



State of Wisconsin

CR 87-75

DEPARTMENT OF NATURAL RESOURCES

Carroll D. Besadny  
Secretary

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File Ref:

STATE OF WISCONSIN )  
DEPARTMENT OF NATURAL RESOURCES )

RECEIVED

MAR 4 1988  
8:45am  
Revisor of Statutes  
Bureau

TO ALL TO WHOM THESE PRESENTS SHALL COME, GREETINGS:

I, Bruce B. Braun, Deputy Secretary of the Department of Natural Resources and custodian of the official records of said Department, do hereby certify that the annexed copy of Natural Resources Board Order No. TS-14-87 was duly approved and adopted by this Department on October 29, 1987. I further certify that said copy has been compared by me with the original on file in this Department and that the same is a true copy thereof, and of the whole of such original.

IN TESTIMONY WHEREOF, I have here-  
unto set my hand and affixed the  
official seal of the Department at  
the Natural Resources Building in  
the City of Madison, this 1<sup>st</sup>  
day of March, 1988.

Bruce B. Braun  
Bruce B. Braun, Deputy Secretary

(SEAL)

5-1-88

ORDER OF THE STATE OF WISCONSIN NATURAL RESOURCES BOARD  
AMENDING, AND REPEALING AND RECREATING RULES

.....  
IN THE MATTER of amending s. NR 149.02(1) .  
and (2), 149.14(3)(c)4, and 219.01, and .  
repealing and recreating, ch. NR 219 .  
Table B and Table E of the Wisconsin .  
Administrative Code, pertaining to .  
laboratory certification and analytical .  
procedures for effluent discharges from .  
point sources .  
.....

TS-14-87

Analysis Prepared by the Department of Natural Resources

Authorizing statutes: ss. 144.95, 147.08(1), and 227.16(2)(e), Stats.  
Statutes interpreted: ss. 144.95, 147.08(1), Stats.

The effect of amending s. NR 149.02(1) and (2) will be to correct several citations which are in error.

The effect of amending s. NR 149.14(3)(c)4. will be to give greater flexibility to the laboratories analyzing 5-day biochemical oxygen demand samples by giving them the option to analyze a known standard once in every 20 samples or once a week. This will lessen the workload on those laboratories analyzing 40 or more samples a week.

The effect of amending s. NR 219.01 will be to correct the citation to the state statutes given in the purpose section of ch. NR 219.

The effect of the revision to ch. NR 219 Tables B and E will be to delete out-of-date analytical references and cite more current analytical references. The Tables revised here will reflect the federal requirements which were revised in the June 30, 1986, federal register.

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SECTION 1. NR 149.02(1) and (2) is amended to read:

NR 149.02 APPLICABILITY (1) Except as provided in subs. (2) and (3), the provisions of subchs. I to III, II, & IV are applicable to laboratories applying for certifications or registrations and laboratories holding valid certification or registration, where department rules require laboratory tests to be done by a certified or registered laboratory.

(2) The provisions of subchs. I and III, & IV are applicable to laboratories applying for certification and laboratories holding valid certifications for the analysis of samples for the safe drinking water program under ss. NR 109.12, 109.13, 109.14, 109.21 and 109.22.

SECTION 2. NR 149.14(3)(c)4. is amended to read:

NR 149.14(3)(c)4. For test category 1, a known standard shall be analyzed after the analysis of 20 samples or once a week. The limits on this quality control check shall be as established in an authoritative source.

SECTION 3. NR 219.01 is amended to read:

NR 219.01 PURPOSE. The purpose of this chapter is to establish analytical test methods, preservation procedures, requirements for laboratories, and procedures applicable to effluent limitations for discharges from point sources as authorized by ss. 147.04(5) 147.08(1) and 144.95, Stats.

SECTION 4. Chapter NR 219 Table B is repealed and recreated to read:

TABLE B  
List of Approved Inorganic Test Procedures

Parameter, Units & Methods	EPA 1979 <sup>A</sup>	Standard Methods <sup>B</sup> 16th Ed.	ASTM <sup>C</sup>	USGS <sup>1</sup>	Other
1. Acidity, as CaCO <sub>3</sub> , mg/L, Electrometric end point or phenolphthalein end point	305.1	402(4.a)	D1067-82(E)		
2. Alkalinity, as CaCO <sub>3</sub> , mg/L; Electrometric or colorimetric: Titration to pH 4.5, manual Or automated	310.1 310.2	403	D1067-82(B)	I-1030-84 I-2030-84	33.014 <sup>2</sup>
3. Aluminum - Total <sup>3</sup> , mg/L: Digestion <sup>3</sup> followed by: AA direct aspiration, AA furnace, Inductively coupled plasma, or colorimetric (Eriochrome cyanine R)	202.1 202.2	303C 304  306B		I-3051-84	200.7 <sup>4</sup>
4. Ammonia (as N), mg/L: Manual distillation <sup>5</sup> (at pH 9.5): Followed by Nesslerization, Titration, Electrode, Automated phenate, or Automated electrode	350.2 350.2 350.2 350.3 350.1	417A 417B 417D 417E or F 417G	D1426-79(A)  D1426-79(D) D1426-79(C)	I-3520-84  I-4523-84	33.057 <sup>2</sup>   ( <sup>6</sup> )
5. Antimony - Total <sup>3</sup> , mg/L: Digestion <sup>3</sup> followed by: AA direct aspiration, AA furnace, or Inductively coupled plasma	204.1 204.2	303A 304			200.7 <sup>4</sup>
6. Arsenic - Total <sup>3</sup> , mg/L: Digestion <sup>3</sup> followed by AA (gaseous hydride), AA furnace, Inductively coupled plasma, Or, colorimetric (SDDC)	206.5 206.3 206.2 206.4	303E 304  307B	D2972-84(B)  D2972-84(A)	I-3062-84  I-3060-84	200.7 <sup>4</sup>
7. Barium - Total <sup>3</sup> , mg/L: Digestion <sup>3</sup> followed by: AA direct aspiration, AA furnace, or Inductively coupled plasma	208.1 208.2	303C 304		I-3084-84	200.7 <sup>4</sup>
8. Beryllium - Total <sup>3</sup> , mg/L: Digestion <sup>3</sup> followed by: AA direct aspiration, AA furnace, Inductively coupled plasma, Or, colorimetric (aluminon)	210.1 210.2	303C 304  309B	D3654-84(A)	I-3095-84	200.7 <sup>4</sup>
9. Biochemical oxygen demand (BOD <sub>5</sub> ), mg/L: Winkler (Azide modifications) Or electrode method	405.1	507		I-1578-78 <sup>7</sup>	P. 17 <sup>8</sup> 33.019 <sup>2</sup>
10. Boron - Total, mg/L: Colorimetric (curcumin) or Inductively coupled plasma	212.3	404A		I-3112-84	200.7 <sup>4</sup>
11. Bromide, mg/L: Titrimetric	320.1		D1246-82(C)	I-1125-84	P.544 <sup>9</sup>

TABLE B  
List of Approved Inorganic Test Procedures  
(continued)

Parameter, Units & Methods	EPA 1979 <sup>A</sup>	Standard Methods <sup>B</sup> 16th Ed.	ASTM <sup>C</sup>	USGS <sup>1</sup>	Other
12. Cadmium - Total <sup>3</sup> , mg/L: Digestion <sup>3</sup> followed by: AA direct aspiration,	213.1	303A or B	D3557-84 (A or B)	I-3135-84 or I-3136-84	33.089 <sup>2</sup> P. 37 <sup>8</sup>
AA furnace, Inductively coupled plasma, Voltametry <sup>10</sup> , or Colorimetric (Dithizone)	213.2	304	D3557-84(C)		200.7 <sup>4</sup>
13. Calcium - Total <sup>3</sup> , mg/L: Digestion <sup>3</sup> followed by: Atomic absorption, Inductively coupled plasma, Or EDTA titration	215.1 215.2	303A 311C	D511-84(B) D511-84(A)	I-3152-84	200.7 <sup>4</sup>
14. Carbonaceous Biochemical oxygen demand (CBOD <sub>5</sub> ), mg/L: with nitrification inhibitor <sup>11</sup>		507(5.e.6)			
15. Chemical oxygen demand (COD), mg/L: Titrimetric	410.1 410.2 410.3	508A	D1252-83	I-3560-84 I-3562-84	33.034 <sup>2</sup> P. 17 <sup>8</sup>
Automated and manual Spectrophotometric	410.4			I-3561-84	( <sup>12</sup> ) or ( <sup>13</sup> )
16. Chloride, mg/L: Titrimetric (silver nitrate) or (Mercuric nitrate), Colorimetric (ferricyanide), manual or automated	325.3 325.1 or 325.2	407A 407B 407D	D512-81(B) D512-81(A) D512-81(C)	I-1183-84 I-1184-84 I-1187-84 I-2187-84	33.067 <sup>2</sup>
17. Chlorine - Total residual, mg/L: amperometric <sup>14</sup> , Back Titration <sup>14</sup> , DPD-FAS, Spectrophotometric, DPD; or Electrode	330.1 330.2 330.4 330.5	408C 408B 408D 408E	D1253-76(A)		( <sup>15</sup> )
18. Chromium VI dissolved, mg/L: 0.45 micron filtration with: Extraction and atomic absorption, or Colorimetric (Diphenylcarbazide)	218.4	303B		I-1232-84 I-1230-84	
19. Chromium - Total <sup>3</sup> , mg/L: Digestion <sup>3</sup> (optional extraction) followed by: AA direct aspiration, AA furnace, Inductively coupled plasma, Or colorimetric (Diphenylcarbazide), Or AA chelation extraction	218.1 218.2 218.3	303A 304 312B 303B	D1687-84(D) D1687-84(A)	I-3236-84	33.089 <sup>2</sup> 200.7 <sup>4</sup>
20. Cobalt - Total <sup>3</sup> , mg/L: Digestion <sup>3</sup> followed by: AA direct aspiration, AA furnace, or Inductively coupled plasma	219.1 219.2	303A or B 304	D3558-84 (A or B)	I-3240-84 or I-3239-84	P. 37 <sup>8</sup> 200.7 <sup>4</sup>

TABLE B  
List of Approved Inorganic Test Procedures  
(continued)

Parameter, Units & Methods	EPA 1979 <sup>A</sup>	Standard Methods <sup>B</sup> 16th Ed.	ASTM <sup>C</sup>	USGS <sup>1</sup>	Other
21. Color, Platinum Cobalt units or dominant wavelength hue, luminance, purity: Colorimetric, ADMI Platinum cobalt; or Spectrophotometric	110.1 110.2 110.3	204D 204A 204B		I-1250-84	( <sup>17</sup> )
22. Copper - Total <sup>3</sup> , mg/L: Digestion <sup>3</sup> followed by: AA direct aspiration,  AA furnace, Inductively coupled plasma, Colorimetric (Neocuproine), Bicinchoninate	220.1  220.2	303A or B  304  313B	D1688-84 (D or E)  D1688-84(A)	I-3271-84 or I-3270-84	33.089 <sup>2</sup> P. 37 <sup>8</sup>  200.7 <sup>4</sup> ( <sup>18</sup> )
23. Cyanide - Total, mg/L: Manual distillation with MgCl <sub>2</sub> Followed by: titrimetric, Manual or Automated <sup>19</sup> spectrophotometric	335.2 335.3	412B 412C 412D	D2036-82(A) D2036-82(A)	I-3300-84	P. 22 <sup>8</sup>
24. Cyanide amenable to chlorination, mg/L: Manual distillation with MgCl <sub>2</sub> followed by titrimetric, manual or automated spectrophotometric	335.1	412F	D2036-82(B)		
25. Fluoride - Total, mg/L: Manual distillation <sup>5</sup> Followed by manual or automated electrode, SPADNS, Or automated complexone	340.2 340.1 340.3	413A 413B 413C 413E	D1179-80(B)  D1179-80(A)	I-4327-84	
26. Gold - Total <sup>3</sup> mg/L: Digestion <sup>3</sup> followed by: AA direct aspiration Or AA furnace	231.1 231.2	303A 304			
27. Hardness - Total as CaCO <sub>3</sub> , mg/L: Automated colorimetric, EDTA titration, (or the sum of Ca and Mg as their respective carbonates by OCP or AA direct aspiration) (See Parameters 13 and 33)	130.1 130.2	314B	D1126-80	I-1338-84	33.082 <sup>2</sup>
28. Hydrogen ion (pH), pH units: Electrometric Measurements or Automated Electrode	150.1	423	D1293-84(A or B)	I-1586-84	33.006 <sup>2</sup> ( <sup>20</sup> )
29. Iridium - Total <sup>3</sup> , mg/L: Digestion <sup>3</sup> followed by: AA direct aspiration Or AA furnace	235.1 235.2	303A 304			
30. Iron - Total <sup>3</sup> , mg/L: Digestion <sup>3</sup> followed by: AA direct aspiration,  AA furnace, Inductively coupled plasma, Or colorimetric (Phenanthroline)	236.1  236.2	303(A or B)  304  315B	D1068-84 (C or D)  D1068-84(A)	I-3381-84	33.089 <sup>2</sup>   200.7 <sup>4</sup> ( <sup>21</sup> )

TABLE B  
List of Approved Inorganic Test Procedures  
(continued)

Parameter, Units & Methods	EPA 1979 <sup>A</sup>	Standard Methods <sup>B</sup> 16th Ed.	ASTM <sup>C</sup>	USGS <sup>1</sup>	Other
31. Kjeldahl nitrogen - Total (as N), mg/L:					
Digestion and distillation	351.3	420A or B	D3590-84(A)		
Followed by titration	351.3	417D	D3590-84(A)		33.051 <sup>2</sup>
Nesslerization or	351.3	417B	D3590-84(A)		
Electrode,	351.3	417E or F			
Automated phenate,	351.1			I-4551-78 <sup>7</sup>	
Semi-automated block digester,	351.2		D3590-84(A)		
Or potentiometric	351.4		D3590-84(A)		
32. Lead - Total <sup>3</sup> , mg/L:					
Digestion <sup>3</sup> followed by:					
AA direct aspiration,	239.1	303A or B	D3559-85(A or B)	I-3399-84	33.089 <sup>2</sup>
AA furnace,	239.2	304			
Inductively coupled plasma,					200.7 <sup>4</sup>
Voltametry <sup>10</sup> or			D3559-85(C)		
Colorimetric (Dithizone)		316B			
33. Magnesium - Total <sup>3</sup> ; mg/L:					
Digestion <sup>3</sup> followed by:					
Atomic absorption	242.1	303A	D511-84(B)	I-3447-84	33.089 <sup>2</sup>
Inductively coupled plasma					200.7 <sup>4</sup>
Or gravimetric		318B	D511-77(A)		
34. Manganese - Total <sup>3</sup> , mg/L:					
Digestion <sup>3</sup> followed by:					
AA direct aspiration,	243.1	303A or B	D858-84	I-3454-84	33.089 <sup>2</sup>
AA furnace,	243.2	304	(B or C)		
Inductively coupled plasma,					200.7 <sup>4</sup>
Colorimetric (Persulfate), or		319B	D858-84(A)		33.126 <sup>2</sup>
Periodate					( <sup>22</sup> )
35. Mercury - Total <sup>3</sup> , mg/L:					
Cold vapor, manual or	245.1	303F	D3223-80	I-3462-84	33.095 <sup>2</sup>
automated	245.2				
36. Molybdenum - Total <sup>3</sup> , mg/L:					
Digestion <sup>3</sup> followed by:					
AA direct aspiration,	246.1	303C		I-3490-84	
AA furnace, or	246.2	304			
Inductively coupled plasma					200.7 <sup>4</sup>
37. Nickel - Total <sup>3</sup> , mg/L:					
Digestion <sup>3</sup> followed by:					
AA direct aspiration,	249.1	303A or B	D1886-84(C or D)	I-3499-84	
AA furnace,	249.2	304			
Inductively coupled plasma,					200.7 <sup>4</sup>
Or colorimetric (Heptoxime)		321B			
38. Nitrate (as N), mg/L:					
Brucine sulfate, or	352.1		D992-71		33.063 <sup>2</sup> , 419D <sup>16</sup> , P. 28 <sup>8</sup>
Nitrate-nitrite N minus Nitrite N (see parameters 39 and 40)					
39. Nitrate-nitrite (as N), mg/L:					
Cadmium reduction, manual	353.3	418C	D3867-85(B)		
Or automated, or	353.2	418F	D3867-85(A)	I-4545-84	
automated hydrazine	353.1				
40. Nitrite (as N), mg/L:					
Spectrophotometric, manual or	354.1	419	D1254-67		( <sup>24</sup> )
automated (Diazotization)				I-4540-84	
41. Oil and grease-Total recoverable, mg/L:					
Gravimetric (extraction)	413.1	503A			

TABLE B  
List of Approved Inorganic Test Procedures  
(continued)

Parameter, Units & Methods	EPA 1979 <sup>A</sup>	Standard Methods <sup>B</sup> 16th Ed.	ASTM <sup>C</sup>	USGS <sup>1</sup>	Other
42. Organic carbon - Total (TOC), mg/L: Combustion or oxidation	415.1	505	D2579-85(A or B)		33.044 <sup>2</sup> P.4 <sup>23</sup>
43. Organic nitrogen (as N), mg/L: Total Kjeldahl N (Parameter 31) minus ammonia N (Parameter 4)					
44. Orthophosphate (as P), mg/L: Ascorbic acid method, automated	365.1	424G		I-4601-84	33.116 <sup>2</sup>
Or manual single reagent or Manual two reagent	365.2 365.3	424F	D515-82(A)		33.111 <sup>2</sup>
45. Osmium - Total <sup>3</sup> , mg/L: Digestion <sup>3</sup> followed by: AA direct aspiration, or AA furnace	252.1 252.2	303C 304			
46. Oxygen, dissolved, mg/L: Winkler (Azide modification) Or electrode	360.2 360.1	421B 421F	D888-81(C)	I-1575-78 <sup>7</sup> I-1576-78 <sup>7</sup>	33.028 <sup>2</sup>
47. Palladium - Total <sup>3</sup> , mg/L: Digestion <sup>3</sup> followed by: AA direct aspiration Or AA furnace	253.1 253.2				P. S27 <sup>9</sup> P. S28 <sup>9</sup>
48. Phenols, mg/L: Manual distillation <sup>25</sup> Followed by manual Or automated <sup>19</sup> colorimetric (4AAP)	420.1 420.1 420.2		D1783-80 (A or B)		( <sup>26</sup> ) ( <sup>26</sup> )
49. Phosphorus (elemental), mg/L: Gas-Liquid chromatography					( <sup>27</sup> )
50. Phosphorus - Total, mg/L: Persulfate digestion Followed by manual or	365.2 365.2 or 365.3	424C(III) 424F	D515-82(A)		33.111 <sup>2</sup>
Automated ascorbic acid Reduction, or semi-automated block digester	365.1 365.4	424G		I-4600-84	33.116 <sup>2</sup>
51. Platinum - Total <sup>3</sup> , mg/L: Digestion <sup>3</sup> followed by: AA direct aspiration, Or AA furnace	255.1 255.2	303A 304			
52. Potassium - Total <sup>3</sup> , mg/L: Digestion <sup>3</sup> followed by: Atomic absorption, Inductively coupled plasma,  Flame photometric, or Colorimetric (cobaltnitrate)	258.1	303A  322B	  D1428-82(A)	I-3630-84	33.103 <sup>2</sup> 200.7 <sup>4</sup>  317B <sup>16</sup>
53. Residue - total, mg/L: Gravimetric 103-105°C	160.3	209A		I-3750-84	
54. Residue - filterable, mg/L: Gravimetric, 180°C	160.1	209B		I-1750-84	

TABLE B  
List of Approved Inorganic Test Procedures  
(continued)

Parameter, Units & Methods	EPA 1979 <sup>A</sup>	Standard Methods <sup>B</sup> 16th Ed.	ASTM <sup>C</sup>	USGS <sup>1</sup>	Other
55. Residue - nonfilterable, (TSS), mg/L: Gravimetric, 103-105°C post washing of residue	160.2	209C		I-3765-84	
56. Residue - settleable, mg/L: Volumetric (Imhoff cone) or gravimetric	160.5	209E			
57. Residue - volatile mg/L: Gravimetric, 550°C	160.4	209D		I-3753-84	
58. Rhodium - Total <sup>3</sup> , mg/L: Digestion <sup>3</sup> followed by: AA direct aspiration Or AA furnace	265.1 265.2	303A 304			
59. Ruthenium - Total <sup>3</sup> mg/L: Digestion <sup>3</sup> followed by: AA direct aspiration Or AA furnace	267.1 267.2	303A 304			
60. Selenium - Total <sup>3</sup> mg/L: Digestion <sup>3</sup> followed by: AA furnace, Inductively coupled plasma, or AA (gaseous hydride)	270.2 270.3	304 303E	D3859-84(A)	I-3667-84	200.7 <sup>4</sup>
61. Silica - Dissolved, mg/L: 0.45 micron filtration: Followed by manual or automated colorimetric (Molybdosilicate), or Inductively coupled plasma	370.1	425C	D859-80(B)	I-1700-84 I-2700-84	200.7 <sup>4</sup>
62. Silver - Total <sup>28</sup> , mg/L: Digestion <sup>3</sup> followed by: AA direct aspiration,  AA furnace, Colorimetric (Dithizone), or Inductively coupled plasma	272.1 272.2	303A or B 304		I-3720-84	33.089 <sup>2</sup> P. 37 <sup>B</sup>  319B <sup>16</sup> 200.7 <sup>4</sup>
63. Sodium - Total <sup>3</sup> , mg/L: Digestion <sup>3</sup> followed by: Atomic absorption, Inductively coupled plasma, Or flame photometric	273.1	303A 325B	D1428-82(A)	I-3735-84	33.107 <sup>2</sup> 200.7 <sup>4</sup>
64. Specific conductance, micromhos/cm at 25°C: Wheatstone bridge	120.1	205	D1125-82(A)	I-1780-84	33.002 <sup>2</sup>
65. Sulfate (as SO <sub>4</sub> ), mg/L: Automated colorimetric (barium chloroanilate), Gravimetric, or Turbidimetric	375.1 375.3 375.4	426A or B	D516-82(A) D516-82(B)		33.124 <sup>2</sup> 426C <sup>29</sup>
66. Sulfide (as S), mg/L: Titrimetric (iodine) or Colorimetric (methylene blue)	376.1 376.2	427D 427C		I-3840-84	228A <sup>30</sup>
67. Sulfite (as SO <sub>3</sub> ), mg/L: Titrimetric (iodine-iodate)	377.1	428A	D1339-84(C)		

TABLE B  
List of Approved Inorganic Test Procedures  
(continued)

Parameter, Units & Methods	EPA 1979 <sup>A</sup>	Standard Methods <sup>B</sup> 16th Ed.	ASTM <sup>C</sup>	USGS <sup>1</sup>	Other
68. Surfactants, mg/L: Colorimetric (methylene blue)	425.1	512B	D2330-82(A)		
69. Temperature, °C: Thermometric	170.1	212			( <sup>31</sup> )
70. Thallium - Total <sup>3</sup> , mg/L: Digestion <sup>3</sup> followed by: AA direct aspiration, AA furnace, or Inductively coupled plasma	279.1 279.2	303A 304			200.7 <sup>4</sup>
71. Tin - Total <sup>3</sup> , mg/L: Digestion <sup>3</sup> followed by: AA direct aspiration or AA furnace	282.1 282.2	303A 304		I-3850-78 <sup>7</sup>	
72. Titanium - Total <sup>3</sup> , mg/L: Digestion <sup>3</sup> followed by: AA direct aspiration or AA furnace	283.1 283.2	303C 304			
73. Turbidity, NTU: Nephelometric	180.1	214A	D1889-81	I-3860-84	
74. Vanadium - Total <sup>3</sup> , mg/L: Digestion <sup>3</sup> followed by: AA direct aspiration, AA furnace, Inductively coupled plasma Or colorimetric (Gallic acid)	286.1 286.2	303C 304	327B	D3373-84(A)	200.7 <sup>4</sup>
75. Zinc - Total <sup>3</sup> , mg/L: Digestion <sup>3</sup> followed by: AA direct aspiration,  AA furnace, Inductively coupled plasma Colorimetric (Dithizone) Or Colorimetric (Zincon)	289.1  289.2	303A or B  304  328C	D1691-84(D) D1691-84(C)	I-3900-84	33.089 <sup>2</sup> P. 37 <sup>8</sup>  200.7 <sup>4</sup>  ( <sup>32</sup> )

TABLE B NOTES

<sup>A</sup> "Methods for Chemical Analysis of Water and Wastes", EPA-600/4-79-020 United States Environmental Protection Agency, March 1979. Available from ORD Publications, CERL, U.S. Environmental Protection Agency, 26 W. St. Claire, Cincinnati, OH 45268.

<sup>B</sup> "Standard Methods for the Examination of Water and Wastewater", Joint Editorial Board, American Public Health Association, American Water Works Association, and Water Pollution Control Federation, 16th Edition, 1985. Available from American Public Health Association, 1015 Fifteenth Street, N.W., Washington, D.C. 20005.

<sup>C</sup> "1986 Annual Book of Standards, Section 11.01 and 11.02, Water and Environmental Technology", American Society for Testing and Materials, 1986. Available from the American Society for Testing and Materials, 1916 Race Street, Philadelphia, PA 19103.

<sup>1</sup> "Methods for Analysis of Inorganic Substances in Water and Fluvial Sediments", U.S. Department of the Interior, U.S. Geological Survey, Open-File Report 85-495, 1986, unless otherwise stated. Available from U.S. Geological Survey, 604 S. Pickett Street, Alexandria, VA 22304.

<sup>2</sup> "Official Methods of Analysis of the Association of Official Analytical Chemists", methods manual, 14th Edition (1985). Available from The Association of Official Analytical Chemists, 1111 N. 19th Street, Suite 210, Arlington, VA 22209.

<sup>3</sup> For the determination of total metals the sample is not filtered before processing. A digestion procedure is required to solubilize suspended material and to destroy possible organic metal complexes. Two digestion procedures are given in "Methods for Chemical Analysis of Water and Wastes, 1979". One (§4.1.3), is a vigorous digestion using nitric acid. A less vigorous digestion using nitric and hydrochloric acids (§4.1.4) is preferred; however, the analyst should be cautioned that this mild digestion may not suffice for all sample types. Particularly, if a colorimetric procedure is to be employed, it is necessary to ensure that all organo-metallic bonds be broken so that the metal is in a reactive state. In those situations, the vigorous digestion is to be preferred making certain that at no time does the sample go to dryness. Samples containing large amounts of organic materials would also benefit by this vigorous digestion. Use of the graphite furnace technique, inductively coupled plasma, as well as determinations for certain elements such as arsenic, the noble metals, mercury, selenium, and titanium require a modified digestion and in all cases the method write-up should be consulted for specific instructions and/or cautions.

Note: If the digestion included in one of the other approved references is different than the above, the EPA procedure will be used.

Dissolved metals are defined as those constituents which will pass through a 0.45 micron membrane filter. Following filtration of the sample, the referenced procedure for total metals will be followed. Sample digestion for dissolved metals may be omitted for AA (direct aspiration or graphite furnace) and ICP analyses provided the sample solution to be analyzed meets the following criteria:

- (a) has a low COD (<20),
- (b) is visibly transparent with a turbidity measurement of 1 NTU or less,
- (c) is colorless with no perceptible odor, and
- (d) is of one liquid phase and free of particulate or suspended matter following acidification.

<sup>4</sup> The full text of Method 200.7, "Inductively Coupled Plasma Atomic Emission Spectrometric Method for Trace Element Analysis of Water and Wastes", is given in Appendix C of the Federal Register, October 26, 1984 (Part VIII, 40 CFR part 136). Available from the Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402.

<sup>5</sup> Manual distillation is not required if comparability data on representative effluent samples are on company file to show that this preliminary distillation step is not necessary; however, manual distillation will be required to resolve any controversies.

<sup>6</sup> Ammonia, Automated Electrode Method, Industrial Method Number 379-75WE, dated February 19, 1976, Technicon AutoAnalyzerII. Available from Technicon Industrial Systems, Benedict Avenue, Tarrytown, NY 10591.

<sup>7</sup> The approved method is that cited in "Methods for Determination of Inorganic Substances in Water and Fluvial Sediments", USGS TWRI, Book 5, Chapter A1 (1979). Available on inter-library loan.

<sup>8</sup> "American National Standard on Photographic Processing Effluents", April 2, 1975. Available from American National Standards Institute, 1430 Broadway, New York, NY 10018.

<sup>9</sup> "Selected Analytical Methods Approved and cited by the United States Environmental Protection Agency", Supplement to the Fifteenth Edition of "Standard Methods for the Examination of Water and Wastewater," from American Public Health Association, 1015 Fifteenth Street, N.W., Washington, D.C. 20005, 1981. Available on inter-library loan.

TABLE B NOTES  
(Continued)

- <sup>10</sup> The use of normal and differential pulse voltage ramps to increase sensitivity and resolution is acceptable.
- <sup>11</sup> Carbonaceous biochemical oxygen demand (CBOD<sub>5</sub>) must not be confused with the traditional BOD<sub>5</sub> test which measures "total BOD." The addition of the nitrification inhibitor is not a procedural option, but must be included to report the CBOD<sub>5</sub> parameter. A discharger whose permit requires reporting the traditional BOD<sub>5</sub> may not use a nitrification inhibitor in the procedure for reporting the results. Only when a discharger's permit specifically states CBOD<sub>5</sub> is required, can the permittee report data obtained using the nitrification inhibitor.
- <sup>12</sup> OIC Chemical Oxygen Demand Method. Available from Oceanography International Corporation, 512 West Loop, P.O. Box 2980, College Station, TX 77840.
- <sup>13</sup> Chemical Oxygen Demand, Method 8000, Hach Handbook of Water Analysis, 1979. Available from Hach Chemical Company, P.O. Box 389, Loveland, CO 80537.
- <sup>14</sup> The back titration method will be used.
- <sup>15</sup> ORION Research Instruction Manual, Residual Chlorine Electrode Model 97-70, 1977. Available from Orion Research Incorporated, 840 Memorial Drive, Cambridge, MA 02138.
- <sup>16</sup> The approved method is that cited in the "Standard Methods for the Examination of Water and Wastewater", 14th Edition, 1976. Available on inter-library loan.
- <sup>17</sup> "An Investigation of Improved Procedures for Measurement of Mill Effluent and Receiving Water Color", NCASI Technical Bulletin No. 253. December, 1971. Available from National Council of the Paper Industry for Air and Stream Improvements, Inc., 260 Madison Avenue, New York, NY 10016.
- <sup>18</sup> Copper, Bicinchoninate Method, Method 8506, Hach Handbook of Water Analysis, 1979. Available from Hach Chemical Company, P.O. Box 389, Loveland, CO 80537.
- <sup>19</sup> After the manual distillation is completed, the auto-analyzer manifolds in EPA Methods 335.03 (Cyanide) or 420.2 (phenols) are simplified by connecting the re-sample line directly to the sampler. When using the manifold setup shown in Method 335.3, the buffer 6.2 should be replaced with the buffer 7.6 found in Method 335.2.
- <sup>20</sup> Hydrogen Ion (pH) Automated Electrode Method, Industrial Method Number 378-75WA, October 1976, Technicon AutoAnalyzer II. Available from Technicon Industrial Systems, Benedict Avenue, Tarrytown, NY 10591.
- <sup>21</sup> 1, 10-Phenanthroline Method for Iron, Hach Method 8008, 1980. Available from Hach Chemical Company, P.O. Box 389, Loveland, CO 80537.
- <sup>22</sup> Periodate Oxidation Method for Manganese, Method 8034. Hach Handbook of Wastewater Analysis, 1979, pp. 2-113 and 2-117. Available from Hach Chemical Company, P.O. Box 389, Loveland, CO 80537.
- <sup>23</sup> "Methods for Analysis of Organic Substances in Water", by D. F. Goerlitz and Eugene Brown: USGS-TWRI, Book 5, Chapter A3, p. 4, 1972. Available from U.S. Geological Survey, 604 S. Pickett Street, Alexandria, VA 22304.
- <sup>24</sup> Nitrite Nitrogen, Hach Method 8507. Available from Hach Chemical Company, P.O. Box 389, Loveland, CO 80537.
- <sup>25</sup> Just prior to distillation, adjust the sulfuric acid preserved sample to pH 4 with 1 + 9 NaOH.
- <sup>26</sup> The approved method is that cited in "Standard Methods for the Examination of Water and Wastewater", 14th Edition. The colorimetric reaction is conducted at a pH of 10.0 ± 0.2. The approved methods are given on pp. 576-81 of the 14th Edition: Method 510A for distillation, Method 510B for the manual colorimetric procedure, or Method 510C for the manual spectrophotometric procedure. Available on inter-library loan.
- <sup>27</sup> "Direct Determination of Elemental Phosphorus by Gas-Liquid Chromatography", by R. F. Addison and R. G. Ackman, Journal of Chromatography, Volume 47, No. 3, pp. 421-426, 1970. Available in most public libraries. Back volumes of the Journal of Chromatography are available from Elsevier/North-Holland, Inc., Journal Information Centre, 52 Vanderbilt Avenue, New York, NY 10164.
- <sup>28</sup> Approved methods for the analysis of silver in industrial wastewaters at concentrations of 1 mg/L and above are inadequate where silver exists as an inorganic halide. Silver halides such as the bromide and chloride are relatively insoluble in reagents such as nitric acid but are readily soluble in an aqueous buffer of sodium thiosulfate and sodium hydroxide to a pH of 12. Therefore, for levels of silver above 1 mg/L, 20 mL of sample should be diluted to 100 mL by adding 40 mL each of 2M Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> and 2M NaOH. Standards should be prepared in the same manner. For levels of silver below 1 mg/L the approved method is satisfactory.

TABLE B NOTES  
(Continued)

<sup>29</sup> The approved method is that cited in "Standard Methods for the Examination of Water and Wastewater", 15th Edition. Available on inter-library loan.

<sup>30</sup> The approved method is that cited in "Standard Methods for the Examination of Water and Wastewater", 13th Edition. Available on inter-library loan.

<sup>31</sup> "Water Temperature-Influential Factors, Field Measurement, and Data Presentation", by H. H. Stevens, Jr., J. Ficke, and G. F. Smoot: USGS-TWRI Book 1, Chapter D1, 1975. Available from U.S. Geological Survey, 604 S. Pickett Street, Alexandria, VA 22304.

<sup>32</sup> Zincon Method of Zinc Method 8009. Hach Handbook for Water Analysis, 1979, pp. 2-231 and 2-333. Available from Hach Chemical Company, P.O. Box 389, Loveland, CO 80537.

SECTION 5. Chapter NR 219 Table E is repealed and recreated to read:

TABLE E

List of Approved Radiological Test Procedures

Parameter and units	Methods	EPA <sup>1</sup>	Standard <sup>1A</sup> Methods 16th Ed.	ASTM <sup>1B</sup>	USGS <sup>2</sup>
1. Alpha-Total, pCi per liter	Proportional or scintillation counter	900.0	703	D1943-81	pp. 75 and 78 <sup>3</sup>
2. Alpha-Counting error, pCi per liter	Proportional or scintillation counter	Note 4.	703	D1943-81	p. 79
3. Beta-Total, pCi per liter	Proportional counter	900.0	703	D1890-81	pp. 75 and 78 <sup>3</sup>
4. Beta-Counting error, pCi per liter	Proportional counter	Note 4.	703	D1890-81	p. 79
5. (a) Radium-Total, pCi per liter	Proportional counter	903.0	705	D2460-70	
(b) <sup>226</sup> Ra, pCi per liter	Scintillation counter	903.1	706	D3454-79	p. 81

TABLE E NOTES

<sup>1</sup> "Prescribed Procedures for Measurement of Radioactivity in Drinking Water", EPA-600/4-80-032 (1980 Update), United States Environmental Protection Agency, 1980. Available from ORD Publications, CERI, U.S. Environmental Protection Agency, 26 W. St. Claire, Cincinnati, OH 45268.

<sup>1A</sup> "Standard Methods for the Examination of Water and Wastewater", Joint Editorial Board, American Public Health Association, American Water Works Association and Water Pollution Control Federation, 16th Edition, 1985. Available from American Public Health Association, 1015 Fifteenth Street, N.W., Washington, D.C. 20005.

<sup>1B</sup> "1984 Annual Book of Standards, Section 11.02, Water and Environmental Technology", American Society for Testing and Materials, 1980. Available from American Society for Testing and Materials, 1916 Race Street, Philadelphia, PA 19103.

<sup>2</sup> "Selected Methods of the U.S. Geological Survey of Analysis of Wastewaters", by M.J. Fishman and Eugene Brown; U.S. Geological Survey Open File Report 76-177 (1976). Available from U.S. Geological Survey, 604 S. Pickett St., Alexandria, VA 22304.

<sup>3</sup> The method found on p. 75 measures only the dissolved portion while the method on p. 78 measures only the suspended portion. Therefore, the two results must be added to obtain the "total".

<sup>4</sup> See Appendix B of the Federal Register, October 26, 1984 (Part VIII, 40 CFR part 136). Available from the Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402.

Note: Copies of the publications referred to in footnotes of the tables under sub. (1) are available for inspection at the offices of the department of natural resources, the secretary of state, the revisor of statutes and the federal register information center, room 8301, 1110 L street, N.W., Washington, D.C. 20408. Sources of the publications are identified in the footnotes.

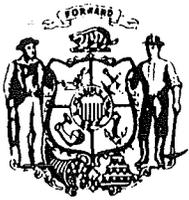
The foregoing rules were approved and adopted by the State of Wisconsin Natural Resources Board on October 29, 1987.

The rules contained herein shall take effect on the first day of the month following publication in the Wisconsin Administrative Register as provided in s. 227.22(2) (intro.), Stats.

Dated at Madison, Wisconsin March 1, 1988

STATE OF WISCONSIN DEPARTMENT OF NATURAL RESOURCES

By Carroll B. Besady  
Carroll B. Besady  
Secretary



State of Wisconsin

DEPARTMENT OF NATURAL RESOURCES

Carroll D. Besadny  
Secretary

BOX 7921  
MADISON, WISCONSIN 53707

March 1, 1988

File Ref: 1020

Mr. Orlan L. Prestegard  
Revisor of Statutes  
Suite 702  
30 W. Mifflin Street

RECEIVED

MAR 4 1988

Revisor of Statutes  
Bureau

Dear Mr. Prestegard:

Enclosed are two copies, including one certified copy, of State of Wisconsin Natural Resources Board Order No. TS-14-87. These rules were reviewed by the Assembly Committee on Environmental Resources and Utilities and the Senate Committee on Urban Affairs, Energy, Environmental Resources and Elections pursuant to s. 227.19, Stats. A summary of the final regulatory flexibility analysis and comments of the legislative review committees is also enclosed.

You will note that this order takes effect following publication. Kindly publish it in the Administrative Code accordingly.

Sincerely,

  
C. D. Besadny  
Secretary

Enc.



State of Wisconsin

DEPARTMENT OF NATURAL RESOURCES

Carroll D. Besadny  
Secretary

BOX 7921  
MADISON, WISCONSIN 53707

File Ref:

RECEIVED

MAR 18 1988

*2100*  
Revisor of Statutes  
Bureau

STATE OF WISCONSIN )  
 )  
DEPARTMENT OF NATURAL RESOURCES ) SS

TO ALL TO WHOM THESE PRESENTS SHALL COME, GREETINGS;

I, Bruce B. Braun, Deputy Secretary of the Department of Natural Resources and custodian of the official records of said Department, do hereby certify that the annexed copy Page 1 of Natural Resources Board Order No. TS-14-87 was duly approved and adopted by this Department on October 29, 1987. I further certify that said copy is the form approved by the legislative review committees, and that said copy has been compared by me with the corrected original on file in this Department and that the same is a true copy thereof.

IN TESTIMONY WHEREOF, I have here-  
unto set my hand and affixed the  
official seal of the Department at  
General Executive Facility #2 in  
the City of Madison, this 16<sup>th</sup>  
day of March, 1988.

*Bruce B. Braun*  
Bruce B. Braun, Deputy Secretary

(SEAL)

ORDER OF THE STATE OF WISCONSIN NATURAL RESOURCES BOARD  
AMENDING, AND REPEALING AND RECREATING RULES

.....  
IN THE MATTER of amending s. NR 149.02(1) .  
and (2), 149.14(3)(c)4, and 219.01, and .  
repealing and recreating. ch. NR 219 .  
Table B and Table E of the Wisconsin .  
Administrative Code, pertaining to .  
laboratory certification and analytical .  
procedures for effluent discharges from .  
point sources .  
.....

TS-14-87

Analysis Prepared by the Department of Natural Resources

Authorizing statutes: ss. 144.95, 147.08(1), and 227.16(2)(e), Stats.  
Statutes interpreted: ss. 144.95, 147.08(1), Stats.

The effect of amending s. NR 149.02(1) and (2) will be to correct several citations which are in error.

The effect of amending s. NR 149.14(3)(c)4. will be to give greater flexibility to the laboratories analyzing 5-day biochemical oxygen demand samples by giving them the option to analyze a known standard once in every 20 samples or once a week. This will lessen the workload on those laboratories analyzing 40 or more samples a week.

The effect of amending s. NR 219.01 will be to correct the citation to the state statutes given in the purpose section of ch. NR 219.

The effect of the revision to ch. NR 219 Tables B and E will be to delete out-of-date analytical references and cite more current analytical references. The Tables revised here will reflect the federal requirements which were revised in the June 30, 1986, federal register.

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SECTION 1. NR 149.02(1) and (2) is amended to read:

NR 149.02 APPLICABILITY (1) Except as provided in subs. (2) and (3), the provisions of subchs. ~~I to III, II, & IV~~ are applicable to laboratories applying for certifications or registrations and laboratories holding valid certification or registration, where department rules require laboratory tests to be done by a certified or registered laboratory.

(2) The provisions of subchs. ~~I and III, & IV~~ are applicable to laboratories applying for certification and laboratories holding valid certifications for the analysis of samples for the safe drinking water program under ss. NR 109.12, 109.13, 109.14, 109.21 and 109.22.

SECTION 2. NR 149.14(3)(c)4. is amended to read:

NR 149.14(3)(c)4. For test category 1, a known standard shall be analyzed after the analysis of 20 samples or once a week. The limits on this quality control check shall be as established in an authoritative source.

SECTION 3. NR 219.01 is amended to read:

NR 219.01 PURPOSE. The purpose of this chapter is to establish analytical test methods, preservation procedures, requirements for laboratories, and procedures applicable to effluent limitations for discharges from point sources as authorized by ss. ~~147.04(5)~~ 147.08(1) and 144.95, Stats.