

## Report From Agency

### REPORT TO LEGISLATURE

NR 219, Wis. Adm. Code

Board Order No. SS-16-08  
Clearinghouse Rule No. 08-076

#### Basis and Purpose of the Proposed Rule

On March 12, 2007, EPA published "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; National Primary Drinking Water Regulations; and National Secondary Drinking Water Regulations; Analysis and Sampling Procedures; Final Rule". In addition, on March 26th, 2007, "Guidelines Establishing Test Procedures for the Analysis of Pollutants; Analytical Methods for Biological Pollutants in Wastewater and Sewage Sludge; Final Rule" was published. In these final rules, EPA updated the approved analytical test methods to be used in the National Pollutant Discharge Elimination System (NPDES) program, which regulates discharges from industrial and municipal wastewater treatment facilities. Wisconsin must incorporate these changes to maintain delegated authority for the Clean Water Act.

#### **Summary of the rule**

The following provisions, changes and requirements are implanted through the proposed rules:

- 1) Sample Preservation Procedures:** The required temperature for sample preservation was updated throughout the chapter to less than or equal to 6°C, to be consistent with the updated federal requirements. The rule also clarified maximum holding times, addressed potential interferences, and extended holding times for specific analytes. Table F, Required Containers, Preservation Techniques, and Holding Time for Wastewater was repealed and recreated to incorporate additional modifications in federal rule.
- 2) Analytical Methods Tables:** The rule retained approximately 500 methods from the previous version, deleted 62 and incorporated 367 additional analytical methods in the following tables: Table A, List of Approved Biological Analytical Methods, Table B, List of Approved Inorganic Analytical Methods in Wastewater, Table C, List of Approved Analytical Methods for Non-Pesticide Organic Compounds, Table D, List of Approved Analytical Methods for Pesticides in Wastewater, Table E, List of Approved Radiological Analytical Methods for Wastewater and Table EM, List of Approved Analytical Methods for Sludge. The rule also removed analytical methods that utilized mercury-containing reagents.

The incorporated methods included those approved through the Office of Water's Alternative Test Procedure program, updated references from "2007 Annual Book of Standards" by ASTM, on-line and the 21<sup>st</sup> Edition of "standard Methods for the Examination of Water and Wastewater", "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, Updates III and IV", and several others developed by instrument manufacturers.

#### Summary of Public Comments

Hearing comments were categorized into three areas of concern: clarification and correction of approved

analytical methods, sample preservation and holding time, and other comments.

#### *Clarification and Correction of Approved Analytical Methods*

- **COMMENT:** Requested clarification regarding the use of the luminescence technique for Biochemical Oxygen Demand (BOD<sub>5</sub>) and Carbonaceous Biochemical Oxygen Demand (CBOD<sub>5</sub>) determinations.  
**RESPONSE:** Approved BOD methods direct laboratories to use methods for dissolved oxygen, to determine oxygen depletion. The approved methods for dissolved oxygen, parameter 47 in table B, includes three analytical technologies- Winkler (azide modification), electrode or luminescence. Laboratories may use any of these methods for the determination of dissolved oxygen during BOD and Carbonaceous BOD analyses.
- **COMMENT:** For Table B, parameter 21- color, why is 2120 E the only cited method versus 2120B or 2120D when comparing the 18-21<sup>st</sup> editions and on-line version of *Standard Methods for the Analysis of Water and Wastewater*.  
**RESPONSE:** For color analyses, EPA only identified *Standard Methods* 2120 B-01 as equivalent to approved methods in the Alternate Test Procedure approval. The on-line versions of methods 2120 C and 2120 E differ dramatically from those previously published in *Standard Methods*. Although EPA only approved a single on-line version, Table B includes thirteen additional approved methods for this parameter.
- **COMMENT:** The prior version of NR 219 included a separate table for metals digestions. The proposed revision drops that table and uses footnotes to address digestion. We find it confusing to determine whether our current practice for silver digestion is allowable under the draft NR 219. We ask that the language be changed to clarify and allow our current practice.  
**RESPONSE:** Metals digestion procedures are contained in Table EM of ch. NR 219. The department did not delete or modify the content of this table in this update effort. Table EM will be included, in the updated version of this chapter, unchanged, when rulemaking is completed. The intent of the footnotes in table B is that laboratories must use an alternative digestion if they anticipate silver concentrations in excess of 1 mg/L.
- **COMMENT:** On Page 14 – Parameter 25 – Fluoride. The ISE method is “C” not “B”. B is the distillation step.  
**RESPONSE:** The table has been corrected to read "4500-F C [18<sup>th</sup>, 19<sup>th</sup>, 20<sup>th</sup>, 21<sup>st</sup>] under the heading "Standard Methods".
- **COMMENT:** On Page 15 – Parameter 28 – pH. Standard method Online is missing a zero. It should read 4500- H<sup>+</sup> B-00.  
**RESPONSE:** The table has been corrected to read "4500- H<sup>+</sup> B-00 under the heading "Standard Methods Online".
- **COMMENT:** On Page 19 – Parameter 40 - Standard method Online is missing a zero. It should read 4500-NO<sub>2</sub> B-00.  
**RESPONSE:** The table has been corrected to read "4500- NO<sub>2</sub> B-00 under the heading "Standard Methods Online".
- **COMMENT:** Table EM appears to list ICP method citations under both EPA and Standard Methods columns for Gaseous Hydride.  
**RESPONSE:** The content of table EM has been corrected to indicate the only approved method for Selenium by Gaseous Hydride is Method 7471A, from "Test Methods for Evaluating Solid Water, Physical/Chemical Methods," SW-846, September 1994.

#### *Sample Preservation and Holding Times*

- **COMMENT:** Composite samples are required to be maintained at  $<6^{\circ}\text{C}$ , and sample temperature must be documented upon receipt by the laboratory. Although the intent of these statements is to ensure sample integrity during transport, we believe this requirement is unnecessary when samples are submitted to the laboratory within 15 minutes of collection and request the note be removed or modified. Our industrial facility's final effluent stream has a temperature of  $30\text{-}35^{\circ}\text{C}$  during the warmer months of the year and no amount of refrigeration will bring these samples to the required temperature within 15 minutes of collection. We believe that documenting that the composite samples and/or refrigerators are maintained at temperatures  $<4^{\circ}\text{C}$  should be sufficient.

**RESPONSE:** It would likely take several hours for your facility's composite sample to drop  $25^{\circ}\text{C}$  ( $\sim 50^{\circ}\text{F}$ ) or more to literally meet these temperature requirements. Provided that your composite samples are collected with a refrigerated autosampler and then either analyzed immediately or stored at  $\leq 6^{\circ}\text{C}$  upon arrival at the laboratory, they would be considered "properly preserved" under these requirements.

- **COMMENT:** Please provide guidance on priority when there are discrepancies between NR 149 and NR 219, such as the determination of sample temperature upon receipt, and to consider this when additional revision are made.

**RESPONSE:** Sample preservation procedures, specified as ss. NR 219.04(2) Wis Adm. Code require immediate cooling to  $\leq 6^{\circ}\text{C}$  after sample collection and that temperature be maintained during shipping. s. NR 219.04(3) Wis Adm. Code, requires that samples not cooled during collection be chilled to  $\leq 6^{\circ}\text{C}$  prior to shipping with a temperature blank.

The sample preservation and holding time requirements listed in s. NR 149.46(4)a, Wis. Adm. Code, establishes that sample preservation and hold time requirements identified in state or federal regulations take precedence over that contained in analytical methods or authoritative sources. The following subsection, b., specifies that samples are properly preserved if, they are either surrounded by ice or actual temperature of a sample, temperature blank or melt water in the shipping container is between  $0\text{-}6^{\circ}\text{C}$ . This language mirrors that contained in ch. NR 219, Wisc. Adm. Code. In addition, permittees may petition the EPA Region V Administrator for a variance from prescribed sample preservation procedures applicable to samples from a specific discharge. The WDNR Laboratory Certification Program may consider clarification of this issue in future revisions of ch. NR 149, Wis Adm. Code.

- **COMMENT:** The language contained in Footnote 6, Table F, which addresses required preservation for cyanide determinations is complex and confusing, especially when dealing with unknown samples. Please provide clarification and guidance on the proper procedures for preserving samples for cyanide.

**RESPONSE:** The language contained in footnotes 5 and 6, were expanded by EPA in the final federal rule, which was based on information gathered during the development of new cyanide methods approved in this rulemaking, and information collected from various commenters and experts in cyanide analyses. All samples for WPDES compliance must be screened for the presence of sulfide at the time of sample collection. Laboratories that perform WPDES-required cyanide analyses must either analyze samples that have been preserved to  $\text{pH}>12$  and  $\leq 6^{\circ}\text{C}$  within 48 hours or document that the presence and removal of all interferences have been carried out for those samples preserved to  $\text{pH}>12$  and  $\leq 6^{\circ}\text{C}$  and analyzed within 14 days. When reporting cyanide results, laboratories should identify any interferences that were removed after sampling or during analytical processes.

The department agrees issuance of guidance that explains interference screening and mitigation processes will develop such materials to assist the regulated community.

- **COMMENT:** I would suggest that all laboratories have a specific data qualifier for exceeding hold times of 15 minutes, or at a minimum have a disclaimer regarding holding times for specific laboratory tests or sample preparation steps.

**RESPONSE:** When field testing is performed after the hold time has been exceeded, these measurements cannot be used to demonstrate compliance with a permit. The only exception would be if a facility's permit specifies "Lab pH", which assumes that the data was not generated within 15 minutes of collection.

Samples that are not immediately analyzed must also be properly preserved. This includes addition of chemical preservatives or storage at  $\leq 6^{\circ}\text{C}$ . Many commercial laboratories provide pre-preserved sample containers to ensure proper preservation after sample is added. Samples that are shipped to external laboratories must also contain sufficient volume of ice to ensure sample temperatures do not exceed  $6^{\circ}\text{C}$  on arrival. When reporting results of samples that have been improperly preserved, data must be qualified.

The WDNR Laboratory Certification and Registration Program, in conjunction with the Watershed Management Permits Section, is developing guidance to more specifically address sample preservation and hold time requirements contained in chs. NR 219 and NR 149, Wis. Adm. Code.

- **COMMENT:** There should be some clarification under the information given in the maximum holding time column for parameter 45, orthophosphate, in table F.

**RESPONSE:** There are nine different forms of orthophosphorus identified in EPA Method 365.1. The requirement for filtration applies only to the determination of dissolved phosphorus species. The department agrees this content is confusing and clarified the intent with the addition of footnote 22, which reads: "Filtration is only required when reporting dissolved orthophosphate, dissolved hydrolyzable phosphorus or dissolved organic phosphorus as described in EPA Method 365.1 (1993). Filtration must be completed within 15 minutes of collection using a  $0.45\mu\text{m}$  filter; sample shall be maintained at  $\leq 6^{\circ}\text{C}$  and analyzed within 48 hours."

#### *Other Comments*

- **COMMENT:** There is only one methodology which is approved for the analysis of mercury in sludge samples, Cold Vapor Atomic Absorption Spectroscopy (CVAAS). EPA SW-846 Method 7474, which is specifically approved for the analysis of sediment and tissue samples uses a combination of microwave digestion, Bromide/Bromate oxidation and Cold Vapor Atomic Fluorescence Spectroscopy (CVAFS) for the determination of total mercury. We are providing data to substantiate the ability to recover mercury from a standard reference material certified by NIST. Please consider inclusion of this method for the analysis of mercury in sludge by CVAFS.  
**RESPONSE:** The department agrees that the fluorescence technique may be appropriate for sludges regulated under this chapter. The rigorous microwave digestion technique described in SW-846 Method 7474, when combined with fluorescence detection will result in data of similar quality to other currently approved analytical methods. Table EM has been modified to incorporate this addition.

- **COMMENT:** Analytical methods contained in *Standard Methods*, 18<sup>th</sup>, 19<sup>th</sup>, 20<sup>th</sup>, and 21<sup>st</sup> editions refer to sampling and handling preservation temperatures of  $4^{\circ}\text{C}$ . The temperatures listed in Table F, Required Containers, Preservation Techniques, and Holding Times lists  $\leq 6^{\circ}\text{C}$ . To avoid confusion between the analytical methods and Table F, we propose the following language be incorporated or referenced in NR 219.04: "Sample preservation procedures, container materials, and maximum allowable holding times for parameters are cited in Table F. Information in the table takes precedence over information in specific methods or elsewhere. Any person may apply for a variance from the prescribes preservation techniques, container materials and maximum holding times applicable to samples taken from a specific discharge. Applications for variances may be made by letters to the..."

**RESPONSE:** The hierarchy for sample preservation for laboratories performing analyses for covered programs, including permitted wastewater discharges under, ch. NR 219, Wis. Adm. Code, is contained in the Laboratory Certification and Registration code chapter, specifically s. NR 149.46(4)(a), Wis. Adm. Code, which states: "Laboratories shall follow the sample preservation procedures and holding times required by state and federal regulations. If the sample preservation

procedures are not required by state or federal regulations, laboratories shall follow the sample preservation procedures and holding times established in the analytical method. If the analytical method does not establish sample preservation procedures and holding times, laboratories shall follow the procedures in authoritative sources specified in Appendix III of this chapter."

This language means that laboratories must follow all sample preservation and holding times included in state regulations, including ch. NR 219, Table F, Wis. Adm. Code, or 40 CFR Part 136 Table II. The sample preservation and holding time language contained in approved methods in ch. NR 219, Wis. Adm. Code, for example, is applicable only when there are no preservation or hold time requirements established in state or federal regulations. The sample preservation and holding time requirements contained in authoritative sources, such as *Standard Methods for the Analysis of Water and Wastewater*, 20th ed., are applicable only if there are no requirements in state or federal regulations or in approved methods for analyses.

The language contained in the Laboratory Certification and Registration Program code clearly dictates the hierarchy for sample preservation and holding time requirements. The department does not believe that inclusion of the suggested language is necessary as the hierarchy is addressed elsewhere in Wisconsin Administrative Code.

#### Modifications Made

Modifications made by the department are detailed in the response to comments.

#### Appearances at the Public Hearing

##### **August 27, 2008 – Madison**

In support:

Sharon Mertens, 250 West Seeboth Street, Milwaukee, WI 53204

In opposition- none

As interest may appear- none

##### **August 27, 2008 – Stevens Point**

In support- none

In opposition- none

As interest may appear- none

#### Changes to Rule Analysis and Fiscal Estimate

No modifications were made to the rules analysis or fiscal estimate as a result of public comments.

#### Response to Legislative Council Rules Clearinghouse Report

The Legislative Council Rules Clearinghouse Report did not contain any comments or suggestions to modify the content of this chapter.

#### Final Regulatory Flexibility Analysis

The proposed rule does not have a significant economic impact on a substantial number of small businesses. The small businesses impacted by the proposed rule are commercial laboratories that perform compliance monitoring for WPDES permittees. The vast majority of these laboratories have previously implemented use of newer analytical methods that were retained in Tables A-EM of this chapter. For most parameters where small businesses may have to update their method references, the Department has maintained at least one method from the current language. There were only four specific techniques eliminated— three of these included mercury-containing reagents for which other alternatives using similar techniques were retained. Hexane extractable materials, an alternative to the freon extraction for oil and grease, has been in use by laboratories for over a decade. All of the small businesses that perform oil and grease determinations currently maintain certification for the hexane method. The Department no longer offers certification for the freon extraction method.

Sample preservation requirements for tests that are typically considered field parameters and are not required to be performed by certified laboratories, were clarified so there is no question as to whether data from these time-sensitive tests is valid. The hold times for hexavalent chromium and polychlorinated biphenyls (PCBs) increased; this will allow small businesses more flexibility in scheduling and performing these analyses. Clarification of procedures for potential interferences in cyanide analyses will allow small business laboratories to continue to perform these analyses in 14 days without requiring investment in new instrumentation required to conduct these analyses.