

NC DEQ/DWR WASTEWATER/GROUNDWATER LABORATORY CERTIFICATION BRANCH

LABORATORY NAME:		CERT #:	
PRIMARY ANALYST:		DATE:	
NAME OF PERSON COMPLETING CHECKLIST (PRINT):			
SIGNATURE OF PERSON COMPLETING CHECKLIST:			

Parameter: **Chloride**
Method: **Standard Methods 4500 Cl⁻ B-2021 (Aqueous)**

EQUIPMENT AND REAGENTS:

Erlenmeyer flask, 250-mL	Potassium chromate indicator solution	Standard silver nitrate titrant 0.0141M (0.0141N)
Buret, 50-mL	Standard sodium chloride, 0.0141M (0.0141N)	Aluminum hydroxide suspension
Phenolphthalein indicator solution	Sodium hydroxide, NaOH, 1N	Sulfuric acid, H ₂ SO ₄ , 1N
Hydrogen peroxide, H ₂ O ₂ , 30%		

PLEASE COMPLETE CHECKLIST IN INDELIBLE INK
Please mark Y, N or NA in the column labeled LAB to indicate the common lab practice and in the column labeled SOP to indicate whether it is addressed in the SOP.

GENERAL		L A B	S O P	EXPLANATION
1	Is the SOP reviewed at least every 2 years? What is the most recent review/revision date of the SOP? [15A NCAC 02H .0805 (a) (7)] Date:			Quality assurance, quality control, and Standard Operating Procedure documentation shall indicate the effective date of the document and be reviewed every two years and updated if changes in procedures are made. Verify proper method reference. During review notate deviations from the approved method and SOP.
2	Are all review/revision dates and procedural edits tracked and documented? [15A NCAC 02H .0805 (a) (7)]			Each laboratory shall have a formal process to track and document review dates and any revisions made in all quality assurance, quality control and SOP documents.
3	Is there North Carolina data available for review?			If not, review PT data
PRESERVATION and STORAGE		L A B	S O P	EXPLANATION
4	What type of containers are used for sample collection? [40 CFR 136.3 Table II] Answer:			Polyethylene, fluoropolymer, or glass must be used for Chloride.
5	Are samples analyzed within 28 days of collection? [40 CFR 136.3 Table II]			
PROCEDURE		L A B	S O P	EXPLANATION
6	Is a 100-mL portion of sample or a suitable portion diluted to 100 mL titrated? [SM 4500 Cl ⁻ B-2021 (4) (a)]			Use a 100-mL sample or a suitable portion diluted to 100 mL.
7	If the sample is highly colored, is 3 mL of the Al(OH) ₃ suspension added, mixed, allowed to settle and then filtered? [SM 4500 Cl ⁻ B-2021 (4) (a)]			If the sample is highly colored, add 3 mL Al(OH) ₃ suspension, mix, let settle, and filter.
8	If sulfide, sulfite, or thiosulfate is present, is the sample boiled to a volume of approximately 70 mL, before adding 3 mL H ₂ O ₂ and then boiled down to 50 mL and allowed to cool? [SM 4500 Cl ⁻ B-2021(4) (a)]			If samples that contain very high concentrations of sulfide, sulfite, or thiosulfate that might interfere with the titration, boil the sample to a volume of approximately 70 mL and add 3 mL H ₂ O ₂ . Continue boiling until the sample volume is approximately 50 mL, and cool to room temperature.
9	If samples are not in the pH range of 8 to 10 S.U., is the sample pH adjusted with H ₂ SO ₄ or NaOH? [SM 4500 Cl ⁻ B-2021 (4) (b)]			Adjust the sample pH to 8-10 with H ₂ SO ₄ or NaOH,
10	Is a non-chloride-type electrode used? [SM 4500 Cl ⁻ B-2021 (4) (b)]			For adjustment to pH 8 to 10 S.U., preferably use a pH meter with a non-chloride-type reference electrode. (If only a chloride-type electrode is available, determine amount of

				<p>acid or alkali needed for adjustment and discard this sample portion. Treat a separate portion with required acid or alkali and continue analysis.)</p> <p>Per Standard Methods committee: <i>The fill solution does not need to be Chloride-free. The chloride in the double junction electrode will have little to no effect on the chloride concentration in the sample. The method was written when double junction electrodes didn't exist, and two electrodes were used.</i></p>
11	Is 1.0 mL K ₂ CrO ₄ added to the sample? [SM 4500 Cl ⁻ B-2021 (4) (b)]			Add 1.0 mL K ₂ CrO ₄ indicator solution.
12	Is sample titrated with AgNO ₃ titrant? [SM 4500 Cl ⁻ B-2021 (4) (b)]			End point of titration is a pinkish yellow color.
13	Is the Silver nitrate titrant standardized against NaCl initially (if prepared in-house) and monthly thereafter? [SM 4500 Cl ⁻ B-2021 (3) (c)] [NC WW/GW LCB Titrant Standardization Policy]			<p>Titrants prepared in the laboratory must be standardized initially and monthly thereafter.</p> <p>All certified titrants which are purchased, may be used initially without standardization. The Certificate of Analysis must be kept on file. The certified titrant must be standardized monthly thereafter, for as long as it is used.</p> <p>Standardize against NaCl by the procedure described in 4500-Cl⁻ B.4b; 1.00 mL = 500 µg Cl⁻. Store in a brown bottle.</p>
	QUALITY CONTROL	L A B	S O P	EXPLANATION
14	Is a reagent/method blank analyzed with each batch of samples? [SM 4500 Cl ⁻ B-2021 (4) (b)]			<p>The reagent/method blank contains the same acid used to preserve samples and is carried through all sample preparatory steps (this would include the distillation step when applicable).</p> <p>SM states: Standardize AgNO₃ titrant and establish a reagent blank value by the titration method outlined above.</p>
15	Are values calculated properly? [SM 4500 Cl ⁻ B-2021 (5)]			<p>Calculation</p> $\text{Cl}^- \text{ mg/L} = \frac{(A - B) \times N \times 35,450}{\text{mL sample}}$ <p>where:</p> <p><i>A</i> = mL titration for sample, <i>B</i> = mL titration for blank, and <i>N</i> = normality of AgNO₃.</p>
16	What is the laboratory's lower reporting limit? Answer:			Based on lowest buret increment.
17	Does the laboratory analyze a laboratory-fortified blank (LFB) at least daily or per batch of 20 or fewer samples? [SM 4020 B-2022 (6)] Concentration:			Standard concentration should be close to majority of sample concentrations. May want to vary concentration.
18	What is the acceptance criterion for the LFB recovery? [SM 4020 B-2022 (6)] Answer:			<p>Must establish acceptance criterion.</p> <p>Evaluate the LFB for percent recovery of the added analytes by comparing results to method-specified limits, control charts, or other approved criteria.</p>
19	What corrective action is taken if the LFB recovery is outside established control limits? [15A NCAC 02H .0805 (a) (7) (B)] [SM 4020 B-2022 (6)] Answer:			<p>Rules: If quality control results fall outside established limits or show an analytical problem, the laboratory shall identify the Root Cause of the failure. The problem shall be resolved through corrective action, the corrective action process documented, and any samples involved shall be reanalyzed, if possible.</p> <p>SM states: If LFB results are out of control, take corrective action, including re-preparation and re-analysis of</p>

			associated samples if required. Use LFB results to evaluate batch performance, calculate recovery limits, and plot control charts.
20	Is a laboratory-fortified matrix (LFM) analyzed with each batch of 20 or fewer samples? [SM 4020 B-2022 (7) and Table 4020:1]		If an LFM is feasible and the method does not specify LFM frequency requirements, then include at least 1 LFM with each sample set (batch) or on a 5% basis, whichever is more frequent.
21	How is the LFM (spike) prepared? [SM 4020 B-2022 (7)] Answer:		Add a concentration that is at least 10 x MRL, less than or equal to the midpoint of the calibration curve, or method-specified level to the selected sample(s). The analyst should use the same concentration as for LFB (4020 B.6) to allow analysts to separate the matrix's effect from laboratory performance. Prepare LFM from the same reference source used for LFB. Make the addition such that sample background levels do not adversely affect recovery (preferably adjust LFM concentrations if the known sample is more than 5 times the background level). At a minimum, the spike must at least equal the background concentration, unless the method specifies otherwise. For example, if the sample contains the analyte of interest, then add approximately as much analyte to the LFM sample as the concentration found in the known sample. See Matrix Spike Technical Assistance document.
22	Is a Laboratory-Fortified Matrix Duplicate (LFMD) analyzed with each batch of 20 or fewer samples? [SM 4020 B-2022 (8) and Table 4020:1]		As a minimum, include 1 duplicate sample or 1 LFM duplicate with each sample set (batch) or on a 5% basis, whichever is more frequent, and process it independently through the entire sample preparation and analysis. Note: Table 4020:1 does not give the option to perform a sample duplicate for this method—an LFM/LFMD is required.
23	What is the acceptance criterion for the LFM/LFMD recovery (accuracy)? [15A NCAC 02H .0805 (a) (7) (A)] Answer:		Each laboratory shall establish performance acceptance criteria for all quality control analyses. Each laboratory shall calculate and document the precision and accuracy of all quality control analyses with each sample set.
24	What corrective action is taken if LFM/LFMD results exceed the acceptance criterion for accuracy ? [15A NCAC 02H .0805 (a) (7) (B)] Answer:		If quality control results fall outside established limits or show an analytical problem, the laboratory shall identify the Root Cause of the failure. The problem shall be resolved through corrective action, the corrective action process documented, and any samples involved shall be reanalyzed, if possible.
25	What is the acceptance criterion for the LFM/LFMD relative percent difference (precision)? [15A NCAC 02H .0805 (a) (7) (A)] Answer:		
26	What corrective action is taken if LFM/LFMD results exceed the acceptance criterion for precision ? [SM 4020 B-2022 (8)] [15A NCAC 02H .0805 (a) (7) (B)] Answer:		SM states: If LFM duplicate results are out of control, then take corrective action to rectify the matrix effect, use another method, use the method of standard addition, or flag the data if reported.
27	Are results qualified to indicate quality control failures or sample anomalies when reporting results? [15A NCAC 02H .0805 (e) (5)]		Reported data associated with Quality Control failures, improper sample collection, holding time exceedances, or improper preservation shall be qualified as such.

Additional Comments:

Inspector: _____ Date: _____

Potassium chromate indicator solution: Dissolve 50 g K₂CrO₄ in a 500 mL of reagent water. Add AgNO₃ solution until a definite red precipitate is formed. Let stand 12 h, filter, and dilute to 1 L with reagent water.

Standard sodium chloride, 0.0141M (0.0141N): Dissolve 824.0 mg NaCl (dried at 140°C) in reagent water and dilute to 1000 mL; 1.00 mL = 500 µg Cl⁻.

Standard silver nitrate titrant 0.0141M (0.0141N): Dissolve 2.395 g AgNO₃ in reagent water and dilute to 1000 mL; Standardize against NaCl by the procedure described in 4500 Cl⁻ B.4b; 1.00 mL = 500 µg Cl⁻. Store in a brown bottle.

Aluminum hydroxide suspension: Dissolve 125 g aluminum potassium sulfate or aluminum ammonium sulfate, AlK(SO₄)₂ · 12H₂O or AlNH₄(SO₄)₂ · 12H₂O, in 1 L reagent water. Warm to 60°C and add 55 mL conc ammonium hydroxide (NH₄OH) slowly with stirring. Let stand about 1 h, transfer to a large bottle, and wash precipitate by successive additions, with thorough mixing and decanting with reagent water, until free from chloride. When freshly prepared, the suspension occupies a volume of approximately 1 L.