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: HEXAVALENT CHROMIUM (Non-aqueous)
Method: SW-846 Method 7196A
with SW-846 Method 3060A

Equipment:

	Spectrophotometer, 540 nm, 1 cm light path or longer		Filter photometer- greenish-yellow, 540 nm, 1 cm light path or longer		Digestion vessel: borosilicate glass or quartz, 250 mL
	Graduated cylinder, 100 ml or equiv.		Volumetric flasks: Class A, 1000 ml and 100 ml with stoppers or equiv.		Vacuum filtration apparatus
	Filter membranes, 0.45 µm		Heating device, 90-95°C with continuous auto-stirring, or equiv.		Volumetric pipettes
	pH meter		Balance		Temperature measurement device, NIST traceable, reading up to 100°C

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 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 revision dates and actions tracked and 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 collected using devices and containers that do not contain stainless steel? [SW-846 3060A Section 6.2]			Samples should be collected using devices and placed in containers that do not contain stainless steel (e.g., plastic or glass).
5	Are samples iced to above freezing but ≤6°C during shipment and storage? [SW-846, Chapter Three, Inorganic Analytes, Table 3-2]			**SW-846 3060A states:** Samples should be stored field-moist at 4 ± 2°C. **SW-846 7196A states**: To retard the chemical activity of hexavalent chromium, the samples and extracts should be stored at 4°C until analyzed. **SW-846 Chapter 3, Table 3-2** however, lists ≤6°C. **We will allow ≤6°C.**
6	Are samples extracted within 30 days of collection? [SW-846, Chapter Three, Inorganic Analytes, Table 3-2]			**SW-846 3060A states:** Hexavalent chromium has been shown to be quantitatively stable in field-moist soil samples for 30 days from sample collection. In addition, Cr(VI) has also been shown to be stable in the alkaline digestate for up to 168 hours after extraction from soil. 168 hours = 7 days. **SW-846 7196A states**: The maximum holding time prior to analysis of the samples or extracts is 24 hr. The 24 hr. holding time

				begins after extraction. **SW-846 Chapter 3, Table 3-2** also lists 30 days to extraction, 7 days from extraction to analysis as the hold time for solid samples. **We will allow 30 days to extraction, 7 days from extraction to analysis.**
7	Are extracts analyzed within 7 days of extraction? [SW-846, Chapter Three, Inorganic Analytes, Table 3-2]			**See above.**
	PROCEDURE – Sample Preparation	**LAB**	**SOP**	**EXPLANATION**
8	Is a temperature blank used to adjust the setting of each heating device? [SW-846 3060A Section 7.1]			Adjust the temperature setting of each heating device used in the alkaline digestion by preparing and monitoring a temperature blank [a 250 mL vessel filled with 50 mLs digestion solution (Section 5.7)]. Maintain a digestion solution temperature of 90-95°C as measured with a NIST-traceable thermometer or equivalent.
9	Is 2.5 ± 0.10 g of a well-mixed field-moist sample analyzed? [SW-846 3060A Section 7.2]			Place 2.5± 0.10 g of the field-moist sample into a clean and labeled 250 mL digestion vessel. The sample should have been mixed thoroughly before the aliquot is removed.
10	Is 50 mL ± 1 mL of digestion solution added to each sample? [SW-846 3060A Section 7.3]			Add 50 mL ± 1 mL of digestion solution (Section 5.7) to each sample using a graduated cylinder
11	Is approximately 0.5 mL of 1.0M phosphate buffer added to each sample? [SW-846 3060A Section 7.3]			add approximately 0.5 mL of 1.0M phosphate buffer (Section 5.5.3).
12	Is approximately 400 $MgCl_2$ added to each sample? [SW-846 3060A Section 7.3]			add approximately 400 mg of MgCl2 (Section 5.4)
13	If Mg^{2+} is not added to samples, can the analytical technique correct for oxidation/reduction of Cr? [SW-846 3060A Section 7.3]			For analytical techniques that can correct for oxidation/reduction of Cr, the addition of Mg2+ is optional.
14	Are samples covered with a watch glass and stirred continuously for at least 5 minutes before heating? [SW-846 3060A Section 7.3] [SW-846 3060A Section 7.4]			Cover all samples with watch glasses. Stir the samples continuously (unheated) for at least five minutes using an appropriate stirring device.
15	Are samples heated to 90-95°C and maintained at that temperature for at least 60 minutes with continuous stirring? [SW-846 3060A Section 7.5]			
16	Are samples gradually cooled with continued stirring to room temperature? [SW-846 3060A Section 7.6]			
17	Are samples quantitatively transferred to the filtration apparatus rinsing the digestion vessel with 3 successive portion of reagent water? [SW-846 3060A Section 7.6]			
18	Are the rinsates transferred to the filtration apparatus? [SW-846 3060A Section 7.6]			
19	Are samples filtered through a 0.45µm membrane filter? [SW-846 3060A Section 7.6]			
20	Are rinsates from the filter flask and filter pad transferred with the filtrate to a clean 250-mL vessel? [SW-846 3060A Section 7.6]			
21	Is 5.0 M nitric acid solution slowly added dropwise to the sample while constantly stirring to adjust the pH to 7.5 ± 0.5 as read from a pH meter? [SW-846 3060A Section 7.7]			
22	If the pH of the digestate deviates from the range, is the solution discarded and sample re-digested? [SW-846 3060A Section 7.7]			If the pH of the digest should deviate from the desired range, discard the solution and re-digest. If overshooting the desired pH range occurs repeatedly, prepare diluted nitric acid solution and repeat digestion procedure.
23	If a flocculent precipitate forms, is the sample filtered through a 0.45µm membrane filter? [SW-846 3060A Section 7.7]			If the filter becomes clogged using the 0.45 µm filter paper, a larger size filter paper (Whatman GFB or GFF) may be used to prefilter samples.
24	Is the stirring device rinsed, collecting the rinsate into the beaker? [SW-846 3060A Section 7.8]			

25	Is the sample transferred quantitatively to a 100 ml volumetric flask and the sample volume adjusted to 100 mL with reagent water and mixed well? [SW-846 3060A Section 7.8]			
	PROCEDURE – Calibration	**LAB**	**SOP**	**EXPLANATION**
26	What is your laboratory's reporting limit? [15A NCAC 2H .0805 (a) (7) (H)] **ANSWER:**			One of the standards shall have a concentration equal to or less than the laboratory's lowest reporting concentration for the parameter involved.
27	List the values of standards used for the daily calibration: [15A NCAC 2H .0805 (a) (7) (H) (v)] **ANSWER:**			**SW-846 7196A states**: Accordingly, pipet a chromium standard solution in measured volumes into 250 ml beakers or conical flasks to generate standard concentrations ranging from 0.5 to 5 mg/L Cr(VI) when diluted to the appropriate volume. **15A NCAC .0805 (a) (7) (H) (v) requires**: 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 lower reporting concentration for the parameter involved. 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.
28	Are calibration standards treated with the same procedure as the samples? [SW-846 7196A, Section 7.2.1 and 7.2.2]			**Section 7.2.1**: To compensate for possible slight losses of chromium during digestion or other operations of the analysis, treat the chromium standards by the same procedure as the sample. **Section 7.2.2**: Develop the color of the standards as for the samples. Transfer a suitable portion of each colored solution to a 1-cm absorption cell and measure the absorbance at 540 nm.
29	Is a reagent blank used to correct the absorbance readings of the standards by subtracting the reagent blank absorbance? [SW-846 7196A, Section 7.2.2]			As reference, use reagent water. Correct the absorbance readings of the standards by subtracting the absorbance of a reagent blank carried through the method.
30	Is a calibration curve constructed by plotting corrected absorbance values against mg/L of Cr(VI)? [SW-846 7196A, Section 7.2.2]			
31	Do calibration curves meet a minimum correlation coefficient of 0.995? [NC WW/GW LC 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**
32	What volume of sample is analyzed? [SW-846 7196A, Section 7.1] **ANSWER:**			Transfer 95 ml of the extract to be tested to a 100-mL volumetric flask. Add 2.0 ml diphenylcarbazide solution and mix. Add H_2SO_4 solution to give a pH of 2 ± 0.5, dilute to 100 ml with reagent water, and let stand 5 to 10 min for full color development.
33	Is H_2SO_4 solution added to give a pH of 2 ± 0.5 s.u.? [SW-846 7196A, Section 7.1]			
34	Is this pH adjustment documented? [15A NCAC 2H .0805 (a) (7) (F) (x)]			All laboratories shall use printable laboratory benchsheets. Certified Data shall be traceable to the associated sample analyses and consist of: sample preparation, where applicable.

35	After pH adjustment, are samples allowed to let stand 5 to 10 minutes for full color development? [SW-846 7196A, Section 7.1]			
36	Is absorbance measured at 540 nm? [SW-846 7196A, Section 7.1]			Transfer an appropriate portion of the solution to a 1-cm absorption cell and measure its absorbance at 540 nm.
	QUALITY ASSURANCE	**LAB**	**SOP**	**EXPLANATION**
37	Are samples diluted when they are more concentrated than the highest calibration standard? [SW-846 7196A, Section 8.2]			Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.
38	Is a preparation blank prepared (including filtering if applicable to samples) and analyzed with each digestion batch? [SW-846 3060A, Section 8.2]			
39	What is the acceptance criterion for the preparation blank? [SW-846 3060A, Section 8.2] [15A NCAC 2H .0805 (a) (7) (A)] **ANSWER:**			**SW-846 3060A:** A preparation blank must be prepared and analyzed with each digestion batch, as discussed in Chapter One and detected Cr(VI) concentrations must be less than the method detection limit or one-tenth the regulatory limit or action level, whichever is greater or the entire batch must be redigested. **NC Rule:** Unless specified by the method or this Rule, 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. When the method of choice specifies performance acceptance criteria for precision and accuracy, and the laboratory chooses to develop laboratory-specific limits, the laboratory-specific limits shall not be less stringent than the criteria stated in the approved method.
40	What corrective action is taken if the preparation blank is not acceptable? [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.
41	Is the initial calibration verified by analyzing a **second source standard**? [15A NCAC 2H .0805 (a) (7) (H) (ii)] **List acceptance criterion and value of standard used:** **ANSWER:**			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. Note: The LCS can be the second source used to verify the initial calibration.
42	What corrective action does the laboratory take if the calibration verification standard is outside established control limits? [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.
43	Is the calibration verified by analyzing a calibration blank initially, after every 10th sample and at the end of the run? [15A NCAC 2H .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.
44	Is the calibration blank concentration less than or equal to ½ the concentration of the lowest calibration standard? [15A NCAC 2H .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.

45	What corrective action is taken if the calibration blank results are greater than one-half the reporting level? [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.
46	Does the laboratory analyze an independently prepared check standard after every 15 samples to verify the calibration? [SW-846 7196A, Section 8.4] **List value of standard used for check standard:**			**SW-846 7196A:** Verify calibration with an independently prepared check standard every 15 samples.
47	What is the acceptance criterion of the check standard? [15A NCAC 2H .0805 (a) (7) (A)] **ANSWER:**			**SW-846 7196A does not prescribe an acceptance criterion.** NC Rule: Unless specified by the method or this Rule, 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. When the method of choice specifies performance acceptance criteria for precision and accuracy, and the laboratory chooses to develop laboratory-specific limits, the laboratory-specific limits shall not be less stringent than the criteria stated in the approved method.
48	What corrective action is taken if the check standard recovery is outside of established control limits? [SW-846 3060A, Section 8.3]] [15A NCAC 2H .0805 (a) (7) (B)] **ANSWER:**			Sample batch must be reanalyzed. 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.
49	Is a laboratory control sample (LCS) prepared with each digestion batch? [SW-846 3060A, Section 8.3]			**SW-846 3060A:** Laboratory Control Sample (LCS): As an additional determination of method performance, utilize the matrix spike solution prepared in Section 5.8.1 or the solid matrix spiking agent $PbCrO_4$ (Section 5.6) to spike into 50 ml of digestion solution (Section 5.7). Alternatively, the use of a certified solid reference material (if available) is recommended. NOTE: SW 846 chapter One states the LCS is prepared and analyzed in exactly the same manner as the other routine samples- meaning that the LCS would be filtered if any samples require filtration
50	What is the acceptance criterion for the LCS? [SW-846 3060A, Section 8.3] **ANSWER:**			**SW-846 3060A:** Recovery must be within the certified acceptance range or a recovery range of 80% to 120% or the sample batch must be reanalyzed.
51	What corrective action is taken if the LCS does not meet the acceptance criterion? [SW-846 3060A, Section 8.3] **ANSWER:**			Recovery must be within the certified acceptance range or a recovery range of 80% to 120% or the sample batch must be reanalyzed.

52	Are both soluble and insoluble pre-digestion matrix spikes analyzed at a frequency of one each per batch of ≤ 20 field samples? [SW-846 3060A, Section 8.5]			Both soluble and insoluble pre-digestion matrix spikes must be analyzed at a frequency of one each per batch of ≤ 20 field samples.
53	Is the spike added directly to the sample after 2.5 ± 0.10 g of sample is added to the digestion vessel and before extraction? [SW-846 3060A Section 7.2]			For the specific sample aliquot that is being spiked (Section 8.5), the spike material **should** be added directly to the sample aliquot at this point. By definition, a spike must go through all preparation and analytical steps.
54	How is the soluble matrix spike prepared? [SW-846 3060A, Section 8.5] **ANSWER:**			The soluble matrix spike sample is spiked with 1.0 ml of the spiking solution prepared in Section 5.8.1 (equivalent to 40 mg Cr(VI).kg) or at twice the sample concentration, whichever is greater.
55	How is the insoluble matrix spike prepared? [SW-846 3060A, Section 8.5] **ANSWER:**			See Matrix Spike Technical Assistance document. It is recommended to use the same solution as the LCS (second source) for the LFM to evaluate bias attributed to matrix and accuracy of the LFM. **SW-846 3060A**: The insoluble matrix spike is prepared by adding 10-20 mg of PbCrO4 (Section 5.6) to a separate sample aliquot. It is used to evaluate the dissolution during the digestion process. More frequent matrix spikes must be analyzed if the soil characteristics within the analytical batch appear to have a significant variability based on visual observation.
56	What is the accuracy acceptance criterion for the soluble and insoluble matrix spikes? [SW-846 3060A, Section 8.5] **ANSWER:**			An acceptance range for matrix spike recoveries is 75-125%.
57	What corrective action does the laboratory take if the matrix spike results are outside of established control limits for accuracy? [15A NCAC 2H .0805 (a) (7) (B)] **ANSWER:**			**15A NCAC 2H .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. **SW-846 3060A Section 8.5 states:** If the matrix spike recoveries are not within these recovery limits, the entire batch must be rehomogenized/redigested/reanalyzed.
58	Is a post-digestion Cr(VI) matrix spike analyzed per batch? [SW-846 3060A, Section 8.6]			A post-digestion Cr(VI) matrix spike must be analyzed per batch as discussed in Chapter One. The post-digestion matrix spike concentration should be equivalent to 40 mg/kg or twice the sample concentration observed in the unspiked aliquot of the test sample, whoever it greater.
59	What is the acceptance criterion for the post-digestion matrix spike? [SW-846 3060A, Section 8.6.2] [15A NCAC 2H .0805 (a) (7) (A)] **ANSWER:**			**SW-846 3060A:** A guideline for the post-digestion matrix spike recovery is 85-115%. NC Rule: Unless specified by the method or this Rule, 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. When the method of choice specifies performance acceptance criteria for precision and accuracy, and the laboratory chooses to develop laboratory-specific limits, the laboratory-specific limits shall not be less stringent than the criteria stated in the approved method.

60	What corrective action does the laboratory take if the post-digestion spike results are outside established control limits for accuracy? [15A NCAC 2H .0805 (a) (7) (B) and SW-846 3060A, Section 8.6.2] **ANSWER:**			If not achieved, consider the corrective actions/guidance on data use specified in Section 8.5 or the Method of Standard Additions (MSA) as specified in Section 8.0 of Method 7000. If the MSA technique is applied post digestion and no spike is observed from the MSA, these results indicate that the matrix is incompatible with Cr(VI) and no further effort on the part of the laboratory is required. These digestates may contain soluble reducing agents for Cr(VI), such as fulvic acids. NC Rule: 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.
61	Is a lower reporting limit standard analyzed or back-calculated with each analysis? [15A NCAC 2H .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.
62	What is the acceptance criterion of the lower reporting limit standard? [15A NCAC 2H .0805 (a) (7) (A)] **ANSWER:**			Establish laboratory control limits Unless specified by the method or this Rule, each laboratory shall establish performance acceptance criteria for all quality control analyses.
63	Is a laboratory-fortified matrix duplicate (LFMD) or sample duplicate analyzed for every 10 samples? [SW-846 7196A, Section 8.4 and SW-846 3060A, Section 8.4]			**SW-846 7196A:** Run one matrix spike replicate or one replicate sample for every ten samples. **SW-846 3060A:** A separately prepared duplicate soil sample must be analyzed at a frequency of one per batch as discussed in Chapter One.
64	What is the precision acceptance criterion for LFMDs or sample duplicates? [SW-846 3060A, Section 8.4] **ANSWER:**			**SW-846 3060A:** Duplicate samples must have a Relative Percent Difference (RPD) of ≤20%, if both the original and the duplicate are ≥ four times the laboratory reporting limit. A control limit of ± the laboratory reporting limit is used when either the original or the duplicate sample is < four times the laboratory reporting limit.
65	What corrective action does the laboratory take if the LFMD or sample duplicate results are outside of established control limits for precision? [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.
66	Are results calculated and reported on a dry-weight basis? [SW-846 3060A Section 7.2]			Percent solids determination, U.S. EPA CLP SOW for Organic Analysis, OLM03.1, 8/94 Rev.) should be performed on a separate aliquot in order to calculate the final result on a dry-weight basis). North Carolina data receiving agencies also require reporting on a dry-weight basis.
67	Is the data qualified on the Discharge Monitoring Report (DMR) or client report if Quality Control (QC) requirements are not met? [15A NCAC 2H .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: 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.

Additional Comments:

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Inspector: _____ Date: _____