AMMONIA/FLUORIDE DISTILLATION TECHNICAL ASSISTANCE (04/17/2019)

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

EPA Office of Water has clarified that the intent of Footnote 6 was that all samples to be used for measurement of ammonia and fluoride for the purpose of reporting compliance monitoring results would be subject to the same requirements. That is, distillation is not required if comparability data on representative samples are on file to show that this preliminary distillation step is not necessary; however, manual distillation will be required to resolve any controversies.

Ammonia/Fluoride Distillation (NC WW/GW LC Policy 04/09/2019)

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 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 another NC WW/GW LC certified 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 spiked samples must meet a 20% RPD acceptance criterion. Both the distilled and undistilled spiked 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 spiked sample be analyzed by the same laboratory. Per 15A NCAC 2H .0805 (e) (2), it would be permissible to have another certified laboratory 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 from each matrix (e.g., effluent, influent, stream, etc.), spiked in duplicate, both with and without the distillation step (a total of 36 samples), to evaluate the need for distillation. These 9 samples may be spread out over a 12-month period. However, at least three samples from each matrix would be required to obtain initial certification.

If the characteristics of any permitted matrix 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, 04/09/2019; based upon Code of Federal Regulations, Title 40, Part 136.3; Federal Register Vol. 82, No. 165, August 28, 2017: Table IB, Footnote 6.

TABLE 1: Ammonia Nitrogen Methods

Ammonia Nitrogen Method	Distillation Required	Study Allowed	Comment
SM 4500 NH_3 C-2011 (Titration)	Yes	No	The distillation study option is not allowed. All samples must be distilled. Method states in Section (1): *The titrimetric method is used only on samples that have been carried through preliminary distillation*.
SM 4500 NH_3 D-2011 (Electrode)	No	N/A	Method states in Section (1) (b): *Sample distillation is unnecessary.*
SM 4500 NH_3 E-2011 (Electrode)	No	N/A	Method refers you SM 4500 NH_3 D-2011 (1) (b), which states that sample distillation is unnecessary.
SM 4500 NH_3 F-2011 (Manual Phenate)	No	N/A	SM 4500 NH_3 A-2011 (1) says that method F may be used either with or without sample distillation. Method states in Section (1) (b): *Remove interfering turbidity by distillation or filtration.*
SM 4500 NH_3 G-2011 (Automated Phenate)	No	N/A	SM 4500 NH_3 A-2011 (1) says that method G may be used either with or without sample distillation. However, the method itself does not discuss distillation and says to address turbidity issues with filtration.
SM 4500 NH_3 H-2011 (Automated Phenate)	No	N/A	SM 4500 NH_3 A-2011 (1) says that method H may be used either with or without sample distillation. However, the method itself does not discuss distillation and says to address turbidity issues with filtration.
EPA 350.1, Rev. 2.0 (1993) (Automated Phenate)	Yes	Yes	Method states in Section 2.1: *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.* **When performing the distillation study, the undistilled samples must be at the same pH as the distilled samples, calibration standards and wash water.**

ASTM D1426-08 (A) (Nesslerization)	Yes	Yes	Method Section 1.4 states: Both test methods A and B are applicable to surface and industrial waters and wastewaters following distillation. The test method for distillation given in Appendix X1 has been used in the past to meet requirements for predistillation of samples being analyzed for ammonia. Method Section 1.7 states: The distillation method now appears as Appendix X1 and is provided as nonmandatory information only.
ASTM D1426-08 (B) (Electrode)	Yes	Yes	See comments above.
USGS I-3520-85 (Nesslerization)	Yes	No	Method Section 2.1 states: *Ammonia is distilled from the buffered solution, and an aliquot of the distillate then is nesslerized.*
USGS I-4523-85 (Automated Phenate)	Yes	Yes	
Timberline Ammonia 001, June 2011 (Continuous Flow Gas Diffusion followed by Conductivity Cell Analysis)	No	N/A	Distillation not required by the method or 40 CFR, Part 136.3, Table IB.

* For requirements of methods not listed, contact us.

TABLE 2: Fluoride Methods

Fluoride Method	Distillation Required	Study Allowed	Comments
SM 4500-F^- C-2011 (Electrode, Manual)	No	N/A	Refer to SM 4500 F^- C-2011 (1) (b) and Table 4500F^-:I for interferences that may require distillation.
SM 4500-F^- D-2011 (Colorimetric)	No	N/A	Refer to Table 4500F^-:I for interferences that may require distillation. Method states in Section (1) (b): *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.*
SM 4500-F^- E-2011 (Automated Complexone)	Yes	No	Distillation is performed inline with the automated method setup. Method states in Section (1) (b): *Interferences normally associated with the determination of fluoride are removed by distillation.*
SM 4110 B-2011 (Ion Chromatography)	Yes	Yes	Sample dilution or gradient elution is used to overcome interferences. Method of Known Additions is used to resolve uncertainties.
SM 4110 C-2011 (Ion Chromatography)	No	N/A	Sample dilution or gradient elution is used to overcome interferences. Method of Known Additions is used to resolve uncertainties.
SM 4140 B-2011 (CIE/UV)	No	N/A	This method has been designed to minimize potential interference typically found in environmental waters, groundwater, drinking water, and wastewater. Formate is a common potential interference with fluoride; it is a common impurity in reagent water, has a migration time similar to that of fluoride, and is an

			indicator of loss of water purification system performance and TOC greater than 0.1 mg/L. The addition of 5 mg formate/L in the mixed working anion standard, and to sample where identification of fluoride is in question, aids in the correct identification of fluoride.
EPA 300.0, Rev. 2.1 (1993) (Ion Chromatography)	No	N/A	
EPA 300.1, Rev. 1.0 (1997) (Ion Chromatography)	No	N/A	
ASTM D1179-10 (B) (Electrode, Manual)	No	N/A	1.3 Test Method B covers the accurate measurement of simple fluoride ion in water by means of an ion selective electrode. With this test method, distillation is eliminated because the electrode is not affected by the interferences common to colorimetric procedures. Concentrations of fluoride from 0.1 to 1000 mg/L may be measured.
ASTM D1179-10 (A) (Electrode, Manual)	Yes	No	1.2 Test Method A covers the accurate measurement of total fluoride in water through isolation of the fluoride by distillation and subsequent measurement in the distillate by use of the ion selective electrode (ISE) method. The procedure covers the range from 0.1 to 2.6 mg/L of fluoride.
USGS I-4327-85 (Electrode, Automated)	Yes	Yes	Method states in Section 2.3: *The method includes a distillation step to decompose organic fluoride compounds and attack minerals such as fluorspar in water suspended sediment.*

* For requirements of methods not listed, contact us.