

Reference Sample Guidance

**A Guide to the Reference Sample Requirements of the
Wisconsin Laboratory Certification Program**



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December 2001



**Bureau of Integrated Science Services
Wisconsin Department of Natural Resources
P.O. Box 7921, Madison, WI 53707**

PUBL-SS-958 2001

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1. Introduction

This document is a guide to the reference sample requirements of the Wisconsin Laboratory Certification Program. Besides clarifying the regulatory definition for reference samples, this document answers many common questions concerning reference samples. Also included are important deadlines, penalties and corrective actions for reference sample failures, and a current list of Wisconsin-approved reference sample providers.

Reference samples, also known as **proficiency testing (PT)** or **performance evaluation (PE) samples**, are samples analyzed by a laboratory to evaluate its ability to perform analyses accurately. The Laboratory Certification Program uses the results of these samples to assess a laboratory's analytical performance between on-site evaluations. All laboratories also must submit acceptable reference sample results annually to the Wisconsin Department of Natural Resources (WDNR) to maintain their certifications or registrations.

2. Terms Defined

Analyte: The chemical substance or physical property being analyzed in a reference sample.

Analyte group: A set of chemical substances possessing structural and reactive similarities that are analyzed as a group using the same method of analysis (e.g. VOCs, PCBs, etc.).

Multi-analyte reference sample: A reference sample containing more than one analyte of interest where certification is granted for each analyte on an individual basis.

Multi-analyte group reference sample: A reference sample containing more than one analyte of interest where certification is granted for the analytes as a group based on acceptable results for all of the existing analytes.

Multi-level reference sample: A reference that includes multiple ampoules with different concentration levels of the same analyte or analytes.

Certified Laboratory: A laboratory which performs tests for hire in connection with a program which requires data from a certified laboratory, and which receives certification or reciprocal recognition under Ch. NR 149, Wis. Adm. Code.

Registered Laboratory: A laboratory which receives registration or reciprocal recognition under Ch. NR 149, Wis. Adm. Code, does not perform tests commercially for hire, and which:

- ✓ performs tests in connection with a program which requires data from a registered laboratory; and
- ✓ performs tests solely on its own behalf or on behalf of a subsidiary or other corporation under common ownership or control, or is owned or controlled by a municipality or two or more municipalities and performs tests solely on the behalf of the municipality or municipalities.

3. Registration

Most laboratories seeking registration only analyze wastewater, and are therefore only interested in registration within the test categories 1-4.

A laboratory must submit an application each time it wishes to become registered for an additional test category, even if it is already currently registered in other test categories. As stated in the introduction, laboratories must also submit acceptable reference sample results annually to the WDNR to maintain their registration.

1) Application

- ✓ A laboratory applying for registration must submit acceptable reference sample results from one of WDNR's approved providers. For a detailed list of the reference samples that must be analyzed when applying for registration in a certain category, consult **Appendix 3** of this document. Part 7 of the application form (Form 4800-002 or 4800-002S) also provides a brief explanation of this requirement. Also see chapter 5, section 3 of this document for an explanation of "key analytes."
- ✓ The study date for the results submitted with applications must be no older than 6 months prior to the date the application is received by the WDNR.

2) Renewal

- ✓ To renew their registration each year, laboratories must submit acceptable reference sample results to the WDNR by September 1. The results must be obtained from reference samples analyzed during the current calendar year (January 1 – September 1). Laboratories are encouraged to report these results to the WDNR by early August to avoid delays in processing the renewal of their registration.
- ✓ Approved providers offer several reference sample options that will meet Wisconsin registration renewal requirements. This *does* include immediate turn-around reference samples (e.g., APG Stat or ERA-Quick Response).
- ✓ Laboratories that have not submitted acceptable reference sample results to the WDNR by early June are sent a letter reminding them that they must provide results to the program before September 1 to retain their registration.

- ✓ DMRQA reference sample results are acceptable for registration renewal purposes as long as certain criteria are satisfied. Refer to chapter 5, section 5 (page 12), for more information on DMRQA.
- ✓ For a detailed list of what reference samples you need to analyze for registration renewal in a certain category, consult **Appendix 3** of this document.

3) Grading

For Water Pollution (**WP**) studies, all WDNR-approved reference sample providers use the same pooled-result grading system used formally by EPA.

- ✓ For specific grading conventions in the case of multi-analyte group, multi-level, and multi-technique reference samples, refer to chapter 4, section 3 (page 7).

4) Failure

Acceptable reference sample results are necessary for renewal of a laboratory's registration.

- ✓ Laboratories must analyze an entirely new reference sample if they fail to report acceptable results initially.
- ✓ If a laboratory fails to report acceptable results for at least 80% of the individual analytes for a multi-analyte group reference sample, it must analyze a second reference sample. The results of *all* individual analytes detected in the reference sample must be reported – *not just the individual analytes that were not acceptable in the first reference sample*.
- ✓ If a laboratory fails *two consecutive* reference samples, it will have to analyze a third reference sample, and may be issued a Notice of Noncompliance (NON). Additional action may also be necessary to close the NON. Such action will be determined on a case-by-case basis.
- ✓ In the event a laboratory fails *three consecutive* reference samples, it may be issued a Notice of Violation (NOV), and its registration may be suspended or revoked.
- ✓ Some laboratories will be registered for multi-analyte groups addressed under Test Categories 10 – 16.
 - If the failure is associated with a multi-component reference sample, the laboratory must report acceptable results for *greater than or equal to* 80% of each of the individual analytes in the sample for the cumulative result of the study to be considered acceptable. This is called the “80% Rule.” For example, if acceptable results are reported for 9 of 15 Volatile Organic

Compounds (VOCs) in a given reference sample study, the cumulative result is not acceptable because only 60% of the analyte results reported fell within the established acceptance limits. The laboratory needs to report correct results for at least 12 of the 15, or 80%, of the analytes in the reference sample for the study to be considered acceptable.

- Laboratories must analyze an entirely new reference sample if they do not attain a score of at least 80%.
- ✓ A comprehensive explanation of enforcement as a consequence of non-drinking water reference sample failure can be found in **Appendix 1** of this document.

4. Certification

A laboratory must submit an application each time it wishes to become certified for an additional test category, even if it is already currently certified in other test categories. As stated in the introduction, laboratories must also submit acceptable reference sample results annually to the WDNR to renew their certifications.

1) Application

- ✓ A laboratory applying for certification must submit acceptable reference sample results from one of the WDNR's approved providers. A detailed list of the reference samples that must be analyzed when applying for certification in a given category is included in **Appendix 3** of this document. Part 7 of the application form (Form 4800-002 or 4800-002S) also provides a brief explanation of this requirement. See chapter 5, section 3 (page 11), for an explanation of "key analytes."
- ✓ The study date for the results submitted with applications must be no older than 6 months prior to the date the application is received by the WDNR.

2) Renewal

- ✓ To renew their certification each year, laboratories must submit acceptable reference sample results to the WDNR by September 1. The results must be obtained from reference samples analyzed during the current calendar year (January 1 – September 1). Laboratories are encouraged to report these results to the WDNR by early August to avoid delays in processing the renewal of their registration.
- ✓ Approved providers offer several reference sample options that will meet Wisconsin certification renewal requirements. This *does* include immediate turn-around reference samples (e.g., APG Stat or ERA-Quick Response).
- ✓ Laboratories that have not submitted acceptable reference sample results to the WDNR by early June are sent a letter reminding them that they must provide results to the program before August 1 to retain their certification.
- ✓ DMRQA reference sample results *are* acceptable for certification renewal purposes. See chapter 5, section 5 (page 12), for more information on DMRQA.
- ✓ For a detailed list of what reference samples you need to analyze to renew certification for any given test category, consult **Appendix 3** of this document.

3) Grading (Non-Drinking Water)

For Water Pollution (WP) studies, all of the WDNR-accepted reference sample providers use the same pooled-result grading system used formally by EPA. WDNR sets acceptance limits only in the event that no established limits exist, which is occasionally the case with some pesticides and other organic analytes. In these cases, the WDNR refers to the method used to establish acceptable limits based on documented performance of that method in an ideal situation.

- ✓ Multi-Analyte Group Reference Samples – For multi-analyte groups (e.g., VOCs), laboratories must report acceptable results for **greater than or equal to** 80% of each of the individual analytes in the reference sample for the overall result to be acceptable. This is called the “80% Rule.” For example, if acceptable results are reported for 9 of 15 VOCs in a given reference sample, the overall result is not acceptable because only 60% of the analyte results reported fell within the established acceptance limits. The laboratory needs to report correct results for at least 12 of the 15, or 80%, of the analytes in the reference sample for the result to be considered acceptable.

It is important to understand how false positive and false negative results affect the acceptability of multi-analyte group reference samples:

- A *false positive* result occurs when a laboratory incorrectly reports an analyte concentration greater than the limit of detection when that analyte is **not** present in the reference sample. Each false positive counts as an individual failure towards the 80% rule.
 - A *false negative* result occurs when a laboratory incorrectly reports an analyte concentration less than the limit of detection for an analyte that is **actually present** in the reference sample. Each false negative counts as an individual failure towards the 80% rule. Unreported results for analytes present in the reference sample are also considered false negatives and count as individual failures toward the 80% rule.
- ✓ Multi-Level Reference Samples - A reference sample study may include multiple ampoules with each one containing a different concentration level of the same analyte or analytes. These reference samples are generally called “multi-level” samples. Laboratories must submit acceptable results on **greater than 50%** of the concentration levels for the cumulative results of the study to be considered acceptable. This is called the “50% Rule.” For example, if a multi-level reference sample consists of two ampoules containing different concentrations of the same group of analytes, the laboratory must report acceptable results for both ampoules for the study to be considered acceptable.

- ✓ Multi-Level Reference Samples for Multi-Analyte Groups - When a reference sample study for a multi-analyte group includes multiple ampules with each one containing a different concentration level, the results reported for each level are first graded separately using the 80% rule. Once the acceptability of each level has been determined, the 50% rule is applied to determine the overall acceptability of the study. ***The acceptability of the study is not determined by the average acceptability rate of the multiple levels.*** For example, consider the case of a laboratory that submits results for a two-level VOC reference sample study. If 98% of the analytes in one study level are reported correctly, but only 70% of the analytes in the other level are reported correctly, the overall study result is unacceptable because only 50% of the individual levels satisfy the 80% rule. The 84% average acceptability rate between the two levels does *not* influence the acceptability of the study.
- ✓ Multiple Methods - When a laboratory employs multiple methods to analyze a reference sample or reference sample group, and the reference sample provider issues an ampule for each method, the 50% rule is applied to determine the acceptability of the overall result.

4) Failure (Non-Drinking Water)

Acceptable reference sample results are necessary for renewal of a laboratory's certification.

- ✓ Laboratories must analyze an entirely new reference sample if they fail to report acceptable results initially.
- ✓ If a laboratory fails to report acceptable results for at least 80% of the individual analytes for a multi-analyte group reference sample, it must analyze a second reference sample. The results of ***all*** individual analytes detected in the reference sample must be reported – ***not just the individual analytes that were not acceptable in the first reference sample.***
- ✓ If a laboratory fails ***two consecutive*** reference samples, it must analyze a third reference sample, and may be issued a Notice of Noncompliance (NON). Additional action also may be necessary to close the NON.
- ✓ In the event a laboratory fails ***three consecutive*** reference samples, the WDNR may not renew or may suspend the laboratory's certification, and the laboratory may be issued a Notice of Violation (NOV). A comprehensive explanation of enforcement as a result of non-drinking water reference sample failures can be found in **Appendix 1** of this document.

5) Certification (Drinking Water)

The requirements for Laboratories certified for Drinking Water (Test Category 18) are often more stringent than those for certified for Non-Drinking Water test categories. The application and renewal processes for laboratories certified to perform drinking water testing is the same as for non-drinking water. However, there are some important differences in regard to grading and failure:

- ✓ Grading requirements for Safe Drinking Water Act (**SDWA**) analytes have been established by the EPA in 40 CFR Part 141. Specific citations are listed in s. NR 149.21, Wis. Adm. Code.
 - Total trihalomethanes (TTHM) grading conventions will be changing with the implementation of revisions to ch. NR 809, Wis. Adm. Code, effective January 2002. Consult this code for revisions to the requirements for disinfection (chlorine) by-products.
 - Laboratories certified for SDWA do not need to analyze reference samples for residual chlorine, pH, and turbidity.
 - PCBs must be determined as decachlorobiphenyl.
- ✓ If a laboratory fails *two consecutive* reference samples, it will be issued a Notice of Violation (NOV) and the WDNR may revoke or decide not to renew the laboratory's certification for that analyte or analyte group.
- ✓ A comprehensive explanation of enforcement as a result of drinking water reference sample failures can be found in **Appendix 2** of this document.

5. Special Considerations

1) PAHs Under Test Category 13

- ✓ The concentrations of reference sample results submitted for polynuclear aromatic hydrocarbons (PAHs) under Test Category 13 must be representative of the lower concentration ranges detectable by high performance liquid chromatography (HPLC).
- ✓ PAH reference samples with higher concentrations representative of the ranges detectable by GC or GC/MS will not be accepted for certification under Test Category 13.
- ✓ When ordering reference samples for PAHs under Test Category 13, request reference samples in the concentration range appropriate for HPLC analysis by the State of Wisconsin.

2) Pesticides

Because of the diversity of pesticides and the way they are accommodated by Wisconsin's test category system, there are special considerations for pesticide reference samples.

- ✓ There are four categories for which the WDNR certifies laboratories for pesticides. The groups of pesticides that make up these categories were chosen for their significant prevalence in this state. Refer to **Appendix 5** of this document for lists of the pesticides that are included in each group.
 - Test Category 13 includes pesticides analyzed by HPLC. This contains "Carbamates by LC" and "Other Pesticides by LC" which could be acid herbicides, nitrogen pesticides, or organophosphorus pesticides.
 - ❑ Laboratories interested in certification for Carbamate Pesticides must analyze a reference sample consisting of representative carbamate pesticides.
 - ❑ For all other pesticides analyzed by LC, the required reference sample will be case-specific and determined by Laboratory Certification Program staff.
 - Test Category 14 includes "Nitrogen Pesticides," "Triazine Pesticides and Metabolites," "Organophosphorus Pesticides," and "Other Pesticides."
 - ❑ For "Organophosphorus Pesticides" and "Acid Herbicides," laboratories must analyze a reference sample consisting of representative organophosphorus and acid herbicides (See **Appendix 5** of this document).

- For “Nitrogen Pesticides” (which includes non-metabolite triazines), both nitrogen and triazine reference samples must be analyzed. These results will also be applied toward certification considerations for “Triazine Pesticides” and their metabolites.
- Test Category 16 includes “Organochlorine Pesticides,” and certification under this category requires a reference sample consisting of representative organochlorine pesticides (See **Appendix 5** of this document).
- Test Category 19 includes any single specific analyte or analyte group, and appropriate reference samples depend on the analyte or analyte group of interest. It is important to note that certification for any pesticide that is not listed in the system of sub-categories can be obtained via Category 19. Certification to perform testing for compliance with Appendix 9 of 40 CFR Part 264 (RCRA) as a separate analyte group can also be obtained under this category.
- ✓ Grading
 - For organophosphorus, carbamates, organochlorines, and acid herbicides, laboratories must report acceptable results for greater than or equal to 80% of the individual analytes in the reference sample for the overall result to be considered acceptable.
 - Nitrogen and triazine pesticide reference samples are graded together as one reference sample. Laboratories must report acceptable results for greater than or equal to 80% of the analytes collectively for the overall result to be considered acceptable. This same result is applied separately toward nitrogen and triazine pesticides.
 - “Other LC Pesticides” are graded individually.

3) Key Analytes

Sometimes producing and distributing a reference sample for a given analyte is not practical for a provider. This is usually because of an inability to successfully isolate the analyte. Other times, it is more economical for a provider to offer a reference sample for a single analyte that represents a large group of very similar analytes. Table 1 of Ch. NR 149, Wis. Adm. Code, designates *key analytes* for each test category to address such instances. All key analytes can be found in **Appendix 3** of this document. There is one exception to this:

- ✓ Certification or registration for **nitrate + nitrite** under Test Category 2, requires a **nitrate** reference sample *only*.

4) Reciprocity

The WDNR may recognize the certification or registration of a laboratory in another state or a federal agency if the standards for that certification or registration are similar enough to that of the WDNR. However, this agreement must be a reciprocal one.

- ✓ Laboratories certified to perform work in Wisconsin through reciprocity with another state are not required to report reference sample results to the WDNR for any purpose. A laboratory's primary state of certification or registration is responsible for providing reference samples to that laboratory.

5) DMRQA

- ✓ Analysis of DMRQA reference sample studies is a requirement of the federal government's NPDES program. DMRQA results are reported to EPA for compliance with the requirements of the Clean Water Act.
- ✓ There is no requirement for labs to report DMRQA results for State of Wisconsin compliance.
- ✓ The Wisconsin Laboratory Certification Program will accept DMRQA reference samples for Wisconsin certification and registration renewal **only if** the results are made available to the WDNR by September 1.
- ✓ If DMRQA results will not be available by September 1, laboratories must purchase reference samples from another WDNR-approved reference sample provider, and submit acceptable results to the WDNR by September 1 to renew their certification or registration.

* **NOTE:** *Just because a laboratory analyzes DMRQA reference samples prior to August 31, it does not mean that those reference samples will be graded and reported to the WDNR by the September 1 deadline.*

6) Providers

Providers are approved by the WDNR with the concurrence of the Certification Standards Review Council. Reference sample providers are required to address specific requirements of the Wisconsin Laboratory Certification Program. When ordering reference samples, it must be stated that they are needed for certification or registration with the *Wisconsin* Laboratory Certification and Registration Program.

Current lists of all of the WDNR-approved providers as well as the analytes and analyte groups that they are approved to provide are found in **Appendix 3** of this document. Contact information for these providers is listed in **Appendix 4**.

Appendix 1

Procedure for Consecutive Reference Sample Failures for Non-Drinking Water Tests

	WDNR Action	Laboratory Action
First Failure	None.	Analyze and pass a second sample. Failure to analyze a second sample will result in a non-renewal.
Second Failure s. 149.13, Wis. Adm. Code	<p>Notice of Noncompliance (NON): WDNR sends a letter requesting corrective actions within 30 days which include:</p> <ul style="list-style-type: none"> • Timetable for analyzing a third sample • Timetable for correcting the problem • Requirement to qualify test data until acceptable results are achieved <p>If these conditions are not met, revocation or suspension may result. If corrective actions are not completed by the renewal deadline, the WDNR will not renew the laboratory's registration or certification.</p>	<ol style="list-style-type: none"> 1) Perform corrective actions with written report within 30 days. 2) Analyze and pass a third reference sample to resolve the NON. 3) Or the laboratory can submit additional results that demonstrate intervening acceptable reference sample results.
Third Failure s. 149.42, Wis. Adm. Code	<p>Notice of Violation (NOV): WDNR sends a letter notifying the laboratory that it has a certain amount of time to respond to this notice. The NOV will be removed if the laboratory can demonstrate that it was the provider's fault or if it has acceptable intervening results.</p> <p>Certified Labs: If the laboratory does not voluntarily withdraw from the program for that test, it will face suspension.</p> <p>Registered Labs: A timeline for correcting the problem will be recommended. Until the laboratory submits two consecutive acceptable results for the test in question, it will not be eligible for renewal for that test or test category.</p> <p>Government Labs: The NOV will include additional information as required by s. 893.80 (1)(b), <i>Wis. Stats.</i>, the Notice of Claim statute. Revocation or suspension occurs after 120 days or if the claim is disallowed.</p>	<p>To regain certification or registration after non-renewal, voluntary withdrawal, or suspension, the laboratory must submit:</p> <ul style="list-style-type: none"> • Revised application and fees. • Two consecutive acceptable reference sample results. • Corrective actions. <p>If a laboratory does not withdraw its certification for the affected test(s), it must either demonstrate that the provider made an error or submit intervening acceptable results to avoid suspension.</p> <p>Government labs have 120 days to disallow the Notice of Claim. Within 120 days, the lab must either disallow the claim or withdraw their certification for the affected tests.</p>

Appendix 2

Procedure for Consecutive Reference Sample Failures for Safe Drinking Water Tests

	WDNR Action	Laboratory Action
First Failure ss. 149.13 and 149.21, Wis. Adm. Code	None.	Laboratories must analyze and pass a second reference sample. Failure to analyze a second reference sample results in non-renewal.
Second Failure s. 149.42, Wis. Adm. Code	<p>Notice of Violation (NOV): WDNR sends a letter notifying the lab that it has 10 days to respond to this notice. The NOV will be removed if the laboratory can demonstrate an error on the part of the provider or if they have additional acceptable intervening results. If the laboratory doesn't voluntarily withdraw from the program for that test, it could face suspension or revocation.</p> <p>Government Labs: The NOV will include additional information as required by s. 893.80 (1)(b), <i>Wis. Stats.</i>, the Notice of Claim statute. After 120 days or if the claim is disallowed, the WDNR may revoke or suspend the laboratory.</p>	<p>To reinstate certification or registration after non-renewal, voluntary withdrawal, or suspension, the lab must submit:</p> <ul style="list-style-type: none"> • Revised application and fees. • Two consecutive acceptable reference sample results. • Corrective actions. <p>If a laboratory does not withdraw its certification for the affected test, it must either demonstrate that the provider made an error or submit intervening acceptable results to avoid suspension.</p> <p>Government labs have 120 days to disallow the Notice of Claim. Within 120 days, the lab must either disallow the claim or withdraw its certification for the affected tests.</p>

Appendix 3

Wisconsin Laboratory Certification and Registration Program Approved Reference Sample Providers

Category	Tests (Key analytes in <i>bold</i> *)	Absolute	Accu-standard	APG	ERA	NSI	RTC	WSLH **
01 Oxygen Utilization								
	BOD	Y	Y	Y	Y	Y	Y	Y
	CBOD	Y	Y	Y	Y	Y	Y	Y
02 Nitrogen								
	Nitrate	Y	Y	Y	Y	Y	Y	Y
	Nitrite	Y	Y	-N-	Y	Y	-N-	-N-
	Nitrate + Nitrite †	Y	Y	Y	Y	Y	-N-	Y
	Ammonia	Y	Y	Y	Y	Y	Y	Y
	TKN	Y	Y	Y	Y	Y	Y	Y
03 Phosphorus								
	Total Phosphorus	Y	Y	Y	Y	Y	Y	Y
	Orthophosphorus	Y	-N-	Y	Y	Y	Y	-N-
04 Physical								
	Total Suspended Solids	Y	Y	Y	Y	Y	Y	Y
	Total Solids	Y	Y	Y	Y	Y	-N-	-N-
	Total Dissolved Solids	Y	Y	Y	Y	Y	Y	-N-
	Total Volatile Solids	Y	-N-	-N-	Y	-N-	-N-	-N-
	Total Volatile Suspended Solids	-N-	-N-	-N-	-N-	-N-	-N-	-N-
	Oil & Grease (Freon)	Y	Y	Y	Y	Y	Y	Y
	Hexane Extractable Material (HEM)	Y	Y	Y	Y	Y	-N-	Y
05 General I								
	Hardness	Y	Y	Y	Y	Y	Y	Y
	Alkalinity/Acidity	Y	Y	Y	Y	Y	Y	-N-
	Bromide	Y	Y	Y	Y	-N-	-N-	-N-
	Chlorophyll a	-N-	-N-	-N-	-N-	-N-	-N-	-N-
	Color	-N-	-N-	Y	Y	-N-	-N-	-N-
	Silica	Y	Y	-N-	Y	-N-	-N-	-N-
	Silicate	-N-	-N-	Y	-N-	-N-	-N-	-N-
	Sulfite	-N-	-N-	-N-	-N-	-N-	-N-	-N-
	Surfactants	Y	Y	Y	Y	Y	-N-	-N-
06 General II								
	Chemical Oxygen Demand	Y	Y	Y	Y	Y	Y	Y
	Chloride	Y	Y	Y	Y	Y	Y	Y
	Cyanide	Y	Y	Y	Y	Y	Y	Y
	Fluoride	Y	Y	Y	Y	Y	Y	Y
	Sulfate	Y	Y	Y	Y	Y	Y	Y
	Total Phenolic Compounds	Y	Y	Y	Y	Y	Y	Y
	Sulfide	-N-	-N-	-N-	Y	Y	-N-	-N-
07 General III								
	Ignitability	-N-	-N-	-N-	Y	-N-	-N-	-N-
	Reactivity	-N-	-N-	-N-	-N-	-N-	-N-	-N-
	Corrosivity	-N-	-N-	-N-	Y	-N-	-N-	-N-
	TOC	Y	Y	Y	Y	Y	Y	-N-
	TOX	-N-	Y	Y	Y	-N-	-N-	-N-

Category	Tests (Key analytes in <i>bold</i> *)	Absolute	Accu- standard	APG	ERA	NSI	RTC	WSLH **
08 Metals I								
	Aluminum	Y	Y	Y	Y	Y	Y	Y
	Antimony	Y	Y	Y	Y	Y	Y	Y
	Arsenic	Y	Y	Y	Y	Y	Y	Y
	Barium	Y	Y	Y	Y	Y	Y	Y
	Beryllium	Y	Y	Y	Y	Y	Y	Y
	Boron	Y	Y	Y	Y	Y	-N-	Y
	Cadmium	Y	Y	Y	Y	Y	Y	Y
	Calcium	Y	Y	Y	Y	Y	Y	Y
	Chromium, Hexavalent	Y	Y	Y	Y	Y	-N-	-N-
	Chromium, Total	Y	Y	Y	Y	Y	Y	Y
	Cobalt	Y	Y	Y	Y	Y	Y	Y
	Copper	Y	Y	Y	Y	Y	Y	Y
	Iron	Y	Y	Y	Y	Y	Y	Y
	Lead	Y	Y	Y	Y	Y	Y	Y
	Magnesium	Y	Y	Y	Y	Y	Y	Y
	Manganese	Y	Y	Y	Y	Y	Y	Y
	Mercury	Y	Y	Y	Y	Y	Y	Y
	Molybdenum	Y	Y	Y	Y	Y	Y	Y
	Nickel	Y	Y	Y	Y	Y	Y	Y
	Potassium	Y	Y	Y	Y	Y	Y	Y
	Selenium	Y	Y	Y	Y	Y	Y	Y
	Silver	Y	Y	Y	Y	Y	Y	Y
	Sodium	Y	Y	Y	Y	Y	Y	Y
	Strontium	Y	Y	Y	Y	Y	Y	Y
	Thallium	Y	Y	Y	Y	Y	Y	Y
	Tin	Y	Y	Y	Y	Y	-N-	Y
	Vanadium	Y	Y	Y	Y	Y	Y	Y
	Zinc	Y	Y	Y	Y	Y	Y	Y
09 Metals II								
	Bismuth	-N-	-N-	-N-	-N-	-N-	-N-	Y
	Gold	Y	Y	-N-	-N-	-N-	-N-	-N-
	Iridium	Y	Y	-N-	-N-	-N-	-N-	-N-
	Lithium	Y	-N-	-N-	-N-	-N-	-N-	Y
	Osmium	-N-	-N-	-N-	-N-	-N-	-N-	-N-
	Palladium	Y	Y	-N-	-N-	-N-	-N-	-N-
	Platinum	Y	Y	-N-	-N-	-N-	-N-	-N-
	Rhodium	Y	Y	-N-	-N-	-N-	-N-	-N-
	Ruthenium	Y	Y	-N-	-N-	-N-	-N-	-N-
	Silicon	Y	-N-	-N-	-N-	-N-	-N-	Y
	Titanium	Y	Y	Y	Y	Y	-N-	Y
	Tungsten	Y	-N-	-N-	-N-	-N-	-N-	-N-
	Zirconium	Y	-N-	-N-	-N-	-N-	-N-	-N-
10 Purgeables by GC or GC/MS								
	VOCs	Y	Y	Y	Y	Y	Y	-N-
	Acrolein & Acrylonitrile	Y	Y	-N-	Y	-N-	-N-	-N-
	Purgeable Aromatics	Y	Y	Y	Y	Y	Y	-N-
	Purgeable Halocarbons	Y	Y	Y	Y	Y	Y	-N-
	Glycols	-N-	-N-	-N-	Y	-N-	-N-	-N-
11 Semivolatiles by GC (no GC/MS methods)								
	Phenols	Y	Y	Y	Y	-N-	Y	-N-
	Phthalate Esters	Y	Y	Y	Y	-N-	-N-	-N-

Category	Tests (Key analytes in <i>bold</i> *)	Absolute	Accu- standard	APG	ERA	NSI	RTC	WSLH **
11 Semivolatile by GC (contd.)								
	Haloethers	Y	Y	Y	Y	-N-	Y	-N-
	Nitroaromatics	Y	Y	Y	Y	-N-	-N-	-N-
	Nitrosamines	Y	Y	Y	Y	-N-	-N-	-N-
	Nonpurgeable Chlorinated	Y	Y	Y	Y	-N-	-N-	-N-
	Hydrocarbons							
	PAHs	Y	Y	Y	Y	-N-	Y	-N-
12 Semivolatiles by GC/MS								
	BNA s	Y	Y	Y	Y	Y	Y	-N-
13 HPLC								
	Benzidines	Y	Y	Y	Y	-N-	-N-	-N-
	PAHs	Y	Y	Y	Y	Y	Y	-N-
	Aldehydes & Ketones	-N-	-N-	-N-	Y	-N-	-N-	-N-
	Carbamate Pesticides	Y	Y	Y	Y	Y	Y	-N-
	Explosive Residues	-N-	-N-	-N-	Y	-N-	-N-	-N-
14 Pesticides								
	Acid Herbs.	Y	-N-	Y	Y	Y	Y	-N-
	2,4-D & Silvex Only	Y	-N-	Y	Y	-N-	-N-	-N-
	Organophosphorous Pests.	Y	-N-	Y	Y	Y	Y	-N-
	Nitrogen Pests. (Incl. Triazine)	Y	-N-	Y	Y	Y	-N-	-N-
	Triazine Pests. & Metabolites	Y	-N-	-N-	Y	-N-	-N-	-N-
15 Petroleum								
	GRO	-N-	-N-	Y	Y	Y	-N-	-N-
	DRO	-N-	-N-	Y	Y	Y	-N-	-N-
	PVOC	-N-	-N-	Y	Y	Y	-N-	-N-
16 Organochlorine Compounds								
	O-CI Pests.	Y	Y	Y	Y	Y	Y	-N-
	PCBs	Y	Y	Y	Y	Y	Y	-N-
17 Dioxins								
	PCDD	-N-	Y	-N-	-N-	-N-	-N-	-N-
	PCDF	-N-	-N-	-N-	-N-	-N-	-N-	-N-
18 SDWA - Inorganics								
	Asbestos	-N-	-N-	-N-	-N-	-N-	-N-	-N-
	Cyanide	Y	Y	Y	Y	Y	Y	Y
	Fluoride	Y	Y	Y	Y	Y	Y	Y
	Nitrate	Y	Y	Y	Y	Y	Y	Y
	Nitrite	Y	Y	Y	Y	Y	Y	Y
	Nitrate + Nitrite ††	Y	Y	Y	Y	Y	Y	Y
	Sulfate	Y	Y	Y	Y	Y	Y	Y
	Antimony	Y	Y	Y	Y	Y	Y	Y
	Arsenic	Y	Y	Y	Y	Y	Y	Y
	Barium	Y	Y	Y	Y	Y	Y	Y
	Beryllium	Y	Y	Y	Y	Y	Y	Y
	Cadmium	Y	Y	Y	Y	Y	Y	Y
	Chromium	Y	Y	Y	Y	Y	Y	Y
	Copper	Y	Y	Y	Y	Y	Y	Y
	Lead	Y	Y	Y	Y	Y	Y	Y
	Mercury	Y	Y	Y	Y	Y	Y	Y
	Nickel	Y	Y	Y	Y	Y	Y	Y
	Selenium	Y	Y	Y	Y	Y	Y	Y
	Sodium	Y	Y	Y	Y	Y	Y	Y
	Thallium	Y	Y	Y	Y	Y	Y	Y

Category	Tests (Key analytes in <i>bold</i> *)	Absolute	Accu-standard	APG	ERA	NSI	RTC	WSLH **
18 SDWA – Organics								
	EDB & DBCP	Y	Y	Y	Y	Y	Y	-N-
	TTHM	Y	Y	Y	Y	Y	Y	-N-
	Regulated VOCs	Y	Y	Y	Y	Y	Y	-N-
	O-CI Pests. by GC	Y	Y	Y	Y	Y	Y	-N-
	O-CL Pests. by GC/MS	Y	Y	Y	Y	Y	Y	-N-
	PCBs	Y	Y	Y	Y	Y	Y	-N-
	N-P Pests. by GC	Y	Y	Y	Y	Y	Y	-N-
	N-P Pests. by GC/MS	Y	Y	Y	Y	Y	Y	-N-
	Acid Herbs by GC	Y	Y	Y	Y	Y	Y	-N-
	Acid Organics by GC/MS	Y	Y	Y	Y	Y	Y	-N-
	HPLC Pests.	Y	Y	Y	Y	Y	Y	-N-
	Chlorinated Hydrocarbons by GC	Y	Y	Y	Y	Y	Y	-N-
	Chlorinated Hydrocarbons by GC/MS	Y	Y	Y	Y	Y	Y	-N-
	Phthalates by GC	Y	Y	Y	Y	Y	Y	-N-
	Phthalates by GC/MS	Y	Y	Y	Y	Y	Y	-N-
	PAH by HPLC	Y	Y	Y	Y	Y	Y	-N-
	PAH by GC/MS	Y	Y	Y	Y	Y	Y	-N-
	Diquat	Y	Y	Y	Y	-N-	Y	-N-
	Endothall	Y	Y	Y	Y	Y	Y	-N-
	Glyphosate	Y	Y	Y	Y	-N-	Y	-N-
	TCDD	-N-	Y	-N-	-N-	-N-	-N-	-N-
18 SDWA – Disinfection By-Products								
	Bromate	Y	Y	Y	Y	Y	Y	-N-
	Chlorite	Y	Y	Y	Y	Y	Y	-N-
	Haloacetic Acids (five)	Y	Y	Y	Y	-N-	Y	-N-
	TTHM	Y	Y	Y	Y	Y	Y	-N-

* Reference samples are required only for key analyte(s) (in bold) in each test category. See to chapter 5, section 3 (page 11) for an explanation of key analytes.

** Effective January 1, 2002, the Wisconsin State Laboratory of Hygiene will no longer provide reference samples for Test Categories 10-17 or reference samples for *organic* analytes under Test Category 18. **The WSLH will continue to provide reference samples for all *inorganic* analytes under Test Category 18.**

† Nitrate + Nitrite certification/registration in Test Category 02 requires a nitrate reference sample only.

†† Nitrate + Nitrite certification in Test Category 18 requires either a *nitrate+nitrite* reference sample, or *both* a nitrate *and* a nitrite reference sample

Appendix 4

Approved Reference Sample Provider Contact Information

Effective January 1, 2001

Please make sure that the provider you select is approved for the specific analyte(s) for which you are seeking registration or certification (see Appendix 3). When contacting providers, specify that you are seeking reference samples for use by the *Wisconsin* DNR Laboratory Certification Program.

Absolute Standards Inc.
P.O. Box 5585
Hamden, CT 06518
800-368-1131
www.absolutestandards.com

NSI Solutions, Inc. (NSI)
7517 Precision Drive, Suite 101
Raleigh, NC 27617
800-234-7837
www.nsi-es.com

Accustandard, Inc.
125 Market Street
New Haven, CT 06513
800-442-5290
www.accustandard.com

Resource Technology Corporation (RTC)
2931 Soldier Springs Road
Laramie, WY 82070
800-576-5690
www.rt-corp.com

Analytical Products Group (APG)
2790 Washington Boulevard
Belpre, OH 45714
800-272-4442
www.apgqa.com

**WI State Laboratory of Hygiene
Proficiency Testing Program (WSLH)**
465 Henry Mall, Room 402
Madison, WI 53706-1578
800-462-5261
www.slh.wisc.edu/pt/
(Note: Effective January 1, 2002, the Wisconsin State Laboratory of Hygiene will no longer provide reference samples for Test Categories 10-17 or reference samples for organic analytes under Test Category 18. The WSLH will continue to provide reference samples for all inorganic analytes under Test Category 18.)

**Environmental Resource Associates
(ERA)**
5540 Marshall Street
Arvada, CO 80002
800-372-0122
www.eraqc.com

Appendix 5

Pesticides Relevant to the Wisconsin DNR Laboratory Certification Program †

Nitrogen Pests (5)

alachlor
bromacil
butylate
EPTC (eptam)
hexazinone
metolachlor
metribuzin
napropamide
propachlor
terbacil
trifluralin
butachlor*
pronamide*
(not included: benefin, dichlobenil, dodine, ethalfluralin, oryzalin, pendimethalin, propanil, triallate)

Triazine Pests (3)

anilazine
atrazine
cyanazine
prometon
propazine
simazine
ametryn*
atraton*
prometryn*
deethyl atrazine*
deisopropyl atrazine*
diaminoatrazine*

Organophos. Pests (5)

chlorpyrifos
diazinon
dimethoate
ethoprop
fonofos
malathion (ethyl)
parathion (ethyl)
parathion methyl
phorate
phosmet
terbuphos
azinophos methyl*
carbophenothion*
dementon-O*
dementon-S*
dioxathion*
disulfoton*
ethion*

famphur*
(not included isophenophos, profenfos)

Acid Herbicides (5)

2,4,5-T
2,4,5-TP (silvex)
2,4-D
2,4-DP
bentazon
bromoxynil
chloramben
DCPA (dacthal)
dicamba
dinoseb
MCPA
MCPP
picloram
dalapon*
pentachlorophenol*
(not included: imazethapyr, MCPB, TCA, sethoxydim)

Carbamates (5)

aldicarb
carbaryl
carbofuran
chlorpropham
oxamyl
propham
aldicarb sulfone*
aldicarb sulfoxide*
aminocarb*
methiocarb*
methomyl*
mexacarbate*
barban*
propoxur*
swep*
(not included: carbosulfan, maneb)

Organochlorine Pests (8)

aldrin
alpha BHC
beta BHC
delta BHC
gamma BHC (lindane)
chlordane (isomer)
chlorothalonil
DDD

DDE*
DDT
dieldrin
endosulfan I
endosulfan II
endosulfan sulfate
endrin
endrin aldehyde
heptachlor
heptachlor epoxide
methoxychlor
toxaphene
captan*
dichloran*
dicofol*
isodrin*
kepone*
mirex*
PCNB*
perthane*
strobane*
(not included: chlordene)

Other LC Pests (4)

diquat
diuron
linuron
paraquat
glyphosate*
endothal*
fenuron*
Fenuron-TCA
monuron*
monuron-TCA*
siduron*
(These are all nitrogen pests.)

(Acid Herbicides analyzable by LC include: 2,4,5-T; 2,4,5-TP, 2,4-D; 2,4-DB; bentazon, chloramben, dalapon, DCPA, dicamba, MCPA, MCPP, pentachlorophenol, picloram, TCA)

(Organophosphorus Pests analyzable by LC include: chlorpyrifos, dimethoate, disulfoton, famphur, parathion methyl, phorate)

* These pesticides are not regulated under ACCP, but are regulated under a different DNR program and may appear in reference samples.

† Note: Number in parentheses denotes number of compounds in list that must be present in reference sample