Chapter NR 149

LABORATORY CERTIFICATION AND REGISTRATION

Subchapter I — General

NR 149.01 Purpose. The purpose of this chapter is to establish a program for the certification and registration of laboratories doing testing under s. 144.95, Stats.

History: Cr. Register, April, 1986, No. 364, eff. 5-1-86.

NR 149.02 Applicability. (1) Except as provided in subs. (2) and (3), the provisions of subchs. I to III 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 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.

(3) This chapter is not applicable to the certification or registration of laboratories for bacteriological or radiological analyses. Laboratories shall be certified or approved by the department of health and social services for such testing where department rules require the testing to be done by a certified or approved laboratory.

Note: Administrative codes requiring analyses to be done by a certified or registered laboratory are: chs. NR 109, 110, 123, 131, 132, 140, 150, 157, 158, 180, 181, 182, 210, 211, 212, 219 and 347.

History: Cr. Register, April, 1986, No. 364, eff. 5-1-86.

NR 149.03 Definitions. In this chapter:

(1) "Acceptance limits" means limits established by a reference sample provider which are used to determine if a laboratory has acceptable accuracy.

(2) "Accuracy" means the closeness of a measured value to its generally accepted value or its value based upon an accepted reference standard.

(3) "Analysis day" means the day in which that specific type of analysis is done.

(4) "Analyte" means the chemical substance or physical property being tested for in a sample.

(5) "Authoritative source" means the following sources:

(a) "Methods for Chemical Analysis of Water and Wastes", EPA-600/4-79-020, Environmental Monitoring and Support Laboratory, 26 West St. Claire, Cincinnati, Ohio 45268, Revised 1983, including EPA-600/4-84-017, March, 1984.

(b) "Test Methods - Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater", EPA-600/4-82-057, Environmental Monitoring and Support Laboratory, 26 West St. Claire, Cincinnati, Ohio 45268, July, 1982.

(c) "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods", SW-846, EPA, Office of Solid Waste and Emergency Response, 401 M Street, S.W., Washington D.C. 20460, July, 1982, including update number 1, 1984.

(d) "Standard Methods for the Examination of Water and Wastewater", 16th ed., American Public Health Association, 1015 Fifteenth Street NW, Washington D.C. 20005, 1985.

(e) "1984 Annual Book of ASTM Standards, Section 11.01 and 11.02, Water and Environmental Technology", American Society for Testing and Materials, 1916 Race Street, Philadelphia, PA 19103.

(f) "Procedures for Handling and Chemical Analysis of Sediment and Water Samples", Technical Report EPA/CE-81-1, Environmental Laboratory, U.S. Army Engineer Waterways Experiment Station, P.O. Box 631, Vicksburg, Mississippi 39180.

(g) "Handbook for Sampling and Sample Preservation of Water and Wastewater", EPA-600/4-82-029, Environmental Monitoring and Support Laboratory, U.S. Environmental Protection Agency, 26 West St. Claire, Cincinnati, Ohio 45268, September, 1982.

(h) "Techniques of Water-Resources Investigations of the United States Geological Survey, Methods for Determination of Inorganic Substances in Water and Fluvial Sediments", Book 5, Chapter A1, U.S. Geological Survey, Lakewood, Colorado 80225.

(i) "Handbook for Analytical Quality Control in Water and Wastewater Laboratories", EPA 600/4-79-019, Environmental Monitoring and Support Laboratory, U.S. Environmental Protection Agency, 26 West St. Claire, Cincinnati, Ohio 45268, March, 1979.

NR 149.14 Quality control. (1) Each laboratory shall maintain a quality control program. The quality control program shall be documented and such documents shall be available, upon request, to the department.

(2) Each subsidiary or branch laboratory shall independently comply with this section.

(3) At a minimum, the quality control program shall consist of:

(a) Calibration and maintenance of test instruments and equipment as necessary to maintain accuracy.

(b) A known standard analyzed or a calibration done on each analysis day. The instrument response for the known standard shall be within the pre-established limits under par. (c).

(c) A known standard analyzed after the analysis of 20 samples, if 20 or more samples are analyzed in an analysis day. The instrument response for the known standard shall be within the following pre-established limits:

1. For test categories 2, 3, 6, 9, 10 and for total organic carbon, total organic halide, chloride, hardness, and sulfate, the pre-established limit shall be $\pm 10\%$.

2. For test categories 11, 12, 13, 14, 15, 16, 17, and 18, the pre-established limits shall be $\pm 15\%$.

3. There is no requirement to analyze a known standard for alkalinity/acidity, corrosivity, EP toxicity, ignitability reactivity, gravimetric tests, titratimetric tests, and test categories 4 and 7.

4. For test category 1, a known standard shall be analyzed after the analysis of 20 samples. The limits on this quality control check shall be as established in an authoritative source.

5. For test category 20 the pre-established limit shall be appropriate for the test.

(d) At least one reagent blank shall be analyzed on each analysis day, for those tests for which reagent blanks are appropriate. For certain tests, a nonreacted sample may be used as a blank.

Note: Reagent blanks are not appropriate for certain tests such as alkalinity/acidity, conductivity, hardness, ignitability, and pH. Nonreacted sample blanks are appropriate for certain colormetric and turbidimetric tests such as the sulfate turbidimetric test, silica molybdosilicate test, and the phosphorus ascorbic acid test.

(e) A duplicate sample shall be run after the analysis of 10 samples. For those methodologies which require that the sample bottle be extracted, duplicate samples shall be taken in the field to insure representative samples.

(f) Spiked samples shall be analyzed except when the method of standard addition is used. The spiking of the sample shall be done before any extraction or digestion. The frequency of spiked analysis shall be:

1. As required in the authoritative sources for test categories 11 to 18, 20, total organic halide and total organic carbon. If no frequency is given in the authoritative source, then the frequency shall be after the analysis of 10 samples.

2. After the analysis of 20 samples, at a minimum, for test categories 2, 3, 6, 9, 10, and for chloride, hardness, sulfate, and bromide.

3. No spiked analysis is required for test categories 1 and 4 and for alkalinity/acidity, color, EP toxicity, pH, oil and grease, specific conductance, sulfide, sulfite, turbidity, corrosivity, ignitability, reactivity, and gravimetric tests, or tests where appropriate standards are not available for spiking.

Note: Spiked samples for organics should be spiked with representative organic analytes for each analyzed extraction. The representative organic analytes should be chosen on the basis of the organic analytes which are identified within a permit, and organic analytes which are typically found in that type of sample.

(g) Quality control limits for duplicate sample and spiked sample analysis shall be calculated using a method from an authoritative source. For laboratories with less than 30 quality control results within 12 months, the laboratory may set quality control limits based on information given in the authoritative sources, or laboratory experience, or the experience of other laboratories.

(h) If the results of known standards or duplicates exceed quality control limits, corrective action shall be taken by the laboratory. If it is determined by the laboratory that the discrepancy has affected past sample results, the laboratory shall reanalyze the samples or qualify the results back to the last acceptable quality control check. The results are qualified by reporting that the laboratory analysis was not within the acceptance limits for this test.

(i) If the analysis of a spiked sample exceeds the quality control limits, corrective action shall be taken by the laboratory. If it is determined by the laboratory that the discrepancy has affected past sample results, the laboratory shall reanalyze the samples or qualify the results, for those samples of the same sample matrix, back to the last acceptable quality control check. The results are qualified by reporting that the laboratory analysis was not within acceptance limits for this test. The impact of the spiked sample results on samples of different sample matrices shall be examined to insure that whatever affected the spiked sample had no impact on those samples of different matrices.

(j) A blind standard shall be analyzed, if available for that analyte, every 4 months for each analyte in test categories 1 to 10, 16, and 20, if the analyte was analyzed during the previous 4-month period. A blind standard shall be analyzed every 4 months for one analyte in each test category in test categories 11 to 15, 17, and 18, if an analyte within those test categories was analyzed during the previous 4-month period. If the result for any analyte does not fall within the limits established by the provider or the laboratory, corrective action shall be taken by the laboratory and an additional blind standard shall be analyzed to verify that the corrective action was successful.

(k) Where duplicate, spikes, and other quality control limits are exceeded, documentation shall be available to the department, upon request, indicating what corrective action was taken to bring the results back within limits.

(4) A copy of the methodology used by the laboratory for each analyte analyzed shall be available to the analyst.

(5) If it has been determined that an organic analyte is present in a sample, the laboratory shall inform the data user if the results have been confirmed by a second analysis with a different methodology.

History: Cr. Register, April, 1986, No. 364, eff. 5-1-86.

Subchapter III - Requirements and Administrative Procedures for the Safe Drinking Water Test Category

Note: This subchapter applies only to laboratories applying for certification in the safe drinking water test category for the purpose of analyzing samples for the safe drinking water program under ch. NR 109.

NR 149.21 Methodology. The analytical methodology used for the safe drinking water test category shall comply with state and federal law. The laboratory instrumentation shall meet the specifications of the required methodology.

Note: A listing of approved methodologies is maintained by the department as specified by ch. NR 109 and this chapter. In addition federal law requirements for methodology can be found in 40 CFR 141 and 143.

(1) SAMPLE COLLECTION, HANDLING, AND PRESERVATION. The following procedures shall be used for sample collection, handling and preservation:

(a) The sample shall be representative of the potable water system. The water tap shall be sampled after maintaining a steady flow for 2 or 3 minutes to clear the service line. The tap shall be free of aerator, strainer, hose attachment, or water purification devices.

(b) The sample report form shall be completed immediately after collection with location, date and time of collection, collector's name, and any special remarks concerning the sample.

(c) The required type of sample container and the required preservation for each inorganic chemical analytes are listed in Table 2.

(d) All samples shall be analyzed within the maximum holding times listed in Table 2. Where these maximum holding times cannot be met, the sample shall be discarded and resampling shall be required.

(e) The required type of sample container and the required preservative for the organic chemical analytes are listed in Table 3.

(f) When sampling chlorinated waters for total trihalomethane analysis, sodium thiosulfate or sodium sulfite shall be added to the empty sample bottles prior to shipping to the sampling site.

(g) The total trihalomethane bottles shall be filled in such a manner that no air bubbles pass through the sample as the bottle is filled. The bottle shall be sealed so that no air bubbles are entrapped in it. The hermetic seal on the sample bottle shall be maintained until analysis.

(h) All organic samples shall be analyzed within the maximum holding times listed in Table 3. Where these maximum holding times cannot be met, the sample shall be discarded and resampling shall be required.

(i) Sodium samples shall be collected in plastic or glass containers. Samples shall be preserved by the addition of concentrated nitric acid to achieve pH of less than 2; analyses shall be performed within 6 months of collection.

(j) Alkalinity samples shall be collected in plastic or glass, and shall be preserved by cooling to 4°C. Analysis shall be performed within 14 days of collection.

(k) Calcium samples shall be collected in plastic or glass containers, cooled to 4°C and shall be preserved by the addition of concentrated nitric acid to achieve a pH of less than 2. Analyses shall be performed within 6 months of collection.

(l) Chloride samples shall be collected in plastic or glass containers. Samples need not be preserved. Analyses shall be performed within 7 days of collection.

(m) Sulfate samples shall be collected in plastic or glass containers, and shall be preserved by cooling to 4°C. Analyses shall be performed within 7 days of collection.

(n) Total dissolved solids samples shall be collected in plastic or glass containers, and shall be preserved by cooling to 4°C. Analyses shall be performed within 7 days of collection.

Note: Sample collection methods required by federal law are in 40 CFR 141.30 Appendix C.

(2) ALTERNATE METHODOLOGY. In order to obtain approval to use an alternate methodology, the procedures in s. NR 149.12 shall be followed.

TABLE 2

Sample Collecting, Handling, and Preservation for Inorganic Analytes[1]

Analyte	Preservation[2]	Containers[3]	Maximum Holding Time[4]
Arsenic	Conc HNO_3 to pH < 2	P or G	6 months
Barium	Conc HNO_3 to pH < 2	P or G	6 months
Cadmium	Conc HNO_3 to pH < 2	P or G	6 months
Chromium	Conc HNO_3 to pH < 2	P or G	6 months
Fluoride	None	P	1 month
Lead	Conc HNO_3 to pH < 2	P or G	6 months
Mercury	Conc HNO_3 to pH < 2	G	38 days
		P	14 days
Nitrate			
Chlorinated supplies	Cool 4°C	P or G	28 days
Nonchlorinated supplies	Conc H_2SO_4 to pH < 2	P or G	14 days
Selenium	Conc HNO_3 to pH < 2	P or G	6 months
Silver	Conc HNO_3 to pH < 2	P or G	6 months

1 If a laboratory has no control over these factors, the laboratory director must reject any samples not meeting these criteria and so notify the authority requesting the analyses.

2 If HNO_3 cannot be used because of shipping restrictions, the sample may be initially preserved by icing and immediately shipping it to the laboratory. Upon receipt in the laboratory, the sample must be acidified with concentrated HNO_3 to pH < 2. At the time of analysis, the sample container should be thoroughly rinsed with 1:1 HNO_3; washings should be added to the sample.

3 P = Polyethylene; G = Glass.

4 In all cases, samples should be analyzed as soon after collection as possible.