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SM 3500-Cr-B – Hexavalent Chromium

Access to this SOP shall be available within the laboratory for reference purposes; the official copy of this SOP resides on the official Georgia EPD website at https://epd.georgia.gov/about-us/epd-laboratory-operations. Printed copies of this SOP will contain a watermark indicating the copy is an uncontrolled copy.

1 Scope and Application

1.1 Hexavalent chromium is determined by the 1,5-Diphenlycarbohydrazide method using a single dry powder formulation called ChromaVer 3 Chromium Reagent. This reagent contains an acidic buffer combined with 1,5-Diphenylcarbohydrazide, which reacts to give a purple color when hexavalent chromium is present. The measurement wavelength is 540 nm for spectrophotometers. Method is modified for use with HACH reagents per HACH Method 8023. Sample absorbance is read at 540 nm.

1.2 Restricted Procedure

This procedure is restricted to use by an analyst experienced in the operation of a HACH DR6000. Additionally, the analyst must complete the requirements of the GAEPD Initial Demonstration of Analyst Proficiency prior to the analysis of actual samples. Analysts are further warned that performance of this analysis involves the use of potentially hazardous chemicals; refer to the GAEPD Chemical Hygiene Plan for additional information regarding chemicals required by this method.

2 Definitions

2.1 Refer to Chapter 3 of the Georgia EPD Laboratory Quality Assurance Manual for Quality Control Definitions.

2.2 Primary Source (PS) – A standard that is used to make up the calibration points of a curve.

2.3 Second Source (SS) – A standard made from a manufacturer other than that of the primary source.

2.4 Initial Calibration Verification (ICV) – An ICV is a second source standard that is used to verify the correctness of the primary source calibration curve. The ICV is run at a level equal to that of a Laboratory Control Sample

(LCS) or the midpoint on the calibration curve.

2.5 Continuing Calibration Check (CCC) or Continuing Calibration Verification (CCV) – A standard used to verify that the response of the instrument has not changed since initial calibration. The CCC is run at a level equal to that of a Laboratory Control Sample (LCS) or the midpoint on the calibration curve.

2.6 Calibration Blank (CB), Initial Calibration Verification Blank (ICB), Method Blank (MBLK), Method Detection Limit Blank (MDLB) or Continuing Calibration Blank (CCB) – A volume of reagent water fortified with the same matrix as the calibration standards, but without the analytes.

2.7 MDLS (Method Detection Limit Spike) – MDLB spiked with analytes at the lowest calibration level to be used for the determination of MDL.

2.8 LCS(Laboratory Control Sample) and LCSD(Laboratory Control Sample Duplicate) are prepared by spiking laboratory reagent water, Ottawa sand or air sampling device with the target analyte or compound. They are used to validate the analytical batch with respect to accuracy and precision.

3 Interferences

3.1 Hexavalent molybdenum and mercury salts will react to from color with the reagent but the intensities are much lower than that for chromium at the specified pH. Concentrations of Mo or Hg as high as 200 mg/L can be tolerated.

3.2 Vanadium interferes strongly but concentrations up to 10 times that of chromium will not result in significant analytical error. Allow 10 minutes for the reaction period before reading.

3.3 Iron may interfere above 1 mg.

3.4 For turbid samples, treat the blank with the contents of one Acid Reagent Powder Pillow. This will make sure that any turbidity dissolved by the acid in the ChromaVer 3 Chromium Reagent will also be dissolved in the blank.

3.5 At high chromium levels, a precipitate may form. Sample dilution may be necessary.

3.6 Highly buffered samples or extreme sample pH can prevent the correct pH adjustment (of the sample) by the reagents. Check pH of each sample, 5 minutes after adding HACH ChromaVer 3 Chromium Reagent Powder Pillows. pH should be 2.0± 0.5. If not, adjust sample pH by adding one Acid Reagent Powder Pillow. See Section 6.3

4 Safety

4.1 Refer to the EPD Laboratory Safety / Chemical Hygiene Plan & Fire Safety Plan, online revision. See SOP Reference 13.7.

5 Apparatus and Equipment

5.1 Sample Container: half gallon plastic

5.2 HACH DR 6000 Spectrophotometer

5.3 Class A volumetric flasks, graduated cylinders and pipettes
Air displacement pipettes of various volumes, auto-pipettor, pipette tips in various sizes. Air displacement pipettes and auto-pipettors may also be describes as mechanical pipettes.

5.4.1 Each day of use, the volume dispensed by each mechanical pipette must be verified for the specific volume for which the pipette is being used.

5.4.1.1 Mechanical pipette volumes are verified by measuring the weight of a volume of water dispensed by the unit. At room temperature, 1 ml of water is equal to 1 g. Mechanical pipettes must be verified to be within ± 2.5% of the expected weight.

5.4.1.2 Auto-pipettors may be verified by measuring the volume dispensed with a graduated cylinder. The volume dispensed must be within ± 2.5% of the nominal volume.

5.4.1.3 Mechanical pipettes must be professionally calibrated every 6 months.

5.5 Balance: analytical, capable of accurately weighing to the nearest 0.0001g.

5.6 Disposable transfer pipettes:

5.6.1 Plastic - VWR® Disposable Transfer Pipets PN# 16001-190 or equivalent
Standard Disposable Transfer Pipettes PN# 13-711-7M or equivalent.

5.7 Laboratory vacuum system

5.8 0.45µm pore size and 47 mm diameter Filter Paper Whatman PN#7184-004 or equivalent.

5.9 Magnetic Filter Funnel with rubber stopper

5.10 Suction flask

5.11 Sample cell: 1” Round Glass 10 ml, HACH PN# 2427606

5.12 Low range pH paper - Fisherbrand™ Paper pH Strips Catalog No. 13-640-511 or equivalent.

6 Reagents

6.1 Reagent Water:
Purified water which does not contain any measurable quantities of target analytes or interfering compounds for each compound of interest. (Deionized, HPLC, Milli-Q water or equivalent. Milli-Q water has a resistivity of 18.2 [MΩ·cm] @ 25° C and a TOC of 50 µg/L or less).

6.2 Color Reagent:
HACH ChromaVer 3 Reagent Powder Pillows 10 ml pk/100 (Hach PN#1271099)

6.3 Acid Reagent Powder Pillow:
HACH PN#212699 100/pkg

6.4 Potassium Dichromate ($Cr_2K_2O_{7)}$: Crystalline, ACS grade or equivalent

6.5 Stock Standard 50 ug/ml Cr^{+6} (50ppm):
Dissolve 141.4 mg $K_2Cr_2O_7$ into a 1L volumetric flask and dilute to volume with reagent water.

6.5.1 Solution is stable for six months. Store at room temperature.

6.6 Working Cr^{+6} Standards:
Using the stock standard 50 ug/ml, prepare calibration standards at five concentrations in reagent water. The calibration standards range from 50 ug/l to 1000 ug/l.

Table 6.6.1 – Working Standards

mL Stock Standard	Reagent Water	Concentration Cr^{+6}
2 ml	100 ml	1000 ug/l
1 ml	100 ml	500 ug/l
0.5 ml	100 ml	250 ug/l
0.2 ml	100 ml	100 ug/l
0.1 ml	100 ml	50 ug/l

6.6.2 Standards are stable for 24 hours.

6.7 Potassium Dichromate ($Cr_2K_2O_{7)}$: Crystalline, ACS grade or equivalent

6.7.1 Must be different lot number or vendor than the Potassium Dichromate ($Cr_2K_2O_{7)}$ used to make standards.

6.8 ICV Stock Standard Solution or Second Source (SS):
Dissolve 141.4 mg $K_2Cr_2O_7$ into a 1L volumetric flask and dilute to volume with reagent water.

6.8.1 Solution is stable for 6 months.

6.9 ICV Solution (500 ug/l Cr^{+6}):
A 1 ml aliquot of ICV Stock Solution (50 ug/ml) is pipetted into a 100 ml volumetric flask and diluted to volume with regent water.

6.9.1 The ICV Solution is stable for 24 hours.

7 Sample Collection

7.1 Samples are collected in plastic half-gallon containers.

7.2 No chemical preservation is required.

7.3 Samples are kept at 0 – 6 ° C (not frozen).

7.4 Sample holding time is 24 hours.

8 Calibration

8.1 Calibration Standards:

The calibration curve consists of the calibration standards at the following concentrations: 0 ug/l Cr^{+6},50 ug/l Cr^{+6}, 100 ug/l Cr^{+6}, 250 ug/l Cr^{+6}, 500 ug/l Cr^{+6}, and 1000 ug/l Cr^{+6}.

8.2 Calibration Curve:

The HACH DR 6000 Hexavalent Chromium curve is calibrated every six months or when the second source calibration verification fails. Minimum acceptable correlation is 0.995 using a linear regression.

8.3 Calibration Verification:

8.3.1 An initial calibration verification standard (ICV) and an initial calibration blank (ICB) must be analyzed immediately after the calibration standards.

8.3.2 The initial calibration verification standard must be prepared with a stock from a different source than the standards used in the calibration of the instrument.

8.3.2.1 The % Drift (see calculation 11.1) of the ICV from the true value must be within ±10% of its true value Repeat once if it fails. If it fails the second attempt, determine the source of the problem, correct and recalibrate.

8.3.3 The ICB/MBLK must be less than the method RL or the run will have to be repeated. The CCB value must be less than the method RL or the samples associated with the out of control CCB will have to be reanalyzed.

8.3.4 A CCC and a Continuing Calibration Blank (CCB) must be analyzed every 10 samples and at the end of the sample run and must meet the same criteria as the ICV and ICB respectively.

8.3.4.1 If the CCC or CCB do not meet acceptance criteria, then all samples affected by the out of control CCC or CCB are to be rerun.

8.3.4.2 The CCC may be from the same source as the calibration standards.

8.4 A MDLB (MDL blank) must be analyzed once per analytical batch to perform an ongoing MDL study. The MDLB may be combined with the MBLK. All batch QC must be valid to report this result.

8.5 A MDLS (low level mdl spike) at the concentration of 50 ug/L must be analyzed with each batch to perform an ongoing MDL study. All batch QC must be valid to report this result.

9 Quality Control

9.1 Refer to Table 14.1 for Reporting Limits (RL's), Table 14.2 for Quality Control Acceptance Criteria. Table 14.3 for Quality Control Procedures associated with this method and the Standard Operating Procedures for Control Charts and Control Limits.

9.1.1 The default control limits for SM3500-CR-B are 90 – 110% recovery for for

LCS recoveries. The EPD Laboratory applies LCS recovery limits to LCSDs. Note, unless specified by method, the EPD Laboratory does not validate batch quality based on LCSD recoveries.

9.1.2 By default, the EPD Laboratory sets LCS/LCSD precision control limits for this method to be 0 – 15% RPD.

9.1.3 LCS/LCSD recovery and precision limits are static by EPA/Method/EPD Lab default.

9.1.4 5% of all routine samples must be spiked. 5% of all samples must be analyzed in duplicate. This criterion will be satisfied if an MSD is analyzed with each MS resulting in 10% of samples being analyzed in duplicate. See Section 9.2 modification below. The EPD Laboratory requires recovery control limits of 90 – 110% for matrix spikes. The EPD Laboratory applies MS recovery limits to MSDs.

9.1.5 By default, the EPD Laboratory sets default sample precision control limits to be 0 – 15% RPD.

9.1.6 MS/MSD recovery and precision limits are adjusted through the use of control charts.

9.1.7 See Administrative SOP for Control Charting and Control Limits for further details.

9.2 Batch samples in groups of 20. For each batch, analyze a Matrix Spike (MS) and a Matrix Spike Duplicate (MSD) for a minimum of 5% of routine samples.

9.2.1 For batches of 1 to 10 routine samples, one MS/MSD pair must be spiked. For batches of 11 to 20 routine samples, two MS/MSD pairs must be spiked using different samples for each pair**.**

9.3 MDL (method detection limit) is the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero.

9.3. 1 The actual MDL varies depending on instrument and matrix.

9.3. 2 The MDL must be determined annually for each instrument prior to results being reported for that instrument. The MDL determined for each compound must be less than the reporting limit for that compound.

9.3.3 The Method Detection Limit Study for all analytes must be performed initially on a new instrument and performed after major instrument repairs or changes to procedures. There are two ways to perform the MDL. The first is with 7 samples and 7 blanks over 3 separate days. The second preferred way the MDL is run as a continuous format.

9.3.4 The 7 MDL samples study is performed by preparing 7 spiked vials, MDLSpike, spiked at the lowest calibration point of the curve, and preparing 7 clean blank vials filled with DI water, MDLBlank. These 7 sets of spiked and blank vial "pairs" are analyzed over 3 separate days, there may or may not be a non-analysis day between each of the 3 days. A total of 14 vials are prepared, 7 spiked and 7 blanks.

9.3.5 A continuous formal MDL study is performed where one vial is spiked as an MDLSpike, at the lowest point of the calibration curve and analyzed with every batch of samples along with the method blank vial as an MDLBlank.

9.3.6 The results of the MDLBlank will be entered into Labworks using the Method Blank test code, B_HEXCR-B. The MDLSpike result will be entered using the MLHEXCR-B. The MDL Spiked Amount will be entered into the test code MAHEXCR-B. The instrument used for the MDL and Blank analysis will be

selected using the test code INSTR-HEXCR-B.

9.3.7 MDL study must be performed every six months and before the MDL for the instrument expires.

9.3.8 MDL data is pulled from a two year period.

10 Procedure

10.1 Procedure for SPEC02 and SPEC03(HACHDR6000)

10.1.1 Procedure for analyzing samples using stored calibration curve

10.1.1.1 Remove sample bottles, standards and reagents from cold storage and allow them to equilibrate to room temperature prior to sample preparation and/ or analysis.

10.1.1.2 Before turning on the instrument make sure the lid is closed. Turn on the instrument by the switch located on the back of the instrument. The power button on the screen will turn green when on.

10.1.1.3 Allow instrument to warm up for 30 minutes prior to use.

10.1.1.4 The instrument must be connected to the network prior to use.

10.1.1.5 To assure that the instrument is connected to the network, complete the following: Select Instrument Setup, then PC and Printer. It should read connected next to network. Press OK to exit.

10.1.1.6 On the main menu display select the “User Program” box, and then select the 9000 for the Hexavalent Chromium program.

10.1.1.7 Select the “Login” on the right side of the display and select your initials. The password will be “Inorganic”.

10.1.1.8 If user initials need to be added select “Instrument Setup” from the main menu. Next select “Operator ID” and then select “Options”. Select “New” then add user initials and select “OK”. Select a symbol as desired and select “Password” and enter “Inorganic” and select “OK”. The new user initials will now be available. Select “Login” and enter password.

10.1.1.9 Once your initials have been selected, select the “Start” button on the bottom of the display.

10.1.1.10 Open the lid place the CCB/MBLK vial into the Round 1” slot in the carousel and close the lid. Ensure to wipe down vials with a Kim-wipe before placing them into the instrument.

10.1.1.11 Press the “Zero” box on the display screen. Once the instrument is zeroed remove vial and place back into sample rack.

10.1.1.12 Select the “Sample ID” box on the right side of the display. Then select the “Option” box on the bottom.

10.1.1.13 Select “Import Sample ID List”. If “Import Sample ID List” is not available refer to “Manual Sample ID Entry”

10.1.1.14 When asked to delete previously imported sample IDs, select the "YES" box.

10.1.1.15 Locate the "csv.file" created and select it, then select the "OK" box on the bottom of the display. *Note to create the "csv.file" reference the" Creating Sample ID list" section.

10.1.1.16 At least 150 ml of ICB/CCB/MBLK/MDLB must be poured into a ½ gallon sample collection container before and measured into the appropriate vials. Record the lot # of the plastic half gallon container.

10.1.1.17 The MDLS 50 µg/L standard must be poured into a ½ gallon sample collection container before it is pipetted into the appropriate vial. Record the lot # of the plastic half gallon container.

10.1.1.18 Prepare the LCS and LCSD by pipetting 0.5 ml of 50 µg/ml Hexavalent Chromium stock standard into a 50 ml volumetric flask and bring to volume with reagent water that has been stored in a plastic half gallon collection container. The LCS amount is 500 µg/L. Record the lot# of the sample container.

10.1.1.19 Prepare the MS and MSD by pipetting 0.5 ml of 50 µg/ml Hexavalent Chromium stock standard into a 50 ml volumetric flask and bring to volume with filtered sample. The spike amount is 500 µg/L.

10.1.1.20 The 500 µg/L hexavalent chromium standard is used for the CCC

10.1.1.21 Fill Dilu-vials ¾ full with sample, MBLK/MDLB,CCB, CCC, MDLS, LCS/LCSD and MS/MSD respectively. MBLK, CCB, LCS/LCSD and MS/MSD are filtered prior to analysis to ensure filtration does not negatively affect results

10.1.1.22 Fill a clear glass threaded sample cell with cap with the Hach Chroma Ver 3 Powder Pillow. After powder has been placed in tube, pipette 10 ml of sample using a mechanical pipette. Place cap on the cell and vortex to mix sample. Note: a purple color will form if hexavalent chromium is present.

10.1.1.23 After all samples are prepared, press the "Timer Icon" to start the 5 minute reaction time.

10.1.1.24 Once the 5 minutes has elapsed, verify that the sample pH is 2.0± 0.5 using Low range pH paper (See 5.12) and disposable transfer pipette. If pH needs adjusting, add one Acid Reagent Powder Pillow to the sample. See Section 6.3. Repeat 10.1.1.22.

10.1.1.25 If a sample in the batch requires pre-treatment, the LCS/LCSD and MBLK must also be pre-treated.

10.1.1.26 Once the 5 minutes has elapsed and samples have been pre-treated if needed, select the "Sample ID" box from the display, then select the first sample from the imported list. Then touch the "Select" box. Open lid and place the vial in the Round 1" slot in the carousel and close the lid.

10.1.1.27 Select the "Read" box. The display will change to reading and then the concentration will be displayed. Next a dialog box will open with "Data Stored" and "Send data to Network".

10.1.1.28 For the next sample in the ID list, select the "Sample ID" box; highlight the desired sample by touching. Then touch the "Select" box, repeat steps 10.1.1.22-10.1.1.27 until all samples have been analyzed.

10.1.1.29 Once all the samples have been analyzed, the data from the instrument is accessed using the network "I" drive. *Note to obtain the data from the network "I" drive; reference the "Accessing data from network drive" section.

10.1.1.30 After reading the last sample, select EXIT and Yes to return to the Main Menu and then turn the spectrophotometer off.

10.1.2 Procedure for creating calibration curve

10.1.2.1 Before turning on the instrument make sure the lid is closed. Turn on the instrument by the switch located on the back of the instrument. The power button on the screen will turn green when on. Allow instrument to warm up for 30 minutes prior to use. During this time the instrument will perform diagnostic testing. Make sure the test passes and record in maintenance log-book.

10.1.2.2 Allow instrument to warm up for 30 minutes prior to use. To assure that the instrument is connected to the network, complete the following: Select Instrument Setup, then PC and Printer. It should read connected next to network. Press OK to exit.

10.1.2.3 On the main menu display select the "User Program" box, and then select the 9000 for the Hexavalent Chromium program. Select the "Login" on the right side of the display and select your initials. If your initials are not present, then they will need to be added (Refer to 10.3.8). The password will be "Inorganic".

10.1.2.4 Once your initials have been selected, select the "Program Option" box on the bottom of the display, then select "Edit".

10.1.2.5 Highlight the calibration line by touching, then select the "Edit" box on the bottom of the display. Select "Read Standards" and press "OK"

10.1.2.6 To add the standards, select the "+" box, type "0" and select "OK". Repeat the process for all the standards 50 µg/L, 100 µg/L, 250 µg/L, 500 µg/L, and 1000 µg/L. *Note the µg/L unit does not need to be typed.

10.1.2.7 Once all the standards have been added. Highlight the "0.000" line by touching it. Open the lid and place the "0 µg/L" standard vial into the Round 1" slot in the carousel and close the lid. Ensure to wipe down vials with a Kim-wipe before placing them into the instrument.

10.1.2.8 With the vial in place press the "Zero" box on the display screen. Once the instrument is zeroed, with the vial still in place press the "Read" box on the bottom. Once it has been read the next standard will be highlighted. Remove the "0 µg/L" standard and place the next standard in the same slot. Select the "Read" box on the bottom. Continue this process for each standard.

10.1.2.9 After all standards have been read, press the “Next” box on the bottom of the display. The calibration will be displayed. Verify the correlation “R” is ≤0.995. Select the “Done” box. The display will change and then select the “Store” box to save the curve. The curve is stored in the folder “PrgData” in the “SPEC02” folder on the “I” drive. You will print the curve from there.

10.1.3 Accessing Data from the Network Drive

10.1.3.1 Open the “I” drive. You will be prompted for a password, the password is “InOrg-5804”

10.1.3.2 Once the “I” drive is open find the folders labeled “SPEC02” and open it. Once the folder is open select the file, labeled “DR6000sampleseqgenver3.accb” and open it. If the security warning pops up click “Enable Content”.

10.1.3.3 Once open select the “LW Results” box. After clicking the box you will be prompted to select a file location. Choose the “I” drive, then select the “SPEC02” folder, then select the “Datalog” folder. Once open select the excel file labeled “DL_DR6000_1849760.csv” file. A dialog box will open indicating the results have been formatted. Select “OK”.

10.1.3.4 After clicking “OK” you will need to go back to the “SPEC02” folder and open the “LWResults” folder. Once open find the excel file of the results that were formatted. (Look at the date and time modified to easily locate the file) The file will be in the format “DR6000_Date_xxxxx.csv”

10.1.3.5 Upon opening the excel file, you will see a mix of data. The data can be filtered by date. To do this use the excel filter function which can be accessed in two different ways.

10.1.3.6 Before the filter function can begin highlight the column labeled “Date”, then select the filter icon under the “Data” tab at the top of excel. After clicking this function a drop down menu will be available to click to the right of the word “Date”. Click this drop down box which will allow you to filter the data by date.

10.1.3.7 If the data is not in run order after Date filter, it can be sorted using the “Sort- A to Z” function of excel, by using the parameters of time.

10.1.3.8 After the data has been sorted, the file needs to be saved. To do this go to “File” then “Save As”, save the file to the “Hexcr sorted batches” folder within the “SPEC02” folder on the “I” drive. The file should be named with the batch # and date.

10.1.4 Creating Sample ID List

10.1.4.1 Before the Sample ID list can be created, you must have already created your batch in Labworks.

10.1.4.2 Open the “I” drive. You will be prompted for a password, the password is “InOrg-5804”

10.1.4.3 Once the "I" drive is open find the folders labeled "SPEC02" and open it.

10.1.4.4 Once the folder is open select the file, labeled "DR6000sampleseqgenver3.accb" and open it. If the security warning pops up click "Enable Content". Once open select "Create Sample Sequence"

10.1.4.5 Type HEXCER-B into the "Test Code" box and hit enter on the keyboard. All the batches with that test code will appear in the "Batch NO. List" box.

10.1.4.6 Select the desired batch. The batch number will appear in the "Batch NO." box once selected. After selected click the "Add" box, this will have the samples related to the selected batch number from Labworks, seen in the "Sample Series" box. If more than one batch is desired repeat the previous process.

10.1.4.7 After all desired batches and samples have been added select the "Create File" box. A dialog box will appear indicating the Sample ID List was created. Close the program.

10.1.4.8 After closing the program the Sample ID list created will appear. Save the created Sample ID List to the "I" drive, under the "SPEC02" folder, in the "SampleID" folder. Name the file HEXCR-b-Batch#.csv.

10.1.5 Manual Sample ID Entry

10.1.5.1 On the main menu display select the "User Program" box, and then select the 9000 for the Hexavalent Chromium program

10.1.5.2 Select the "Sample ID" on the right of the screen and then select "Options".

10.1.5.3 From the options select "New" to create a new Sample ID or "Edit" to edit previously store Sample IDs.

10.1.5.4 Create a "New" Sample ID by selecting "New". Then type in the sample ID as desired then select "OK'. Next ensure the "Add Date/Time" option is selected then select "OK"

10.1.5.5 Editing a previously stored Sample ID by selecting the appropriate Sample ID from list of stored Sample IDs. Then select "Options". Next select "Edit". Edit Sample ID as desired and select "OK". Next ensure the "Add Date/Time" option is selected then select "OK"

10.1.5.6 After new/edited Sample IDs have been created, highlight the desired Sample ID and hit "Select" and insert sample and then select "Read". Repeat for each sample ID needed.

11 Calculations

11.1 The weighted external standard calibration is calculated by the instrument software and is documented in the instrument software.

11.2 Mean ($\overline{X}$):

$$\overline{X} = \frac{X_1 + X_2 + \cdots X_n}{n}$$

11.2.1 Where:

$X_1 + X_2 + \cdots X_n$ = The sum of a set of values X_i, i = 1 to n

n = The number of values in the set

11.3 Standard Deviation (n – 1) (σ_{n-1}):

$$\sigma_{n-1} = \sqrt{\sum_{i=1}^{n} \frac{(X_i - \overline{X})^2}{n-1}}$$

11.3.1 Where:

$\overline{X}$ = Mean of the values

X_i = Individual values 1 through i

n = Number of values

11.4 Percent Relative Standard Deviation (%RSD):

$$\%RSD = \frac{\sigma_{n-1}}{\overline{X}} * 100$$

11.4.1 Where:

σ_{n-1} = Sample Standard Deviation

$\overline{X}$ = Mean of the values

11.5 Relative Percent Difference (%RPD or RPD):

$$\%RPD = \frac{|X_1 - X_2|}{\frac{(X_1 + X_2)}{2}} * 100$$

11.6 Percent Drift, %Drift:

$$\%Drift = \frac{(Concentration_{Calculated} - Concentration_{Expected})}{Concentration_{Expected}} * 100$$

11.6.1 Where:

$Concentration_{Calculated}$ = Concentration calculated from result

$Concentration_{Expected}$ = Theoretical concentration of the standard

11.7 Extract Concentration:
The extract concentration is calculated relative to the calibration curve by the instrument software.

11.8 Percent Recovery:

11.8.1 *LCS/LCSD*:

$$\%\text{Recovery} = \frac{\text{Conc}_{\text{spiked}}}{\text{Conc}_{\text{expected}}} * 100$$

11.8.1.1 Where:
$\text{Conc}_{\text{spiked}}$= Concentration found in the spiked sample
$\text{Conc}_{\text{expected}}$= Expected concentration

11.8.2 *MS/MSD*:

$$\%\text{Recovery} = \frac{\text{Conc}_{\text{spiked}} - \text{Conc}_{\text{unspiked}}}{\text{Conc}_{\text{expected}}} * 100$$

11.8.2.1 Where:
$\mathbf{Conc_{spiked}}$ = Concentration found in the spiked sample
$\mathbf{Conc_{unspiked}}$ = Concentration found in unspiked sample
$\mathbf{Conc_{expected}}$ = Expected concentration

11.9 Calculation of Dilution Factors

C x D = F

11.9.1 Where:
C = concentration from instrument in ug/l
D = dilution factor, if any
F = final concentration in ug/l

12 Waste Management

12.1 See GA EPD Laboratory SOP-EPD Laboratory Waste Management Standard Operating procedures, reference 13.7.

13 References

13.1 Standard Methods for the Examination of Water and Wastewater, Method 3500-Cr-B, 2009, Editorial revision 2011.

13.2 EPD Laboratory Quality Assurance Plan, online revision.

13.3 GA EPD Laboratory SOP's – Initial Demonstration of Capability SOP 6-001, online revision or Continuing Demonstration of Capability SOP 6-002, online revision.

13.4 GA EPD Laboratory SOP-EPD Laboratory Procedures for Control Charts and Control Limits SOP, SOP 6-025, online revision.

13.5 GA EPD Laboratory SOP-EPD Laboratory Waste Management SOP, SOP 6-015, online revision.

13.6 GA EPD Laboratory SOP – Determination of Method Detection Limit, Method Detection Limit SOP 6-007, online revision.

13.7 GA EPD Laboratory Safety Plan – EPD Laboratory Safety / Chemical Hygiene Plan & Fire Safety Plan, online revision.

14 Reporting Limits (RL's), Precision and Accuracy Criteria, and Quality Control Approach

Table 14.1 RL's for Method SM 3500-Cr-B

Parameter/Method	Analyte	Matrix (aqueous)	
		RL	Unit
SM 3500-Cr-B	Hexavalent Chromium	50	ug/L

Table 14.2 Acceptance Criteria for Method SM 3500-Cr-B

Method	Analyte	Accuracy Water (%R)	Precision Water (RPD)
SM 3500-Cr-B	Hexavalent Chromium	90-110	15

Table 14.3 Summary of Calibration and QC Procedures for Method SM 3500-Cr-B

Method	Applicable Parameter	QC Check	Minimum Frequency	Acceptance criteria	Corrective Action	Flagging Criteria
SM 3500-Cr-B	Hexavalent Chromium	Initial Calibration for all analytes	Calibration performed every 6 months	Correlation coefficient ≥ 0.995 linear regression	Correct problem then repeat initial calibration	
SM 3500-Cr-B	Hexavalent Chromium	Initial Demonstration: Demonstrate ability to generate acceptable accuracy and precision using four analysis of a QC check sample, a method blank and a blind sample. In addition, the analyst must prepare one standard.	Once per analyst	QC Acceptance Criteria Table 14.2 and Initial demonstration SOP	Recalculate results: locate and fix problem with system and then rerun demonstration for those analytes that did not meet criteria	
		Continuing Demonstration: Demonstrate ability to generate acceptable accuracy and precision using a variety of analysis options of a QC sample(s)	Every 6 months	QC Acceptance Criteria Table, SOP 3-026 Appendix A and Continuing Demonstration of Capability SOP (Reference 13.3)	Recalculate results: locate and fix problem with system and then rerun demonstration for those analytes that did not meet criteria	
		Second source calibration verification (ICV)	Once per run or quarterly whichever is sooner	Value must be within 10% of expected value	Correct problem, then reanalyze results	
		Initial Calibration Blank (ICB)	Prior to sample analysis	Value must be below reporting limit	Correct problem, then repeat initial calibration	
		Method Blank (MBLK/MDLB)	One per batch	Cr value must be < RL	Correct problem then analyze method blank and all samples processes with the contaminated blank	If unable to re-analyze, flag with a "B"
		Laboratory Control Sample (LCS/ LCSD)	One LCS/LCSD per analytical batch	QC Acceptance Criteria Table, SOP 3-026 Appendix A	Correct problem, then reanalyze the LCS/LCSD and all samples in the affected batch	If unable to re-analyze, flag with a "J"
		MDL low level Spike (50 ug/L) (MDLS)	Once per analytical batch	All batch QC must be valid	Correct problem and reanalyze affected batch	

Table 14.3 Summary of Calibration and QC Procedures for Method SM 3500-Cr-B						
Method	**Applicable Parameter**	**QC Check**	**Minimum Frequency**	**Acceptance criteria**	**Corrective Action**	**Flagging Criteria**
		Matrix Spike (MS/MSD)	One MS/MSD per analytical batch	QC Acceptance Criteria Table, SOP 3-026 Appendix A	Evaluate out of control event, reanalyze or flag data	
SM 3500-Cr-B	Hexavalent Chromium	Continuing Calibration Check (CCC)	After every 10 samples and at the end of the sample run	Cr concentration within 10% of expected value	Correct problem then reanalyze all samples associated with out of control CCC.	
		Continuing Calibration Blank (CCB)	After every 10 samples and at the end of sample run	Cr value must be < RL	Correct problem then reanalyze all samples associated with out of control CCB	
		MDL study	Every six months or after major maintenance of the instrument	All Spiked MDLs must have a value greater than 0. Minimum Detection Limits established shall be < the RLs in Table 14.1	Re-do MDL Study	
		MDL analysis	Once per batch or as needed to acquire data points per SOP 6-007, online revision	All Spiked MDLs must have a value greater than 0. All other QC in the MDL blank and MDL sample (i.e. Surrogate Spike or Internal Standard, etc. if included) must meet established criteria	Correct problem and re-run the MDL sample or MDL blank once and initiate a corrective action. If the re-run fails a second time, do not use MDL data. Update corrective action, and use associated sample data	

Appendix A – Quality Assurance Criteria for Method SM3500-Cr-B- Hexavalent Chromium

Table A.1 Quality Assurance Criteria for Method SM5310C					
QC Type	**Analyte**	**Accuracy(%R) LCL**		**UCL**	**Precision (%RPD)**
LCS/LCSD	Hexavalent Chromium	90	-	110	15
MS/MSD	Hexavalent Chromium	90*	-	110*	15

Table A.1 Quality Assurance Criteria for Method SM5310C				
QC Type	Analyte	Accuracy(%R) LCL	UCL	Precision (%RPD)
*MS/MSD Control limits are static by EPD Lab default. Control Chart data generated from 01/01/2018 -01/01/2021				

Updates to Previous Version:
Section 6
Section 9
Section 10
Table A.1
Table 14.3