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 s. 147.04 (5), 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 ch. 147, Stats.

(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," 14th Edition, 1976. 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 31, Water, 1975." 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 Waste, 1974", Methods Development and Quality Assurance Research Laboratory, National Environmental Research Center, Cincinnati, Ohio 45268; U.S. Environmental Protection Agency, Office of Technology Transfer, Industrial Environmental Research Laboratory, Cincinnati, Ohio 45268. This publication is available from the Office of Technology Transfer.

(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 1 through 3, 5 through 10, 12, 13, 15 through 17, and 22 through 24 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; am. (1), (2), (3) and (4m), Register, January, 1978, No. 265, eff. 2-1-78.

NR 219.04 Application for alternate test procedures. (1) Any person may apply to the regional administrator for approval of an alternate test procedure for a specific discharge. Such application shall be made in the following manner:

(a) The applicant shall submit an application to the regional administrator through the department.

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

1. 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,

2. Identify the pollutant or parameter for which approval of an alternate testing procedure is being requested,

3. Provide justification for using testing procedures other than those specified in NR 219, and

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

(2) Any person may apply to the director, environmental monitoring and support laboratory, Cincinnati, Ohio 45268 for approval of an alternate test procedure for nationwide use. Such application shall be made in the following manner:

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

1. Provide the name and address of the responsible person or firm making the request,

2. Identify the pollutant (s) or parameter (s) for which nationwide approval of an alternate testing procedure is being requested,

3. Provide a detailed description of the proposed alternate test procedure, together with references to published or other studies confirming the general applicability of the alternate test procedure to the pollutant (s) or parameter (s) in wastewater from representative or specified industrial or other categories, and

4. Provide comparability data for the performance of the proposed alternate test procedure compared to the approved test procedures.

History: Cr. Register, August, 1976, No. 248, eff. 9-1-76; r. and recr. January, 1978, No. 265, eff. 2-1-78.

NR 219.05 Approval of alternate test procedures. (1) The regional administrator has final responsibility for approval of any alternate test procedure proposed by responsible person or firm making the discharge.

(2) Within 30 days of receipt of an application, the department will forward such application proposed by responsible person or firm making the discharge, together with its recommendations, to the regional administrator. Where the director recommends rejection of the application for scientific and technical reasons which the director provides, the regional adminstrator shall deny the application.

(3) Within 90 days of the receipt of an application for an alternate test procedure proposed by responsible person or firm making the discharge, 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.

(4) Within 90 days of the receipt by the director of the environmental monitoring and support laboratory, Cincinnati, of an application for an alternate test procedure for nationwide use, the director of the environmental monitoring and support laboratory, Cincinnati, shall notify the applicant of his/her recommendation to the administrator to approve or reject the application or shall specify additional information which is required to determine whether to approve the proposed test procedure. After such notification, an alternate method determined by the administrator to satisfy the applicable requirements of this chapter shall be approved for nationwide use: alternate test procedures determined by the administrator not to meet the requirements of 40 CFR part 136 shall be rejected. Notice of these determinations shall be submitted for publication in the federal register not later than 15 days after such notification and determination is made.

History: Cr. Register, August, 1976, No. 248, eff. 9-1-76; am. (1) to (3) and cr. (4), January, 1978, No. 265, eff. 2-1-78.

NR 219.06 - LIST OF APPROVED TEST PROCEDURES[1]

	Parameter and Units	Method	References (page numbers) EPA Methods	Standard Methods	ASTM	USGS[2] Methods	Other
General Parameters							
1.	Acidity, as $CaCO_3$, mg/l	Electrometric end point (pH of 8.2) or phenolphthalein end point.	1	273(4d)	116	40	[3](607)
2.	Alkalinity as $CaCO_3$, mg/l	Electrometric titration (to pH 4.5) manual or automated, or equivalent automated methods.	3 5	278	111	41	[3](607)
3.	Ammonia (as N), mg/l	Manual distillation[4] (at pH 9.5), followed by nesslerization, titration electrode, automated phenolate.	159 165 168	410 412 616	237	116	[3](614)
4.	Benzidine, mg/l						
5.	Biochemical oxygen demand, five-day (BOD_5), mg/l	Oxidation - colorimetric.[5] Winkler (Azide modification) or eletrode.		543		[6](50)	[7](17)
6.	Bromide, mg/l	Titrimetric, iodine-iodate.	14		323	58	
7.	Chemical oxygen demand (COD), mg/l	Dichromate reflux.	20	550	472	124	[3](610) [7](17)
8.	Chloride, mg/l	Silver nitrate; mercuric nitrate; automated colorimetric-ferricyanide.	29 31	303 304 613	267 265	[8](46)	[3](615)
9.	Chlorinated organic compounds (except pesticides), mg/l	Gas chromatography.[9]					
10.	Chlorine-total residual, mg/l	Iodometric titration, amperometric or starch-iodine endpoint; DPD colorimetric or titrimetric methods (these last two methods are interim methods pending laboratory testing).	35	318 322 332 329	278		
11.	Color, platinum cobalt units or dominant wavelength, hue, luminance, purity	Colorimetric; spectrophotometric; or ADMI procedure.[10]	36 39	64 66		82	
12.	Cyanide, total,[11] mg/l	Distillation followed by silver nitrate titration or pyridine pyrazolone (or barbituric acid) colorimetric.	40	361	503	85	[7](22)

	Parameter and Units	Method	References (page numbers) EPA Methods	Standard Methods	ASTM	USGS[2] Methods	Other
13.	Cyanide amenable to chlorination, mg/1	...do	49	376	505		
14.	Dissolved oxygen, mg/1	Winkler (Azide modification) or electrode method.	51 56	443 450	368	126	[3](609)
15.	Fluoride, mg/1	Distillation[4] followed by ion electrode; SPADNS; or automated complexone.	 65 59 61	389 391 393 614	 307 305	 93	
16.	Hardness, total, as $CaCO_3$, mg/1	EDTA titration; automated colorimetric; or atomic absorption (sum of Ca and Mg as their respective carbonates).	68 70	202	161	94	[3](617)
17.	Hydrogen ion (pH), pH units	Electrometric measurement.	239	460	178	129	[3](606)
18.	Kjeldahl nitrogen (as N), mg/1	Digestion and distillation followed by nesslerization, titration or electrode; automated digestion automated phenolate.	175 165 182	437		122	[3](612)
19.	Nitrate (as N), mg/1	Cadmium reduction; brucine sulfate; automated cadmium or hydrazine reduction.[13]	201 197 207	423 427 620	358	119	[3](614)-[7](28)
20.	Nitrite (as N), mg/1	Manual or automated colorimetric (Diazotization)	215	434		121	
21.	Oil and grease, mg/1	Liquid-liquid extraction with trichlorotrifluoro-ethane-gravimetric.	229	515			
22.	Organic carbon, total (TOC) mg/1	Combustion-infrared method.[14]	236	532	467	[15](4)	
23.	Organic nitrogen (as N), mg/1	Kjeldahl nitrogen minus ammonia nitrogen.	175,159	437		122	[3](612,614)
24.	Orthophosphate (as P), mg/1	Manual or automated ascorbic acid reduction.	249 256	481 624	384	131	[3](621)
25.	Pentachlorophenol, mg/1	Gas chromatography.[9]					
26.	Pesticides, mg/1	...do[9]		555	529	[15](24)	
27.	Phenols, mg/1	Distillation followed by colorimetric (4AAP).	241	574	545		
28.	Phosphorus (elemental), mg/1	Gas chromatography.[16]					

	Parameter and Units	Method	References (page numbers) EPA Methods	Standard Methods	ASTM	USGS[2] Methods	Other
29.	Phosphorus, total (as P), mg/1	Persulfate digestion followed by manual or automated ascorbic acid reduction.	249 256	476,481 624	384	133	[3](621)
30.	Specific conductance, micromhos per centimeter at 25°C	Wheatstone bridge conductimetry.	275	71	120	148	[3](606)
31.	Sulfate (as SO_4), mg/1	Gravimetric; turbidimetric; or automated colorimetric (barium chloranilate).	 277 279	493 496	424 425		[3](624) [3](623)
32.	Sulfide (as S), mg/1	Titrimetric-iodine for levels greater than 1 mg/1; methylene blue photometric.	284	505 503		154	
33.	Sulfite (as SO_3), mg/1	Titrimetric, iodine-iodate.	285	508	435		
34.	Surfactants, mg/1	Colorimetric (methylene blue).	157	600	494	[15](11)	
35.	Temperature, degrees C	Calibrated glass or electrometric thermometer.	286	125		[17](31)	
36.	Turbidity, NTU	Nephelometric.	295	132	223	156	
Bacteria							
37.	Coliform (fecal)[18], number per 100 ml	MPN;[19] membrane filter.		922 937		[6](45)	
38.	Coliform (fecal)[18], in presence of chlorine, number per 100 ml	...do[19,20]		922 928,937			
39.	Coliform (total)[18], number per 100 ml	...do[19]		916 928		[6](35)	
40.	Coliform (total)[18], in presence of chlorine, number per 100 ml	MPN;[19] membrane filter with enrichment.		916 933			
41.	Fecal streptococci,[18] number per 100 ml.	MPN;[19] membrane filter; plate count.		943 944 947		[6](50)	
Metals[21]							
42.	Aluminum, total, mg/1	Digestion[22] followed by atomic absorption[23] or by colorimetric (Eriochrome Cyanide R).	92	152 171		[8](19)	
43.	Antimony, total, mg/1	Digestion[22] followed by atomic absorption[23].	94				

	Parameter and Units	Method	References (page numbers) EPA Methods	Standard Methods	ASTM	USGS[2] Methods	Other
44.	Arsenic, total, mg/l	Digestion followed by silver diethyldithio-carbamate; or atomic absorption.[23],[24]	9 95	285 283 159		[8](31) [8](37)	
45.	Barium, total, mg/l	Digestion[22] followed by atomic absorption.[23]	97	152			52
46.	Beryllium, total, mg/l	Digestion[22] followed by atomic absorption[22] or by colorimetric (aluminon)	99	152 177		53	
47.	Boron, total, mg/l	Colorimetric (Curcumin).	13	287			
48.	Cadmium, total, mg/l	Digestion[22] followed by atomic absorption[23] or by colorimetric (Dithizone).	101	148 182	345	62	[3](619)-[7](37)
49.	Calcium, total, mg/l	Digestion[22] followed by atomic absorption; or EDTA titration.	103	148 189	345	66	
50.	Chromium VI, mg/l	Extraction and atomic absorption; colorimetric (Diphenylcarbazide).	89,105	192		76 75	
51.	Chromium, total, mg/l	Digestion[22] followed by atomic absorption[23] or by colorimetric (Diphenylcarbazide).	105	148 192	345 286	78 77	[3](619)
52.	Cobalt, total, mg/l	Digestion[22] followed by atomic absorption.[23]	107	148	345	80	[7](37)
53.	Copper, total, mg/l	Digestion[22] followed by atomic absorption[23] or by colorimetric (Neocuproine).	108	148 196	345 243	83	[3](619)-[7](37)
54.	Gold, total, mg/l	Digestion[22] followed by atomic absorption.[12]					
55.	Iridium, total, mg/l	Digestion[22] followed by atomic absorption.[12]					
56.	Iron, total, mg/l	Digestion[22] followed by atomic absorption[23] or by colorimetric (Phenanthroline).	110	148 208	345 326	102	[3](619)
57.	Lead, total, mg/l	Digestion[22] followed by atomic absorption[23] or by colorimetric (Dithizone).	112	148 215	345	105	[3](619)
58.	Magnesium, total, mg/l	Digestion[22] followed by atomic absorption; or gravimetric.	114	148 221	345	109	[3](619)

	Parameter and Units	Method	References (page numbers) EPA Methods	Standard Methods	ASTM	USGS[7] Methods	Other
59.	Manganese, total, mg/1	Digestion[22] followed by atomic absorption[23] or by colorimetric (Persulfate or periodate).	116	148 225,227	345	111	[3](619)
60.	Mercury, total, mg/1	Flameless atomic absorption.	118	156	338	[8](51)	
61.	Molybdenum, total, mg/1	Digestion[22] followed by atomic absorption.[23]	139		350		
62.	Nickel, total, mg/1	Digestion[22] followed by atomic absorption[23] or by colorimetric (Heptoxime).	141	148	345	115	
63.	Osmium, total, mg/1	Digestion[22] followed by atomic absorption[12].					
64.	Palladium, total, mg/1	Digestion[22] followed by atomic absorption[12].					
65.	Platinum, total, mg/1	Digestion[22] followed by atomic absorption[12].					
66.	Potassium, total, mg/1	Digestion[22] followed by atomic absorption, colorimetric (Cobaltinitrite), or by flame photometric.	143	 235 234	 403	134	[3](620)
67.	Rhodium, total, mg/1	Digestion[22] followed by atomic absorption.[12]					
68.	Ruthenium, total, mg/1	Digestion[22] followed by atomic absorption.[12]					
69.	Selenium, total, mg/1	Digestion[22] followed by atomic absorption.[12,24]	145	159			
70.	Silica, dissolved, mg/1	0.45 micron filtration[21] followed by colorimetric (Molybdosilicate).	274	487	398	139	
71.	Silver, total[25], mg/1	Digestion[22] followed by atomic absorption[23] or by colorimetric (Dithizone).	146	148 243		142	[3](619) - [7](37)
72.	Sodium, total, mg/1	Digestion[22] followed by atomic absorption or by flame photometric.	147	 250	 403	143	[3](621)
73.	Thallim, total, mg/1	Digestion[22] followed by atomic absorption.[23]	149				
74.	Tin, total, mg/1	Digestion[22] followed by atomic absorption.[23]	150			[8](65)	
75.	Titanium, total, mg/1	Digestion[22] followed by atomic absorption.[23]	151				

	Parameter and Units	Method	References (page numbers) EPA Methods	Standard Methods	ASTM	USGS[2] Methods	Other
76.	Vanadium, total, mg/1	Digestion[22] followed by atomic absorption[23] or by colorimetric (Gallic acid).	153	152 260	441	[8](67)	
77.	Zinc, total, mg/1	Digestion[22], followed by atomic absorption[23] or by colorimetric (Dithizone).	155	148 265	345	159	[3](619)- [7](37)
Radiological							
78.	Alpha, total, pCi/1	Proportional or scintillation counter		648	591		[8 26](75+78)
79.	Alpha, Counting Error, pCi/1	...do		648	594		[8](79)
80.	Beta, total, pCi/1	Proportional counter.		648	601		[8 26](75+78)
81.	Beta, counting error, pCi/1	...do		648	606		[8](79)
82.	Radium, total, pCi/1	...do		661	661		
83.	226 Radium, pCi/1	Scintillation counter.		667			[8](81)
Residue							
84.	Total, mg/1	Gravimetric, 103 to 105°C.	270	91			
85.	Total dissolved (filterable), mg/1	Glass fiber filtration, 180°C.	266	92			
86.	Total suspended (nonfilterable), mg/1	Glass fiber filtration, 103 to 105°C.	268	94			
87.	Settleable, ml/1 or mg/1.	Volumetric or gravimetric.		95			
88.	Total volatile, mg/1	Gravimetric, 550°C.	272	95			

[1]Recommendation for sampling and preservation of samples according to parameter measured may be found in "Methods for Chemical Analysis of Water and Wastes, 1974" U.S. Environmental Protection Agency, table 2, pp. vii-xii.

[2]All page references for USGS methods, unless otherwise noted, are to Brown, E., Skougstad, M.W., and Fishman, M.J., "Methods for Collection and Analysis of Water Samples for Dissolved Minerals and Gases," U.S. Geological Survey Techniques of Water-Resources Inv., book 5, ch. A1, (1970).

[3]EPA comparable method may be found on indicated page of "Official Methods of Analysis of the Association of Official Analytical Chemists" methods manual, 12th ed. (1975).

[4]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.

[5]Adequately tested methods for benzidine are not available. Until approved methods are available, the following interim method can be used for the estimation of benzidine: "Method for Benzidine and its Salts in Wastewaters," available from Environmental Monitoring and Support Laboratory, U.S. Environmental Protection Agency, Cincinnati, Ohio 45268.

[6]Slack, K.V., and others, "Methods for Collection and Analysis of Aquatic Biological and Microbiological Samples," U.S. Geological Survey Techniques of Water-Resources Inv., book 5, ch. A4, (1973).

[7]American National Standard on Photographic Processing Effluents, April 2, 1975. Available from NASI, 1430 Broadway, New York, New York 10018.

[8]Fishman, M.J. and Brown, Eugene, "Selected Methods of the U.S. Geological Survey for Analysis of Wastewaters," (1976) open-file report, 76-117.

[9]Procedures for pentachlorophenol, chlorinated organic compounds and pesticides can be obtained from the Environmental Monitoring and Support Laboratory, U.S. Environmental Protection Agency, Cincinnati, Ohio 45268.

[10]Color method (ADMI procedure) available from the Environmental Monitoring and Support Laboratory, U.S. Environmental Protection Agency, Cincinnati, Ohio 45268.

[11]For samples suspected of having thiocyanate interference, magnesium chloride is used as the digestion catalyst. In the approved test procedure for cyanides, the recommended catalysts are replaced with 20 ml of a solution of 510 g/l magnesium chloride ($MgC1.6H_2O$). This substitution will eliminate thiocyanate interference for both total cyanide and cyanide amenable to chlorination measurements.

[12]Method available from the Environmental Monitoring and Support Laboratory, U.S. Environmental Protection Agency, Cincinnati, Ohio 45268.

[13]An authomated hydrazine reduction method is available from the Environmental Monitoring and Support Laboratory, U.S. Environmental Protection Agency, Cincinnati, Ohio 45268.

[14]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.

[15]Goerlitz, D., Brown, E., "Methods for Analysis of Organic Substances in Water," U.S. Geological Survey Techniques of Water-Resources Inv., book 5, ch. A3 (1972).

[16]Addison, R.F., and Ackman, R.G., "Direct Determination of Elemental Phosphorus by Gas-Liquid Chromatography," "Journal of Chromatography," vol. 47, No. 3, pp. 421-426, 1970.

[17]Stevens, H.H., Ficke, J.F., and Smoot, G.F., "Water Temperature-Influential Factors, Field Measurement and Data Presentation," U.S. Geological Survey Techniques of Water Resources Inv., book 1 (1975).

[18]The method used must be specified.

[19]The 5 tube MPN is used.

[20]Since the membrane filter technique usually yields low and variable recovery from chlorinated wastewaters, the MPN method will be required to resolve any controversies.

[21]Dissolved metals are defined as those constituents which will pass through a 0.45 micron filter. A prefiltration is permissable to free the sample from larger suspended solids. Filter the sample as soon as practical after collection using the first 50 to 100 ml to rinse the filter flask. (Glass or plastic filtering apparatus are recommended to avoid possible contamination). Discard the portion used to rinse the flask and collect the required volume of filtrate. Acidify the filtrate with 1:1 redistilled HNO_3 to a pH of 2. Normally, 3 ml of (1:1) acid per liter should be sufficient to preserve the samples.

[22]For the determination of total metals the sample is not filtered before processing. Because vigorous digestion procedures may result in a loss of certain metals through precipitation, a less vigorous treatment is recommended as given on page 83 (4.1.4) of "Methods for Chemical Analysis of Water and Wastes" (1974). In those instances where a more vigorous digestion is desired, the procedure on page 82 (4.1.3) should be followed. For the measurement of the noble metal series

(gold, iridium, osmium, palladium, platinum, rhodium and ruthenium), an aqua regia digestion is to be substituted as follows: Transfer a representative aliquot of the well-mixed sample to a Griffin beaker and add 3 ml of concentrated redistilled HNO_3. Place the beaker on a stream bath and evaporate to dryness. Cool the beaker and cautiously add a 5 ml portion of aqua regia. (Agua regia is prepared immediately before use by carefully adding 3 volumes of concentrated HCl to one volume of concentrated HNO_3). Cover the beaker with a watch glass and return to the steam bath. Continue heating the covered beaker for 50 minutes. Remove cover and evaporate to dryness. Cool and take up the residue in a small quantity of 1:1 HCl. Wash down the beaker and 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 volume based on the expected metal concentration. The sample is now ready for analysis.

[23]As the various furnace devices (flameless A.A.) are essentially atomic absorption techniques, they are considered to be approved test methods. Methods of standard addition are to be followed as noted in p. 78 of "Methods for Chemical Analysis of Water and Wastes," 1974.

[24]See "Atomic Absorption Newsletter," vol. 13,75 (1974). Avaiable from Perkin-Elmer Corp., Main Ave., Norwalk, Conn. 06852.

[25]Recommended methods for the analysis of silver in industrial wastewaters at concentrations of 1 mg/1 and above are inadequate where silver exists as 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/1, 20 ml of sample should be diluted to 100 ml by adding 40 ml each of 2M $Na_2S_2O_3$ and 2M NaOH. Standards should be prepared in the same manner. For levels of silver below 1 mg/1 the recommended procedure is satisfactory.

[26]The method found on page 75 measures only the dissolved portion while the method on page 78 measures only suspended. Therefore the two results must be added together to obtain "total."

History: Cr. Register, August, 1976, No. 248, eff. 9-1-76; r. and recr. Register, January, 1978, No. 265, eff. 2-1-78.