OKLAHOMA DEPARTMENT OF ENVIRONMENTAL QUALITY

Effective Date: __March 31, 2020_____

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*, -2011 (22nd Edition) *(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 file to show that this preliminary distillation step is not necessary: However, manual distillation will be required to resolve any controversies. In general, the analytical method should be consulted regarding the need for distillation. If the method is not clear, the laboratory may compare a minimum of 9 different sample matrices to evaluate the need for distillation. For each matrix, a matrix spike and matrix spike duplicate are analyzed both with and without the distillation step. (A total of 36 samples, assuming 9 matrices). If results are comparable, the laboratory may dispense with the distillation step for future analysis. Comparable is defined as <20% relative percent difference (RPD) for all tested matrices. Alternatively the two populations of spike recovery percentages may be compared using a recognized statistical test".

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 analysis must be performed by a minimum Class C wastewater laboratory technician or by an appropriately accredited commercial laboratory.
- 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 and a matrix spike duplicate utilizing a known addition, shall be performed on both the distilled and non-distilled samples for each set of samples. The level of the known addition must be between 1 to 10 times the ambient level or 5 to 50 times the MDL, whichever is higher. This data is crucial in evaluating test recovery and matrix interference.

Comparability data should consist of nine (9) to twelve (12) samples each with and without pre-distillation. Sample sets must be collected and analyzed at the normal sampling frequency and location as required by the OPDES Permit. Data will be considered comparable if the following criteria for the spike recovery percentages with and without pre-distillation are met;

- Quality Control Criteria:

  - Percent recovery of the sample spike, between 80 and 120%.
  - Quality control sample (QCS) between 90-110%.
  - Blank analysis must be less than 1/2 the laboratory reporting limit.
  - Duplication of matrix spike per sample.
  - Control charts for the matrix spike and matrix spike duplicate.

- The spiked matrices achieve a <20% RPD; or

- The comparison utilizes a recognized statistical test of the two populations of spike recovery percentages.

St**atistical Analysis of the Laboratory Results**

Relative Percent Difference (%RPD)

RPD = (|difference| ÷ average)*100

		BAD						**Good**		
	Test Data						Test Data			
		Matrix:	WasteWater					Matrix:	WasteWater	
		Units:	% Difference Decimal Form					Units:	% Difference Decimal Form	
	Date:	Distilled	Non-Distilled	RPD (%)			Date:	Distilled	Non-Distilled	RPD (%)
1	9/4/19	0.08047	0.08657	7.30		1	2/19/18	0.4087	0.40	0.07
2	9/8/19	0.08767	0.07712	12.80		2	2/17/18	0.2594	0.25	0.77
3	9/11/19	0.08957	0.07661	15.59		3	2/12/18	2.052	2.04	0.48
4	9/10/19	0.08667	0.0737	16.17		4	2/10/18	0.9930	1.00	1.49
5	9/5/19	0.09317	0.07848	17.11		5	2/9/18	1.138	1.11	1.68
6	9/9/19	0.09507	0.07582	22.52		6	2/18/18	1.510	1.53	1.511
7	9/12/19	0.08367	0.06189	29.92		7	2/3/18	0.1713	0.14	15.13
8	9/18/19	0.09877	0.06878	35.79		8	2/13/18	2.959	3.00	1.37
9	8/29/19	0.0779	0.1278	48.51		9	2/20/18	2.795	2.75	1.51
						10	2/15/18	0.4504	0.54	18.35