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Confidential

Subject: Temperature (SM 2550 B-2010)

Approval

Title	Name	Signature	Date
Laboratory Supervisor	Kelley E. Keenan		05-01-24
Quality Assurance Officer	Jim Sumner		05-01-24

Document Revision History

Effective Date	Revision number	Review Type	Evaluators	Revisions
12-01-00	0	Internal	Jim Sumner (ETS)	Original document
09-01-09	1	External (TVA, Environmental Standard, Inc.) Internal	William Rogers (TVA) Cynthia Russell (TVA) Rick Sherrard (TVA) Rock Vitale (Environmental Standards, Inc.) Jim Sumner (ETS)	• SOP G12 section B moved to this SOP (incubator, refrigerator, and drying oven temperatures). • Corrective action included if measured temperatures are outside acceptance limits.
06-01-11	2	Internal	Jim Sumner (ETS)	• Updated exhibits during document review.
01-01-13	3	Internal	Jim Sumner (ETS)	• Updated procedure and references to the approved analytical method identified in USEPA Method Update Rule II (MUR II), May 18, 2012.
10-01-17	4	Internal	Jim Sumner (ETS)	• Updated procedure to include NELAP requirements. • Verification of thermometers using NIST thermometers changed to annually. • Additional guidance included in SOP. • Method number revised based on 2017 MUR.
01-04-19	5	External (SC HDEC) Internal	Haley Anderson (SC DHEC) Jim Sumner (ETS)	• Updated procedure to indicate: When equipment is in use, measurements must be recorded twice daily (at least 4 hours apart). • Updated procedure to include requirement of quarterly verification of thermometers used record temperatures of incubators/water baths and digital thermometers.
07-01-21	6	Internal	Jim Sumner (ETS)	• Updated procedure and references to the approved analytical method identified in USEPA Method Update Rule, May 19, 2021.
05-01-24	7	Internal	Jim Sumner (ETS)	• Updated reference to 24th Edition of Standard Methods.

Subject: Temperature (SM 2550 B-2010)

Scope and Application

This method is used to measure temperature of water samples used in toxicity tests, wastewater, receiving water, drinking water and testing equipment.

Summary of Method

The temperature is measured with a mercury or red spirit-filled, hand-held or digital thermometer. Measurements are recorded in degrees Celsius (^{o}C) and reported to the nearest 0.1^{o}C or 1^{o}C, depending on the accuracy of the thermometer.

Temperature measurement procedures are based on Standard Methods 2550 B-2010.

Quality Control

Standardization: All mercury, red spirit-filled, hand-held thermometers, and meters, which measure temperature, must be verified at least **annually** (once every calendar year) with traceable NIST thermometers (SOP-G12).

In addition, any thermometers used to monitor the temperature of incubators or water baths must be verified at least **quarterly** with traceable NIST thermometers (SOP-G12).

All digital thermometers must be verified at least **quarterly** with traceable NIST thermometers (SOP-G12).

Additional quality control guidance is provided in QAP-Q5.

Equipment and Materials

Mercury or red spirit-filled thermometers, Hand-held thermometers, Digital thermometers
NIST traceable thermometers
Scienceware® Mercury Collectors
Rinse bottle
Deionized water
Waste container
Various logsheets

Subject: Temperature (SM 2550 B-2010)

Procedure

A. Measuring the Temperature of Water Samples.

1. Place the tip of the thermometer in the sample. If an immersion line is present on the thermometer, the thermometer must be submerged in the sample below this line.

2. Wait until the reading has stabilized.

3. Adjust the temperature for the correction factor located on the thermometer tag.

4. Record the reading on the appropriate logsheet or benchsheet. Measurements must be in ^{o}C and reported to the nearest 0.1^{o}C or 1^{o}C, depending on the accuracy of the thermometer.

5. Remove the thermometer from the sample and rinse area that came in contact with the sample with deionized water.

Corrective Action: Corrective action for samples, which exceed acceptable temperature upon receipt, are addressed in SOP-G4: Receipt, Handling and Storage of Samples.

B. Incubator, Refrigerator and Drying Oven Temperatures.

1. At least one thermometer, submerged in water (or sand for ovens), is maintained within each incubator, refrigerator, drying oven or item that requires temperature monitoring. If the thermometer has an immersion line, the thermometer must be submerged in the water (or sand for ovens) below this line.

2. Adjust the temperature for the correction factor located on the thermometer tag.

3. Record the reading on the appropriate logsheet or benchsheet. Refer to Exhibit C1.1 for an example Temperature Logsheet for Incubators and Refrigerators. Measurements must be in ^{o}C and reported to the nearest 0.1^{o}C or 1^{o}C, depending on the accuracy of the thermometer.

4. Temperature measurements of incubators and refrigerators are documented at least once daily, during normal business operation (excluding weekends, holidays, and laboratory closings). When equipment is in use, measurements must be recorded twice daily (at least 4 hours apart). The minimum and maximum temperatures over a 24-hour

period are recorded daily, during normal business operation, from digital thermometers in aquatic toxicity incubators.

5. Temperature measurements of drying ovens are taken when the oven is in use and are documented on the appropriate test benchsheet (i.e. Fathead Minnow Chronic Toxicity Test Benchsheet, Total Suspended Solids Benchsheet, Total Dissolved Solids Benchsheet, etc.).

Corrective Action: Incubator or refrigerator temperatures, which exceed acceptance limits, are documented in the comments section with a possible cause and resolution (temperature adjusted and samples/tests moved). The temperature of individual tests and/or samples within the incubator or refrigerator are monitored to ensure that they have not exceeded acceptance limits. Dependent on the degree of deviation from testing protocols, those tests and/or samples may be invalidated. Refer to test specific SOPs for additional corrective action requirements.

Safety and Hazardous Waste Management

Safety glasses, gloves and lab coats should always be worn while handling samples. Excess samples may be flushed down the sink.

Scienceware® Mercury Collectors are used to clean mercury spills from broken thermometers. Instructions are identified on the bottom of the collector.

Review Policy-P6: General Safety Policy and Policy-P9: Radiation Protection Policy for additional safety requirements.

References

Standard Methods for the Examination of Water and Wastewater, 24th Edition, 2023. American Public Health Association, 800 I Street, NW, Washington DC 20001-3710.

- Method: 2550 B-2010.

TNI Standard. Management and Technical Requirements for Laboratories Performing Environmental Analysis. The NELAC Institute, PO Box 2439, Weatherford, TX 76086.

Exhibits

Exhibit C1.1: Example Temperature Logsheet for Incubators and Refrigerators.

Subject: Temperature (SM 2550 B-2010)

Exhibit C1.1: Example Temperature Logsheet for Incubators and Refrigerators.

ETS

Toxicity Incubator #1 – Temperature Log (°C)

Month and Year: May 2024

Initial thermometer calibration date: 12-21-23 by J. Sumner

Thermometer location	Serial number	Correction factor (°C)
Toxicity Incubator #1	WB41340472	Calibrated to 25.0°C
Top	6272	0
Bottom	4673	0
Digital Min / Max	160724968	+0.2

Day	AM Time	Analyst	Location		PM Time	Analyst	Location		24-hour Range		
			Top	Bottom			Top	Bottom	Analyst	Minimum	Maximum
1											
2											
3											
4								WE			
5								WE			
6											
7											
8											
9											
10											
11								WE			
12								WE			
13											
14											
15											
16											
17											
18								WE			
19								WE			
20											
21											
22											
23											
24											
25								WE			
26								WE			
27											
28											
29											
30											
31											

Note: WE = Weekend, H = Holiday, NT = No samples or tests present.

Comments:

SOP C1-Revision 7–Exhibit C1.1

Subject: Dissolved Oxygen (SM 4500-O H-2021)

Approval

Title	Name	Signature	Date
Laboratory Supervisor	Kelley E. Keenan		05-01-25
Quality Assurance Officer	Jim Sumner		05-01-25

Document Revision History

Effective Date	Revision number	Review Type	Evaluators	Revisions
12-01-00	0	Internal	Jim Sumner (ETS)	Original document
09-01-09	1	Internal	Jim Sumner (ETS)	• Updated exhibits during document review.
06-01-11	2	Internal	Jim Sumner (ETS)	• Updated exhibits during document review.
01-01-13	3	Internal	Jim Sumner (ETS)	• Updated procedure and references to the approved analytical method identified in USEPA Method Update Rule II (MUR II), May 18, 2012.
10-01-17	4	Internal	Jim Sumner (ETS)	• Updated procedure to include NELAP requirements. • Verification of thermometers using NIST thermometers changed to annually. • Additional guidance included in SOP. • Method number revised based on 2017 MUR.
01-04-19	5	External (SC HDEC) Internal	Haley Anderson (SC DHEC) Jim Sumner (ETS)	• Updated procedure to clarify: Follow the posted chart to find the correct reading based on the temperature, altitude, and salinity table (Exhibit C2.2). If the dissolved oxygen reading is not within ± 0.2 mg/L if the theoretical value in the table, then the meter must be calibrated.
02-17-20	6	External (TVA) Internal	Rick Sherrard (TVA) Jim Sumner (ETS)	• Updated procedure and benchsheet to include the serial number of the meter used to perform dissolved oxygen.
07-01-21	7	Internal	Jim Sumner (ETS)	• Updated procedure and references to the approved analytical method identified in USEPA Method Update Rule, May 19, 2021.
05-01-24	8	Internal	Jim Sumner (ETS)	• Updated procedure and references to the approved analytical method identified in USEPA Method Update Rule, April 16, 2024.
05-01-25	9	Internal	Jim Sumner (ETS	• Changed procedure to LDO method for measuring dissolved oxygen.

Subject: Dissolved Oxygen (SM 4500-O H-2021)

Scope and Application

This method is used to measure the dissolved oxygen of water samples used in toxicity tests, wastewater, receiving water, and drinking water.

Summary of Method

The dissolved oxygen is measured by the optical-probe method. The optical probe uses luminescence-based oxygen sensors to measure the light-emission characteristics of a luminescent reaction: oxygen quantitatively quenches the luminescence. The change in luminescence signal's lifetime correlates to the DO concentration. Measurements are recorded to the nearest 0.1 mg/L.

Dissolved oxygen measurement procedures are based on Standard Methods 4500-O H-2021.

Quality Control

Calibration: The dissolved oxygen meter must be calibrated each day **before use**. The meter internal calibration adjusts for temperature, altitude and salinity for determining dissolved oxygen solubility.

The temperature reading of the dissolved oxygen meter must be verified at least **annually** (once every calendar year) with a traceable NIST thermometer (SOP-G12).

Additional quality control guidance is provided in QAP-Q5.

Interferences

Chlorine dioxide interferes with this reaction. Biofouling due to bacteria or algal growth can prevent oxygen permeation through the window. Bacteria and algae may also generate or consume oxygen, resulting in erroneous readings; this can be minimized by rinsing the probe between readings to keep the sensor clean. Oils can close the membrane and sensor cap, prohibiting oxygen from diffusing to the sensor; frequent rinsing between measurements can minimize this problem.

Subject: Dissolved Oxygen (SM 4500-O H-2021)

Equipment and Materials

HACH HQ430d Flexi meter equipped with a LDO probe
BOD bottle
Rinse bottle
Deionized water
Waste container
Solubility of Dissolved Oxygen Table (Compensation for Temperature, Altitude, and Salinity)
Daily Meter Calibration and Standardization Benchsheet

Procedure (Meter: HACH HQ430d Flexi, SN250100050300 equipped with a LDO101 probe)

A. Air Calibration.

1. Each day before analysis, calibrate the meter. The calibration is recorded on the Daily Meter Calibration and Standardization Benchsheet (Exhibit C2.1).

2. Turn the meter **ON**. Wait for the meter to connect to the LDO101 probe.

3. Remove the probe from the BOD bottle partially filled with deionized water (so that the probe is not submerged in the water), rinse the probe with deionized water, shake off any excess water, and gently dry the cap with a clean towel. Place the probe back in the BOD bottle.

4. Press the **CALIBRATE** button and then press **READ**. Wait for the meter to stabilize. The meter will calibrate to 100% saturation, adjusted for temperature, altitude and salinity (0 ppt salinity). Press **DONE** to review the calibration, then press **STORE**. Follow the posted chart to find the correct reading based on the temperature, altitude, and salinity table (Exhibit C2.2). The dissolved oxygen reading displayed must be within ± 0.5 mg/L if the theoretical value in the table. If the reading is not within the acceptance limits, then the meter must be calibrated.

5. Record the calibration readings in the Daily Meter Calibration and Standardization Benchsheet.

Corrective Action: If the meter does not calibrate properly, check the probe cap. Gently clean the cap with deionized water and dry with a clean towel. Refer to the instrument manual for instructions on the care and maintenance of the LDO probe. Maintenance activities are recorded following SOP-G9: Instrument Maintenance and Repair.

B. Measurement of Sample DO.

1. Once the meter has been calibrated, submerge the probe in the sample and stir gently. Allow the reading to stabilize and record the value on the appropriate logsheet. Rinse the probe with deionized water prior to measuring the DO of the next sample. Continue reading and recording values for all other samples.

2. Read directly in mg/L and report to the nearest 0.1 mg/L.

Corrective Action: Corrective actions for toxicity samples, which exceed dissolved oxygen tolerance limits for organisms in toxicity tests, are addressed in test specific SOPs.

Safety and Hazardous Waste Management

Safety glasses, gloves and lab coats should always be worn while handling samples. Excess samples may be flushed down the sink.

Review Policy-P6: General Safety Policy and Policy-P9: Radiation Protection Policy for additional safety requirements.

References

Standard Methods for the Examination of Water and Wastewater, 24th Edition, 2023. American Public Health Association, 800 I Street, NW, Washington DC 20001-3710.

- Method: 4500-O H-2021.

TNI Standard. Management and Technical Requirements for Laboratories Performing Environmental Analysis. The NELAC Institute, PO Box 2439, Weatherford, TX 76086.

Instrument Manual

USEPA. October 2002. Methods for Measuring the Acute Toxicity of Effluents and Receiving Waters to Freshwater and Marine Organisms, 5th ed. EPA-821-R-02-012. US Environmental Protection Agency, Cincinnati, OH.

USEPA. October 2002. Short-Term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to Freshwater Organisms, 4th ed. EPA-821-R-02-013. US Environmental Protection Agency, Cincinnati, OH.

USEPA. October 2002. Short-Term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to Marine and Estuarine Organisms, 3rd ed. EPA-821-R-02-014. US Environmental Protection Agency, Cincinnati, OH.

Exhibits

Exhibit C2.1: Daily Meter Calibration and Standardization Benchsheet.
Exhibit C2.2: Solubility of Dissolved Oxygen Table
(Compensation for Temperature, Altitude, and Salinity).

Subject: Dissolved Oxygen (SM 4500-O H-2021)

Exhibit C2.1: Daily Meter Calibration and Standardization Benchsheet.

ETS

Page _____

Daily Meter Calibration and Standardization

Analyst(s) _____ Calibration date _____

Reagent Incubator #1 (Thermometer SN 5030) temperature (°C): _____ (Standards and samples must be warmed to 25.0 ± 1.0°C before taking measurements

Conductivity (SM 2510 B-2021, Meter: Accumet Model AR20, SN 93312452) RL = 14.9 µmhos/cm

Calibration:

Reference standard	True value (µmhos/cm)	Internal Cell Constant
INSS	1000	

Standardization:

Reference standard	True value (TV) (µmhos/cm)	Conductivity corrected to µmhos/cm (C)	% RS = C / TV x 100
INSS	14.9		
INSS	146.9		
INSS	717.5		
INSS	1412		
INSS	2000		
INSS	6667		

Salinity (SM 2520 B-2021, Meter: YSI PRO30, SN 18D104324) RL = 1.0 ppt

Calibration:

Reference standard	Initial Salinity (ppt)	Correction (ppt)	Final Salinity (True value = 25.0) (ppt)
INSS			25.0

Laboratory control standards:

Reference standard	True value (TV) (ppt)	Salinity ppt (C)	% RS = C / TV x 100
INSS	0.71		
INSS	35.0		

Duplicate sample precision:

Sample ID	Conductivity / Salinity corrected to µmhos/cm or ppt	%RPD = ((S - D) /[(S+D)/2]} x 100 (acceptable range = ± 10%)
	S	
Duplicate	D	

Note: The duplicate sample precision should be performed on an effluent or control sample used for a toxicity test.

Dissolved Oxygen (SM 4500-O H-2021, Meter: HACH HQ430d Flexi, SN 250100050330)

Air calibration (based on laboratory DO Saturation table):

Ambient temperature (°C)	DO Saturation (mg/L)	Meter calibration reading (mg/L)	Difference (mg/L) Acceptance Limits = ± 0.5 mg/L

pH (SM 4500-H⁺ B-2021, Meter: Accumet Model AR20, SN 93312452)

Calibration:

	pH 4.00	pH 7.00	Slope (%)
Reference standard number	INR	INR	

Laboratory control standard:

Reference standard	True value (S.U.)	Measured value (S.U.)	Control Limits
INR	10.00		9.90 – 10.10

Duplicate sample precision:

Sample ID	pH S.U.	Acceptable range = ± 0.20 S.U.
	S	
Duplicate	D	

Note: The duplicate sample precision should be performed on an effluent or control sample used for a toxicity test.

SOP C2-Revision 9–Exhibit C2.1, SOP C3-Revision 10–Exhibit C3.1, SOP C4-Revision 9–Exhibit C4.1, SOP C5-Revision 7– Exhibit C5.1

Subject: Dissolved Oxygen (SM 4500-O H-2021)

Exhibit C2.2: Solubility of Dissolved Oxygen Table (Compensation for Temperature, Altitude and Salinity).

Solubility of Dissolved Oxygen (mg/L)
Correction for Temperature, Altitude and Salinity

(SM 4500 O H-2021, Meter: HACH HQ430d Flexi, SN250100050330)

Temperature (°C)	Dissolved Oxygen (mg/L)	
	Freshwater	Saltwater (25 ppt)
17.0	8.99	7.63
17.5	8.90	7.56
18.0	8.81	7.49
18.5	8.72	7.41
19.0	8.63	7.34
19.5	8.54	7.27
20.0	8.45	7.21
20.5	8.37	7.14
21.0	8.30	7.07
21.5	8.21	7.01
22.0	8.13	6.95
22.5	8.05	6.89
23.0	7.98	6.82
23.5	7.91	6.76
24.0	7.83	6.70
24.5	7.76	6.65
25.0	7.68	6.60
25.5	7.61	6.54
26.0	7.54	6.47
26.5	7.48	6.42
27.0	7.41	6.37
27.5	7.35	6.31
28.0	7.28	6.26
28.5	7.22	6.21
29.0	7.15	6.16
29.5	7.09	6.11
30.0	7.03	6.06

Note: Solubility corrected for elevation in Asheville, NC (1984 feet = 707 mm Hg Atmospheric Pressure (946 hPa), 0.93 correction).

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Subject: Hydrogen Ion, pH (SM 4500-H+ B- 2021; SW846 9040C-2004; SW846 9045D-2004)

Approval

Title	Name	Signature	Date
Laboratory Supervisor	Kelley E. Keenan		05-01-24
Quality Assurance Officer	Jim Sumner		05-01-24

Document Revision History

Effective Date	Revision number	Review Type	Evaluators	Revisions
12-01-00	0	Internal	Jim Sumner (ETS)	Original document
09-01-09	1	Internal	Jim Sumner (ETS)	• Updated exhibits during document review. • Corrective action included if LCS exceed acceptance criteria.
06-01-11	2	Internal	Jim Sumner (ETS)	• Updated exhibits during document review.
01-03-12	3	Internal	Kelley E. Keenan Jim Sumner (ETS)	• Provided guidance on SW846 9040C and SW846 9045 D methods. • Updated exhibits during document review.
01-01-13	4	Internal	Jim Sumner (ETS)	• Updated procedure and references to the approved analytical method identified in USEPA Method Update Rule II (MUR II), May 18, 2012.
10-01-17	5	Internal	Jim Sumner (ETS)	• Updated procedure to include NELAP requirements. • Additional guidance included in SOP. • Method number revised based on 2017 MUR.
01-04-19	6	External (SC HDEC) Internal	Haley Anderson (SC DHEC) Jim Sumner (ETS)	• Updated procedure to indicate: Samples must be analyzed within 15 minutes of collection. • Corrected typographical error to indicate: pH measurement procedures of water samples are based on Standard Methods 4500-H+ B-2011.
02-17-20	7	External (TVA) Internal	Rick Sherrard (TVA) Jim Sumner (ETS)	• Updated procedure and benchsheet to include the serial number of the meter used to perform pH. Clarified the temperature requirements of calibration standards.
12-22-20	8	External (SC HDEC) Internal	Haley Anderson (SC DHEC) Jim Sumner (ETS)	• Corrected duplicate acceptance criteria to ± 0.20 S.U.
07-01-21	9	Internal	Jim Sumner (ETS)	• Updated procedure and references to the approved analytical method identified in USEPA Method Update Rule, May 19, 2021.
05-01-24	10	Internal	Jim Sumner (ETS)	• Updated procedure and references to the approved analytical method identified in USEPA Method Update Rule, April 16, 2024.

Subject: Hydrogen Ion, pH (SM 4500-H+ B- 2021; SW846 9040C-2004; SW846 9045D-2004)

Scope and Application

This method is used to measure the pH of water samples used in toxicity tests, wastewater, receiving water, drinking water, liquid/multiphase waste and soil/solid waste.

Summary of Method

The pH of a sample is determined electrometrically using either a glass electrode in combination with a reference potential or a combination electrode. Measurements are recorded to the nearest 0.01 S.U. Wastewater measurements are rounded to the nearest 0.1 S.U.

pH measurement procedures of water samples are based on Standard Methods 4500-H+ B-2021, liquid/multiphase waste samples are based on SW846 9040C-2004 and soil/solid waste samples are based on SW846 9045D-2004

Sample Collection, Preservation, Shipment and Storage

Samples must be analyzed within 15 minutes of collection.

Samples received in the laboratory are stored at 0 to 6.0°C. Samples are warmed to 25.0 ± 1.0°C prior to analysis. Calibration standards are maintained at 25.0 ± 1.0°C.

Quality Control

Calibration: The pH meter must be calibrated each day **before use**. The calibration slope should be 92% to 102%.

Precision: Analyze a **duplicate** with each batch of water, liquid/multiphase waste or soil/ solid waste samples (a batch of samples is considered samples analyzed on the same date). At a minimum, a duplicate must also be performed after every 20 samples. If these results differ by more than ± 0.20 S.U., then the results associated with this duplicate must be reanalyzed. For samples in association with toxicity tests, a duplicate is only performed initially, each day that samples are analyzed.

***Laboratory Control Sample (LCS)*:** An LCS must be analyzed initially to verify the calibration curve and with each batch of samples. At a minimum, an LCS must be performed after every 20 samples and at the end of each batch of samples. The LCS must be ± 0.10 S.U. from the true value. Depending on the pH value of the samples, the final LCS used is dependent on the pH values within the batch and must be in the range of the samples. The final LCS analysis may be 4.00, 7.00, 10.00 or 12.45 S.U. For samples in association with toxicity tests, an LCS is only performed initially, each day that samples are analyzed.

PE: Annually (once every calendar year), a single-blind QC check sample (QCS) or performance evaluation sample (PE) is analyzed. This sample is provided by an approved proficiency testing (PT) provider.

Additional quality control guidance is provided in QAP-Q5.

Interferences

Coatings of oily material or particulate matter can impair electrode response. These coatings can be removed by gently wiping or detergent washing, followed by rinsing with deionized water.

Temperature effects on the electrometric measurement of pH arise from two sources. The first is caused by the change in electrode output at various temperatures. This interference is controlled by calibrating the meter at the same temperature of the samples (25.0 ± 1.0°C). The second source is the change of pH inherent in the sample at various temperatures. This error is sample dependent and cannot be controlled. It is therefore noted by reporting both the pH and temperature at the time of analysis.

Equipment and Materials

Ion analyzer equipped with a pH probe
pH buffers: 4.00, 7.00, 10.00 and 12.45
50-ml beaker
Analytical balance (accurate to 0.0001 g)
Spatula
Conductance and Reagent Incubator #1
Rinse bottle
Deionized water
1-oz Medicine cups
Waste container
Daily Meter Calibration and Standardization Benchsheet
pH Benchsheet

Subject: Hydrogen Ion, pH (SM 4500-H+ B- 2021; SW846 9040C-2004; SW846 9045D-2004)

Procedure (Meters: Accumet AR20, SN 93312452)

A. Calibration

1. Each day before analysis, calibrate the meter. The calibration is recorded on the Daily Meter Calibration and Standardization Benchsheet (Exhibit C3.1). For analytical samples, calibration and sample results are recorded on the pH benchsheet (Exhibit C3.2).

2. Pour the 4.00, 7.00, and 10.00 buffers into 1-oz medicine cups. Record the reference standard numbers for each buffer on the benchsheet.

3. Turn on the pH meter by touching the screen twice.

4. Press the **pH** on the screen.

5. Remove the probe's protective cap and rinse the tip with deionized water. Submerge the tip in the 4.00 buffer and gently agitate the sample with the tip of the probe.

   a. Press **STD** and then **CLEAR** to clear existing standards.
   b. Press **STD** to update or add existing standards.
   c. Once the reading has stabilized the meter will accept the standard.

6. Rinse the probe tip with deionized water and place into the 7.00 buffer and gently agitate the sample with the tip of the probe. Follow the directions as indicated in section A.5.b through c above. Discard the aliquots of buffers after calibration.

7. The meter will indicate if the slope is out of range. If the slope is out of range, recalibrate the meter following steps A.5 and A.6. Record the slope, indicated on the bottom of the screen, on the benchsheet.

8. Rinse the probe tip with deionized water and place in the 10.00 buffer and gently agitate the sample with the tip of the probe. This is the laboratory control standard (LCS). Allow the reading to stabilize; the meter will indicate a stable measurement with a beep.

9. The LCS must be 9.90 to 10.10 S.U. If it is out of range, reanalyze. Record the LCS value on the benchsheet.

10. Once the LCS standard has been analyzed, perform a duplicate on the first unbuffered sample. Measure and record the values on the benchsheet. These results must not differ by more than ± 0.20 S.U. Reanalyze the duplicate if the results differ by more than ± 0.20 S.U.

11. At this time, the meter is ready to measure the pH of samples.

Corrective Action: If the meter does not calibrate properly, gently wipe the probe to remove any oily material and rinse with deionized water. Recalibrate the meter and verify the LCS.

B. Sample Analysis

1. Samples must be warmed to 25.0 ± 1.0°C prior to analysis. Samples may be placed in the Reagent Incubator #1, which is maintained at this temperature, to reach temperature.

2. Analyze the first sample in duplicate by pouring and measuring a second aliquot of the sample, as indicated below. A duplicate must be performed with every 10 samples analyzed.

3. For water samples, pour an aliquot into a 1-oz medicine cup.

4. For liquid multiphase waste samples, pour an aliquot into a labeled 50-ml beaker.

5. For soil/solid waste samples, carefully weigh 20 g of solid waste/soil into a 50-ml glass beaker using a calibrated top-loading balance (SOP-G10). Add 20-mL of deionized water to the beaker and stir the suspension for 5 minutes. Let the suspension settle for 1 hour.

6. Submerge the probe tip in the prepared aliquot and gently agitate the sample with the tip of the probe. The meter will indicate a stable measurement for each sample with a beep. Gently agitate the samples with the tip of the probe until a stable measurement is obtained. Read directly in pH units (S.U.), measure to the nearest 0.01 S.U. and round to the nearest 0.1 S.U. Rinse the probe tip with deionized water between measuring each sample. Record the measurement on the appropriate logsheet.

7. Analyze an LCS at the end of the sample batch and/or at the end of each 10 samples within a batch. The LCS must be within the range of the samples analyzed and either the pH 4.00, 7.00, 10.00 or 12.45 buffer can be used.

8. Turn the meter off after all measurements have been completed, by pressing **MODE** and then **STDBY**.

Corrective Action: Corrective actions for toxicity samples, which exceed pH tolerance limits for organisms in toxicity tests, are addressed in test specific SOPs.

Safety and Hazardous Waste Management

Safety glasses, gloves and lab coats should always be worn while handling samples. Excess samples may be flushed down the sink.

Review Policy-P6: General Safety Policy and Policy-P9: Radiation Protection Policy for additional safety requirements.

References

Standard Methods for the Examination of Water and Wastewater, 24th Edition, 2023. American Public Health Association, 800 I Street, NW, Washington DC 20001-3710.

- Method: 4500-H+ B-2021.

USEPA. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846). On-line. US Environmental Protection Agency, Cincinnati, OH.
ww.epa.gov/osw/hazard/testmethods/sw846/index.html

- Method: 9040C, 2004. Revision 3.
- Method: 9045D, 2004. Revision 4.

TNI Standard. Management and Technical Requirements for Laboratories Performing Environmental Analysis. The NELAC Institute, PO Box 2439, Weatherford, TX 76086.

Instrument Manual

USEPA. October 2002. Methods for Measuring the Acute Toxicity of Effluents and Receiving Waters to Freshwater and Marine Organisms, 5th ed. EPA-821-R-02-012. US Environmental Protection Agency, Cincinnati, OH.

USEPA. October 2002. Short-Term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to Freshwater Organisms, 4th ed. EPA-821-R-02-013. US Environmental Protection Agency, Cincinnati, OH.

USEPA. October 2002. Short-Term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to Marine and Estuarine Organisms, 3rd ed. EPA-821-R-02-014. US Environmental Protection Agency, Cincinnati, OH.

Exhibits

Exhibit C3.1: Daily Meter Calibration and Standardization Benchsheet.
Exhibit C3.2: pH Benchsheet.

Subject: Hydrogen Ion, pH (SM 4500-H+ B- 2021; SW846 9040C-2004; SW846 9045D-2004)

Exhibit C3.1: Daily Meter Calibration and Standardization Benchsheet.

ETS

Page _____

Daily Meter Calibration and Standardization

Analyst(s) _____ Calibration date _____

Reagent Incubator #1 (Thermometer SN 5030) temperature (°C): _____ (Standards and samples must be warmed to 25.0 ± 1.0°C before taking measurements)

Conductivity (SM 2510 B-2021, Meter: Accumet Model AR20, SN 93312452) RL = 14.9 µmhos/cm

Calibration:

Reference standard	True value (µmhos/cm)	Internal Cell Constant
INSS	1000	

Standardization:

Reference standard	True value (TV) (µmhos/cm)	Conductivity corrected to µmhos/cm (C)	% RS = C / TV x 100
INSS	14.9		
INSS	146.9		
INSS	500		
INSS	717.5		
INSS	1412		
INSS	2000		
INSS	6667		

Salinity (SM 2520 B-2021, Meter: YSI PRO30, SN 18D104324) RL = 1.0 ppt

Calibration:

Reference standard	Initial Salinity (ppt)	Correction (ppt)	Final Salinity (True value = 25.0) (ppt)
INSS			25.0

Laboratory control standards:

Reference standard	True value (TV) (ppt)	Salinity ppt (C)	% RS = C / TV x 100
INSS	0.71		
INSS	35.0		

Duplicate sample precision:

Sample ID	Conductivity / Salinity corrected to µmhos/cm or ppt	%RPD = ((S - D) /[(S+D)/2]) x 100 (acceptable range = ± 10%)
	S	
Duplicate	D	

Note: The duplicate sample precision should be performed on an effluent or control sample used for a toxicity test.

Dissolved Oxygen (SM 4500-O G-2021, Meter: YSI Model 52CE, SN 08A100271)

Air calibration:

Ambient temperature (°C)	Initial reading (mg/L)	Correction	Final reading (mg/L)

pH (SM 4500-H+ B-2021, Meter: Accumet Model AR20, SN 93312452)

Calibration:

	pH 4.00	pH 7.00	Slope (%)
Reference standard number	INR	INR	

Laboratory control standard:

Reference standard	True value (S.U.)	Measured value (S.U.)	Control Limits
INR	10.00		9.90 – 10.10

Duplicate sample precision:

Sample ID	pH S.U.	Acceptable range = ± 0.20 S.U.
	S	
Duplicate	D	

Note: The duplicate sample precision should be performed on an effluent or control sample used for a toxicity test.

SOP C2-Revision 8–Exhibit C2.1, SOP C3-Revision 10–Exhibit C3.1, SOP C4-Revision 9–Exhibit C4.1, SOP C5-Revision 7– Exhibit C5.1

Subject: Hydrogen Ion, pH (SM 4500-H+ B- 2021; SW846 9040C-2004; SW846 9045D-2004)

Exhibit C3.2: pH Benchsheet.

Page _____
Page _____ of _____

pH

Meter: Accumet Model AR20, SN 93312452

Sample temperature (°C): _____

Check	
	Matrix: Water **Method: SM 4500 H+ B-2021**
	Matrix: Liquid **Method: SW846 9040C-2004**
	Matrix: Solid **Method: SW846 9045D-2004**

Analyst		**Start time**	
Date analyzed		**End time**	

Calibration:

	pH 4.00	pH 7.00	Slope (%)
Reference standard number	INR	INR	

Laboratory control standard (LCS):

Reference standard number	True value (SU)	Measured value (S.U.) (acceptable range = 9.90 to 10.10 S.U.)
INR	10.00	

Duplicate sample precision:

Sample number	Sample ID	pH (S.U.)	Acceptable range = ± 0.20 S.U.
		S	
	Duplicate	D	

Sample measurements:

Sample number	Sample ID	pH (S.U.)	Comments
INR	LCS, TV =		Acceptable range TV ± 0.10 S.U.

Note: All samples were analyzed in excess of holding time, unless otherwise noted.

Reviewed by _____
Date reviewed _____

SOP C3-Revision 10–Exhibit C3.2

Subject: Specific Conductance, Conductivity (SM 2510 B-2021)

Approval

Title	Name	Signature	Date
Laboratory Supervisor	Kelley E. Keenan		05-01-24
Quality Assurance Officer	Jim Sumner		05-01-24

Document Revision History

Effective Date	Revision number	Review Type	Evaluators	Revisions
12-01-00	0	Internal	Jim Sumner (ETS)	Original document
09-01-09	1	External (TVA, Environmental Standard, Inc.) Internal	William Rogers (TVA) Cynthia Russell (TVA) Rick Sherrard (TVA) Rock Vitale (Environmental Standards, Inc.) Jim Sumner (ETS)	• Updated exhibits during document review. • Corrective action included if LCSs exceed acceptance criteria.
06-01-11	2	Internal	Jim Sumner (ETS)	• Updated exhibits during document review.
01-01-13	3	Internal	Jim Sumner (ETS)	• Updated procedure and references to the approved analytical method identified in USEPA Method Update Rule II (MUR II), May 18, 2012.
10-01-17	4	Internal	Jim Sumner (ETS)	• Updated procedure to include NELAP requirements. • Additional guidance included in SOP. • Method number revised based on 2017 MUR.
01-04-19	5	External (SC HDEC) Internal	Haley Anderson (SC DHEC) Jim Sumner (ETS)	• Clarified procedure to indicate under Standardization that second source standards are used, and these must recover within ± 15% of the true value.
02-17-20	6	External (TVA) Internal	Rick Sherrard (TVA) Jim Sumner (ETS)	• Updated procedure and benchsheet to include the serial number of the meter used to perform conductivity. Clarified the temperature requirements of calibration standards.
12-22-20	7	External (SC HDEC) Internal	Haley Anderson (SC DHEC) Jim Sumner (ETS)	• Second source standard frequency corrected to every 10 samples and at the end of every sample batch.
07-01-21	8	Internal	Jim Sumner (ETS)	• Updated procedure and references to the approved analytical method identified in USEPA Method Update Rule, May 19, 2021.
05-01-24	9	Internal	Jim Sumner (ETS)	• Updated procedure and references to the approved analytical method identified in USEPA Method Update Rule, April 16, 2024.

Subject: Specific Conductance, Conductivity (SM 2510 B-2021)

Scope and Application

This method is used to measure the conductivity of water samples used in toxicity tests, wastewater, receiving water and drinking water.

Summary of Method

The conductivity of a sample is determined with a self-contained conductivity meter.

Conductivity measurement procedures are based on Standard Methods 2510 B-2021.

Sample Collection, Preservation, Shipment and Storage

Samples must be analyzed within **28-days** of collection.

Samples received in the laboratory are stored at 0 to 6.0°C. Samples are warmed to 25.0 ± 1.0°C prior to analysis. Calibration standards are maintained at 25.0 ± 1.0°C.

Quality Control

Calibration: The conductivity meter must be calibrated each day **before use**. The meter is calibrated using a purchased 1000 µmhos/cm standard. This standard is used to determine the internal cell constant of the meter.

Standardization: Second source standards must be analyzed initially to verify the calibration cell constant and must be performed with each batch of samples. At a minimum, a second source standard must be performed after every 10 samples and at the end of each batch of samples. The percent recovery of the second source standard must be ± 15% of the true value. Depending on the conductivity values of the samples, the final second source standard used is dependent on the conductivity values within the batch and must be in the range of the samples. The final second source standard analysis may be 14.9, 146.9, 500, 717.5, 1412, 2000, or 6667 µmhos/cm. For samples in association with toxicity tests, second source standards are only performed initially, each day that samples are analyzed.

Precision: Analyze a **duplicate** with each batch of samples (a batch of samples is considered samples analyzed on the same date). At a minimum, a duplicate must also be performed after every 20 samples. The relative percent difference (%RPD) should be ± 10% or within established limits determined through control charts. If these results differ by more than the established limits, results associated with this duplicate must be qualified (with a footnote in the analytical report) identifying the deviation. For

samples in association with toxicity tests, a duplicate is only performed initially, each day that samples are analyzed.

RL: The lowest standard (14.9 µmhos/cm standard) is set as the Reporting Limit (RL). The %R of the RL must be ± 25%.

ATC: The automatic temperature compensation of the conductivity meter must be verified annually (once every calendar year). This verification determines the upper and lower temperature thresholds that will maintain an LFB within ± 10% of the true value.

PE: Annually (once every calendar year), a single-blind QC check sample (QCS) or performance evaluation sample (PE) is analyzed. This sample is provided by an approved proficiency testing (PT) provider.

Additional quality control guidance is provided in QAP-Q5.

Interferences

Coatings of oily material or particulate matter can impair cell response. These coatings can be removed by gently wiping or detergent washing, followed by rinsing with deionized water

Air bubbles which adhere to the electrode surface can increase the resistance of the sample within the cell and lower the conductivity reading. Unstable signals can be an indication of air bubbles in the measuring cell. Before every measurement (and before every calibration and verification) it should be ensured that there are no air bubbles inside the cell. Remove bubbles by tapping the sensor or alternately raising and lowering the sensor to flush them out.

Temperature will greatly influence the conductivity of a sample. An increase in a sample's temperature will cause a decrease in its viscosity and an increase in the mobility of the ions in solution. An increase in temperature may also cause an increase in the number of ions in solution due to dissociation of molecules. As the conductivity of a solution is dependent on these factors then an increase in the solution's temperature will lead to an increase in its conductivity. This interference is controlled by calibrating the meter at the same temperature of the samples (25.0 ± 1.0^{o}C). Both the conductivity and temperature at the time of analysis are reported.

Subject: Specific Conductance, Conductivity (SM 2510 B-2021)

Equipment and Materials

Ion analyzer equipped with a conductivity probe
Balance (Fisher Scientific ACCU-224, or equivalent)
Certified Weights
Anti-static brush
Forceps
Spatula
Weigh boats
Balance Logbook
Potassium chloride (KCl, reagent grade)
1000-ml volumetric flask
10-ml volumetric pipette
Pipette bulb
100-ml volumetric flask
500 µmhos/cm Conductivity Standard for Calibration (purchased – certified standard)
2000 µmhos/cm Conductivity Standard for Calibration (purchased – certified standard)
14.9 µmhos/cm Conductivity Standard for Standardization (laboratory prepared)
149.6 µmhos/cm Conductivity Standard for Standardization (laboratory prepared)
717.5 µmhos/cm Conductivity Standard for Standardization (laboratory prepared)
1000 µmhos/cm Conductivity Standard for Standardization (purchased – certified standard)
1412 µmhos/cm Conductivity Standard for Standardization (laboratory prepared)
6667 µmhos/cm Conductivity Standard for Standardization (laboratory prepared)
Mercury or red spirit-filled or hand-held thermometer
Nalgene bottles
Rinse bottle
Deionized water
1-oz Medicine cups
Waste container
Daily Meter Calibration and Standardization Benchsheet,
Conductivity Benchsheet

Subject: Specific Conductance, Conductivity (SM 2510 B-2021)

Procedure (Meter: Accumet AR20, SN 93312452)

A. Preparation of Conductivity Standards.

1. Preparation of the **1412** µmhos/cm conductivity standard.

   a. Carefully weigh out 0.7456 g of KCl using a calibrated top-loading balance (SOP-G10).
   b. Place approximately 500 ml of deionized water in a 1000-ml volumetric flask.
   c. Add the KCl to the flask and dissolve the KCl by swirling the flask.
   d. Bring to volume with deionized water.
   e. Pour the standard into clean nalgene bottles.
   f. Using the Stock Standard Log, assign an INSS number for the standard as indicated in SOP-G15.
   g. Label the bottles with the standard concentration, preparation date, analyst's initials, and the INSS number.

2. Preparation of the **14.9** µmhos/cm conductivity standard.

   a. Using a 10-ml volumetric pipette, carefully pipette 10 ml of the 1412 µmhos/cm standard into approximately 500 ml of deionized water in a 1000-ml volumetric flask.
   b. Mix the solution by swirling the flask
   c. Bring to volume with deionized water.
   d. Follow steps A.1.e through f as indicated above.

3. Preparation of the **146.9** µmhos/cm conductivity standard.

   a. Using a 100-ml volumetric flask, carefully measure 100 ml of the 1412 µmhos/cm standard and pour into approximately 500 ml of deionized water in a 1000-ml volumetric flask.
   b. Mix the solution by swirling the flask
   c. Bring to volume with deionized water.
   d. Follow steps A.1.e through f as indicated above.

4. Preparation of the **717.5** µmhos/cm conductivity standard.

   a. Carefully weigh out 0.3728 g of KCl using a calibrated top-loading balance (SOP-G10).
   b. Place approximately 500 ml of deionized water in a 1000-ml volumetric flask.

c. Add the KCl to the flask and dissolve the KCl by swirling the flask.
d. Bring to volume with deionized water.
e. Follow steps A.1.e through f as indicated above.

5. Preparation of the **6667** µmhos/cm conductivity standard.

a. Carefully weigh out 3.7280 g of KCl using a calibrated top-loading balance (SOP-G10).
b. Place approximately 500 ml of deionized water in a 1000-ml volumetric flask.
c. Add the KCl to the flask and dissolve the KCl by swirling the flask.
d. Bring to volume with deionized water.
e. Follow steps A.1.e through f as indicated above.

Note: The expiration date of the laboratory prepared conductivity standards is 1-year from the preparation date.

6. **500**, **1000**, and **2000** µmhos/cm conductivity standards are purchased from an approved supplier.

Note: The expiration date of the purchased certified conductivity standards is according to the manufacturer's specifications.

B. Meter Calibration and Standardization.

Note: All standards and samples must be warmed to 25.0 ± 1.0°C prior to measuring conductivity.

1. Prepare the Daily Meter Calibration and Standardization Benchsheet (Exhibit C4.1).

2. Each time before analysis, standardize the meter.

3. **Conductivity Calibration and Measurement.**

a. Pour the 1000, 14.9, 146.9, 500, 717.5, 1412, 2000, and 6667 µmhos/cm standards into 1-oz medicine cups. Record the reference standard numbers on the benchsheet.
b. Plug the low-level conductivity probe (13-620-160) into the **Conductivity 2 Cell** connection on back of the meter.
c. Turn on the meter by touching the screen twice.
d. Press the **COND** for the correct probe connection.

e. Remove the probe from the beaker containing deionized water and rinse the tip with deionized water. Submerge the tip in the 1000 µmhos/cm standard and gently agitate the sample with the tip of the probe.
f. Press **STD** and then **CLEAR** to clear existing standards.
g. Press **STD** to update or add existing standards.
h. Once the reading has stabilized the meter will prompt to enter the true value. Press **1000** and then **ENTER**.
i. The meter will indicate if the cell constant is out of range. If the cell constant is out of range, recalibrate the meter following steps 3.e through h. Record the cell constant (**Cell K**), indicated on the bottom of the screen, on the benchsheet.
j. Rinse the probe with deionized water and place into the 14.9 µmhos/cm standard and gently agitate the sample with the tip of the probe. This standard measurement is the reporting limit (RL) and should be ± 25% of the true value. Allow the reading to stabilize and record the measurement on the benchsheet. If the measurement is out of range, reanalyze.
k. Rinse the probe with deionized water and place in the 146.9 µmhos/cm standard. Gently agitate the sample with the tip of the probe until a stable measurement is obtained. This standard measurement is one of the laboratory-fortified blanks (LFB) and should be ± 10% of the true value. Allow the reading to stabilize and record the measurement on the benchsheet. If the measurement is out of range, reanalyze.
l. Repeat step 3.k with the 500, 717.5, 1412, 2000 and 6667 µmhos/cm standards. Discard each aliquot of standard after use.
m. Once all of the LFB standards have been analyzed, the meter is ready to measure the conductivity of samples.
n. Rinse the probe with deionized water and place in the sample. Gently agitate the sample with the tip of the probe until a stable measurement is obtained. Record the measurement of the sample.
o. Continue measuring and recording the conductivity of the samples. Gently agitate the samples with the tip of the probe and rinse the probe with deionized water between samples.
p. Turn the meter off after all measurements have been completed, by pressing **MODE** and then **STDBY**.

C. Calculation of Conductivity.

1. Read in µmhos/cm and report to 2 significant figures.

2. µS is the equivalent of µmhos/cm. To calculate µmhos/cm from MS, multiply the value by 1000.

D. Precision and Accuracy, Calculations.

1. Standard determination,
True value = 14.9, 146.9, 500, 717.5, 1412, 2000 or 6667 µmhos/cm.

Percent Recovery of the Standard (%RS)
%RS = (Measured value) / (True value) x 100

2. Duplicate acceptance (as indicated below) or determined through control charts.

Relative Percent Difference (%RPD)
%RPD = (Sample value – Duplicate value) / [(Sample value + Duplicate value)/2] x 100

Safety and Hazardous Waste Management

Safety glasses, gloves and lab coats should always be worn while handling samples. Excess samples may be flushed down the sink.

Review Policy-P6: General Safety Policy and Policy-P9: Radiation Protection Policy for additional safety requirements.

References

Standard Methods for the Examination of Water and Wastewater, 24th Edition, 2023. American Public Health Association, 800 I Street, NW, Washington DC 20001-3710.

- Method: 2510 B-2021.

TNI Standard. Management and Technical Requirements for Laboratories Performing Environmental Analysis. The NELAC Institute, PO Box 2439, Weatherford, TX 76086.

Instrument Manual

Exhibits

Exhibit C4.1: Daily Meter Calibration and Standardization Benchsheet.
Exhibit C4.2: Conductivity Benchsheet.

Subject: Specific Conductance, Conductivity (SM 2510 B-2021)

Exhibit C4.1: Daily Meter Calibration and Standardization Benchsheet.

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Daily Meter Calibration and Standardization

Analyst(s) _____ Calibration date _____

Reagent Incubator #1 (Thermometer SN 5030) temperature (°C): _____ (Standards and samples must be warmed to 25.0 ± 1.0°C before taking measurements)

Conductivity (SM 2510 B-2021, Meter: Accumet Model AR20, SN 93312452) RL = 14.9 µmhos/cm

Calibration:

Reference standard	True value (µmhos/cm)	Internal Cell Constant
INSS	1000	

Standardization:

Reference standard	True value (TV) (µmhos/cm)	Conductivity corrected to µmhos/cm (C)	% RS = C / TV x 100
INSS	14.9		
INSS	146.9		
INSS	500		
INSS	717.5		
INSS	1412		
INSS	2000		
INSS	6667		

Salinity (SM 2520 B-2021, Meter: YSI PRO30, SN 18D104324) RL = 1.0 ppt

Calibration:

Reference standard	Initial Salinity (ppt)	Correction (ppt)	Final Salinity (True value = 25.0) (ppt)
INSS			25.0

Laboratory control standards:

Reference standard	True value (TV) (ppt)	Salinity ppt (C)	% RS = C / TV x 100
INSS	0.71		
INSS	35.0		

Duplicate sample precision:

Sample ID	Conductivity / Salinity corrected to µmhos/cm or ppt	%RPD = {(S - D) / [(S+D)/2]} x 100 (acceptable range = ± 10%)
	S	
Duplicate	D	

Note: The duplicate sample precision should be performed on an effluent or control sample used for a toxicity test.

Dissolved Oxygen (SM 4500-O G-2021, Meter: YSI Model 52CE, SN 08A100271)

Air calibration:

Ambient temperature (°C)	Initial reading (mg/L)	Correction	Final reading (mg/L)

pH (SM 4500-H⁺ B-2021, Meter: Accumet Model AR20, SN 93312452)

Calibration:

	pH 4.00	pH 7.00	Slope (%)
Reference standard number	INR	INR	

Laboratory control standard:

Reference standard	True value (S.U.)	Measured value (S.U.)	Control Limits
INR	10.00		9.90 – 10.10

Duplicate sample precision:

Sample ID	pH S.U.	Acceptable range = ± 0.20 S.U.
	S	
Duplicate	D	

Note: The duplicate sample precision should be performed on an effluent or control sample used for a toxicity test.

SOP C3-Revision 8-Exhibit C2.1, SOP C3-Revision 10-Exhibit C3.1, SOP C4-Revision 9-Exhibit C4.1, SOP C5-Revision 7- Exhibit C5.1

Subject: Specific Conductance, Conductivity (SM 2510 B-2021)

Exhibit C4.2: Conductivity Benchsheet.

ETS

Page _____
Page _____ of _____

Conductivity (SM 2510 B-2021, Meter: Accumet Model AR20, SN 93312452)

RL = 14.9 µmhos/cm

Analyst _____ Reviewed by _____
Date analyzed _____ Date reviewed _____

Sample temperature (°C): _____ (Samples must be warmed to 25.0 ± 2.0°C before taking conductivity measurements.)

Calibration:

Reference standard	True value (µmhos/cm)	Internal Cell Constant
INSS	1000	

Standardization:

Reference standard	True value (TV) (µmhos/cm)	Conductivity corrected to µmhos/cm (C)	% RS = C / TV x 100
INSS	14.9		
INSS	146.9		
INSS	500		
INSS	717.5		
INSS	1412		
INSS	2000		
INSS	6667		

Duplicate sample precision:

Sample number	Sample ID	Conductivity corrected to µmhos/cm	%RPD = {(S - D) /[(S+D)/2]} x 100 (acceptable range = ± 10%)
		S	
	Duplicate	D	

Sample measurements:

Sample number	Sample ID	Conductivity corrected to µmhos/cm	Reported conductivity (µmhos/cm)
TV = ND	Blank – Deionized water		

Standardization:

Reference standard	True value (TV) (µmhos/cm)	Conductivity corrected to µmhos/cm (C)	% RS = C / TV x 100
INSS			

SOP C4-Revision 9 Exhibit C4.2

Subject: Salinity (SM 2520 B-2021)

Approval

Title	Name	Signature	Date
Laboratory Supervisor	Kelley E. Keenan		05-01-24
Quality Assurance Officer	Jim Sumner		05-01-24

Document Revision History

Effective Date	Revision number	Review Type	Evaluators	Revisions
12-01-00	0	Internal	Jim Sumner (ETS)	Original document
09-01-09	1	External (TVA, Environmental Standard, Inc.) Internal	William Rogers (TVA) Cynthia Russell (TVA) Rick Sherrard (TVA) Rock Vitale (Environmental Standards, Inc.) Jim Sumner (ETS)	• Updated exhibits during document review. • Corrective action included if LFBs exceed acceptance criteria.
06-01-11	2	Internal	Jim Sumner (ETS)	• Updated exhibits during document review.
01-01-13	3	Internal	Jim Sumner (ETS)	• Updated procedure and references to the approved analytical method identified in USEPA Method Update Rule II (MUR II), May 18, 2012.
10-01-17	4	Internal	Jim Sumner (ETS)	• Updated procedure to include NELAP requirements. • Additional guidance included in SOP. • Method number revised based on 2017 MUR.
02-17-20	5	External (TVA) Internal	Rick Sherrard (TVA) Jim Sumner (ETS)	• Updated procedure and benchsheet to include the serial number of the meter used to perform salinity. Clarified the temperature requirements of calibration standards.
07-01-21	6	Internal	Jim Sumner (ETS)	• Updated procedure and references to the approved analytical method identified in USEPA Method Update Rule, May 19, 2021.
05-01-24	7	Internal	Jim Sumner (ETS) Jaydon Perez (ETS)	• Updated procedure and references to the approved analytical method identified in USEPA Method Update Rule, April 16, 2024. • Changed the upper operational range to 70 ppt. • Changed salinity meter procedure for using the YSI Pro 30.

Subject: Salinity (SM 2520 B-2021)

Scope and Application

This method is used to measure the salinity of water samples used in toxicity tests, wastewater, receiving water and drinking water.

Summary of Method

The salinity of a sample is determined with a self-contained salinity meter.

Salinity measurement procedures are based on Standard Methods 2520 B-2021.

Sample Collection, Preservation, Shipment and Storage

Samples must be analyzed within **28-days** of collection.

Samples received in the laboratory are stored at 0 to 6.0°C. Samples are warmed to 25.0 ± 1.0°C prior to analysis. Calibration standards are maintained at 25.0 ± 1.0°C.

Quality Control

Calibration: The salinity meter must be calibrated each day **before use**. The meter is calibrated using a laboratory prepared 25 ppt standard.

Precision: Analyze a **duplicate** with each batch of samples (a batch of samples is considered samples analyzed on the same date). At a minimum, a duplicate must also be performed after every 20 samples. The relative percent difference (%RPD) should be ± 10% or within established limits determined through control charts. If these results differ by more than the established limits, results associated with this duplicate must be qualified (with a footnote in the analytical report) identifying the deviation. For samples in association with toxicity tests, a duplicate is only performed initially, each day that samples are analyzed.

Laboratory Fortified Blank (LFB, referred to LCS on benchsheets): An LFB must be analyzed initially to verify the calibration cell constant and must be performed with each batch of samples. At a minimum, an LFB must be performed after every 20 samples and at the end of each batch of samples. The percent recovery of the LFB (%R) must be ± 25% for the 0.71 ppt standard and ± 10% for the 35 ppt standard. For samples in association with toxicity tests, the LFB is only performed initially, each day that samples are analyzed.

Subject: Salinity (SM 2520 B-2021)

Operational Range: The operational range of the salinity meter is 1 ppt to 70 ppt. Measurements less than 1 ppt and greater than 70 ppt are displayed as ***UR*** and ***OR***, respectively, on the salinity meter.

RL: The lower operational range (1 ppt) is set as the Reporting Limit (RL).

ATC: The automatic temperature compensation of the salinity meter must be verified annually (once every calendar year). This verification determines the upper and lower temperature thresholds that will maintain the LFB within ± 10% of the true value.

PE: A single-blind QC check sample (QCS) or performance evaluation (PE) is not available by an approved proficiency testing (PT) provider.

Additional quality control guidance is provided in QAP-Q5.

Interferences

Coatings of oily material or particulate matter can impair cell response. These coatings can be removed by gently wiping or detergent washing, followed by rinsing with deionized water.

Air bubbles which adhere to the electrode surface can increase the resistance of the sample within the cell and lower the salinity reading. Unstable signals can be an indication of air bubbles in the measuring cell. Before every measurement (and every calibration and verification) it should be ensured that there are no air bubbles inside the cell. Remove bubbles by tapping the sensor or alternately raising and lowering the sensor to flush them out.

Temperature will greatly influence the salinity of a sample. An increase in a sample's temperature will cause a decrease in its viscosity and an increase in the mobility of the ions in solution. An increase in temperature may also cause an increase in the number of ions in solution due to dissociation of molecules. As the salinity of a solution is dependent on these factors then an increase in the solution's temperature will lead to an increase in its salinity. This interference is controlled by calibrating the meter at the same temperature of the samples (25.0 ± 1.0^{o}C). Both the salinity and temperature at the time of analysis are reported.

Subject: Salinity (SM 2520 B-2021)

Equipment and Materials

YSI Pro 30 Salinity Meter (Professional Series)
Balance (Fisher Scientific ACCU-224, or equivalent)
Certified weights
Anti-static brush
Forceps
Spatula
Weigh boats
Balance logbook
Potassium chloride (KCl, reagent grade)
Sodium chloride (NaCl, reagent grade)
1000-ml volumetric flask
Pipette bulb
25 ppt Salinity standard for calibration
0.71 and 35 ppt Salinity standards for standardization
Rinse bottle
Deionized water
Salt synthetic water
100-mL plastic bottles
Waste container
Daily Meter Calibration and Standardization Benchsheet

Procedure (Meter: YSI Pro 30 Salinity Meter, Professional series)

A. Preparation of Salinity Standards.

1. Preparation of the **25.0** ppt salinity calibration standard.

   a. Carefully weigh out 23.0 g of NaCl using a calibrated top-loading balance (SOP-G10).
   b. Place approximately 500 ml of deionized water in a 1000-ml volumetric flask.
   c. Add the NaCl to the flask and dissolve the NaCl by swirling the flask.
   d. Bring to volume with deionized water.
   e. Pour the standard into clean nalgene bottles.
   f. Using the Stock Standard Log, assign an INSS number for the standard as indicated in SOP-G15.
   g. Label the bottles with the standard concentration, preparation date, analyst's initials, and the INSS number.

2. Preparation of the **0.71** ppt salinity standard.

   a. Carefully weigh out 0.7455 g of KCl using a calibrated top-loading balance (SOP-G10).
   b. Place approximately 500 ml of deionized water in a 1000-ml volumetric flask.
   c. Add the KCl to the flask and dissolve the KCl by swirling the flask.
   d. Bring to volume with deionized water.
   e. Pour the standard into clean nalgene bottles.
   f. Using the Stock Standard Log, assign an INSS number for the standard as indicated in SOP-G15.
   g. Label the bottles with the standard concentration, preparation date, analyst's initials, and the INSS number.

3. Preparation of the **35.0** ppt salinity standard.

   a. Carefully weigh out 32.4356 g of KCl using a calibrated top-loading balance (SOP-G10).
   b. Place approximately 500 ml of deionized water in a 1000-ml volumetric flask.
   c. Add the KCl to the flask and dissolve the KCl by swirling the flask.
   d. Bring to volume with deionized water.
   e. Pour the standard into clean nalgene bottles.
   f. Using the Stock Standard Log, assign an INSS number for the standard as indicated in SOP-G15.
   g. Label the bottles with the standard concentration, preparation date, analyst's initials, and the INSS number.

Note: The expiration date of the laboratory prepared standards is 1-year from the preparation date.

B. Meter Calibration and Standardization.

Note: All standards and samples must be warmed to 25.0 ± 1.0°C prior to measuring salinity.

1. Prepare the Daily Meter Calibration and Standardization Benchsheet (Exhibit C5.1).

2. Each time before analysis, calibrate the meter.

3. **Salinity is measured by the YSI Pro 30 Salinity Meter. The meter internally converts measurements to salinity in ppt.**

a. Pour the 25.0 ppt, 0.71 ppt and 35.0 ppt standards into 100-mL plastic bottles. Record the reference standard numbers on the benchsheet.
b. Turn on the meter by pressing and holding the **Power** button.
c. Rinse the tip of the probe with deionized water and carefully shake excess water off the probe. Submerge the tip in the 25.0 ppt standard and gently agitate the sample with the tip of the probe.
d. Press and hold **Cal** to calibrate the meter.
e. Select **Salinity** using the ▲ ▼ buttons. Press **ENTER.**
f. Once the reading has stabilized adjust the measurement to **25.0** using the ▲ ▼ buttons. Press **ENTER** to accept this measurement. Record the initial measurement and the amount the measurement was adjusted on the benchsheet.
g. Remove the probe from the 25.0 ppt standard, rinse the tip with deionized water and carefully shake excess water off the probe. Submerge the probe tip in the 0.71 ppt standard and gently agitate the sample with the tip of the probe. This standard measurement is the laboratory-fortified blank (LFB) and should be ± 25% of the true value. Allow the reading to stabilize and record the measurement on the benchsheet. If the measurement is out of range, reanalyze.
h. Remove the probe from the 0.71 ppt standard, rinse the tip with deionized water and carefully shake excess water off the probe. Submerge the probe tip in the 35.0 ppt standard and gently agitate the sample with the tip of the probe. This standard measurement is the laboratory-fortified blank (LFB) and should be ± 10% of the true value. Allow the reading to stabilize and record the measurement on the benchsheet. If the measurement is out of range, reanalyze.
i. Once the LFBs have been analyzed, the meter is ready to measure the salinity of samples.
j. Rinse the probe with deionized water, carefully shake excess water off the probe and place in the sample. Gently agitate the sample with the tip of the probe until a stable measurement is obtained. Record the measurement of the sample.
k. Continue measuring and recording the salinity of the samples. Gently agitate the samples with the tip of the probe, rinse the probe with deionized water and carefully shake excess water off the probe between samples.
l. Turn the meter off after all measurements have been completed, by pressing and holding **Power** button.

C. Calculation of Salinity.

1. Read in ppt and report to 2 significant figures.

D. Precision and Accuracy, Calculations.

1. Laboratory fortified blank (LFB) determination, True value = 0.71 or 35.0 ppt.

   Percent Recovery of the Standard (%RS)
   %RS = (Measured value) / (True value) x 100

2. Duplicate acceptance.

   Relative Percent Difference (%RPD)
   %RPD = (Sample value – Duplicate value) / [(Sample value + Duplicate value)/2] x 100

Safety and Hazardous Waste Management

Safety glasses, gloves and lab coats should always be worn while handling samples. Excess samples may be flushed down the sink.

Review Policy-P6: General Safety Policy and Policy-P9: Radiation Protection Policy for additional safety requirements.

References

Standard Methods for the Examination of Water and Wastewater, 24th Edition, 2023. American Public Health Association, 800 I Street, NW, Washington DC 20001-3710.

- Method: 2520 B-2021.

TNI Standard. Management and Technical Requirements for Laboratories Performing Environmental Analysis. The NELAC Institute, PO Box 2439, Weatherford, TX 76086.

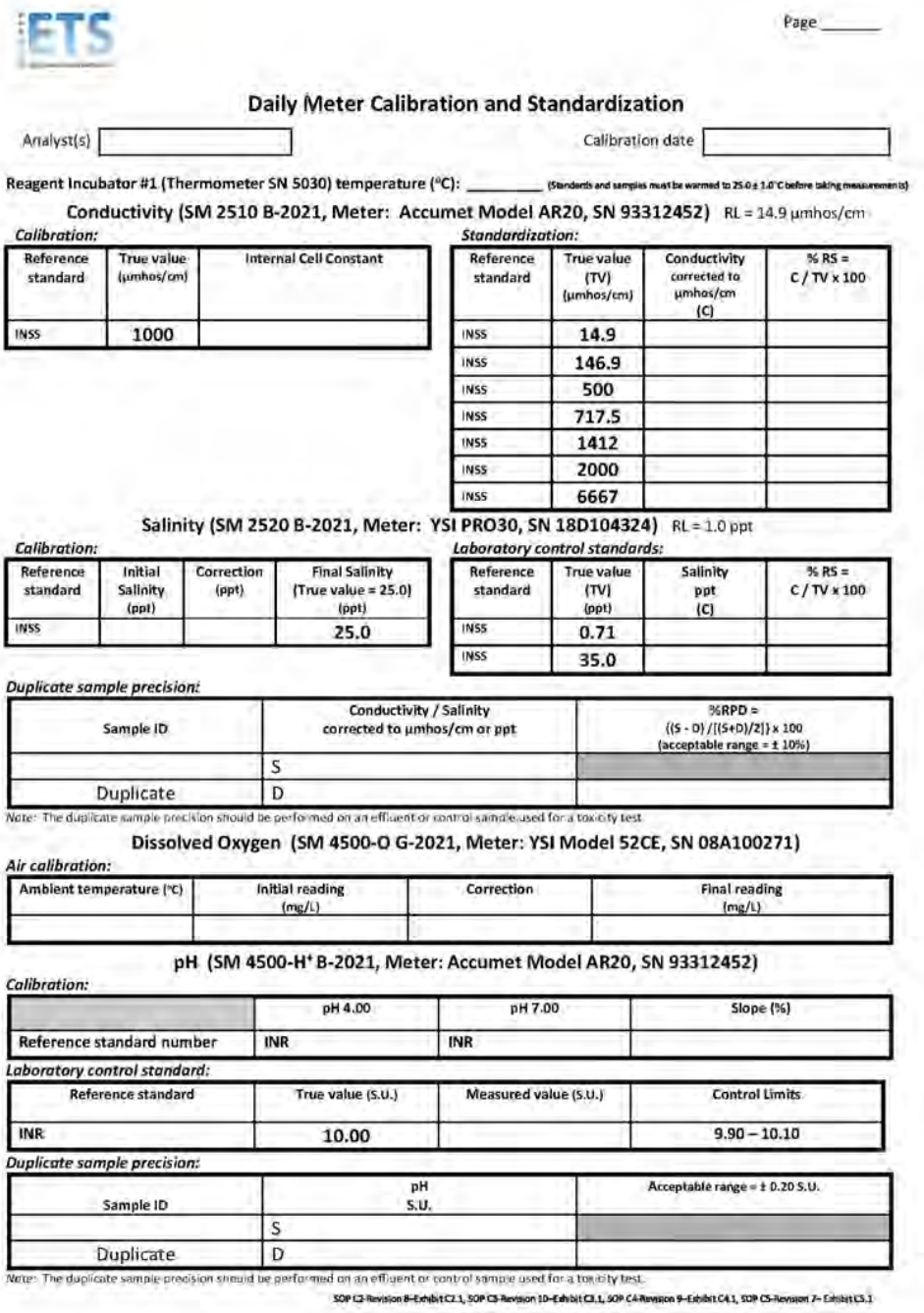
Instrument Manual

Exhibits

Exhibit C5.1: Daily Meter Calibration and Standardization Benchsheet.
Exhibit C5.2: Salinity Benchsheet.

Subject: Salinity (SM 2520 B-2021)

Exhibit C5.1: Daily Meter Calibration and Standardization Benchsheet.



ETS

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Daily Meter Calibration and Standardization

Analyst(s) _____ Calibration date _____

Reagent Incubator #1 (Thermometer SN 5030) temperature (°C): _____ (Standards and samples must be warmed to 25.0 ± 1.0°C before taking measurements)

Conductivity (SM 2510 B-2021, Meter: Accumet Model AR20, SN 93312452) RL = 14.9 µmhos/cm

Calibration:

Reference standard	True value (µmhos/cm)	Internal Cell Constant
INSS	1000	

Standardization:

Reference standard	True value (TV) (µmhos/cm)	Conductivity corrected to µmhos/cm (C)	% RS = C / TV x 100
INSS	14.9		
INSS	146.9		
INSS	500		
INSS	717.5		
INSS	1412		
INSS	2000		
INSS	6667		

Salinity (SM 2520 B-2021, Meter: YSI PRO30, SN 18D104324) RL = 1.0 ppt

Calibration:

Reference standard	Initial Salinity (ppt)	Correction (ppt)	Final Salinity (True value = 25.0) (ppt)
INSS			25.0

Laboratory control standards:

Reference standard	True value (TV) (ppt)	Salinity ppt (C)	% RS = C / TV x 100
INSS	0.71		
INSS	35.0		

Duplicate sample precision:

Sample ID	Conductivity / Salinity corrected to µmhos/cm or ppt	%RPD = ((S - D) / [(S+D)/2]) x 100 (acceptable range = ± 10%)
	S	
Duplicate	D	

Note: The duplicate sample precision should be performed on an effluent or control sample used for a toxicity test.

Dissolved Oxygen (SM 4500-O G-2021, Meter: YSI Model 52CE, SN 08A100271)

Air calibration:

Ambient temperature (°C)	Initial reading (mg/L)	Correction	Final reading (mg/L)

pH (SM 4500-H⁺ B-2021, Meter: Accumet Model AR20, SN 93312452)

Calibration:

	pH 4.00	pH 7.00	Slope (%)
Reference standard number	INR	INR	

Laboratory control standard:

Reference standard	True value (S.U.)	Measured value (S.U.)	Control Limits
INR	10.00		9.90 – 10.10

Duplicate sample precision:

Sample ID	pH S.U.	Acceptable range = ± 0.20 S.U.
	S	
Duplicate	D	

Note: The duplicate sample precision should be performed on an effluent or control sample used for a toxicity test.

SOP C2-Revision 8-Exhibit C2.1, SOP C3-Revision 10-Exhibit C3.1, SOP C4-Revision 9-Exhibit C4.1, SOP C5-Revision 7- Exhibit C5.1

Subject: Salinity (SM 2520 B-2021)

Exhibit C5.2: Salinity Benchsheet.

Page _____
Page _____ of _____

Salinity (SM 2520 B-2021, Meter: YSI PRO30, SN 18D104324)
RL = 1.0 ppt

Analyst		Reviewed by	
Date analyzed		Date reviewed	

Sample temperature (°C): _____ (Samples must be warmed to 25.0 ± 1.0°C before taking salinity measurements.)

Calibration

Reference standard	Initial Salinity (ppt)	Correction (ppt)	Final Salinity (True value = 25.0) (ppt)
INSS			25.0

Laboratory control standard (LCS)

Reference standard	True value (TV) (ppt)	Salinity ppt (C)	% RS = C / TV x 100
INSS	0.71		
INSS	35.0		

Duplicate sample precision:

Sample ID	Salinity (ppt)	%RPD = [(S - D) / [(S+D)/2]] x 100 (acceptable range = ± 10%)
	S	
Duplicate	D	

Sample measurements:

Sample number	Sample ID	Salinity (ppt)	Reported Salinity (ppt)
TV = ND	Blank – Deionized Water		

Laboratory control standard (LCS)

Reference standard	True value (TV) (ppt)	Salinity (ppt) (C)	% RS = C / TV x 100
INSS	0.71 or 35.0		

SOP C5-Revision 7– Exhibit C5.2

Subject: Alkalinity (SM 2320 B-2021)

Approval

Title	Name	Signature	Date
Laboratory Supervisor	Kelley E. Keenan		05-01-24
Quality Assurance Officer	Jim Sumner		05-01-24

Document Revision History

Effective Date	Revision number	Review Type	Evaluators	Revisions
12-01-00	0	Internal	Jim Sumner (ETS)	Original document
09-01-09	1	External (TVA, Environmental Standard, Inc.) Internal	William Rogers (TVA) Cynthia Russell (TVA) Rick Sherrard (TVA) Rock Vitale (Environmental Standards, Inc.) Jim Sumner (ETS)	• Updated exhibits during document review. • Corrective action included if LFBs exceed acceptance criteria.
06-01-11	2	Internal	Jim Sumner (ETS)	• Updated exhibits during document review.
01-01-13	3	Internal	Jim Sumner (ETS)	• Updated procedure and references to the approved analytical method identified in USEPA Method Update Rule II (MUR II), May 18, 2012.
10-01-17	4	Internal	Jim Sumner (ETS)	• Updated procedure to include NELAP requirements. • Additional guidance included in SOP. • Method number revised based on 2017 MUR. • Increased RL to 5.0 mg/L $CaCO_3$. • Changed QCs performed to reflect SM requirements.
02-17-20	5	External (TVA) Internal	Rick Sherrard (TVA) Jim Sumner (ETS)	• Updated procedure and benchsheet to include the serial number of the meter used to perform pH. Clarified the temperature requirements of calibration standards.
07-01-21	6	Internal	Jim Sumner (ETS)	• Updated procedure and references to the approved analytical method identified in USEPA Method Update Rule, May 19, 2021.
05-01-24	7	Internal	Jim Sumner (ETS)	• Updated procedure and references to the approved analytical method identified in USEPA Method Update Rule, April 16, 2024.

Subject: Alkalinity (SM 2320 B-2021)

Scope and Application

This method is used to measure the alkalinity of water samples used in toxicity tests, wastewater, receiving water and drinking water. Since this analysis is currently only used in support of toxicity tests, the extrapolation technique is not used for the determination of low alkalinity samples (< 20 mg/L $CaCO_3$).

Summary of Method

The alkalinity of a sample is determined by titration to an electrometrically determined endpoint of pH 4.5 S.U.

Alkalinity measurement procedures are based on Standard Methods 2320 B-2021.

Sample Collection, Preservation, Shipment and Storage

Samples must be analyzed within **14-days** of collection.

Samples received in the laboratory are stored at 0 to 6.0°C. Samples are warmed to 25.0 ± 1.0°C prior to analysis. Calibration standards are maintained at 25.0 ± 1.0°C.

Quality Control

Calibration: The pH meter must be calibrated each day **before use**. The calibration slope should be 92% to 102%.

Standardization: Verify the **normality** of titrant reagents by re-standardizing at least monthly. If the titration reagent's normality (titer value) has changed, then use the measured value, adjust the normality (titer value) as the procedure describes.

Precision: Analyze a **duplicate** with each batch of samples (a batch of samples is considered samples analyzed on the same date). At a minimum, a duplicate must also be performed after every 20 samples. The relative percent difference (%RPD) should be ± 10% or within established limits determined through control charts. If these results differ by more than the established limits, results associated with this duplicate must be qualified (with a footnote in the analytical report) identifying the deviation.

Laboratory Fortified Blank (LFB, referred to LCS on benchsheet): A LFB must be analyzed initially and must be performed with each batch of samples. At a minimum, an LFB must be performed after every

20 samples and at the end of each batch of samples. The percent recovery of the LFB (%R) must be ± 10% from the true value.

Method Blank (MB): An MB must be analyzed initially and must be performed with each batch samples (a batch of samples is considered samples analyzed on the same date). In addition, a MB must be performed after every 20 samples. The MB must be ≤ one half the reporting limit (RL).

Reporting Limit (RL): The RL for alkalinity is 5.0 mg/L.

PE: Annually (once every calendar year), a single-blind QC check sample (QCS) or performance evaluation sample (PE) is analyzed. This sample is provided by an approved proficiency testing (PT) provider.

Additional quality control guidance is provided in QAP-Q5.

Interferences

Coatings of oily material or particulate matter can impair electrode response. These coatings can be removed by gently wiping or detergent washing, followed by rinsing with deionized water.

Temperature effects on the electrometric measurement of pH arise from two sources. The first is caused from by the change in electrode output at various temperatures. This interference is controlled by calibrating the meter at the same temperature of the samples (25.0 ± 1.0°C). The second source is the change of pH inherent in the sample at various temperatures. This error is sample dependent and cannot be controlled.

The addition of excessive titrant (> 15 mL) due to high alkalinity in a sample can interfere with sample analysis. Based on prior sample history, samples may be diluted to prevent excessive titrant volume. Samples in support of toxicity tests from saltwater dischargers commonly have alkalinity in excess of 1000 mg/L $CaCO_3$. If a sluggish pH response is noted, interferences may be present, and the samples should not be diluted.

Subject: Alkalinity (SM 2320 B-2021)

Equipment and Materials

50-mL burette and burette stand with clamps
Ion analyzer equipped with a pH probe
150-mL beakers
Stir bars
Stir plate
100-mL graduated cylinder
5-mL serological pipettes
10-mL serological pipettes
Pipette bulb
Rinse bottle
Waste container
pH buffer 4.00 for standardization
pH buffer 7.00 for standardization
pH buffer 10.00 for the Laboratory Control Standard (LCS)
Deionized water
0.020N Sulfuric Acid (H_2SO_4) titrant (Specifications: 0.0200 ± 0.00005 N at 20°C)
0.1N Sodium Carbonate (Na_2CO_3) normality check standard (Specifications: 0.1000 ± 0.0001 N at 20°C)
0.02N Sodium Carbonate (Na_2CO_3) laboratory fortified blank standard (LFB) and spike standard (Specifications: 0.0200 ± 0.00005 N at 20°C)
Alkalinity Benchsheet

Procedure

A. Preparation of Alkalinity Titrant and Standards.

1. Preparation of 0.020 N Sulfuric Acid (H_2SO_4) **(titrant)**.

   a. Place approximately 500 ml of deionized water in a 1000-ml volumetric flask.
   b. Add 555.6 µL concentrated H_2SO_4 to the flask and bring to volume with deionized water.
   c. Pour the titrant into clean plastic bottles.
   d. Using the Reagent Log, assign an INR number for the titrant as indicated in SOP-G15.
   e. Label the bottles with the titrant concentration, preparation date, analyst's initials, and the INR number.
   f. Pour the standard into clean plastic bottles.

2. Preparation of 0.1N Sodium Carbonate (Na_2CO_3) **(normality check standard)**.

   a. Carefully weigh out 5.3000 g of Na_2CO_3 (dried overnight at 105°C and stored in a desiccator) using a calibrated top-loading balance (SOP-G10).
   b. Place approximately 500 ml of deionized water in a 1000-ml volumetric flask.
   c. Add the Na_2CO_3 to the flask and dissolve the Na_2CO_3 by swirling the flask.
   d. Bring to volume with deionized water.
   e. Pour the standard into clean plastic bottles.
   f. Using the Stock Standard Log, assign an INSS number for the standard as indicated in SOP-G15.
   g. Label the bottles with the standard concentration, preparation date, analyst's initials, and the INSS number.

3. Preparation of 0.020N Sodium Carbonate (Na_2CO_3) **(laboratory fortified blank standard)**.

   a. Carefully weigh out 1.0606 g of Na_2CO_3 (dried overnight at 105°C and stored in a desiccator) using a calibrated top-loading balance (SOP-G10).
   b. Place approximately 500 ml of deionized water in a 1000-ml volumetric flask.
   c. Add the Na_2CO_3 to the flask and dissolve the Na_2CO_3 by swirling the flask.
   d. Bring to volume with deionized water.
   e. Pour the standard into clean plastic bottles.
   f. Using the Stock Standard Log, assign an INSS number for the standard as indicated in SOP-G15.
   g. Label the bottles with the standard concentration, preparation date, analyst's initials, and the INSS number.

A. Titration Procedure.

1. Prepare the Alkalinity Benchsheet (Exhibit C6.1).

2. Calibrate the pH meter according to SOP-C3. An Accumet model AR20 (SN 93312452) is used for pH analysis.

3. Samples must be warmed to 25.0°C ± 1.0°C prior to analysis (the same temperature as calibration standards). Samples may be placed in the Reagent Incubator #1, which is maintained at this temperature, to reach temperature.

4. Close the burette tip and securely clamp the burette to the stand. Over-fill the burette with 0.020N H_2SO_4.

5. Drain the excess. This will fill the tip and help remove air bubbles.

6. Determine the normality of the titrant.

   a. Use a 100-mL graduated cylinder, to make the normality check standard. Mix 2.5 mL of 0.1N Na_2CO_3 into 97.5 mL of deionized water. Use a 10 mL serological pipette to prepare the standard.

   b. Pour the standard into a 150-mL beaker with a stir bar. Place the beaker on the stir plate and stir. Put the pH probe in the solution and titrate to 4.5 S.U. Record the begin mL, end mL and total mL of titrant required to reach the 4.5 S.U. endpoint.

   c. Calculate the normality of the standard to find the multiplier. If the normality is out of range, reanalyze.

7. Analyze an MB.

   a. Using a 100-mL graduated cylinder, pour 100 mL of deionized water in a 150-mL beaker with a stir bar.

   b. Place the beaker on the stir plate. If the pH of deionized water is greater than 4.5 S.U., then titrate the deionized water sample and record the begin mL, end mL and total mL of titrant required to reach the 4.5 S.U. endpoint. Multiply the total mL of titrant required by the multiplier to determine the MB. If the pH is less than 4.5 S.U., then there is no alkalinity and MB is not detected (ND).

8. Analyze a LFB.

   a. Use a 100-mL graduated cylinder, to make the LFB. Mix 10 mL of 0.020N Na_2CO_3 into 90 mL of deionized water. Use a 10-mL serological pipette to make the standard. Pour into a 150-mL beaker with a stir bar.

   b. Place the beaker on the stir plate. Put the pH probe in the solution and titrate to 4.5 S.U. Record the begin mL, end mL and total mL of titrant required to reach the 4.5 S.U. endpoint. Multiply the total mL of titrant required by the multiplier to determine the LFB.

   c. Calculate the %RS of the LFB. The %RS must be ± 10%. If the LFB is out of range, reanalyze.

9. To analyze samples, use 100 mL of sample. If the sample requires more than 15 mL of titrant, dilute the sample to accommodate (make dilutions that evenly divide into 100, e.g. use 50, 25, or 10 mL of sample). Based on prior sample history, samples may be diluted to prevent excessive titrant volume. For each sample, record the begin mL, end mL and total mL of tritant required to reach the 4.5 S.U. endpoint. Multiply the total mL of titrant required by the multiplier to determine the sample result.

10. Analyze a sample in duplicate with every 20 samples performed. The %RPD should be ±10. If the duplicate result is out of range, reanalyze the sample.

Note: All samples must be stirring during analysis.

B. Calculation of Alkalinity.

1. Total mL = End mL – Begin mL

2. Dilution factor = Sample volume mL/100

3. Alkalinity (mg $CaCO_3$/L) = Total mL X Dilution factor X Multiplier

4. Read directly in mg/L and report to 2 significant figures.

D. Precision and Accuracy, Calculations.

1. Normality determination. The normality should calculate to be 0.018 – 0.022.
   Normality = 0.25 / Total mL of H_2SO_4

2. Multiplier determination.
   Multiplier = (Normality x 50000) / 100 mL of Sample

3. Laboratory fortified blank (LFB) determination, True value = 100 mg/L.
   Percent Recovery of the Standard (%RS)
   %RS = (Measured value) / (True value) x 100

4. Duplicate acceptance (as indicated below) or determined through control charts.
   Relative Percent Difference (%RPD)
   %RPD = (Sample value – Duplicate value) / [(Sample value + Duplicate value)/2] x 100

Subject: Alkalinity (SM 2320 B-2021)

Safety and Hazardous Waste Management

Safety glasses, gloves and lab coats should be worn at all times while handling samples. Excess samples may be flushed down the sink.

Review Policy-P6: General Safety Policy and Policy-P9: Radiation Protection Policy for additional safety requirements.

References

Standard Methods for the Examination of Water and Wastewater, 24th Edition, 2023. American Public Health Association, 800 I Street, NW, Washington DC 20001-3710.

- Method: 2320 B-2021.

TNI Standard. Management and Technical Requirements for Laboratories Performing Environmental Analysis. EL-V1-ISO-2016-Rev2.0. The NELAC Institute, PO Box 2439, Weatherford, TX 76086.

Instrument Manual

Exhibits

Exhibit C6.1: Alkalinity Benchsheet.

Subject: Alkalinity (SM 2320 B-2021)

Exhibit C6.1: Alkalinity Benchsheet.

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Analyst
Date analyzed

Alkalinity (SM 2320 B-2021)

Matrix: Water, RL = 5.0 mg $CaCO_3$/L, Samples are titrated to pH = 4.5 S.U.

pH Meter: Accumet Model AR20, SN 93312452

Titrant normality and multiplier determination:

Titrant reference number	Normality check standard number	Begin mL	End mL	Total mL (E)	Normality (N) of H_2SO_4 = (5 mL Na_2CO_3 x 0.05)/E = 0.25/E (acceptable range = 0.0180 - 0.0220)	pH Factor or Multiplier = (N x 50000)/ 100 mL sample = N x 500
INR	INSS					

Laboratory control standard (LCS):

Reference standard number	True value (TV) (mg $CaCO_3$/L)	Sample volume (mL)	Begin mL	End mL	Total mL	Multiplier	Alkalinity (MV) (mg $CaCO_3$/L)	% RS = MV / TV x 100 (acceptable range = 90 to 110%)
INSS	100	100						

Duplicate sample precision:

Sample number	Sample ID	Sample volume (mL)	Begin mL	End mL	Total mL	Multiplier	Alkalinity (mg $CaCO_3$/L)	%RPD = [(S - D) /[(S+D)/2]] x 100 (acceptable range = ± 10%)
							S	
	Duplicate (D)						D	

Sample measurements:

Sample number	Sample ID	Sample volume (mL)	Begin mL	End mL	Total mL	Multiplier	Alkalinity (mg $CaCO_3$/L)
MB (TV < 2.5 mg/L)	Deionized water, pH = _____s.u.	100					

Laboratory control standard (LCS):

Reference standard number	True value (TV) (mg $CaCO_3$/L)	Sample volume (mL)	Begin mL	End mL	Total mL	Multiplier	Alkalinity (MV) (mg $CaCO_3$/L)	% RS = MV / TV x 100 (acceptable range = 90 to 110%)
INSS	100	100						

Reviewed by: _____ Date reviewed: _____

SOP C6-Revision 7-Exhibit C6.1

Subject: Hardness (SM 2340 C-2021)

Approval

Title	Name	Signature	Date
Laboratory Supervisor	Kelley E. Keenan		05-01-24
Quality Assurance Officer	Jim Sumner		05-01-24

Document Revision History

Effective Date	Revision number	Review Type	Evaluators	Revisions
12-01-00	0	Internal	Jim Sumner (ETS)	Original document
09-01-09	1	External (TVA, Environmental Standard, Inc.) Internal	William Rogers (TVA) Cynthia Russell (TVA) Rick Sherrard (TVA) Rock Vitale (Environmental Standards, Inc.) Jim Sumner (ETS)	• Updated exhibits during document review. • Corrective action included if LFBs exceed acceptance criteria.
06-01-11	2	Internal	Jim Sumner (ETS)	• Updated exhibits during document review.
01-01-13	3	Internal	Jim Sumner (ETS)	• Updated procedure and references to the approved analytical method identified in USEPA Method Update Rule II (MUR II), May 18, 2012.
10-01-17	4	Internal	Jim Sumner (ETS)	• Updated procedure to include NELAP requirements. • Additional guidance included in SOP. • Method number revised based on 2017 MUR. • Increased RL to 5.0 mg/L $CaCO_3$. • Changed QCs performed to reflect SM requirements.
02-17-20	5	External (TVA) Internal	Rick Sherrard (TVA) Jim Sumner (ETS)	• Clarified the temperature requirements of standards.
07-01-21	6	Internal	Jim Sumner (ETS)	• Updated procedure and references to the approved analytical method identified in USEPA Method Update Rule, May 19, 2021.
05-01-24	7	Internal	Jim Sumner (ETS)	• Updated procedure and references to the approved analytical method identified in USEPA Method Update Rule, April 16, 2024.

Subject: Hardness (SM 2340 C-2021)

Scope and Application

This method is used to measure the hardness of water samples used in toxicity tests, wastewater, receiving water and drinking water.

Summary of Method

The hardness of a sample is determined by titration to colorimetric endpoint. Calcium and magnesium ions in the sample are sequestered upon the addition of disodium ethylenediamine tetraacetate (Na_2EDTA). The end point of the reaction is detected by means of Eriochrome Black T indicator, which has a red color in the presence of calcium and magnesium and a blue color when the cations are sequestered.

Hardness measurement procedures are based on Standard Methods 2320 B-2021.

Sample Collection, Preservation, Shipment and Storage

Samples must be analyzed within **6 months** of collection if preserved with $HN0_3$. Samples are preserved at the time of collection with $HN0_3$ at a pH < 2 S.U. Samples in support of toxicity tests are <u>not</u> preserved with HNO_3.

Samples are warmed to 25.0 ± 1.0°C prior to analysis. Standards are maintained at 25.0 ± 1.0°C.

Quality Control

Standardization: Verify the **normality** of titrant reagents by re-standardizing at least monthly. If the titration reagent's normality (titer value) has changed, then use the measured value, adjust the normality (titer value) as the procedure describes.

Precision: Analyze a **duplicate** with each batch of samples (a batch of samples is considered samples analyzed on the same date). At a minimum, a duplicate must also be performed after every 20 samples. The relative percent difference (%RPD) should be ± 10% or within established limits determined through control charts. If these results differ by more than the established limits, results associated with this duplicate must be qualified (with a footnote in the analytical report) identifying the deviation.

Laboratory Fortified Blank (LFB, referred to LCS on the benchsheets): A LFB must be analyzed initially and must be performed with each batch of samples. At a minimum, an LFB must be performed after every 20 samples and at the end of each batch of samples. The percent recovery of the LFB (%R) must be ± 10% from the true value.

Method Blank (MB): An MB must be analyzed initially and must be performed with each batch samples (a batch of samples is considered samples analyzed on the same date). In addition, a MB must be performed after every 20 samples. The MB must be ≤ one half the reporting limit (RL).

Reporting Limit (RL): The RL for hardness is 5.0 mg/L.

PE: Annually (once every calendar year), a single-blind QC check sample (QCS) or performance evaluation sample (PE) is analyzed. This sample is provided by an approved proficiency testing (PT) provider.

Additional quality control guidance is provided in QAP-Q5.

Interferences

Some metal ions interfere by causing fading or indistinct endpoints or by stoichiometric consumption of EDTA. This interference may be reduced by adding certain inhibitors before titration.

Cold sample temperature may slow color changes during titration. To avoid this interference, samples are warmed to 25.0 ± 1.0°C prior to analysis.

Subject: Hardness (SM 2340 C-2021)

Equipment

50-mL burette and burette stand with clamps
Spatula
150-mL beakers
Stir bars
Stir plate
50-mL graduated cylinder
5-mL serological pipettes
10-mL serological pipettes
Pipette bulb
Waste container
Rinse bottle
Deionized water
0.01M EDTA titrant (Specifications: 0.01000 ± 0.00001 M at 20°C)
Normality check standard: 1 mL = 1 mg $CaCO_3$ (Specifications: 0.01000 ± 0.00001 M at 20°C)
Laboratory control standard (LFB), and spike standard: 1 mL = 1 mg $CaCO_3$
(Specifications: 0.01000 ± 0.00001 M at 20°C)
Water hardness buffer, reagent grade
Eriochrome Black T indicator
Sodium Chloride (NaCl)
Eriochrome Black T
100-mL Plastic bottle
Balance (Fisher Scientific ACCU-224, or equivalent)
Certified Weights
Anti-static brush
Forceps
Spatula
Weigh boats
Balance Logbook
Hardness Benchsheet

Subject: Hardness (SM 2340 C-2021)

Procedure

A. Preparation of Hardness Titrant and Standards.

1. Preparation of Eriochrome Black T (indicator).

   a. Carefully weigh out 100 g of NaCl and 0.50 g of Eriochrome Black T using a calibrated top-loading balance (SOP-G10).
   b. Combine the NaCl and Eriochrome Black T in a 100-mL plastic bottle and mix well.
   c. Using the Chemical Log, assign a CHM number for the standard as indicated in SOP-G15.
   d. Label the bottle with the chemical name, preparation date, analyst's initials and the CHM number.
   e. The expiration date of this chemical is 1-year from the preparation date.

2. Preparation of 0.01M EDTA (Ethylenediaminetetraacetic acid, disodium salt) **(titrant)**.

   a. Carefully weigh out 3.7230 g of EDTA using a calibrated top-loading balance (SOP-G10).
   b. Place approximately 500 ml of deionized water in a 1000-ml volumetric flask.
   c. Add the EDTA to the flask and dissolve the EDTA by swirling the flask.
   d. Bring to volume with deionized water.
   e. Pour the titrant into clean plastic bottles.
   f. Using the Reagent Log, assign an INR number for the titrant as indicated in SOP-G15.
   g. Label the bottles with the titrant concentration, preparation date, analyst's initials, and the INR number.

B. Titration Procedure.

1. Prepare the Hardness Benchsheet (Exhibit C7.1).

2. Close the burette tip and securely clamp the burette onto the stand. Over fill the burette with 0.01 M EDTA titrant.

3. Drain the excess. This will fill the tip and help remove air bubbles.

4. Determine the normality of the titrant.

   a. Using a 50-mL graduated cylinder, mix 10 mL of $CaCO_3$ Normality Standard in 40 mL of deionized water and pour into a 150-mL beaker with a stir bar and place on the stir plate. This is the normality check. Use a 10-mL serological pipette to measure the $CaCO_3$ standard.

   b. Add 2 mL of water hardness buffer to the sample. The sample must be analyzed within 5 minutes of adding the buffer.

   c. Using a spatula, add a small amount of Eriochrome Black T indicator to the sample. The sample should turn a pale pink/red color. **DO NOT** add too much or too little because the color change will not be evident.

   d. Titrate to a blue color. Record the begin mL, end mL and total mL of titrant required to reach the blue color endpoint.

   e. Calculate the normality of the standard to find the multiplier. If the normality is out of range, reanalyze.

5. Analyze an MB.

   a. Using a 50-mL graduated cylinder, pour 50 mL of deionized water in a 150-mL beaker with a stir bar.

   b. Place the beaker on the stir plate.

   c. Add 2 mL of water hardness buffer to the sample. The sample must be analyzed within 5 minutes of adding the buffer.

   d. Using a spatula, add a small amount of Eriochrome Black T indicator to the sample. **DO NOT** add too much or too little because the color change will not be evident. If the blank sample turns blue with no titration, then there is no hardness. If titration is required (sample is a pale pink/red color), titrate to a blue color. Record the begin mL, end mL and total mL of titrant required to reach the blue color endpoint. Multiply the total mL of titrant required by the multiplier to determine the MB.

6. Analyze a LFB.

   a. Use a 50-mL graduated cylinder to make the LFB. Mix 2 mL of $CaCO_3$ standard in 48 mL of deionized water. Use a 10-mL serological pipette to make the standard. Pour into a 150-mL beaker with a stir bar.

   b. Add 2 mL of water hardness buffer to the sample. The sample must be analyzed within 5 minutes of adding the buffer.

   c. Using a spatula, add a small amount of Eriochrome Black T indicator to the sample. The sample should turn a pale pink/red color. **DO NOT** add too much or too little because the color change will not be evident.

   d. Titrate to a blue color. Record the begin mL, end mL and total mL of titrant required to reach the blue color endpoint. Multiply the total mL of titrant required by the multiplier to determine the LFB.

   e. Calculate the %RS of the LFB. The %RS must be ± 10%. If the LFB is out of range, reanalyze.

5. To analyze samples, use 50 mL of sample. If the sample requires more than 15 mL of titrant, then dilute the sample to accommodate (make dilutions that evenly divide into 50, e.g. use 25, 10, or 5 mL of sample using a graduated cylinder). Based on prior sample history, samples may be diluted to prevent excessive titrant volume. For each sample, record the begin mL, end mL and total mL of titrant required to reach the blue color endpoint. Multiply the total mL of titrant required by the multiplier to determine the sample result.

7. Analyze a sample in duplicate with every 20 samples performed. The %RPD should be ±10. If the duplicate result is out of range, reanalyze the sample.

Note: All samples must be stirred during analysis.

C. Calculation of Hardness.

1. Total mL = End mL – Begin mL

2. Dilution factor = Sample volume mL/100 mL

3. Hardness (mg $CaCO_3$/L) = Total mL X Dilution factor X Multiplier

4. Read directly in mg/L and report to 2 significant figures.

D. Precision and Accuracy, Calculations.

1. Normality determination. The normality should calculate to be 0.018 – 0.022.
   Normality = 0.20 / Total mL of 0.01 M EDTA titrant

2. Multiplier determination.
   Multiplier = (Normality x 50000) / 50 mL of Sample

3. Laboratory control sample (LFB), True value = 40 mg/L.
   Percent Recovery of the Standard (%RS)
   %RS = (Measured value) / (True value) x 100

2. Duplicate acceptance (as indicated below) or determined through control charts.
   Relative Percent Difference (%RPD)
   %RPD = (Sample value – Duplicate value) / [(Sample value + Duplicate value)/2] x 100

Safety and Hazardous Waste Management

Safety glasses, gloves and lab coats should always be worn while handling samples. Excess samples may be flushed down the sink.

Review Policy-P6: General Safety Policy and Policy-P9: Radiation Protection Policy for additional safety requirements.

References

Standard Methods for the Examination of Water and Wastewater, 24th Edition, 2023. American Public Health Association, 800 I Street, NW, Washington DC 20001-3710.

- Method: 2340 C-2021.

TNI Standard. Management and Technical Requirements for Laboratories Performing Environmental Analysis. EL-V1-ISO-2016-Rev2.0. The NELAC Institute, PO Box 2439, Weatherford, TX 76086.

Exhibits

Exhibit C7.1: Hardness Benchsheet.

Subject: Hardness (SM 2340 C-2021)

Exhibit C7.1: Hardness Benchsheet.

ETS

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Analyst
Date analyzed

Hardness (SM 2340 C-2021)
Matrix: Water, RL = 5.0 mg $CaCO_3$/L

Titrant normality and multiplier determination:

Titrant reference number	Normality check standard number	Begin mL	End mL	Total mL (E)	Normality (N) of EDTA = 0.2/E (acceptable range = 0.0180 - 0.0220)	pH Factor or Multiplier = (N x 50000)/ 50 mL sample = N x 1000
INR	INSS					

Laboratory control standard (LCS):

Reference standard number	True value (TV) (mg $CaCO_3$/L)	Sample volume (mL)	Begin mL	End mL	Total mL	Multiplier	Hardness (MV) (mg $CaCO_3$/L)	% RS = MV / TV x 100 (acceptable range = 90 to 110%)
INSS	40	50						

Duplicate sample precision:

Sample number	Sample ID	Sample volume (mL)	Begin mL	End mL	Total mL	Multiplier	Hardness (mg $CaCO_3$/L)	%RPD = ((S - D) /[(S+D)/2]) x 100 (acceptable range = ± 10%)
							S	
	Duplicate (D)						D	

Sample measurements:

Sample number	Sample ID	Sample volume (mL)	Begin mL	End mL	Total mL	Multiplier	Hardness (mg $CaCO_3$/L)
MB (TV < 2.5 mg/L)	Deionized water	50					

Laboratory control standard (LCS):

Reference standard number	True value (TV) (mg $CaCO_3$/L)	Sample volume (mL)	Begin mL	End mL	Total mL	Multiplier	Hardness (mg $CaCO_3$/L)	% RS = MV / TV x 100 (acceptable range = 90 to 110%)
INSS	40	50						

Reviewed by: _____ Date reviewed: _____

SOP C6-Revision 7–Exhibit C6.1

Subject: Total Residual Chlorine (ORION-97-70-1977)

Approval

Title	Name	Signature	Date
Laboratory Supervisor	Kelley E. Keenan		05-01-24
Quality Assurance Officer	Jim Sumner		05-01-24

Document Revision History

Effective Date	Revision number	Review Type	Evaluators	Revisions
12-01-00	0	Internal	Jim Sumner (ETS)	Original document
09-01-09	1	External (TVA, Environmental Standard, Inc.) Internal	William Rogers (TVA) Cynthia Russell (TVA) Rick Sherrard (TVA) Rock Vitale (Environmental Standards, Inc.) Jim Sumner (ETS)	• Updated exhibits during document review. • Corrective action included if LFBs exceed acceptance criteria.
06-01-11	2	Internal	Jim Sumner (ETS)	• Updated exhibits during document review.
01-01-13	3	Internal	Jim Sumner (ETS)	• Updated procedure and references to the approved analytical method identified in USEPA Method Update Rule II (MUR II), May 18, 2012.
10-01-17	4	Internal	Jim Sumner (ETS)	• Updated procedure to include NELAP requirements. • Additional guidance included in SOP. • Method number revised based on 2017 MUR. • Provided a screening method for samples in association with toxicity tests.
02-17-20	5	External (TVA) Internal	Rick Sherrard (TVA) Jim Sumner (ETS)	• Updated procedure and bench sheet to include the serial number of the meter used to perform chlorine.
12-22-20	6	External (SC HDEC) Internal	Haley Anderson (SC DHEC) Jim Sumner (ETS)	• Corrected LFB frequency to every 10 samples and at the end of every batch. • Updated calibration curve to 0.05, 0.50 and 5.00 mg/L. Changed MDL standard to 0.25 mg/L. Lowered reporting limit to 0.05 mg/L.
07-01-21	7	Internal	Jim Sumner (ETS)	• Updated procedure and references to the approved analytical method identified in USEPA Method Update Rule, May 19, 2021.
05-01-24	8	Internal	Jim Sumner (ETS)	• Updated reference to 24th Edition of Standard Methods.

Subject: Total Residual Chlorine (ORION-97-70-1977)

Scope and Application

This method is used to provide both a screening method for total residual chlorine and a method for measuring the concentration of total residual chlorine in samples associated with toxicity tests.

Summary of Method

Total residual chlorine is determined electrometrically using a residual chlorine ion selective electrode.

The electrode method is based on iodometric measurements of chlorine. An iodide reagent and an acid reagent are added to a sample, and the iodide reacts completely with the chlorine to form iodine. The iodine concentration after reaction is equal to the chlorine concentration before reaction. Acid must be present for the conversion of chloramines to iodine. The electrode contains a platinum (redox) sensing element and iodide-sensing reference element. The platinum element develops a potential that depends on the relative levels of iodine and iodide ion in solution. The iodine-sensing element develops a potential that depends on the iodide level in solution. The meter measures the difference between the potentials developed by the two elements. The combination of the platinum and the iodide-sensing elements measure the iodine concentration, which is equal to the total residual chlorine concentration before reaction with the iodide reagent.

Total residual chlorine measurement procedures are based on ORION-97-70-1977.

Sample Collection, Preservation, Shipment and Storage

Samples must be analyzed within **15-minutes** of collection.

All samples analyzed for total residual chlorine are associated with whole effluent toxicity tests performed in the laboratory. Since this total residual chlorine is used as an indicator of potential toxic effects to the testing organisms, samples are analyzed on the day they are used for testing. This exceeds the 15-minute hold time required for NPDES reporting.

Samples received in the laboratory are stored at 0 to 6.0°C.

Subject: Total Residual Chlorine (ORION-97-70-1977)

Quality Control for Confirmation and Measurement Procedures

Calibration: The ion analyzer must be calibrated for total residual chlorine each day **before use**. The calibration curve uses 0.05, 0.25 and 0.50 mg/L standards. The average mV change between the calibration standards should be 26 to 30 mV.

Precision: Analyze a **duplicate** with each batch of samples (a batch of samples is considered samples analyzed on the same date). At a minimum, a duplicate must also be performed after every 20 samples. The relative percent difference (%RPD) should be ± 10% or within established limits determined through control charts. If these results differ by more than the established limits, results associated with this duplicate must be qualified (with a footnote in the analytical report) identifying the deviation.

Laboratory fortified blank (LFB): A LFB must be analyzed initially and must be performed with each batch of samples. At a minimum, an LFB must be performed after every 10 samples and at the end of each batch of samples. The percent recovery of the LFB (%R) must be ± 10% from the true value. The same standard as the MDL is used.

Operational Range: The operational range of the ion analyzer for total residual chlorine is 0.05 mg/L to 0.50 mg/L (calibration range). Measurements less than 0.05 mg/L are reported as < 0.05 mg/L. Samples with total residual chlorine concentrations greater than 0.50 mg/L are diluted to obtain a measured value within the 0.05 to 0.50 mg/L calibration range. The dilution factor is applied prior to reporting the final result.

Method Blank (MB): An MB must be analyzed initially and must be performed with each batch of samples. In addition, a MB must be performed after every 20 samples. The MB must be ≤ one half the reporting limit (RL).

Method Detection Limit (MDL): An MDL standard prepared at 0.25 mg/L is analyzed at least 7 times per year in separate batches of samples analyzed. The MDL may be analyzed by multiple analysts. The values obtained are pooled and used to determine the method detection level for this procedure.

Reporting Limit (RL): The RL for total residual chlorine is 0.05 mg/L.

PE: Annually (once every calendar year), a single-blind QC check sample (QCS) or performance evaluation sample (PE) is analyzed. This sample is provided by an approved proficiency testing (PT) provider.

Additional quality control guidance is provided in QAP-Q5.

Interferences

Coatings of oily material or particulate matter can impair electrode response. These coatings can be removed by gently wiping or detergent washing, followed by rinsing with deionized water.

Strong oxidizing agents that can convert iodide to iodine, including iodate, bromine, cupric ion and manganese dioxide, interfere with the method. These are interferences in all iodometric methods. Silver and mercuric ions must be below 10 to 20 mg/L in the sample. Chromate ion, an interference for the amperometric method, does not interfere with the electrode method. Color or turbidity are not interferences.

Equipment and Materials

Ion analyzer equipped with a residual chlorine probe
Residual chlorine standard (100 mg/L potassium iodate as chlorine)
Acid reagent
Iodide reagent
Rinse bottle
Deionized water
Tap water
1-oz medicine cups
DPD-2 (N,N-Diethyl-p-Phenylenediamine) Powder Pop Dispenser®, 5-mL
150-mL beakers
Stir bars
Stir plate
Serological pipettes
100-mL graduated cylinder
Pipette bulb
Timer
Waste container
Total Residual Chlorine Bench Sheet

Procedure

A. Screening Samples upon Receipt using DPD (N,N-Diethyl-p-Phenylenediamine)

1. Samples received in the laboratory for toxicity testing are screened for total residual chlorine using a color indicator, DPD (N,N-Diethyl-p-Phenylenediamine). Confirmation testing, providing the total residual chlorine measurement, is only performed if DPD screening provides a positive result (pink to red color).

2. Prepare the Total Residual Chlorine, Screening Whole Effluent Toxicity Samples benchsheet (Exhibit C8.1).

3. Perform a positive and negative control to validate that the DPD color indicator will provide accurate results with each batch of samples (a batch of samples is considered samples analyzed on the same date).

   a. For a negative control, pour a small aliquot of deionized water into a 1-oz medicine cup (approximately 5 mL). Using the DPD-2 Powder Pop Dispenser®, dispense one dose of DPD to the medicine cup. There should be no color change.
   b. For a positive control, pour a small aliquot of tap water into a 1-oz medicine cup (approximately 5 mL). Dispense one dose of DPD to the medicine cup. The color of the tap water should change to pink or red.
   c. Record the results of the negative and positive controls on the bench sheet. If either control does not provide the expected result, repeat the process, and obtain a new DPD dispenser if necessary.

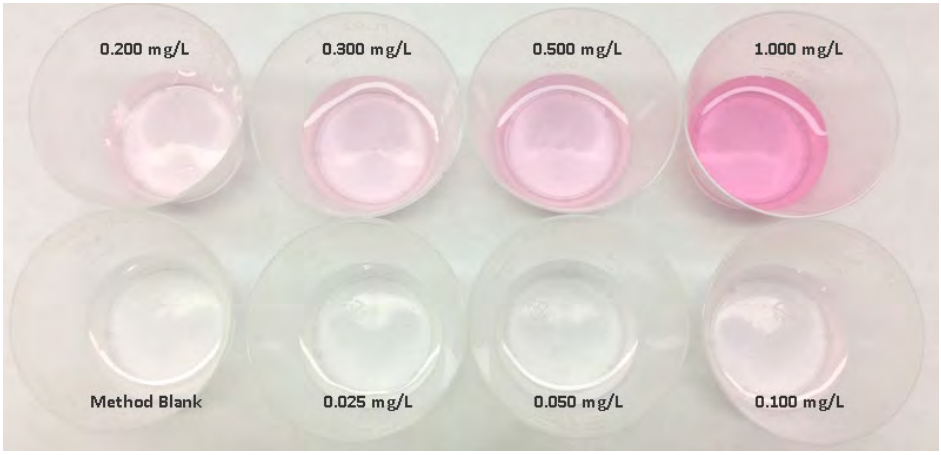
4. Once the positive and negative control tests are complete, samples may be screened for total residual chlorine. Pour a small aliquot of each sample received into a 1-oz medicine cup (approximately 5 mL). Dispense one dose of DPD to each medicine cup containing the samples.

5. Record on the bench sheet the sample number, sample ID, physical characteristics of the unaltered sample (color, clarity, particles, odor, etc.) and the result (positive for pink/red color or negative for no color change)

6. If total residual chlorine is present, the concentration of total residual chlorine must be measured following confirmation procedures identified in Section B.

   Note: The visible detection limit of DPD (N,N-Diethyl-p-Phenylenediamine) is less than 0.10 mg/L total residual chlorine (as indicated in Figure 8.1).

Figure 8.1: Visible detection of DPD (N,N-Diethyl-p-Phenylenediamine).



B. Confirmation and Measurement of Whole Effluent Toxicity Samples for Total Residual Chlorine (Meter: Accumet Model AB250, SN 92349123).

1. Toxicity samples, which have been identified as positive for total residual chlorine, are analyzed to determine the concentration of total residual chlorine.

2. Prepare the Total Residual Chlorine (ORION-97-70-1977) bench sheet (Exhibit C8.2).

3. Each time before analysis, calibrate the meter. The ORION method recommends a calibration curve using a reagent blank and 0.2, 1.0, and 5.0 mg/L standards; however, the Accumet Model AB250 pH/mV/Ion Meter will not accommodate this calibration curve. As a result, a two-point calibration curve using 0.05 and 0.50 mg/L standards is used.

4. Turn on the meter by pressing the **POWER/LIGHT** button.

5. Prepare the method blank (MB), calibration standards and method detection limit spike sample (MDL_s).

6. Pipette 0.05 mL residual chlorine standard into a 150 mL beaker for the 0.05 mg/L calibration standard, 0.25 mL (for the LFB / MDL_s), and 0.50 mL (for the 0.50 mg/L calibration standard). The MB will consist of 150 mL beaker without any residual chlorine standard.

7. Add 1 mL acid reagent and 1 mL iodide reagent to each of the beakers.

8. Set a timer for 2 minutes.

9. After 2 minutes, bring to each volume (100 mL) with deionized water.

10. Remove the probe's cover. Rinse the probe tip with deionized water and place into the 0.05 mg/L calibration standard.

11. Press **DISPLAY** and then **STD**. Press **CLEAR** to clear existing standards. Use the ▲ to select **0.05**. Gently agitate the sample with the tip of the probe. When a stable reading is obtained, the meter will indicate **PRESS STD TO STANDARDIZE**. Press **STD**.

12. Rinse the probe tip with deionized water and place into the 0.50 mg/L calibration standard.

13. Press **DISPLAY** and then **STD**. Use the ▲ to select **0.50**. Gently agitate the sample with the tip of the probe. When a stable reading is obtained, the meter will indicate **PRESS STD TO STANDARDIZE**. Press **STD**. Slope will be displayed and should be 26 to 30 mV.

14. If the average slope is out of range, recalibrate the meter following steps 5 through 13 above.

15. If the average slope is within range, record the mV on the bench sheet and then analyze the LFB / MDL_s.

16. Rinse the probe tip with deionized water and place into the 0.25 mg/L LFB / MDL_s. Gently agitate the sample with the tip of the probe and allow the reading to stabilize. The meter will indicate **STABLE** when the measurement has stabilized.

17. Record the LFB / MDL_s measurement on the bench sheet and calculate the %RS. The LFB must be ± 10% of the true value. If it is out of range, the meter must be recalibrated.

18. Analyze the MB. Rinse the probe tip with deionized water and place into the MB. Gently agitate the sample with the tip of the probe and allow the reading to stabilize. The meter will indicate **STABLE** when the measurement has stabilized.

19. Record the MB measurement on the benchsheet. The MB must be < 0.025 mg/L (less than ½ the reporting limit). If it is out of range, then reanalyze a MB.

20. To analyze a sample, pour 100 mL of the sample into a 150-mL beaker.

21. Add 1 mL of acid reagent and 1 mL of iodide reagent to the sample. Set a timer for 2 minutes.

22. After 2 minutes, rinse the probe tip with deionized water and place into the sample. Gently agitate the sample with the tip of the probe and allow the reading to stabilize. The meter will indicate **STABLE** when the measurement has stabilized.

23. Record the measurement on the Total Residual Chlorine Benchsheet. If the measurement is greater than 0.50 mg/L (highest standard in the calibration curve), then the sample must be diluted. Dilute the sample to evenly divide into 100 (e.g. use 25, 10, or 5 mL of sample diluted to a final volume of 100 mL with deionized water using a graduated cylinder). Re-analyze the sample according to steps 22 through 24 above and multiply the value by the dilution factor (e.g. if 25 mL of sample was used, multiply the value by 4).

24. Continue measuring and recording the total residual chlorine of samples.

25. Once all samples have been analyzed, rinse the probe tip with deionized water and place the cap on the probe. Turn the meter off by pressing and holding the **POWER/LIGHT** button until the screen goes blank.

Note: All samples must be stirring during analysis.

C. Calculation of Total Residual Chlorine.

1. Read directly in mg/L and report to the nearest 0.01 mg/L.

D. Precision and Accuracy, Calculations.

1. Laboratory fortified blank, True value = 0.25 mg/L.
   Percent Recovery of the Standard (%RS)
   %RS = (Measured value) / (True value) x 100

2. Duplicate acceptance.
   Relative Percent Difference (%RPD)
   %RPD = (Sample value – Duplicate value) / [(Sample value + Duplicate value)/2] x 100

Subject: Total Residual Chlorine (ORION-97-70-1977)

Safety and Hazardous Waste Management

Safety glasses, gloves and lab coats should always be worn while handling samples. Excess samples may be flushed down the sink.

Review Policy-P6: General Safety Policy and Policy-P9: Radiation Protection Policy for additional safety requirements.

References

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Thermo Fisher Scientific, Inc. 2008. User Guide Residual Chlorine Ion Selective Electrode, Thermo Scientific, 166 Cummings Center Beverly, MA 01915.

TNI Standard. Management and Technical Requirements for Laboratories Performing Environmental Analysis. EL-V1-ISO-2016-Rev2.0. The NELAC Institute, PO Box 2439, Weatherford, TX 76086.

Instrument Manual

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USEPA. October 2002. Short-Term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to Freshwater Organisms, 4th ed. EPA-821-R-02-013. US Environmental Protection Agency, Cincinnati, OH.

USEPA. October 2002. Short-Term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to Marine and Estuarine Organisms, 3rd ed. EPA-821-R-02-014. US Environmental Protection Agency, Cincinnati, OH.

Subject: Total Residual Chlorine (ORION-97-70-1977)

Exhibits

Exhibit C8.1: Total Residual Chlorine, Screening Whole Effluent Toxicity Samples Benchsheet.
Exhibit C8.2: Total Residual Chlorine, Confirmation of Whole Effluent Toxicity Samples Benchsheet.

Subject: Total Residual Chlorine (ORION-97-70-1977)

Exhibit C8.1: Total Residual Chlorine, Screening Whole Effluent Toxicity Samples Benchsheet.

ETS Environmental Testing Solutions, Inc.

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Total Residual Chlorine (4500-Cl G-2011), Screening Whole Effluent Toxicity Samples

Matrix: Water, RL = 0.10 mg/L

Analyst _____ DPD: INR

Test initiation date _____

Samples are analyzed as they are received in the laboratory.
The test initiation date indicates the date the sample is analyzed for toxicity.

Positive and Negative Control:

Control Type	Sample ID	Result (✓)	
		Positive	Negative
Negative control	Deionized water		
Positive control	Tap water		

Sample screening:

Sample number	Sample ID	Sample characteristics (color – clarity – particles – odor)	Result (✓)	
			Positive	Negative

Note: All samples were analyzed in excess of EPA recommended holding time (15 minutes) unless otherwise noted. A positive result indicates the presence of total residual chlorine above detection (> 0.10 mg/L), which results in a pink to red color change with the addition of the DPD indicator. A negative result indicates the absence of total residual chlorine, which results in no color change with the addition of the DPD indicator. If a color change cannot be determined due to the initial sample color, then the probe method must be performed.

Reviewed by _____

Date reviewed _____

SOP C8-Revision 8 – Exhibit C8.1

Subject: Total Residual Chlorine (ORION-97-70-1977)

Exhibit C8.2: Total Residual Chlorine, Confirmation of Whole Effluent Toxicity Samples Benchsheet.

ETS

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Total Residual Chlorine (ORION-97-70-1977), Confirmation of Whole Effluent Toxicity Samples

Matrix: Water, RL = 50 µg/L, Meter: Accumet Model AB250, SN 92349123

Analyst		Iodide reagent:	INR
Date analyzed		Acid reagent:	INR

Calibration:

	0.050 mg/L	0.500 mg/L	Slope Values (mV) (suggested range = 26 to 30 mV)
Reference standard #	INSS	INSS	

Note: For samples with a residual chlorine of > 0.50 mg/L, the samples must be diluted to be within the calibration range.

Laboratory control sample:

Reference standard number	True value (TV) (mg/L)	Measured value (MV) (mg/L)	% RS = MV / TV x 100 (acceptable range = 90 to 110%)
INSS	**0.250**		

Duplicate sample precision:

Sample number	Sample ID	Total residual chlorine		%RPD = {(S - D) /[(S+D)/2]} x 100 (acceptable range = ± 10%)
		Meter Reading mg/L	Reported Value (Meter Reading x 1000) µg/L	
			S	
	Duplicate		**D**	

Sample measurements:

Sample number	Sample ID	Total residual chlorine	
		Meter Reading mg/L	Reported Value (Meter Reading x 1000) µg/L
TV < 25 µg/L	**Method Blank (MB)**		

Note: All samples were analyzed in excess of EPA recommended holding time (15 minutes) unless otherwise noted.

Laboratory control sample:

Reference standard number	True value (TV) (mg/L)	Measured value (MV) (mg/L)	% RS = MV / TV x 100 (acceptable range = 90 to 110%)
INSS	**0.250**		

Reviewed by _____ Date reviewed _____

SOP C8-Revision 8–Exhibit C8.2

Subject: Solids, Total Suspended (SM 2540 D-2020)

Approval

Title	Name	Signature	Date
Laboratory Supervisor	Kelley E. Keenan		05-01-24
Quality Assurance Officer	Jim Sumner		05-01-24

Document Revision History

Effective Date	Revision number	Review Type	Evaluators	Revisions
06-18-01	0	Internal	Kelley Keenan (ETS)	Original document
10-01-10	1	Internal	Kelley Keenan, Jim Sumner (ETS)	• Updated exhibits during document review. • Corrective action included if LFBs exceed acceptance criteria.
01-03-12	2	Internal	Kelley Keenan, Jim Sumner (ETS)	• Updated exhibits during document review.
04-01-13	3	Internal	Jim Sumner (ETS)	• Updated procedure and references to the approved analytical method identified in USEPA Method Update Rule II (MUR II), May 18, 2012.
10-01-17	4	Internal	Jim Sumner (ETS)	• Updated procedure to include NELAP requirements. • Additional guidance included in SOP. • Method number revised based on 2017 MUR.
05-01-24	5	Internal	Jim Sumner (ETS)	• Updated procedure and references to the approved analytical method identified in USEPA Method Update Rule, April 16, 2024.

Scope and Application

This gravimetric method is used to measure total suspended solids in drinking, surface, saline waters, domestic and industrial wastes.

Summary of Method

Total suspended solids (TSS) is defined as those solids which are retained by a glass fiber filter and dried to constant weight at 103 to 105^{o}C.

Total suspended solid measurement procedures are based on SM 2540 D-2020.

Sample Collection, Preservation, Shipment and Storage

Samples must be analyzed within **7-days** of collection.

Samples received in the laboratory are stored at 0 to 6.0^{o}C.

Subject: Solids, Total Suspended (SM 2540 D-2020)

Quality Control

Precision: Analyze a **duplicate** with each batch of samples (a batch of samples is considered samples analyzed on the same date). At a minimum, a duplicate must also be performed after every 20 samples. The relative percent difference (%RPD) should be ± 10% or within established limits determined through control charts. If these results differ by more than the established limits, results associated with this duplicate must be qualified (with a footnote in the analytical report) identifying the deviation. Qualification may include any sample interferences that may have resulted in the deviation.

Laboratory Fortified Blank (LFB, referred to LCS on benchsheets): A LFB must be analyzed initially and must be performed with each batch of samples. At a minimum, an LFB must also be performed after every 20 samples. The percent recovery of the LFB (%R) must be ± 10% from the true value. If the %RS is out of range, results associated with this LFB must be qualified (with a footnote on the analytical report) identifying the deviation.

Method Blank (MB): Both a dry and wet blank must be analyzed initially and must be performed with each batch of samples. In addition, both a dry and wet blank must be performed after every 20 samples. The dry and wet blanks must be less than 4% of the previous weighing or 0.5 mg, whichever is less. If either of the blank results exceeds these limits, results associated with this dry and/or wet blank must be qualified (with a footnote on the analytical report) identifying the deviation.

Reporting Limit (RL): The RL for total suspended solids is 5.0 mg/L.

QCS: Annually (once every calendar year), a single-blind QC check sample (QCS) is analyzed. This sample is provided by an approved proficiency testing (PT) provider.

Additional quality control guidance is provided in QAP-Q5.

Interferences

Certain sample characteristics may increase error rate and interfere in the analysis of total suspended solids. Below are a few of the interferences that may be encountered with samples received in the laboratory. Unusual observations during the analysis and/or unusual sample characteristics should be recorded on the test benchsheet. Samples, which have identifiable interferences, will be qualified in the wastewater report with a description of the possible interference. If these interferences are readily identified in a sample, a duplicate analysis on the sample may be necessary.

1. Samples with high concentrations of calcium, magnesium, chloride, and/or sulfate may have hydroscopic characteristics, requiring additional drying and rapid weighing (where sample filter exposure to the ambient air is minimized). In addition, samples containing high dissolved solids may require additional washing to ensure that the dissolved material passes through the filter.

2. Large floating particles, submerged agglomerates, and organisms (e.g. chironomids, daphnids) may affect the final result and should be excluded if it is determined that their inclusion is not representative of the sample. These particles/organisms may be removed directly from the filter surface with forceps, being careful not to remove additional solids.

3. Samples that have particles that adhere to the sides of the sample container or contain high concentrations or oil and grease should be documented on the test benchsheet. Samples with high oil and grease may require additional drying time.

4. Multiphase samples may require stirring on a magnetic stir plate to keep the sample homogeneous during transfer. If this technique is required during the analysis, it should be documented on the test benchsheet.

Subject: Solids, Total Suspended (SM 2540 D-2020)

Equipment and Materials

Forced air oven (103 –105° C)
Thermometer (1°C increment)
500-mL graduated cylinders
100-mL graduated cylinders
10-mL serological pipettes
Glass fiber filters (4.7 cm)
Aluminum pans (approximately 5.0 cm)
Cookie sheets
Desiccators
Analytical balance (accurate to 0.0001 g)
Rinse bottle
Deionized water
Total suspended solids (TSS) benchsheet
Pipette bulb
Filtration apparatus with filter funnel
Paper pulp
Forceps
Spatula
1000mL- volumetric flask
1-oz medicine cup
Sharpie® marker

Procedure

A. Glass Fiber Filter Preparation.

1. Glass fiber filters (e.g. Millipore, AP4004705) are used for the analysis of total suspended solids.

2. Glass fiber filters must be washed and dried prior to use.

    a. Determine the number of samples to be analyzed (including duplicates, laboratory fortified blanks, wet and dry blanks). For each sample, a uniquely identified aluminum pan is needed. Using a Sharpie® marker, write a unique identification number on each aluminum pan and place them in order on a cookie sheet.

b. Using forceps, place a glass fiber filter on the filtration apparatus (wrinkle side up). Wash the filter with 3 consecutive washings using 20 mL portions of deionized water.

c. After all traces of water are removed, remove the filter from the filtration apparatus (using forceps) and place in an aluminum pan.

d. Repeat this process until all aluminum pans are full.

e. Place the cookie sheet holding the aluminum pans into the forced air oven at 103 – 105°C for at least one hour.

f. After at least one hour, remove the cookie sheet from the oven and place the aluminum pans in a desiccator. Filters must remain in the desiccator at least 30 minutes before initial weight measurements of the filters are determined.

B. Preparation of Laboratory Fortified Blank (LFB).

1. Using a calibrated top-loading balance, carefully weigh 0.250 g of paper pulp in a 1-oz medicine cup (SOP-G10).

2. Place approximately 900 mL of deionized water in a 1000-mL volumetric flask. Add the paper pulp to the flask, rinse any remaining paper pulp contained in the medicine cup into the volumetric flask using deionized water, and bring to volume with deionized water.

3. Vigorously mix the solution and pour the solution into a 1-L plastic bottle.

4. Assign this standard an INSS number (SOP-G15).

5. Label the 1-L plastic bottle with the INSS number, preparation date, analyst's initials, and expiration date.

C. Analysis of Total Suspended Solids.

1. Remove the aluminum pans containing washed glass fiber filters from the desiccator (prepared in Section A) and place them in order on a cookie sheet.

2. Using a calibrated top-loading balance (SOP-G10), weigh each filter (using forceps) and record the pan identification number and the filter tare weight weight for each sample to be analyzed on the TSS benchsheet.

3. The first sample to be analyzed is the dry blank. Water is not filtered through this filter. This filter is dried, desiccated, and reweighed following procedures beginning in Section C.12.

4. Using forceps, place the next glass fiber filter on the filtration apparatus (wrinkle side up). Make sure that the filter is seated properly by using deionized water in the ring on the bottom of the filter funnel.

5. Analyze the Laboratory Fortified Blank (LFB). Vigorously shake the LFB and measure 50-mL of the LFB in a 100-mL graduated cylinder. Turn on the vacuum pump and pour the LFB onto the filter. Wash the cylinder and the filter with 3 successive volumes of 10-mL of deionized water. After all traces of water are removed, remove the filter from the filtration apparatus (using forceps) and place in the assigned aluminum pan.

6. Using forceps, place the next glass fiber filter on the filtration apparatus (wrinkle side up). Make sure that the filter is seated properly by using deionized water.

7. Analyze a wet blank by filtering 30-mL deionized water through the glass fiber filter. After all traces of water are removed, remove the filter from the filtration apparatus (using forceps) and place in the assigned aluminum pan.

8. Using forceps, place the next glass fiber filter on the filtration apparatus (wrinkle side up). Make sure that the filter is seated properly by using deionized water.

9. Analyze the first sample. Vigorously shake the sample and measure the volume of the sample to be filtered into a 500-mL, 100-ml graduated cylinder or 10-mL serological pipette (wide-bore). The sample volume may be adjusted based on the amount of solids in the sample. Turn on the suction and slowly pour (or pipette) the sample through the filter, being sure not to clog the filter. Repeat this process until there is at least 2.5 mg suspended solids weight gain on the filter or 1000 mL of sample has been filtered. If it takes longer than 10 minutes to filter the sample, it may be necessary to reanalyze the sample and decrease the sample volume. On the TSS benchsheet, record the number of milliliters filtered. Wash the cylinder and the filter with 3 successive volumes of 10-mL of deionized water. After all traces of water are removed, remove the filter from the filtration apparatus (using forceps) and place in the assigned aluminum pan.

10. Repeat steps 8 through 9 until all samples are filtered.

11. Each batch of samples (10 samples) must have a duplicate. A duplicate is a replicate of one of the samples contained in the batch.

12. Initial Weight Determination:

    a. Place the cookie sheet into the forced air oven at 103 – 105°C. Samples must remain in the oven at least one hour. On the benchsheet, record the temperature and time the samples were placed into the oven.
    b. After at least one hour, remove the cookie sheet from the oven and place the aluminum pans in a desiccator. Filters must remain in the desiccator at least 30 minutes before final weight measurements of the filters are determined. On the benchsheet, record the time the samples were removed from the oven and placed in a desiccator.
    c. Remove the aluminum pans from the desiccator and place them in order on a cookie sheet. The amount of time the sample filters are exposed to the ambient air should be minimized to prevent the absorption of additional moisture before weighing.
    d. Using a calibrated top-loading balance (SOP-G10), weigh each filter (using forceps) and record the initial weight for each sample on the TSS benchsheet.

13. Final Weight Determination:

    a. Place the cookie sheet into the forced air oven at 103 – 105°C. Samples must remain in the oven at least one hour. On the benchsheet, record the temperature and time the samples were placed into the oven.
    b. After at least one hour, remove the cookie sheet from the oven and place the aluminum pans in a desiccator. Filters must remain in the desiccator at least 30 minutes before final weight measurements of the filters are determined. On the benchsheet, record the time the samples were removed from the oven and placed in a desiccator.
    c. Remove the aluminum pans from the desiccator and place them in order on a cookie sheet. The amount of time the sample filters are exposed to the ambient air should be minimized to prevent the absorption of additional moisture before weighing.
    d. Using a calibrated top-loading balance (SOP-G10), weigh each filter (using forceps) and record the final weight for each sample on the TSS benchsheet.
    e. The initial and final weights should not differ by more than 0.5 mg. If the values differ by more than 0.5 mg, redry the filters following procedures identified in Step C.13 and document on the benchsheet.

14. Determine the weight difference by subtracting the Filter Tare Weight from the Final Sample Weight.

15. Calculate the total suspended solids in mg/L (Section D).

D. Calculation of Total Suspended Solids.

1. TSS in mg/L = $\frac{(A - B) \times 1000}{C}$

A = final weight of filter (filter + sample residue) in mg
B = filter tare weight in mg
C = volume of sample filtered in mL

2. Reporting Limit (RL) in mg/L = $\frac{1000}{C} \times 2.5$

C = volume of sample filtered in mL

3. Each sample filtered must have at least 2.5 mg weight gain. If the sample does not weigh at least 2.5 mg/L then the RL must have a dilution factor multiplied based on the amount of sample used (i.e. if 400 mL of sample was used and the result is less that 2.5 mg/L then the result will be < 6.2 mg/L and the new RL will be 6.2 mg/L).
Calculation: 1000mL/400mL x2.5mg = 6.2mg/L

E. Precision and Accuracy, Calculations.

1. Laboratory fortified blank (LFB) determination, True value = 250 mg/L.

Percent Recovery of the Standard (%RS)

%RS = (Measured value) / (True value) x 100

2. Duplicate acceptance.

Relative Percent Difference (%RPD)

%RPD = (Sample value – Duplicate value) / [(Sample value + Duplicate value)/2] x 100

Subject: Solids, Total Suspended (SM 2540 D-2020)

Safety and Hazardous Waste Management

Safety glasses, gloves and lab coats should always be worn while handling samples. Excess samples may be flushed down the sink.

Review Policy-P6: General Safety Policy and Policy-P9: Radiation Protection Policy for additional safety requirements.

References

Standard Methods for the Examination of Water and Wastewater, 24th Edition, 2023. American Public Health Association, 800 I Street, NW, Washington DC 20001-3710.

- Method: 2540 D-2020.

TNI Standard. Management and Technical Requirements for Laboratories Performing Environmental Analysis. EL-V1-ISO-2016-Rev2.0. The NELAC Institute, PO Box 2439, Weatherford, TX 76086.

Exhibits

Exhibit C9:1: Total Suspended Solids Benchsheet.

Subject: Solids, Total Suspended (SM 2540 D-2020)

Exhibit C9:1: Total Suspended Solids Benchsheet.

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Solids, Total Suspended (SM 2540 D-2020)

Matrix: water, RL = 2.5 mg/L

Date analyzed: _____ Reviewed by: _____

Analyst: _____ Reviewed date: _____

Sample Initial Weight

Analyst: _____

Oven Temp (°C): _____

Date in: _____ Time in: _____

Date out: _____ Time out: _____

Sample Final Weight

Analyst: _____

Oven Temp (°C): _____

Date in: _____ Time in: _____

Date out: _____ Time out: _____

Sample Number	Sample Identification	Tared Filter #	Filter Tare Weight (mg)	Sample Vol. (ml)	*Sample Weight (mg)		Weight Diff. (mg) –Tare = Final Sample Weight	Final TSS Result (mg/L)
					Initial	Final		
	Dry Blank							
	LCS							
	Duplicate							
	Wet Blank							

*Note: Filters must be dried to a constant weight (initial – final weight must not differ by more than 0.5 mg).

CALCULATIONS

Final TSS (mg/L) = {(Final weight - filter tare weight)/(sample volume)} x 1000

Final RPD = {(S - D) / [(S + D) / 2]} x 100%

Reference standard recovery (%RS) = (X / Y) x 100%

QUALITY CONTROL

Precision (duplicate):

Sample number: _____

Sample result (S): _____ mg/L

Duplicate result (D): _____ mg/L

Final RPD = _____

Laboratory control standard (LCS):

Reference standard number _____

Value obtained (X) = _____ mg/L True value (Y) = _____ mg/L %RS= _____

SOP C9-Revision 5–Exhibit C9.2

Subject: Solids, Total Dissolved (SM 2540 C-2020)

Approval

Title	Name	Signature	Date
Laboratory Supervisor	Kelley E. Keenan		05-01-24
Quality Assurance Officer	Jim Sumner		05-01-24

Document Revision History

Effective Date	Revision number	Review Type	Evaluators	Revisions
06-18-01	0	Internal	Kelley Keenan (ETS)	Original document
10-01-10	1	Internal	Kelley Keenan, Jim Sumner (ETS)	• Updated SOP and exhibits during document review. Provided additional procedural guidance where required.
01-03-12	2	Internal	Kelley Keenan, Jim Sumner (ETS)	• Updated SOP and exhibits during document review. Provided additional procedural guidance where required.
04-01-13	3	Internal	Jim Sumner (ETS)	• Updated procedure and references to the approved analytical method identified in USEPA Method Update Rule II (MUR II), May 18, 2012.
10-01-17	4	Internal	Jim Sumner (ETS)	• Updated procedure to include NELAP requirements. • Additional guidance included in SOP. • Method number revised based on 2017 MUR.
05-01-24	5	Internal	Jim Sumner (ETS)	• Updated procedure and references to the approved analytical method identified in USEPA Method Update Rule, April 16, 2024.

Scope and Application

This gravimetric method is used to measure total dissolved solids in drinking, surface, saline waters, domestic and industrial wastes.

Summary of Method

Total dissolved solids (TDS) is defined as those solids capable of passing through a glass fiber filter and dried to constant weight at 180°C.

Total dissolved solids measurement procedures are based on SM 2540 C-2020.

Sample Collection, Preservation, Shipment and Storage

Samples must be analyzed within **7-days** of collection.

Samples received in the laboratory are stored at 0 to 6.0°C.

Subject: Solids, Total Dissolved (SM 2540 C-2020)

Quality Control

Precision: Analyze a **duplicate** with each batch of samples (a batch of samples is considered samples analyzed on the same date). At a minimum, a duplicate must also be performed after every 20 samples. The relative percent difference (%RPD) should be ± 10% or within established limits determined through control charts. If these results differ by more than the established limits, results associated with this duplicate must be qualified (with a footnote in the analytical report) identifying the deviation. Qualification may include any sample interferences that may have resulted in the deviation.

Laboratory Fortified Blank (LFB, referred to LCS on benchsheets): An LFB must be analyzed initially and must be performed with each batch of samples. At a minimum, an LFB must also be performed after every 20 samples. The percent recovery of the LFB (%R) must be ± 10% from the true value. If the %RS is out of range, results associated with this LFB must be qualified (with a footnote on the analytical report) identifying the deviation.

Method Blank (MB): An MB must be analyzed initially and must be performed with each batch of samples. In addition, an MB must be performed after every 20 samples. The MB must be less than 4% of the previous weighing or 0.5 mg, whichever is less. If the blank result exceeds these limits, results associated with this blank must be qualified (with a footnote on the analytical report) identifying the deviation.

Reporting Limit (RL): The RL for total dissolved solids is 10 mg/L.

QCS: Annually (once every calendar year), a single-blind QC check sample (QCS) is analyzed. This sample is provided by an approved proficiency testing (PT) provider.

Additional quality control guidance is provided in QAP-Q5.

Interferences

Certain sample characteristics may increase error rate and interfere in the analysis of total dissolved solids. Below are a few of the interferences that may be encountered with samples received in the laboratory. Unusual observations during the analysis and/or unusual sample characteristics should be recorded on the test benchsheet. Samples, which have identifiable interferences, will be qualified in the wastewater report with a description of the possible interference. If these interferences are readily identified in a sample, a duplicate analysis on the sample may be necessary.

1. Samples with high concentrations of calcium, magnesium, chloride, and/or sulfate may have hydroscopic characteristics, requiring additional drying and rapid weighing (where the evaporating dish exposure to the ambient air is minimized). In addition, samples containing high

dissolved solids may require additional rinsing into the filter flask to ensure that the dissolved material passes through the filter.

2. Multiphase samples may require stirring on a magnetic stir plate to keep the sample homogeneous during transfer. If this technique is required during the analysis, it should be documented on the test benchsheet.

Equipment and Materials

Forced air draft oven (103 –105°C)
Drying oven (180 ± 2°C)
100-mL Graduated Cylinder
Glass fiber filters (4.7 cm)
0.45µm filters (4.7 cm)
Thermometer (1°C increment)
150-mL evaporating dishes
Cookie sheet
Dessicator
Analytical balance (accurate to 0.0001 g)
Spatula
1-oz medicine cup
Rinse bottle
Tongs
Deionized water
Total dissolved solids (TDS) benchsheet
Filtration apparatus
Sodium chloride
1000-mL volumetric flask
1000-mL vacuum flasks
Sharpie® marker

Procedure

NOTE: DO NOT TOUCH EVAPORATING DISHES EXCEPT WITH TONGS.

A. Preparation of Drying Dishes.

1. Determine the number of samples to be analyzed (including duplicates, laboratory control standards, and blanks). For each sample, a uniquely identified 150-mL evaporating dish is needed. Using a Sharpie® marker, write a unique identification

number on each dish and place into the drying oven (180 ± 2°C). Dishes must remain in the drying oven at least one hour.

2. Using tongs remove the dishes from the oven and place in a desiccator. Dishes should remain in the desiccator at least 30 minutes. To ensure proper cooling, leave all TDS dishes in the desiccator overnight.

B. Preparation of Laboratory Fortified Blank (LFB).

1. Using a calibrated top-loading balance, carefully weigh 0.250 g of sodium chloride in a 1-oz medicine cup (SOP-G10).

2. Place approximately 900 mL of deionized water in a 1000-mL volumetric flask. Add the sodium chloride to the flask, rinse any remaining sodium chloride contained in the medicine cup into the volumetric flask using deionized water, and bring to volume with deionized water.

3. Vigorously mix the solution and pour into a 1-L plastic bottle.

4. Assign this standard an INSS number (SOP-G15).

5. Label the 1-L plastic bottle with the INSS number, preparation date, analyst's initials, and expiration date.

C. Analysis of Total Dissolved Solids.

NOTE: Groundwater monitoring wells must be filtered through a 0.45 µm filter. Refer to the groundwater monitoring well list that is provided by NCDEQ groundwater division. All other samples must be filtered with a glass fiber filter.

1. Using tongs remove the evaporating dishes from the desiccator (prepared in Section A) and place them in order on a cookie sheet.

2. Using a calibrated top-loading balance (SOP-G10), weigh each evaporating dish (using tongs) and record the dish identification number and the dish tare weight for each sample to be analyzed on the TDS benchsheet.

3. Analyze a <u>blank</u> by filling a 100-mL graduated cylinder with deionized water and pour into the appropriate evaporating dish.

4. Vigorously shake the Laboratory Fortified Blank (LFB) and measure 50 mL into a 100-mL graduated cylinder and pour into the appropriate evaporating dish.

5. Vigorously shake the first sample to be analyzed and measure 110 mL into a graduated cylinder. Seat a glass fiber filter (0.45 µm filter is used for groundwater samples) on the filtration apparatus using deionized water. Slowly pour the sample through the filter. If the filter becomes clogged, remove the filter and place a clean filter on the apparatus. Repeat this process until 110 mL of sample is filtered. **Do not rinse the cylinder into the filtered sample.** After the sample is filtered, measure 100-mL of the filtered sample in a graduated cylinder and pour into the appropriate evaporating dish. Wash the cylinder with 3 successive volumes of 10-mL of deionized water and pour each wash into the evaporating dish. Remove the flask from the filtration apparatus and place a waste flask on the apparatus. Rinse the filter into the waste flask. **Do not filter any deionized water into the original flask.**

6. Follow step C.6 until all samples have been filtered.

7. Place the cookie sheet into the drying oven at 103 – 105 ^{o}C. Samples must remain in the oven until dry.

8. Initial Weight Determination:

   a. Once dried, remove the cookie sheet and place the dishes into the 180 ± 2^{o}C drying oven for at least one hour.
   b. After one hour, remove the dishes using tongs and place them in a desiccator.
   c. After at least 30 minutes, the dishes may be removed and weighed. To ensure proper cooling, leave all TDS dishes in the desiccator overnight.
   d. Weigh each dish and record the initial sample weight on the TDS benchsheet.

9. Final Weight Determination:

   a. Place the dishes into the 180 ± 2^{o}C drying oven for at least one hour.
   b. After one hour, remove the dishes using tongs and place them in a desiccator.
   c. After at least 30 minutes, the dishes may be removed and weighed. To ensure proper cooling, leave all TDS dishes in the desiccator overnight.
   d. Weigh each dish and record the final sample weight on the TDS benchsheet.
   e. The initial and final weights should not differ by more than 0.5 mg. If the values differ by more than 0.5 mg, redry the dishes following procedures identified in Step C.9 and document on the benchsheet.

10. Determine the weight difference by subtracting the Dish Tare Weight from the Final Sample Weight.

11. Calculate the total dissolved solids in mg/L.

D. Calculation of Total Dissolved Solids.

1. TDS, mg/L = $\frac{(A - B) \times 1000}{C}$

A = weight of dried residue + dish in mg
B = weight of dish in mg
C = volume of sample used in mL

2. Reporting Limit (RL) in mg/L = 10 mg/L

3. Each sample filtered must have at least 1.0 mg weight gain. If the sample does not weigh at least 10 mg/L then the result is ND (not detected).

E. Precision and Accuracy, Calculations.

1. Laboratory fortified blank (LFB) determination, True value = 250 mg/L.

Percent Recovery of the Standard (%RS)

%RS = (Measured value) / (True value) x 100

2. Duplicate acceptance.

Relative Percent Difference (%RPD)

%RPD = (Sample value – Duplicate value) / [(Sample value + Duplicate value)/2] x 100

Safety and Hazardous Waste Management

Safety glasses, gloves and lab coats should always be worn while handling samples. Excess samples may be flushed down the sink.

Review Policy-P6: General Safety Policy and Policy-P9: Radiation Protection Policy for additional safety requirements.

Subject: Solids, Total Dissolved (SM 2540 C-2020)

References

Standard Methods for the Examination of Water and Wastewater, 24th Edition, 2023. American Public Health Association, 800 I Street, NW, Washington DC 20001-3710.

- Method: 2540 C-2020.

TNI Standard. Management and Technical Requirements for Laboratories Performing Environmental Analysis. EL-V1-ISO-2016-Rev2.0. The NELAC Institute, PO Box 2439, Weatherford, TX 76086.

Exhibits

Exhibit C10:1: Total Dissolved Solids Benchsheet.

Subject: Solids, Total Dissolved (SM 2540 C-2020)

Exhibit C10:1: Total Dissolved Solids Benchsheet.

Page _____

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Solids, Total Dissolved (SM 2540 C-2020)

Matrix: water, RL = 10 mg/L

Reviewed by: _____

Reviewed date: _____

Initial Drying at 103-105°C

Analyst: _____

Oven Temp (°C): _____

Date in: _____ Time in: _____

Date out: _____ Time out: _____

Sample Initial Weight

Analyst: _____

Oven Temp (°C): _____

Date in: _____ Time in: _____

Date out: _____ Time out: _____

Sample Final Weight

Analyst: _____

Oven Temp (°C): _____

Date in: _____ Time in: _____

Date out: _____ Time out: _____

Sample Number	Sample Identification	Tared Dish #	Dish Tare Weight (mg)	Sample Vol. (ml)	*Sample Weight (mg)		Weight Diff. (mg) = Tare – Final Sample Weight	Final TDS Result (mg/L)
					Initial	Final		
	Method Blank							
	LCS							
	Duplicate							

*Note: Dishes must be dried to a constant weight (initial – final weight must not differ by more than 0.5 mg).

CALCULATIONS

Final TDS (mg/L) = {(Final weight - dish tare weight)/(sample volume)} x 1000

Final RPD = {(S - D) / [(S + D) / 2]} x 100%

Reference standard recovery (%RS) = (X / Y) x 100%

QUALITY CONTROL

Precision (duplicate):

Sample number: _____

Sample result (S): _____ mg/L

Duplicate result (D): _____ mg/L

Final RPD = _____

Laboratory control standard (LCS):

Reference standard number _____

Value obtained (X) = _____ mg/L True value (Y) = _____ mg/L %RS= _____

SOP C10-Revision 5–Exhibit C10.2

Subject: Solids, Settleable (SM 2540 F-2020)

Approval

Title	Name	Signature	Date
Laboratory Supervisor	Kelley E. Keenan		05-01-24
Quality Assurance Officer	Jim Sumner		05-01-24

Document Revision History

Effective Date	Revision number	Review Type	Evaluators	Revisions
06-18-01	0	Internal	Jim Sumner (ETS)	Original document
10-01-10	1	Internal	Kelley Keenan, Jim Sumner (ETS)	• Updated SOP and exhibits during document review. Provided additional procedural guidance where required. Corrected typographical errors.
01-03-12	2	Internal	Kelley Keenan, Jim Sumner (ETS)	• Updated SOP and exhibits during document review.
01-27-12	3	Internal	Jason Smith (NC DENR)	• Updated laboratory benchsheet to document 45-minute stir time.
04-01-13	4	Internal	Jim Sumner (ETS)	• Updated procedure and references to the approved analytical method identified in USEPA Method Update Rule II (MUR II), May 18, 2012.
04-01-18	5	Internal	Jim Sumner (ETS)	• Updated procedure to include NELAP requirements. • Additional guidance included in SOP. • Method number revised based on 2017 MUR.
05-01-24	6	Internal	Jim Sumner (ETS)	• Updated procedure and references to the approved analytical method identified in USEPA Method Update Rule, April 16, 2024.

Scope and Application

This method is used to measure settleable matter volumetrically with an Imhoff cone in surface, and saline waters, domestic and industrial wastes.

Summary of Method

Settleable matter is measured volumetrically with an Imhoff cone.

Settleable solids measurement procedures are based on SM 2540 F-2020.

Subject: Solids, Settleable (SM 2540 F-2020)

Sample Collection, Preservation, Shipment and Storage

Samples must be analyzed within **48 hours** of collection.

Samples received in the laboratory are stored at 0 to 6.0°C.

Quality Control

Precision: If the client collected sufficient volume, a duplicate may be analyzed. The relative percent difference (%RPD) should be ± 10% or within established limits determined through control charts. If these results differ by more than the established limits, results associated with this duplicate must be qualified (with a footnote in the analytical report) identifying the deviation. Qualification may include any sample interferences that may have resulted in the deviation.

Reporting Limit (RL): The RL for settleable solids is 0.1 ml/L.

QCS: Annually (once every calendar year), a single-blind QC check sample (QCS) is analyzed. This sample is provided by an approved proficiency testing (PT) provider.

Additional quality control guidance is provided in QAP-Q5.

Interferences

A separation of settleable and floating materials may occur. In such instances, floating materials are not measured.

Equipment and Materials

Imhoff cone
Ring Stand
Glass stir rod
Pipette
Timer
Settleable Solids Benchsheet

Subject: Solids, Settleable (SM 2540 F-2020)

Procedure

A. Analysis of Settleable Solids.

1. Vigorously shake the sample and pour the 1-liter contents into a clean Imhoff cone.
2. Place the Imhoff cone in the ring stand.
3. Set a timer for 45 minutes.
4. Allow the sample to settle for 45 minutes, then gently swirl the contents with a glass stir rod or pipette and document on benchsheet.
5. Reset the timer for 15 minutes.
6. After 15 minutes, read the settled matter in ml/L and record the results on the Settleable Solids Benchsheet (Exhibit C12.1).
7. If there are pockets of liquid that settle between the solids, they must be subtracted out from the final results.

B. Precision and Accuracy, Calculations.

1. Duplicate acceptance.

   Relative Percent Difference (%RPD)

   %RPD = (Sample value – Duplicate value) / [(Sample value + Duplicate value)/2] x 100

Safety and Hazardous Waste Management

Safety glasses, gloves and lab coats should always be worn while handling samples. Excess samples may be flushed down the sink.

Review Policy-P6: General Safety Policy and Policy-P9: Radiation Protection Policy for additional safety requirements.

Subject: Solids, Settleable (SM 2540 F-2020)

References

Standard Methods for the Examination of Water and Wastewater, 24th Edition, 2023. American Public Health Association, 800 I Street, NW, Washington DC 20001-3710.

- Method: 2540 F-2020.

TNI Standard. Management and Technical Requirements for Laboratories Performing Environmental Analysis. EL-V1-ISO-2016-Rev2.0. The NELAC Institute, PO Box 2439, Weatherford, TX 76086.

Exhibits:

Exhibit C12:1: Settleable Solids Benchsheet.

Subject: Solids, Settleable (SM 2540 F-2020)

Exhibit C12:1: Settleable Solids Benchsheet.

Page _____

Page _____of _____

Solids, Settleable (SM 2540 F-2020)

Matrix: water, RL = 0.1 mL/L

Date analyzed: _____
Date entered: _____
Entered by: _____

Analyst: _____
Reviewed by: _____
Reviewed date: _____

45-minute Stir Time (check) ☐

Sample Number	Sample Identification	Date Collected	Start Time	End Time	Sample Volume (mL)	Final Settleable Solid Result (mL/L)

CALCULATIONS
Final concentration settleable solids (mL/L) = settled volume after 1 hour

SOP C12-Revision 6–Exhibit C12.1

Subject: Solids, Percent and Percent Moisture (SM 2540 G-2020)

Approval

Title	Name	Signature	Date
Laboratory Supervisor	Kelley E. Keenan		05-01-24
Quality Assurance Officer	Jim Sumner		05-01-24

Document Revision History

Effective Date	Revision number	Review Type	Evaluators	Revisions
06-18-01	0	Internal	Jim Sumner (ETS)	Original document
10-01-10	1	Internal	Kelley Keenan, Jim Sumner (ETS)	• Updated SOP and exhibits during document review. Provided additional procedural guidance where required.
01-03-12	2	Internal	Kelley Keenan, Jim Sumner (ETS)	• Updated SOP and exhibits during document review.
04-01-13	3	Internal	Jim Sumner (ETS)	• Updated procedure and references to the approved analytical method identified in USEPA Method Update Rule II (MUR II), May 18, 2012.
04-01-18	4	Internal	Jim Sumner (ETS)	• Updated procedure to include NELAP requirements. • Additional guidance included in SOP. • Method number revised based on 2017 MUR.
05-01-24	5	Internal	Jim Sumner (ETS)	• Updated procedure and references to the approved analytical method identified in USEPA Method Update Rule, April 16, 2024.

Scope and Application

This method is used to measure percent solids and percent moisture in solid, semi-solid and liquid samples.

Summary of Method

A well-mixed aliquot of sample is quantitatively transferred to a pre-weighed pan and evaporated to dryness at 103 – 105°C.

Percent solids measurement procedures are based on SM 2540 G-2020.

Subject: Solids, Percent and Percent Moisture (SM 2540 G-2020)

Sample Collection, Preservation, Shipment and Storage

Samples must be analyzed within **7-days** of collection.

Samples received in the laboratory are stored at 0 to 6.0°C.

Quality Control

Precision: Analyze a **duplicate** with each batch of samples (a batch of samples is considered samples analyzed on the same date). At a minimum, a duplicate must also be performed after every 20 samples. The relative percent difference (%RPD) should be ± 10% or within established limits determined through control charts. If these results differ by more than the established limits, results associated with this duplicate must be qualified (with a footnote in the analytical report) identifying the deviation. Qualification may include any sample interferences that may have resulted in the deviation.

Additional quality control guidance is provided in QAP-Q5.

Interferences

Highly mineralized water with a significant concentration of calcium, magnesium, chloride and/or sulfate may be hygroscopic and require prolonged drying, proper desiccation and rapid weighing. Exclude large, floating particles or submerged agglomerates of nonhomogeneous materials from the sample if it is determined that their inclusion is not desired in the final result. Disperse visible floating oil and grease with a blender before withdrawing a sample portion for analysis.

Equipment and Materials

Forced air drying oven (103 –105 °C)
Aluminum pans
Spatula
Analytical balance (accurate to 0.0001g)
Sharpie® marker
Tongs
Disposable pipette
Percent Solids/Percent Moisture Benchsheet

Subject: Solids, Percent and Percent Moisture (SM 2540 G-2020)

Procedure

NOTE: DO NOT TOUCH THE PANS EXCEPT WITH TONGS.

A. Preparation of aluminum pans.

1. Using a Sharpie® marker, write a unique identification number on each aluminum pan and place into the drying oven (103 - 105°C). Pans must remain in the drying oven at least one hour.

2. Using tongs, remove the pans and place in a desiccator. Pans should remain in the desiccator at least 30 minutes.

B. Analysis of Percent Solids.

1. Using tongs, remove the appropriate number of pans from the dessicator and place on a cookie sheet.

2. Using a calibrated top-loading balance (SOP-G10), weigh each pan (using tongs) and record the dish identification number and the initial weight for each sample to be analyzed on the Percent Solids / Percent Moisture benchsheet (Exhibit C13.1).

3. Leaving the pan on the balance tray, auto zero.

4. If the sample is a solid, thoroughly mix the sample with a spatula and place approximately 10 g into the pan. If the sample is a liquid, vigorously shake the container and pipette approximately 10 g into the pan.

5. Record the weight of the solids in the percent solids/percent moisture benchsheet.

6. Follow steps B 3 – 6 to complete all samples.

7. Initial Weight Determination (1st Drying Time):

   a. Place the cookie sheet into the forced air oven at 103 – 105°C. Samples must remain in the oven until dry.
   b. Remove the cookie sheet from the oven and place the aluminum pans in a desiccator. Pan must remain in the desiccator at least 30 minutes before final weight measurements of the filters are determined.

c. Remove the aluminum pans from the desiccator and place them in order on a cookie sheet. The amount of time the samples are exposed to the ambient air should be minimized to prevent the absorption of additional moisture before weighing.
d. Using a calibrated top-loading balance (SOP-G10), weigh each pan (using forceps) and record the initial weight for each sample on the Percent Solids benchsheet.

8. Final Weight Determination (2nd Drying Time):

a. Place the cookie sheet into the forced air oven at 103 – 105°C. Samples must remain in the oven at least one hour.
b. After at least one hour, remove the cookie sheet from the oven and place the aluminum pans in a desiccator. Pans must remain in the desiccator at least 30 minutes before final weight measurements of the filters are determined.
c. Remove the aluminum pans from the desiccator and place them in order on a cookie sheet. The amount of time the samples are exposed to the ambient air should be minimized to prevent the absorption of additional moisture before weighing.
d. Using a calibrated top-loading balance (SOP-G10), weigh each pan (using forceps) and record the final weight for each sample on the Percent Solids benchsheet.
e. The initial and final weights should not differ by more than 0.5 mg. If the values differ by more than 0.5 mg, redry the filters following procedures identified in Step C.13 and document on the benchsheet.

9. Determine the Percent Solids using the calculations identified in Section C.

C. Calculation.

1. $$\% \text{ Solids} = \frac{(A - B) \times 100}{C}$$

A = weight of dried residue + dish in mg
B = weight of dish in mg
C = volume of sample used in mL

2. % Moisture = % Solids – 100

D. Precision and Accuracy, Calculations.

1. Duplicate acceptance.

Relative Percent Difference (%RPD)
%RPD = (Sample value – Duplicate value) / [(Sample value + Duplicate value)/2] x 100

G. Exhibits:

Exhibit C13.1: Percent Moisture/Percent Solids Benchsheet.

Safety and Hazardous Waste Management

Safety glasses, gloves and lab coats should always be worn while handling samples. Excess samples may be flushed down the sink.

Review Policy-P6: General Safety Policy and Policy-P9: Radiation Protection Policy for additional safety requirements.

References

Standard Methods for the Examination of Water and Wastewater, 24th Edition, 2023. American Public Health Association, 800 I Street, NW, Washington DC 20001-3710.

- Method: 2540 G-2020.

TNI Standard. Management and Technical Requirements for Laboratories Performing Environmental Analysis. EL-V1-ISO-2016-Rev2.0. The NELAC Institute, PO Box 2439, Weatherford, TX 76086.

Exhibits:

Exhibit C13:1: Percent Solids / Percent Moisture Benchsheet.

Subject: Solids, Percent and Percent Moisture (SM 2540 G-2020)

Exhibit C13:1: Percent Solids / Percent Moisture Benchsheet.

ETS Environmental Testing Solutions, Inc.

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Percent Solids / Percent Moisture (SM 2540 G-2020)

Date analyzed	Sample number	Dish identification	Dish weight (g)	Sample weight (g)	1st Drying Time		2nd Drying Time (must not differ by more than 0.5 mg or 4% from 1st drying time)		Analyst initials
					Final weight (g)	% Total Solids	Final weight (g)	% Total Solids	

CALCULATIONS
% Total Solids = Final weight (g) – Dish weight (g) / Sample weight (g) X 100

SOP C13-Revision 5–Exhibit C13.1

Subject: Biochemical Oxygen Demand (SM 5210 B-2016)

Approval

Title	Name	Signature	Date
Laboratory Supervisor	Kelley E. Keenan		05-01-24
Quality Assurance Officer	Jim Sumner		05-01-24

Document Revision History

Effective Date	Revision number	Review Type	Evaluators	Revisions
06-18-01	0	Internal	Jim Sumner (ETS)	Original document
09-01-09	1	Internal	Jim Sumner (ETS)	• Updated exhibits during document review. • Corrective action included if LFB exceed acceptance criteria.
01-11-11	2	Internal	Jim Sumner (ETS)	• Updated exhibits during document review.
01-03-12	3	Internal	Kelley Keenan, Jim Sumner (ETS)	• Updated exhibits during document review. • Provided additional guidance and clarification.
04-01-13	4	Internal	Kelley Keenan, Jim Sumner (ETS)	• Updated procedure and references to the approved analytical method identified in USEPA Method Update Rule II (MUR II), May 18, 2012. • Updated new NC WW/GW LC Policy for drift checks.
09-02-14	5	Internal	Kelley Keenan (ETS)	• Updated procedure to include additional requirements in the 22nd Edition of Standard Methods.
10-01-17	6	Internal	Jim Sumner (ETS)	• Updated procedure to include NELAP requirements. • Additional guidance included in SOP. • Revised based on 2017 MUR.
07-01-21	7	Internal	Jim Sumner (ETS)	• Updated procedure and references to the approved analytical method identified in USEPA Method Update Rule, May 19, 2021.
05-01-24	8	Internal	Jim Sumner (ETS)	• Updated procedure and references to the approved analytical method identified in USEPA Method Update Rule, April 16, 2024.

Subject: Biochemical Oxygen Demand (SM 5210 B-2016)

Scope and Application

This method is used to measure the biochemical oxygen demand of wastewater and effluent samples.

Summary of Method

Biochemical oxygen demand (BOD) testing determines the relative oxygen requirements of wastewaters, effluents, and polluted waters. Its widest application is in measuring waste loadings to treatment plants and in evaluating a plant's efficiency in removing BOD. The BOD test measures the molecular oxygen used during a 5-day incubation period to biochemically degrade organic material (carbonaceous demand), oxidize inorganic material (e.g. sulfide and ferrous iron) and oxidize reduced forms of nitrogen (nitrogenous demand) unless an inhibitor is added to prevent such reduction.

BOD procedures are based on Standard Methods 5210 B-2016.

Quality Control

Blanks: Analyze two blanks with each batch of samples. The blank can deplete up to 0.2 mg/L of oxygen. If at least one of the blank samples is not less than or equal to 0.2 mg/L, then all samples in the batch must be footnoted.

Seed Controls*:* Two seed controls are used to calculate the amount of oxygen that has been used by the seeded blank. This value is subtracted from each sample. The average value should be 0.6 – 1.0 mg/L. The average value should be about the same value as the seeded blank.

Laboratory Fortified Blank (LFB, referred to LCS): Analyze at least three LCS's with each batch of samples. The final value must be between ± 30.5 mg/L of the true value. If the value is outside of the established limits, then all samples in the batch must be footnoted. All LCS bottles must be averaged.

For CBOD, LCS values, analyze at least three LCS's with each batch of samples. The final value must be between ± 30.7 mg/L of the true value. If the value is outside of the established limits, then all samples in the batch must be footnoted. All LCS bottles must be averaged.

Precision: Analyze a **duplicate** with each batch of samples (a batch of samples is considered samples analyzed on the same date). At a minimum, a duplicate must also be performed after every 20 samples. The relative percent difference (%RPD) should be ± 10% or within established limits determined through control charts. If these results differ by more than the established limits, results associated with this duplicate must be qualified (with a footnote in the analytical report) identifying the deviation.

Subject: Biochemical Oxygen Demand (SM 5210 B-2016)

Drift Checks: An air blank correction (drift check) must be checked after 10 samples and at the end of each batch. This value must be recorded when the initial DO is measured and when the final DO is measured. The drift check reading must be no more than ± 0.2 mg/L. If the drift check is not within this range, recalibrate the meter and measure all sample bottles that were in between the drift check.

A bottle blank correction (drift check) must be checked after 10 samples and at the end of each batch. This value must be recorded when the initial DO is measured and when the final DO is measured. The drift check reading must be no more than ± 0.2 mg/L. If the drift check is not within this range, recalibrate the meter and measure all sample bottles that were in between the drift check.

Consumables:
Once opened, the glucose glutamic acid solution must be discarded after 30 days.

The sodium sulfite solution must be prepared daily.

Sample results:
Sample results are calculated based on the amount of DO in mg/L that has been used. Samples must deplete 2.0 mg/L of oxygen in each dilution before the results can be used. If the dilution does not deplete the required oxygen, the Envio rules are used to determine the BOD of the sample.

If a sample is initiated with one dilution being 300 mL, and that dilution does not meet the 2.0-mg/L requirement, then the value of the 300 mL sample which is reported as the result and a footnote will not be required.

If a sample is initiated and both dilutions used meet the 2.0 mg/L requirement, then an average will be calculated from both samples and that result will be reported and no footnote will be required.

If a sample is initiated and both dilutions do not meet the 2.0 mg/L requirement, then the result of the highest dilution will be used, and a footnote will be required. The reporting limit will also be increased based on the sample value after the seed correction x the dilution factor. (final DO – seed correction x dilution factor)

If a sample is initiated and both dilutions deplete all the oxygen in the sample, where less than 1.0 mg/L is left, then a calculation will be used to determine the greater than value. You must read the first dilution and record the value, even though the result is less than 1.0 mg/L. Follow the normal calculations and report a greater than value. All samples in the batch must be footnoted.

Additional quality control guidance is provided in QAP-Q5.

Interferences

Several factors (e.g. soluble versus particulate organics, settleable and floating solids, oxidation of reduced iron and sulfur compounds, or lack of mixing) may affect the accuracy and precision of BOD measurements. Presently, there are no effective adjustments or corrections to compensate for these factors.

Equipment and Materials

300-mL BOD bottles
BOD racks
BOD stoppers
10-L and 20-L Nalgene water jugs
Masking tape
Sharpie®
Ferric chloride 0.025%
Calcium chloride 2.75%
Magnesium sulfate 2.25%
Phosphate buffer 7.2 S.U.
HACH nutrient pillows
HACH Nitrification Inhibitor pop
1000-mL beaker
800-mL beaker
400-mL beakers
150-mL beakers
Stir rods
Stir bars
Stir plate
Aquarium pump
Aquarium tubing
10-mL serological pipettes
5-mL serological pipette
2-mL serological pipette
Glass pipette
DO meter with stirring BOD probe
BOD probe filling solution
BOD probe nodules
Polyseed ®
DPD powder pops
1-oz medicine cups

1000-mL volumetric flask
100-mL volumetric flask
Spatula
Concentrated H_2SO_4
Potassium iodide
Sodium sulfite
Sodium hydroxide pellets
100-mL graduated cylinders
250-mL graduated cylinders
pH meter and probe
Analytical balance (0.001 mg)
Deionized water
Rinse bottle
Bleach
Refrigerator (0 – 4^0C)
Incubator (20 ± 1^0C)
Thermometer (1°C increments)
Sparkleen®
BOD benchsheet
Environotes
Conditions when BOD data must be qualified
BOD History Log

Procedure

A. Preparation of BOD Water.

1. Add a splash of bleach to a 10-L or 20-L Nalgene® water jug.
2. Rinse the jug with tap water until there is no smell of bleach.
3. Once clean, fill the water jug with 10-L or 20-L of deionized water.
4. Loosen the cap before storing.
5. On a strip of masking tape, write with a Sharpie® marker, "BOD H_2O", the date BOD water was prepared and initial. Tape to the jug.
6. Water must be aged and used between 5 and 15 days before use.

7. On the day that the BOD H_2O is to be used, add 1-mL of calcium chloride, magnesium sulfate, ferric chloride and phosphate buffer to each liter of water.

B. Preparation of Polyseed®.

1. Before a new bottle of Polyseed® is used, open all the capsules into the original bottle.
2. Measure 800-mL of BOD water into a 1000-mL beaker with a stir bar.
3. Calibrate the balance (SOP-G10).
4. With a spatula, measure between 0.25 – 0.30 mg of Polyseed® into a 1-oz medicine cup. This value will vary with each new batch of Polyseed. **NOTE**: Each new batch of Polyseed® may have a different measurement.
5. Empty the contents into the 1000-mL beaker containing the BOD water.
6. Place aquarium tubing on the tip of a glass pipette. Slip the other end of the tubing into an aquarium pump and plug the pump in.
7. Place the open end of the pipette into the 1000-mL beaker so that the Polyseed® mixture is aerating.
8. Place the beaker on a stir plate.
9. Aerate and stir the mixture for a least 1-hour.
10. After the hour, remove the pipette from the beaker and turn off the stir plate.
11. Tip the beaker towards the lip and let the stir bar rest on the side of the beaker. This will keep the solids from being stirred up when the liquid is decanted.
12. After the solids have settled, slowly decant the liquid into an 800-mL beaker being careful not to get any large solids into the liquid. Sample should settle for ~ 1-2 hours.
13. Write “BOD SEED”, the date and initials of the analyst that prepared the mixture on the side of the glass beaker.
14. Keep the Polyseed® mixture refrigerated until use. Polyseed® must be used within 48-hours of being mixed.

C. Preparation of Sodium Sulfite.

1. Calibrate the balance (SOP-G10).
2. Measure 0.1575g of sodium sulfite into a 1-oz medicine cup.
3. Fill a 100-mL volumetric flask with approximately 70-mL of deionized water.
4. Add the sodium sulfite to the 100-mL volumetric flask and mix until dissolved.
5. Bring to volume with deionized water and shake.
6. Sodium sulfite must be made daily.

D. Preparation of Potassium Iodide.

1. Calibrate the balance (SOP-G10).
2. Measure 100-g of potassium iodide into a 1-oz medicine cup.
3. Fill a 1000-mL volumetric flask with 800-mL of deionized water.
4. Place a funnel in the flask and pour the potassium iodide into the funnel.
5. Mix the solution until dissolved.
6. Bring to volume with deionized water and mix.
7. Assign the reagent an INR number according to SOP-G15.
8. Pour the standard into a 1-L glass bottle.
9. Label the standard with the directions, date made, INR number, expiration date and analyst's initials. Reagents that are made in the laboratory have a year expiration date.

E. Preparation of the 1+50 Sulfuric Acid.

1. Pour approximately 40 mL of concentrated sulfuric acid into a 150-ml beaker.
2. Fill a 1000-mL volumetric flask with 800-mL of deionized water.

3. Using a glass serological pipette, measure 20-mL into the flask and mix. Caution should be used when working with sulfuric acid.

4. Bring to volume with deionized water and mix.

5. Assign the reagent an INR number according to SOP-G15.

6. Pour the standard into a 1-L glass bottle.

7. Label the standard with the directions, date made, INR number, expiration date and analyst's initials. Reagents that are made in the laboratory have a year expiration date.

F. Preparation of 1N Sodium Hydroxide.

1. Calibrate the balance (SOP-G10).

2. Measure 40-g of sodium hydroxide pellets into a 1-oz medicine cup.

3. Fill a 1000-mL volumetric flask with 800-mL of deionized water.

4. Slowly pour the sodium hydroxide pellets into the flask and mix. Caution should be used when working with sodium hydroxide.

5. Bring to volume with deionized water and mix.

6. Assign the reagent an INR number according to SOP-G15.

7. Pour the standard into a 1-L plastic bottle.

8. Label the standard with the directions, date made, INR number, expiration date and analyst's initials. Reagents that are made in the laboratory have a 1-year expiration date.

G. Preparation of 1 N Sulfuric Acid.

1. Pour approximately 40-mL of concentrated sulfuric acid into a 150-oz beaker.

2. Fill a 1000-mL volumetric flask with 800-mL of deionized water.

3. Using a glass serological pipette, measure 28-mL of sulfuric acid into the flask and mix. Caution should be used when working with sulfuric acid.

4. Bring to volume with deionized water and mix.

5. Assign the reagent an INR number according to SOP-G15.

6. Pour the standard into a 1-L plastic bottle.

7. Label the standard with the directions, date made, INR number, expiration date and analyst's initials. Reagents that are made in the laboratory have a year expiration date.

H. Preparation of Glucose Glutamic Acid Solution.

1. Pour a small amount of glucose in an evaporating dish.

2. Pour a small amount of glutamic acid in an evaporating dish.

3. Both chemicals must be dried at 103^{o} for one hour.

4. Remove chemicals from the oven and desiccate overnight.

5. Calibrate the balance according to SOP-G10.

6. Measure 150 mg of each into a 1-oz medicine cups.

7. Fill a 1-L volumetric flask with 800-mL deionized water.

8. Pour the chemicals in the flask.

9. Bring to volume with deionized water and mix.

10. Pour the standard into a 1-L glass bottle and refrigerate.

11. Label the standard with the directions, date made, INSS number, expiration date and analyst's initials. The glucose glutamic acid standard MUST to be used within 30 days.

12. If the glucose glutamic acid is purchase as a large quantity, the expiration date is 30 days from the date opened. If glucose glutamic acid is bought in individual vials, the expiration date will be the manufacture's expiration date.

Subject: Biochemical Oxygen Demand (SM 5210 B-2016)

I. Preparation of the BOD bottles.

1. Wash all bottles and stoppers in the dishwasher with dishwasher safe Sparkleen® or Alconox®.

2. After bottles and stoppers are washed, remove from the dishwasher and store bottles upside down in the BOD rack and the stoppers in a bucket.

2. If bottles or stoppers do not get clean in the dishwasher, fill a sink with hot water and add approximately 2 tablespoons of Sparkleen® or Alconox®.

3. Place the BOD bottles into the sink and soak.

4. Using a bottlebrush, scrub the inside of the bottles until clean.

5. Rinse each bottle with tap water and turn upside down to dry.

6. Bottles must be stored upside down until use.

7. Wash all stoppers with hot soapy water and rinse with tap water. Store stoppers in a bucket/box.

J. Preparation of starch solution.

1. Starch solution should be purchased. Follow the manufacturer's expiration date.

K. Preparation of DPD powder pops or dispenser.

1. DPD powder pops/dispenser should be purchased. Be sure to check the volume of sample that each pop will be used. Follow the manufactures expiration date.

L. Preparation of BOD samples.

1. All BOD samples must have the pH and chlorine checked before analysis. Make sure the temperature of the samples is 20°C ± 3°C. (room temperature). Place the samples in a sink of hot water, leave the samples out on the counter long enough to reach room temperature, or place on the 103 – 105°C oven.

2. Calibrate the pH meter (SOP-C3).
3. Pour approximately 30-mL of sample into a 1-oz medicine cup.

4. Measure the pH of each sample. The pH must be 6.0 – 8.0 S.U. If the pH is not in this range the sample must be adjusted with 1N Sodium Hydroxide or 1N Sulfuric Acid. If the pH is out of range, record on the BOD benchsheet the pH value and ↑or ↓. The adjusted pH must be between 7.0 – 7.2 S.U.

5. After the pH is measured, dispense a DPD powder pop into each medicine cup.

6. If the sample turns pink, a titration for chlorine must be performed.

M. Titration of BOD samples to determine the amount of dechlorination.

1. Pour 100-mL of sample into a 150-mL beaker with a stir bar.

2. Add 10-mL of 1+50 sulfuric acid and 10-mL of potassium iodide.

3. Place the sample on stir plate and stir.

4. Add few drops of starch solution until the sample turns blue. If the sample does not turn a blue color, then the sample gave a false positive chlorine result.

5. Add a drop of the sodium sulfite mixture until the sample turns clear.

6. Record the number of drops used to dechlorinate the sample in the BOD benchsheet.

7. If a sample has an excessive amount of chlorine present, a stronger concentration of Sodium Sulfide Anhydrous may be mixed. (Example: Mix a 10x stronger concentration)

N. Preparation of the DO Meter.

1. Calibrate the DO meter (SOP-C2).

O. Dilution Technique.

1. A minimum of three dilutions must be set on each sample. Refer to the BOD History Book for prior sample dilutions and results. If the sample is new and there is no history for results, a minimum of four dilutions must be set.

2. Observe the sample color, smell, clarity, and type. Dilutions are made based on these observations. Dilutions that are 1 mL or lower, must be made using a serial dilution.

3. Samples that are dark have a septic smell or chemical smell should be set at lower dilutions.

4. Samples that are clear and have few solids should be set at higher dilutions.

5. Record the first bottle number on the BOD benchsheet. Dilutions are set from the lowest to the highest dilution.

P. Procedure for setting up BOD Samples.

1. Remove the samples, glucose glutamic acid, Polyseed®, DPD powder pops/dispenser and starch solution from the refrigerator and warm the liquids to room temperature (20^{o} C ± 3^{o} C). Liquids may be warmed to room temperature in a hot water bath, by leaving out long enough to reach room temperature, or by placing on the top of the 103 – 105°C oven.

2. Fill out the BOD benchsheet (Exhibit C14.1) with the sample identification number, date collected, sample name, and dilutions to be used.

3. Take a rack of BOD bottles and turn upright. Record the bottle identification number on the benchsheet.

4. Make sure that all samples have the chlorine and pH checked and the amount of sodium sulfite that is needed to dechlorinate the sample is documented according to SOP-C14 L and M. If a stronger sodium sulfite solution is needed, make a note on the benchsheet.

5. Calibrate the DO meter (SOP-C2).

6. Using a 100-mL graduated cylinder, add 1-mL each of calcium chloride, magnesium sulfate, ferric chloride and phosphate buffer to each liter of water. For 20-L there will be 20-mL of each reagent. At the time that the phosphate buffer is opened, the pH must be checked and recorded on the bottle. The true value is 7.2 S. U.

7. Start with the blanks (two bottles). Fill the first bottle with BOD water.

8. Take a glass stopper and gently tap out any air bubbles.

9. Measure the initial DO of the water. The DO must be between 7.5 and 9.0 mg/L. If the BOD water is not in this range, vigorously shake the jug and recheck. Fill the second bottle and record both values. BOD water that should be around the DO required for the room temperature.

10. Take a glass stopper and tap the top of the bottle to remove any air bubbles.

11. Place a stopper in the top of each bottle and cover with a plastic cap. Make sure that the water in the bottle covers the stopper. If there is not enough water add a small amount of BOD water so that the stopper is covered.

12. Fill the next three bottles with 5, 20, and 30-mL of Polyseed®. The 5-mL bottle is the seeded blank. The 20 and 30-mL bottles are used for the seed blank correction. This correction should be relatively close to the value of the seeded blank.

13. Fill each bottle with BOD water.

14. Take a glass stopper and gently tap out any air bubbles.

15. Measure and record the initial DO of the samples on the BOD benchsheet.

16. Place a stopper in the top of each bottle and cover with a plastic cap. Make sure that the water in the bottle covers the stopper. If there is not enough water add a small amount of BOD water so that the stopper is covered.

17. Add 5-mL of Polyseed® to all remaining bottles.

18. The next three bottles are the laboratory control standards (LCS). Add 6-mL of the LCS (glucose glutamic acid) to each bottle or if you are using vials, break each vial, pour the liquid into a bottle with 5-mL of Polyseed® and approximately 100-mL of BOD H_2O. Put the glass top and bottom of each vial into each LCS BOD bottle. Swirl around until there are no air bubbles in the glass vials. **NOTE**: You may use more than 3 LCS bottles if problems are noted with LCS recovery values.

19. Fill each bottle with BOD water.

20. Take a glass stopper and gently tap out any air bubbles.

21. Measure and record the initial DO of the LCS on the BOD benchsheet.

22. Place a stopper in the top of each bottle and cover with a plastic cap. Make sure that the water in the bottle covers the stopper. If there is not enough water add a small amount of BOD water so that the stopper is covered.

23. After the LCS has been set up, start preparing the samples.
24. Set at minimum of three dilutions for each sample.

25. If the sample needs to be dechlorinated, pour the appropriate volume into a 400-mL beaker and add the pre-determined amount of sodium sulfite.

26. Using a glass stir rod, vigorously stir the sample.

27. Measure the proper dilutions into the appropriate bottles. Use 100 and 250-mL graduated cylinders, and 10-mL pipettes.

28. If the sample needs to have the pH adjusted, pour the appropriate volume into a 400-mL beaker and measure the pH.

29. Using 1N sodium hydroxide or 1N sulfuric acid, adjust the pH between 7.0 and 7.2 S.U. **NOTE**: If the sample required both dechlorination and pH adjustment, dechlorinate the sample first. Check the pH and adjust with 1N sodium hydroxide or 1N sulfuric acid.

30. Measure the proper dilutions into the appropriate bottles. Use 100 and 250-mL graduated cylinders, and 10-mL pipettes.

31. For sample dilutions that are over 201 mL, then a nutrient pillow must be added to each bottle. Cut the top off the nutrient pillow and pour the entire contents into each BOD bottle.

32. Fill all the bottles with BOD water.

33. Take a glass stopper and gently tap the top of each bottle to remove any air bubbles.

34. Measure and record the initial DO in mg/L. Place stoppers in the top of each bottle and cover with a plastic cap. Make sure that the sample in the bottle covers the stopper. If there is not enough water in the bottle add a small amount of BOD water to cover the stopper.

35. Follow steps P25 – 34 to complete the remaining samples.

36. On day 1, a DO Meter Drift using air calibration must be recorded. After every ten samples and at the end of the batch record the day 1 drift check. Rinse the probe with deionized water and shake all the excess water off the probe. Place the probe in the BOD bottle partially filled with deionized water. Check the temperature reading and subtract the difference from the correct reading and record on the BOD benchsheet.

i.e. If the temperature is 20.2°C the correct reading will be 8.4 mg/L. If the meter is reading 8.3 mg/L then -0.1 will be placed in the drift check column for day 1. The drift check reading must be no more than ± 0.2 mg/L. If the drift check is not within this range, recalibrate the meter and measure all sample bottles that were in between the drift check.

37. On day 1, a DO Meter Drift on a bottle blank must be recorded. After every ten samples and at the end of each batch, record the initial DO in mg/L on the benchsheet in the sample identification – BLANK. The measurement will be from the 2nd bottle blank at the beginning of each batch. The Drift check reading must be no more than ± 0.2 mg/L. If the drift check is not within this range, recalibrate the meter and measure all sample bottles that were in between the DO Meter Drift check.

Q. Procedure for setting up CBOD Samples.

1. Remove the samples, glucose glutamic acid, Polyseed®, DPD powder pops/dispenser and starch solution from the refrigerator and warm the liquids to room temperature (20° C ± 3° C). Liquids may be warmed to room temperature in a hot water bath, by leaving out long enough to reach room temperature, or by placing on the top of the 103 – 105°C oven.

2. Get out the HACH Nitrification Inhibitor pop.

3. Fill out the BOD benchsheet (Exhibit C14.1) with the sample identification number, date collected, sample name, and dilutions to be used.

4. Take a rack of BOD bottles and turn upright. Record the bottle identification number on the benchsheet.

5. Make sure that all samples have the chlorine and pH checked and the amount of sodium sulfite that is needed to dechlorinate the sample is documented according to SOP-C14 L and M. If a stronger sodium sulfite solution is needed, make a note on the benchsheet.

6. Calibrate the DO meter (SOP-C2).

7. Using a 100-mL graduated cylinder, add 1-mL each of calcium chloride, magnesium sulfate, ferric chloride and phosphate buffer to each liter of water. For 20-L there will be 20-mL of each reagent. At the time that the phosphate buffer is opened, the pH must be checked and recorded on the bottle. The true value is 7.2 S. U.

8. Start with the blanks (two bottles). Fill the first bottle with BOD water.

9. Take a glass stopper and gently tap out any air bubbles.

10. Measure the initial DO of the water. The DO must be between 7.5 and 9.0 mg/L. If the BOD water is not in this range, vigorously shake the jug and recheck. Fill the second bottle and record both values. BOD water that should be around the DO required for the room temperature.

11. Take a glass stopper and tap the top of the bottle to remove any air bubbles.

12. Place a stopper in the top of each bottle and cover with a plastic cap. Make sure that the water in the bottle covers the stopper. If there is not enough water add a small amount of BOD water so that the stopper is covered.

13. Fill the next three bottles with 5, 20, and 30-mL of Polyseed®. The 5-mL bottle is the seeded blank. The 20 and 30-mL bottles are used for the seed blank correction. This correction should be relatively close to the value of the seeded blank.

14. Fill each bottle with approximately 100-mL BOD water. Add 2 pops of the nitrification inhibitor and swirl each bottle to mix. Finish filling up each bottle with BOD water.

15. Take a glass stopper and gently tap out any air bubbles.

16. Measure and record the initial DO of the samples on the BOD benchsheet.

17. Place a stopper in the top of each bottle and cover with a plastic cap. Make sure that the water in the bottle covers the stopper. If there is not enough water add a small amount of BOD water so that the stopper is covered.

18. Add 5-mL of Polyseed® to all remaining bottles.

19. The next three bottles are the laboratory control standards (LCS). Add 6-mL of the LCS (glucose glutamic acid) to each bottle or if you are using vials, break each vial, pour the liquid into a bottle with 5-mL of Polyseed® and approximately 100-mL of BOD H_2O. Put the glass top and bottom of each vial into each LCS BOD bottle. Swirl around until there are no air bubbles in the glass vials. **NOTE**: you may use more than 3 LCS bottles if problems are noted with LCS recovery values.

20. Fill each bottle with approximately 100-mL BOD water. Add 2 pops of the nitrification inhibitor and swirl each bottle to mix. Finish filling up each bottle with BOD water.

21. Take a glass stopper and gently tap out any air bubbles.

22. Measure and record the initial DO of the LCS on the BOD benchsheet.

23. Place a stopper in the top of each bottle and cover with a plastic cap. Make sure that the water in the bottle covers the stopper. If there is not enough water add a small amount of BOD water so that the stopper is covered.

24. After the LCS has been set up, start preparing the samples.

25. Set at minimum of three dilutions for each sample.

26. If the sample needs to be dechlorinated, pour the appropriate volume into a 400-mL beaker and add the pre-determined amount of sodium sulfite.

27. Using a glass stir rod, vigorously stir the sample.

28. Measure the proper dilutions into the appropriate bottles. Use 100 and 250-mL graduated cylinders, and 10-mL pipettes.

29. If the sample needs to have the pH adjusted, pour the appropriate volume into a 400-mL beaker and measure the pH.

30. Using 1N sodium hydroxide or 1N sulfuric acid, adjust the pH between 6.5 and 7.5 S.U. **NOTE**: If the sample required both dechlorination and pH adjustment, dechlorinate the sample first. Check the pH and adjust with 1N sodium hydroxide or 1N sulfuric acid.

31. Measure the proper dilutions into the appropriate bottles. Use 100 and 250-mL graduated cylinders, and 10-mL pipettes.

32. For sample dilutions that are over 201 mL, then a nutrient pillow must be added to each bottle. Cut the top off the nutrient pillow and pour the entire contents into each BOD bottle.

33. Fill all the bottles with BOD water. Add 2 pops of the nitrification inhibitor and swirl each bottle to mix. For samples that are set up at 300 mL, fill the BOD 2/3 full of sample, add 2 pops of the nitrification inhibitor and swirl each bottle to mix. Finish filling up each bottle with sample.

34. Take a glass stopper and gently tap the top of each bottle to remove any air bubbles.

35. Measure and record the initial DO in mg/L. Place stoppers in the top of each bottle and cover with a plastic cap. Make sure that the sample in the bottle covers the stopper. If there is not enough water in the bottle add a small amount of BOD water to cover the stopper.

36. Follow steps Q26 – 35 to complete the remaining samples.

37. On day 1, a DO Meter Drift using air calibration must be recorded. After every ten samples and at the end of the batch record the day 1 drift check. Rinse the probe with deionized water and shake all the excess water off the probe. Place the probe in the BOD bottle partially filled with deionized water. Check the temperature reading and subtract the difference from the correct reading and record on the BOD benchsheet. i.e. If the temperature is 20.2°C the correct reading will be 8.4 mg/L. If the meter is reading 8.3 mg/L then -0.1 will be placed in the drift check column for day 1. The drift check reading must be no more than ± 0.2 mg/L. If the drift check is not within this range, recalibrate the meter and measure all sample bottles that were in between the drift check.

38. On day 1, a DO Meter Drift on a bottle blank must be recorded. After every ten samples and at the end of each batch, record the initial DO in mg/L on the benchsheet in the sample identification – BLANK. The measurement will be from the 2nd bottle blank at the beginning of each batch. The Drift check reading must be no more than ± 0.2 mg/L. If the drift check is not within this range, recalibrate the meter and measure all sample bottles that were in between the DO Meter Drift check.

R. Incubation of BOD samples.

1. After initial set up has been completed, place BOD racks in the BOD incubator.

2. Samples must be incubated in the dark at 20° C ± 1° C for 5 days.

3. On the fifth day, remove the appropriate rack from the incubator. Samples may be read-out ± 6-h of the set up time. If samples can not be read-out during this time, then note the benchsheet with the reason.

S. Read-out of BOD samples.

1. Calibrate the DO meter (SOP-C2).

2. Remove the plastic tops from each bottle.

3. Remove the stoppers from each bottle.

4. Starting with the blank samples, measure and record the final DO in mg/L.

5. Measure and record the final DO in mg/L of the Polyseed® control.

6. Measure and record the final DO in mg/L of the LCS.

7. Continue this procedure until the final DO in mg/L has been recorded for each sample.

8. Rinse the DO probe with deionized water after each sample.

9. On day 5, a DO Meter Drift using air calibration must be recorded. After every ten samples and at the end of the batch record the day 1 drift check. Rinse the probe with deionized water and shake all the excess water off the probe. Place the probe in the BOD bottle partially filled with deionized water. Check the temperature reading and subtract the difference from the correct reading and record on the BOD benchsheet. i.e. If the temperature is 20.2°C the correct reading will be 8.4 mg/L. If the meter is reading 8.3 mg/L then -0.1 will be placed in the drift check column for day 1. The drift check reading must be no more than ± 0.2 mg/L. If the drift check is not within this range, recalibrate the meter and measure all sample bottles that were in between the drift check.

10. On day 5, a DO Meter Drift on a bottle blank must be recorded. After every ten samples and at the end of each batch, record the final DO in mg/L on the benchsheet in the sample identification – Blank. The measurement will be from the 2nd bottle blank at the beginning of each batch. The Drift check reading must be no more than ± 0.2 mg/L. If the drift check is not within this range, recalibrate the meter and measure all sample bottles that were in between the DO Meter Drift check.

Subject: Biochemical Oxygen Demand (SM 5210 B-2016)

T. Calculation of BOD results.

1. Oxygen used mg/L = Initial DO mg/L – Final DO mg/L

2. % Oxygen Depleted mg/L = $\frac{\text{Oxygen Used mg/L}}{\text{Initial DO mg/L}}$

3. Corrected DO mg/L = $\frac{\text{Oxygen Used mg/L}}{\text{Final Seed Correction}}$

4. Dilution Factor = $\frac{300\ \text{mL}}{\text{mL of sample used}}$

5. BOD of the sample mg/L= Corrected DO mg/L X Dilution Factor

V. Precision and Accuracy, Calculations.

1. Blank calculation.

   Final DO mg/L – Initial DO mg/L

2. Seed correction calculation.

   a. 20-mL seed correction.
   $$\frac{\text{Final DO mg/L – Initial DO mg/L}}{20} \times 5$$
   b. 30-mL seed correction.
   $$\frac{\text{Final DO mg/L – Initial DO mg/L}}{30} \times 5$$
   c. Add the 20-mL and 30-mL values and average.

3. Laboratory control standard (LCS) determination, True value = 198 mg/L.
   Final DO mg/L – Initial DO mg/L – Seed Correction

   Multiply this value x 50

   Determined value – True value

4. CBOD Laboratory control standard (LCS) determination, True value = 164 mg/L.
   Final DO mg/L – Initial DO mg/L – Seed Correction

   Multiply this value x 50

   Determined value – True value

5. Duplicate acceptance. Relative Percent Difference (%RPD)

   %RPD = (Sample value – Duplicate value) / [(Sample value + Duplicate value)/2] x 100

6. Greater than calculation.

   Initial DO mg/L – Seed Correction X Dilution factor

Safety and Hazardous Waste Management

Safety glasses, gloves and lab coats should always be worn while handling samples. Excess samples may be flushed down the sink.

Review Policy-P6: General Safety Policy and Policy-P9: Radiation Protection Policy for additional safety requirements.

References

Standard Methods for the Examination of Water and Wastewater, 24th Edition, 2023. American Public Health Association, 800 I Street, NW, Washington DC 20001-3710.

- Method: 5210 B-2016.

TNI Standard. Management and Technical Requirements for Laboratories Performing Environmental Analysis. The NELAC Institute, PO Box 2439, Weatherford, TX 76086.

Instrument Manual

Exhibits

Exhibits C14.1: BOD benchsheet.

Subject: Biochemical Oxygen Demand (SM 5210 B-2016)

Exhibit C14:1: BOD Benchsheet

BOD
SM 5210 B-2016
RL = 2.0 mg/L

Page _____
Page _____ of _____

Date Started: _____ Time Started: _____ Analyst: _____
Date Completed: _____ Time Completed: _____ Analyst: _____
Initial D.O. Calibration: _____ Final D.O. Calibration: _____ Reviewed By: _____
Seed Date: Dilution Water Date: Reviewed Date: _____

Sample Number	Date Collected	Sample Identification	Bottle Number	(#1) Initial D.O. mg/L	(#2) Final D.O. mg/L	(#3) Oxygen Used, mg/L (#1-#2)	% Oxygen Depleted (#3 / #1)	Averaged Dilution, mg/L	(#4) Final Seed Correction	(#5) Corrected D.O., mg/L (#3-#4)	(#6) Dilution factor (300 / ml of sample)	BOD of sample, mg/L (#5 x #6)	Dilution Reported	mls of sample	v if extra nutrients added	pH 6.0 - 8.0, No (pH value)	If pH is (N), adjust pH Up (U) or down (D)	Amount of S. S. added to dechlorinate 100 ml sample	Drift Check every 10 samples - Day 1	Day 5

CALCULATIONS

Initial Seed Correction: (5) (final oxygen used in 20 ml seed bottle / 20)
(5) (final oxygen used in 30 ml seed bottle / 30)
( ) = _____ mg/l **Average** = _____

Final RPD = [(S - D) / ((S + D / 2)] x 100%
Laboratory Control Standard (LCS) RS = A - B (True Value = 198mg/l)
Sodium Sulfite Anhydrous = S.S. (made fresh daily)

Quality Control

Precision (duplicate):
Sample number:
Sample result (S): _____
Duplicate result (D):
Final RPD: _____ %

Precision (duplicate):
Sample number:
Sample result (S): _____
Duplicate result (D):
Final RPD: _____ %

Reference Standard (LCS):
Reference standard number:
Value Obtained (A): _____
True Value (B):
RS: _____ mg/L Difference

SOP C14-Revision 8-Exhibit C14.1

Subject: Ammonia Nitrogen (SM 4500 NH_3 D-2021)

Approval

Title	Name	Signature	Date
Laboratory Supervisor	Kelley E. Keenan		05-01-24
Quality Assurance Officer	Jim Sumner		05-01-24

Document Revision History

Effective Date	Revision number	Review Type	Evaluators	Revisions
06-18-01	0	Internal	Kelley E. Keenan (ETS)	Original document
01-11-11	1	Internal	Jim Sumner (ETS)	• Updated SOP and exhibits during document review. Provided additional procedural guidance where required
01-03-12	2	Internal	Kelley Keenan Jim Sumner (ETS)	• Updated SOP and exhibits during document review.
01-27-12	3	External	Jason Smith (NC DENR)	• Midpoint analyzed at the end of every batch (or 10 samples) instead of LFB.
04-01-13	4	Internal	Jim Sumner (ETS)	• Updated procedure and references to the approved analytical method identified in USEPA Method Update Rule II (MUR II), May 18, 2012.
04-01-18	5	Internal	Jim Sumner (ETS)	• Updated procedure to include NELAP requirements. • Additional guidance included in SOP. • Method number revised based on 2017 MUR.
05-01-24	6	Internal	Jim Sumner (ETS)	• Updated procedure and references to the approved analytical method identified in USEPA Method Update Rule, April 16, 2024.

Subject: Ammonia Nitrogen (SM 4500 NH_3 D-2021)

Scope and Application

This method is used to provide a method for measuring the concentration of ammonia nitrogen in water samples.

Summary of Method

Ammonia nitrogen is determined electrometrically using a glass electrode in combination with a reference potential or a combination electrode.

The ammonia-selective electrode uses a hydrophobic gas permeable membrane to separate the sample solution from an electrode internal solution of ammonium chloride. Dissolved ammonia ($NH_{3(ag)}$ and NH_4^+) is converted to $NH_{3(ag)}$ by raising the pH to above 11 S.U. with a strong base. $NH_{3(ag)}$ diffuses through the membrane and changes the internal solution pH that is sensed by a pH electrode. The fixed level of chloride in the internal solution is sensed by a chloride ion-selective electrode that serves as the reference electrode. Potentiometric measurements are made with a pH meter having an expanded millivolt scale or with a specific ion meter.

Ammonia nitrogen measurement procedures are based on SM 4500 NH_3 D-2021.

Sample Collection, Preservation, Shipment and Storage

Samples must be analyzed within **28-days** of collection if preserved with H_2SO_4. Samples are preserved at the time of collection with H_2SO_4 at a pH < 2 S.U. In addition, samples containing chlorine are dechlorinated at the time of collection with $Na_2S_2O_3$.

Samples must be received and stored in the laboratory at 0 to 6.0°C.

Quality Control

Calibration: The ion analyzer must be calibrated for ammonia nitrogen each day **before use**.

Precision: Analyze a **duplicate** with each batch of samples (a batch of samples is considered samples analyzed on the same date). At a minimum, a duplicate must also be performed after every 20 samples. The relative percent difference (%RPD) should be ± 10% or within established limits determined through control charts. If these results differ by more than the established limits, results associated with this duplicate must be qualified (with a footnote in the analytical report) identifying the deviation.

Laboratory Fortified Blank (LFB, referred to LCS on benchsheets): A LFB must be analyzed initially and must be performed with each batch of samples. At a minimum, a LFB must be performed after every 20

samples and at the end of each batch of samples. The percent recovery of the LFB (%R) must be ± 10% from the true value.

Matrix Spike Recovery (MS): A MS must be analyzed initially and must be performed with each batch of samples. At a minimum, a MS must be performed on 5% of samples on a monthly basis. If fewer than 20 samples are analyzed in a month, at least one MS must be performed within that month. The percent recovery of the MS (%R) must be ± 25% from the true value. If these results differ by more than the established limits, results associated with the spike must be qualified (with a footnoted on the analytical report) identifying the deviation. Qualification may include any sample interferences that may have resulted in the deviation.

Matrix Spike Duplicate (MSD): A MSD must be analyzed initially and must be performed with each batch of samples. At a minimum, a MSD must be performed on 5% of samples on a monthly basis. If fewer than 20 samples are analyzed in a month, at least one MSD must be performed within that month. The relative percent difference (%RPD) should be ± 10% or within established limits determined through control charts. If these results differ by more than the established limits, results associated with this MSD must be qualified (with a footnote in the analytical report) identifying the deviation. Qualification may include any sample interferences that may have resulted in the deviation.

Method Blank (MB): A MB must be analyzed initially and must be performed with each batch of samples (a batch of samples is considered samples analyzed on the same date). The MB must be ≤ one half the reporting limit (RL).

Reporting Limit (RL): The RL for ammonia nitrogen is 0.10 mg/L.

PE: Annually (once every calendar year), a single-blind QC check sample (QCS) or performance evaluation sample (PE) is analyzed. This sample is provided by an approved proficiency testing (PT) provider.

Additional quality control guidance is provided in QAP-Q5.

Interferences

Amines are a positive interference and may be enhanced by acidification. Mercury and silver interfere by complexing with ammonia, unless NaOH/EDTA solution is used.

Subject: Ammonia Nitrogen (SM 4500 NH_3 D-2021)

Equipment and Materials

Ion analyzer equipped with an ammonia nitrogen probe
Ammonia nitrogen standard for the Laboratory Fortified Blank (LFB)
Ammonia nitrogen standard for standardization
10N Sodium Hydroxide
Eppendorf pipettes
Rinse bottle
Deionized water
150-mL beakers
Stir bars
Stir plate
Serological pipettes
100-mL graduated cylinder
100-mL volumetric flasks
Pipette bulb
pH strips
Waste container
Ammonia Nitrogen Benchsheet

Procedure

A. Calibration and Measurement (Meter: Accumet Model AB250 pH/mV/Ion Meter)**.**

1. Prepare the Ammonia Nitrogen benchsheet (Exhibit C15.1).

2. Each time before analysis, calibrate the meter.

3. Turn on the meter by pressing the **POWER/LIGHT** button.

4. Prepare the method blank (MB), calibration standards, midpoint standard and laboratory fortified blank (LFB).

5. To prepare the 1.0 mg/L calibration standard, pipette 0.10 mL ammonia nitrogen standard into a 100 mL volumetric flask and bring to volume using deionized water. Pour the calibration standard into a 150 mL beaker with a stir bar. 1.00 mL ammonia nitrogen standard is used to prepared the 10.0 mg/L calibration standard, 0.50 mL ammonia nitrogen standard for midpoint standard, 0.50 mL ammonia nitrogen standard using a second source for the LFB, and 0.01 mL ammonia nitrogen standard for the RL. The MB will consist of 100 mL deionized water without any ammonia nitrogen standard.

Subject: Ammonia Nitrogen (SM 4500 NH_3 D-2021)

1. Place the 1.00 mg/L calibration standard on a stir plate and stir. Remove the probe from the beaker containing ammonia solution. Rinse the probe tip with deionized water and submerge the probe into the 1.00 mg/L calibration standard. Add 1 mL 10*N* NaOH to the beaker. Check the pH of the sample by submerging a pH strip into the stirring mixture. The pH must be greater than 11 S.U. If the sample is less than 11 S.U., add a drop of 10*N* NaOH until the pH is greater than 11 S.U. Record the extra volume used.

2. Press **DISPLAY** and then **STD**. Press **CLEAR** to clear existing standards. Use the ▲ to select **1.00**. When a stable reading is obtained, the meter will indicate **PRESS STD TO STANDARDIZE**. Press **STD**.

3. Rinse the probe tip with deionized water and place into the 10.0 mg/L calibration standard on the stir plate and add 1 mL 10*N* NaOH to the beaker. Check the pH of the sample by submerging a pH strip into the stirring mixture. The pH must be greater than 11 S.U. If the sample is less than 11 S.U., add a drop of 10*N* NaOH until the pH is greater than 11 S.U. Record the extra volume used.

4. Press **DISPLAY** and then **STD**. Use the ▲ to select **10.00**. When a stable reading is obtained, the meter will indicate **PRESS STD TO STANDARDIZE**. Press **STD**.

5. The slope will be displayed. The meter will indicate a bad slope, if the slope is out of range. If the slope is out of range, recalibrate the meter following steps 1 through 5 above.

6. If the slope is within range, record the slope on the benchsheet and then analyze the midpoint standard.

7. Rinse the probe tip with deionized water and place into the 5.00 mg/L midpoint standard on the stir plate and add 1 mL 10*N* NaOH to the beaker. Check the pH of the sample by submerging a pH strip into the stirring mixture. The pH must be greater than 11 S.U. If the sample is less than 11 S.U., add a drop of 10*N* NaOH until the pH is greater than 11 S.U. Record the extra volume used. The meter will indicate **STABLE** when the measurement has stabilized.

8. Record the midpoint standard measurement on the benchsheet and calculate the %RS. The midpoint standard must be ± 10% of the true value. If it is out of range, the meter must be recalibrated.

9. Rinse the probe tip with deionized water and place into the 5.00 mg/L LFB on the stir plate and add 1 mL 10*N* NaOH to the beaker. Check the pH of the sample by submerging a pH strip into the stirring mixture. The pH must be greater than 11 S.U. If the sample is less than 11 S.U., add a drop of 10*N* NaOH until the pH is greater than 11 S.U. Record the extra volume used. The meter will indicate **STABLE** when the measurement has stabilized.

10. Record the LFB measurement on the benchsheet and calculate the %RS. The LFB must be ± 10% of the true value. If it is out of range, the meter must be recalibrated.

11. Analyze the MB. Rinse the probe tip with deionized water and place into the MB on the stir plate and add 1 mL 10*N* NaOH to the beaker. Check the pH of the sample by submerging a pH strip into the stirring mixture. The pH must be greater than 11 S.U. If the sample is less than 11 S.U., add a drop of 10*N* NaOH until the pH is greater than 11 S.U. Record the extra volume used. The meter will indicate **STABLE** when the measurement has stabilized.

12. Record the MB measurement on the benchsheet. The MB must be < 0.05 mg/L (less than ½ the reporting limit). If it is out of range, then reanalyze a MB.

13. Analyze the RL. Rinse the probe tip with deionized water and place into the RL on the stir plate and add 1 mL 10*N* NaOH to the beaker. Check the pH of the sample by submerging a pH strip into the stirring mixture. The pH must be greater than 11 S.U. If the sample is less than 11 S.U., add a drop of 10*N* NaOH until the pH is greater than 11 S.U. Record the extra volume used. The meter will indicate **STABLE** when the measurement has stabilized.

14. Record the RL measurement on the benchsheet and calculate the %RS. The RL must be ± 25% of the true value. If it is out of range, reanalyze the RL.

15. The RL must be < 0.05 mg/L (less than ½ the reporting limit). If it is out of range, then reanalyze a MB.

16. Analyze the 1st sample. Pour 100 mL of the sample into a 150 ml beaker with a stir bar. Add 1 mL 10*N* NaOH to the beaker. Check the pH of the sample by submerging a pH strip into the stirring mixture. The pH must be greater than 11 S.U. If the sample is less than 11 S.U., add a drop of 10*N* NaOH until the pH is greater than 11 S.U. Record the extra volume used. Rinse the probe tip with deionized water and place into the 1st sample. The meter will indicate **STABLE** when the measurement has stabilized.

17. Record the measurement on the benchsheet.

18. If any sample is over 10.0 mg/L, then it must be diluted. Adjust dilutions to allow readings between 1.0 mg/L and 10.0 mg/L.

19. If any samples are diluted, adjust the RL according to the dilution factor. Multiple the original RL and the dilution factor for the adjusted value.

20. The 1st sample is used for performing a duplicate, spike and spike duplicate.

21. To measure the duplicate, pour 100 mL of the same sample into a 150-ml beaker. Add 1 mL of 10*N* NaOH. Check the pH of the sample by submerging a pH strip into the stirring mixture. The pH must be over 11 S.U. If the sample is less than 11 S.U., add a drop of 10*N* NaOH until the pH is greater than 11 S.U. Record the extra volume used. Rinse the probe tip with deionized water and place into the sample. The meter will indicate **STABLE** when the measurement has stabilized.

22. Record the duplicate measurement on the benchsheet and calculate the RPD.

23. After the sample duplicate has been analyzed, pipette 0.25 mL ammonia nitrogen standard into the duplicate sample on the stir plate. The meter will indicate **STABLE** when the measurement has stabilized.

24. Record the spike measurement on the benchsheet. The spike value must be ± 25% of the true value. If the spike sample is out of range, reanalyze or footnote the samples in the batch.

25. To measure the spike duplicate, pour 100 mL of a second aliquot of the 1st sample into a 150 mL beaker with a stir bar. Pipette 0.25 mL ammonia nitrogen standard into the spike duplicate sample on the stir plate. Add 1 mL of 10*N* NaOH. Check the pH of the sample by submerging a pH strip into the stirring mixture. The pH must be over 11 S.U. If the sample is less than 11 S.U., add a drop of 10*N* NaOH until the pH is greater than 11 S.U. Record the extra volume used. Rinse the probe tip with deionized water and place into the sample. The meter will indicate **STABLE** when the measurement has stabilized.

26. Record the spike duplicate measurement on the benchsheet. Calculate the %RPD. The %RPD must be within laboratory established control limits. If these results outside of the laboratory control limits, it is noted on the laboratory benchsheet that matrix interferences may have caused the deviation.

27. Continue measuring and recording the ammonia nitrogen of samples. If any sample is over 10.00 mg/L, then it must be diluted. Adjust dilutions to allow readings between 1.0 mg/L and 10.0 mg/L.

28. If any samples are diluted, adjust the RL according to the dilution factor. Multiply the original RL and the dilution factor for the adjusted value.

29. After every 10 samples and at the end of the batch, prepare and measure a midpoint standard and a method blank. If an intermediate midpoint standard is out of range, then reanalyze all samples between the last in range standard and the out of range standard.

30. At the end of the batch, measure a method blank.

31. Once all samples have been analyzed, rinse the probe tip with deionized water and place the probe in the beaker of ammonia solution. Turn the meter off by pressing and holding the **POWER/LIGHT** button until the screen goes blank.

Note: All samples must be stirring during analysis.

B. Calculation of Ammonia Nitrogen.

1. Read directly in mg/L and report to the nearest 0.10 mg/L.

2. If the sample required more than 1 ml of 10 N NaOH, then follow the calculation below.

$$\text{mg/L } NH_3 = A \times B \times \frac{[\,100 + D\,]}{100 + C}$$

A = dilution factor
B = concentration of NH_3 mg/L
C = volume of 10N NaOH added to calibration standards (mL)
D = volume of 10N NaOH added to sample (mL)

C. Precision and Accuracy, Calculations.

1. Laboratory fortified blank (LFB) determination, True value = 0.50 mg/L.

Percent Recovery of the Standard (%RS)

%RS = (Measured value) / (True value) x 100

2. Duplicate, spike duplicate acceptance.

   Relative Percent Difference (%RPD)

   %RPD = (Sample value – Duplicate value) /
   [(Sample value + Duplicate value)/2] x 100

3. Spike recovery, True value = 0.50 mg/L.

   Percent Recovery of the Spike (%R)

   %R = (Spike value – Sample value) / (True value) x 100

Safety and Hazardous Waste Management

Safety glasses, gloves and lab coats should always be worn while handling samples. Excess samples may be flushed down the sink.

Review Policy-P6: General Safety Policy and Policy-P9: Radiation Protection Policy for additional safety requirements.

References

Standard Methods for the Examination of Water and Wastewater, 24th Edition, 2023. American Public Health Association, 800 I Street, NW, Washington DC 20001-3710.

- 4500-NH_3 D-2021.

TNI Standard. Management and Technical Requirements for Laboratories Performing Environmental Analysis. EL-V1-ISO-2016-Rev2.0. The NELAC Institute, PO Box 2439, Weatherford, TX 76086.

Instrument Manual

Exhibits

Exhibit C15.1: Ammonia Nitrogen Benchsheet.

Subject: Ammonia Nitrogen (SM 4500 NH_3 D-2021)

Exhibit C15.1: Ammonia Nitrogen Benchsheet.

Page _____
Page ____ of _____

Ammonia (SM 4500 NH_3 D- 2021)

Matrix: water, RL = 0.10 mg/L NH_3-N

Analyst: _____ Reviewed by: _____
Date analyzed: _____ Reviewed date: _____

Stock standard: _____
Working standard: Daily from stock standard
10 *N* NaOH: _____
Slope: _____

Calibration Standards

Calibration:	1.0	mg/L
Calibration:	10	mg/L
RL:		mg/L
Midpoint (TV = 5.0):		mg/L

Sample Number	Sample Identification	Sample volume (mL)	Concentration (mg/L)	Dilution Factor	Final conc. NH_3-N (mg/L)	pH check >12 S.U.
TV = ND	Blank					
TV = 5.00	LCS					
	Duplicate					
	Spike					
	Spike Duplicate					
TV = 5.00	Midpoint					

CALCULATIONS

Final Ammonia Result mg/L: concentration X dilution factor
Spike recovery (%R) = [(A-B) / C)] X 100
Final RPD = [(S-D) / [(S+D) / 2)] X 100
Reference standard recovery (%RS) = (X / Y) X 100

QUALITY CONTROL

Precision (duplicate):

Sample number: _____
Sample result (S): _____ mg/L Spike result (S): _____ mg/L
Duplicate result (D): _____ mg/L Spike Duplicate result (D): _____ mg/L
Final RPD = _____ Final RPD = _____ mg/L

Accuracy (spike):

Spiked sample result (A): _____ mg/L
Sample conc, (B): _____ mg/L
Spike value (C): _____ mg/L
%RS = _____ %

Laboratory control standard (LCS):

Reference standard number _____
Value obtained (X) = _____ mg/L True value (Y) = _____ mg/L %RS= _____ %

SOP C15-Revision 6–Exhibit C15.1

Subject: Chloride (SM 4500 Cl^- C-2021)

Approval

Title	Name	Signature	Date
Laboratory Supervisor	Kelley E. Keenan		05-01-24
Quality Assurance Officer	Jim Sumner		05-01-24

Document Revision History

Effective Date	Revision number	Review Type	Evaluators	Revisions
06-18-01	0	Internal	Jim Sumner (ETS)	Original document
01-03-12	1	Internal	Kelley Keenan Jim Sumner (ETS)	• Updated SOP and exhibits during document review.
04-01-13	2	Internal	Jim Sumner (ETS)	• Updated procedure and references to the approved analytical method identified in USEPA Method Update Rule II (MUR II), May 18, 2012.
04-01-18	3	Internal	Jim Sumner (ETS)	• Updated procedure to include NELAP requirements. • Additional guidance included in SOP. • Method number revised based on 2017 MUR.
05-01-24	4	Internal	Jim Sumner (ETS)	• Updated procedure and references to the approved analytical method identified in USEPA Method Update Rule, April 16, 2024.

Scope and Application

This method is used to measure the chloride of water samples used in wastewater, receiving water and drinking water.

Summary of Method

Chloride is titrated with mercuric nitrate because of the formation of soluble, slightly dissociated mercuric chloride. In the pH range 2.3 – 2.8 S.U., diphenylcarbazone indicates the titration end point by formation of a purple complex with the excess mercuric ions. Xylene cyanol FF serves as a pH indicator and end-point enhancer. Increasing the strength of the titrant and modifying the indicator mixtures extend the range of measurable chloride concentrations.

Chloride measurement procedures are based on Standard Methods 4500 Cl^- C-2021.

Subject: Chloride (SM 4500 Cl^- C-2021)

Sample Collection, Preservation, Shipment and Storage

Samples must be analyzed within **28-days** of collection.

Samples received in the laboratory are stored at 0 to 6.0°C. Samples are warmed to 25.0 ± 1.0°C prior to analysis. This is the same temperature standards are maintained for calibration.

Quality Control

Calibration: The pH meter must be calibrated each day **before use**. The calibration slope should be 92% to 102%.

Standardization: Verify the **normality** of titrant reagents by re-standardizing at least monthly. If the titration reagent's normality (titer value) has changed, then use the measured value, adjust the normality (titer value) as the procedure describes.

Precision: Analyze a **duplicate** with each batch of samples (a batch of samples is considered samples analyzed on the same date). At a minimum, a duplicate must also be performed after every 20 samples. The relative percent difference (%RPD) should be ± 10% or within established limits determined through control charts. If these results differ by more than the established limits, results associated with this duplicate must be qualified (with a footnote in the analytical report) identifying the deviation.

Laboratory Fortified Blank (LFB, referred to LCS on benchsheets): An LFB must be analyzed initially and must be performed with each batch of samples. At a minimum, an LFB must be performed after every 20 samples and at the end of each batch of samples. The percent recovery of the LFB (%R) must be ± 10% from the true value.

Matrix Spike Recovery (MS): A MS must be analyzed initially and must be performed with each batch of samples. At a minimum, a MS must be performed on 5% of samples on a monthly basis. If fewer than 20 samples are analyzed in a month, at least one MS must be performed within that month. The percent recovery of the MS (%R) must be ± 25% from the true value. If these results differ by more than the established limits, results associated with the spike must be qualified (with a footnote on the analytical report) identifying the deviation. Qualification may include any sample interferences that may have resulted in the deviation.

Matrix Spike Duplicate (MSD): A MSD must be analyzed initially and must be performed with each batch of samples. At a minimum, a MSD must be performed on 5% of samples on a monthly basis. If fewer than 20 samples are analyzed in a month, at least one MSD must be performed within that month. The relative percent difference (%RPD) should be ± 10% or within established limits determined through control charts. If these results differ by more than the established limits, results associated with

this MSD must be qualified (with a footnote in the analytical report) identifying the deviation. Qualification may include any sample interferences that may have resulted in the deviation.

Method Blank (MB): A MB must be analyzed initially and must be performed with each batch of samples (a batch of samples is considered samples analyzed on the same date). The MB must be ≤ one half the reporting limit (RL).

Reporting Limit (RL): The RL for chloride is 1.0 mg/L.

PE: Annually (once every calendar year), a single-blind QC check sample (QCS) or performance evaluation sample (PE) is analyzed. This sample is provided by an approved proficiency testing (PT) provider.

Additional quality control guidance is provided in QAP-Q5.

Interferences

Bromide and iodide are titrated with $Hg(NO_3)_2$ in the same manner as chloride. Chromate, ferric and sulfite ions interfere when present in excess of 10 mg/L.

Equipment and Materials

50-mL buret and buret stand with clamps
Ion analyzer equipped with a pH probe
150-mL beakers
Stir bars
Stir plate
100- mL graduated cylinder
1-mL volumetric pipettes
5-mL volumetric pipettes
Pipette bulb
Rinse bottle
Waste container
Mercury or red spirit-filled or hand-held thermometer
pH buffer 4.00 for standardization
pH buffer 7.00 for standardization
pH buffer 10.00 for the Laboratory Control Standard (LCS)
Deionized water
0.1 *N* HNO_3
0.0141 *N* Mercuric Nitrate titrant

Subject: Chloride (SM 4500 Cl^- C-2021)

Diphenylcarbazone-Xylene Cyanol Indicator
0.05 mg/L chloride standard normality check standard
0.05 *N* chloride standard laboratory fortified blank (LFB) and spike standard
Water bath
Chloride Benchsheet

Subject: Chloride (SM 4500 Cl^- C-2021)

Procedure

A. Titration Procedure.

1. Prepare the Chloride Benchsheet (Exhibit C16.1).

2. Calibrate the pH meter according to SOP-C3.

3. Remove samples from the refrigerator and warm to 25.0 ± 2.0°C. Check the temperature with thermometer. Warm samples by placing in a warm water bath or by leaving samples out long enough to reach room temperature.

4. While the samples are warming, close the buret tip and securely clamp the buret to the stand. Over fill the buret with 0.0141 *N* mercuric nitrate.

5. Drain the excess. This will fill the tip and remove air bubbles.

6. Analyze an MB.

   a. Using a 100-mL graduated cylinder, pour 100 mL of deionized water in a 150-mL beaker with a stir bar.

   b. Place the beaker on the stir plate. Put the pH probe in the solution and add 0.1 N NHO_3 drop wise until the pH is 2.5 ±1 S.U. Add 1-mL of Diphenylcarbazone-Xylene Cyanol Indicator. Titrate the sample until the blue color turns purple. Record the difference. This blank correction value will be subtracted from the remaining samples.

7. Determine the normality of the titrant.

   a. Use a 100-mL graduated cylinder, to make the normality check standard. Mix 5.0 mL of 0.05 mg/L chloride standard into 95 mL of deionized water. Use a 10 mL serological pipette to prepare the standard.

   b. Pour the standard into a 150-mL beaker with a stir bar. Place the beaker on the stir plate and stir. Put the pH probe in the solution and add 0.1 N NHO_3 drop wise, until the pH is 2.5 ± 1.0 S.U. Add 1-mL of Diphenylcarbazone-Xylene Cyanol Indicator. Titrate the sample until the blue color turns purple. Record the begin mL, end mL and total mL of titrant required to reach the purple color endpoint. Subtract the blank correction from the total mL of titrant to determine the normality.

c. Calculate the normality of the standard to find the multiplier. If the value is out of range, reanalyze.

8. Analyze a LFB.

a. Use a 100-mL graduated cylinder, to make the laboratory control standard. Mix 5.0 mL of 0.05 mg/L chloride standard into 95 mL of deionized water. Use a 10 mL serological pipette to prepare the standard.

b. Pour into a 150-mL beaker with a stir bar and place on the stir plate. Put the pH probe in the standard and add 0.1 *N* NHO_3 drop wise, until the pH is 2.5 ± 1.0 S.U. Add 1-mL of Diphenylcarbazone-Xylene Cyanol Indicator. Titrate the sample until the blue color turns purple. Record the begin mL, end mL and total mL of titrant required to reach the purple color endpoint. Subtract the blank correction from the total mL of titrant to determine the LFB.

9. To analyze samples, use 100 mL and pour into a 150-mL beaker with a stir bar and place on the stir plate. Put the pH probe in the solution and add 0.1 N NHO_3 drop wise, until the pH is 2.5 ±1 S.U. Add 1-mL of Diphenylcarbazone-Xylene Cyanol Indicator. Titrate the sample until the blue color turns purple. Record the difference. If there is no initial purple color, dilute the sample to accommodate (make dilutions that evenly divide into 100, e.g. use 50, 25, or 10 mL of sample).

10. Each batch of samples must have a duplicate, spike and a spike duplicate. A duplicate is a replicate of the sample.

11. To perform a spike, take 100 mL of the sample and add 1 mL of 0.05 mg/L chloride standard and titrate to the purple color.

Note: All samples must be stirring during analysis.

Subject: Chloride (SM 4500 Cl^- C-2021)

B. Calculation of Chloride.

1. Read directly in mg/L and report to the nearest 0.1 mg/L.

C. Precision and Accuracy, Calculations.

1. Normality Acceptable range. The normality should calculate to be 4.7 – 5.3 mL.

2. Blank Correction.

   Blank Correction = End mL of Mercuric Nitrate – Begin mL of Mercuric Nitrate

3. Laboratory fortified blank (LFB) determination, True value = 25 mg/L.

   Percent Recovery of the Standard (%RS)

   %RS = (Measured value) / (True value) x 100

4. Duplicate, spike duplicate acceptance.

   Relative Percent Difference (%RPD)

   %RPD = (Sample value – Duplicate value) /
   [(Sample value + Duplicate value)/2] x 100

5. Spike recovery, True value = 50 mg/L.

   Percent Recovery of the Spike (%R)

   %R = (Spike value – Sample value) / (True value) x 100

Safety and Hazardous Waste Management

Safety glasses, gloves and lab coats should be worn at all times while handling samples. Excess samples may be flushed down the sink.

Review Policy-P6: General Safety Policy and Policy-P9: Radiation Protection Policy for additional safety requirements.

Subject: Chloride (SM 4500 Cl^- C-2021)

References

Standard Methods for the Examination of Water and Wastewater, 24th Edition, 2023. American Public Health Association, 800 I Street, NW, Washington DC 20001-3710.

- Method: 4500 Cl^- C-2021.

TNI Standard. Management and Technical Requirements for Laboratories Performing Environmental Analysis. EL-V1-ISO-2016-Rev2.0. The NELAC Institute, PO Box 2439, Weatherford, TX 76086.

Instrument Manual

Exhibits

Exhibit C16.1: Chloride Benchsheet.

Subject: Chloride (SM 4500 Cl^- C-2021)

Exhibit C16.1: Chloride Benchsheet.

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Chloride (SM 4500 Cl^- C-2021)

Matrix: water, RL = 1.0 mg/L

Analyst: _____ Reviewed by: _____

Date analyzed: _____ Reviewed date: _____

Blank Correction

Deionized Water	Begin (mL)	End (mL)	Total (mL)
100 mL			

Normality Check Reference Number (INSS#): _____

Titrant Reference Number	Begin (mL)	End (mL)	Total (mL)	Blank Correction (mL)	Acceptable Range 4.7 – 5.3 mL	Multiplier Normality (0.0141N) x 35450
INR#						499.8

Sample Number	Sample Identification	Sample Volume (mL)	Begin (mL)	End (mL)	Total (mL)	Blank Correction (mL)	Final Chloride Result (mg/L)
	LCS						
	Duplicate						
	Spike						
	Spike Duplicate						

CALCULATIONS

Final Chloride Result mg/L: Total mL – Blank Correction X titrant normality X 35450 / mL of sample

Final RPD = [(S-D) / [((S+D) / 2)] X 100

Spike recovery (%R) = [(A-B) / C)] X 100

Reference standard recovery (%RS) = (X / Y) X 100

QUALITY CONTROL

Precision (duplicate):

Sample number: _____

Sample result (S): _____ mg/L Spike result (S): _____ mg/L

Duplicate result (D): _____ mg/L Spike Duplicate result (D): _____ mg/L

Final RPD = _____ Final RPD = _____ mg/L

Accuracy (spike):

Spiked sample result (A): _____ mg/L

Sample conc, (B): _____ mg/L

Spike value (C): _____ mg/L

%RS = _____ %

Laboratory control standard (LCS):

Reference standard number (INSS#) _____

Value obtained (X) = _____ mg/L True value (Y) = _____ mg/L %RS= _____ %

SOP C16-Revision 4–Exhibit C16.1

Subject: Turbidity (SM 2130 B-2020)

Approval

Title	Name	Signature	Date
Laboratory Supervisor	Kelley E. Keenan		05-01-24
Quality Assurance Officer	Jim Sumner		05-01-24

Document Revision History

Effective Date	Revision number	Review Type	Evaluators	Revisions
06-18-01	0	Internal	Kelley E. Keenan (ETS)	Original document
01-03-12	1	Internal	Jim Sumner (ETS)	• Updated SOP and exhibits during document review. Provided additional procedural guidance where required
01-27-12	2	External	Jason Smith (NC DENR)	• Removed requirement of diluting samples, if they exceed the range of the meter.
04-01-13	3	Internal	Jim Sumner (ETS)	• Updated procedure and references to the approved analytical method identified in USEPA Method Update Rule II (MUR II), May 18, 2012.
04-01-18	4	Internal	Jim Sumner (ETS)	• Updated procedure to include NELAP requirements. • Additional guidance included in SOP. • Method number revised based on 2017 MUR.
05-01-24	5	Internal	Jim Sumner (ETS)	• Updated procedure and references to the approved analytical method identified in USEPA Method Update Rule, April 16, 2024.

Subject: Turbidity (SM 2130 B-2020)

Scope and Application

This method is used to provide a method for measuring the turbidity in water samples.

Summary of Method

Nephelometric method is based on a comparison of the intensity of light scattered by the sample under defined conditions with the intensity of light scattered by a reference suspension under the same conditions. The higher the intensity of scattered light, the higher the turbidity. Formazin polymer is used as the primary standard reference suspension.

Turbidity measurement procedures are based on SM 2130 B-2020.

Sample Collection, Preservation, Shipment and Storage

Samples must be analyzed within **48-hours** of collection.

Samples received in the laboratory are stored at 0 to 6.0°C. Samples are warmed to room temperature prior to analysis. This is the same temperature standards are maintained for calibration.

Quality Control

Calibration: The turbidity meter must be calibrated each day **before use**.

Precision: Analyze a **duplicate** with each batch of samples (a batch of samples is considered samples analyzed on the same date). At a minimum, a duplicate must also be performed after every 20 samples. The relative percent difference (%RPD) should be ± 10% or within established limits determined through control charts. If these results differ by more than the established limits, results associated with this duplicate must be qualified (with a footnote in the analytical report) identifying the deviation.

Laboratory Fortified Blank (LFB, referred to LCS on benchsheets): A LFB must be analyzed initially and must be performed with each batch of samples. At a minimum, a LFB must be performed after every 20 samples and at the end of each batch of samples. The percent recovery of the LFB (%R) must be ± 10% from the true value.

Method Blank (MB): A MB must be analyzed initially and must be performed with each batch of samples (a batch of samples is considered samples analyzed on the same date). The MB must be ≤ one half the reporting limit (RL).

Reporting Limit (RL): The RL for ammonia nitrogen is 1.0 NTU.

PE: Annually (once every calendar year), a single-blind QC check sample (QCS) or performance evaluation sample (PE) is analyzed. This sample is provided by an approved proficiency testing (PT) provider.

Additional quality control guidance is provided in QAP-Q5.

Interferences

Dirty glassware and the presence of air bubbles provide false results. Water color due to the presence of dissolved substances may cause measured turbidities to be low.

Equipment and Materials

100-mL graduated cylinder
10-mL serological pipette
2, 150-mL beakers
10 – 100 µL Eppendorf pipette
100 – 1000 µL Eppendorf pipette
2 - 4000 NTU Turbidity standard
HACH 2100A Turbidity meter
Glass sample tubes
Pipette tips
Rinse bottle
Deionized water
Turbidity benchsheet
Pipette bulb

Subject: Turbidity (SM 2130 B-2020)

Procedure

A. Preparation of the Turbidity Meter (HACH Model 2100A Turbidimeter).

1. Turn on the turbidity meter by turning the left dial to any of the turbidity levels.

2. The meter should be turned on approximately 15 minutes before use to warm the light source.

B. Preparation of the Samples.

1. Warm all samples to room temperature by placing them in a hot water bath, leaving out long enough to reach room temperature, or by placing them on the top of the 103 – 105^{o}C oven.

2. Fill out the Turbidity benchsheet (Exhibit C17.1) with the sample number, date collected, and sample name.

C. Calibration Standards and Calibration Levels.

DO NOT TOUCH THE GLASS SAMPLE TUBES.

1. There are two levels of calibration for turbidity.

2. To calibrate on the **low level**, turn the calibration dial to 1.0 NTU.

3. The low level is 1.0 – 9.9 NTU. To make the standard and the Laboratory Control Standard (LCS), shake the 4000 NTU calibration standard and the 4000 NTU LCS standard and pipette 0.10 ml of standard into each 150-mL beaker. Each standard concentration is 4.0 NTU.

4. Measure 100-ml of deionized water into a 100-ml graduated cylinder and pour into each of the beakers.

5. Using a Kim-wipe or paper towel, hold a glass tube in your hand and pour approximately 25-mL of the calibration standard into the glass tube.

6. Place the glass tube into the top of the turbidity meter and rotate the tube in a circle to remove any air bubbles. Cover the top of the glass tube with the black cover.

7. Turn the calibration dial (on the right) until the meter reads 4.0 NTU. This will calibrate the meter to 4.0 NTU.

8. Swirl the LCS standard. Using a Kim-wipe or paper towel, hold a glass tube in your hand and pour approximately 25-mL of the LCS standard into the glass tube.

9. Place the glass tube into the top of the turbidity meter and rotate the tube in a circle to remove any air bubbles. Cover the top of the glass tube with the black cover.

10. Record the value on the Turbidity benchsheet (Exhibit C17.1). If the value is out of range, reanalyze.

11. To calibrate on the **high level**, turn the calibration dial to 10 NTU.

12. The high level is 10 – 40 NTU. To make the standard, shake the 4000 NTU calibration standard and pipette 1.0 ml of standard into one 150-ml beaker. To make the Laboratory Control Standard (LCS), shake the 4000 NTU LCS standard and pipette 0.5 ml of standard into one 150-mL beaker. The standard value is 40 NTU and the LCS is 20 NTU.

13. Measure 100-mL of deionized water into a 100-mL graduated cylinder and pour into each of the beakers.

14. Using a Kim-wipe or paper towel, hold a glass tube in your hand and pour approximately 25-mL of the calibration standard into the glass tube.

15. Turn the calibration dial (on the right) until the meter reads 40 NTU. This will calibrate the meter to 40 NTU.

16. Swirl the LCS standard. Using a Kim-wipe or paper towel, hold a glass tube in your hand and pour approximately 25-mL of the LCS standard into the glass tube.

17. Place the glass tube into the top of the turbidity meter and rotate the tube in a circle to remove any air bubbles. Cover the top of the glass tube with the black cover.

18. Record the value on the Turbidity benchsheet (Exhibit C17.1). If the value is out of range, reanalyze.

Subject: Turbidity (SM 2130 B-2020)

D. Analysis of Turbidity Samples.

1. To analyze samples, shake the sample and remove the cap.

2. Using a Kim-wipe or paper towel, hold a glass tube in your hand and pour approximately 25-mL of the calibration standard into the glass tube.

3. Place the glass tube into the top of the turbidity meter and rotate the tube in a circle to remove any air bubbles. Cover the top of the glass tube with the black cover.

4. Record the sample value on the turbidity benchsheet (Exhibit C17.1). If the value is less than 1.0 NTU then record a ND for the result.

E. Calculation of Ammonia Nitrogen.

1. Read directly in NTU and report to the nearest 1.0 NTU.

2. If the sample required dilution, then follow the calculation below.

Turbidity (NTU) = Measurement X Dilution Factor

F. Precision and Accuracy, Calculations.

1. Laboratory fortified blank (LFB) determination, True value = 4.0 NTU (Low Level) and 20 NTU (High Level).

Percent Recovery of the Standard (%RS)

%RS = (Measured value) / (True value) x 100

2. Duplicate acceptance.

Relative Percent Difference (%RPD)

%RPD = (Sample value – Duplicate value)

Subject: Turbidity (SM 2130 B-2020)

Safety and Hazardous Waste Management

Safety glasses, gloves and lab coats should always be worn while handling samples. Excess samples may be flushed down the sink.

Review Policy-P6: General Safety Policy and Policy-P9: Radiation Protection Policy for additional safety requirements.

References

Standard Methods for the Examination of Water and Wastewater, 24th Edition, 2023. American Public Health Association, 800 I Street, NW, Washington DC 20001-3710.

- 2130 B-2020.

TNI Standard. Management and Technical Requirements for Laboratories Performing Environmental Analysis. EL-V1-ISO-2016-Rev2.0. The NELAC Institute, PO Box 2439, Weatherford, TX 76086.

Instrument Manual

Exhibits

Exhibit C17.1: Turbidity Benchsheet**.**

Subject: Turbidity (SM 2130 B-2020)

Exhibit C17.1: Turbidity Benchsheet.

Page _____
Page ____ of _____

Turbidity (SM 2130 B- 2020)

Matrix: water, RL = 1.0 NTU, RL = 10 NTU

Analyst: _____
Date analyzed: _____

Reviewed by: _____
Reviewed date: _____

Calibration Standards
Reference standard #
4.0 NTU: _____
40 NTU: _____

Sample Number	Sample Identification	Date Collected	Turbidity Reading (NTU)	Dilution Factor	Final Turbidity (NTU)
TV = ND	Blank				
TV =	LCS				
	Duplicate				

CALCULATIONS
Final Turbidity (NTU): turbidity reading X dilution factor
Final RPD = S – D
Reference standard recovery (%RS) = (X / Y) X 100

QUALITY CONTROL
Precision (duplicate):

Sample number: _____ Sample number: _____
Sample result (S): _____ NTU Sample result (S): _____ NTU
Duplicate result (D): _____ NTU Duplicate result (D): _____ NTU
Final RPD = _____ NTU Final RPD = _____ NTU

Laboratory control standard (LCS):
Reference standard number _____
Value obtained (X) = _____ NTU True value (Y) = _____ NTU %RS= _____ %

Reference standard number _____
Value obtained (X) = _____ NTU True value (Y) = _____ NTU %RS= _____ %

SOP C17-Revision 5–Exhibit C17.1

Subject: Nitrate (SM 4500 NO_3^- D-2019)

Approval

Title	Name	Signature	Date
Laboratory Supervisor	Kelley E. Keenan		05-01-24
Quality Assurance Officer	Jim Sumner		05-01-24

Document Revision History

Effective Date	Revision number	Review Type	Evaluators	Revisions
11-01-04	0	Internal	Kelley E. Keenan (ETS)	Original document
06-01-11	1	Internal	Kelley E. Keenan (ETS)	• Corrected typos. • Updated method changes. • Updated exhibits during document review.
04-01-13	2	Internal	Jim Sumner (ETS)	• Updated procedure and references to the approved analytical method identified in USEPA Method Update Rule II (MUR II), May 18, 2012. • Changed LFB preparation.
09-14-15	3	Internal	Kelley Keenan (ETS)	• Updated section G for reporting using Public Water Supply Laboratory Data Submittal (LDS) system.
04-01-18	4	Internal	Jim Sumner (ETS)	• Updated procedure to include NELAP requirements. • Additional guidance included in SOP. • Method number revised based on 2017 MUR.
05-01-24	5	Internal	Jim Sumner (ETS)	• Updated procedure and references to the approved analytical method identified in USEPA Method Update Rule, April 16, 2024.

Scope and Application

This method is used to provide a method for measuring the concentration of nitrate in drinking water samples.

Summary of Method

Nitrate is determined electrometrically using a NO_3^- ion selective electrode.

The NO_3^- ion electrode is a selective sensor that develops a potential across a thin, porous, inert membrane that holds in place a water-immiscible liquid ion exchanger. The electrode responds to NO_3^- ion activity between about 0.14 to 1400 mg/L NO_3^--N. The lower limit of detection is determined by the small but finite solubility of the liquid ion exchanger.

Nitrate measurement procedures are based on SM 4500 NO_3^- D-2021.

Subject: Nitrate (SM 4500 NO_3^- D-2019)

Sample Collection, Preservation, Shipment and Storage

Non-chlorinated samples must be analyzed within **48-hours** of collection. To extend the hold time, samples may be preserved upon receipt using 2 mL concentrated H_2SO_4 (currently samples are not preserved). Chlorinated samples and/or preserved samples must be analyzed within **14-days** of collection.

Samples received must be received and stored in the laboratory at 0 to 6.0°C.

Quality Control

Calibration: The ion analyzer must be calibrated for nitrate each day **before use**.

Precision: Analyze a **spike duplicate** with each batch of samples (a batch of samples is considered samples analyzed on the same date). At a minimum, a duplicate must also be performed after every 10 samples. The relative percent difference (%RPD) should be ± 10% or within established limits determined through control charts. If these results differ by more than the established limits, results associated with this duplicate must be qualified (with a footnote in the analytical report) identifying the deviation.

Laboratory fortified blank (LFB, referred to LCS on benchsheets): A LFB must be analyzed initially and must be performed with each batch of samples. At a minimum, a LFB must be performed after every 10 samples and at the end of each batch of samples. The percent recovery of the LFB (%R) must be ± 10% from the true value.

Method Blank (MB): An MB must be analyzed initially and must be performed with each batch of samples. In addition, a MB must be performed after every 10 samples and at the end of each batch of samples. The MB must be ≤ one half the reporting limit (RL).

Method Detection Limit (MDL): An MDL standard is analyzed at least 7 times per year in separate batches of samples analyzed. The MDL may be analyzed by multiple analysts. The values obtained are pooled and used to determine the method detection level for this procedure.

Reporting Limit (RL): The RL for nitrate is 1.0 mg/L.

PE: Twice every calendar year (January and July), a single-blind QC check sample (QCS) or performance evaluation sample (PE) is analyzed. This sample is provided by an approved proficiency testing (PT) provider.

Subject: Nitrate (SM 4500 NO_3^- D-2019)

Additional quality control guidance is provided in QAP-Q5.

Interferences

Chloride and bicarbonate ions interfere when their weight ratios to NO_3^--N are >10 or >5, respectively. Ions that are potential interferences but do not normally occur at significant levels in potable waters are NO_2^-, CN^-, S^{2-}, Br^-, I^-, ClO_3^- and ClO_4^-. Although the electrodes functions satisfactorily in buffers over the range pH 3 to 9, erratic responses have been noted where pH is not held constant. Because the electrode responds to NO_3^- activity rather than concentration, ionic strength must be constant in all samples and standards. Minimize these problems by using a buffer solution containing Ag_2SO_4 (ISA) to remove CN^-, S^{2-}, Br^-, I^- and Cl^-.

Equipment and Materials

150-mL beakers
Stir bars
Stir plate
1-L Amber bottle
Deionized water
Deionized water bottle
Nitrate double junction reference probe
Nitrate probe
Sensing modules
Ion analyzer
103 – 105 °C drying oven
Kimwipe
Disposable gloves
500-mL volumetric flask
100 ppm Nitrate stock standard
Nitrate double junction reference inner filling solution
Nitrate double junction reference outer filling solution
Nitrate ionic strength adjuster (ISA)
Potassium Nitrate (KNO_3)
1-mL glass pipette
10-mL glass pipette
10-100 µl Eppendorf pipette
100-100 µl Eppendorf pipette
Chloroform
DPD dispenser pops
1-oz medicine cups

Thermometer (0.1°C increments)

Procedure

A. **Preparation of samples.**

1. Samples must be received and analyzed within 48-hours of collection. If the sample is chlorinated, then the hold time can be extended to 14-days. If samples are not analyzed within 48-hours and the sample is not chlorinated, then add 2 mL concentrated H_2SO_4 to preserve the sample.

2. When samples are received, they must be checked for temperature and chlorine. The temperature must be recorded on the nitrate state form (example form: Exhibit C18.1).

3. Temperature must be < 6.0°C when received at the laboratory. If samples are not received within temperature requirements, the sample will be rejected and a resample must be collected.

4. Check each sample for chlorine by pouring 10 mL of sample into a 1-oz medicine cup.

5. Dispense one pop from the DPD dispenser.

6. If the sample turns pink, then chlorine is present. On the top of the sample container, note that chlorine is present with a **C.**

B. Preparation of Nitrate and Double Junction Reference Probe.

1. Nitrate Probe

   a. The nitrate probe must be conditioned before initial use.
   b. Remove a sensing module from the package and screw the module onto the end of the nitrate probe. Make sure the washer is between the electrode body and the sensing module.
   c. After the module is screwed to the nitrate body, shake the probe like a thermometer.
   d. Rinse the probe with deionized water and soak in a 100 ppm nitrate standard one to two hours before use.

2. Nitrate Double Junction Reference Probe.

a. The nitrate double junction reference probe must be conditioned before initial use.
b. Unscrew the top (cap) from the body of the probe. This will allow the spring to be released and the plastic outer body sleeve to be freed from the inner sleeve.
c. Push the inner sleeve out the bottom of the outer sleeve.
d. The inner sleeve contains two O-rings, the sensing module, and the sensing membrane.
e. Fill the inner sleeve with the green AgCl Reference Electrode Inner Filling Solution by inserting the tip of the bottle into the small hole at the top of the sleeve.
f. Slowing fill the inner sleeve. Gently shake the solution down in the inner sleeve.
g. Once filled, slip the white cover over the hole in the inner sleeve.
h. After checking all the probe parts, hold the outer sleeve in one hand and gently push the inner sleeve into the outer sleeve. This can be done by firmly holding your thumb on the end of the sensing membrane. **DO NOT TOUCH THE MEMBRANE WITH YOUR BARE HANDS**. Use a Kim-Wipe® or gloves. Make sure that the inner sleeve is level with the outer sleeve.
i. Slide the spring and cap onto the top of the outer sleeve and screw the top down until they are firmly in place. **DO NOT OVER TURN**.
j. Fill the outer sleeve with the clear KNO_3 Reference Outer Filling Solution by inserting the tip of the bottle into the small hole at the top of the sleeve. This solution is a mixture of 2 mL of ISA and 98 mL of deionized water and can be prepared. If prepared, use a transfer pipette to fill the outer sleeve.
k. Slowly fill the outer sleeve. Gently shake the solution down in the outer sleeve and close the hole with the white cap.
l. Rinse the probe with deionized water and place in a beaker of deionized water.

C. Preparation of the Nitrate Stock Standard

1. KNO_3 must be dried at 105° C for 24 hours. The chemical must be desiccated at least 24 h before use.

2. Add 0.3609 g KNO_3 anhydrous to a 500-mL volumetric flask.

3. Add 1-mL of chloroform.

4. Pour standard into a 1-L amber bottle.

5. Following SOP G-15 to check in a stock standard.

Subject: Nitrate (SM 4500 NO_3^- D-2019)

D. Calibration and Measurement (Meter: Accumet Model AB250 pH/mV/Ion Meter)**.**

1. Prepare the Nitrate benchsheet (Exhibit C18.2).

2. Each time before analysis, calibrate the meter.

3. Turn on the meter by pressing the **POWER/LIGHT** button.

4. Prepare the method blank (MB), calibration standards , midpoint standard and laboratory fortified blank (LFB).

5. To prepare the 1.00 mg/L calibration standard, pipette 1.00 mL nitrate standard into a 100 mL graduated cylinder and bring to volume using deionized water. Pour the calibration standard into a 150 mL beaker with a stir bar. 10.00 mL nitrate standard is used to prepared the 10.00 mg/L calibration standard, 5.00 mL nitrate standard for midpoint standard, 5.00 mL nitrate standard using a second source for the LFB. The MB will consist of 100 mL deionized water without any nitrate standard.

6. Place the 1.00 mg/L calibration standard on a stir plate and stir. Remove the probe from the beaker containing nitrate stock solution. Rinse the probe tip with deionized water and submerge the nitrate probe and the nitrate double junction reference electrode into the 1.00 mg/L calibration standard. Add 2 mL ISA to the beaker.

7. Press **DISPLAY** and then **STD**. Press **CLEAR** to clear existing standards. Use the ▲ to select **1.00**. When a stable reading is obtained, the meter will indicate **PRESS STD TO STANDARDIZE**. Press **STD**.

8. Rinse the probe tip with deionized water and place into the 10.00 mg/L calibration standard on the stir plate and add 2 mL ISA to the beaker.

9. Press **DISPLAY** and then **STD**. Use the ▲ to select **10.00**. Gently agitate the sample with the tip of the probe. When a stable reading is obtained, the meter will indicate **PRESS STD TO STANDARDIZE**. Press **STD**.

10. The slope will be displayed. The meter will indicate a bad slope, if the slope is out of range. If the slope is out of range, recalibrate the meter following steps 5 through 9 above.

11. If the slope is within range, record the slope on the benchsheet and then analyze the midpoint standard.

12. Rinse the probe tip with deionized water and place into the 5.00 mg/L midpoint standard on the stir plate and add 2 mL ISA to the beaker. The meter will indicate **STABLE** when the measurement has stabilized.

13. Record the midpoint standard measurement on the benchsheet and calculate the %RS. The midpoint standard must be ± 10% of the true value. If it is out of range, the meter must be recalibrated.

14. Rinse the probe tip with deionized water and place into the 5.00 mg/L LFB on the stir plate and add 2 mL ISA to the beaker. The meter will indicate **STABLE** when the measurement has stabilized.

15. Record the LFB measurement on the benchsheet and calculate the %RS. The LFB must be ± 10% of the true value. If it is out of range, the meter must be recalibrated.

16. Analyze the MB. Rinse the probe tip with deionized water and place into the MB on the stir plate and add 2 mL ISA to the beaker. The meter will indicate **STABLE** when the measurement has stabilized.

17. Record the MB measurement on the benchsheet. The MB must be < 0.50 mg/L (less than ½ the reporting limit). If it is out of range, then reanalyze a MB.

18. Analyze the 1st sample. Pour 100 mL of the sample into a 150 mL beaker with a stir bar. Add 2 mL of ISA to the beaker. Rinse the probe tip with deionized water and place into the 1st sample. The meter will indicate **STABLE** when the measurement has stabilized.

19. Record the measurement on the benchsheet. The 1st sample is used for performing a spike and spike duplicate.

20. To measure the spike, pipette 5.00 mL nitrate standard into the sample on the stir plate. The meter will indicate **STABLE** when the measurement has stabilized.

21. Record the measurement on the benchsheet.

22. To measure the spike duplicate, pour 100 mL of a second aliquot of the 1st sample into a 150 mL beaker with a stir bar. Add 2 mL of ISA to the beaker and pipette 5.00 mL nitrate standard into the sample. Rinse the probe tip with deionized water and place into the spike duplicate. The meter will indicate **STABLE** when the measurement has stabilized.

23. Record the measurement on the benchsheet. Calculate the %RPD. The %RPD must be within laboratory established control limits. If these results outside of the laboratory control limits, it is noted on the laboratory benchsheet that matrix interferences may have caused the deviation.

24. Continue measuring and recording the nitrate of samples. If any sample is over 10.00 mg/L, then it must be diluted. Adjust dilutions to allow readings between 1.0 mg/L and 10.0 mg/L. If any sample must be diluted, notify your supervisor. Public water supply must be notified the same day of testing by entering the results through the NC PWS LDS site, if results are over 10 mg/L.

25. If any samples are diluted, adjust the RL according to the dilution factor. Multiply the original RL and the dilution factor for the adjusted value.

26. Once all samples have been analyzed, rinse the probe tip with deionized water and place the probe in the beaker of nitrate stock solution. Turn the meter off by pressing and holding the **POWER/LIGHT** button until the screen goes blank.

Note: All samples must be stirring during analysis.

E. Calculation of Nitrate.

1. Read directly in mg/L and report to the nearest 0.1 mg/L.

2. Samples that are analyzed, which are < 1.00 mg/L and the reading continues to read lower than the RL, are recorded as < the value displayed.

F. Precision and Accuracy, Calculations.

1. Laboratory control standard, True value = 5.0 mg/L.
   Percent Recovery of the Standard (%RS)
   %RS = (Measured value) / (True value) x 100

2. Duplicate acceptance.
   Relative Percent Difference (%RPD)
   %RPD = (Sample value – Duplicate value) / [(Sample value + Duplicate value)/2] x 100

G. Reporting results to clients and the North Carolina Public Water Supply (PWS).

1. If the results for state clients are over 10 mg/L, results must be reported to the state on the day that the test results are completed. Note in the comment section on the state

form that the client has been notified or a message has been left. Make sure that the result section is marked. All the appropriate dates, times and signatures must be completed. All data must be uploaded into the Public Water Supply Laboratory Data Submittal (LDS) system (refer to SOP-B6, Exhibit B6.3).

2. All results must be uploaded into the LDS system before the 10th of the following month.

Safety and Hazardous Waste Management

Safety glasses, gloves and lab coats should always be worn while handling samples. Excess samples may be flushed down the sink.

Review Policy-P6: General Safety Policy and Policy-P9: Radiation Protection Policy for additional safety requirements.

References

Standard Methods for the Examination of Water and Wastewater, 24th Edition, 2023. American Public Health Association, 800 I Street, NW, Washington DC 20001-3710.

- 4500-NO_3^- D-2011.

TNI Standard. Management and Technical Requirements for Laboratories Performing Environmental Analysis. EL-V1-ISO-2016-Rev2.0. The NELAC Institute, PO Box 2439, Weatherford, TX 76086.

Instrument Manual

Exhibits

Exhibit C18.1: Example NC State Nitrate From**.**
Exhibit C18.2: Nitrate Benchsheet**.**

Subject: Nitrate (SM 4500 NO_3^- D-2019)

Exhibit C18.1: Example NC State Nitrate From.

PO Box 7565
Asheville NC 28802
Phone: (828) 350-9364
Fax: (828) 350-9368

NITRATE/NITRITE ANALYSIS

Note: All appropriate information must be supplied for compliance credit.

WATER SYSTEM ID #: 1 0 - 8 8 - 0 0 1 **County:** Transylvania

Name of Water System: Adventure Village

Sample Type: ☒ Entry Point ☐ Special/Non-compliance

Location Where Collected: Storage Tank

Facility ID No.: P 0 1

Sample Point: E 0 1

Collected By: _____ (Please Print)

Collection Date	Collection Time
__/__/__ (MM/DD/YY)	__:__ M (Specify AM or PM)

Mail Results to (water system representative):

Trevco

Mr. Trevor McMinn **Phone #:** (828) 691-7191

2020 Howard Gap Road **Fax #:**

Hendersonville, NC 28792 **Responsible Person's e-mail:**

LABORATORY ID# 3 7 7 8 6 ☐ SAMPLE UNSATISFACTORY ☐ RESAMPLE REQUIRED

CONTAM CODE	CONTAMINANT	METHOD CODE	REQUIRED REPORTING LIMIT (R.R.L)	NOT DETECTED (i.e. < R.R.L.) (X)	QUANTIFIED RESULTS*	ALLOWABLE LIMIT
1040	Nitrate	4500NO3D	1.00 mg/L	☐	__.__ mg/L	10.00 mg/L
1041	Nitrite		0.10 mg/L	☐	__.__ mg/L	1.00 mg/L

***Note:** If result exceeds allowable limit, the laboratory must fax analytical results to the State on day test completed.

	DATE:	TIME:
ANALYSIS BEGUN:	__/__/__ (MM/DD/YY)	__:__ M (Specify AM or PM)
ANALYSIS COMPLETED:	__/__/__ (MM/DD/YY)	__:__ M (Specify AM or PM)

Laboratory Log #: _____ **Certified By:** _____ Kelley E. Keenan

Temperature upon reciept at laboratory (°C): _____

COMMENTS: _____

2008

Laboratory should Mail Results to:
Public Water Supply Section, Attn: Data Entry, 1634 Mail Service Center, Raleigh, NC 27699-1634
Fax: 919.715.6637

Subject: Nitrate (SM 4500 NO_3^- D-2019)

Exhibit C18.2: Nitrate Benchsheet.

Page _____
Page ____ of _____

Nitrate (SM 4500 NO_3^- D- 2019)

Matrix: water, RL = 1.0 mg/L NO_3^-N

Analyst: _____ Reviewed by: _____
Date analyzed: _____ Reviewed date: _____

Stock standard: _____ Time started: _____
Working standard: Daily from stock standard Time ended: _____
ISA: _____
Slope: _____

Calibration Standards
Calibration: 1.0 mg/L
Calibration: 10 mg/L
Midpoint (TV = 5.0): _____ mg/L

Sample Number	Date Collected	Chlorine (Y/N)	Sample Identification	Sample volume (mL)	Concentration Nitrate (mg/L)	Dilution Factor	Final Concentration Nitrate (mg/L)
TV = ND			Blank				
TV = 5.00			LCS				
			Spike				
			Spike Duplicate				
TV = ND			Blank				
TV = 5.00			LCS				

CALCULATIONS

Final Nitrate Result mg/L: concentration X dilution factor
Final RPD = [(S-D) / [(S+D) / 2)] X 100
Reference standard recovery (%RS) = (X / Y) X 100

QUALITY CONTROL

Precision (spike duplicate):

Sample number: _____
Spike result (S): _____ mg/L
Spike Duplicate result (D): _____ mg/L
Final RPD = _____ %

Laboratory control standard (LCS):

Reference standard number _____
Value obtained (X) = _____ mg/L True value (Y) = _____ mg/L %RS= _____ %

SOP C18-Revision 5–Exhibit C18.1

Subject: Chemical Oxygen Demand (HACH 8000)

Approval

Title	Name	Signature	Date
Laboratory Supervisor	Kelley E. Keenan		05-01-24
Quality Assurance Officer	Jim Sumner		05-01-24

Document Revision History

Effective Date	Revision number	Review Type	Evaluators	Revisions
01-30-06	0	Internal	Kelley E. Keenan (ETS)	Original document
01-03-12	1	Internal	Kelley Keenan Jim Sumner (ETS)	• Updated SOP and exhibits during document review.
01-27-12	2	External	Jason Smith (NC DENR)	• Midpoint analyzed at the end of every batch (or 10 samples) instead of LFB.
04-01-13	3	Internal	Jim Sumner (ETS)	• Updated procedure and references to the approved analytical method identified in USEPA Method Update Rule II (MUR II), May 18, 2012.
04-01-18	4	Internal	Jim Sumner (ETS)	• Updated procedure to include NELAP requirements. • Additional guidance included in SOP. • Method number revised based on 2017 MUR.
05-01-24	5	Internal	Jim Sumner (ETS)	• Updated procedure and references to the approved analytical method identified in USEPA Method Update Rule, April 16, 2024.

Scope and Application

This method is used to determine the quantity of oxygen required to oxidize the organic matter in water samples.

Summary of Method

Chemical oxygen demand (COD) is defined as the amount of a specific oxidant that reacts with the sample under controlled conditions. The quantity of oxidant consumed is expressed in terms of oxygen equivalence. Both organic and inorganic components of a sample are subject to oxidation, but in most cases the organic component predominates.

COD measurement procedures are based on HACH 8000.

Subject: Chemical Oxygen Demand (HACH 8000)

Sample Collection, Preservation, Shipment and Storage

Samples must be analyzed within **28-days** of collection if preserved with H_2SO_4. Samples are preserved at the time of collection with H_2SO_4 at a pH < 2 S.U.

Samples must be received and stored in the laboratory at 0 to 6.0°C.

Quality Control

Calibration curve: A five-point calibration curve, consisting of a blank and 5 standards (50, 150, 450, 750, 1200 and 1500 mg/L COD) must be analyzed yearly. Using linear regression, the minimum correlation coefficient must be ≥0.995. If COD vial or chemical lot numbers have changed, new standards are prepared or bacterial growth is identified in the standards, the calibration curve must be reanalyzed.

Precision: Analyze a **duplicate** with each batch of samples (a batch of samples is considered samples analyzed on the same date). At a minimum, a duplicate must also be performed after every 20 samples. The relative percent difference (%RPD) should be within established limits determined through control charts. If these results differ by more than the established limits, results associated with this duplicate must be qualified (with a footnote in the analytical report) identifying the deviation.

Laboratory Fortified Blank (LFB, referred to LCS on benchsheets): A LFB must be analyzed initially and must be performed with each batch of samples, using a second source standard. At a minimum, a LFB must be performed after every 20 samples and at the end of each batch of samples. The percent recovery of the LFB (%R) must be ± 10% from the true value.

Midpoint: A midpoint standard must be analyzed at the end of each batch of samples to verify that the instrument calibration has not drifted. The percent recovery of the midpoint standard (%R) must be ± 10% from the true value. If an intermediate midpoint %RS is out of range, all samples between the last in range midpoint and the out-of-range midpoint must be reanalyzed.

Matrix Spike Recovery (MS): A MS must be analyzed initially and must be performed with each batch of samples. At a minimum, a MS must be performed on 5% of samples on a monthly basis. If fewer than 20 samples are analyzed in a month, at least one MS must be performed within that month. The percent recovery of the MS (%R) must be ± 25% from the true value. If these results differ by more than the established limits, results associated with the spike must be qualified (with a footnote on the analytical report) identifying the deviation. Qualification may include any sample interferences that may have resulted in the deviation.

Method Blank (MB): A MB must be analyzed initially and must be performed at the end of each batch of samples (a batch of samples is considered samples analyzed on the same date). The MB must be ≤ one half the reporting limit (RL).

Reporting Limit (RL): The RL for COD is 50 mg/L.

PE: Annually (once every calendar year), a single-blind QC check sample (QCS) or performance evaluation sample (PE) is analyzed. This sample is provided by an approved proficiency testing (PT) provider.

Additional quality control guidance is provided in QAP-Q5.

Interferences

Chloride is the primary interference when determining the COD concentration. Each COD vial contains mercuric sulfate that will eliminate chloride interference up to 2000 mg/L. Samples with higher chloride concentrations should be diluted to < 4000 mg/L.

Subject: Chemical Oxygen Demand (HACH 8000)

Equipment and Materials

Potassium Acid Phthalate PAP – 2 different lot numbers
110 °C forced air oven
Dessicator
Glass chemical containers for Potassium Acid Phthalate
Medicine cups
Spatulas
Balance
Deionized water
Water bottle
1000-mL volumetric flask
500-mL volumetric flask
100-mL volumetric flask
50-mL volumetric flask
Sharpie®
Volumetric caps
Parafilm
Stir bars
Stir plate
Plastic test tube holder
HACH COD High level vials
1-mL volumetric pipets
2-mL volumetric pipets
3-mL volumetric pipets
5-mL volumetric pipets
10-mL volumetric pipets
COD Digester Reactor with thermometer
KimWipes
HACH DR400 Spectrophotometer
EZ COD ™ Recycling Container
Calculator with 3rd Function

Subject: Chemical Oxygen Demand (HACH 8000)

Procedure

A. Standard Preparation Procedure.

1. Pour the Potassium Acid Phthalate (PAP) into two glass chemical containers. There must be two separate lot numbers used. Using a Sharpie®, write on each container the lot # of each chemical.

2. Place each container into a 110°C forced air oven until the chemical is at a constant weight.

3. After the chemical has reached a constant weight, remove the container and place it into a desiccator overnight.

4. Calibrate the balance according to SOP-G10.

5. Place a medicine cup on the balance pan and weigh 12.75 g of PAP this will be used to make the working standards.

6. Fill a 1000-mL volumetric flask with 500 mL of deionized water. Rinse the contents of the medicine cup into the flask and swirl. Completely fill the flask with deionized water. Cut a small piece of Parafilm and cover the top of the flask. Place a stir bar into the flask and place on a stir plate. Stir until the entire amount of chemical is dissolved. The value of this standard is 15,000 mg/L.

7. Assign the stock standard an INSS number (SOP-G15).

8. Place a medicine cup on the balance pan and weigh 0.2125 g of PAP from the second source. This standard will be used to make the LFB and RL standards.

9. Fill a 500-mL volumetric flask with 250 mL of deionized water. Rinse the contents of the medicine cup into the flask and swirl. Completely fill the flask with deionized water. Cut a small piece of Parafilm and cover the top of the flask. Place a stir bar into the flask and place on a stir plate. Stir until the entire amount of chemical is dissolved. The value of this standard is 500 mg/L.

10. Assign the stock standard an INSS number (SOP –G15).

11. Place a medicine cup on the balance pan and weigh 1.7 g of PAP from the second source. This standard will be used to make the spike standard. The value of this standard is 20, 000 mg/L.

12. Fill a 100-mL volumetric flask with 50 mL of deionized water. Rinse the contents of the medicine cup into the flask and swirl. Completely fill the flask with deionized water. Cut a small piece of Parafilm and cover the top of the flask. Place a stir bar into the flask and place on a stir plate. Stir until the entire amount of chemical is dissolved.

13. Assign the stock standard an INSS number (SOP-G15).

14. Standards must be refrigerated between uses.

B. Working Standard Preparation Procedure.

1. To make the working standards, place 5, 100-mL volumetric flasks on the benchtop and fill with approximately 50 mL of deionized water. Use a Sharpie® to write the standard values on the flask.

2. Using volumetric pipettes make the standards following the directions below.

    150 mg/L = 1 mL of 15,000 mg/L standard
    450 mg/L = 3 mL of 15,000 mg/L standard
    750 mg/L = 5 mL of 15,000 mg/L standard
    1200 mg/L = 8 mL of 15,000 mg/l standard
    1500 mg/L = 10 mL of 15,000 mg/L standard

3. After each amount has been added, fill to the 100-mL mark on the flask with deionized water.

4. Place a cap on each flask and shake to mix the standards.

5. To make the RL, place a 50-mL volumetric flask on the benchtop and fill with approximately 25-mL of deionized water. Use a Sharpie marker and write RL on the flask. TV = 50 mg/L.

6. Using a volumetric pipet, place 5 mL of the RL/LFB standard into the flask.

7. Fill to the 50-mL mark with deionized water.

8. Place a cap on the flask and shake to mix the standard.

9. Turn on the COD digester reactor to reach 150°C. Turn the on/off switch on the back of the digester to On. Press the ADJ and the ∞ on the front of the digester.

10. Place 8 COD vials in a plastic test tube rack.

11. Take a Sharpie® and write the following on the caps:

    Blank, LFB, 50, 150, 450, 750, 1200, 1500

12. Remove the caps. Use glass volumetric pipettes and pipet 2-mL of each standard into the appropriate COD vial. For the blank, pipit 2-mL of Deionized water into the appropriate COD vial.

13. To make the LFB standard, put 2 mL of the RL/LFB standard will be used directly into the COD vial mark LFB.

14. Cap each vial and shake. Place each vial into the preheated 150°C digester reactor for 2 hours. To set the digester, turn the timer to the 120 min mark.

15. After the timer has sounded, remove the vials and place into the plastic test tube rack to cool.

C. Analysis of Chemical Oxygen Demand.

1. Turn on the spectrophotometer and wait until the pre-check has been completed. Spectophotometer must be on for at least 15 minutes before use.

2. Set the method program to 2720. The wavelength should be 620 nm vis. Use the 1st ^ button to change the program.

3. Make sure that the correct vial holder is inserted into the spectrophotometer before use. Using a Kim-Wipe, clean the outside of the blank vial and insert it into the vial holder.

4. Zero the meter by pressing the 1st ^ button until the Zero appears. Select from the options until view ABS. Press the enter key to zero. Once the spectrophotometer is zeroed, remove the vial.

5. Wipe off the 50 vial and place into the vial holder. Record the answer on the COD benchsheet. Remove the vial.

6. Wipe off the 150 mg/L vial and place in the vial holder. Record the absorbance on the COD benchsheet. Remove the vial.

7. Repeat the procedure for the 450 mg/L, 750 mg/L, 1200 mg/L, 1500 mg/L and LFB vials.

8. Plot the curve on a 3rd function calculator. Record the correlation coefficient and the y intercept on the benchsheet.

   a. Press 3rd Key, then Stat 2
   b. Enter first point (0) by pressing X<>Y key twice, then the ∑+ key. A "1" will appear.
   c. Enter the absorbance of your first standard and press the X<>Y key.
   d. Now enter the known value of your first standard and press the X<>Y key again.
   e. Press the ∑+ key. The number "2" will appear.
   f. Continue entering all the remaining values. After pressing the ∑+ key each time, a number will appear to indicate the total number of points plotted.
   g. When you have entered the last data point and value, press the 3rd key and the COR key. This will display your correlation coefficient. This value must be between 0.995 and 1.0. Record the value on the benchsheet.
   h. Press the 2nd key and the ITC key. This will display your y intercept. The number may be positive or negative. Record the value on the benchsheet.

* **This curve can be used for 1 year, unless the COD vial lot number or chemical lot numbers are changed, any new standards are made, or any bacteria growth is noticed in the standards.**

9. With each COD sample batch, a blank, midpoint (750 mg/L standard), LFB, duplicate and spike must be analyzed. A duplicate and a spike must be analyzed with each batch of 10 samples.

10. To make the duplicate, choose a sample. Using a Sharpie®, mark the cap of the vial with the identifying information. Always use the sample volume for the original sample and the duplicate.

11. To make the spike, choose a sample. Using a Sharpie, mark the cap of the vial with the identifying information. Take 25 µg of the spike standard to a 2 – mL sample volume. Spike must be pipetted into the solution after the sample volume has been added.

12. Once all samples have been analyzed, place the vials into the EZ COD ™ Recycling Container. When the container is ¾ full, please let the supervisor know.

D. Precision and Accuracy, Calculations.

1. Laboratory fortified blank (LFB) determination, True value = 500 mg/L.

   Percent Recovery of the Standard (%RS)

   %RS = (Measured value) / (True value) x 100

2. Duplicate, spike duplicate acceptance.

   Relative Percent Difference (%RPD)

   %RPD = (Sample value – Duplicate value) /
   [(Sample value + Duplicate value)/2] x 100

3. Spike recovery, True value = 250 mg/L.

   Percent Recovery of the Spike (%R)

   %R = (Spike value – Sample value) / (True value) x 100

4. Midpoint recovery, True value = 750 mg/L.

   Percent Recovery of the Midpoint (%R)

   %R = (Midpoint value) / (True value) x 100

Safety and Hazardous Waste Management

Safety glasses, gloves and lab coats should always be worn while handling samples. Excess samples may be flushed down the sink.

Review Policy-P6: General Safety Policy and Policy-P9: Radiation Protection Policy for additional safety requirements.

Subject: Chemical Oxygen Demand (HACH 8000)

References

HACH Handbook of Water Analysis. 1979. HACH Company, Loveland, CO 80539

- Method 8000

HACH Water Analysis Handbook 4th Edition, Revision 2. 2003. HACH Company, Loveland, CO 80539

Standard Methods for the Examination of Water and Wastewater, 24th Edition, 2023. American Public Health Association, 800 I Street, NW, Washington DC 20001-3710.

TNI Standard. Management and Technical Requirements for Laboratories Performing Environmental Analysis. EL-V1-ISO-2016-Rev2.0. The NELAC Institute, PO Box 2439, Weatherford, TX 76086.

Instrument Manual

Exhibits

Exhibit C19.1: COD Benchsheet**.**

Subject: Chemical Oxygen Demand (HACH 8000)

Exhibit C19.1: COD Benchsheet.

Page _____

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Chemical Oxygen Demand (HACH 8000)

Matrix: water, RL = 50 mg/L

Analyst: _____ Reviewed by: _____

Date analyzed: _____ Reviewed date: _____

Date of curve: _____

Stock standard: _____ Time in Reactor: _____

RL standard: _____ Time out of Reactor: _____

Spike standard _____ Time completed: _____

Correlation coefficient: _____

y intercept: _____

Calibration Standards

Blank mg/L: _____

50 mg/L: _____

150 mg/L: _____

450 mg/L: _____

750 mg/L: _____

1200 mg/L: _____

1500 mg/L: _____

Sample Number	Sample Identification	Sample volume (ml)	Absorbance	Concentration	Dilution Factor	Final conc. COD (mg/L)
	Blank					
	Laboratory Control					
	Duplicate					
	Spike					
	Midpoint					

CALCULATIONS

Final COD Result mg/L: concentration X dilution factor

Spike recovery (%R) = [(A-B) / C)] X 100

Final RPD = [(S-D) / [(S+D) / 2)] X 100

Reference standard recovery (%RS) = (X / Y) X 100

QUALITY CONTROL

Precision (duplicate):

Sample number: _____

Sample result (S): _____ mg/L

Duplicate result (D): _____ mg/L

Final RPD = _____ %

Accuracy (spike):

Spiked sample result (A): _____ mg/L

Sample conc, (B): _____ mg/L

Spike value (C): _____ mg/L

%RS = _____ %

Laboratory control standard (LCS):

Reference standard number _____

Value obtained (X) = _____ mg/L True value (Y) = _____ mg/L %RS= _____ %

SOP C19-Revision 5–Exhibit C19.1

Subject: Sulfate (SM 4500 SO_4^2 E-2021)

Approval

Title	Name	Signature	Date
Laboratory Supervisor	Kelley E. Keenan		05-01-24
Quality Assurance Officer	Jim Sumner		05-01-24

Document Revision History

Effective Date	Revision number	Review Type	Evaluators	Revisions
01-30-06	0	Internal	Kelley E. Keenan (ETS)	Original document
01-03-12	1	Internal	Kelley Keenan Jim Sumner (ETS)	• Updated SOP and exhibits during document review.
01-27-12	2	External	Jason Smith (NC DENR)	• Midpoint analyzed at the end of every batch (or 10 samples) instead of LFB.
04-01-13	3	Internal	Jim Sumner (ETS)	• Updated procedure and references to the approved analytical method identified in USEPA Method Update Rule II (MUR II), May 18, 2012.
04-01-18	4	Internal	Jim Sumner (ETS)	• Updated procedure to include NELAP requirements. • Additional guidance included in SOP. • Method number revised based on 2017 MUR.
05-01-24	5	Internal	Jim Sumner (ETS)	• Updated procedure and references to the approved analytical method identified in USEPA Method Update Rule, April 16, 2024.

Scope and Application

This method is used to determine the quantity of sulfate in water samples.

Summary of Method

Turbidimetric method for sulfate measurement: Sulfate ion is precipitated in an acetic acid medium with barium chloride to form barium sulfate crystals of uniform size. Light absorbance of the barium sulfate suspension is measured by a photometer and the sulfate concentration is determined by comparison of the reading with a standard curve.

Sulfate measurement procedures are based on Standard Methods 4500 SO_4^2 E-2021.

Subject: Sulfate (SM 4500 SO_4^2 E-2021)

Sample Collection, Preservation, Shipment and Storage

Samples must be analyzed within **28-days** of collection.

Samples must be received and stored in the laboratory at 0 to 6.0°C.

Quality Control

Calibration curve: A five-point calibration curve, consisting of a blank and 5 standards (5.0, 10, 20, 25, 30 and 35 mg/L sulfate) must be analyzed yearly. Using linear regression, the minimum correlation coefficient must be ≥0.995. If COD vial or chemical lot numbers have changed, new standards are prepared or bacterial growth is identified in the standards, the calibration curve must be reanalyzed.

Precision: Analyze a **duplicate** with each batch of samples (a batch of samples is considered samples analyzed on the same date). At a minimum, a duplicate must also be performed after every 20 samples. The relative percent difference (%RPD) should be within established limits determined through control charts. If these results differ by more than the established limits, results associated with this duplicate must be qualified (with a footnote in the analytical report) identifying the deviation.

Laboratory Fortified Blank (LFB, referred to LCS on benchsheets): A LFB must be analyzed initially and must be performed with each batch of samples, using a second source standard. At a minimum, a LFB must be performed after every 20 samples and at the end of each batch of samples. The percent recovery of the LFB (%R) must be ± 10% from the true value.

Midpoint: A midpoint standard must be analyzed at the end of each batch of samples to verify that the instrument calibration has not drifted. The percent recovery of the midpoint standard (%R) must be ± 10% from the true value. If an intermediate midpoint %RS is out of range, all samples between the last in range midpoint and the out-of-range midpoint must be reanalyzed.

Matrix Spike Recovery (MS): A MS must be analyzed initially and must be performed with each batch of samples. At a minimum, a MS must be performed on 5% of samples on a monthly basis. If fewer than 20 samples are analyzed in a month, at least one MS must be performed within that month. The percent recovery of the MS (%R) must be ± 25% from the true value. If these results differ by more than the established limits, results associated with the spike must be qualified (with a footnote on the analytical report) identifying the deviation. Qualification may include any sample interferences that may have resulted in the deviation.

Method Blank (MB): A MB must be analyzed initially and must be performed at the end of each batch of samples (a batch of samples is considered samples analyzed on the same date). The MB must be ≤ one half the reporting limit (RL).

Subject: Sulfate (SM 4500 SO_4^2 E-2021)

Reporting Limit (RL): The RL for sulfate is 5.0 mg/L.

PE: Annually (once every calendar year), a single-blind QC check sample (QCS) or performance evaluation sample (PE) is analyzed. This sample is provided by an approved proficiency testing (PT) provider.

Additional quality control guidance is provided in QAP-Q5.

Interferences

Color and suspended matter in large amounts will interfere. Suspended matter may be removed by filtration. If the absorbance of the sample before adding the barium chloride is lower in the response than the lowest concentration standard, correct for interference by running blanks without the addition of barium chloride. Silica in excess of 500 mg/L interferes and in waters containing large quantities of organic material it may not be possible to precipitate barium sulfate satisfactorily.

Subject: Sulfate (SM 4500 SO_4^2 E-2021)

Equipment and Materials

2, Sulfate Standards – 1000 ppm
Sulfa Ver 4 packets for 25 ml sample
Deionized water
Water bottle
100-ml volumetric flasks
50-ml volumetric flask
150-ml beakers
Whatman 40 glass fiber filters
Sharpie®
Volumetric caps
2 25 – ml square glass sample cells
0.5 – ml volumetric pipet
1-ml volumetric pipet
2-ml volumetric pipet
3-ml volumetric pipes
5-ml volumetric pipet
KimWipes
Waste bucket
Scissors
Timer
HACH DR400 Spectrophotometer
Calculator with 3rd Function

Subject: Sulfate (SM 4500 SO_4^2 E-2021)

Procedure

A. Preparation of Spectrophotometer.

1. Turn on the spectrophotometer and wait until the pre-check has been completed. Spectophotometer must be on for at least 15 minutes before use.

2. Set the method program to 3450. The wavelength should be 450 nm vis. Use the 1st ^ button to change the program.

B. Working Standard Preparation Procedure.

1. To make the working standards, place 6, 100-ml volumetric flasks on the benchtop and fill with approximately 50 ml of deionized water. Use a Sharpie® to write the standard values on the flask.

2. Using volumetric pipettes make the standards following the directions below.

   5.0 mg/L = 0.5 ml of 1000 ppm standard
   10 mg/L = 1.0 ml of 1000 ppm standard
   20 mg/L = 2.0 ml of 1000 ppm standard
   25 mg/L = 2.5 ml of 1000 ppm standard
   30 mg/L = 3.0 ml of 1000 ppm standard
   35 mg/L = 3.5 ml of 1000 ppm standard

3. After each amount has been added, fill to the 100-ml mark on the flask with deionized water.

4. Place a cap on each flask and shake to mix the standards.

5. To make the LCS, use a volumetric pipette and place 2 ml of the 1000 ppm standard into a 1000 ml volumetric flask.

6. Fill to the 50-ml mark with deionized water.

7. Place a cap on the flask and shake to mix the standard.

C. Preparation of Samples.

1. Remove samples from the refrigerator.

2. If samples are turbid or have particles, place a 150-ml beaker on the benchtop. Using a Sharpie® mark the beaker with the sample name or number.

3. Fold a Whatman 40 glass fiber filter into quarters and place into the top of the beaker.

4. Shake the sample and pour an aliquot into the filter. Repeat this process, until you have filtered approximately 100-ml of sample.

5. Place the beakers on an oven to warm them to room temperature.

D. Analysis of Sulfate.

1. Pour 25-ml of Deionized water into the sample cell and add 1 packet of Sulfa Ver 4 Reagent into the sample cell and swirl. This is the blank.

2. Turn on timer for 5 minutes.

3. After 5 minutes, place the sample cell in the vessel holder.

4. Zero the meter by pressing the 1st ^ button until the Zero appears. Select from the options until view ABS. Press the enter key to zero. Once the spectrophotometer is zeroed, remove the vial and record your answer.

5. Pour 25 ml of the 5.0 ml/L standard into the sample cell and add 1 packet of Sulfa Ver 4 Reagent into the sample cell and swirl.

6. Turn on timer for 5 minutes.

7. After 5 minutes, place the vessel in the vessel holder and record the absorbance.

8. Repeat the D.5 – D.7 for the 5, 10, 15, 20, 25 and 35 mg/L standards.

9. Plot the curve on a 3rd function calculator. Record the correlation coefficient and the y intercept on the benchsheet.

   a. Press 3rd Key, then Stat 2
   b. Enter first point (0) by pressing X<>Y key twice, then the ∑+ key. A “1” will appear.
   c. Enter the absorbance of your first standard and press the X<>Y key
   d. Now enter the known value of your first standard and press the X<>Y key again
   e. Press the ∑+ key. The number “2” will appear.

f. Continue entering all the remaining values. After pressing the ∑+ key each time, a number will appear to indicate the total number of points plotted.
g. When you have entered the last data point and value, press the 3rd key and the COR key. This will display your correlation coefficient. This value must be between 0.995 and 1.0. Record the value on the benchsheet.
h. Press the 2nd key and the ITC key. This will display your y intercept. The number may be positive or negative. Record the value on the benchsheet.

* **This curve can be used for 1 year, unless the COD vial lot number or chemical lot numbers are changed, any new standards are made, or any bacteria growth is noticed in the standards.**

10. To analyze the LCS, pour 25-ml of the LCS standard into the sample cell and add 1 Sulfa Ver 4 packet to the cell and swirl.

11. Set a timer for 5 minutes.

12. After 5 minutes, place the cell in the vessel holder and record the absorbance. To calculate the LCS result, push the 2nd Function button and then the 6 (x').

13. To analyze samples, pour 25-ml into the sample cell. Place the cell into the vessel holder and record the value. This is the sample blank.

14. After you have recorded the blank, remove the cell and add 1 Sulfa Ver 4 packet to the cell and swirl.

15. Set a timer for 5 minutes.

16. After 5 minutes, place the cell in the vessel holder and record the absorbance.

17. To calculate the sample result, subtract the sample blank from the sample absorbance. Once you have the difference, you will push the 2nd Function button and the 6 (x'). This will display the sample result. Make sure to apply any dilution factors to get the final result.

18. With each Sulfate sample batch, a blank, midpoint (20 mg/L standard), LCS, duplicate and spike must be analyzed. A duplicate and a spike must be analyzed with each batch of 10 samples.

19. To make the duplicate, choose a sample. Always use the sample volume for the original sample and the duplicate.

20. To make the spike, choose a sample. Take a 50-ml volumetric flask and add approximately 25-ml of sample. Add 0.5 ml of the 1000 ppm standard and fill to the 50-ml mark. Follow sample procedure D.5 – D.7.

E. Precision and Accuracy, Calculations.

1. Laboratory fortified blank (LFB) determination, True value = 20 mg/L.

   Percent Recovery of the Standard (%RS)

   %RS = (Measured value) / (True value) x 100

2. Duplicate, spike duplicate acceptance.

   Relative Percent Difference (%RPD)

   %RPD = (Sample value – Duplicate value) /
   [(Sample value + Duplicate value)/2] x 100

3. Spike recovery, True value = 25 mg/L.

   Percent Recovery of the Spike (%R)

   %R = (Spike value – Sample value) / (True value) x 100

4. Midpoint recovery, True value = 20 mg/L.

   Percent Recovery of the Midpoint (%R)

   %R = (Midpoint value) / (True value) x 100

Safety and Hazardous Waste Management

Safety glasses, gloves and lab coats should always be worn while handling samples. Excess samples may be flushed down the sink.

Review Policy-P6: General Safety Policy and Policy-P9: Radiation Protection Policy for additional safety requirements.

Subject: Sulfate (SM 4500 SO_4^2 E-2021)

References

Standard Methods for the Examination of Water and Wastewater, 24th Edition, 2023. American Public Health Association, 800 I Street, NW, Washington DC 20001-3710.

- SM 4500 SO_4^2 E-2021

HACH Water Analysis Handbook 4th Edition, Revision 2. 2003. HACH Company, Loveland, CO 80539

TNI Standard. Management and Technical Requirements for Laboratories Performing Environmental Analysis. EL-V1-ISO-2016-Rev2.0. The NELAC Institute, PO Box 2439, Weatherford, TX 76086.

Instrument Manual

Exhibits

Exhibit C20.1: Sulfate Benchsheet**.**

Subject: Sulfate (SM 4500 SO_4^2 E-2021)

Exhibit C20.1: Sulfate Benchsheet.

Page _____

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Sulfate (SM 4500 SO_4^2 E-2021)

Matrix: water, RL = 5.0 mg/L

Analyst: _____
Date analyzed: _____

Reviewed by: _____
Reviewed date: _____

Date of curve: _____

Calibration Standards
Blank mg/L: _____
5.0 mg/L: _____
10 mg/L: _____
20 mg/L: _____
25 mg/L: _____
30 mg/L: _____
35 mg/L: _____

Stock standard: _____
Correlation coefficient: _____
y Intercept: _____

Sample Number	Sample Identification	Sample volume (ml)	Absorbance	Concentration	Dilution Factor	Final conc. Sulfate (mg/L)
	Blank					
	Laboratory Control					
	Duplicate					
	Spike					
	Midpoint					

CALCULATIONS

Final Sulfate Result mg/L: concentration X dilution factor
Spike recovery (%R) = [(A-B) / C)] X 100
Final RPD = [(S-D) / [(S+D) / 2]] X 100
Reference standard recovery (%RS) = (X / Y) X 100

QUALITY CONTROL

Precision (duplicate):

Sample number: _____
Sample result (S): _____ mg/L
Duplicate result (D): _____ mg/L
Final RPD = _____ %

Accuracy (spike):

Spiked sample result (A): _____ mg/L
Sample conc, (B): _____ mg/L
Spike value (C): _____ mg/L
%RS = _____ %

Laboratory control standard (LCS):

Reference standard number _____
Value obtained (X) = _____ mg/L True value (Y) = _____ mg/L %RS= _____ %

SOP C20-Revision 5–Exhibit C19.1