NC DEQ/DWR LABORATORY CERTIFICATION BRANCH

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

Parameter: Inorganic **Phenols**
Method: **EPA 420.1, Rev. 1978 (Aqueous)**
Manual Colorimetric

Phenol is considered a method-defined parameter per the definition in the Code of Federal Regulations, Part 136.6, Section (a) (5). This means that the method may not be modified per Part 136.6, Section (b) (3).

EQUIPMENT:

	Spectrophotometer **Model:** **Wavelength: 460 or 510 nm**		Funnels
	pH meter **Model:** **Electrode:**		Distillation apparatus
	Filters **Type:** **Pore Size:**		Filter paper
	Nessler tubes, short or long form		Separatory funnels, 500 or 1,000 mL

ANALYSIS REAGENTS:

	Phosphoric acid 1+9		Copper sulfate solution		Buffer solution
	4-Aminoantipyrine solution		Potassium ferricyanide solution		Stock phenol solution
	Standard phenol Solution A		Standard phenol Solution B		Chloroform
	Ferric ammonium sulfate				

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	**LAB**	**SOP**	**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)] **Answer:**			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 Standard Operating Procedure documents.
3	Is there North Carolina data available for review?			If not, review PT data.
4	What is the laboratory's reporting limit? [15A NCAC 02H .0805 (a) (7) (H)] **Answer:**			For analytical procedures requiring analysis of a series of standards, the concentrations of these standards shall bracket the range of the sample concentrations measured. One of the standards shall have a concentration equal to or less than the laboratory's lowest reporting concentration for the parameter involved.
	PRESERVATION and STORAGE	**LAB**	**SOP**	**EXPLANATION**
5	Are samples checked for Residual Chlorine at the time of collection and prior to pH preservation adjustment? [EPA 420.1, Rev. 1978 (Section 5.2)]			Oxidizing agents such as chlorine, detected by the liberation of iodine upon acidification in the presence of potassium iodide, are removed immediately after sampling.

6	What action is taken if chlorine is present? [EPA 420.1, Rev. 1978 (Section 5.2)] **Answer:**			The method states to use an excess of ferrous ammonium sulfate. Note: the proposed MUR 22 includes an update to Phenols in Table II, which states to use 0.008% sodium thiosulfate to treat for chlorine at collection
7	Is the residual chlorine check and any necessary mitigation documented? [Sample Collection, Preservation, Storage and Transport Requirements for Non-Field Laboratories Policy]			Dechlorinating agents used at the time of sampling must be documented to have been effective (either by the sample collector or the receiving laboratory) by verifying a chlorine residual <0.5 mg/L at a neutral pH. If measuring chlorine concentration in an acidified sample, pour off a small portion of the sample and neutralize the pH prior to testing. Use sufficiently strong base to not dilute the sample. Discard that portion after testing.
8	If residual chlorine is not checked prior to acidification in the field, is a portion of the preserved sample neutralized in the laboratory and checked for residual chlorine prior to distillation? [Sample Collection, Preservation, Storage and Transport Requirements for Non-Field Laboratories Policy]			Note: Guidance from EPA Region IV confirms that the residual chlorine removal is not required to be performed at collection. It may be removed prior to distillation, or analysis if distillation is not required. Removal is not required at all if the permittee does not use chlorine for disinfection.
9	Is the residual chlorine check documented? [15A NCAC 02H .0805 (a) (7) (M)]			Sample preservation shall be verified and documented.
10	Are samples preserved at the time of collection with H_2SO_4 to a pH of <2 S.U.? [40 CFR 136.3, Table II]			
11	Is pH checked and documented to be <2 S.U. upon receipt in the laboratory? [15A NCAC 02H .0805 (a) (7) (M)]			
12	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.
13	Are samples iced to above freezing but ≤ 6 ºC during transport? [40 CFR 136.3 Table II and footnote 18]			
14	Are samples refrigerated above freezing and ≤ 6 °C during storage? [40 CFR 136.3, Table II]			
15	Are samples analyzed within 28 days of collection? [40 CFR 136.3, Table II]			
	PROCEDURE – Calibration	**LAB**	**SOP**	**EXPLANATION**
16	How often is the spectrophotometer calibrated? [15A NCAC 02H .0805 (a) (7) (H) (v)]			For colorimetric analyses, a series of five or more non-zero standards for a curve prepared every 12 months or three or more non-zero standards for curves established each day, or standards as set forth in the analytical procedure, shall be analyzed to establish a calibration curve. A manufacturer's factory-set calibration (internal curve) shall be verified with the same number of standards and frequency as a prepared curve.

17	Is the laboratory calibrating with the method specified number of standards? [EPA Method 420.1, Rev. 1978, Section 8.2.1 and 8.3.1] **List the calibration standard concentrations:**			Direct photometric method - blank plus 6 standards. Chloroform extraction method - blank plus 5 standards.
18	Does each standard curve have a correlation coefficient ≥ 0.995? [NC WW/GW LCB Correlation Coefficient for Linear Calibration Curves Policy, 12/23/2014]			When linear regression is used, use the minimum correlation coefficient specified in the method. If the minimum correlation coefficient is not specified, then a minimum value of 0.995 (or a coefficient of determination, r^2, of 0.99) is required.
19	Are sample results read directly from standard curve? [EPA 420.1, Rev. 1978, Section 9.2]			Obtain concentration value of sample directly from standard curve.
	DISTILLATION PROCEDURE	**LAB**	**SOP**	**EXPLANATION**
20	Is 500 mL of sample distilled? [EPA 420.1, Rev. 1978 (Section 8.1.1)]			Measure 500 mL sample into a beaker.
21	Is the sample pH adjusted to 4 S.U. with 1 + 9 NaOH prior to distillation? [40 CFR 136.3, Table IB, Footnote 26]			Just prior to distillation, adjust the sulfuric-acid-preserved sample to pH 4 with 1 + 9 NaOH
22	Is this documented? [15A NCAC 02H .0805 (a) (7) (E)]			All analytical data and records pertinent to each certified analysis shall be available for inspection upon request.
23	Is 5 mL $CuSO_4$ solution (7.2) added after adjusting the pH? [EPA 420.1, Rev. 1978, Section 8.1.1]			
24	Is distillation stopped after 450 mL of distillate has been collected and 50 mL of warm distilled water added to the flask? [EPA 420.1, Rev. 1978 (Section 8.1.2)]			
25	Is distillation resumed until 500 mL of distillate has been collected? [EPA 420.1, Rev. 1978 (Section 8.1.2)]			
26	Is the distillate filtered through a prewashed membrane filter if the distillate is turbid? [EPA 420.1, Rev. 1978 (Section 8.1.3)]			
	Direct photometric method	**LAB**	**SOP**	**EXPLANATION**
27	Is 100 mL of standard and 100 mL of distillate or an aliquot diluted to 100mL used? [EPA 420.1, Rev. 1978, Section 8.2.2]			To 100 mL of distillate or an aliquot diluted to 100 mL and/or standards, add 2 mL of buffer solution (7.3) and mix.
28	Is 2 mL of buffer added to the samples and/or standards? [EPA 420.1, Rev. 1.0, 1978, Section 8.2.2]			
29	Is the pH of the sample and/or standard documented to be 10.0 ± 0.2 S.U.? [EPA 420.1, Rev. 1.0, 1978, Section 8.2.2]			EPA 420.1: The pH of the sample and standards should be 10±0.2 S.U. Footnote 27 in 40 CFR Part 136.3, Table IB on SM 5530 D-2021 states: The colorimetric reaction must be conducted at a pH of 10.0 +/- 0.2 S.U. Even though method 420.1 uses “should” to describe the pH range, the addition of the footnote for SM 5530 D, which is listed in the equivalent methodology row in Table IB, suggests that it is required for both methods.
30	Is 2 mL of aminoantipyrine solution added and mixed? [EPA 420.1, Rev. 1978, Section 8.2.3]			
31	Is 2.0 mL of potassium ferricyanide solution added and mixed? [EPA 420.1, Rev. 1978, Section 8.2.4.]			
32	Is the sample read after 15 minutes? [EPA 420.1, Rev. 1978, Section 8.2.5.]			After 15 minutes read absorbance at 510 nm.

33	Are the samples and standards read at 510 nm? [EPA 420.1, Rev. 1978, Section 8.2.5]			510 nm
	Chloroform extraction method	**LAB**	**SOP**	**EXPLANATION**
34	Is 500 mL of distillate or an aliquot diluted to 500 mL used? [EPA 420.1, Rev. 1978, Section 8.3.2]			Place 500 mL of distillate or an aliquot diluted to 500 mL in a separatory funnel.
35	Is 10 mL of buffer solution added to standards and samples and mixed? [EPA 420.1, Rev. 1978, Section 8.3.3]			
36	What is the pH of the distillate? [EPA 420.1, Rev. 1978. Section 8.2.2] **Answer:**			The pH of the sample and standards should be 10±0.2 S.U.
37	Is this documented? [15A NCAC 02H .0805 (a) (7) (E)]			All analytical data and records pertinent to each certified analysis shall be available for inspection upon request.
38	Is 3.0 mL of aminoantipyrine solution added and mixed? [EPA 420.1, Rev. 1978, Section 8.3.4]			
39	Is 3.0 mL of potassium ferricyanide solution added and mixed? [EPA 420.1, Rev. 1978, Section 8.3.5]			
40	After 3 minutes is the distillate extracted with 25 mL of chloroform? [EPA 420.1, Rev. 1978, Section 8.3.6] **Describe procedure:**			Shake the separatory funnel at least 10 times, let $CHCl_3$ settle, shake again 10 times and let chloroform settle again. Vent chloroform fumes into hood.
41	Is the chloroform extract filtered through filter paper? [EPA 420.1, Rev. 1978, Section 8.3.7]			Filter chloroform extracts through filter paper. Do not add more chloroform. Carry out filtration in a hood. Dispose of chloroform in environmentally acceptable manner.
42	Are samples and standards read against the blank at 460 nm? [EPA 420.1, Rev. 1978, Section 8.3.8]			Read the absorbance of the samples and standards against the blank at 460 nm.
	QUALITY ASSURANCE	**LAB**	**SOP**	**EXPLANATION**
Note: EPA Method 420.1, Rev. 1978 does not include QA/QC procedures. 40 CFR Part 136.7 states that if a method lacks QA/QC procedures, the permittee/laboratory has specific options to comply with QA/QC requirements. The options are to follow QA/QC published in the "equivalent" EPA method (of which there are none), refer to the appropriate QA/QC sections of an approved part 136 method from a consensus organization (i.e., Standard Methods), or incorporate 12 quality control elements as applicable that are listed in 136.7 (c) (1). As such, the following QC requirements are collected from NC WW/GW LCB Rules and Standard Methods 5020 B-2022			
43	Has each analyst performing this analysis completed an Initial Demonstration of Capability (IDC)? [SM 5020 B-2022 (3)] **Attach a copy of each analyst's IDC to this checklist.**			IDCs should be performed before producing data and then periodically. Specific frequency is not stated in SM, but should be in the labs QA manual. IDC should contain a reagent blank at least 4 LFBs at a concentration between 10x the MDL and the mid-point of the calibration curve.
44	Has an MDL been established according to 40 CFR 136 Appendix B?			Process a minimum of seven spiked samples and seven method blank samples through all steps of the method. The samples used for the MDL must be prepared in at least three batches on three separate calendar dates and analyzed on three separate calendar dates.
45	Is ongoing MDL data being collected quarterly? [Method Detection Limit Procedure, Rev. 2, (3) (a)]			During any quarter in which samples are being analyzed, prepare and analyze a minimum of two spiked samples on each instrument, in separate batches, using the same spiking concentration used in Section 2.
46	Is the MDL recalculated at least once every 13 months? [Method Detection Limit Procedure, Rev. 2, (4) (a)]			At least once every thirteen months, re-calculate MDLs and MDLb from the collected spiked samples and method blank results using the equations in Section 2.
47	Is a lower reporting limit standard analyzed or back-calculated with each analysis? [15A NCAC 02H .0805 (a) (7) (H)]			Laboratories shall analyze or back-calculate a standard at the same concentration as the lowest reporting concentration each day samples are analyzed.

48	What is the acceptance criterion for the lower reporting limit standard? [15A NCAC 02H .0805 (a) (7) (A)] **Answer:**			Unless specified by the method or this Rule, each laboratory shall establish performance acceptance criteria for all quality control analyses.
49	What corrective action does the laboratory take if the lower reporting limit standard does not meet the acceptance criterion? [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. Recalibrate/re-verify the curve.
50	Is a calibration blank analyzed before sample analysis, after every 10 samples and at the end of analysis? [15A NCAC 02H .0805 (a) (7) (H)]			A calibration blank and calibration verification standard shall be analyzed prior to sample analysis, after every tenth sample, and at the end of each sample group, unless otherwise specified by the method, to check for carryover and calibration drift.
51	Is a reagent blank (method blank) analyzed with each sample set before analyzing samples or on a 5% basis, whichever is more frequent? [SM 5020 B-2022 (5)]			A reagent blank (method blank) consists of reagent water (see Section 1080) and all reagents (including preservatives) that normally are in contact with a sample during the entire analytical procedure. As a minimum, include one reagent blank with each sample set (batch) or on a 5% basis, whichever is more frequent. Analyze a blank after the initial CCV standard and before analyzing samples.
52	Is the acceptance criterion for all blanks ≤50% of the reporting limit? [15A NCAC 02H .0805 (a) (7) (H) (i)]			The concentration of reagent, method, and calibration blanks shall not exceed 50 percent of the lowest reporting concentration or as otherwise specified by the reference method.
53	What corrective action is taken if the blank does not meet the acceptance criterion? [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.
54	Is a calibration verification standard analyzed initially (i.e., prior to sample analysis), after every tenth sample and at the end of each sample group to check for carry over and calibration drift? [15A NCAC 02H .0805 (a) (7) (H)]			Rule: A calibration blank and calibration verification standard shall be analyzed prior to sample analysis, after every tenth sample, and at the end of each sample group, unless otherwise specified by the method, to check for carryover and calibration drift.
55	What is the acceptance criterion for the calibration verification standard? [15A NCAC 02H .0805 (a) (7) (A)] **Answer:**			Unless specified by the method or this Rule, each laboratory shall establish performance acceptance criteria for all quality control analyses.
56	What corrective action is taken if the standard does not meet the acceptance criterion? [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.
57	Is a second source standard analyzed after each initial calibration prior to sample analysis to verify the calibration? [15A NCAC 02H .0805 (a) (7) (H) (ii)]			Laboratories shall analyze one known second source standard to verify the accuracy of standard preparation if an initial calibration is performed and in accordance with the referenced method requirements thereafter. All standards are second source when using a factory-set curve, so an additional standard is not needed to meet this requirement.

58	What is the acceptance criterion for the second source standard? [15A NCAC 02H .0805 (a) (7) (A)] **Answer:**			
59	What corrective action is taken if the second source standard is outside the acceptance criterion? [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.
60	Is a laboratory-fortified blank (LFB) analyzed with each sample set or on a 5% basis, whichever is more frequent? [SM 5020 B-2022 (6)]			A laboratory-fortified blank (LFB) is a reagent-water sample (with associated preservatives) to which a known concentration of the analyte(s) of interest has been added. The LFB may be used as the LCS (5020B.4) if the method requires a preliminary sample extraction or digestion. As a minimum, include one LFB with each sample set (batch) or on a 5% basis, whichever is more frequent. Process the LFB through all sample-preparation and -analysis steps.
61	What is the concentration of the LFB? [SM 5020 B-2022 (6)] **Answer:**			Use an added concentration of at least 10 X MDL, at or below the midpoint of the calibration curve, a method-specified level, or a level specified in a project plan's data quality objectives. Ideally, the LFB concentration should be less than the MCL (if the contaminant has one).
62	What is the acceptance criterion for the LFB? [15A NCAC 02H .0805 (a) (7) (A)] **Answer:**			None specified in 5020 B
63	What corrective action is taken if the LFB does not meet the acceptance criterion? [SM 5020 B-2022 (6)] **Answer:**			If LFB results are out of control, take corrective action, including re-preparation and re-analysis of associated samples if required.
64	At what frequency is a Matrix Spike (MS) analyzed? [SM 5020 B-2022 (7)] **Answer:**			If an LFM is feasible and the method does not specify LFM frequency requirements, then include at least one LFM with each sample set (batch) or on a 5% basis, whichever is more frequent.
65	How is the MS prepared? [NC WW/GW LCB Matrix Spiking Policy 05/07/2020] **Answer:**			See Matrix Spiking Policy and Technical Assistance document.
66	What is the acceptance criterion for MS recovery? [15A NCAC 02H .0805 (A) (7) (A)] Answer:			Unless specified by the method or this Rule, each laboratory shall establish performance acceptance criteria for all quality control analyses.
67	What corrective action is taken if the MS results do not meet the acceptance criterion? [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

68	At what frequency are duplicates and/or Matrix Spike Duplicates (MSD) analyzed? [SM 5020 B-2022 (8)] **Answer:**			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.
69	What is the acceptance criterion for duplicates and/or MS/MSD? [15A NCAC 02H .0805 (a) (7) (A)] **Answer:**			Unless specified by the method or this Rule, each laboratory shall establish performance acceptance criteria for all quality control analyses.
70	What corrective action does the laboratory take if the duplicate and/or MS/MSD results are outside of established control limits? [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.
71	Is the data qualified on the Discharge Monitoring Report (DMR) or client report if Quality Control (QC) requirements are not met? [15A NCAC 02H .0805 (a) (7) (B)]			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. If data qualifiers are used to qualify samples not meeting QC requirements, the data may not be useable for the intended purposes. It is the responsibility of the laboratory to provide the client or end-user of the data with sufficient information to determine the usability of the qualified data.

Note: If chlorine is present, the phenolic compounds may be partially oxidized and the results may be low. Dechlorinate samples that are known to have residual chlorine.

Analytical Reagents & Standards Prep:

Phosphoric acid solution, 1+9: Dilute 10 mL of 85% H_3PO_4 to 100 mL with distilled water.

Copper sulfate solution: Dissolve 100 g $CuSO_4 \cdot 5H_2O$ in distilled water and dilute to 1 liter.

Buffer solution: Dissolve 16.9 g NH_4Cl IN 143 mL conc. NH_4OH and dilute to 250 mL with distilled water. Two mL should adjust 100 mL of distillate to pH 10.

4-Aminoantipyrine solution: Dissolve 2 g of 4AAP in distilled water and dilute to 100 mL.

Potassium ferricyanide solution: Dissolve 8 g of $K_3Fe(CN)_6$ in distilled water and dilute to 100 mL.

Stock phenol solution: Dissolve 1.0 g phenol in freshly boiled and cooled distilled water and dilute to 1 liter. 1 mL = 1 mg phenol.

Working solution A: Dilute 10 mL stock phenol solution to 1 liter with distilled water. mL = 10 µg phenol.

Working solution B: Dilute 100 mL of working solution A to 1000 mL with distilled water. 1 mL = 1 µg phenol.

Ferrous ammonium sulfate: Dissolve 1.1 g ferrous ammonium sulfate in 500 mL distilled water containing 1 mL conc. H_2SO_4 and dilute to 1 liter

Additional Comments:

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Inspector: _____ Date: _____