NC DEQ/DWR WASTEWATER/GROUNDWATER LABORATORY CERTIFICATION

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

Parameter: CHROMIUM VI, DISSOLVED (Aqueous)
Method: SM 3500-Cr-B-2011

Equipment:

	Spectrophotometer, 530 or 540 nm		Filter photometer, greenish yellow filter with max transmittance at 530 or 540 nm		pH meter
	Cuvettes, 1 cm light path or longer				

Reagents:

	Buffer Solution - Dissolve 33 g of ammonium sulphate in 75 mL of ASTM Type I water and add 6.5 mL of ammonium hydroxide. Dilute to 100 mL with ASTM Type I water.		Diphenylcarbazide solution: Dissolve 250 mg 1,5-diphenylcarbazide (1,5-diphenylcarbohydrazide) in 50 mL acetone. Store in a brown bottle. Prepare weekly. Discard if the solution becomes discolored.
	Phosphoric acid (H_3PO_4), concentrated		Sodium Hydroxide (NaOH), 5*N* and 1*N*
	Nitric acid (HNO_3), concentrated		Sulfuric acid (H_2SO_4), concentrated, 18N, and 6N
	Stock chromium solution: Dissolve 141.4 mg K2Cr2O7 in water and dilute to 100 mL; 1.00 mL = 500 µg Cr. **CAUTION: Hexavalent chromium is toxic and a suspected carcinogen. Handle with care.**		Sulfuric acid (H_2SO_4), 0.2N: Dilute 17 mL 6N H_2SO_4 to 500 mL with water.

NOTE: Do not use Nitric Acid that has a yellow tinge. This yellow color indicates reduction of nitrate to nitrite and will interfere with the test.

PLEASE COMPLETE CHECKLIST IN INDELIBLE INK

	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 2H .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 documented? [15A NCAC 2H .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	**LAB**	**SOP**	**EXPLANATION**
4	Are samples filtered through a 0.45 µm filter within 15 minutes and before preservation? [40 CFR Part 136.3, Table II, footnote 20, SM 3500 Cr A-2011 (3) and EPA 218.6, Section 8.2]			
5	Are filtered unpreserved samples analyzed within 24 hours of collection? [SM 3500 Cr B-2011 (4) (b)]			
6	To achieve a 28-day holding time, are filtered samples preserved within 15 minutes of collection by adding ammonium sulfate buffer solution dropwise until the pH of the sample is 9.3-9.7 S.U.? [40 CFR Part 136.3, Table II, footnote 20 and EPA 218.6, Section 8.2]			**Footnote 20:** To achieve the 28-day holding time, use the ammonium sulfate buffer solution specified in EPA Method 218.6. The allowance in this footnote supersedes preservation and holding time requirements in the approved hexavalent chromium methods, unless this supersession would compromise the measurement, in which case requirements in the method must be followed.
7	Are filtered samples preserved with ammonium sulfate buffer solution analyzed within 28 days of collection? [40 CFR Part 136.3, Table II, footnote 20]			

8	Are samples iced to above freezing but ≤6° C during shipment and storage? [40 CFR 136.3 Table II and footnote 18]			
	PROCEDURE – Calibration	**LAB**	**SOP**	**EXPLANATION**
9	Is a calibration curve consisting of at least three standards and a blank analyzed daily or a curve consisting of at least five standards and a blank analyzed annually? [15A NCAC 2H .0805 (a) (7) (H) (v) and SM 3020 B-2017 (1) (b)] **List the values of standards used for the calibration curve:**			**SM 3020 B-2017 (1) (b):** Perform initial calibration using at least three concentrations of standards and one blank. **15A NCAC .0805 (a) (7) (H) (v) requires**: 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.
10	Are calibration standards treated with the same procedure as the samples? [SM 3500 Cr B-2011 (4) (a)]			To compensate for possible slight losses of chromium during analytical operations, treat standards and samples with the same procedure.
11	Is a reagent blank used to correct the absorbance readings of the standards by subtracting the reagent blank absorbance? [SM 3500 Cr B-2011 (4) (a)]			Correct absorbance readings of standards by subtracting absorbance of a reagent blank carried through the method.
12	Is a calibration curve constructed by plotting corrected absorbance values against µg of Cr(VI) in 102 mL final volume? [SM 3500 Cr B-2011 (4) (a)]			Construct a calibration curve by plotting corrected absorbance values against micrograms chromium in 102 ml final volume.
13	Do calibration curves meet a minimum correlation coefficient of 0.995? [NC WW/GW LCB Correlation Coefficient for Linear Calibration Curves Policy]			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.
	PROCEDURE – Sample Analysis	**LAB**	**SOP**	**EXPLANATION**
14	Are samples brought to room temperature before analysis? [SM 3500 Cr B-2011 (4) (c)]			
15	What volume of sample is analyzed? **Answer:**			
16	Is 0.25 ml (5 drops) of H_3PO_4 added to each sample? [SM 3500 Cr B-2011 (4) (c)]			
17	Is H_2SO_4 solution added to give a pH of 2 ± 0.5 S.U.? [SM 3500 Cr B-2011 (4) (c)]			
18	Is this pH adjustment documented? [15A NCAC 2H .0805 (a) (7) (F)]			
19	Is the solution transferred to a 100-ml volumetric flask, diluted to 100 mL and mixed? [SM 3500 Cr B-2011 (4) (c)]			
20	Is 2.0 ml diphenylcarbazide solution added to each sample and mixed? [SM 3500 Cr B-2011 (4) (c)]			
21	Are samples allowed to let stand 5 to 10 minutes for full color development? [SM 3500 Cr B-2011 (4) (c)]			
22	Is absorbance measured at 530 or 540 nm? [SM 3500 Cr B-2011 (4) (c)]			Transfer an appropriate portion to a 1-cm absorption cell and measure its absorbance at 530 or 540 nm, using reagent water as reference.
23	Is the absorbance reading of samples corrected by subtracting the absorbance of a blank carried through the method? [SM 3500 Cr B-2011 (4) (c)]			
24	If the solution is turbid after dilution to 100 mL, what actions are taken? [SM 3500 Cr B-2011 (4) (c)]			NOTE: If the solution is turbid after dilution to 10 mL in ¶c above, take an absorbance reading before adding carbazide reagent and correct

	Answer:			absorbance reading of final colored dilution by subtracting the absorbance measured previously.
	QUALITY ASSURANCE	**LAB**	**SOP**	**EXPLANATION**
25	Are samples diluted when they are more concentrated than the highest calibration standard? [SM 3020 B-2017 (1) (b)]			Make sure the calibration range encompasses the concentrations expected in method samples or required dilutions.
26	Is each calibration point back-calculated against the curve? [SM 3020 B-2017 (1) (b)]			
27	What is the acceptance criterion for back calculation? [SM 3020 B-2017 (1) (b)] **Answer:**			Compare each calibration point to the curve and recalculate its concentration. If any recalculated values are not within the method's acceptance criteria—up to twice the MRL ±50%; between 3 and 5 times the MRL ±20%; or greater than 5 times the MRL ±10%—unless otherwise specified in individual methods, identify the source of any outlier(s) and correct before sample quantitation.
28	Is the calibration verified by analyzing a second-source standard at a concentration near the mid-point of the calibration curve? [SM 3020 B-2017 (1) (b)] **List value of standard used.** **ANSWER:**			Verify the initial calibration by analyzing a standard prepared from a different stock standard than that used to create the calibration curve; its concentration should be near the midpoint of the calibration range.
29	What is the acceptance criterion of the second source standard? [SM 3020 B-2017 (1) (b)] **Answer:**			The analytical results for this second source mid-range standard must be within 10% of its true value.
30	What corrective action is taken if the second source standard recovery is outside of established control limits? [SM 3020 B-2017 (1) (b)] **Answer:**			The analytical results for this second source mid-range standard must be within 10% of its true value. If not, determine the cause of the error, take corrective action, and re-verify the calibration. If the re-verification passes, continue the analyses; otherwise, repeat the initial calibration.
31	Is a Continuing Calibration Verification (CCV) standard analyzed prior to sample analysis, after every ten samples and at the end of the sample set? [SM 3020 B-2017 (1) (c) and 15A NCAC 02H .0805 (a) (7) (H)]			**SM 3020 B-2017 (1) (c):** In CCV, analysts periodically use a calibration standard to confirm that instrument performance has not changed significantly since initial calibration. Base the CCV interval on the number of samples analyzed (e.g., after every 10 samples and at least once per batch). Verify calibration by analyzing one standard whose concentration is near the midpoint of the calibration range. **Rules:** 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.
32	What is the acceptance criterion for the CCV? [SM 3020 B-2017 (1) (c)] **Answer:**			The results must be within allowable deviations (within 10% of its true value) from either initial-calibration values or specific points on the calibration curve.

33	What corrective action is taken when the CCV is not within the acceptance criterion? [SM 3020 B-2017 (1) (c)]			If the CCV is out of control, then take corrective action—including re-analysis of any samples analyzed since the last acceptable CCV.
34	Is a continuing calibration blank (CCB) analyzed prior to sample analysis, after every ten samples and at the end of the sample set? [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.
35	What is the acceptance criterion for the CCB? [15A NCAC 02H .0805 (a) (7) (H) (i)] **Answer:**			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.
36	What corrective action is taken when the CCB is not within the acceptance criterion? [15A NCAC 2H .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. 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.
37	What is the laboratory's reporting limit? [15A NCAC 2H .0805 (a) (7) (H)] **Answer:**			
38	Is a reporting limit verification standard analyzed with each analytical batch? [SM 3020 B-2017 (9)]			With each analytical batch, analyze a reagent-water sample spiked at MRL and ensure that it meets MRL acceptance criteria (generally ±50%). If not, re-analyze the entire batch or flag results for all samples in the batch.
39	What is the acceptance criterion for the reporting limit verification standard? [SM 3020 B-2017 (9)] **Answer:**			
40	What corrective action is taken when the reporting limit verification standard exceeds the acceptance criterion? [SM 3020 B-2017 (9)] **Answer:**			
41	Is a Laboratory Fortified Matrix (LFM) analyzed with each sample set or on a 5% basis, whichever is more frequent? [SM 3020 B-2017 (7)]			The LFM is used to evaluate analyte recovery in a sample matrix. 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.
42	How is the LFM (spike) prepared? [NC WW/GW LCB Matrix Spiking Policy and SM 3020 B-2017 (7)] **Answer:**			**Policy:** The volume of spike solution used in MS preparation must in all cases be ≤ 5% of the total MS volume. It is preferable that the spike solution constitutes ≤1% of the total MS volume so that the MS can be considered a whole volume sample with no adjustment (i.e., volume correction) by calculation necessary. If the spike solution volume constitutes >1% of the total sample volume, the sample concentration must be adjusted by calculation.

				SM 3020 B-2017 (7): 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 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 five times the background level). For example, if the sample contains the analytes of interest, then add approximately as much analyte to the LFM sample as the concentration found in the known sample.
43	What is the acceptance criterion for LFM recovery (accuracy)? [SM 3020 B-2017 (7)] **Answer:**			If the method does not provide limits, use the calculated preliminary limits from the IDC (3020B.3). LFM control limits may be wider than for LFB or LCS, and batch acceptance generally is not contingent upon LFM results.
44	What corrective action does the laboratory take if the LFM results are outside of established control limits for accuracy? [15A NCAC 2H .0805 (a) (7) (B)] **Answer:**			Evaluate LFM results for percent recovery; if they are not within control limits, then take corrective action to rectify the matrix effect, use another method, use the method of standard addition, or flag the data if reported.
45	Is a sample duplicate or Laboratory Fortified Matrix Duplicate (LFMD) analyzed with each sample set or on a 5% basis, whichever is more frequent? [SM 3020 B-2017 (8)]			Duplicate samples are analyzed to estimate precision. If an analyte is rarely detected in a matrix type, use an LFM duplicate. As a minimum, include one duplicate sample or one 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.
46	What acceptance criterion is used to evaluate precision? [SM 3020 B-2017 (8)] **Answer:**			When the value of one or both duplicate samples is ≤5 X MRL, the laboratory may use the MRL as the control limit for percent recovery, and the duplicate results are not used. See method for specific acceptance criteria for LFM duplicates or duplicate samples until the laboratory develops statistically valid, laboratory-specific performance criteria. If the method does not provide limits, use the calculated preliminary limits from the IDC.
47	What corrective action does the laboratory take if the LFMD or sample duplicate results are outside of established control limits for accuracy or precision? [15A NCAC 2H .0805 (a) (7) (B)] **Answer:**			Evaluate LFM/LFMD results for accuracy and precision; if they are not within control limits, then take corrective action to rectify the matrix effect, use another method, use the method of standard addition, or flag the data if reported. In general, batch acceptance is not contingent upon LFM duplicate results.
48	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 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 limits show an analytical problem, the results shall be qualified as such.

Additional Comments:

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Inspector: _____Date:_____

mg Cr/L = $\frac{\mu g\ Cr\ (in\ 102\ mL\ final\ volume)}{A}$ where: A = mL original sample