

WISCONSIN DEPARTMENT OF NATURAL RESOURCES

Laboratory Accreditation Program

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2.9.23 | DNR.WI.GOV



TOPICS

1. *Laboratory Accreditation Program Background*
2. *Hach Method 10206*
3. *Becoming a WI DNR Accredited Laboratory*
4. *Program Communications*
5. *Bacteria Testing for Municipal WWTF*

- *DNR groundwater (GW) staff / WI legislators*
- *Protect GW*
- *1983 – Laboratory accreditation law*
- *1986 – first rule completed: NR 149*

- *Establish minimum testing requirements*
- *Help increase likelihood that data received was defensible and high quality*
- *Allow DNR to make sound environmental decisions*

- *330 Labs*
- *146 Certified; 186 Registered*
- *199 Municipal WWTF*
- *64 Commercial*
- *39 Industrial WWTF*
- *21 Public health*
- *6 Hazardous waste TSD*
- *1 Public water system*

2022 DW LAB ACCREDITATION STAFF

**Steve
Geis**

**Brandy
Baker-
Muhich**

**Autumn
Farrell**

**Janelle
Nehs**

**Tom
Trainor**

- *Work with stakeholders to update minimum requirements*
- *Perform evaluations to assess compliance*
- *Explain code and method requirements*
- *Provide technical assistance*
- *Provide example forms, spreadsheets, technical information*

HACH Method 10206: Nitrate by Colorimetry

- This method **cannot** be used for nitrite certification.
- This method can be used for certification of nitrate (on unpreserved samples) and “nitrate + nitrite” (on preserved samples).
- The approved version is January 2011, Rev 2.0.

Hach Company TNTplus 835/836 Method 10206

Revision 2.0
January 2011

From 40 CFR 141:

Nitrate	Ion Chromatography		4110 B	4110 B	4110 B		D 4327-11, -17	
	Automated Cadmium Reduction		4500-NO ₃ ⁻ F	4500-NO ₃ ⁻ F	4500-NO ₃ ⁻ F			
	Manual Cadmium Reduction		4500-NO ₃ ⁻ E	4500-NO ₃ ⁻ E	4500-NO ₃ ⁻ E			
	Ion Selective Electrode		4500-NO ₃ ⁻ D	4500-NO ₃ ⁻ D	4500-NO ₃ ⁻ D			
	Reduction/Colorimetric							Systema Easy (1-Reagent). ⁸ NECi Nitrate-Reductase. ⁴⁰
	Colorimetric; Direct							Hach TNTplus™ 835/836 Method 10206. ²³
	Capillary Ion Electrophoresis						D 6508-15	

HACH Method 10206: Nitrate by Colorimetry

- TNT 835 vials = 0.2 – 13.5 mg/L
- Analyze room temperature
- Unpreserved sample holding time 48 hours
- Sulfuric acid preserved sample holding time 28 days

HACH Method 10206: Nitrate by Colorimetry

- Acid preserved samples must be neutralized to pH 7 before adding Solution A
- Use 1 mL sample with TNT 835
- Add 0.2 mL Solution A with TNT 835

HACH Method 10206: Nitrate by Colorimetry

- Factory programmed calibration curves not allowed.
- Zero spectrophotometer with reagent water before run starts (no Solution A).
- Include calibration blank (zero concentration standard treated same as other standards in curve; i.e., with Solution A) in curve.
- At least 3 non-zero concentration standards must be used in curve.
- A correlation coefficient ≥ 0.995 is required.

HACH Method 10206: Nitrate by Colorimetry

- ICV required after calibration curve analyzed.
- ICV from different source than standards in curve.
- ICV concentration typically midpoint of curve.
- ICV limits = 90 – 110%
- ICV not required on days when curve not analyzed.

HACH Method 10206: Nitrate by Colorimetry

- CCV required at beginning, after every 20 field samples, and at end.
- First CCV must be 0.3 mg/L or concentration lowest standard in curve.
- Other CCVs should be midpoint or higher concentration (w/i curve).
- CCV may be from same source as standards used in curve.
- CCV limits = 85 – 115%

HACH Method 10206: Nitrate by Colorimetry

- On non-curve days, each batch requires a minimum:



- Method blank required each analysis day and every 20 samples.
- Method blank limits = < LOD or < 0.5 (5%) of MCL
- LCS / OPR is same as CCV in method; therefore, additional QC sample not required.

HACH Method 10206: Nitrate by Colorimetry

- Matrix spike (MS) and matrix spike duplicate (MSD) are required each analysis day.
- MS limits = 85 – 115%
- MS/MSD RPD limits = 20%
- MDL study is required.

HACH Method 10206: Nitrate by Colorimetry

- Initial demonstration of capability (IDC per NR 149, IPR per 10206)
- Each analyst must pass IDC before performing analysis.
- Analyze 4 replicate standards at 5 mg/L or lower concentration.
- IDC/IPR limits:
 - average recovery = 90 - 110% (ideally each)
 - RSD \leq 10%
- Do not report any results with failed quality control, re-run samples.

HACH Method 10206: Nitrate by Colorimetry

Sample
Calibration Blank
Standard 1
Standard 2
Standard 3
Standard 4
Standard 5
Standard 6
Standard 7
Standard 8
ICV
CCV 1 (Low)
Method Blank

LCS/CCV 2 (med/high)

MS

MSD

Spiked Sample ID:

Steps to Become a Certified Lab

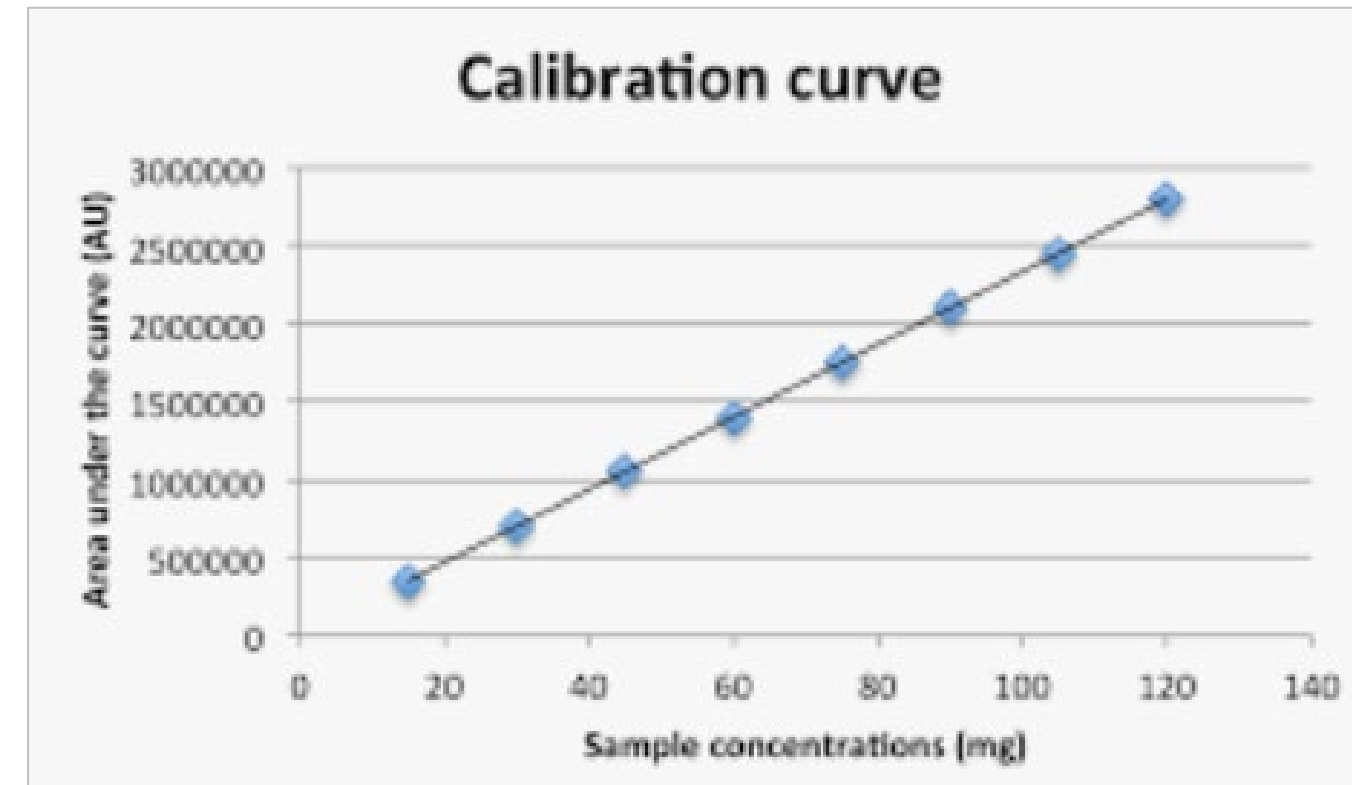
- Decide what tests to get certified for.
- Read pertinent sections NR 149 (Subchapter VII – Quality Systems).
https://docs.legis.wisconsin.gov/code/admin_code/nr/100/149.pdf
- Read pertinent sections SDWA Manual and supplements.
<https://www.epa.gov/dwlabcert/laboratory-certification-manual-drinking-water>
- Decide which approved method to follow (obtain and read it).

Steps to Become a Certified Lab

- Obtain instrumentation, reagents and standards.
- Create Standard Operating Procedure.
- Create Quality Assurance Manual.

Steps to Become a Certified Lab

- Perform calibration curve and ICV.
- Perform initial demonstration of capability.
- Perform initial MDL study.
- Perform WS PT.



Initial LOD/LOQ Calculation and Validation Worksheet (Single Instrument) Revised 10/13/20				
Facility:				
Analytical Method:		Calculation Date:		
Matrix: Wastewater		Calculation Analyst:		
Spiked Blanks				
	Date Prepped	Date Analyzed	Result	% Recovery
1				
2				
3				
4				
5				
6				
7				
8				
Spike Level:		mg/L		
Average:				
Standard Deviation:				
Student's t-value to use:				
Calculated LOD _s :		<7 Spk Blks	mg/L	
Method Blanks				
	Date Analyzed	Result		
1				
2				
3				
4				
5				
6				
7				
8				
Average:				
Standard Deviation:				
Student's t-value to use:				
Calculated LOD _b :		<7 MBs	mg/L	
Calculated LOD:		NA	mg/L	(calculated from the greater of LOD _s and LOD _b)
Calculated LOQ*:		NA	mg/L	(= 10/3 x LOD)

Steps to Become a Certified Lab

- Send application to Tom Trainor to review before cutting check.
- After Tom's comments, send in required materials.
 - Application form 4800-002, FEIN 9400-568, and attachment A3
 - Check for application costs.

<https://dnr.wisconsin.gov/topic/labCert/applications>

Steps to Become a Certified Lab

- Passing WS PT study (pdf from PT provider)
- Passing MDL study (summary data)
- Passing IDC study (summary data)
- Complete SOP and Quality Assurance Manual
- Calibration curve and analysis run raw data from IDC study

Steps to Become a Certified Lab

- Tom reviews materials submitted to determine if good.
- Tom informs assigned auditor they can review your data and schedule audit.
- Auditor performs audit and provides an audit report, if necessary.

Steps to Become a Certified Lab

- Once findings, if any, are resolved, auditor will let me know you are ready to be granted certification.
- Tom updates database to reflect new certification status.
- Tom sends certification documents.
- Thereafter, annual certification fees need to be paid and WS PTs passed.

Lab Accreditation Program Communications

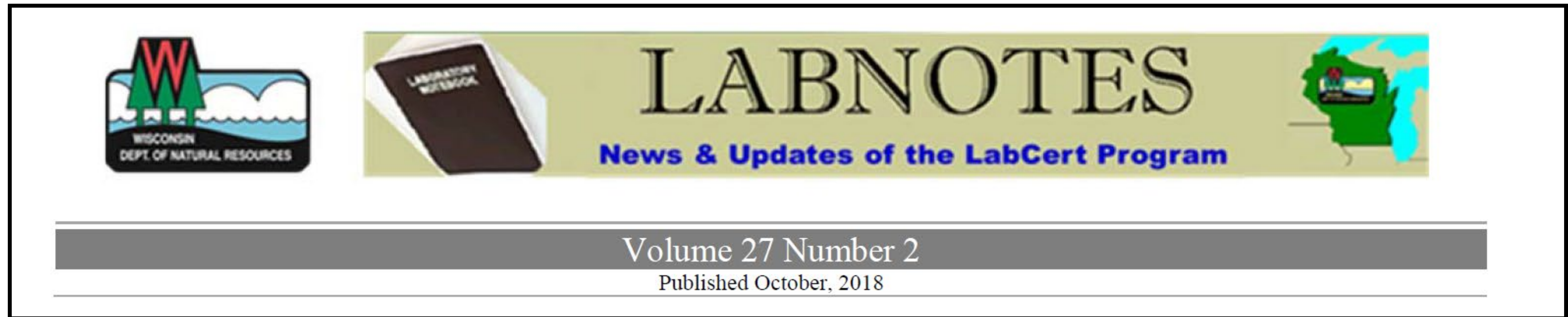
Question:

How does the Program keep labs up to date with the latest happenings?

Answer:

In many ways ...

In the old days:



Lab Accreditation Program Communications

Ways we communicate with labs now

- FAQ documents (2022 WW and DW PFAS)
- Bulletins (PFAS, NR 812 and NR 809 metals requirements, flashpoint PT requirements)
- Annual renewal emails
- GovDelivery
- Quarterly Lab Certification Standards Review Council meeting minutes
- Lab Accreditation website (presentations, documents, training, FAQ soon)

Lab Accreditations Program Communications

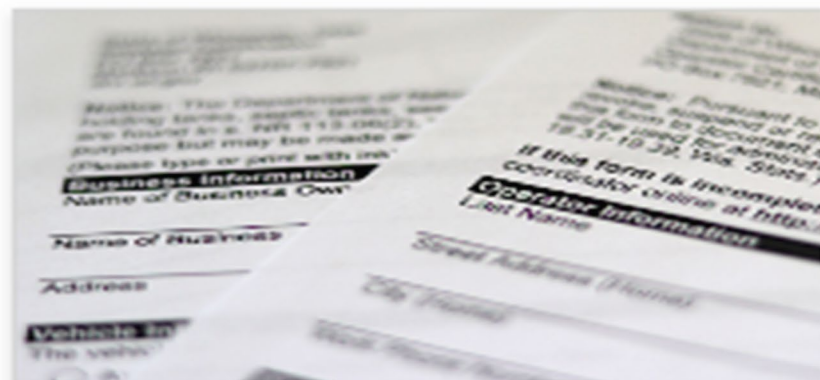
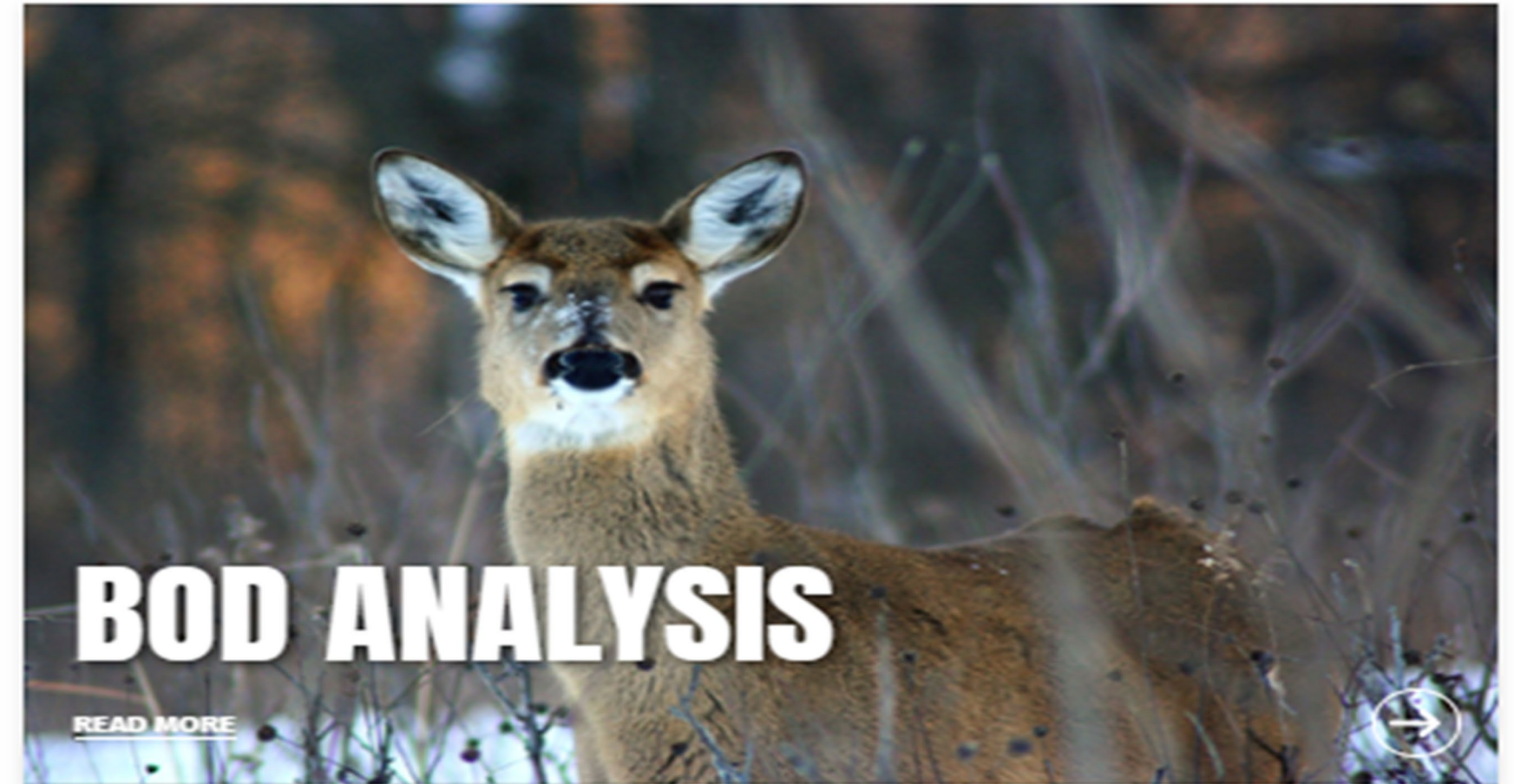
[Lab Accreditation Website](https://dnr.wisconsin.gov/topic/LabCert)

<https://dnr.wisconsin.gov/topic/LabCert>



Lab Accreditation Program Communications

[Lab Accreditation Website](#)



DOCUMENTS

Spreadsheets, forms, checklists and documents to help with laboratory testing



TRAINING

Information and resources related to performing laboratory testing



APPLICATIONS

Applications for registration and certification

Lab Accreditation Program Communications

[Lab Accreditation Website](#)

ANNUAL RENEWAL

Registration and certification requirements for annual renewal



PRIVATE WELLS

Information and resources for homeowners related to private well testing



LABORATORY STANDARDS REVIEW COUNCIL

Council meeting announcements and minutes



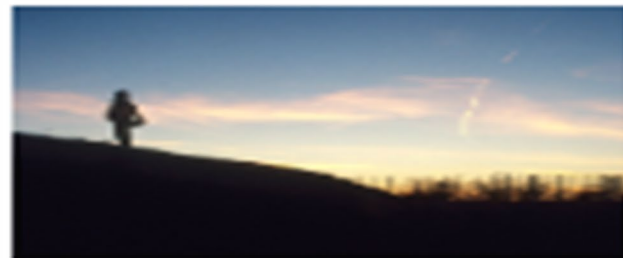
PROFICIENCY TESTING

Resources related to WI PT requirements



LAB OF THE YEAR

Past award winners and a description about the award



ANALYTE GROUPS

Information on which compounds are included in the analyte groups offered



ADDITIONAL RESOURCES



Lab Accreditation Program Communications

[GovDelivery](#)

<https://public.govdelivery.com/accounts/WIDNR/subscriber/new?preferences=true>

Receive emails from

widnr@service.govdelivery.com

WPDES Bacteria Testing for Municipal WWTF

- Fecal coliform and *E. coli* testing needed in wastewater (→ *E. coli*).
- Fecal coliform testing may be needed in sludge (not *E. coli*).
- Certification is not required for wastewater or sludge.
- Certification is required for drinking water.

WPDES Bacteria Testing for Municipal WWTF

- Busy time seasonal disinfection (May – September).
- Minor facilities need help as major facilities do themselves.
- Sampling requirements are weekly for minor facilities.
- 331 minor facilities

WPDES Bacteria Testing for Municipal WWTF

Approved Methods – NR 219

- Wastewater Fecal Coliform
 - MPN – EPA 1680, EPA 1681, SM 9221E-2014, SM 9221 F.2-2015
 - Membrane Filter (single step) – SM 9222D-2015
 - Multiple tube/Multiple well – Colilert-18
- Sludge Fecal Coliform
 - MPN – EPA 1680, EPA 1681, SM 9221E-2014
 - Membrane Filter (single step) – SM 9222D-2015

WPDES Bacteria Testing for Municipal WWTF

Approved Methods

- Wastewater *E. coli*
 - MPN – SM 9221E B.3-2014, SM 9221 F-2014
 - Membrane Filter (single step) – SM 9222B-2015, SM 9222I-2015
 - Multiple tube/Multiple well – Colilert, Colilert-18, SM 9223B-2016

WPDES bacteria testing for municipal WWTF

Number 1 Issue

Wastewater

Parameter Number/Name	Container ¹	Preservation ^{2,3}	Maximum Holding Time ⁴
Table A — Bacterial Tests			
1–5. Coliform, total, fecal and <i>E. coli</i>	PA, G	Cool, <10°C, 0.0008% Na ₂ S ₂ O ₃ ⁵	8 hours. ^{22,23}

WPDES bacteria testing for municipal WWTF

Laboratories That May Be Interested

- Bayfield County
- Iron County
- Madison/Dane County
- Rock County
- Walworth County
- Waukesha County
- Wood County

WPDES bacteria testing for municipal WWTF

To Facilities That May Be Interested

- Excel table that can be sent to interested labs
 - includes minor facilities and locations
- Labs can reach out to close ones to see if interested
- Expectation is that the municipality takes the samples and would drive them by car to your lab