Chapter NR 219

ANALYTICAL TEST METHODS AND PROCEDURES APPLICABLE TO INTERIM EFFLUENT LIMITATIONS WISCONSIN POLLUTANT DISCHARGE ELIMINATION SYSTEM

Note: Pursuant to Chapter 74, Laws of 1973, in sections 147.04 (3) and (5) and under the procedure of section 227.027, Wis. Stats., the department of natural resources has promulgated interim effluent limitations which become effective February 1, 1974 and will remain in effect for a period of one year. These interim effluent limitations will be periodically replaced by permanent effluent limitations.

NR 219.01 Purpose. The purpose of this chapter is to establish analytical test methods and procedures applicable to interim effluent limitations for discharges from point sources as authorized by section 147.04 (5), Wis. Stats.

History: Emerg. cr. eff. 2-1-74.

NR 219.02 Applicability. The procedures prescribed herein shall, except as provided in NR 219.05, be used in the determination of concentrations and quantities of pollutant parameters as required for:

(1) An application submitted to the department for a permit under chapter 147, Wis. Stats.

(2) Reports required to be submitted by dischargers in accordance with the conditions of issued permits.

History: Emerg. cr. eff. 2-1-74.

NR 219.03 Definitions. As used in this chapter:

(1) Standard Methods—means "Standard Methods for the Examination of Water and Waste Water," 13th Edition, 1971. This publication is available from the American Public Health Association, 1015 18th Street NW, Washington, D. C. 20036.

(2) ASTM—means "Annual Book of Standards, Part 23, Water, Atmospheric Analysis, 1972." This publication is available from the American Society for Testing and Materials, 1916 Race Street, Philadelphia, Pennsylvania 19103.

(3) EPA Methods—means "Methods for Chemical Analysis of Water and Wastes," 1971, Environmental Protection Agency, Analytical Quality Control Laboratory, Cincinnati, Ohio. This publication is

available from the Superintendent of Documents, U.S. Government Printing Office, Washington, D. C. 20402 (Stock Number 5501–0067).

(4) Regional Administrator—the term "Regional Administrator" means the Regional Administrator of Region V, U.S. Environmental Protection Agency.

Note: Standards used in this chapter have not received consent from the attorney general or the revisor of statutes pursuant to section 227.025 Wis. Stats.

History: Emerg. cr. eff. 2–1–74.

NR 219.04 Application for alternate test procedures. (1) Any person may apply to the regional administrator for approval of an alternative test procedure.

(2) The applicant shall submit his application to the regional administrator through the department.

(3) An application for an alternate test procedure shall be made by letter in triplicate, and

(a) Provide the name and address of the responsible person or firm making the discharge (if not the applicant), the number of the existing or pending permit, the name of the issuing agency, and the discharge serial number,

(b) Identify the pollutant or parameter for which approval of an alternate testing procedure is being requested,

(c) Provide justification for using testing procedures other than those specified in NR 219, and

(d) Provide a detailed description of the proposed alternate test procedure, together with references to published studies of the applicability of the alternate test procedure to the effluents in question.

History: Emerg. cr. eff. 2–1–74.

NR 219.05 Approval of alternate test procedures. (1) The regional administrator has final responsibility for approval of any alternate test procedure.

(2) Within 30 days of receipt of an application, the department will forward such application, together with its recommendations, to the regional administrator. Where the director recommends rejection of the application for scientific and technical reasons which he provides, the regional administrator shall deny the application.

(3) Within 90 days of his receipt of an application for an alternate test procedure, the regional administrator will notify the applicant and the department agency of approval or rejection, or shall specify the additional information which is required to determine whether to approve the proposed test procedure.

History: Emerg. cr. eff. 2–1–74.

219.06 Table listing approved test procedures.

Parameter and units	Method	References		
		Standard methods	ASTM	EPA methods
General analytical method:				
1. Alkalinity as $CaCO_3$ mg $CaCO_3$/liter.	Titration: electrometric, manual or automated method—methyl orange.	p. 370	p. 143	p. 6. p. 8.
2. B.O.D. five day mg/liter	Modified winkler or probe method	p. 489		
3. Chemical oxygen demand (C.O.D.) mg/liter.	Dichromate reflux	p. 495	p. 219	p. 17.
4. Total solids mg/liter	Gravimetric 103–105° C	p. 535		p. 280.
5. Total dissolved (filterable) solids mg/liter.	Glass fiber filtration 180° C			p. 275.
6. Total suspended (nonfilterable) solids mg/liter.	Glass fiber filtration 103–105° C	p. 537		p. 278.
7. Total volatile solids mg/liter.	Gravimetric 550° C	p. 536		p. 282.
8. Ammonia (as N) mg/liter.	Distillation—nesslerization or titration automated phenolate.			p. 134. p. 141.
9. Kjeldahl nitrogen (as N) mg/liter.	Digestion + distillation—nesslerization or titration automated digestion phenolate.	p. 469		p. 149. p. 157.
10. Nitrate (as N) mg/liter	Cadmium reduction; brucine sulfate; automated cadmium or hydrazine reduction.	p. 458 p. 461	p. 124	p. 170. p. 175. p. 185.
11. Total phosphorus (as P) mg/liter.	Persulfate digestion and single reagent (ascorbic acid), or manual digestion, and automated single reagent or stannous chloride.	p. 526 p. 532	p. 42	p. 235. p. 246. p. 259.
12. Acidity mg $CaCO_3$/liter	Electrometric end point or phenolphthalein end point.		p. 148	
13. Total organic carbon (TOC) mg/liter.	Combustion—infrared method[1]	p. 257	p. 702	p. 221.
14. Hardness—total mg $CaCO_3$/liter.	EDTA titration; automated colorimetric atomic absorption.	p. 179	p. 170	p. 76. p. 78.
15. Nitrite (as N) mg/liter.	Manual or automated colorimetric diazotization.			p. 185. p. 195.
Analytical methods for trace metals:				
16. Aluminum—total[2] mg/liter.	Atomic absorption	p. 210		p. 98.
17. Antimony—total[2] mg/liter.	Atomic absorption[4]			
18. Arsenic—total mg/liter.	Digestion plus silver diethyldithiocarbamate; atomic absorption.[3]	p. 65 p. 62		p. 13.
19. Barium—total[2] mg/liter	Atomic absorption[4]	p. 210		
20. Beryllium—total[2] mg/liter.	Aluminon; atomic absorption	p. 67 p. 210		
21. Boron—total mg/liter	Curcumin	p. 69		
22. Cadmium—total[3] mg/liter.	Atomic absorption; colorimetric	p. 210 p. 422	p. 692	p. 101.
23. Calcium—total[2] mg/liter	EDTA titration; atomic absorption	p. 84	p. 692	p. 102.
24. Chromium VI mg/liter.	Extraction and atomic absorption; colorimetric.	p. 429		p. 94.
25. Chromium—total[2] mg/liter.	Atomic absorption; colorimetric	p. 210 p. 426	p. 692 p. 403	p. 104.
26. Cobalt—total[2] mg/liter.	Atomic absorption[4]		p. 692	
27. Copper—total[2] mg/liter	Atomic absorption; colorimetric	p. 210 p. 430	p. 692 p. 410	p. 106.
28. Iron—total[3] mg/liter	do	p. 210 p. 433	p. 692 p. 152	p. 108.
29. Lead—total[3] mg/liter	do	p. 210 p. 436	p. 692	p. 110.
30. Magnesium—total[3] mg/liter.	Atomic absorption; Gravimetric	p. 210 p. 416 p. 201	p. 692	p. 112.
31. Manganese—total[3] mg/liter.	Atomic absorption	p. 210	p. 692	p. 114.
32. Mercury—total mg/liter	Flameless atomic absorption[5]			
33. Molybdenum—total[3] mg/liter.	Atomic absorption[4]			
34. Nickel—total[3] mg/liter.	Atomic absorption; colorimetric[4]	p. 443	p. 692	
35. Potassium—total[2] mg/liter.	Atomic absorption; colorimetric; flame photometric.	p. 283 p. 285	p. 326	p. 115.

Parameter and units	Method	References		
		Standard methods	ASTM	EPA methods
36. Selenium—total mg/liter	Atomic absorption[3]			
37. Silver—total[2]	Atomic absorption[4]	p. 210		
38. Sodium—total[2] mg/liter	Flame photometric; atomic absorption	p. 317	p. 326	p. 118.
39. Thallium—total[2] mg/liter.	Atomic absorption[4]			
40. Tin—total[3] mg/liter	do			
41. Titanium—total mg/liter	do			
42. Vanadium—total[3] mg/liter.	Atomic Absorption;[4] Colorimetric	p. 157		
43. Zinc—total[3] mg/liter	Atomic Absorption; Colorimetric	p. 210 p. 444	p. 692	p. 120.
Analytical methods for nutrients, anions, and organics:				
44. Organic nitrogen (as N) mg/liter.	Kjeldahl nitrogen minus ammonia nitrogen.	p. 468		p. 149.
45. Ortho-phosphate (as P) mg/liter.	Direct single reagent; automated single reagent or stannous chloride.	p. 532	p. 42	p. 235. p. 246. p. 259.
46. Sulfate (as SO_4) mg/liter.	Gravimetric; turbidimetric; automated colorimetric—barium chloranilate.	p. 331 p. 334	p. 51 p. 52	p. 286. p. 288.
47. Sulfide (as S) mg/liter	Titrimetric—iodine	p. 551		p. 294.
48. Sulfite (as SO_3) mg/liter.	Titrimetric; iodide-iodate	p. 337	p. 261	
49. Bromide mg/liter	do		p. 216	
50. Chloride mg/liter	Silver nitrate; mercuric nitrate; automated colorimetric-ferricyanide.	p. 96 p. 97	p. 23 p. 21	p. 29. p. 31.
51. Cyanide—total mg/liter.	Distillation—silver nitrate titration or pyridine pyrazolone colorimetric.	p. 397	p. 556	p. 41.
52. Fluoride mg/liter	Distillation—SPADNS	p. 171 p. 174	p. 191	p. 64.
53. Chlorine—total residual mg/liter.	Colorimetric; amperometric titration	p. 382	p. 223	
54. Oil and grease mg/liter	Liquid-Liquid extraction with trichlorotrifluoroethane.	p. 254		
55. Phenols mg/liter	Colorimetric, 4 AAP	p. 502	p. 445	p. 232.
56. Surfactants mg/liter	Methylene blue colorimetric	p. 339	p. 619	p. 131.
57. Algicides mg/liter	Gas chromatography[6]			
58. Benzidine mg/liter	Diazotization—colorimetric[7]			
59. Chlorinated organic compounds (except pesticides) mg/liter.	Gas chromatography[6]			
60. Pesticides mg/liter	Gas chromatography[6]			
Analytical methods for physical and biological parameters:				
61. Color platinum-cobalt units or dominant wave-length, hue, luminance, purity.	Colorimetric; spectrophotometric	p. 160 p. 392		p. 38.
62. Specific conductance mho/cm at 25° C.	Wheatstone bridge	p. 323	p. 163	p. 284.
63. Turbidity jackson units.	Turbidimeter	p. 350	p. 467	p. 308.
64. Fecal streptococci bacteria number/100 ml.	MPN; membrane filter; plate count	p. 689 p. 690 p. 691		
65. Coliform bacteria (fecal) number/100 ml.	MPN; Membrane filter	p. 669 p. 684		
66. Coliform bacteria (total) number/100 ml.	do	p. 664 p. 679		
Radiological parameters:				
67. Alpha—total pCi/liter	Proportional counter; scintillation counter	p. 598	p. 509	
68. Alpha—counting error pCi/liter.	do	p. 598	p. 512	
69. Beta—total pCi/liter	Proportional counter†	p. 598	p. 478	
70. Beta—counting error pCi/liter.	do	p. 598	p. 478	
71. Radium—total pCi/liter.	Proportional counter; scintillation counter	p. 611 p. 617	p. 674	

[1] A number of such systems manufactured by various companies are considered to be comparable in their performance. In addition, another technique, based on Combustion-Methane Detection, is also acceptable.

[2] For the determination of total metals the sample is not filtered before processing. Choose a volume of sample appropriate for the expected level of metals. If much suspended material is present, as little as 50-100 ml. of

well-mixed sample will most probably be sufficient. (The sample volume required may also vary proportionally with the number of metals to be determined.)

Transfer a representative aliquot of the well-mixed sample to a Griffin beaker and add 3 ml. of concentrated distilled HNO_3. Place the beaker on a hotplate and evaporate to dryness making certain that the sample does not boil. Cool the beaker and add another 3 ml. portion of distilled concentrated HNO_3. Cover the beaker with a watch glass and return to the hotplate. Increase the temperature of the hotplate so that a gentle reflux action occurs. Continue heating, adding additional acid as necessary until the digestion is complete, generally indicated by a light colored residue. Add (1:1 with distilled water) distilled concentrated HCl in an amount sufficient to dissolve the residue upon warming. Wash down the beaker walls and the watch glass with distilled water and filter the sample to remove silicates and other insoluble material that could clog the atomizer. Adjust the volume to some predetermined value based on the expected metal concentrations. The sample is now ready for analysis. Concentrations so determined shall be reported as "total".

[3]See D. C. Manning, "Technical Notes", Atomic Absorption Newsletter, Vol. 10, No. 6, p. 123, 1971. Available from Perkin-Elmer Corporation, Main Avenue, Norwalk, Connecticut 06852.

[4]Atomic absorption method available from Methods Development and Quality Assurance Research Laboratory, National Environmental Research Center, USEPA, Cincinnati, Ohio 45268.

[5]For updated method see: Journal of the American Water Works Association 64, No. 1, pp. 20-25 (Jan. 1972) or ASTM Method D 3223-73, American Society for Testing and Materials Headquarters, 1916 Race St., Philadelphia, Pa. 19103.

[6]Interim procedures for algicides, chlorinated organic compounds, and pesticides can be obtained from the Methods Development and Quality Assurance Research Laboratory, National Environmental Research Center, USEPA, Cincinnati, Ohio 45268.

[7]Benzidine may be estimated by the method of M.A. El-Dib, "Colorimetric Determination of Aniline Derivatives in Natural Waters", El-Dib, M.A., Journal of the Association of Official Analytical Chemists, Vol. 54, No. 6, Nov., 1971, pp. 1383-1387.

†As a prescreening measurement.

History: Emerg. cr. **eff. 2–1–74.**