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SM 5220D – Chemical Oxygen Demand

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 This method covers the determination of COD in surface waters, domestic and industrial wastes. The COD method determines the quantity of oxygen required to oxidize organic matter under specific conditions of oxidizing agent, temperature and time. Since the test utilizes a specific chemical oxidation, the result has no definite relationship to the BOD or TOC tests. COD should be considered an independent measure of organic material in a sample. Method is modified for use with HACH reagents per HACH Method 8000. High level samples are read at 620 nm and low level samples are read at 420 nm. This procedure is modified using HACH Method 8000. Volumes of standards and reagents may be changed, provided the quality control and performance requirements stated in this SOP are met.

1.2 Restricted Procedure

This procedure is restricted to use by an analyst experienced in the operation of a HACH DR6000 and COD reactor. 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 Section 3 and Section 4 of the Georgia EPD Laboratory Quality Assurance Plan (see SOP reference 13.2) 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), 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 Volatile organic compounds are more completely oxidized in the closed system because of longer contact with the oxidant.

4 Safety

4.1 Refer to the EPD Laboratory Safety / Chemical Hygiene Plan & Fire Safety Plan, online revision (See Section 13.8)

5 Apparatus and Equipment

5.1 Sample Container: 250 mL Nalgene bottle containing 2.5 mL of 10% H_2SO_4.

5.2 Analytical Balance, capable of accurately weighing to the nearest 0.0001 g

5.3 COD heating block capable of reaching a temperature of 150°C ± 2°C

5.4 COD vials

5.4.1 COD Digestion Vials, High Range – Hach Catalog # 2125915 or equivalent

5.4.2 COD Digestion Vials, Low Range – Hach Catalog # 2125815 or equivalent

5.5 Hach spectrophotometer DR/6000 set at 420nm (low level) and 620nm (high level).

5.6 Air displacement pipettes of various volumes, auto-pipettors, pipette tips in various sizes. Air displacement pipettes and auto-pipettors may also be described as mechanical pipettes.

5.6.1 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.

5.6.2 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 1g. Mechanical pipettes must be verified to be within ± 2.5 percent of the nominal volume.

5.6.3 Mechanical pipettes must be professionally calibrated every 6 months.

5.6.4 Auto-pipettors may be verified by measuring the volume dispensed with a Class "A" graduated cylinder. The volume dispensed must be within ± 2.5 percent of the nominal volume.

5.7 HDPE bottles, various sizes, for storage of standards.

5.8 Disposal pipette tips, 100-1000 µl - Fisher PN# 02-707-507 or equivalent.

5.9 Disposal pipette tips, 1ml – 5ml – VWR PN# 82018-840 or equivalent

5.9.1 Disposable transfer pipettes:

5.9.2 Plastic - VWR® Disposable Transfer Pipets PN# 16001-190 or Fisherbrand™ Standard Disposable Transfer Pipettes PN# 13-711-7M

5.10 Glassware -- Class "A" volumetric flasks, graduated cylinders, and pipettes

5.11 NIST traceable thermometer for measuring temperature of COD reactor. Fisher PN# 06-664-31 or equivalent.

6 Reagents

6.1 Reagent Water:

6.2.1 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] @ 25ºC and a TOC of 50 ug/L or less).

6.2 High Range Potassium Acid Phthalate (KHP) Standard Solution (10,000 mg/L) Primary Source (PS) Stock Standard:

6.2.1 Add 8.496 g of ACS grade, KHP and dilute to 1000 mL with reagent water. KHP previously dried to constant weight.

6.2.2 Prepare every 6 months and keep under refrigeration.

6.3 Low Range Potassium Acid Phthalate (KHP) Standard Solution (3000 mg/L) Primary Source (PS) Stock Standard :

6.3.1 Pipette 150 mL of High Range Potassium Acid Phthalate (KHP) Standard Solution (10,000 mg/L) into a 500 mL volumetric flask and dilute to volume with reagent water.

6.3.2 Prepare every 3 months and keep under refrigeration.

6.4 10% Sulfuric Acid Solution:

6.4.1 Purchased from VWR, Part # BDH3358-4 or equivalent.

6.4.2 This solution is used for preservation of standards and blanks.

6.4.3 This purchased chemical is stable until expiration date on bottle or within 1 year of opening date, whichever is sooner. Store at room temperature.

6.5 Calibration standards:

6.5.1 Prepare calibration standards at nine concentrations in reagent water. The calibration standards range from 10 mg/L – 1400 mg/L. After the standards are brought to volume, add 1.0 mL of 10% H_2SO_4 per 100 mL of standard is added.

6.5.2 Prepare every 3 months.

6.5.3 Keep standards under refrigeration.

WORKING STANDARDS (High Range)

Potassium Acid Phthalate Standard High Range (10,000 mg/L)	Reagent water	Concentration mg/L
14 mL	100 mL	1400
11 mL	100 mL	1100
7.5 mL	100 mL	750
4.5 mL	100 mL	450
1.5 mL	100 mL	150

WORKING STANDARDS (Low Range)

Potassium Acid Phthalate Standard Low Range (3,000 mg/L)	Reagent water	Concentration mg/L
5.0 mL	100 mL	150
3 mL	100 mL	90
2 mL	100 mL	60
1 mL	100 mL	30
0.33 mL	100 mL	10

6.6 0.00 mg/L Standard, ICB, CCB, MBLK, MDLB and Dilution water):
To prepare an ICB/CCB, Pipette 10 mL of 10% H2SO4 into a 1L volumetric flask that already contains 1L of reagent water. This solution is stable for 28 days. The volume of the reagent may be altered as long as the final concentration remains the same. Keep under refrigeration. Note: must be poured into a 250ml sample collection bottle before it is placed into the appropriate vial. Record lot # of bottle used.

6.7 Low Range Continuing Calibration Check (CCC) 60.0 mg/L Standard:
To prepare the CCC, pipette 2 mL of the Low Range Potassium Acid Phthalate (KHP) Standard Solution (3000 mg/L) into a 100 mL volumetric flask. Once the standard is diluted to volume with reagent water, preserve the solution with 1.0 mL of 10% Sulfuric Acid Solution.

6.7.1 This solution is stable for 3 months. Keep under refrigeration.

6.8 High Range Continuing Calibration Check (CCC) 750 mg/L Standard:
To prepare the CCC, pipette 7.5 mL of the High Range Potassium Acid Phthalate (KHP) Standard Solution (10,000 mg/L) into a 100 mL volumetric flask. Once the standard is diluted to volume with reagent water, preserve the solution with 1.0 mL of 10% Sulfuric Acid Solution.

6.8.1 This solution is stable for 3 months. Keep under refrigeration.

6.9 Method Detection Limit Spike (MDLS) 10.0 mg/L Standard:
To prepare the MDLS, pipette 0.33 mL of the (PS) 3000 mg/L Stock standard Solution into a 100 mL volumetric flask. Once the standard is diluted to volume with reagent water, preserve the solution with 1.0 mL of 10% Sulfuric Acid Solution. 10.1. The MDLS standard must be poured into a 250ml sample collection bottle before it is placed into the appropriate vial. Record lot # of bottle used.

6.9.1 This solution is stable for 3 months. Keep under refrigeration.

6.10 Low Range LCS/LCD 60 mg/L concentration:

6.10.1 Prepare the low range LCS and LCSD by pipetting 0.20 mL of the Low Range Potassium Acid Phthalate (KHP) Standard Solution (3000 mg/L) Primary Source (PS) Stock Standard into a 10mL volumetric flask and bring to volume with dilution water that was stored in a 250ml sample collection sample bottle. (See Section 6.6). Record lot # of bottle used.

6.11 Low Range MS/MSD 60 mg/L concentration:

6.11.1 Prepare the low range MS and MSD by pipetting 0.20 mL of the Low Range Potassium Acid Phthalate (KHP) Standard Solution (3,000 mg/L) Primary

Source (PS) Stock Standard into a 10mL volumetric flask and bring to volume with bring to volume with sample chosen as the spike.

6.12 High Range LCS/LCD 750 mg/L concentration:

6.12.1 The matrix spike should be prepared at the 750 mg/l concentration. To prepare the matrix spike and matrix spike duplicate, pipette 0.75 mL of the High Range Potassium Acid Phthalate (KHP) Standard Solution (10,000 mg/L) Primary Source (PS) Stock Standard into a 10 mL volumetric flask and bring to volume with dilution water (See Section 6.6) that was stored in a 250ml sample collection sample bottle.

6.13 High Range MS/MSD 750 mg/L concentration:

6.13.1 Prepare the high range MS and MSD by pipetting 0.75 mL of the High Range Potassium Acid Phthalate (KHP) Standard Solution (10,000 mg/L) Primary Source (PS) Stock Standard into a 10 mL volumetric flask and bring to volume with bring to volume with sample chosen as the spike.

6.14 ICV Stock Standard Solution, 1000 mg/L - Second Source (SS) Stock standard:

6.14.1 The ICV stock standard is used as a second source standard.

6.14.2 This stock standard must be from a different source than the stock standard used to make the calibration standards.

6.14.3 The prepared standard is stable until expiration date on bottle or within 6 months of opening date, whichever is sooner. Keep under refrigeration.

6.14.4 Hach COD 1000 mg/L standard, Catalog No. 2253929, or equivalent is used.

6.15 Low Range ICV Solution 60 mg/L Second Source (SS) Standard:

6.15.1 A 6 mL aliquot of the ICV Stock Standard Solution (1000 mg/L) is pipetted into a 100 mL volumetric flask and diluted to volume with reagent water. Once the ICV is diluted to volume with reagent water, preserve the solution using 1mL of 10% Sulfuric Acid Solution.

6.15.2 The ICV solution must be prepared fresh every 3 months. Keep under refrigeration.

6.16 High Range ICV Solution 750 mg /L (SS) Second Source (SS) Standard:

6.16.1 A 75 mL aliquot of the ICV Stock Standard Solution (1000 mg/L), is pipetted into a 100 mL volumetric flask and diluted to volume with reagent water. Once the ICV is diluted to volume with reagent water, preserve the solution using 1mL of 10% Sulfuric Acid Solution.

6.16.2 The ICV solution must be prepared fresh every 3 months. Keep under refrigeration.

6.17 Volumes and amounts of reagents, chemicals and standards may be altered as long as final concentrations remain the same. Sample volumes and amounts may be altered as long as required detection limits can be met and sample/reagent ratios remain the same.

7 Sample Collection

7.1 Samples are collected in 250 mL HDPE bottles.

7.2 The sample bottles are pre-preserved with 2.5mL of 10% Sulfuric Acid to a pH of < 2 in the field.

7.3 Sample preservation is checked in the receiving lab at time of receipt.

7.4 Samples are cooled and stored at 0-6° C (not frozen).

7.5 Sample holding time is 28 days.

8 Calibration

8.1 Calibration Standards

The calibration curve for low range CODs consists of calibration standards at the following concentrations: 0 mg/L O_2, 10 mg/L O_2, 30 mg/L O_2, 60 mg/L O_2, 90 mg/L O_2, and 150 mg/L O_2. The calibration curve for high range CODs consists of calibration standards at the following concentrations: 0 mg/L O_2, 150 mg/L O_2, 450 mg/L O_2, 750 mg/L O_2, 1100 mg/L O_2, and 1400 mg/L O_2.

8.2 Calibration Curve

The Hach Spectrophotometer using Hach Method 8000 is calibrated every time a new lot of COD vials is used or every six months, whichever is sooner. The calibration is verified once per batch. Two calibrations curves are stored in memory, one for high range and one for low range. Minimum acceptable correlation is 0.995 using a linear regression. Dilute, re-digest and reanalyze all samples with a response greater than 1400 mg/L on high range curve. Digest and analyze all samples greater than 150 mg/L on high range curve.

8.3 Calibration Verification

8.3.1 An Initial Calibration Verification standard (ICV), a Continuing Calibration Check (CCC) 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 ICV value must be within 10% of its true value.

8.3.2.2 The %Drift (see calculation 11.6) of the ICV from the true value must be within ±10%. 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, CCB, MDLB and MBLK values must be less than the method RL or the run will have to be repeated.

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

8.3.4.2 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.

8.3.5 A MDLS (low level spike) at the concentration of 10.0 mg/L must be analyzed with each batch to perform ongoing MDL study. All batch QC must be valid to report this result.

8.3.6 A MDLB (MDLB) must be analyzed once per low-level COD analytical 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 EPD Lab default control limits from SM5220D are 85 – 115% recovery for

COD 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 – 25% RPD.

9.1.3 LCS/LCSD recovery and precision limits are monitored through the use of control charts every 6 months.

9.1.4 5% of all routine samples must be spiked. The EPD Laboratory requires recovery control limits of 85-115% 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 – 25% RPD.

9.1.6 MS/MSD recovery and precision limits are static by EPD Lab default. These limits are monitored through the use of control charts every 6 months.

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.

9.3 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 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 blank.

9.3.5 A continuous format 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_COD. The MDLSpike result will be entered using the MLCOD. The MDL Spiked Amount will be entered into the test code MACOD. The instrument used for the MDL and Blank analysis will be selected using the test code INSTR-COD.

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

9.3.8 Data for the MDL study is pulled from a two year period.

10 Procedure

10.1 Procedure for preheating 3-COD02 and 3-COD03

10.1.1 Press power switch on the back of the COD reactor. Make sure "COD Start" is listed on the left and right of display. If not, follow instructions in 10.2.1.1 and 10.2.1.2.

10.1.1.1 Block 1 COD program: Press middle key, left key, left key and left key again to accept.

10.1.1.2 Block 2 COD program: Press middle key, right key, left key and left key again to accept.

10.1.2 Press the left key under the start command in display for block #1 or right key under start command in display for block #2. The corresponding block will begin to preheat to 150ºC. Place a COD vial filled with sand and NIST traceable thermometer into one of the positions (1-15). ***Note- the position must be rotated from the previous digestion and noted on the digestion worksheet and diagram.**

10.1.3 Once the 150ºC is reached 2 beeps will be heard and "start" and a timer icon will appear. *** note – to stop heating at any time press the left button twice or right button twice to stop heating to the corresponding block.**

10.1.4 Place the prepped sample vials into the block(s). Close lid and press the start key for the block (left or right key). The Counter will begin to count down from 120 minutes. *Note-the timing process should always be verified with a NIST timer.

10.1.5 When the 120 minutes has elapsed 3 beeps will be heard. The heating process will stop.

10.1.6 Allow the vials to cool to 70ºC, or less, and mix vials by inverting twice.

10.2 Procedure for Preparing Samples:

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

10.2.2 Turn on COD reactor to preheat to 150ºC ± 2ºC. See 10.1 or 10.2.

10.2.3 Choose either High or Low range vials. Different standards are run for each.

10.2.4 Prepare MS and MSD for low level COD. Refer to Section 6.13.

10.2.5 Prepare MS and MSD for high level COD. Refer to Section 6.15.

10.2.6 Prepare LCS and LSCD for low level COD. Refer to Section 6.12.

10.2.7 Prepare LCS and LSCD for high level COD. Refer to Section 6.14.

10.2.8 Pipette 2 mL of sample, standard or QC sample per vial and replace cap tightly.

10.2.9 Vortex to homogenize.

10.2.10 Put all the vials into the preheated reactor (set to150ºC ± 2ºC) and set block timer for 2 hours. When the vials are placed in the block digester, the positions of the QC and thermometer should be shifted with each batch so that over time, the QC and the thermometer are checked in each position.

10.2.11 When digestion is complete, allow vials to cool to 70ºC or less.

10.2.12 Mix vials by inverting twice and allow them to cool to the touch before reading on the spectrophotometer.

10.3 Procedure for using SPEC02 and SPEC03- (HACH DR/6000

10.3.1 Turn on HACH Spectrophotometer. Allow ample time for warm-up. Approximately 30 minutes.

10.3.2 Instrument must be connected to the network prior to use.

10.3.2.1 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.

10.3.3 On the main menu display select the "User Program" box, and then select the 9001 for the COD Low Level program or select 9002 for the COD High Level program.

10.3.4 Select the "Login" on the right side of the display and select your initials. The password will be "Inorganic".

10.3.4.1 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.

10.3.5 Once your initials have been selected, select the "Start" button on the bottom of the display.

10.3.6 Open the lid place the CCB/MBLK vial into the slot on the left side of the carousel and close the lid. Ensure to wipe down vials with a Kim-wipe before placing them into the instrument.

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

10.3.8 Select the "Sample ID" box on the right side of the display. Then select the "Option" box on the bottom.

10.3.9 Select "Import Sample ID List". When asked to delete previously imported sample IDs, select the "YES" box. If "Import Sample ID List" not available refer to section 10.7.

10.3.10 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" refer to section 10.5.3.

10.3.11 Select the "Sample ID" box from the display and then select the first sample from the imported list. Then touch the "Select" box.

10.3.12 Open lid and place the vial in the slot on the left side of the carousel and close the lid.

10.3.13 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".

10.3.14 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 10.4.12-10.4.14 until all samples have been analyzed.

10.3.15 After 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 refer to section 10.5.

10.4 Procedure for Accessing Data on Network Drive for SPEC02 and SPEC03

10.4.1 Open the "I" drive by selecting and entering the password; the password is "InOrg-5804"

10.4.2 On the "I" drive open folder labeled "SPEC02" or "SPEC03" and select the file, labeled "DR6000sampleseqgenver3.accb" and open it. If the security warning pops up click "Enable Content.

10.4.3 Click the “LW Results” box and select a file location. Choose the “I” drive, then select the “SPEC02” or “SPEC03” 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”.

10.4.4 Return to the “SPEC02” or “SPEC03” 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”

10.4.5 Open the excel file and 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”.

10.4.6 After the data has been sorted, save the file to the “COD sorted batches” folder within the “SPEC02” or “SPEC03” folder on the “I” drive. The file should be named with the batch # and date.

10.5 Procedure for Creating Sample ID List for SPEC02 and SPEC03

10.5.1 Before Sample ID list can be created, batches must have been created in Labworks.

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

10.5.3 Open folders labeled “SPEC02” or “SPEC03” and open select the file, labeled “DR6000sampleseqgenver3.accb”.

10.5.4 Once open select “Create Sample Sequence” and type COD into the “Test Code” box. All the batches with that test code will appear in the “Batch NO. List” box.

10.5.5 Select the desired batch. 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.

10.5.6 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.

10.5.7 After closing the program the Sample ID list created will appear. Save the created Sample ID List to the “I” drive, under the “SPEC02” or “SPEC03” folder, in the “SampleID” folder. Name the file COD-Batch#.csv.

10.6 Procedure for Manual Sample ID Entry for SPEC02 and SPEC03

10.6.1 On the main menu display select the “User Program” box, and then select the 9001 for COD Low Level program or 9002 for COD High Level program.

10.6.2 Select the “Sample ID” on the right of the screen and then select “Options”.

10.6.3 From the options select “New” to create a new Sample ID or “Edit” to edit previously store Sample IDs.

10.6.4 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”

10.6.5 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"

10.6.6 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.

10.7 Procedure for Calibration for Low Level and High Level for SPEC02 and SPEC03

10.7.1 Turn on HACH Spectrophotometer. Allow ample time for warm-up. Approximately 30 minutes.

10.7.2 On the main menu display select the "User Program" box, and then select the 9001 for the COD Low Level program or select 9002 for the COD High Level program.

10.7.3 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 10.4.4.1). The password will be "Inorganic".

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

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

10.7.6 To add the standards, select the "+" box, type "0" and select "OK". Repeat the process for the rest of the standards either COD Low Level or COD High Level. COD Low Level Standards: 10 mg/L, 30 mg/L, 60 mg/L, 90 mg/L, and 150 mg/L. COD high level Standards: 150mg/L, 450 mg/L, 750 mg/L, 1100 mg/L and 1400 mg/L. *Note the mg/L unit does not need to be typed.

10.7.7 Once all the standards have been added. Highlight the "0.000" line by touching it. Then open the lid and place the "0 mg/L" standard vial into the slot on the side of the carousel and close the lid. Ensure to wipe down vials with a Kim-wipe before placing them into the instrument.

10.7.8 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 mg/L" standard and place the next standard in the same slot. Select the "Read" box on the bottom. Repeat this process for each standard.

10.7.9 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.

11 Calculations

11.1 The standard curve is prepared by plotting the response of processes standards against known concentration values. The concentrations of the samples are computed by comparing the response with the standard curve.

$$\text{COD as mg } O_2 \text{ /L} = \frac{\text{mg } O_2 \text{ in final volume}}{\text{mL sample}} \times 1000$$

C x D = F

where:

C = concentration from instrument in mg/L
D = dilution factor, if any
F = final concentration in mg/L

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):

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

11.5.1 Where:

$|X_1 - X_2|$ = Absolute difference between two values

$\frac{(X_1 + X_2)}{2}$ = Average of two values

11.6 Percent Drift, %Drift:

$$\%\text{Drift} = \frac{(\text{Concentration}_{\text{Calculated}} - \text{Concentration}_{\text{Expected}})}{\text{Concentration}_{\text{Expected}}} * 100$$

11.6.1 Where:

Concentration $_{\text{Calculated}}$ = Concentration calculated from result
Concentration $_{\text{Expected}}$ = Theoretical concentration of the standard

11.7 Extract Concentration:

11.7.1 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:

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

11.9 Calculation of Dilution Factors

$$C \times D = F$$

11.9.1 Where:

C = concentration from instrument in mg/L

D = dilution factor, if any

F = final concentration in mg/L

12 Waste Management

12.1 See GA EPD Laboratory SOP-EPD Laboratory Waste Management Standard Operating procedures, SOP reference 13.6.

13 References

13.1 Standard Methods for the Examination of Water and Wastewater, 20th Edition, 5-15, 5-16, Method 5220D. Closed Reflux Colorimetric Method (1997), 2011 Online Edition.

13.2 HACH Method 8000, Chemical Oxygen Demand, Reactor Digestion Method, based on SM5220D method.

13.3 EPD Laboratory Quality Assurance Plan, online revision.

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

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

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

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

13.8 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 5220D

		Matrix (Aqueous)	
Parameter	**Analyte**	**RL**	**Unit**
SM 5220D	COD	10	mg/L

Table 14.2 Acceptance Criteria for Method SM 5220D

Method	Analyte	Accuracy Water (%R)	Precision Water (RPD)
SM 5220D	COD	85-115	25

Table 14.3 Summary of Calibration and QC Procedures for Method SM 5220D

Method	Applicable Parameter	QC Check	Minimum Frequency	Acceptable Criteria	Corrective Action	Flagging Criteria
SM 5220D	COD	Initial calibration for high level COD analytes and initial calibration for low level COD analytes	Curve regenerated for each new lot # of COD ampules or every six months.	Correlation Coefficient $\geq$ 0.995 linear regression	Correct problem then repeat initial calibration	
		Second source calibration verification (ICV)	Prior to sample analysis	COD concentration within 10% of expected value	Correct problem then repeat initial calibration	
		Initial Calibration Blank (ICB)	Once per analytical run	Value must be < RL	Correct problem and repeat initial calibration	
		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, SOP 3-031 Appendix A and Initial Demonstration SOP(SOP Reference 13.4)	Recalculate results: locate and fix problem with system and then rerun demonstration for those analytes that did not meet criteria	
SM5220D	COD	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 3-031 Appendix A and Continuing Demonstration of Capability SOP (SOP Reference 13.4)	Recalculate results: locate and fix problem with system and then rerun demonstration for those analytes that did not meet criteria	
		Method Blank (MBLK)	Once per analytical batch	COD value must be < RL	Correct problem then analyze method blank and	If unable to re-analyze, flag with a "B"

Table 14.3 Summary of Calibration and QC Procedures for Method SM 5220D

Method	Applicable Parameter	QC Check	Minimum Frequency	Acceptable Criteria	Corrective Action	Flagging Criteria
					all samples processed with the contaminated blank	
		Laboratory Control Sample (LCS/ LCSD)	One LCS/LCSD per analytical batch	QC Acceptance Criteria Table, SOP 3-031 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"
		Matrix Spike (MS/MSD)	One MS/MSD per analytical batch	QC Acceptance Criteria Table, SOP 3-031 Appendix A	Evaluate out of control event, reanalyze or flag data.	
		Continuing Calibration Check (CCC) 60 mg/L (Low Range) 750 mg/L (High Range)	After every 10 samples and at the end of the sample run	COD concentration within 10% of expected value	Correct problem then reanalyze CCC and all samples associated with affected batch	
		Continuing Calibration Blank (CCB)	After every 10 samples and at the end of the sample run	COD concentration must be < 10 mg/L	Correct problem then reanalyze CCB and all samples associated with affected batch	
		MDL Low level Spike (MDLS) 10 mg/L	Once per analytical batch	All batch QC must be valid	Correct problem then reanalyze the affected batch	
		MDL Blank (MDLB)	Once per analytical batch	All batch QC must be valid	Correct problem then reanalyze the affected batch	
		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	None
		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	None

Appendix A – Quality Assurance Criteria for Method SM5220D

Table A.1 Quality Assurance Criteria for Method SM5220D					
QC Type	Analyte	Accuracy(%R) LCL		UCL	Precision (%RPD)
LCS/LCSD	COD	85	-	115	25
MS/MSD	COD	85*	-	115*	25
*MS/MSD Control limits are static by EPD Lab default. Control Chart data generated from 01/01/2019 -01/01/2021					

Updates to Previous Version:

Appendix A added.
Updated for online revision.
Section 2
Section 5
Section 6
Section 8
Section 9
Section 10
Table 14.3