

AMMONIA/FLUORIDE DISTILLATION TECHNICAL ASSISTANCE (5/31/2016)

Background

40 CFR Part 136.3, Table IB – List of Approved Inorganic Test Procedures, requires manual distillation or gas diffusion (pH>11) followed by any of the approved reference methods for Ammonia Nitrogen and manual distillation followed by any of the approved reference methods for Fluoride analyses. This requirement is footnoted.

Footnote 6 reads:

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% RPD for all tested matrices). Alternatively, the two populations of spike recovery percentages may be compared using a recognized statistical test.

Ammonia/Fluoride Distillation (NC WW/GW LC Policy 05/31/2016)

It is the responsibility of the permittee to ensure that monitoring is conducted according to test procedures approved under 40 CFR Part 136 even if the permittee does not operate the laboratory that performs the analytical testing on the waste stream. In terms of Ammonia Nitrogen and Fluoride monitoring, this means that the permittee must ensure that their effluent is appropriately characterized as to whether distillation is required. Methods that specifically state that distillation is not required may only require distillation to resolve controversies. Additionally, manual distillation may not be 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. A comparison study may be performed in-house or contracted to another certified laboratory. Permittees that do not perform the analyses in-house, and contract the analyses or the distillation study to a NC WW/GW LC certified commercial laboratory must obtain a copy of the initial comparison data and all subsequent comparison data, keep it on file at their facility and make these records available to the Department upon request.

Samples must be spiked according to the NC WW/GW LC Matrix Spike Policy, in duplicate, to allow for a meaningful statistical comparison. It is recommended that samples are spiked to yield a value within the verified calibration range so that sample dilution is not needed. Comparisons between the matrix spike and matrix spike duplicate, as well as between distilled and undistilled samples must meet a 20% RPD acceptance criterion. Both the distilled and undistilled samples must be analyzed using the same method technology used to report compliance data for the permitted facility. It is recommended that both the distilled and undistilled portions of the sample be analyzed by the same laboratory. Per 15A NCAC 2H .0805 (e) (2), it would be permissible to have a contract lab distill the samples and send the distillates back to the permittee for analysis within the prescribed holding time. It is the responsibility of the permittee to ensure that when only the distillation portion is contracted, that samples are distilled into the proper receiving solution required by the analytical method to be used. That means when the titration method will be employed, samples must be distilled into a boric acid solution. When the phenate method will be employed, samples must be distilled into a sulfuric acid solution.

The following frequencies are required:

Initially, compare a minimum of 9 samples, spiked in duplicate, both with and without the distillation step (a total of 36 samples), to evaluate the need for distillation.

Subsequently, each year analyze a minimum of 2 samples, spiked in duplicate, approximately 6 months apart, both with and without the distillation step (a total of 8 samples). If effluent characteristics change (e.g., contributing industries are added or lost, major change in plant processes, etc.), or if the laboratory changes to another analytical method that requires the comparison, a minimum of two additional samples must be spiked in duplicate and analyzed, both with and without the distillation step, to demonstrate that that distillation is still not required.

Refer to the tables below to determine if distillation studies are allowed. NOTE: By following the previous NC WW/GW LC Ammonia/Fluoride Distillation Studies policy, a laboratory may have historical data on file that meets these requirements.

Ref: North Carolina Wastewater/Groundwater Laboratory Certification (NC WW/GW LC) Policy, 05/31/2016; based upon Code of Federal Regulations, Title 40, Part 136.3; Federal Register Vol. 77, No. 97, May 18, 2012: Table IB, Footnote 6.

TABLE 1: Ammonia Nitrogen Methods

Ammonia Nitrogen Method	Distillation Required	Study Allowed	Comment
SM 4500 NH3 C-1997 (Titration)	Yes	No	The distillation study option is not allowed. All samples must be distilled. Method states in Section (1): <i>The titrimetric method is used only on samples that have been carried through preliminary distillation.</i>
SM 4500 NH3 D-1997 (Electrode)	No	N/A	Method states in Section (1) (b): <i>Sample distillation is unnecessary.</i>
SM 4500 NH3 E-1997 (Electrode)	No	N/A	Method refers you SM 4500 NH3 D 1., which states that sample distillation is unnecessary.
SM 4500 NH3 F-1997 (Manual Phenate)	Yes	Yes	Method states in Section (1) (b): <i>Remove interfering turbidity by distillation or filtration.</i>
SM 4500 NH3 G-1997 (Automated Phenate)	Yes	Yes	
SM 4500 NH3 H-1997 (Automated Phenate)	Yes	Yes	
EPA 350.1, Rev. 2.0 (1993) (Automated Phenate)	Yes	Yes	Method states in Section 2.1: <i>The sample is buffered at a pH of 9.5 with a borate buffer in order to decrease hydrolysis of cyanates and organic nitrogen compounds, and is distilled into a solution of boric acid.</i>
ASTM D1426-08 (A) (Nesslerization)	Yes	Yes	
ASTM D1426-08 (B) (Electrode)	Yes	Yes	
USGS I-3520-85 (Nesslerization)	Yes	No	Method states in Section 2.1: <i>Ammonia is distilled from the buffered solution, and an aliquot of the distillate then is nesslerized.</i>
USGS I-4523-85 (Automated Phenate)	Yes	Yes	

* For requirements of methods not listed, contact us.

TABLE 2: Fluoride Methods

Fluoride Method	Distillation Required	Study Allowed	Comments
SM 4500-F C-1997 (Electrode, Manual)	Maybe	Yes	Refer to Table 4500F:1 for interferences that may require distillation.
SM 4500-F D-1997 (Colorimetric)	Maybe	Yes	Refer to Table 4500F:1 for interferences that may require distillation. Method states in Section (1) (b): <i>Whenever any one substance is present in sufficient quantity to produce an error of 0.1 mg/L or whenever the total interfering effect is in doubt, distill the sample. Also distill colored or turbid samples.</i>
SM 4500-F E-1997 (Automated Complexone)	Yes	No	Distillation is performed inline with the automated method setup. Method states in Section (1) (b): <i>Interferences normally associated with the determination of fluoride are removed by distillation.</i>
SM 4110-F B-2000 (Ion Chromatography)	Yes	Yes	
SM 4110-F C-2000 (Ion Chromatography)	Yes	Yes	
SM 4140 B-1997 (CIE/UV)	Yes	Yes	
EPA 300.0, Rev. 2.1 (1993) (Ion Chromatography)	Yes	Yes	
EPA 300.1, Rev. 1.0 (1997) (Ion Chromatography)	Yes	Yes	
ASTM D1179-04 (B) (Electrode, Manual)	Yes	Yes	No laboratories currently certified by this method. Standard has not been purchased.
ASTM D1179-04 (A) (Colorimetric)	Yes	Yes	No laboratories currently certified by this method. Standard has not been purchased.
USGS I-4327-85 (Electrode, Automated)	Yes	Yes	Method states in Section 2.3: <i>The method includes a distillation step to decompose organic fluoride compounds and attack minerals such as fluorspar in water suspended sediment.</i>

* For requirements of methods not listed, contact us.