Chapter NR 219

ANALYTICAL TEST METHODS AND PROCEDURES

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

History: Cr. Register, August, 1976, No. 248, eff. 9-1-76.

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, Wisconsin Statutes.

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

History: Cr. Register, August, 1976, No. 248, eff. 9-1-76.

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.

(4m) Copies of the publications identified above, and of the publications referred to in footnotes (3) through (7) of NR 219.06 are available for inspection at the offices of the department of natural resources, the secretary of state, and the revisor of statutes.

History: Cr. Register, August, 1976, No. 248, eff. 9-1-76.

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: Cr. Register, August, 1976, No. 248, eff. 9-1-76.

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 adminstrator 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: Cr. Register, August, 1976, No. 248, eff. 9-1-76.

NR 219.06 - List of approved test procedures

Parameter and units	Method	References: Standard Methods	References: ASTM	References: EPA Methods
General analytical methods:				
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.	Aluminum; atomic absorption.	p. 67 p. 210		
21. Boron—total mg/liter.	Curcumin.	p. 69		
22. Cadmium—total[2] 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[2] mg/liter.	do	p. 210 p. 433	p. 692 p. 152	p. 108
29. Lead—total[2] mg/liter.	do	p. 210 p. 436	p. 692	p.110
30. Magnesium—total[2] mg/liter.	Atomic absorption; Gravimetric.	p. 210	p. 692	p. 112

			p. 416		
			p. 201		
31.	Manganese—total[2] mg/liter.	Atomic absorption.	p. 210	p. 692	p. 114
32.	Mercury—total mg/liter.	Flameless atomic absorption.[5]			
33.	Molybdenum—total[2] mg/liter.	Atomic absorption.[4]			
34.	Nickel—total[2] 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
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[2] mg/liter.	do			
41.	Titanium—total mg/liter.	do			
42.	Vanadium—total[2] mg/liter.	Atomic absorption;[4] colorimetric.	p. 357		
43.	Zinc—total[2] 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 chloranllate.	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.	Oxidation—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		
	See Note at end of Table I				
65.	Coliform bacteria (fecal) number/100 ml.	MPN; membrane filter.	p. 669 p. 684		
66.	Coliform bacteria (total)	do	p. 664		

	number/100 ml.		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 additon, 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 materials 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 Othicial Analytical Chemists, Vol. 54, No. 6, Nov., 1971. pp. 1383-1387.

†As a prescreening measurement.

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