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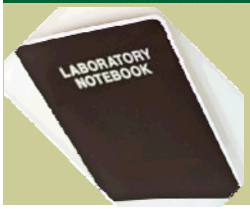

LABNOTES

Newsletter of the Wisconsin Laboratory Certification and Registration Program

INSIDE THIS ISSUE:

Remember: *Annual renewal does not require an application. An invoice for fees will be sent in late May payable by July 1.*

PTs for renewal (Study close date ≥ 1/1/13) are accepted up until 8/15/2013.

LabNotes Returns!

We are excited to be publishing a LabNotes Newsletter again and hope you find it helpful. I have been the manager of the Lab Certification program for two years now and we are continuing to improve our program every year.

However, we want to continue to make improvements and I encourage you to contact me at any time if you have any comments or concerns. We are here to serve the laboratory community and will do whatever we can to improve those services. We want to work together with you to ensure that the most reliable data possible is being generated. The data is very important for making sound decisions about the protection of our natural resources.

If you have questions about your audit, our program, technical issues, rule changes, input on the newsletter, or anything else please contact me. If I cannot answer your questions I will find someone who can help you. Keep up the great laboratory work that you do!

--Camille Turcotte
Chief, Environmental Science Services

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LabNotes

Newsletter of the Laboratory Certification Program

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Council Corner

As I sat down to write this message, I looked back to past issues of LabNotes to give myself some clue on what to write. I noticed the most recent issue was Fall 2009. It started with the words '*Tempus Fugit* is Latin for time flies…' and was about the first anniversary of the 'new' revised NR149. And the last Council Corner articles were in the Spring 2008 edition and were written by outgoing chair Katie Edgington and new small WWTP representative Judy Tholen. Yours truly was not even on the council at that time.

Here it is Fall 2012 and Katie and Judy are long gone from the council. I am well into my second term on the council and first as chair. In addition new (or in some cases renewed) members have joined the council. You should find a table of the members elsewhere in this newsletter.

One thing we all share in common is a commitment to serve the certified and registered laboratory and customer community of this state. We exist at least in part to be the conduit between the department program and staff and the laboratories and stakeholders. So if you have any questions or concerns about the program and don't want to contact the staff yourself, please feel free to contact your council representative.

Program staff has gone through a number of changes as well, with a new section chief, former audit chemist Camille Turcotte, and new auditors on board. Despite disruptions from established auditors leaving and short staffing while new auditors are hired and trained, the staff has strived to keep up the pace with laboratory audits. And as always, they take great care to make sure the audits are done fairly and with as much consistency as possible. I want to personally thank Camille and the staff for their efforts.

And about that new NR149, it has now been four years from implementation and most if not all the labs should have at least one routine audit under their belts under this version. So maybe you have gotten a little nonchalant about it. But as that opening statement three years ago stated, time flies and it is time to start thinking about revisiting the code. This time it should only be a minor tweaking, but if you have any suggestions of things you would like to see addressed please contact staff or a council member.

--Randy Thater
Chairman, Certification Standards Review Council

What is the Certification Standards Review Council?

The council shall review the laboratory certification and registration program and shall make recommendations to the department concerning the specification of test categories, reference sample testing and standards for certification, registration, suspension and revocation and other aspects of the program.

--- s. 299.11 (3), Wis. Stats

Certification Standards Review Council Members

Representation	Name	Organization	Phone # E-mail
Large Municipal Wastewater Plant	Mr. Randall Thater • Chair •	City of Waukesha	(262) 524-3631 RThater@ci.waukesha.wi.us
Public Water Utility	Ms. Kirsti Sorsa • Vice-Chair •	Public Health Madison-Dane County Lab	(608) 266-4821 KSorsa@publichealthmdc.com
Small Municipal Wastewater Plant	Mr. Kurt Birkett • Secretary •	Fort Atkinson Wastewater Utility	(920) 563-7766 KBirkett@fortatkinsonwi.net
Industrial Laboratory	Ms. Jennifer Peth	Flambeau River Papers	(715) 762-5368 JPeth@flambeauriverpapers.com
Commercial Laboratory	Mr. Paul Junio	Northern Lake Service, Inc.	(262) 547-3406 PaulJ@nlslab.com
State Laboratory of Hygiene	Mr. Patrick Gorski	State Lab of Hygiene	(608) 224-6226 Patrick.Gorski@slh.wisc.edu
Demonstrated Interest in Lab Certification	Mr. Paul Harris	Davy Laboratories	(608)782-3130 PHarris@davyinc.com

The membership of the Certification Standards Review Council is established under s. 15.107 (12), Wisconsin Statutes

LabCert website gets a makeover

Effective September 1, 2012, the Department launched a whole new look to its website, switching to a "topic" based approach. Supplying a keyword in response to the keyword search box will also direct you to a subject of interest. LabCert program pages have been relocated to fall under one of three "tabbed" pages (see sidebar). All of the content you are used to seeing can be found on one of the "tabs" in one of the three pages". Bookmark http://dnr.wi.gov/regulations/labcert/ for the LabCert "Home" page. This page contains the following tabs:

Overview | Application | Fees | Proficiency testing (PT) | Contacts | Rules | Water testing

LabCert "Program Information" page

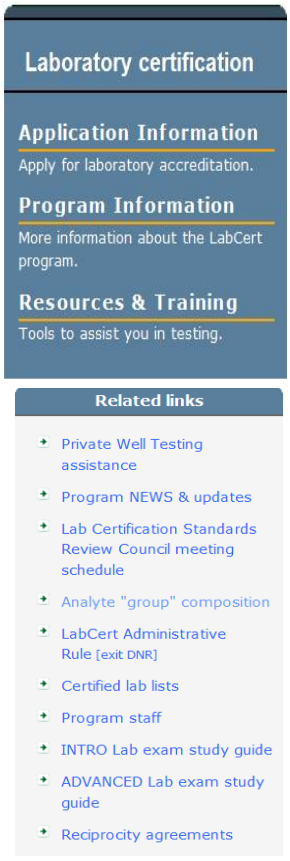
Directing your browser to http://dnr.wi.gov/regulations/labcert/info.html will take you to a page containing tabbed links to the following:

Background | Analyte groups | Newsletter | Lab-of-the-Year awards | Low level mercury

LabCert "Resources" page

Directing your browser to http://dnr.wi.gov/regulations/labcert/Resources.html will take you to a page containing tabbed links to the following:

BOD resource | Forms | Checklists | Benchsheets | Methods | Guidance | Training



"Popular pages" on the LabCert homepage.

…for wastewater testing

Administrative code updates

NR 219 ……..

The EPA did an evaluation of our wastewater program here at the WDNR. As part of that evaluation they found that we were allowing the use of SW 846 methods for wastewater analysis. Although those methods are often better than the counterpart methods, the EPA does not consider those methods to be approved for wastewater analysis.

Therefore, **we have been mandated to remove all SW 846 methods from NR 219 that apply to wastewater samples and will no longer allow their use for wastewater sample analysis.** SW846 methods will still be allowed for sludge sample analysis. The good news is that we have to go through the code revision process to make this change so **it will be close to 2 years before the change is in place.**

You will also have a chance to comment during the public comment phase of the rule revision. As we go through the revision process we will also be adding new federally promulgated methods to NR 219. If you currently follow SW 846 methods for wastewater analysis you should begin finding different methods to transition to and update your documents accordingly (method citations in SOPs, QM, benchsheets).

NR 149 ……..

We have received Governor approval to begin revision of NR 149. We will be **making minor changes to clarify requirements and update the code**.

This will not be a major change like our last revision. We will ask for input from labs during the process so make note of things in the code you would like improved and let us know about them. **This will be a 2-3 year process due to current legislative requirements**.

–Camille Turcotte

Information required on reports of sample results

The WDNR requires that certain elements be presented on test reports. NR 149.47 (1) (e) details these requirements.

There are **some exceptions to the requirements** which are presented below.

1. When the test report is prepared for an internal client.
2. When the laboratory has a written agreement with the client that certain elements are not needed.
3. When the laboratory provides the results to the WDNR in a format specified by the WDNR (e.g. drinking water data, wastewater data).

For the third point we are extending that exception to include facilities that provide the data to their client in the WDNR format. For example, some laboratories provide data to their wastewater clients in DMR format and that is acceptable. All the requirements presented in NR 149 need to be included on your test reports unless you meet one of the exemptions listed above. In any case, be sure that the client is receiving all the data qualifiers, the appropriate laboratory IDs and other information they need to make the best use of the data.

–Camille Turcotte

Verification of sample container cleanliness

NR 149 requires labs to establish procedures which address concerns that sample collection containers used do not contribute to the contamination of samples at levels that will affect sample results.

Labs generally follow some protocol to ensure that sample containers are appropriately clean. So, how can labs ensure their sample bottles are clean ENOUGH?

Certified sample containers

Many larger, commercial laboratories use new sample containers that come with certificates of cleanliness supplied by the manufacturer. These are not always adequate to show that the containers do not contribute to the contamination of samples at the concentration levels that they are used for. What auditors typically find is that "certificates of cleanliness" for a given lot of sample containers only "certify" that they are free of target analytes greater than levels that are substantially higher than the lab's LOD or even LOQ. Some things to watch for with certificates are the units which may be in ug/mL (ppm) instead of ug/L (ppb).

In addition, manufacturer certificates may not address all of the parameters that the containers are used for, For example, bottles certified clean for trace metals analysis may not make any statement about elements such as boron, strontium, or titanium, yet the lab will use these bottles for analysis of those elements.

Consequently, we encourage labs to establish some type of "bottle blank" protocol to satisfy the requirements in NR 149. One way to do this is to prepare and analyze container blanks at least once (but preferably routinely to check different "lots" of bottles), for each bottle type and vendor used, and for each parameter for which the containers are used. Bottle blanks can be prepared by filling a cleaned sample container with reagent water and letting it sit for 24 hours, then an aliquot of sample is analyzed for each analytical parameter. Results should be less than the LOD for all parameters.

For parameters where field blanks/ trip blanks are analyzed the results of those samples (as long as they are reported to the limit of detection) would suffice for demonstrating bottle cleanliness.

Specific method requirements

Remember, some methods (particularly EPA Method 1631E, ultra-trace mercury) have more prescriptive requirements for documenting sample bottle cleanliness. If the method you reference contains requirements for bottle blanks, then you will be required to demonstrate that you have met them.

Cleaning and re-using your containers

Smaller, municipal or industrial labs that typically clean and reuse larger sample containers also need to demonstrate the cleaning procedure and frequency is sufficient. This can be done by pouring reagent water into the sample container (after cleaning), letting it sit for at least 24 hours, then testing it for each of the tests the laboratory is certified for. Repeat the test if the cleaning procedure or frequency is changed

Document, Document, Document…

Don't forget to document your results and file them so they can be easily accessed. If you do not choose to establish a bottle blank program, be prepared to demonstrate to your auditor that you have another way of demonstrating sample container cleanliness.

-- Brandy Baker-Muhich

	Clean to:	PAL
Aluminum	100 ug/L	40 ug/L
Antimony	5	1.2
Arsenic	2	1
Beryllium	1	0.4
Cadmium	1	0.5
Thallium	10	0.4
Vanadium	10	6
1,4-Dioxane	N/A	0.3
Vinyl chloride	1	0.02
Benzo(a)pyrene	5.0	0.02
Benzo(b)fluoranthene	5.0	0.02
Chrysene	5.0	0.02
Pentachlorophenol	20.0	0.1

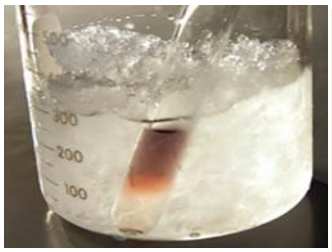
PAL = NR 140 Preventive Action Limit

"How do you know your sample containers are clean enough?"

This may not be good enough

Excerpts from bottle cleanliness certificates

For groundwaters, the relevant standard is the PAL. If bottles are only certified at levels above the PAL, the bottles will not be adequate for sample collection.



Thermometer calibration

Thermometers used in the lab to monitor equipment that have specified temperature requirements **need to be calibrated or verified annually to make sure they are accurate**.

Laboratories can make sure they complete these checks when required by using the calibration due date on the certificate received with each thermometer as its "expiration date".

While some laboratories decide to replace each of these NIST traceable thermometers, others may decide to send them out for calibration, and still others to check/verify them at the laboratory by comparing them to another thermometer that is traceable to NIST (and is still within *its* calibration due date) at the temperature or range of use.

Another option which may be acceptable for most thermometers is to verify the thermometer by comparing it to known standardized temperatures such as the ice point (0°C) and/or steam / boiling point (100°C).

Verifying thermometers may be a way of reducing purchasing costs ($). The verification process requires generation of clear documentation **and**, in some cases, thermometers may need a correction factor in order to be acceptable for continued use.

If the laboratory is interested in department guidance documents further explaining these verification options, including procedures and examples of what to document, please email your auditor or brandy.bakermuhich@wisconsin.gov.

-- Brandy Baker-Muhich

" Thermometers need to be calibrated or verified annually to make sure they are accurate. "

Meet the newest addition to our staff

Hi everyone, my name in Brandy Baker-Muhich (please just call me Brandy, that last name is a handful!). I have been with the department for 10 months now and have been able to visit seventeen laboratories already. I have a degree in chemistry but my real experience comes from working in several laboratories, as a laboratory technician, analyst, quality assurance officer and eventually laboratory manager. I really hope to be of service to the laboratories I visit and have enjoyed meeting so many great people and learning new things along the way. It has been great to be a part of the DNR laboratory certification team - they really care about helping labs produce defensible data and have developed many tools for labs to use.

Brandy Baker-Muhich

On a personal note, I love spending time with my family, especially when we get to enjoy the outdoors - camping, canoeing, and fishing, but my real favorite times are the holidays- hope everyone out there enjoys them this year!

BOD blank criteria

Each time that samples are prepared for BOD analysis a method blank (BOD blank) must be prepared along with the samples. The BOD blank serves as a measure of contamination present in your laboratory and an indicator of contamination that could possibly be present in all of the samples prepared on that day.

The control limit for the BOD blank is 0.24 mg/L. *(Note that the 0.24 mg/L allowance stems from rounding.)*

If a BOD blank has a BOD of 0.25 mg/L or higher the BOD blank "failed", is out of control, and corrective action must be taken. The BOD results for all samples prepared with the failing BOD blank must be qualified on the DMR.

--Tom Trainor

blank ?

0.24 mg/L allowance accounts for rounding

Solids: No 1/4ly re-dry if dry time ≥8 hrs

Prior to November 28, 2011, a quarterly "re-dry" analysis for solids testing (TS, TDS, TSS, TVS) was required if samples were dried for at least 8 hours with documented proof.

For our program, labs have the following options to comply with method prescribed constant weight requirements associated with solids (TS, TSS, TVS, TDS) determinations:

1. Follow the method - If the approved method used requires samples to be dried until a constant weight is achieved, all samples can be performed as per the method and brought to a constant weight.

2. Dry samples for at least 8 hours - In lieu of a method requirement to dry samples to a constant weight, laboratories may dry samples for a minimum of 8 hours (with supporting documentation of date/time in and out of the oven). There is no longer a requirement to perform quarterly re-dry verification with this option.

This allowance applies to all solids testing and effectively eliminates any requirement to perform a quarterly "re-dry" verification, introduced by the LabCert program in May 2001.

To summarize, labs must either: dry to constant weight (if required by the method they cite) or dry for a minimum of 8 hours.

One exception: %Solids determinations

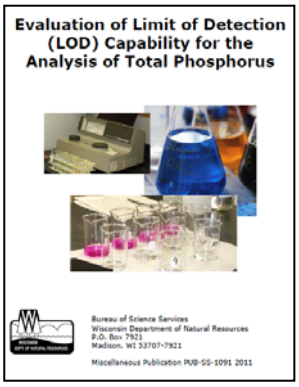
For total solids (TS) determinations performed for moisture determination or to convert wet weight results to dry weight for non-aqueous samples ONLY, labs may dry samples for the minimum time required by the method (usually 1 hour) and not dry to constant weight.
This determination of percent solids, specifying a drying time and without mention of constant weight, is included as part of many promulgated analytical methods.

Drying to constant weight

Drying at least 8 hours

" Dry solids for at least 8 hours and avoid drying to a constant weight! "

"Our experience is that drying samples for at least 8 hours is equivalent to method minimum drying times and a determination of constant weight. "



"Routine testing will require an LOD of 0.03 mg/L but Adaptive Management required testing may require an LOD of 0.01 mg/L."

Phosphorus LODs must be ≤ 0.03 mg/L

Revisions to Wisconsin's water quality standards for phosphorus discharges require laboratories to attain a level of detection (LOD) no greater than 0.03 mg/L (as P) for total phosphorus. We surveyed accredited labs to evaluate their potential to meet this new LOD expectation. It was determined that 41% of laboratories were unable to achieve a valid LOD of 0.03 mg/L or less. Labs that use the Test 'N Tube (TNT) procedure had particular difficulty in meeting the new LOD. Our findings suggest that one of the primary reasons for this is that each TNT vial serves as its own cuvette, rather than using a single cuvette for all color measurements. It was determined that if absorbance measurements were made using a single, high quality cuvette, the LOD of the Test 'N Tube procedure could be improved (lowered) by as much as 60%. Other procedures which can be used to improve LODs are discussed as well.

A copy of the report, "Evaluation of Limit of Detection (LOD) Capability for the Analysis of Total Phosphorus", can be obtained at http://dnr.wi.gov/files/PDF/pubs/ss/SS1091.pdf

NOTE: As Adaptive Management guidance is being developed, the Watershed Program is looking at requiring an LOD on the order of 0.01 mg/L.

"The bisulfate/water preservative in method 5035 is approved, but methanol remains the preferred approach."

Alternative to Methanol; SW-846 5035A approved for VOCs in Solids

The current promulgated version of s. NR 700.13, Wis. Admin. Code, specifies that soil samples collected for VOC analysis must be preserved in methanol or collected in an approved sampling device and then lab-preserved with methanol within a prescribed timeframe. The rule further requires that the samples be processed by purge-and-trap using EPA's "Test Methods for Evaluating Solid Waste (SW-846) Method 5030A.

The Remediation and Redevelopment (RR) Program is currently in the process of revising the NR 700 rule series. One of the proposed changes will allow for the use of the updated purge-and-trap procedure, SW-846 Method 5035A. This procedure introduces sodium bisulfate and water as a preservative option to methanol. The bisulfate alternative allows the direct purge and trap of soil samples, rather than purging a small volume of methanol extract for soils. This in turn allows for lower limits of detection (LOD).

The proposed revisions to the NR 700 series will not be completed for approximately 12 - 18 months. In the interim however, effective immediately, the RR program will accept results generated using Method 5035A.

Note that the RR Program strongly prefers the use of methanol preservative, particularly when the range of soil VOC concentration is unknown. The program also recommends against the use of water-only preservative or no preservative when a soil sample is packed into a container, even though these options are included in Method 5035A. The RR program may reject sample results if either of these preservative methods is used.

If you have questions or require additional information, please feel free to contact Resty Pelayo at 608-267-3539 or aristeo.pelayo@wisconsin.gov.

--Tom Trainor

Reduced volume extractions allowed

One of the more recent innovations in lab analysis involves the use of smaller sample extraction volumes prior to analysis of semivolatile organic parameters. The modification involves extracting a smaller sample volume (typically 100 mL instead of 1 L of sample) with a proportional reduction in solvent volume. This modification alone would effectively result in a 10-fold increase in the LOD. To offset the impact of the reduced volume extraction, the protocol calls for a ten-fold increase in the injection volume (10 uL instead of 1 uL). To minimize the impact of additional solvent volume on the GC or GC/MS system, a guard column is typically employed as well as precision venting of solvent.

Some of the benefits of using a reduced volume extraction are a reduction in solvent use, lower sample shipping costs, and more efficient field sampling. Keep in mind that this modification (reductions to sample volume and solvent combined with increased injection volume) to the methods is something built into the method flexibility afforded by SW-846. Such flexibility is allowed provided that the modification does not result in a change to the chemistries, and the required ratio of reagents to sample volume is maintained.

Subsequently, the WDNR accepts the use of reduced volume extractions coupled with large volume injections for SW846 methods and WDRO. In order to utilize these method modifications the following criteria must be met prior to conducting any analysis of compliance samples:

- Changes to the method or extraction chemistry (including solvent choice) are not allowed unless specifically allowed by the reference method.
- The ratio of sample volume to solvent volume and must be maintained; method specified sequential extractions must be conducted.
- All method quality control, including initial demonstration of capability and chromatography, must meet or exceed method or code required acceptance criteria.
- Quantitation sensitivity must not be affected for any parameters where a regulatory limit or project required limit is critical.

Special Note: Wisconsin DRO

Approval for this approach for analysis of Wisconsin DRO is based on using a minimum of 100 mL (nominal) of aqueous sample and performing three successive extractions with methylene chloride.

Special Note: PAHs

Approval for the analyses of PAHs is based on achieving a detection limit of 0.02 µg/L for benzo(a)pyrene, benzo(b)fluoranthene, and chrysene in ground water. This may require labs to slightly optimize the full-scan mode Method 8270 when those analytes are requested in groundwater, or to analyze all Wisconsin groundwaters in the SIM mode.

--Tom Trainor

1L ➔ 100 mL

Reduced extraction volume allowed for organic extractables

10x ↓ sample volume

10x ↓ solvent

10x ↑ injection volume

LODs: no change

Applications & PTs Reminders

Please remember that in order to be complete, applications must include PTs for those parameters requiring them. WP PTs are acceptable for aqueous and solid matrices. WS PTs are valid for drinking water only. Please do not include any PTs with study close dates more than 6 months prior to the date you submit the application. Also, please do not submit solid matrix PT results, as we do not accept those. Lastly, if a parameter requires a PT, the analyte MUST be included in the PT at a non-zero concentration.

NO!

NO!

NO!

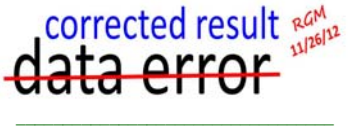
Proper error correction

Laboratory records must insure that:

- A permanent record is created. *(This means permanent ink or a computer record. Pencil or correction fluid is not allowed.)*
- The records are legible *(we know you can read your handwriting…but can the rest of the world?)*

Original entries of hardcopy records must not be obliterated by "scribbling" or overwritten with a permanent marker.

The proper protocol for correction is to draw a single line through the erroneous result and write the new result above it. These changes should also be accompanied by the initials and date of the individual making the correction.



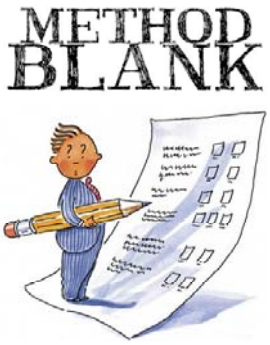
The proper way to correct errors

Electronic records should not allow the user to delete or replace the original entry completely but rather "archive" the original record while creating a separate amended record. Some electronic records capture the user ID and date of the individual who created the original record as well as the individual who modified the record. If you use a LIMS for electronic record-keeping, ask the vendor about "audit trail" functionality.

Please contact your laboratory auditor if you have questions about correcting handwritten records.

--John Condron

Proper assessment of method blanks



Auditors are finding that many labs are assessing method blanks relative to "reporting limits", which are frequently arbitrarily determined and can be significantly greater than the limit of detection (LOD). NR 149 (see below) is clear in the hierarchy of method blank evaluation, and reporting limit is not discussed. In addition, the acceptance criteria for initial and continuing calibration blanks must be the same as those used for the method blanks unless the method specifies otherwise.

- NR 149.48 (3) (d) states-

When the method employed does not specify method blank acceptance criteria, the laboratory must refer to NR 149 for the method blank acceptance criteria. NR 149 specifies that samples in a batch be re-analyzed or qualified if the concentration in the associated method blank exceeds the highest of any of the following values:

a. The limit of detection
b. 5% of the regulatory limit
c. 10% of the measured concentration in the sample

"NR 149 is clear in the hierarchy of method blank evaluation, and reporting limit is not discussed.

Example:
ACME Labs analyzes a groundwater sample for copper by flame AA. The result is 90 ug/L. The method blank analyzed with the sample measured 23 ug/L. The lab did not qualify its data.

The lab's LOD for copper by ICP is 10 ug/L, but uses a reporting limit for copper, which has been established at 50 ug/L, corresponding to the concentration of the lowest calibration standard.

The "regulatory" limit for copper in this case would be the preventive action limit (PAL) of 130 ug/L established in NR 140.

The lab's rationale reporting results without qualification was that the concentration of copper in the method blank was well below the reporting limit.

The assessment should have been:

a. The limit of detection = 10 ug/L
b. 5% of the regulatory limit = 6.5 ug/L
c. 10% of the sample result = 9 ug/L

The highest of the three (in this situation) is 10 ug/L. Since the method blank measured 23 ug/L, the method blank fails. **Therefore, the associated sample must be re-analyzed or the data qualified**.

Reminder: QCS Required for Flame AA

One of the changes that occurred with the 2008 revision to NR 149 was the elimination of the requirement to analyze PT samples for metals analyzed by flame atomic absorption (FLAA). **Instead of PTs**, the program requires the analysis of quality control samples (**QCS), three times annually at "evenly spaced intervals".**

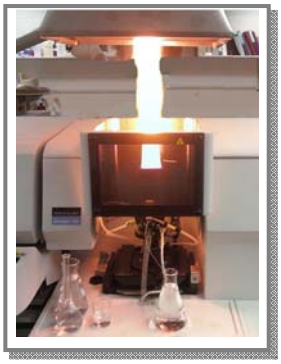
While several have asked, unfortunately the choice by a lab to continue analyzing PT samples does not exempt them from the requirement to analyze QCS three times annually.

Please note that the definition of QCS in NR 149 is quite specific. A lab may not prepare its own QCS.

> *"Quality control standard" or "QCS" means a solution or sample containing method analyte of known concentration, accompanied by specified analytical acceptance limits, and obtained from a source external to the laboratory and different from the source of calibration standards. These samples are distinguished from proficiency test samples in that the acceptance limits are provided with the sample, rather than after analysis.*
>
> ---NR 149.03 (57), Definitions

PT Providers list QCS as…

Absolute: xxx-IN
ERA: WastewateR Type=QC)
NSI: QCI-xxx
Phenova: QC-xxx-WP
RTC: QCxxx



Is your LOD realistic? Defensible?

We all know how to generate an LOD the traditional way (40 CFR Part 136, App. B). However, the LOD generated using this procedure is often unrealistically low. Reporting results using unrealistic LODs may give the data user a false sense of security. The test report may indicate that the parameter reported was not detected at the LOD - when in fact often the lab cannot really detect the parameter at the LOD concentration derived from the EPA protocol.

To address this, we suggest following the protocol listed below:

1. **Compare the LOD response to the method blank response.**

Prepare a standard at the same concentration as the LOD. After analysis of this standard, compare its response to the response of the method blank. If the response of the LOD standard is at least 3 times the response of the method blank, this check passes. If this check does not pass, then the calculated LOD is not significantly different from background and it is too low.

2. **Determine the recovery at the LOQ concentration.**

Prepare a standard at or near the LOQ concentration (the LOQ should be approximately 3 times the LOD). Treat the LOQ standard the same as a sample by subjecting it to all of the steps in the method. This is equivalent to performing an LCS at or near the LOQ concentration. If the recovery of this standard is between 50-150% for organic compounds and 60 – 140% for inorganic compounds then this check indicates that a quantifiable recovery was achieved at this concentration. For Total Phosphorus (TP) and NH3-N a recovery between 70 – 130% should be achievable. If this check does not pass, then the LOD is too low because a reasonable recovery cannot be achieved at the LOQ.

If either of these checks fail then the calculated LOD is too low. To resolve this, the lab should increase their LOQ concentration, incrementally, performing an LCS at each concentration, until recoveries listed in step 2 above are achieved. At that point, the LOQ is divided by 3 to determine a nominal LOD. Using the nominal LOD perform step 1 above. If that passes, then a defensible, realistic LOD has been determined.

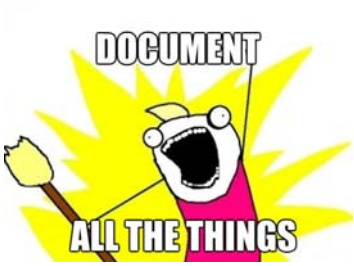
Be sure to retain all data so that if an auditor asks to see how you arrived at the nominal LOD you have data to show your process.

--Tom Trainor

"If the response observed for your blanks exceeds the response at the LOD… your LOD is unrealistically low."

Leave a trail others can follow, but…

don't reinvent THE WHEEL



"Good corrective action requires good follow through.

Leave a trail for others to follow."

Documenting Corrective Action

The foundation of a quality system is to develop policies to ensure data quality. When lab testing does not conform to policy, then corrective action is in order. The LabCert administrative rule, NR 149, requires corrective action to be taken any time lab activities deviate from established policy. Of course what goes without saying is that you must have established a quality system including clear and comprehensive policies (SOPs).

Corrective action is required when ANY quality control (QC) sample exceeds acceptance criteria. By QC sample, we're talking things like method blanks, LCS, spikes and replicates (if you are required to analyze them). If you choose to analyze QC samples above and beyond those required by this program, then your quality system should be clear about what action you should take. In nutshell, there's no point in analyzing QC samples if you have not established acceptance criteria, and there's no point in analyzing them if you aren't going to take some action when they exceed criteria….right? If your smoke or carbon monoxide detector sounds , you take immediate action…don't you?

Corrective action has three elements:

• **Identify –** Corrective action must identify the source of the problem.

• **Triage, Treatment, and Follow-up** – This is a multi-faceted stage that begins with a diagnosis. What caused the QC exceedance or deviation from policy? We need to assign a preliminary diagnosis as to the root cause and take action to resolve the problem. At times, our initial diagnosis is incorrect and we must try something else. Ultimately, we need to continue taking action until we are certain that the problem has been addressed. Follow-up on the problem in case it sparks up again like a slowly simmering wildfire.

How will you know whether or not the corrective action worked or not? Good corrective action requires good follow through. If the corrective action worked then you need to document how you know that it worked. If the problem still exists, then you need to re-diagnose and try other corrective actions measures.

This iterative process continues until the problem is resolved….but don't let it linger until it becomes a "cold case". Keep after it. And don't hesitate to call for back-up. Check in with other labs/analysts or check in with your DNR auditor.

• **Documentation –** Learning from the experience, and providing a means to guide others in the future, should this recur, is the most critical phase of corrective action. We need a roadmap which outlines the treatment provided and how they were—or were not—successful.

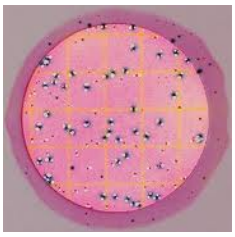
Hansel and Gretel marked their path home with a trail of bread crumbs…and we know how that almost worked out for them. So we need to forge a better trail of documentation. This problem may rear its head again, and future analysts need to know how it was corrected in the past. Documentation has to be such that others do not have to re-invent the wheel, so to speak. Document what was tried and what the outcomes were. Use a form or develop your own.

Here is an example of a basic corrective action form; it may not include all instances in which corrective action is needed, but it's a start:

http://dnr.wi.gov/regulations/labcert/documents/formsCorrActionLog.doc

-- John Condron

30 Hour Holding Time for Public Drinking Water Microbiology Samples



EPA has required that public drinking water microbiology samples over 30 hours old cannot be analyzed. If you have problems getting your samples to a laboratory in time, then you need to look at other ways that you can meet this requirement. **This change in requirement was effective 10/01/2012**. If your sample is over 30 hours old, then you will need to resample. This does not affect private drinking water microbiology samples. For more information go to http://dnr.wi.gov/regulations/labCert/News.html.

--Ron Arneson

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Drinking Water Data Submittals

In order to submit your data to us you need to have a user ID and password. This allows you access to DNR data systems via the Switchboard. You should not share you user ID and password with others at your facility. Each person should have their own user ID and password. The user agreement states:

> *"Your Wisconsin User ID* **[WAMS ID]** *and password are your keys to doing secure business with the State of Wisconsin over the Internet. They should be considered as important as your signature. Do not share your Wisconsin User ID or password with anyone. You are the only person who will know your password. It will be secured and unavailable to anyone, including State security officers and administrators. It is your obligation to protect it by keeping it confidential and known only to you. "*

Information systems, and the data that is stored and managed by the State of Wisconsin, are governed by State and Federal laws, rules and regulations. Violators may be subject to prosecution, fines or other sanctions.

If you need to get a user ID and password go to http://dnr.wi.gov/topic/switchboard/ for addition information.

--Ron Arneson

WAMS
WEB ACCESS MANAGEMENT SYSTEM

Lab IDs and Method Codes for PTs.

☑ Please remember to report an "EPA ID" to your PT provider for all PT results. If you do not have one, report your 9-digit Wisconsin Lab ID (on your certificate); it will always work. Without an ID, your results do not get loaded.

☑ Also remember to report the proper TNI method code with all PT results. Your PT Provider should have a system to convert your method to the proper Method Code. Without a method code your PT results may get "lost".

" In order to submit your data to us you need to have a user ID and password. "

Proper verification of balances

"Don't just record the weight for your certified weights. The bottom line is that you need to establish acceptance criteria for your certified weights."

NR 149.44(3)(g) deals with monthly analytical balance accuracy checks. Labs are reminded that:

Your analytical balance should be verified for accuracy on each day you use it. At a minimum, analytical balances must be checked monthly with at least 2 certified weights (i.e., ASTM E617 class 1 that are NIST traceable), one weight in the gram range and one weight in the milligram range. These weights must be sent to an outside metrology lab for re-certification at least every 5 years. This re-certification must be performed sooner if balance checks performed using these weights suggest that a change in the certified weight has occurred. Alternatively, it may be more cost effective to simply purchase two new weights every 5 years.

It is important to choose weights that reflect the weights that you are measuring during your analyses. The best practice is to evaluate your TSS bench sheets to see what the typical weight ranges are that you use. However, keep in mind that you may use the analytical balance for more than just TSS. Standard and reagent preparation should also be considered when deciding which weights to use for verification. There is no reason that you cannot use more than just the required minimum of two if you choose.

Each time you perform your balance accuracy verification you need to document the true value of the weight tested and the observed value of that weight. These two records coupled with the date of verification and identity of the analyst need to be documented.

Once the measurements have been made, you must then evaluate the accuracy of the observed weight. Optimally, you should establish acceptance criteria for each weight based on a mean +/- 3 standard deviations of 20 replicate weighings. Alternatively, we think the fixed "control limits" below are appropriate. **The bottom line is that you need to establish acceptance criteria for your certified weights!**

Optional "fixed" weight control limits

- ± 0.3 mg for weights <10 mg
- ± 0.5 mg for weights 10 mg to 100 mg
- ± 1-2% for weights >100 mg

Your balance-weight verification records need to clearly indicate what control limits you used for assessing whether or not your balance-weight verification was in control.

If the measured values are not within the control limits then corrective action is needed. Some examples of corrective actions are:

- Perform an internal calibration
- Clean the pan
- Check for static electricity
- Check for air drafts or other excessive air flow (balances should not be placed near doors or HVAC vents)
- Check the balance spirit level
- Have your balance re-certified by a third party
- Have your weights re-certified by a third party
- Send your balance in for repair

Record the corrective actions you take and note if it solved the problem.

Don't forget top-loader balances!
Your top loading balance needs to be checked at least monthly with at least one weight in the expected working mass range. The weights used to perform these checks may be traceable to or verified against those traceable to the NIST.

For further reading on balances and an interesting tip to see if static electricity is causing your balance not to stabilize (Yes, coffee is involved!) see: http://labmed.ascpjournals.org/content/35/1/48.full.pdf

-- Dave Ekern

Impact: the 2012 Methods Update Rule

On May 18, 2012, EPA promulgated changes to the list of Clean Water Act (CWA) methods at 40 CFR Part 136.3. This action, referred to as the Methods Update Rule (MUR), approves new methods or changes to existing methods, that affects over 100 EPA methods, Standard Methods, ASTM methods, and other test procedures in Part 136 of Title 40 of the Code of Federal Regulations (CFR). The final rule is located at:

http://water.epa.gov/scitech/methods/cwa/update_index.cfm

And a clarification letter is found at:

http://www.standardmethods.org/PDF/EPA_Acceptable_Version_WW_6-20-2012_final.pdf

One major change with this MUR is the format for referencing methods from Standard Methods (SM). The old system of referencing by editions of the Standard Methods compendium is no longer used. Instead, individual methods are now referenced by the year they were approved by that particular method's committee.

For example, the current identification of approved methods for BOD in NR219 is "Standard Methods 5210B [18th, 19th, 20th, 21st]". Under the new Federal rule, the designation of the approved method has simply become "Standard Methods 5210 B-2001" and "Standard Methods 5210 B-2011". The 2011 version is only found online and in the 22nd edition of the compendium. The 2011 version is identical to the 2001 version save editorial revisions. The requirements within the method itself have not changed.

The approved date is found by checking the footnote located on the method introduction, e.g.,:

5210 BIOCHEMICAL OXYGEN DEMAND (BOD)*

* Approved by Standard Methods Committee, 2001. Editorial revisions, 2011.

So what you need to do is check the methods that you cite for their "Approved by Standard Methods Committee" date. If your compendium edition does not contain the correct "Approved by Standard Methods Committee" date, you will need to change the method that you cite. If you are currently using an older edition of Standard Methods that does not include all the approved methods, purchasing the 22nd Edition should include all methods found in the MUR. Alternatively, purchasing methods from the Standard Methods website will guarantee access to the most recent version of all methods.

For the "basic four' of BOD, TSS, TP, and Ammonia as N, the acceptable SM methods will become:

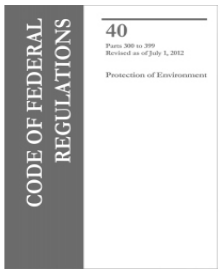
BOD: 5210 B-2001 and 5210 B-2011

TSS: 2540 D–1997 and 2540 D–2011

TP: 4500–P B,E,F, H-1999 and
4500–P B,E,F, H-2011

NH_3-N: 4500–NH3 C, D, F, G, H–1997
4500–NH3 C, D, F, G, H–2011

NR 219 will be updated to reflect this change in Federal law. Until then, the methods currently listed in NR 219 are still allowed by the WI LabCert program. Labs are strongly encouraged to begin changing the way methods are cited in order to comply with the future NR 219 update.



40 CFR Part 136.3

Standard Methods
For the Examination of Water and Wastewater

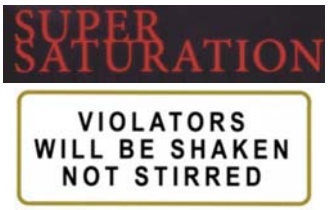
" Which Standard Methods procedure is approved?

. . . individual methods are now referenced by the year they were approved by that particular method's committee. "

Which SM wastewater methods are approved?: http://www.standardmethods.org/PDF/Total_CWA_Table_NEMC.pdf

DO Super-saturation and BOD Testing

Probably one of the most forgotten and misunderstood issues in BOD testing is dissolved oxygen (DO) super-saturation. In fact, it is one of the most cited deficiencies during on-site evaluations. So what do we mean by super-saturation? Water only has a limited capacity to hold oxygen. This capacity, or saturation point, is driven by temperature and barometric pressure. Cold water will hold more oxygen than warm water. In early spring, late fall and during the winter DO concentrations in effluent samples can become super-saturated. Concentrations of up to 13 mg/L are not uncommon during the cold winter months. Many people, including me, incorrectly believed that Standard Methods establishes the maximum DO concentration allowed in the BOD test as 9.0 mg/L. Actually, this is not correct. The point of super-saturation could occur at a much lower oxygen concentration. If the sample DO is greater than the saturation point when the bottles are placed in the incubator, oxygen will physically come out of solution and appear to be an oxygen demand. The resulting BOD will be falsely high.



" 9.0 mg/L is not the definitive saturation point.
For many samples, saturation occurs as low as 8.2-8.5 mg/L. "

So how do you deal with super-saturation?

1. Warm samples to 20-22ºC. Standard Methods allows a temperature range of 17-23ºC. However, you will not be able to drive off the excess DO easily unless the temperature is above 20ºC but less than 23ºC.

2. Pour the sample into a suitable size bottle but only fill about ½ to ¾ full. For effluent samples, a 2 L bottle is generally adequate. The key here is to have plenty of head-space so the sample can be vigorously agitated.

3. Shake the ½ to ¾ filled bottle vigorously for about 1 to 2 minutes. Some try stirring samples in large beakers but this does not provide enough agitation. IT DOESN'T WORK!! Use the "James Bond approach"…shaken, not stirred.

4. Vent the bottle by removing the cap after shaking and allow the sample sit for 2-3 minutes to allow the micro-bubbles to dissipate. Like a good wine, it should breathe a few minutes before it is used. Do the same with the sample.

5. Measure the DO of the sample and compare the value to the theoretical DO saturation point from the saturation chart: http://dnr.wi.gov/regulations/labCert/documents/methods/DO_Sat_Table.pdf
The sample DO should be near (but not higher than) the theoretical (e.g., ~0.2 mg/L).

6. If the sample is still above the theoretical saturation point, shake the sample a few more minutes and allow it to breathe again for 2-3 minutes. Re-check the sample DO before proceeding with the test. DO NOT proceed with testing if the sample is still super-saturated.

7. The sample is now ready for BOD testing.

-- George Bowman

Please…do not over-pay for your application.

We receive a lot of applications for which a check far in excess of the required fee is submitted. Maybe labs are just used to paying exorbitant prices elsewhere ☺. The single greatest mistake is paying a "technology" fee when none is required. Use your scope of accreditation as a resource. If you already have the technology "ion chromatography" (IC) but now want to add bromine by IC, you do not pay for the technology fee…you've already paid it!
We encourage calling us first or making use of our application fee calculator : http://dnr.wi.gov/regulations/labcert/documents/AppFeeCalc.xls

We're on the Web!
dnr.wi.gov/regulations/labcert/