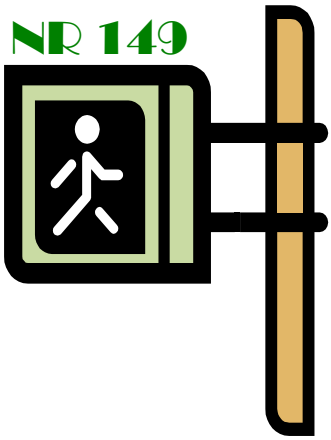
The Newsletter of the Wisconsin Laboratory Certification and Registration Program




LABNOTES

Winter 2005-06

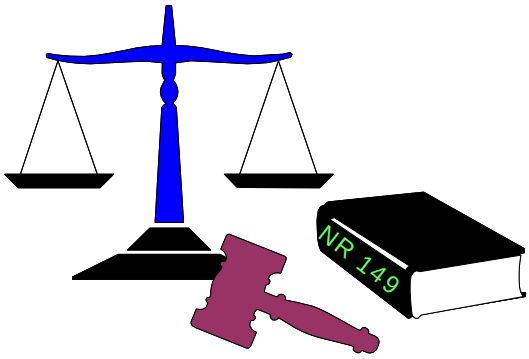
Chapter NR 149 Revision: "In the Green"



The Laboratory Certification Program has completed the analysis and documents required to take a draft of the proposed Certification and Registration Code to the Natural Resources Board and seek authorization to conduct public hearings on the revision. The package the Board reviewed is topped by a green-colored memorandum; in DNR lingo, the Chapter NR 149 revision is at the first green sheet stage. The Board approved the requested authorization at its meeting on December 7, 2005.

Public hearings are anticipated to take place in the spring and early summer of 2006 at several locations throughout the State. Once all comments have been received and reviewed, the Department will produce another draft of the Code incorporating any changes needed to address comments. The program will then prepare a second green sheet sometime in 2006 seeking adoption by the Natural Resources Board of the final version of the Chapter.

The proposed rule information can be obtained at: https://apps4.dhfs.state.wi.us/admrules/public/Rmo?nRmoId=727 and clicking on the "Initial Proposed Rulemaking Order" link. For more information, contact David Webb (608) 266-0245.



Also in this Issue:

Contact us at: (608) 267-7633 or LabCert@dnr.state.wi.us
Web Site: www.dnr.state.wi.us/org/es/science/lc

Exams, Meetings & Training Opportunities

Operator Certification Exams

DNR will hold Wastewater, Drinking Water, and Septage Operator Certification exams on May 3, 2006 (postmark deadline April 5, 2006) and November 1, 2006 (postmark deadline October 4, 2006) in DNR Regions around the state. Check the Op Cert. web site for details, as they become available. The DNR's Central Office in Madison will send an exam application 3 months prior to the upcoming exam date to those operators that have taken an exam(s) in the last 3 exam cycles.

www.dnr.state.wi.us/org/es/science/opcert

Training for Lab Analysts

March 21-23, 2006 "Detection of Ascaris and other Parasite Eggs and Cysts in Sewage Sludge"
College of Veterinary Medicine
Cornell University, Ithaca, NY.
www.vet.cornell.edu/conferences/parasite06/

March 28-30, 2006 Intro to Wastewater Lab
Green Bay - WWTS

April 4-5, 2006 Advanced Wastewater Lab
Madison - WWTS

WWTS: Wastewater Training Solutions.
Contact Dan Tomaro at (608) 770-5144
www.wastewatertrainingsolutions.com/

www.dnr.state.wi.us/org/es/science/opcert/training.pdf

LabNotes

Newsletter of the Laboratory Certification Program

LabNotes is published twice annually by the Wisconsin DNR Laboratory Certification and Registration Program. For information about distribution or to make suggestions for future articles, contact the editor.

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LabNotes Editor
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2005-06 Conferences & Meetings

MWAA Winter EXPO

The Midwest Water Analysts Association has scheduled its Winter EXPO 2006 for January 27, 2005 at the Bratstop Banquet Center in Kenosha. Contact Larry Dressel at (630) 369-5586 for info.

www.midwestwateranalysts.org

Forum on Laboratory Accreditation

The Forum on Laboratory Accreditation, consisting of consecutive meetings of the National Environmental Laboratory Accreditation Conference (NELAC), the Institute for National Environmental Laboratory Accreditation (INELA) and the Environmental Laboratory Advisory Board (ELAB) will take place at the Westin Chicago River North in Chicago, Illinois on January 28 - February 4, 2006. Three training courses will be offered in conjunction with the Forum: "Data Review for Conformance to the NELAC Standard" (Jan. 28 - 29), "Staged Electronic Data Deliverables" (SEDD, Feb. 4), and "Requirements for a NELAC QA Manager" (February 4). A workshop for first time attendees will be presented on January 30. For registration materials and more information contact INELA via their website (listed below).

http://www.inela.org

1st Annual Midwest Water Industry Expo

Central States Water Environment Association & Wisconsin Water Association are jointly sponsoring the EXPO. It is being held at the Kalahari Water Park Resort and Conference Center in the Wisconsin Dells on February 1-2, 2006.

www.cswea.org or www.wih2oassoc.org

Government Affairs Seminar

The Government Affairs Seminar (jointly sponsored by Wisconsin DNR, the Wisconsin Section of the Central States WEA, Wisconsin Wastewater Operators Association, Municipal Environmental Group and Wisconsin League of Municipalities) will be held February 23, 2006 at the Marriott Inn in Madison

FET's Environment '06 Conference

The Federation of Environmental Technology's (FET) annual conference will be held March 6-8, 2005 at the Four Points Sheraton – Milwaukee Airport, in Milwaukee.

www.fetinc.org/

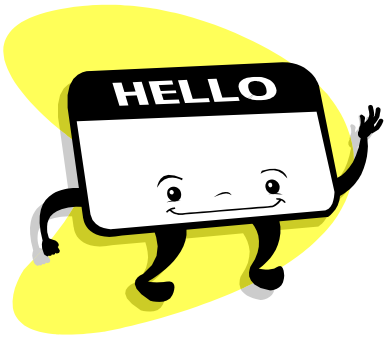
24th Annual Spring BioSolids Symposium

The Spring BioSolids Symposium will be held March 21, 2006 at the Country Springs & Convention Center (fka Holiday Inn) in Stevens Point. For more information contact: Greg Kester at (608) 267-7611.

Rural Water (WRWA) Association

The Wisconsin Rural Water Association holds its annual conference March 29 - 31, 2006 at the Green Bay Regency Suites and KI Convention Center complex. Call (715) 344-7778 or visit their web site for more information.

www.wrwa.org



Wisconsin Water Association

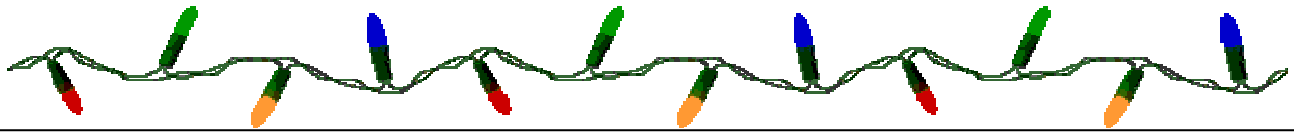
The Wisconsin Water Association (formerly AWWA WS) 85th annual conference is scheduled for September 20 through 22, 2006 at the Kalahari Resort in Wisconsin Dells. Contact Jack Albrechtson at (608) 831-6554 for more information.

www.wih2oassoc.org

Wastewater Operators Association (WWOA)

The 40th Wisconsin Wastewater Operators Association annual conference will be held October 3 through 6, 2006 at the Kalahari Resort in Wisconsin Dells. Check the WWOA web site for more details.

www.wwoa.org



Program Administration

n-Hexane Options for Method 1664A

By Greg Pils

The cessation of domestic production of 85% pure n-hexane solvent has many laboratories wondering what their solvent options for method 1664A will be once the supply runs out.

We recently received confirmation from the Engineering and Analysis Division of EPA's Office of Water (the authority responsible for method 1664A) that laboratories must continue to use n-hexane of 85% purity or greater when analyzing samples for hexane extractable material (HEM) by method 1664A.

This may seem unduly restrictive, given that 1664A is a performance-based method. However, the method was validated using 85% purity n-hexane, and EPA noted during the validation that significant changes in results occurred when an alternate solvent was used. Consequently, modifications to the extraction solvent – including the use of n-hexane of less than 85% purity – are not permitted.

Rumors abound that certain vendors will continue to have amply supplies of 85% pure solvent available for several months. However, feedback from the laboratory community on this front has been mixed. One laboratory informed us that they specifically ordered 85% pure n-hexane, but were instead shipped a much less pure solvent. The purity level was not printed on the solvent jug labels, but a review of the accompanying certificates of analysis revealed an n-hexane purity level of 68%, which is unacceptable for method 1664A.

The bottom line: If you are analyzing samples for HEM, contact your solvent vendor to verify the purity level of the n-hexane they have in stock before ordering. If the solvent jugs are not labeled, check the certificate of analysis. If no certificate is shipped with your order, call to request one. Anything less than 85% pure n-hexane is unacceptable, and laboratories will be cited as deficient for its use. Purity levels greater than 85% will always be considered acceptable.

If you have further questions, please contact Greg Pils at (608-267-9564, or via e-mail at gregory.pils@dnr.state.wi.us).

Certification vs. Registration

By Camille Johnson

Did you know that there are two categories of approval for laboratories in the WI DNR Lab Certification Program? The two categories are registration and certification. These are fully defined in NR 149 – the Lab Certification and Registration Code. There are a total of 435 labs in our program, with more than sixty percent of those in the registered category and the remainder certified.

Registration is allowed for laboratories analyzing samples only for their own facility. This primarily applies to wastewater treatment plant labs and small industrial labs. Registration can also apply to a facility that is testing for other facilities that are all under common ownership. For example, if Company X has two manufacturing plants the Company X Lab can do analysis for both the manufacturing plants with only registration status. However, the Company X Lab could not do analysis for the city wastewater treatment plant. All the parties involved need to be under common ownership for registration to be acceptable.

So, who has to be certified? Certification is required for laboratories performing analytical testing commercially, either for regulated facilities or for special DNR projects. This can range from a large commercial lab to a small wastewater treatment plant lab that wants to do testing for some neighboring municipalities.

If you are currently testing for other facilities (under different ownership) and are not certified you need to contact the Lab Certification program as soon as possible. It is a fairly simple process to change your status. There are some forms to file and different fees that will be assessed. However, if you do not correct your status and it is discovered at a lab evaluation, your facility is likely to be issued enforcement action. It is preferable to maintain compliance and correct this if it has been overlooked. If you need further information about revising your certification status the best contact is our Program Chemist, Rick Mealy, at 608-264-6006.

Evaluation Checklists

(BOD, NH3, P & TSS)

By Camille Johnson

The Lab Certification program has developed a set of five checklists covering the following parameters: biochemical oxygen demand (BOD), ammonia (ISE method), phosphorus (ascorbic acid method) and total suspended solids (TSS).

One checklist was developed for each of those parameters, with an additional "Quality Control and Records Requirement Checklist" which covers QC and records for all four parameters.

You may wonder why those four parameters were chosen. The primary reason is that they are the most common parameters tested by the labs we register. They are also less complicated parameters than some, so made a good starting point.

… labs may find that the checklists are a good self-auditing tool to make sure there aren't any major requirements being overlooked.

The main focus of these checklists is to cover procedures or requirements that are specifically mandated by code or method. They do not cover good lab practices and may not cover every single requirement. It remains the lab's responsibility to ensure that all proper procedures are followed. However, labs may find that the checklists are a good self-auditing tool to make sure there aren't any major requirements being overlooked. Your auditor will review these requirements at an evaluation, but they may also go beyond these lists to provide required changes and procedural recommendations that should improve your lab results.

The checklists are available on the Lab Certification website - address:

http://www.dnr.state.wi.us/org/es/science/lc/. They are downloadable in Microsoft© Excel or PDF format. If you prefer a paper copy you can call the Lab Certification Program and copies will be sent to you. If you have questions or comments about the checklists please contact Camille Johnson at 715-831-3272 or camille.johnson@dnr.state.wi.us

Standard Methods 21st ed Released

By Rick Mealy

In September 2005, the 21st edition of Standard Methods for the Examination of Water and Wastewater (aka "Standard Methods") hit the streets.

The logical question that follows this and every other new edition's release is: "Can I use it?" The answer, unfortunately is, "No." To make a long story short, the reason why we cannot allow the use of the 21st edition at this time is that the EPA has not yet recognized this version and updated the Code of Federal Regulations to allow it. That has to happen FIRST.

Once the EPA promulgates it as an approved method source under the Clean Water Act (40 CFR Part 136) the next step is for us to make a similar change in NR 219, WI Admin. Code, for it to be allowed for the analysis of wastewater samples. Similarly, if the 21st edition is to be referenced for drinking water analysis, then the EPA must approve it under 40 FR Part 141 and then Wisconsin, in turn, must make changes to NR 809, Wis. Admin. Code.

Standard Methods: Which Edition?

By Rick Mealy

If Standard Methods is your authoritative source for methods, make sure you clearly document which edition of Standard Methods you are following.

While some methods are not changed between editions (e.g. procedures for TSS), substantial changes are made to others—most notably the procedure for BOD. Consequently, it's not quite enough to say that your procedure for BOD is "Standard Methods 5210 B". We also need to know which edition you reference, because there are significant differences in analytical requirements.

One good example is that if you reference the 20th ed. For BOD, take note that this edition specifically requires not just a minimum of two dilutions, but a minimum of two dilutions that meet method-specified depletion criteria. This slight change could mean that many labs will have to prepare at least three dilutions to ensure this requirement is fulfilled.

Reporting Data Down to the LOD

By Rick Mealy

Certified and registered laboratories are required to report data down to their limit of detection (LOD) for many analytes that have a health-based environmental standard in chapters NR 105, 140, 720 and 809, Wis. Adm. Code, below or near the analytical limit of detection (NR 149.15 (3)). This requirement became effective January 1, 1997.

The table below contains the list of compounds of concern at low levels. A note following s. NR 149.15, Wis. Adm. Code specifies that the LabCert Program publish a list of these compounds annually. Laboratories are required to report all data for these substances down to their limit of detection. All results greater than the LOD, yet less than the LOQ, must be reported and appropriately qualified (consult ch. NR 149, Wis. Adm. Code, for definitions of the LOD and LOQ).

Data reporting requirements are found in many of the agency's administrative rules and can be confusing. To help eliminate some confusion, below is an abbreviated guide of <u>when laboratories are required to report data down to the LOD</u>:

1. If a client requests data reported down to the LOD.
2. If it is a sample for the Groundwater or Landfill Programs, then report all analytes to the LOD.
3. If it is a sample for a WPDES permit established under chapter NR 105, report data down to the LOD.
4. If it is a sample for the Drinking Water Program, then report all analytes with an MCL to the LOD.
5. If (1), (2), (3) & (4) do not apply to the sample, then report to the LOD if the substance is on the NR149 Compounds of Concern reporting list (Table 4.9).
6. If (1), (2), (3), (4) or (5) do not apply, then it is not necessary to report to the LOD.

Knowing when to report results to the LOD is complex. However, there is a way to make it easy. A laboratory may report all data to its LOD, with the appropriate qualifiers, and be assured of meeting all program specific requirements. Laboratory clients may specify data reporting requirements that exceed those set by WDNR.

Low level Reporting Requirement – Substances of Concern (1-1-06)

1. INORGANICS

Metals
Antimony
* Arsenic [1]
Beryllium
Cadmium
Lead
Thallium
Mercury
Chromium (Hexavalent)

2. ORGANICS

Acids/Phenols
Pentachlorophenol (PCP)

Benzidines
Benzidine

Haloethers
Bis(chloromethyl)ether

Nitroaromatics 2,4-Dinitrotoluene 2,6-Dinitrotoluene

Polynuclear Aromatic Hydrocarbons
Benzo(a)pyrene
* Chrysene [2]
* Benzo (b) fluoranthene [2]

Phthalates & Adipates
Bis (2-ethylhexyl) phthalate

Nitrosamines
* N-nitroso-diphenylamine [3]

Nonpurgeable Chlorinated Hydrocarbons
Hexachlorobenzene

Dioxins/Furans
Dioxin

PCBs
Polychlorinated biphenyls

Chlorinated Pesticides
DDT and Metabolites
Heptachlor
Heptachlor epoxide
Lindane
Toxaphene

Carbamate Pesticides
Aldicarb

Nitrogen Pesticides
Alachlor
Trifluralin
* Cyanazine [1]

Phosphorus Pesticides
Dimethoate
Parathion

Volatiles
1,1,2,2-Tetrachloroethane
1,1,2-Trichloroethane
1,3-Dichloropropene (cis/trans)
* Benzene [3]
Bromodichloromethane
Bromoform
Bromomethane
Chloroform
Chloromethane
Methyl tert-butyl ether (MTBE)
Methylene Chloride
Vinyl Chloride
Dibromochloropropane (DBCP)
Ethylene dibromide (EDB)

Changes, since the previous list, are identified by an "*".

[1] PAL recently reduced [2] Recent addition to NR 140, PAL same as Benzo(a)pyrene [3] earlier omission

DNR & State Take Action against Falsification and Lab Fraud

By Stefan Fabian and Rick Mealy

DNR enforcement staff have unfortunately had to deal with several cases of laboratory fraud in recent months. The case against a Green Lake man has recently been completed, but several other incidents are still in the investigatory or preliminary criminal phase and therefore cannot be discussed.

Laboratory fraud is an offense that can put all of the public at risk. The disturbing rise in violations of this nature makes it important to underscore the severity of the offense and the ramifications imposed on the offender.

In a press release issued June 9, 2005, Attorney General Peg Lautenschlager stated, "Waste water treatment plant records must be reported accurately and honestly for the sake of our citizens' health and the quality of our clean water." "Falsifying such records puts us all at risk", Lautenschlager said.

In that press release, Lautenschlager said that James L. Bradley, of Green Lake, was charged with submitting false information on reports required to be filed with the DNR concerning the level of pollutants in waste water discharged by the City of Green Lake Waste Water Treatment Plant. Bradley was the operator of the waste water treatment plant at the time the false reports were filed.

According to the state's complaint, Bradley, in 14 monthly reports filed between December 2002 and December 2003, falsified required waste water testing analytical results on reports submitted to the DNR. The reports included fictitious required test results on waste water discharged from the plant during certain months when in fact no such testing occurred.

The City of Green Lake operates its own lab out of its wastewater treatment plant. James L. Bradley was the former operator. In September 2005, he was prosecuted for falsification of monthly Discharge Monitoring Reports (DMRs). During the investigation phase, DNR enforcement staff determined that Mr. Bradley wasn't performing some of the laboratory tests and simply made up some of the data. He was subsequently fined $15,000 and the Department revoked all wastewater certifications. In addition, Mr. Bradley lost his employment with the City of Green Lake.

During interviews, when questioned about his rationale behind the decision to falsify results, Mr. Bradley said that he began falsifying the results because he was too busy to perform the analysis because of dealing with personnel issues with employees that he supervised as well as dealing with the rest of his responsibilities as the Public Works Director.

While the consequences of this case may seem severe, they could have been even worse. It's critical for anyone analyzing environmental samples for regulatory compliance — whether an operator in a wastewater treatment plant lab, or a technician in a major commercial laboratory— to understand that falsification is never the answer. No matter how much pressure is on you, you must speak up and let someone know that there are too many priorities and not enough time. You will get caught eventually, whether it's by an auditor from the LabCert program or a basin engineer. Most of these analyses are inter-related and a trained eye can easily detect abnormal trends. The consequences are far to great for falsification to ever be an option. 🕮

Lab-of-the-Year Candidates Needed

By Camille Johnson

Yes, it's that time of year already – we are looking for your nominations for the 2006 Lab of the Year Award! Anyone can nominate a laboratory except the facility themselves. The hard work that goes on in most labs is often overlooked by many of us, but it serves numerous important functions. If you know of a registered lab that deserves some recognition, please consider nominating them.

One award is presented in each of two categories: Small Registered Facility and Large Registered Facility. Small facilities include municipal wastewater treatment laboratories with a flow of less than 1 mgd, or labs that perform limited types of testing (e.g., BOD, nitrogen, phosphorus, and solids). Large facilities may include major municipal wastewater treatment laboratories with flows greater than 1 mgd, or labs that perform tests of greater complexity (e.g., metals, PCBs, VOCs). Nominees for the award must be ***registered*** facilities located in the State of Wisconsin. Certified laboratories will not be considered.

There is no limit on the number of times that a laboratory may be nominated, and a laboratory may be nominated for (or receive) an award in consecutive years. In the event that insufficient nominations are received for either category, the Department reserves the right to not issue either award. Nominations are due by January 15, 2005. For a nomination form or more information please contact: Camille Johnson at (715) 831-3272 or Camille.Johnson@dnr.state.wi.us

Proficiency Testing

WSLH Proficiency Testing Update

By Barb Burmeister

Acceptance Criteria Update

As of June 1, 2005, the Wisconsin State Laboratory of Hygiene Proficiency Testing (WSLH PT) Program revised the environmental PT acceptance criteria to be consistent with other Wisconsin-approved PT providers. Historically, WSLH PT has used the following procedure for calculating acceptable ranges:

> Outlying results are removed using a 3-step protocol. The protocol consists of two 3 SD passes followed by a modified USGS fence calculation. The mean and standard deviation are then calculated. The lower and upper limits of the acceptable range are calculated using the mean ± 2.78 standard deviations for all analytes with ≥10 results.

The other Wisconsin-approved PT providers use acceptance criteria found in the USEPA NERL-Ci-0045 "*National Standards for Water Proficiency Testing Studies, Criteria Document*," December 30, 1998 and the NELAC Fields of Proficiency Testing tables, December 2004. These acceptance criteria were revised, became effective June 1, 2005 and are located on the NELAC website (www.epa.gov/nelac/). The lower and upper limits of the acceptable range are calculated using the assigned value and a regression equation. The mean & standard deviation are calculated using 4 regression factors (F1, F2, F3, F4):

> Mean = (True value x F1) + F2
> SD = (True value x F3) + F4
>
> The acceptable range is calculated using the mean and standard deviation:
>
> Potable water acceptable range = Mean ± 2.0 SD
> Non-potable acceptable range = Mean ± 3.0 SD

After reviewing comparison data, the change in acceptance criteria will have a minimal effect to laboratories participating in WSLH PT programs. If you have any questions regarding acceptance criteria, please contact Barb Burmeister, Environmental PT Coordinator at (800) 462-5261, ext. 107.

Now Available: Potable Water Blind Standards

Starting in 2006, WSLH PT is offering four quality assurance chemistry samples for potable water that will satisfy the quality control sample requirements of the USEPA *Manual for the Certification of Laboratories Analyzing Drinking Water*, Fifth Edition. These blind standard samples ship three times a year and include cyanide, metals, minerals and nitrite at potable water concentration ranges.

As with the blind standards for non-potable water, the analytes contained in each sample are identical to the analytes found in the corresponding reference sample. See the list in the 2006 WSLH PT Environmental catalog or on the WSLH PT website (www.wslhpt.org) for the analytes specific to each sample.

Council Corner

By Paul Junio, Council Chair

All things must change (or nothing is constant except change). Next June marks the end of 6 years serving on the Laboratory Certification Council for George Bowman, Marcia Kuehl, and me. We'll all be cycling off the Council then. While there will be another LabNotes published between then and now, I won't be the Council Chair at that point, so I'll say my good-byes now.

I'd like to thank the Council members with whom I served (and hope that I don't miss anyone): George Bowman, Debbie Cawley, Katie Edgington, Randy Herwig, Steve Jossart, Jim Kinscher, Kurt Knuth, Dave Kollakowsky, Marcia Kuehl, Ruth Klee Marx, and Gilbert Williams. I'd also like to thank all of the DNR staff who have been involved: Brenda Howald, Diane Drinkman, Rick Mealy, Greg Pils, Alfredo Sotomayor, Phil Spranger, Jack Sullivan, and David Webb.

As we rotate off of the Council, this allows for new voices to be heard, not that you can't already do that by attending our meetings. So, if you'd like to be one of those voices by filling an upcoming vacancy, feel free to contact me.

So long until the next Council meeting!

Current Council Members

Representation	Name	Phone # / e-mail
Commercial Laboratory	Paul Junio ***(Chair)***	(920) 261-1660 PJunio@testamericainc.com
State Laboratory of Hygiene	George Bowman ***(Vice Chair)***	(608) 224-6279 gtb@mail.slh.wisc.edu
Demonstrated Interest in Lab Certification	Marcia A. Kuehl ***(Secretary)***	(920) 469-9113 makuehl@aol.com
Public Water Utility	Katie Edgington	(608) 755-3115 edgingtonk@ci.janesville.wi.us
Small Municipal Wastewater Plant	Randy Herwig	(608) 592-3247 rherwig@wppisys.org
Industrial Laboratory	Steve Jossart	(920) 438-2898 steve.jossart@gapac.com
Large Municipal Wastewater Plant	Kurt Knuth	(608)222-1201 x293 kurtk@madsewer.org

Drinking Water

Electronic Reporting Will Be Required in 2006

By Gail North (WDNR)

The Public Drinking Water Program in the Bureau of Drinking Water and Groundwater is moving forward with mandatory electronic reporting of all laboratory analytical results for sampling required under the Safe Drinking Water Act (SDWA). Our goal is to have all SDWA analytical results reported electronically by January 1, 2006. Per Chapter NR809, Wis Adm Code, laboratories are responsible for reporting these results directly to the DNR.

The good news is that the majority of labs have already met that goal. The DNR's web data entry form became available in July 2005 and a large number of labs immediately took that opportunity to begin reporting electronically. Within the first two months, DNR received almost 4000 samples via the web form. Very few problems were encountered and most labs reported that they found the form to be straightforward and easy to use. Other labs have created a process to transfer files of sample results directly to DNR. Between July 1 and November 30, 2005, approximately 80% of the SDWA samples were reported via one of these electronic means.

Whichever route your laboratory chooses to follow, whether it's the web data entry form or a file transfer process, all SDWA samples need to be submitted electronically as of January 1, 2006.

If you would like more information, please visit http://www.dnr.state.wi.us/org/water/dwg/ereport.htm

You can also contact Gail North at (608) 264-6131 or gail.north@dnr.state.wi.us .

Certification Required to Analyze Sodium in Drinking Water

Just a brief reminder to laboratories that certification under test category 18 (Drinking Water) for sodium is required to perform testing for sodium on drinking water samples. Many people incorrectly assume that since sodium is not a "primary" contaminant, and has no MCL, that certification is not required.

Wastewater

EPA Proposes Tests for 4 Types of Bacteria in Wastewater & BioSolids

(from the Region V "Quality Assurance Update" Vol. 10. No. 4 September 2005.)

The United States Environmental Protection Agency (EPA) published a Federal Register Proposed Rule entitled, "Guidelines Establishing Test Procedures for the Analysis of Pollutants; Analytical Methods for Biological Pollutants in Wastewater and Sewage Sludge" on August 16, 2005 [70 FR 482561].

With this notice, EPA is proposing new methods that use culture-based approaches to detect enterococci and Escherichia coli (E. coli) in wastewater. Additional tests will also identify Salmonella and fecal coliform bacteria in sewage sludge. This proposed regulation would amend the "Guidelines Establishing Test Procedures for the Analysis of Pollutants" under section 304(h) of the Clean Water Act (CWA), by adding analytical test procedures for enumerating the bacteria, *Escherichia coli* (E. *coli*) and enterococci, in wastewater; and by adding analytical test procedures for enumerating fecal coliforms and Salmonella in sewage sludge to the list of Agency-approved methods. Specifically, EPA is proposing both membrane filter (MF) and multiple-tube fermentation (MTF, i.e., multiple-tube, multiple-well) methods for E. coli and enterococci bacteria in wastewater, and MTF methods for fecal coliforms and Salmonella in sewage sludge. EPA's approval of these methods will help Regions, States, communities, and environmental laboratories better assess public health risks from microbiological pollutants**.**

EPA is seeking comment on the technical merit of these methods and their applicability to monitoring under the Clean Water Act. EPA is also asking stakeholders to suggest any other test methods for these pollutants that would be useful for monitoring in wastewater or sewage sludge. The comment period closed on October 17, 2005. The complete document of this proposed rule can be browsed or downloaded from the EPA website at: www.epa.gov/waterscience/methods or www.epa.gov/fedrgstr/EPA-WATER/2005/August/Day-16/w16195.pdf.

Interim Guidance for Bacteria and WPDES Permits

The following information was condensed from information received from Toni Glymph, DNR Bureau of Watershed Management

If your permit is coming up for review, the Department is moving forward according to the following guidance:

Effluent Monitoring

For Municipal Facilities: If the determination has been made that disinfection is required for a municipal facility in accordance with NR 210.06(3), monitoring for both fecal coliforms and E. coli should be included in the permit.

For Industrial Facilities: The recent detection of E. coli in industrial wastewater discharges that do not contain sanitary wastewater has prompted the need to perform an initial screening for bacteria during the permit application process. Permit applications should request both E. coli and fecal coliform sampling including at least 5 samples collected evenly spaced apart within a 30-day period. If the results of samples collected during the application exceeds the geometric mean specified in Table 2 (*see page 11*), the determination for monitoring and/or limitations will be made on a case-by-case basis.

Effluent Limitations:

In the absence of a full recreational use assessment, facilities with outfalls located within a 5-mile radius of a designated beach area should meet the ambient water criteria of 126 cfu/100mL as an effluent limitation for E. coli at the end of pipe. Links to County maps identifying all designated Great Lakes beaches can be found in the left margin at the following location: http://dnr.wi.gov/org/water/wm/wqs/beaches/index.html.

In the interim, all other permittees that discharge directly to Lake Michigan and Lake Superior should include 206 cfu/100mL as an effluent limitation for E. coli at the end of pipe.

Disinfection Requirements

Year round disinfection is required to protect drinking water supplies. Great Lakes dischargers with permits that currently contain requirements to disinfect year round should continue to do so. If year round disinfection is not required see NR 210.06(3) to determine if year round disinfection should be included in the permit.

Analytical Test Methods

NR 219.04 Table A contains a list of state approved biological test procedures for bacteria. Table 1 (below) identifies test methods may be used for enumerating E. coli in the wastewater effluent. For more information, please contact Toni Glymph at (608) 264-8954 or toni.glymph@dnr.state.wi.us.

Table 1: Test methods allowed for enumerating E. coli in wastewater effluent

Method Sponsor	Method	Method Name	Method Type
Standard Methods	9221 B.1	LTB – EC MUG	MPN
Standard Methods	9221 F	LTB – EC MUG	Direct Count
Standard Methods	9223 B [1]	Colilert ®; Colilert-18®	MPN
Standard Methods	9213 D	MColiBlue24	Direct Count
EPA	1103.1	mTEC	Direct Count
EPA	1603	Modified mTEC	Direct Count
EPA	1604	MI Medium	Direct Count

[1] This test method may yield significantly higher results when used with effluents that have been disinfected using chlorine.

Table 2: Applicable Effluent limitations

Category	Indicator	Distance	Geometric Mean	Maximum
Great Lakes[1]	**Fecal Coliform**		200 cfu/100mL	400 cfu/100mL[4]
	E. coli	< 5 mile radius	126 cfu/100mL[2A]	235 cfu/100mL[3]
	E. coli	> 5 mile radius	206 cfu/100mL[2B]	235 cfu/100mL[3]
Inland Waters	**Fecal Coliform**	----------	200 cfu/100mL	400 cfu/100mL[4]

[1]Great Lakes includes all open waters of Lake Michigan and Lake Superior, but explicitly excludes "inland waters or waters upstream of the mouth of a river or stream having an unimpaired natural connection with the open sea."

[2]The geometric mean criterion applies to beach areas designated as "frequent use."
[A] Criterion based on a risk level of swimmer illness of 8 per 1000. [B] Criterion based on a risk level of 10 per 1000

[3]The single sample maximum criterion for *E. coli* is applicable for use in beach closure or advisory decisions only.

[4] This maximum criterion shall not be exceeded in more than 10% of the samples collected during any month.

Wastewater Samples: Reconciling Sample Date and Holding Time

By Rick Mealy

ACME Laboratories receives a wastewater effluent sample from Pinebluff WWTP on Wednesday December 14, 2005. The sample bottle says the sample date is Monday, December 12, but the chain-of-custody form indicates the sample was collected at 07:00 am on Tuesday the 13th. The sample receipt clerk sounds the alarm to report that the discrepancy means that the 48 hour holding time for BOD may have been exceeded. Sound familiar???

This question comes up frequently and can be explained fairly easily. Wastewater effluent (and influent samples) are 24-hour composite samples, therefore, unless the sampler is started (and sample removed) exactly at midnight, the sample is collected over 2 days.

The sample DATE (for DMR reporting purposes) is the date on which most of the sample was collected. Most wastewater operators work 7:00am – 3:30 pm shifts. The first task of the day is to get the sample from the autosampler, which means the sample consists of 17 hours from the previous day (7:00 am to midnight) and 7 hours from the current day (midnight to 7:00 am). Using ACME Labs' scenario, this is how it plays out:

- Monday 12/12/2005: Start up autosampler 7:00 am
- Tuesday 12/13/2005: MONDAY Dec 12 sample is pulled from the autosampler. Collection date is 12/13/2005. Holding time begins now.
- Wednesday 12/14/2005: MONDAY's sample arrives at lab. The lab has 24 hours to get the BOD sample prepped and in the incubator to meet the holding time. Holding time is 48 hours from the END of compositing period.

Bottom line: the results for the sample collected on Tuesday 12/13/2005 get reported as the sample results for Monday 12/12/2005.

Solid Waste

NR 700 Rule Revisions

The Natural Resources Board (NRB) has approved a request to proceed with numerous limited changes to the NR 700 series of administrative rules, *Investigation and Remediation of Environmental Contamination*. This is a rule "clean up" proposal, intended to ensure that our rules remain internally consistent, consistent with statutes and consistent with current practices. The next steps in rule making will be to:

- Prepare the first "green sheet" for approval by the NRB. This will contain the actual changes proposed for rule language. The NRB will also establish the public hearing schedule at this time. ***Plans are to go to the Board as soon as code language is finalized.***
- Conduct hearings and accept written comments during the public comment period.
- Prepare the second "green sheet" to propose the final draft language for the rule. This will include a response to public comments and a fiscal estimate.
- The NRB will then decide whether or not to approve the final draft rule language. If approved, the proposed changes are sent to legislative committees in the Assembly and Senate.
- The legislative committees then decide whether to hold their own hearings on the rule changes. If no legislative hearings are held, the rules are approved as written and become effective when published by the state Revisor of Statutes. Legislative committees may approve the rules as written or send them back to the agency for revision.

The following is a summary of the proposed rule changes affecting analytical procedures:

- Eliminate the gasoline range organic & diesel range organic (GRO/DRO) standards for disposal and land-spreading of petroleum contaminated soil, and for closure approval. Instead, rely on standards for specific contaminants of concern such as benzene (VOCs) and PAHs. Consider retaining the DRO standard for hydraulic fluids, where specific compounds don't show up in analytic scans.
- Eliminate the soil sampling product names contained in NR 700. Eliminating names associated with soil sampling devices and preservation/storage techniques, opens the door for allowing alternate devices
- Allow the SW-846-5035 method for preservation of soil samples. The proposal would allow the use of SW-846 method 5035 for analyzing VOCs in soil. This change would not replace existing methods, but will offer the use of method 5035 as well.
- Change the level at which volatile organic compound and petroleum volatile organic compound (VOC/PVOC) contamination must be reported to DNR to the level at which these contaminants can be detected, rather than the limit at which they can be quantified. Currently a reporting limit of 25 ppb is required for VOCs in soil. This rule change would require labs to report individual VOC analytes down to the respective LOD, as required under s. NR 149.15.
- Consider adding sampling holding time limits for certain metals and other contaminants.
- Move all the analytical requirements to one location within the rules.

For more information, contact Jane Lemcke, Bureau of Remediation and Redevelopment, at (608) 267-0554) or visit the website:

www.dnr.state.wi.us/org/aw/rr/wi_regs/pending_nr700_rule_changes.pdf.

General Interest

Monitoring Reagent Water Quality

By Rick Mealy and
George Bowman (WI State Lab of Hygiene)

We all know that ASTM has established a standard for reagent water quality, but how many have actually read ASTM Standard D-1193? Be honest, you haven't either, have you? I'm certain you've seen a table of "ASTM" requirements for reagent water, but it's considerably more likely that you found that table in some other publication (e.g., Standard Methods, EPA publications) than from the original ASTM document.

ASTM D-1193: The Myth

There **is** a table included in ASTM Method D-1193, but what there **is no** reference within the text of the procedure that relates back to the table. In fact, if one were to delete the table, the text of the procedure would still read clearly and make perfect sense. Unlike standard technical writing protocol, the table everyone is so familiar with carries no label or numbering. Other than the seemingly misplaced table, the standard could be described as a set of procedures to be followed to obtain water of a specific purity.

Monitoring "Requirements"

At least having seen a table purported to be taken from ASTM D-1193, you likely know that conductivity measurement is a "requirement", but did you know that the table suggests that monitoring of sodium, chloride, silica, and TOC are also critical. Actually the more important question is **why** these parameters are even included.

Conductivity

Measuring conductivity is absolutely an essentially tool with which to monitor water quality. Unfortunately, the conductivity measurement "requirements" listed in ASTM D-1193 simply are not realistically achievable with conventional laboratory conductivity instrumentation. Even if a lab were to use a conductivity probe with a more appropriate cell constant (0.1 or 0.01), the fact is that one cannot accurately measure conductivity of high purity water in an "open" system. The concentration of carbon dioxide (CO_2) in the atmosphere is such that pure water will rapidly absorb CO_2. At this point carbonate chemistry comes into play. Sparing you the boring details, the bottom line is that reactions associated with carbonate chemistry result in the conversion of CO_2 to bicarbonate (HCO_3^-). Bicarbonate is an ion, and the introduction of dissolved ions means an increase in conductivity. Upon reaching equilibrium with air, the conductivity of pure water has been scientifically demonstrated to exceed 0.7 µS/cm. This means that meeting the conductivity requirements of ASTM Type 1 and III is not possible and even Type II water becomes a challenge.

ASTM Standard D1193

Limit	Type I	Type II	Type III	Type IV
Conductivity, max, uS/cm [*resistivity, MOhms*] at 25°C	**0.056** [*18.2*]	1.0 [*10*]	0.25 [*4*]	**5.0** [*0.2*]
pH at 298 K (25°C)	[A]	[A]	[A]	**5.0 to 8.0**
Total organic carbon (**TOC**), max, ug/L	**50**	50	200	n/a
Sodium, max, ug/L	1	5	10	**50**
Chlorides max, ug/L	1	5	10	**50**
Total silica, max, ug/L	**3**	**3**	500	n/a

[A] The measurement of pH in Type I, II, and III reagent waters has been eliminated from this specification because these grades of water do not contain constituents in sufficient quantity to significantly alter the pH.

Try it yourself: take a sample of purified reagent water from your system. Insert the conductivity probe and a magnetic star bar. Keep the solution stirring to ensure fresh solution comes in contact with the probe, but without generating a vortex. Turn the meter to "READ" and once it stabilizes, take and hold in a deep breath and then blow it out across the surface of the beaker. You should see a rapid increase in conductivity as the CO_2 reacts with the water.

Bottom Line on Conductivity

The only way to accurately measure the conductivity of reagent water is to use a flow-through system that is closed from the atmosphere. If your water system does not have a built-in conductivity monitoring device, consider having one installed. If your reagent water system does have built-in flow through conductivity device, we recommend that you record the daily conductivity measurements in a logbook,. Use these data to track performance of the ion exchange cartridges and to determine when the maintenance is required.

Sodium? Chloride?

There are two concerns with sodium and chloride being listed in the ASTM table. First, since conductivity will indirectly measure dissolved concentrations of these parameters, isn't this a redundancy? In addition, the maximum levels for sodium and chloride associated with Type I and Type II represent values well below the detection capability of current instrumentation.

Continued on next page.

***Reagent Water Monitoring**; continued from pg. 13*

A little research explains the levels of these two parameters and why they might be appear in the table. Interestingly enough, it turns out that 1 ppb of NaCl dissolved in pure water will increase the conductivity from 0.055 to 0.057 uS/cm at 25 °C. In other words, 1 ppb of sodium chloride dissolved in pure water will increase the conductivity just enough to exceed the criteria (0.056 uS/cm) for Type I water. Since we've already established that it is not realistically feasible for labs to measure conductivity at these levels, there is no need to monitor these parameters

Total Silica?

Recently, Dr. Erich L. Gibbs, a member of the ASTM D19 (Water) committee and president of a water purification instrumentation firm inquired about the need for silica in this table. He conducted both a search of over 20,000 journals and an international e-mail poll of 23,000 other bio-scientists asking the question, "Is silica contamination a source of non-specific interference in laboratory applications?"

The bottom line is that while the presence of silica may be an early indicator of the failure of mixed bed ion-exchange columns, conductivity remains a better measure of system performance.

Total Organic Carbon (TOC)

This one **does** make sense. TOC actually replaced the original permanganate 60 minute color retention time test in the 1991 update to D1193. Measuring conductivity will not tell you if organic contamination is present which can interfere with many analyses, including BOD. In fact, up to 1000 ug/L of sugar can be added to a water system before the conductivity maximum for ASTM Type I is exceeded. Organics Organics can leach from ion exchange resin, can cross ion-exchange systems, and even pass through exhausted carbon filters. . Labs may wish to check their reagent water for TOC if they are having problems with high BOD blanks.

What does this mean for Audits?

The LabCert Program has made an internal decision to not cite labs for failing to verify the quality of laboratory reagent water (with an external method), or to calibrate in-line conductivity meters. Auditors will want to see that you have a system in place to evaluate the suitability of your reagent water for intended use. Obviously, that will mean different things for different labs; work with your auditor.

ICP & Single-point calibration

By Rick Mealy and
George Bowman (WI State Lab of Hygiene)

Ever since the early 80's, when ICP emission technology came into vogue in environmental analysis, the calibration protocol has been subject to great debate. The wonder of the ICP was a single instrument could simultaneously quantitate 24 or more elements, at concentrations spanning four (4) or more orders of magnitude. All this capability was based on calibration using a blank and a single "high-level" standard for each element. At that time, and yet today, other than electrometric techniques that are bound by the laws of the Nernst equation, multi-point calibration was the rule for virtually all analytical techniques. The logical question was: why should ICP be any different?

It takes a great deal of restraint not to answer that question with, "Because that's the way it is". We **could** talk about plasma physics and the chemistry of the technology. We **could** point out the phenomenal temperatures (8,000-10,000 °C)—that's equivalent to the temperature of the sun's surface, folks—at which the elements are analyzed and discuss the complete absence of physical or chemical interferences that contribute to the extreme linearity. Or….we could demonstrate the point with real data.

In 2003, as part of an ICP training workshop, the Wisconsin State Laboratory of Hygiene produced a set of data that demonstrated the superiority of using a single-point calibration over multi-point calibration for ICP. That was nice, but it was generated with a relatively old fixed-wavelength polychromator system in an ICP world that is now heavily populated with instruments equipped with solid state detector systems and dual view technology. This of course generated the question, "Is it possible that multi-point calibration is more appropriate (than single point calibration) with solid state detection and dual view technology?"

Two years later, the State Laboratory of Hygiene has since purchased a state-of-the-art, solid state detection, "dual-view" ICP instrument. To answer the calibration question once and for all, the metals chemists at the Wisconsin State Lab of Hygiene designed a study to compare the effectiveness of single-point calibration vs. multi-point calibration.

The following calibration approaches were used:

1. Single point: A blank and a single, upper level standard (1 blank & 4 standard solutions)

Continued on next page.

***ICP Calibration**; continued from pg. 13*

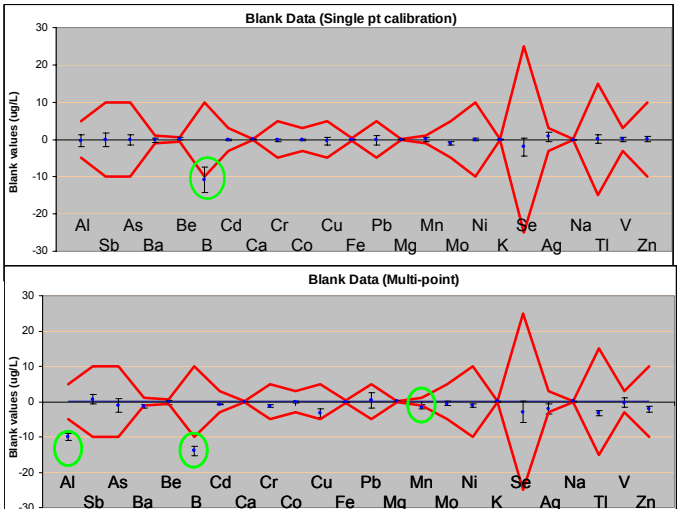
2. Multipoint: A blank, a LOQ level, mid-level and upper level standard (A blank & 12 standard solutions)

After calibrating the instrument using a blank and a single, upper level standard, the chemists analyzed:

- 7 replicates of a calibration blank (Figs. 1 &2)
- 7 replicates of the ICS-A standard, which contained 200 ppm each of interferents Ca and Na, 100 ppm of Mg, and 20 ppm each of Fe and K. (*Theoretically equal to a blank for all non-interferent elements*)
- 7 replicates of an "LOQ standard", containing each of 24 elements at a concentration approximately equal to their respective LOQ (Table1)
- 7 replicates of an IPC standard (Instrument Performance Check) containing all 24 elements at 100, 250, 500, or 1000 ppb.
- 7 replicates of a QC standard (QCS), containing all 24 elements at 80 - 1000 ppb.

Here's what the data show:

- Blanks should fall within ± the LOD
- The single point calibration data (Fig. 1) show that all but one element (B) are within + the LOD while 3 elements (Al, B & Mn) were outside the limit for the multipoint calibration.
- LOQ data (Table 1) show a mean recovery of 98.6% (70.5-116.1%) for the single point calibration and a mean of 90.8% (44.1-121.9%)



Comparison of blank analysis using single-point (top) and multipoint calibration. *The dark lines on the graph enclose a range of ± LOD for each element. The average result, including 3-sigma error bar is plotted.*

for the multipoint calibration.

- Only 3 standards required for the 1-point calibration; 12 for the multipoint calibration
- Performance on the IPC and QC standards was similar for both calibration approaches.

As a result of these efforts, it is clear that both calibration approaches have been shown to work. On closer examination, however, the nod has to be given to single-point calibration. The reason for this is the better demonstration of control at low levels (blanks, ICS-A, LOQ standard). Not only is there better accuracy at low concentrations using single-point calibration, (*see below*) but better precision as well. Consequently single-point calibration is the more economical (time and money).

****

The following table summarizes mean recovery from the analysis of seven (7) replicates of a standard prepared to contain each element at a concentration approximating the LOQ. The sample was analyzed seven (7) times following single point calibration and then seven (7) times following multipoint calibration.

		LOQ sample results	
	LOQ	1 pt	multi-pt
Analyte λ	µg/L	%R	%R
Axial elements (µg/L)----------			
Al 396.153	15	104.8%	44.1%
Sb 206.836	30	98.7%	103.0%
As 188.982	30	95.7%	97.2%
Ba 233.525	3	107.5%	66.3%
Be 313.042	1.5	116.1%	94.9%
B 249.772	30	70.5%	70.6%
Cd 228.802	9	99.3%	94.4%
Cr 205.560	15	102.7%	97.3%
Co 228.615	9	101.4%	101.6%
Cu 327.399	15	94.6%	77.4%
Pb 220.353	15	104.3%	109.0%
Mn 257.608	3	99.8%	48.0%
Mo 202.032	15	96.1%	99.3%
Ni 231.606	30	99.0%	96.9%
Se 196.025	75	100.6%	99.8%
Ag 338.289	9	102.7%	79.2%
Tl 190.793l	45	100.5%	91.8%
V 292.402	9	102.8%	103.3%
Zn 206.198	30	100.1%	97.4%
Radial elements (mg/L)----------			
Ca 317.993	0.3	103.3%	81.8%
Fe 238.203	0.9	103.7%	102.1%
Mg 279.075	*0.3*	*101.1%*	*121.9%*
K 766.475	*0.3*	*82.7%*	*103.1%*
Na 589.592	*0.3*	*77.5%*	*98.7%*
	Mean	**98.6%**	**90.8%**
	Min	**70.5%**	**44.1%**
	Max	**116.1%**	**121.9%**

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