OKLAHOMA DEPARTMENT OF ENVIRONMENTAL QUALITY

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RECOMMENDED COMPARABILITY DATA REQUIREMENTS FOR NH_3-N DATA

In Method 4500-NH_3 "Nitrogen Ammonia" of *Standard Methods for the Examination of Water and Wastewater*, 18th, 19th, 20th Editions *(Standard Methods)*, Section A.1 "Introduction: Selection of Method" states, "Methods D, E, F, G, and H may be used with or without sample distillation." The Federal requirement, however, is that distillation is required unless a facility can demonstrate that the distillation step in the analysis for ammonia (NH_3-N) in its wastewater is not necessary, i.e., the facility must show that the results of ammonia analysis with and without the pre-distillation step are comparable. This requirement for comparability data comes from Note 6 to Table I.B "List of Approved Inorganic Test Procedures" in Title 40 of the Code of Federal Regulations Section 136.3 (40 CFR §136.3). Note 6 states, "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 controversies."

The purpose of this document is to establish a standard protocol that facilities can use to develop the required comparability data.

Comparability data should be based on samples collected during normal sampling events and analyzed at the frequency required by the OPDES Permit. Samples must be collected during times representative of normal operating conditions.

Whenever requirements for comparability are met, comparability data should be regenerated thereafter as part of the OPDES permitting application process, i.e., normally once every five years. Generation of comparability data also may be required any time that new process flows or significant new sources are introduced into the treatment system or the treatment process changes.

For commercial laboratories, comparability data must be developed separately for each permitted outfall of each facility and must be available at each facility for inspection. Questions about this procedure should be directed to the Laboratory Accreditation section of the Department of Environmental Quality. DEQ will perform the statistical analysis of the comparability data for a facility upon request.

Laboratory and Analysis Requirements:

- A single laboratory must be involved in performing all of the required chemical analyses.
- All comparability data shall be generated using the approved analytical method that the facility will use for OPDES reporting, e.g., titration, ion-specific electrode, etc., as authorized in 40 CFR §136.3.
- QC analyses in accordance with *Standard Methods*, Section 1020 shall be run along with replicate sample analyses.

  Analysis of a matrix spike by known addition shall be performed on both the distilled and non-distilled samples for each set of samples. The level of the known addition will be between 1 and 10 times the ambient level or 5 to 50 times the MDL whichever is higher. Do

not use a known addition above the demonstrated linear range of the method. These data will be used to evaluate test recovery and matrix interference.

- Comparability data should consist of the following:
  - Between eight (8) and twelve (12) samples from each permitted outfall collected and analyzed at the normal sampling frequency as required by the OPDES Permit;
  - Chemical analysis of each sample with and without pre-distillation following the QC guidelines above;
  - Statistical analysis of the laboratory results utilizing the Wilcoxon Signed-Ranks (WSR) test with a significance level of $\alpha = 0.05$ (see the attached sample calculations).
- Data will be considered comparable if the following criteria are met.
  - All test conditions as described above are met.
  - There is no significant difference between the test populations at the 5% significance level ($\alpha = 0.05$).
  - The percent recovery of the spike QA/QC data is satisfactory, i.e., between 80 and 120%.

Statistical Analysis of the Laboratory Results

The Wilcoxon Signed-Rank (WSR) test is a non-parametric statistical method to evaluate data when the data may not be distributed normally. Basically, it is a method to determine whether the median of differences between two sets of paired data (in this case analyses of a single sample with and without the pre-distillation step) is zero (the sets are comparable) or not zero (the sets are not comparable).

Evaluation of the Sample Data Using the WRS Test

The null hypothesis, H_o: $m_d = 0$, is that the median of the differences between the results with pre-distillation and those without pre-distillation is zero, i.e., the results of the analyses with and without the pre-distillation step are the same and comparable.

The alternative hypothesis: H_a: $m_d \neq 0$, is that the median of the differences between the results with pre-distillation and those without pre-distillation is **not** zero, i.e., the results of the analyses with and without the pre-distillation step are **not** the same and **not comparable**.

The validity of the WSR test is higher the more pairs are included in the test. However, to limit the amount of time, effort, and expense required to obtain the comparability data, the number of samples to demonstrate comparability can be as low as eight (8).

Following are two examples of analyses with and without pre-distillation. The first example demonstrates that the data are comparable and, therefore, conducting the analyses without pre-distillation is appropriate. The second example shows that the data are not comparable and, therefore, pre-distillation must be conducted for ammonia analyses.

Sample Data Set #1

Date	NH_3-N concentration mg/L	
	With Distillation	Without Distillation
01/01/06	5.3	5.6
01/02/06	4.7	4.5
01/03/06	6.1	6.5
01/04/06	2.1	2.0
01/05/06	5.2	5.8
01/06/06	7.3	7.0
01/07/06	8.4	8.3
01/08/06	2.1	1.9
01/09/06	3.5	4.3
01/10/06	4.2	3.7

Steps in Performing the WSR Test

1. Calculate the difference between paired analyses.
2. Rank the differences between paired values from smallest to largest without regard to sign, i.e., rank the absolute values of the differences. If the difference between paired values is zero, then that set of paired values can be eliminated from further consideration, which reduces the number of sample pairs by one.
3. Assign to the ranks the sign of the original difference.
4. Compute the sum of the positive ranks and sum the negative ranks separately. The value of the "T-statistic" is the lesser of the absolute values of the two sums.
5. Compare the T-statistic to the two-sided Critical Values in the WSR Table corresponding to the number of sample pairs, *n* (at the end of this document).
6. If the T statistic is greater than the critical value, then the two sets of analyses are comparable.

1. Date	2. With Distillation	3. Without Distillation	4. Difference	5. Absolute Value of the Difference	6. Rank	7. Signed Ranks	8. Positive Ranks	9. Negative Ranks
01/07/06	8.4	8.3	0.1	0.1	1.5	1.5	1.5	
01/04/06	2.1	2.0	0.1	0.1	1.5	1.5	1.5	
01/02/06	4.7	4.5	0.2	0.2	3.5	3.5	3.5	
01/08/06	2.1	1.9	0.2	0.2	3.5	3.5	3.5	
01/01/06	5.3	5.6	-0.3	0.3	5.5	-5.5		-5.5
01/06/06	7.3	7.0	0.3	0.3	5.5	5.5	5.5	
01/03/06	6.1	6.5	-0.4	0.4	7	-7		-7
01/10/06	4.2	3.7	0.5	0.5	8	8	8	
01/05/06	5.2	5.8	-0.6	0.6	9	-9		-9
01/09/06	3.5	4.3	-0.8	0.8	10	-10		-10

Column 4 is the difference between the results with and without distillation in columns 2 and 3. In the case of this example none of the samples pairs has a difference equal to zero, so the number of sample pairs, n, is 10.

Column 5 is the absolute values of the differences in column 4.

Column 6 is the ranks of the absolute values of the differences. In the case when two or more absolute values are the same, their ranks are equal to the average rank, i.e., if the 1st and 2nd ranked values are the same, the rank assigned would be the average of 1 + 2 = 3 or 1.5.

Column 7 has the sign of the difference in column 4 assigned to the rank in column 6.

Column 8 has the positive ranks

Column 9 has the negative ranks

The sum of the positive ranks is $T^+ = 1.5 + 1.5 + 3.5 + 3.5 + 5.5 + 8.0 = 23.5$

The absolute value of the sum of the negative ranks is $T^- = \left| - (5.5 + 7.0 + 9.0 + 10.0) \right| = 31.5$

The absolute value of the sum of the positive ranks is less than the absolute value of the sum of the negative ranks, so the T-statistic, $T = 23.5$. (A check to see if the calculation was done correctly is that $T^- + T^+ = 31.5 + 23.5 = 55 = (n * (n+1) / 2 = (10 * 11) / 2 = 55$

Compare the value of $T = 23.5$ with the Critical Value for $n = 10$ in the WRS Table, $CV_{10} = 8$. Since $T > CV_{10}$, the results with and without pre-distillation are comparable and, therefore, analysis for NH_3-N without the pre-distillation step is appropriate. The null hypothesis is accepted.

Sample Data Set #2

Date	NH_3-N concentration mg/L	
	With Distillation	Without Distillation
01/01/06	5.3	5.2
01/02/06	4.7	5.3
01/03/06	6.1	6.1
01/04/06	2.1	2.6
01/05/06	5.2	5.4
01/06/06	7.3	7.8
01/07/06	8.4	8.9
01/08/06	2.1	2.5
01/09/06	3.5	3.2
01/10/06	4.2	5.1

Performing the same operations on Data Set #2 as was done on Data Set #1 yields the following table:

1. Date	2. With Distillation	3. Without Distillation	4. Difference	5. Absolute Value of the Difference	6. Rank	7. Signed Ranks	8. Positive Ranks	9. Negative Ranks
01/03/06	6.1	6.1	0.0	0.0				
01/01/06	5.3	5.2	-0.1	0.1	1	-1		-1
01/05/06	5.2	5.4	0.2	0.2	2	2	2	
01/09/06	3.5	3.2	-0.3	0.3	3	-3		-3
01/08/06	2.1	2.5	0.4	0.4	4	4	4	
01/04/06	2.1	2.6	0.5	0.5	6	6	6	
01/07/06	8.4	8.9	0.5	0.5	6	6	6	
01/06/06	7.3	7.8	0.5	0.5	6	6	6	
01/02/06	4.7	5.3	0.6	0.6	8	8	8	
01/10/06	4.2	5.1	0.9	0.9	9	9	9	

In Sample Data Set #2, the difference between the paired analyses for 01/03/06 is zero, so $n = 9$.

The sum of the positive ranks is $T^+ = 41$

The absolute value of the sum of the negative ranks is $T^- = |-4| = 4$

Since 4 < 41 the T-statistic is 4. [$T^- + T^+ = 45$, $(n * (n+1))/2 = (9 * 10) / 2 = 45$]

Compare $T = 4$ with the Critical Value for $n = 9$ in the WSR table, $CV_9 = 5$

Since $T < CV_9$, the results with and without pre-distillation are not comparable and, therefore, all analyses for NH_3-N require the pre-distillation step. The null hypothesis is rejected.

Wilcoxon Signed-Ranks Test: Critical Values* $\alpha = 0.05$, Two-Sided

Number (n)	Critical Value (CV)
8	3
9	5
10	8
11	10
12	13
13	17
14	21
15	25
16	29
17	34
18	40
19	46
20	52
21	58
22	65
23	73
24	81
25	89

*http://www.euronet.nl/users/warnar/demostatistiek/tables/WILCOXONTABEL.htm

References for the WSR Test

- Steele, Robert and James Torrie: *Principals and Procedures of Statistics*, McGraw-Hill, 1960.
- Helsel, D.R. and R.M Hirsch: *Statistical Methods in Water Resources*, USGS, 2002. This document is also on the Internet at: http://pubs.usgs.gov/twri/twri4a3/
- Most statistics and/or probability books discuss the WSR test.
- The Internet has many sites that discuss the WSR test, such as the following.
  - http://www.nist.gov/speech/tests/sigtests/wilcoxon.htm
  - http://faculty.vassar.edu/lowry/wilcoxon.html