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Subject: Temperature (SM 2550 B-2010)

Approval

Title	Name	Signature	Date
Laboratory Supervisor	Kelley E. Keenan		07-01-21
Quality Assurance Officer	Jim Sumner		07-01-21

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.

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 °C and reported to the nearest 0.1°C or 1°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 °C and reported to the nearest 0.1°C or 1°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, 23rd Edition, 2017. 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. EL-V1-ISO-2016-Rev2.0. 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

1

Toxicity Incubator #1 – Temperature Log (°C)

Month and Year: January 2021

Initial thermometer calibration date: 12-23-20 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	+0.5

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

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

Comments:

Subject: Dissolved Oxygen (SM 4500-O G-2016)

Approval

Title	Name	Signature	Date
Laboratory Supervisor	Kelley E. Keenan		07-01-21
Quality Assurance Officer	Jim Sumner		07-01-21

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.

Subject: Dissolved Oxygen (SM 4500-O G-2016)

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 with a dissolved oxygen meter equipped with a dissolved oxygen probe. Measurements are recorded to the nearest 0.1 mg/L.

Dissolved oxygen measurement procedures are based on Standard Methods 4500-O G-2011.

Quality Control

Calibration: The dissolved oxygen meter must be calibrated each day **before use** (this may be several times within a day). Calibration procedures correct 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

Probes with membranes respond to partial pressure of oxygen which in turn is a function of dissolved inorganic salts. Conversion factors for brackish water and seawater are calculated from dissolved oxygen saturation versus salinity to remove this interference.

Plastic films used with membrane electrode systems are permeable to a variety of gasses besides oxygen, although none are depolarized easily at the indicator electrode. Prolonged use of membrane electrodes in waters containing gases such as hydrogen sulfide tends to lower cell sensitivity. This interference is eliminated by changing the membrane electrode on a regular basis and calibrating the meter before each use.

Subject: Dissolved Oxygen (SM 4500-O G-2016)

Equipment and Materials

Dissolved oxygen (DO) meter equipped with a DO 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: YSI Model 52CE, SN 18D104324 equipped with a YSI 5905 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 to the **O_2-TEMP** setting. Wait for the meter to cycle through the internal check.

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, and shake off any excess water. Place the probe back in the BOD bottle.

4. Check the temperature and dissolved oxygen readings.

5. 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.

6. Turn the dial to the **CALIBRATE** setting. The meter will prompt to **Calibrate in percent**. Press the **SKIP** button and the meter will prompt to **Calibrate in mg/L**. Press the **CONFIRM** button. The meter will prompt **Enter cal value. Last = X.XX mg/L**. Adjust the DO reading to the correct measurement (based on Exhibit C2.2) using the ↑ ↓ buttons and press **CONFIRM**. Turn the dial back to the **O_2-TEMP** setting.

7. Remove the probe from the BOD bottle and submerge the tip of the probe in a sample.

8. Remove the probe from the sample and rinse with deionized water. Place the probe back in the BOD bottle.

9. Once the display has stabilized, check the reading again for the correct DO calibration. If the reading is not correct, follow steps A.5 through A.9.

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

Corrective Action: If the meter does not calibrate properly, check the probe membrane for tears and/or air bubbles under the membrane. If a tear occurs, the membrane and filling solution must be replaced, and the meter must be recalibrated. Refer to the instrument manual for instructions on the care and maintenance of the DO 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, 23rd Edition, 2017. American Public Health Association, 800 I Street, NW, Washington DC 20001-3710.

- Method: 4500-O G-2016.

Subject: Dissolved Oxygen (SM 4500-O G-2016)

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

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 G-2016)

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

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-2011, 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-2011, 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-2016, 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-2011, 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 7–Exhibit C2.1, SOP C3-Revision 9–Exhibit C3.1, SOP C4-Revision 8–Exhibit C4.1, SOP C5-Revision 6– Exhibit C5.1

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

	Dissolved Oxygen (mg/L)	
Temperature (°C)	Freshwater	Saltwater (25 ppt)
17.0	9.0	8.9
18.0	8.8	8.7
19.0	8.6	8.6
20.0	8.4	8.4
21.0	8.3	8.2
22.0	8.1	8.1
23.0	8.0	8.0
24.0	7.8	7.8
25.0	7.7	7.7
26.0	7.6	7.6
27.0	7.4	7.5
28.0	7.3	7.4
29.0	7.2	7.2
30.0	7.0	7.0

Note: Solubility corrected for elevation in Asheville, NC (2200 feet = 698 mm Atmospheric Pressure, 1.09 correction).

Subject: pH (SM 4500-H+ B- 2011; SW846 9040C-2004; SW846 9045D-2004)

Approval

Title	Name	Signature	Date
Laboratory Supervisor	Kelley E. Keenan		07-01-21
Quality Assurance Officer	Jim Sumner		07-01-21

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, May 19, 2021.

Subject: pH (SM 4500-H+ B- 2011; 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-2011, 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: pH (SM 4500-H+ B- 2011; 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, 23rd Edition, 2017. American Public Health Association, 800 I Street, NW, Washington DC 20001-3710.

- Method: 4500-H+ B-2011.

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. EL-V1-ISO-2016-Rev2.0. 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: pH (SM 4500-H+ B- 2011; SW846 9040C-2004; SW846 9045D-2004)

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

ETS Environmental Testing Solutions, Inc.

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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-2011, 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-2011, 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-2016, 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-2011, 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 7–Exhibit C2.1, SOP C3-Revision 9–Exhibit C3.1, SOP C4-Revision 8–Exhibit C4.1, SOP C5-Revision 6– Exhibit C5.1

Subject: pH (SM 4500-H+ B- 2011; SW846 9040C-2004; SW846 9045D-2004)

Exhibit C3.2: pH Benchsheet.

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ETS Environmental Testing Solutions, Inc.

pH

Meter: Accumet Model AR20, SN 93312452

Sample temperature (°C): _____

Check	
	Matrix: Water **Method: SM 4500 H+ B-2011**
	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	

Subject: Conductivity (SM 2510 B-2011)

Approval

Title	Name	Signature	Date
Laboratory Supervisor	Kelley E. Keenan		07-01-21
Quality Assurance Officer	Jim Sumner		07-01-21

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.

Subject: Conductivity (SM 2510 B-2011)

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-2011.

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 also 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: Conductivity (SM 2510 B-2011)

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: Conductivity (SM 2510 B-2011)

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.

Subject: Conductivity (SM 2510 B-2011)

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, 23rd Edition, 2017. American Public Health Association, 800 I Street, NW, Washington DC 20001-3710.

- Method: 2510 B-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 C4.1: Daily Meter Calibration and Standardization Benchsheet.
Exhibit C4.2: Conductivity Benchsheet.

Subject: Conductivity (SM 2510 B-2011)

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-2011, 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-2011, 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-2016, 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-2011, 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 7–Exhibit C2.1, SOP C3-Revision 9–Exhibit C3.1, SOP C4-Revision 8–Exhibit C4.1, SOP C5-Revision 6– Exhibit C5.1

Subject: Conductivity (SM 2510 B-2011)

Exhibit C4.2: Conductivity Benchsheet.

Environmental Testing Solutions, Inc.

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Conductivity (SM 2510 B-2011, 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 ± 1.0°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 8 Exhibit C4.2

Subject: Salinity (SM 2520 B-2011)

Approval

Title	Name	Signature	Date
Laboratory Supervisor	Kelley E. Keenan		07-01-21
Quality Assurance Officer	Jim Sumner		07-01-21

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.
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.

Subject: Salinity (SM 2520 B-2011)

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-2011.

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 Control Standard (LCS): An LCS must be analyzed initially to verify the calibration cell constant and must be performed 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 percent recovery of the LCS (%R) must be ± 0.10 S.U. from the true value. The LCS's are laboratory prepared standards at 0.71 and 35 ppt. For samples in association with toxicity tests, the LCS is only performed initially, each day that samples are analyzed.

Subject: Salinity (SM 2520 B-2011)

Operational Range: The operational range of the salinity meter is 1 ppt to 100 ppt. Measurements less than 1 ppt and greater than 100 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°C). Both the salinity and temperature at the time of analysis are reported.

Subject: Salinity (SM 2520 B-2011)

Equipment and Materials

Oakton Salt 6 Salinity Meter (Acorn 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: Oakton Salt 6 Salinity Meter, Acorn 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 Oakton Salt 6 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 the **ON/OFF** button.
c. Remove the probe from the beaker containing deionized water, rinse the tip 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 **CAL** to calibrate the meter.
e. Once the reading has stabilized adjust the measurement to **25.0** using the ▲ ▼ buttons. Press **HOLD/ENTER** to accept this measurement. Record the initial measurement and how many ppt the measurement was adjusted on the benchsheet .
f. 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 ± 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.
g. 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.
h. Once the LFBs have been analyzed, the meter is ready to measure the salinity of samples.
i. 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.
j. 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.
k. Turn the meter off after all measurements have been completed, by pressing **ON/OFF** button.

C. Calculation of Salinity.

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

Subject: Salinity (SM 2520 B-2011)

D. Precision and Accuracy, Calculations.

1. Laboratory control standard (LCS) 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, 23rd Edition, 2017. American Public Health Association, 800 I Street, NW, Washington DC 20001-3710.

- Method: 2520 B-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 C5.1: Daily Meter Calibration and Standardization Benchsheet.
Exhibit C5.2: Salinity Benchsheet.

Subject: Salinity (SM 2520 B-2011)

Exhibit C5.1: 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-2011, 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-2011, 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-2016, 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-2011, 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 7–Exhibit C2.1, SOP C3-Revision 9–Exhibit C3.1, SOP C4-Revision 8–Exhibit C4.1, SOP C5-Revision 6– Exhibit C5.1

Subject: Salinity (SM 2520 B-2011)

Exhibit C5.2: Salinity Benchsheet.

Environmental Testing Solutions, Inc.

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Salinity (SM 2520 B-2011, 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 6– Exhibit C5.2

Subject: Alkalinity (SM 2320 B-2011)

Approval

Title	Name	Signature	Date
Laboratory Supervisor	Kelley E. Keenan		07-01-21
Quality Assurance Officer	Jim Sumner		07-01-21

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. • 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.

Subject: Alkalinity (SM 2320 B-2011)

Scope and Application

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

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-2011.

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 Control Standard (LCS): An LCS must be analyzed initially and must be performed with each batch samples. At a minimum, an LCS must be performed after every 20 samples and at the end of each batch of samples. The percent recovery of the LCS (%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-2011)

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 control standard (LCS) and spike standard
(Specifications: 0.0200 ± 0.00005 N at 20°C)
Alkalinity Benchsheet

Procedure

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 an LCS.

   a. Use a 100-mL graduated cylinder, to make the LCS. 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 LCS.

   c. Calculate the %RS of the LCS. The %RS must be ± 10%. If the LCS 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 control standard (LCS) 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-2011)

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, 22nd Edition, 2012. American Public Health Association, 800 I Street, NW, Washington DC 20001-3710.

- Method: 2320 B-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 C6.1: Alkalinity Benchsheet.

Subject: Alkalinity (SM 2320 B-2011)

Exhibit C6.1: Alkalinity Benchsheet.

ETS Environmental Testing Solutions, Inc.

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Analyst
Date analyzed

Alkalinity (SM 2320 B-2011)
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 6–Exhibit C6.1

Subject: Hardness (SM 2340 C- 2011)

Approval

Title	Name	Signature	Date
Laboratory Supervisor	Kelley E. Keenan		07-01-21
Quality Assurance Officer	Jim Sumner		07-01-21

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. • 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.

Subject: Hardness (SM 2340 C- 2011)

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-2011.

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 Control Standard (LCS): An LCS must be analyzed initially and must be performed with each batch samples. At a minimum, an LCS must be performed after every 20 samples and at the end of each batch of samples. The percent recovery of the LCS (%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- 2011)

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 (LCS), 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- 2011)

Procedure

A. Preparation of Eriochrome Black T Indicator.

1. Carefully weigh out 100 g of NaCl and 0.50 g of Eriochrome Black T using a calibrated top-loading balance (SOP-G10).

2. Combine the NaCl and Eriochrome Black T in a 100-mL plastic bottle and mix well.

3. Using the Chemical Log, assign a CHM number for the standard as indicated in SOP-G15.

4. Label the bottle with the chemical name, preparation date, analyst's initials and the CHM number.

5. The expiration date of this chemical is 1-year from the preparation date.

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 an LCS.

a. Use a 50-mL graduated cylinder, to make the LCS. 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 LCS.

e. Calculate the %RS of the LCS. The %RS must be ± 10%. If the LCS 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 stirring 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 (LCS), 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

Subject: Hardness (SM 2340 C- 2011)

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, 23rd Edition, 2017. American Public Health Association, 800 I Street, NW, Washington DC 20001-3710.

- Method: 2340 C-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.

Exhibits

Exhibit C7.1: Hardness Benchsheet.

Subject: Hardness (SM 2340 C- 2011)

Exhibit C7.1: Hardness Benchsheet.

ETS Environmental Testing Solutions, Inc.

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Analyst
Date analyzed

Hardness (SM 2340 C-2011)
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 6–Exhibit C6.1

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

Approval

Title	Name	Signature	Date
Laboratory Supervisor	Kelley E. Keenan		07-01-21
Quality Assurance Officer	Jim Sumner		07-01-21

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. • 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 LCS 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.

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, 0.50 and 5.00 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 control standard (LCS): An LCS must be analyzed initially and must be performed with each batch samples. At a minimum, an LCS must be performed after every 10 samples and at the end of each batch of samples. The percent recovery of the LCS (%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 5.00 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 5.00 mg/L are diluted to obtain a measured value within the 0.05 to 5.00 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 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.

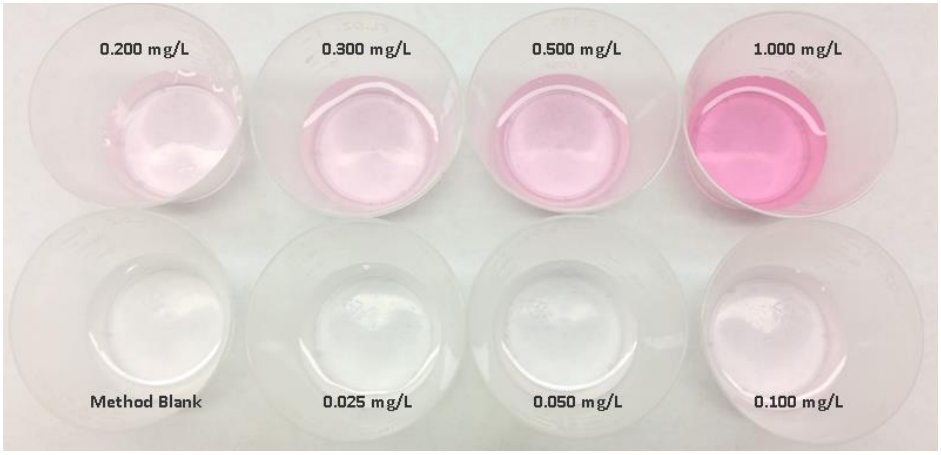
4. Once the positive and negative control tests are complete, samples may be screened for total residual chlorine. Pour a small aliquot of each sample received into a 1-oz medicine cup (approximately 5 mL). Dispense one dose of DPD to each medicine cup containing the samples.

5. Record on the bench sheet the samples 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 three point calibration curve using 0.05, 0.50 and 5.00 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 LCS / MDL_s), 0.50 mL (for the 0.50 mg/L calibration standard) and 5.00 mL (for the 5.00 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 the 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. Rinse the probe tip with deionized water and place into the 5.00 mg/L calibration standard.

15. Press **DISPLAY** and then **STD**. Use the ▲ to select **5.00**. 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**. Slope will be displayed and should be 26 to 30 mV.

16. If the average slope is out of range, recalibrate the meter following steps 5 through 15 above.

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

18. Rinse the probe tip with deionized water and place into the 0.25 mg/L LCS / 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.

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

20. 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.

21. 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.

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

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

24. After the 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.

25. Record the measurement on the Total Residual Chlorine Benchsheet. If the measurement is greater than 5.00 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).

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

27. 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 control standard, 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

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, 23rd Edition, 2017. American Public Health Association, 800 I Street, NW, Washington DC 20001-3710.

- 4500-Cl G-2011.

Thermo Electron Corporation. 2003. Orion Residual Chlorine Electrode Instruction Manual, Orion 97-70. Thermo Electron Corporation, 166 Cummings Center Beverly, MA 01915.

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

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.

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

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 C8.1: Total Residual Chlorine (45001-Cl G-2011), Screening Whole Effluent Toxicity Samples Benchsheet.

Exhibit C8.2: Total Residual Chlorine (ORION-97-70-1977), Confirmation of Whole Effluent Toxicity Samples Benchsheet.

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

Exhibit C8.1: Total Residual Chlorine (45001-Cl G-2011), Screening Whole Effluent Toxicity Samples Benchsheet.

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

Matrix: Water, RL = 0.10 mg/L

Analyst

Date analyzed

DPD: INR

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 7– Exhibit C8.1

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

Exhibit C8.2: Total Residual Chlorine (ORION-97-70-1977), Confirmation of Whole Effluent Toxicity Samples Benchsheet.

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

Matrix: Water, RL = 0.05 mg/L, Meter: Accumet Model AB250, SN 92349123

Analyst		Iodide reagent:	INR
Date analyzed		Acid reagent:	INR

Calibration:

	0.05 mg/L	0.50 mg/L	5.00 mg/L	Slope Values (mV) (suggested range = 26 to 30 mV)	
Reference standard #	INSS	INSS	INSS		

Note: For samples with a residual chlorine of > 5.00 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	**0.25**		

Duplicate sample precision:

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

Sample measurements:

Sample number	Sample ID	Total residual chlorine (mg/L)
TV < 0.025 mg/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	**0.25**		

Reviewed by _____ Date reviewed _____

SOP C8-Revision 7–Exhibit C8.2