency, accuracy and precision.

Controlling (??) contamination in the Lab

...Got phosphate additives?

How do laboratories ensure sample containers, glassware and bulk composite containers are adequately cleaned and not contributing analytes of interest to the sample? Most laboratories take great pains to clean their sample containers and glassware to reduce the risk of contamination. They wash with hot tap water and non-phosphate detergent and then rinse with dilute hydrochloric acid followed by *tap water* and a little distilled water. With all this care, they are confident they have done everything possible to prevent contamination, particularly from phosphorus. Even the "Fonz" from Happy Days might have to admit he was wr-wrrr-wrong in believing that.

Laboratories often fail to recognize there are other potential sources of contamination.

Many wastewater laboratories are unaware that their community water supply may be treated with orthophosphate or polyphosphate to control corrosion (unless you're Flint, Michigan) or to sequester iron and manganese. Average feed rates for phosphate levels (PO_4) in treated water supplies range from 1 to 3 ppm as PO_4 which translates to about 0.3 to 1 ppm as P. However, levels of up to 5 ppm PO_4 (that's about 1.6 ppm as P) are not uncommon. So a lab goes to great lengths to remove phosphorus only to add it back in the rinsing process if tap water is used to rinse glassware. In other words they go to great effort to remove the phosphorus as a contaminant only to add it back in the final steps of cleaning. To make matters worse, most labs are not even aware this is happening.



These same labs that take great care to wash sample bottles and glassware rarely take the same precautions to clean their composite containers. Most rinse with tap water only on a daily basis and only wash the composite containers with detergent on an occasional basis. If the water supply is treated with phosphate, again they are likely adding phosphorus to the samples during the sampling process. The bottom line here is if the city water is treated with phosphate then sample phosphorus levels may be biased high. This means a facility may be reporting results biased high on their discharge monitoring report and they may be paying more than their fair share of NR101 fees. Other costs are incurred due to the need for additional treatment chemicals to remove phosphorus at the wastewater treatment facility, that was added by the municipality itself!

The situation can be further complicated if the facility has a discharge limit for metals. Metals such as copper can build up in the composite container, sampler pump tubing and sampler lines which, in turn, can cause elevated metals levels in samples. In some cases facilities could violate discharge limits because of contributions from the sampling process.

What steps can be taken to deal with these issues?

- Check with the water utility to see if the water supply is treated with phosphate. Find out what is being added to the water (i.e., polyphosphate, orthophosphate or a blended phosphate mixture) and what concentrations. Common products used include names such as AquaMag or AquaDene.

- If the water utility adds phosphate, consider treating the water used for glassware and sample containers with reverse osmosis followed by anion exchange.
- Consider purchasing a laboratory grade dishwasher for glassware and sample container cleaning. Most washers designed for laboratory use are equipped with a pump to allow the laboratory to feed the washer with water that has been treated to remove phosphate. Lab grade dishwashers can also be setup to include a wash cycle using a mild acid such as sulfamic or citric acid. Joe Panek from the Bristol Wastewater Treatment Plant has successfully used this approach for many years. He installed a 20 gallon polyethylene reservoir which he feeds with deionized water. The washer draws all water used for washing and rinsing from this reservoir.
- If hand washing, use distilled or deionized (anion and cation exchange) treated water for washing and rinsing.
- Instead of washing the sampler carboys consider using a food grade polyethylene bag as a liner for carboys. Mike Suha from the City of Appleton Wastewater Treatment Facility uses a relatively inexpensive food grade polyethylene bag as a liner. Mike says they cost \$0.15 each so he has them changed daily. Contact the LabCert program for more information.
- If a facility has a discharge permit for metals and requires monthly sampling, consider using the food grade polyethylene bag and changing the sampler line and pump tubing immediately before sampling for metals. Sam Warp and Ted Bratton from the City of Marshfield Wastewater Utility began using Clavies plastic bags as carboy liners in 2014 to address copper and phosphorus contamination issues. They found copper levels in their effluent samples decreased significantly after switching to the carboy liners. They determined prior samples were elevated due to sample contamination during the sampling process.
- Finally, a word about acid washing. Don't go crazy using strong acid to wash glassware and sample containers. Use dilute hydrochloric acid; limit it to 1%. DO NOT USE stronger acid. Remember, strong acids pose an increased safety hazard and do not improve cleaning efficiency. **When it comes to acid, less is more.**



From little known secret sources of contamination (phosphates used in the water supply) to carboy liners

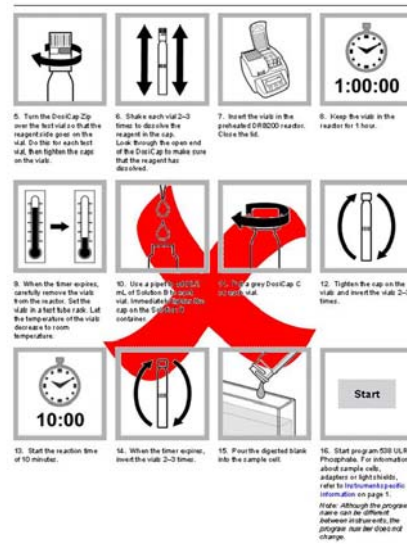
to using too much acid, there are many things that detract from an operator's ability to do the job well. Always feel free to contact your auditor for assistance as needed.

Considerations when using Hach methodologies

...Not everything goes!

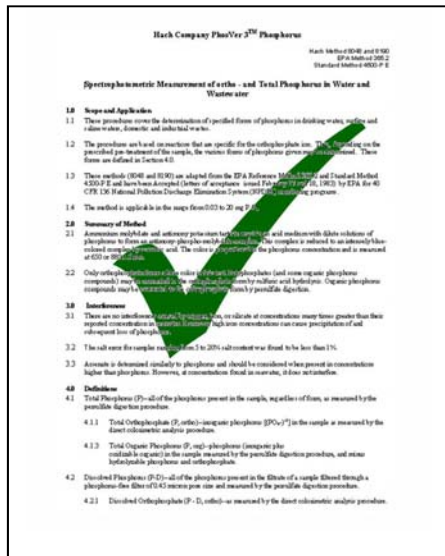
They say that a picture tells 1000 words, but when it comes to approved methods to be used for compliance testing, pictures don't cut it.

In their desire to be customer friendly, Hach has developed quick "picture" versions of its methods. Unfortunately, these **"picture" methods are NOT approved for compliance.** You must actually have (and use) a paper or electronic copy of an approved Hach Method in EPA format when using and citing Hach Methods for any compliance monitoring. The "EPA Format" method version of methods can be found on the Hach website or contact a Hach representative.



Phosphorus, Reactive and Total, Ascorbic Acid TRV plus Method (1500 µg/L)

The Hach Co. has developed a number of test kit methods that have been approved outright (as standalone methods) by the EPA. These EPA approved methods will appear in 40 CFR Parts 136 [wastewater] or 141 [drinking water]. These methods are acceptable for compliance testing under the programs that approved them. Other Hach (and similar vendors' test kits) methods have been deemed "equivalent" to approved methods under those federal programs.



A listing of Hach EPA compliant methods, by program, is available at:

<http://www.hach.com/cms/documents/pdf/EPA/HachEPACompliantMethods.pdf>

- A. For drinking water you may only use methods that appear in 40 CFR Part 141 or the methods that are “EPA-approved” for the Drinking Water program.
- B. For all other environmental programs you may use methods that are “Approved”, “Accepted” or “Equivalent”.
- C. If you’re unsure...contact your auditor or the program general contact.

There are a number of other considerations when using Hach methods:

What method should I report with my results?

For wastewater compliance monitoring (WPDES) labs must report the authoritative method (the approved reference method listed in the Hach method). Do not cite the Hach method unless it is approved as a standalone method in the Federal Register. The reference method is provided in the table on the

[\[http://www.hach.com/cms/documents/pdf/EPA/HachEPACompliantMethods.pdf\]](http://www.hach.com/cms/documents/pdf/EPA/HachEPACompliantMethods.pdf) link.

For example, if a lab is using the TNT Plus 843, Hach Method 10210 for Total Phosphorus, the method to be reported is EPA 365.1 [automated] or EPA 365.3 [manual].

Note that this approach will also help when reporting PT sample results.

How do I indicate I’m using a Hach method for testing if my reference is something else?

If you are using a Hach Method, that information must be included in your SOP.

There are method numbers and product numbers for Hach. For instance, for Total Phosphorus the product numbers are TNT843, TNT844, and TNT845 but the Hach Method number is 10210 for all of these. Use the Hach Method number in your SOP, but also be sure to include the product number used under the consumables section of your SOP.

What quality control is required?

Labs must perform the required quality control samples listed in the approved reference method – not what is in the Hach method. If there are no required QC samples in the reference method then defer to NR 149 for required QC.

My vendor says I can use the pre-programmed calibration on my DR-xxx. Is that true?

Sorry, but no. No matter what any vendor representative or method may proclaim, **WI does not allow the use of pre-programmed calibration curves**. Each lab must generate their own calibration curve, at the frequency required by NR 149, using their own equipment, standards, reagents, and lab conditions.

My vendor says I never have to calibrate my new LDO probe for BOD. Is that true?

Again, no. This is not true in Wisconsin. DO/BOD probes must be calibrated daily.

Is there anything else I need to be concerned about?

Even some of the allowable Hach versions have errors and here are TWO common ones that you need to be aware of.

A. Total Phosphorus method 10210 contains two clear errors.

- Samples must be digested for **30** minutes at **150** °C at a minimum. (*Many versions indicate to heat for 60 minutes at 100 °C*).
- Samples must be **neutralized** before digesting. (*All versions indicate that a pH between 2 and 10 is acceptable*).

B. Ammonia by method 10205 contains an error as well.

- Samples must be preserved with **sulfuric acid** --not hydrochloric acid (HCl), (*as many Hach versions indicate*).

Analyte Groups – a flexible option

...is ACME Labs certified for tetramethyltoast?

Many regulatory agencies drill down and certify to the analyte level. We find these Scopes of Accreditation to be decidedly user UNfriendly. The average client procuring lab services would be hard pressed to wade through scores of analytes for different regulatory programs and analytical methods to determine that a lab is capable of providing its testing needs.



Trying to make sense of long certificate analyte lists

While the Wisconsin Laboratory Certification and Registration Program can provide accreditation on the analyte level for those analytes we offer accreditation for; we also provide an array of discrete "Analyte Group" offerings in the aqueous and solid matrices to make your life easier.

These offerings are as follows:

- PAH group (lists for GC, GCMS, & HPLC)
- BNA group (GCMS)
- VOC group (lists for GC & GCMS)
- Organochlorine Pesticides group (lists for GC & GCMS)
- PCB as Aroclors group (lists for GC & GCMS)
- PCB Congeners group (lists for GC, GCMS, & HRMS)
- Dioxin & Furans group (lists for GCMS, & HRMS)

The benefits of utilizing the analyte group accreditation, instead of individual analytes are:

- Your certification scope is more concise and easier to read
- Proficiency testing (PT) samples are not required for each analyte in the group – instead we only require the analysis of a standard (VOC/BNA/PAH/Organochlorine pesticide/PCB/Dioxins-Furans] PT sample from an approved Provider. Note, however, that:
 - Our program does not assess PTs as the NELAC program does,

- Our program has established minimum numbers of analytes which must have non-zero assigned values,
 - Only analytes with non-zero assigned values "count",
 - At least 80% of non-zero analytes must have acceptable results,
 - False positive and false negatives will adversely affect your score.
- Less PT requirements means less money and time spent on the annual requirement.

While certifying by analyte groups is a great bonus for labs, **labs need to remember that there is a specific list of analytes associated with each analyte group and that those are the only analytes you are certified for** – not every possible analyte that can fall under the description of a PAH, BNA, VOC, etc. analyte.


So how does a lab know which analytes fall under each analyte group?

We provide a list of those analytes on our website (<http://dnr.wi.gov/regulations/labcert/info.html#tabx2>)

Each analyte group that we offer accreditation for is listed along with the technologies that are associated with them. Click on any of those groups and a pdf that is downloadable is available that lists all of the analytes covered by the "analyte group" accreditation.

So when a laboratory is checking to verify proper WI accreditations they need to review these analyte group lists versus their project lists to make sure they are not performing any work without certification.


This complete list?



...repeated several times for different methods

OR

VOLATILE ORGANICS [VOC] (group) by GC/MS



Ammonium? Or Ammonia? Which is it?

...Hint: they're really the same thing!

The Land Application section of Wastewater Permits often requires that the nutrient parameter "Nitrogen, Ammonium (NH₄-N) Total" analysis testing be performed.

Examples of how this can appear in Wastewater Permits:

List 2 Nutrients	
See the Monitoring Requirements and Limitations table above for monitoring frequency for the List 2 parameters.	
Solids, Total (percent)	
Nitrogen Total Kjeldahl (percent)	
Nitrogen Ammonium (NH ₄ -N) Total (percent)	
Phosphorus Total as P (percent)	
Phosphorus Water Extractable (as percent of Total P)	
Potassium Total Recoverable (percent)	

4.2.1 Sampling Point (Outfall) 002 - SLUDGE			
Monitoring Requirements			
Parameter	Limit Type	Limit and Units	Sample Frequency
Solids, Total		Percent	Quarterly
Nitrogen, Total Kjeldahl		Percent	Quarterly
Nitrogen, Ammonium (NH ₄ -N) Total		Percent	Quarterly
Phosphorus, Total		Percent	Quarterly
Phosphorus, Water Extractable		% of Tot P	Quarterly

However, these requests and lists, asking for NH₄-N are actually a long-ignored error. Instead, the requirement should read NH₃-N (Nitrogen, Ammonia) Total! Simply stated, there is no test that measures for ammonium. Ammonia -N exists in a perpetual equilibrium between ammonia (NH₃) and ammonium (NH₄⁺). Ammonia (NH₃) is a gas and is predominant at pHs over 10. This is the reason why the analysis of ammonia by ISE requires addition of sodium hydroxide to a pH of at least 11.

The Wastewater Program is aware of this mistake and are working on revising this section of municipal permits such that updated permits reflect the requirement to perform NH₃-N analysis instead of NH₄-N. Revised forms will eventually be made available.

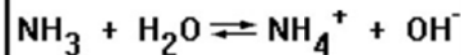
What do we do in the meantime...?

When a request for NH₄-N analysis is made on a sludge/biosolids sample, the test that needs to be

performed is NH₃-N and reported as NH₃-N regardless of what the permit may say.

Keep in mind the following

- There are no test methods that directly measure for ammonium (NH₄-N) – and none that differentiate between NH₃-N and NH₄-N.
- Once the total NH₃-N concentration is determined, the concentrations of NH₃-N and NH₄-N can be estimated based on sample pH – both are always present, the ratio just shifts based on the sample pH.
- NH₃-N is prevalent when pH > 8.5, which is why we adjust the pH to at least 11 and use a gas-permeable membrane for analysis of ammonia by ISE.
- NH₄-N is prevalent when pH < 8.5, which is why we preserve samples using acid.
- Furthermore, all of the approved methods for measuring NH₃-N (total ammonia) actually measure the sum of "NH₃-N + NH₄-N" because before analytical measurement occurs the pH is increased until all NH₄-N present is converted to NH₃-N.
- Over time the DNR will work on revising the Land Application Requirements section of municipal permits and change the NH₄-N requirement to NH₃-N but requests for NH₄-N now can be accomplished by performing NH₃-N.



Bottom line: you can't measure for ammonium (NH₄⁺)...period. If analysis of ammonium is requested, the intention is for ammonia.

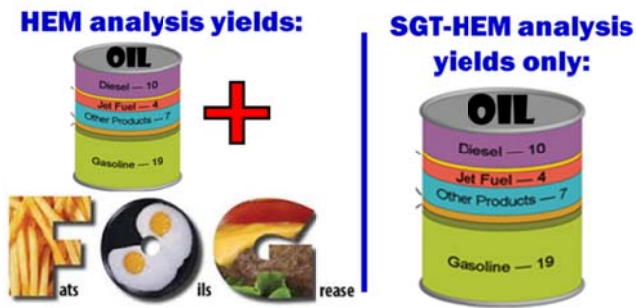
F.O.G. advisory: H.E.M. vs. SGT-HEM

...Alphabet soup only further muddles things

Back in 1997, the EPA made changes to the original Freon extraction procedure for oil & grease and replaced the ozone-depleting Freon with hexane as the extraction solvent. Thus was born "Hexane Extractable Material", or HEM. The terms "F.O.G." (fats, oils, and grease) and oil & grease are effectively retired in favor of hexane extractable material (HEM).

But there's a twist. There's also this thing called "Silica Gel Treated N-Hexane Extractable Material", or "SGT-HEM". Make no mistake, although both HEM and SGT-HEM are listed under "oil & grease" in federal

rule (40 CFR Part 136) and the Wisconsin counterpart (NR 219), these are two very different animals.



Oil and grease is made up of both polar and non-polar material. The silica gel treatment (SGT) removes the polar fraction (natural oils and fats) of the sample leaving the non-polar (petroleum oils). Just because SGT is an option in the method that does not mean it can be performed and results reported instead of HEM. The two are different parameters.

In our checking with DNR staff and the administrative code we have found nothing that indicates that SGT-HEM should be reported to the DNR. Some Federal categorical standards (coil coating and can making (40 CFR 465) and transportation equipment cleaning (40 CFR 442) require testing for petroleum hydrocarbons. SGT-HEM can be used for this testing. Also, some wastewater pretreatment programs may require SGT-HEM. If you are reporting SGT-HEM results, you should verify that you should be. Never report SGT-HEM as oil & grease, or HEM. They are different results and each must be reported with a different parameter code.

So...generally speaking, permits are written to require the analysis of HEM as a measure of the conventional pollutant known as oil & grease. There may be situations where you may be able to use the analysis of SGT-HEM as a process control approach to identify the source of oils and greases coming into your wastewater plant.

For example, if you suspect that the source of oil and grease impacting your WWTP or the collection system, is a restaurant (i.e., the offending material is polar fats and greases), then HEM is the best analysis. However, if you suspect the source to be a local metals finishing plant, auto service station, or some other manufacturing operation that uses large volumes of lubricants or cutting oils, then an analysis of SGT-HEM could help identify the source. But this testing is more properly labelled process control or investigative—not compliance monitoring.

SGT-HEM provides a measure of what is formerly known as “total petroleum hydrocarbons” (TPH), but is now known as “non-polar material (NPM). Monitoring of TPH (now SGT-HEM or “non-polar material;” NPM) is presently required in the monitoring and reporting requirements under the Coil Coating point source category at 40 CFR 465.03(c).

Bottom Line: For 99+% of labs, HEM analysis is required for permit compliance. Analysis of SGT-HEM may help you meet a permit limit, but your results will be biased low and karma will manifest itself in the form of grease blocks in your collections system!

Hexavalent chromium reminder

If your lab is certified for Hexavalent Chromium in an aqueous matrix, keep in mind that NR 219 is applicable to “Hexavalent Chromium, dissolved”, therefore WPDES samples require filtering.

Ensure that any sample handling requirements in the methods are met when required. This may be of particular concern if the sample will be made basic to increase the sample hold time to 28 days.

To obtain a pdf copy of NR 219, go to: https://docs.legis.wisconsin.gov/code/admin_code/nr/200/219.pdf.

Rejection of Drinking Water Samples

...It's a lab's responsibility

Did you know that it is a laboratory's responsibility for rejection of drinking water samples – that do not meet specific criteria – upon sample receipt?



Our auditors have noticed that laboratories struggle with the age old question “Who do we listen to – our clients who pay the bills or the regulatory body that grants us certification?”

When it comes to drinking water, for Wisconsin, that answer is easy - drinking water samples must be handled according to law – regardless of the client's wishes.

NR 149 indicates the following

NR 149.46 (4) SAMPLE PRESERVATION AND HOLDING TIME. (a) Laboratories shall follow the sample preservation procedures and holding times required by state and federal regulations.

*NR 149.46 (2) SAMPLE ACCEPTANCE POLICY. (a) The laboratory shall have and follow a written policy that clearly outlines the conditions under which samples will be accepted or **rejected for analysis**, or under which associated reported results will be qualified.*

*1. Drinking water samples received beyond holding time, improperly preserved, in inappropriate containers or showing evidence that they have not been collected according to approved or accepted protocols **shall be rejected for analysis**, unless the laboratory can document that it has been instructed by the client to proceed with analyses, and all associated results are accompanied by a disclaimer attesting that results may not be used to determine or evaluate compliance with the safe drinking water act.*

So the laboratory must have a written sample acceptance policy and include in that policy the criteria the laboratory is using to determine whether drinking water samples will be rejected or accepted.

This is a decision that the laboratory makes based on the law – neither the client nor the water system can indicate that a rejected sample is acceptable for compliance analysis.

The following elements, at a minimum, must be assessed and addressed in the sample acceptance policy: improper temperature preservation, improper chemical preservation, improper containers, expired holding time, and unsecure receipt.

The sample acceptance policy must also discuss the action the laboratory takes for communicating the rejected samples to the client and how this communication is documented.

The client can request that the rejected samples be analyzed by the laboratory **for informational purposes**

- **if** that instruction is received in writing
- **and if** the results are qualified with a **“not to be used for compliance purposes”** qualifier.

If it is discovered that the laboratory is not rejecting drinking water samples appropriately and they are not qualifying the results appropriately the consequence is a likely Notice of Non-compliance enforcement action from Wisconsin. Repeat offenses will result in escalation to a Notice of Violation.

If any laboratory would like assistance in explaining this requirement to a client, contact us and we would be glad to intervene. We need only look to Flint, Michigan to be reminded of our collective responsibility in protecting public health.

LabNotes

Newsletter of the Laboratory Certification Program
LabNotes is published by the Wisconsin DNR
Laboratory Certification and Registration Program.

Bureau of Science Services
(608) 267-9753

Steve Geis, Chief
Environmental Science Services Section
(608) 266-0245

Rick Mealy
LabNotes Editor
(608) 264-6006