

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: **Hardness**

Method: **Standard Methods 2340 C-2021 (Aqueous)**

Analytical Reagents:

Buffer Solution	Standard Calcium Solution (see recipe at the end of the checklist)
Indicators: Eriochrome Black T or Calmagite	Sodium Hydroxide, NaOH, 0.1N
Standard EDTA Titrant, 0.01M	Complexing agents (if necessary): Inhibitor I, Inhibitor II, or MgCDTA

Digestion Reagents and Equipment (if necessary):

Nitric Acid- Sulfuric Acid Digestion	Nitric Acid-Perchloric Acid Digestion	Hot plate
concentrated HNO ₃	concentrated HNO ₃	Erlenmeyer flask or griffin beaker; acid-washed and rinsed
concentrated H ₂ SO ₃	Concentrated HClO ₄	Watch glasses
		Volumetric flasks

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	Is the sample preserved at the time of collection to pH <2 S.U. with HNO ₃ or H ₂ SO ₄ ? [40 CFR 136.3 Table II]			Preservation not required if analyzed within 15 minutes.
5	Is pH checked and documented to be <2 S.U. upon receipt in the laboratory? [15A NCAC 02H .0805 (a) (7) (M)]			
6	What action is taken if pH is >2 S.U.? [15A NCAC 02H .0805 (a) (7) (M)] Answer:			Sample preservation shall be verified and documented. If a laboratory receives a sample subject to G.S. 143-215.1 and 143-215.63 that does not meet sample collection, holding time, or preservation requirements, the laboratory shall document the incident, notify the sample collector or client, and secure another sample that meets the regulatory requirements, if possible. If another viable sample cannot be secured, the original sample may be analyzed but the results reported shall be qualified with the nature of the sample collection, holding time, or preservation infractions and the laboratory shall notify the State Laboratory of the infractions. The notification shall include a statement indicating corrective action taken to prevent future infractions.
7	Are samples analyzed within 6 months of collection? [40 CFR 136.3 Table II]			
	PROCEDURE – Interferences	L A B	S O P	EXPLANATION

8	<p>What is done if interference by metal ions is suspected? [SM 2340 C-2021 (1) (b)]</p> <p>Answer:</p>			<p>Some metal ions interfere by causing fading or indistinct end points or by stoichiometric consumption of EDTA. Reduce this interference by adding certain inhibitors before titration. MgCDTA (see 2340 C.2b3), selectively complexes heavy metals, releases magnesium into the sample, and may be used as a substitute for toxic or malodorous inhibitors. It is useful only when the magnesium substituted for heavy metals does not contribute significantly to the total hardness. With heavy metal or polyphosphate concentrations below those indicated in Table 2340:1, use Inhibitor I or II. When higher concentrations of heavy metals are present, determine calcium and magnesium by a non-EDTA method (see Sections 3500-Ca and 3500-Mg) and obtain hardness by calculation. The values in Table 2340:1 are intended as a rough guide only and are based on using a 25-mL sample diluted to 50 mL.</p>
9	<p>If CaCO₃ precipitation occurs causing a drifting end point and low results, what is done to reduce precipitation loss? [SM 2340 C-2021 (1) (c)]</p> <p>Answer:</p>			<p>The specified pH may produce an environment conducive to CaCO₃ precipitation. Although the titrant slowly redissolves such precipitates, a drifting endpoint often yields low results. Completion of the titration within 5 min minimizes the tendency for CaCO₃ to precipitate. The following three procedures also reduce precipitation loss:</p> <p>1) Dilute the sample with reagent water to reduce CaCO₃ concentration. This simple expedient has been incorporated in the procedure. If precipitation occurs at this dilution of 1 + 1 use procedure 2 or 3. Using too small a sample contributes a systematic error due to the buret-reading error.</p> <p>2) If the approximate hardness is known or is determined by a preliminary titration, add 90% or more of titrant to the sample before adjusting the pH with buffer.</p> <p>3) Acidify the sample and stir for 2 min to expel CO₂ before pH adjustment. Determine alkalinity to indicate the amount of acid to be added.</p>
	PROCEDURE – Sample Digestion	L A B	S O P	EXPLANATION
10	Are polluted water or wastewater samples digested prior to analysis? [SM 2340 C-2021 (3) (a)]			Pretreatment of polluted water and wastewater samples: Use nitric acid-sulfuric acid or nitric acid-perchloric acid digestion (Section 3030)
11	Is a digestion log maintained that includes all pertinent information? [15A NCAC 02H .0805 (a) (7) (E)]			
	Nitric Acid-Sulfuric Acid Digestion			
12	<p>What sample volume is used for digestion? [SM 3030 G-2020 (3)]</p> <p>Answer:</p>			The method does not specify, but the final digestate is diluted to the mark in a 100-mL volumetric flask.
13	Is 5 mL of concentrated HNO ₃ added to the flask or beaker with sample? [SM 3030 G-2020 (3)]			
14	Is the flask placed on a hot plate and covered with a ribbed watch glass? [SM 3030 G-2020 (3)]			
15	Is the sample brought to a slow boil and evaporated to 15 to 20 mL? [SM 3030 G-2020 (3)]			
16	Is 5 mL concentrated HNO ₃ and 10 mL concentrated H ₂ SO ₃ added, cooling flask between additions? [SM 3030 G-2020 (3)]			
17	Is the sample evaporated on the hot plate until dense white fumes just appear? [SM 3030 G-2020 (3)]			
18	If the solution does not clear at this point, is an additional 10 mL of concentrated HNO ₃ added? [SM 3030 G-2020 (3)]			
19	Is the sample heated until the solution is clear and no brownish fumes are evident? [SM 3030 G-2020 (3)]			
20	Is the sample kept from drying out during digestion? [SM 3030 G-2020 (3)]			
21	Is the sample cooled and diluted to 50 mL with water? [SM			

	3030 G-2020 (3)]			
22	Is the sample heated to almost boiling to dissolve salts? [SM 3030 G-2020 (3)]			
23	If it is necessary to filter the sample, is the flask rinsed with 2 portions of reagent water, and added to an additional flask containing the filtrate? [SM 3030 G-2020 (3)]			
24	Is the sample cooled, diluted to final volume, and mixed thoroughly? [SM 3030 G-2020 (3)] Final volume:			
	Nitric Acid-Perchloric Acid Digestion			
25	What sample volume is used for digestion? [SM 3030 H-2020 (3)] Answer:			The method does not specify, but the final digestate is diluted to the mark in a 100-mL volumetric flask.
26	Is 5 mL of concentrated HNO ₃ added to the flask or beaker with sample? [SM 3030 H-2020 (3)]			
27	Is the flask placed on a hot plate and covered with a ribbed watch glass? [SM 3030 H-2020 (3)]			
28	Is the sample brought to a slow boil and evaporated to 15 to 20 mL? [SM 3030 H-2020 (3)]			
29	Is 10 mL each of concentrated HNO ₃ and HClO ₄ added, cooling flask between additions? [SM 3030 H-2020 (3)]			Caution: Heated mixtures of HClO ₄ and organic matter may explode violently. Precautions to avoid this are in SM 3030 H-2020 (3).
30	Is the sample evaporated on the hot plate until dense white fumes just appear? [SM 3030 H-2020 (3)]			
31	If solution is not clear, is sample kept just at the boiling point until it clears? [SM 3030 H-2020 (3)]			
32	Is an additional 10 mL of concentrated HNO ₃ added to complete digestion, if necessary? [SM 3030 H-2020 (3)]			
33	Is the sample flask cooled and rinsed with water, diluting to about 50 mL? [SM 3030 H-2020 (3)]			
34	Is the sample brought to boil? [SM 3030 H-2020 (3)]			
35	If it is necessary to filter the sample, is the flask rinsed with 2 portions of reagent water, and added to an additional flask containing the filtrate? [SM 3030 H-2020 (3)]			
36	Is the sample cooled, diluted to final volume, and mixed thoroughly? [SM 3030 H-2020 (3)] Final volume:			
	PROCEDURE – Sample Analysis	L A B	S O P	EXPLANATION
37	Is the titration conducted at or near room temperature? [SM 2340 C-2021 (1) (c)]			Conduct titrations at or near room temperature. The color change becomes impractically slow as the sample approaches freezing temperature. Indicator decomposition becomes a problem in hot water.
38	Is a volume of sample selected that required less than 15 mL of EDTA titrant? [SM 2340 C-2021 (3) (b)]			
39	Is the titration completed within 5 minutes, measured from time of buffer addition? [SM 2340 C-2021 (3) (b)]			
40	Is 25mL of sample diluted to about 50 mL with distilled water? [SM 2340 C-2021 (3) (b)]			Dilute to a ratio of 1:1 to reduce CaCO ₃ precipitation.
41	Is the appropriate amount of buffer added to reach a pH of 10.0 ± 0.1 S.U.? [SM 2340 C-2021 (1) (a)]			Add 1 to 2 mL buffer solution. Usually 1mL will be sufficient to achieve pH 10.0 to 10.1 S.U.
42	Is the buffer discarded after one month or sooner if 1 or 2 mL added to the sample fails to produce a pH of 10.0±0.1 S.U. at the titration endpoint? [SM 2340 C-2021 (2) (a) (2)]			
43	Are 1 to 2 drops of indicator solution or appropriate amount of dry powder indicator formulation added? [SM 2340 C-2021 (3) (b)]			
44	Is standard EDTA titrant added slowly, with continuous stirring, until the last reddish tinge disappears? [SM 2340 C-2021 (3) (b)]			

45	Are samples titrated to the blue end-point? [SM 2340 C-2021 (3) (b)]			The endpoint of the solution is usually blue. Daylight or a daylight fluorescent lamp is recommended highly because ordinary incandescent lights tend to produce a reddish tinge in the blue at the endpoint.
46	If there is not a sharp end-point color change to the titration, is the appropriate inhibitor added? [SM 2340 C-2021 (3) (b)]			The absence of sharp end-point color change in the titration usually means that an inhibitor must be added after the pH adjustment or that the indicator has deteriorated.
47	What calculation is used to determine Hardness? [SM 2340 C-2021 (4)] Answer:			Hardness (EDTA) as mg/L CaCO ₃ = $\frac{A \times B \times 1000}{\text{mL sample}}$ where: A = mL titration for sample B = mg CaCO ₃ equivalent to 1.00 mL EDTA titrant
	If your reporting limit is ≥ 5 mg/L, skip to question 51			
48	Is a larger sample volume used for titration for samples <5 mg/L? [SM 2340 C-2021 (3) (c)]			Use 100 to 1000mL of sample and add proportionately larger amounts of buffer, inhibitor (if needed), and indicator.
49	Is a blank analyzed using the same volume as samples <5 mg/L? [SM 2340 C-2021 (3) (c)]			Add standard EDTA slowly from a microburet to the same volume of reagent water as used for the sample which contains identical amounts of buffer, inhibitor (if needed), and indicator.
50	Is the volume of EDTA used for the blank subtracted from the volume of EDTA used for samples <5 mg/L? [SM 2340 C-2021 (3) (c)]			Hardness (EDTA) as mg/L CaCO ₃ = $\frac{(A-C) \times B \times 1000}{\text{mL sample}}$ where: A = mL titration for sample B = mg CaCO ₃ equivalent to 1.00 mL EDTA titrant C = mL titration for blank
	QUALITY ASSURANCE	L A B	S O P	EXPLANATION
51	What is the laboratory's lower reporting limit? Answer:			
52	Is the Standard EDTA titrant standardized against a standard calcium solution? [SM 2340 C-2021 (2) (d)]			Standardize prepared titrant using the same method as titrating samples. Purchased titrant does not need initial standardization as long as the laboratory maintains the COA.
53	Is the Standard EDTA titration reagent re-standardized monthly or when improper storage occurs? [SM 2020 B-2021 (2) (b)]			Re-standardize reagents once per month or when improper storage occurs.
54	What is done if the reagent's normality has changed? [SM 2020 B-2021 (2) (b)] Answer:			If the titration reagent's normality (titer value) has changed, then use the measured value, adjust the normality (titer value) as the procedure describes, or prepare and standardize fresh titration reagent as needed.
55	Is a method blank (MB) analyzed daily or with each batch or 20 or fewer samples? [SM 2020 B-2021 (2) (d) and Table 2020:2]			Include at least one method blank daily or with each batch of 20 or fewer samples, whichever is more frequent. The method blank must be digested if any samples are digested.
56	Is the method blank acceptance criterion less than the reporting level? [SM 2020 B-2021 (2) (d)]			If any MB measurements are at or above the reporting level, take immediate corrective action as outlined in Section 1020 B.5. This may include reanalyzing the sample batch. It is recommended that any results over ½ the reporting level be investigated.
57	What corrective action is taken if the method blank does not meet the acceptance criterion? [15A NCAC 02H .0805 (a) (7) (B)] [SM 2020 B-2021 (2) (d)] Answer:			Our Rule requires corrective action any time quality control results indicate a problem. SM states: If any MB measurements are at or above the reporting level, take immediate corrective action as

			outlined in Section 1020 B.5. This may include re-analyzing the sample batch.
58	Does the laboratory analyze a laboratory-fortified blank (LFB) at least daily or per batch of 20 or fewer samples? [SM 2020 B-2021 (2) (e) and Table 2020:2]		If any samples are digested, the LFB must be digested.
59	What is the true value of the LFB? [15A NCAC 02H .0805 (a) (7) (A)] [SM 2020 B-2021 (2) (e)] Answer:		SM States: Using stock solutions preferably prepared with the second source, prepare fortified concentrations so they are within the calibration curve. Ideally, vary LFB concentrations to cover the range from the midpoint to the lower part of calibration curve, including the reporting limit. Since there is no calibration curve included in this analysis, try to approximate the midpoint of your routine samples. The lab will set their own acceptance criterion.
60	What is the acceptance criterion of the LFB? [15A NCAC 02H .0805 (a) (7) (A)] Answer:		
61	What corrective action is taken if the LFB does not meet the acceptance criterion? [15A NCAC 02H .0805 (a) (7) (B)] [SM 2020 B-2021 (2) (e)] Answer:		Our Rule requires corrective action any time quality control results indicate a problem. SM states: Establish corrective actions to take if the LFB does not satisfy acceptance criteria.
62	Are duplicate samples analyzed daily or with each batch of 20 or fewer samples? [SM 2020 B-2021 (2) (f) and table 2020:2]		Include at least one duplicate for each matrix type daily or with each batch of 20 or fewer samples.
63	What is the acceptance criterion for the duplicates? [SM 2020 B-2021 (2) (f)] Answer:		Calculate control limits for duplicates when method-specific limits are not provided.
64	What corrective action is taken if the duplicates do not meet the acceptance criterion? [15A NCAC 02H .0805 (a) (7) (B)] Answer:		Our Rule requires corrective action any time quality control results indicate a problem.
65	Is the data qualified on the electronic Discharge Monitoring Report (eDMR) or client report if Quality Control (QC) requirements are not met? [15A NCAC 02H .0805 (a) (7) (B)]		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. If the sample cannot be reanalyzed, or if the quality control results continue to fall outside established limits or show an analytical problem, the results shall be qualified as such.

Additional Comments:

Inspector: _____ Date: _____