Georgia Department of Natural Resources

Environmental Protection Division laboratory

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SM4500-H+B – pH

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1. Scope and Application

1.1. This method is applicable to drinking and surface water, and aqueous domestic, and industrial wastes. The pH of a sample is determined electrometrically using a reference electrode.

1.2. Restricted Procedure

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

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2. Definitions

2.1 Refer to Section 3 and Section 4 of the Georgia EPD Laboratory Quality Assurance Plan (see SOP reference 13.5) for Quality Control Definitions.

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

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

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

2.5 Continuing Calibration Check (CCC) or Continuing Calibration Verification (CCV) – A standard used to verify that the response of the instrument has not changed since initial calibration.

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

2.7 LCS (Laboratory Control Sample) and LCSD (Laboratory Control Sample Duplicate) are prepared by spiking laboratory reagent water, Ottawa sand or air sampling device with the target analyte or compound. They are used to validate the analytical batch with respect to accuracy and precision. In this method, the CCC results are used for LCS/LCSD for Labworks purposes.

3. Interferences

3.1. The glass electrode is relatively free from interference from color, turbidity, colloidal matter, oxidants, reductants, or high salinity, except for a sodium error at pH> 10.

3.2. pH measurements are affected by temperature in two ways: mechanical effects that are caused by changes in the properties of the electrodes and chemical effects caused by equilibrium changes. Always report temperature at which pH is measured.

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3.3. Coatings of oily material or particulate matter can impair electrode response. These coatings can usually be removed by gentle wiping or detergent washing, followed by reagent water rinsing. An additional treatment with Markson electrode cleaning solution (Cat # 6200-0004) or equivalent may be necessary to remove any remaining film.

4. Safety

4.1. Refer to the EPD Laboratory Safety/Chemical Hygiene Plan and Fire Safety Plan, online revision, Reference 13.6.

5. Apparatus and Equipment

5.1. Sample Container: plastic half-gallon container

5.2. 50 ml and 150 ml glass beakers

5.3. Approved pH meter with pH electrode and reference electrode with automatic temperature compensation.

5.3.1. Glass electrode

5.3.2. Reference electrode- a silver-silver chloride or other reference electrode with automatic temperature compensation. Note: Combination electrodes incorporating both measuring and referenced functions are convenient to use and are available with solid, gel-type filling materials that require minimal maintenance.

5.3.3. Stir plate and stir bar

5.3.4. Class A graduated cylinders and pipettes

5.3.5. Thermometer and/or temperature sensor for automatic compensation.

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6. Reagents

6.1 Reagent Water:

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

6.2 Calibration Standards:

6.2.1 The calibration standards are buffer solutions at the following concentrations: 4.00, 7.00, and 10.0. These buffer solutions are certified, commercially prepared and purchased.

6.2.2 Additional checks may be performed using other buffer values if samples are outside the 4.00 to 10.0 range.

6.2.2.1 Use calibration standards 2.00, 4.00 and 7.00 for samples with pH values less than 4.00.

6.2.2.2 Use calibration standards 7.00, 10.0 and 12.0 for samples with pH values above 10.0.

6.2.3 All sample results must be bracketed by valid calibration levels.

6.2.4 The purchased buffers are stable until the expiration date on the bottle or within 6 months of opening date, whichever is sooner.

6.3 Initial Calibration Verification Standard (ICV):

6.3.1 A 7.00 buffer solution from an alternate source is used to verify the initial calibration of the measurement system.

6.3.2 The ICV value must be within 0.1 pH units of the true value, or the calibration must be repeated.

6.3.3. A different lot from the same vendor as the calibration standards is also acceptable.

6.3.4 The purchased buffer is stable until the expiration date on the bottle or within 6 months of opening date, whichever is sooner.

6.4 Reference Filling Solution:

6.4.1 Thermo Scientific™ Orion™ pH Electrode Filling Solution Thermo Scientific™ 900011, Fisher Catalog# 13-641-686 or equivalent.

7. Sample Collection

7.1. Samples are collected in plastic half gallon containers.

7.2. No chemical preservation is required.

7.3. Samples should be placed on ice as soon as possible after collection.

7.4. Samples are stored at 0–6º C (not frozen) until analysis if necessary.

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7.7. Samples should be placed on ice as soon as possible after collection.

7.8. Samples are stored at 0–6º C (not frozen) until analysis if necessary.

7.9. Source Samples

7.9.1. The holding time for pH is 15 minutes.

7.9.2. All source samples that require pH analysis by the laboratory must be flagged with a J and commented in Labworks. These samples should be analyzed as soon as practical.

7.9.3. Comment as follows:

7.9.3.1. "Source-pH-SM4500-H+B-pH - <J> -Value Estimated- pH analysis should be performed in the field within 15 minutes of sample collection (Manual for Certification of Laboratories Analyzing Drinking Water, Table IV-6 Sample Containers, Preservation and Holding Times for Regulated Parameters)." See SOP reference 13.7.

7.10. All other samples that require pH analysis are reported as laboratory pH.

8. Calibration

8.1. Calibration Standards

8.1.1 The calibration consists of calibration buffers at the following concentrations: 4.00, 7.00, and 10.0. These buffer solutions are certified, commercially prepared and purchased.

8.1.2 Use calibration standards 2.00, 4.00 and 7.00 for samples with pH values less than 4.00.

8.1.3 Use calibration standards 7.00, 10.0 and 12.0 for samples with pH values greater than 10.0.

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8.1.4 The purchased buffers are stable until the expiration date on the bottle or within 6 months of opening date, whichever is sooner.

8.2 Calibration Curve

8.2.1 The pH meter is calibrated daily.

8.2.2 The slope should be between 92 -102%. If it is not, clean the electrode according to manufacturer instructions and recalibrate.

8.2.3 Once the pH meter is calibrated, the calibration standards must be analyzed against the curve and the readings must be within ± 0.1 pH units of the buffer solution value.

8.3 Calibration Verification

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

8.3.1.1 The ICV standard must be from an alternate source than the standards used in the calibration of the pH meter.

8.3.2 A Continuing Calibration Check Standard (CCC) must be analyzed every 10 samples and at the end of a sample run.

8.3.2.1 The CCC must be within ± 0.1 pH units of the expected value

8.3.2.2 If the CCC does not meet acceptance criteria, then all samples affected by out of control CCC are to be rerun.

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

8.3.2.4 Either the 4.00, 7.00 or 10.0 buffer used for the calibration is also used for the CCC.

8.3.2.5 If the 2.0, 4.0, and 7.00 calibration curve is used, the 4.00 buffer is to be used for the CCC.

8.3.2.6 If the 4.00, 7.00 and 10.0 calibration curve is used, the 7.00 buffer is to used for the CCC.

8.3.2.7 If the 7.00, 10.0 and 12.0 curve is used, the 10.0 buffer is to be used for the CCC.

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9. Quality Control

9.1. Refer to Table 14.1 for Reporting Limits (RL's), Table 14.2 for Quality Control Acceptance Criteria, and Table 14.3 for Quality Control Procedures associated with this method, and standard operating procedures for the control charts and control limits.

9.2. Refer to the GA EPD Laboratory SOP's- Initial Demonstration of Capability SOP 6-001, online revision, or Continuing Demonstration of Capability SOP 6-002, online revision, SOPs for training criteria. pH samples for IDCs and CDCs must be within ± 0.1 pH units of the expected values. See SOP references in section 13.2.

9.3. The temperature compensation probe must be verified at least quarterly using a NIST traceable thermometer. The allowable temperature deviation of the pH probe temperature sensor compared to a NIST traceable thermometer is ± 2^{o} C. This verification must be recorded in the pH maintenance log.

9.4. Source pH is analyzed at the EPD laboratory as quickly as is practical and is reported as estimated. All other samples that require pH are reported as laboratory pH.

9.4.1. Because Source samples only have a 15 min. hold time for pH, all Source pH samples are considered out of hold when analyzed at the laboratory. Source pH sample must be <J> flagged and commented on as estimated. All other pH samples are reported as laboratory pH.

9.5. Sample duplicates must be analyzed at a rate of no less than 10% of all samples analyzed over time.

9.5.1. At least one sample duplicate should be analyzed for each batch of 1 to 9 samples and two sample duplicates analyzed for each batch of 10 – 18 samples.

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9.6. Every sample requesting pH must have an independent temperature recorded for it on the bench sheet.
9.7. Record manufacturer, serial number, and model number in maintenance log when pH probe is replaced.
9.8. All pH acceptance criteria are static (i.e. not based on control charts).
9.9. pH analyses are exempt from the requirement to perform MDL studies.

10. Procedure

10.1. Remove sample bottles from the cold storage and allow equilibration to room temperature prior to sample preparation and/or analysis. The samples should be at the same temperature as the buffers used for calibration.
10.2. Remove the pH electrode from the pH ICV storage solution.
10.2.1. Inspect the electrode and the level of the reference electrode filling solution.
10.2.2. Rinse probe well with reagent water.
10.2.3. If filling solution is below the filling hole by more than ¼ inch, add filling solution (See Section 6.4).
10.2.4. If reference chamber has layers of KCl crystals, empty chamber by gently pressing air in chamber with disposable pipette while holding probe upside down.
10.2.5. Refill with reagent water and shake several times to dissolve crystals. Empty chamber and repeat again with reagent water. Empty chamber and refill with Reference filling solution (See Section 6.4) to the top of the chamber hole.
10.2.6. Allow one hour for probe readings to stabilize after replacing filling solution.
10.2.7. Record in maintenance
10.3. Rinse the probe well with reagent water and gently blot dry.
10.4. Press the POWER button on the meter and wait for the pH numbers to appear and the meter to warm up. Important: Always ensure that the reference electrode with the automatic temperature compensation is plugged in securely to the rear of the meter and check the temperature adjustment when monitoring samples. Note: If the temperature is staying at 25ºC then the temperature compensation is not working.
10.5. Pour up fresh 4.0, 7.0, and 10 buffer solutions daily into 3 separate 50 ml beakers containing stir bars. Keep buffer solutions covered with parafilm when not in use.
10.6. Calibration procedure:
10.6.1. Press calibrate button.
10.6.2. When 'CAL 1' appears on screen, place the beaker with the 4.0 buffer on stir plate under the probe, turn stirrer on to stir gently. Immerse electrode into the 4.0 buffer solution. Allow the reading to stabilize. When the pH symbol stops blinking, the meter is stable.
10.6.3. Before removing the 4.00 buffer solution, press the calibrate button and turn off the stirrer. When 'CAL 2' appears, raise electrode out of the 4.00 buffer

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solution, rinse well with reagent water, and blot excess water from the electrode with a tissue.

10.6.4. Place the beaker containing the 7.0 buffer solution on the stir plate, turn on the stirrer to stir gently, immerse the pH probe into the 7.0 buffer solution and wait for the meter to stabilize and the pH symbol to stop blinking.

10.6.5. Press the calibrate button on the pH meter and wait for "CAL 3" to appear, turn off the stirrer, raise the probe out of the 7.0 buffer solution, rinse well with reagent water and blot excess water off of the probe with a tissue.

10.6.6. Place the beaker containing the 10.0 buffer on the stir plate, turn on the stirrer to gently stir and immerse the probe into the 10.0 buffer solution.

10.6.7. Allow the meter to stabilize, wait for pH symbol to stop blinking.

10.6.8. Press the measure/save/print button to save the calibration curve and the "SLOPE' reading will appear on the screen. Make sure to record the "SLOPE" reading on the sample bench sheet.

10.6.9. The slope should be between 92% - 102%. If not, clean the electrode according to manufacturer's instructions and calibrate the meter again following the instructions above.

10.6.10. Read the 4.0, 7.0 and 10.0 buffers and record the results on the worksheet. Results must be within ± 0.1 pH units of true value.

10.6.11. Verify the calibration by checking a second source standard (ICV). Record the result on the bench sheet.

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10.7. Perform a backlog of pending samples. Batch samples in groups of 17. For each batch choose a QC sample and analyze a sample duplicate for a minimum of 10% of the samples.

10.8. <u>Analyzing samples for pH</u>:

10.8.1. Pour 100 ml of sample into a 150 ml beaker containing a stir bar and place on stir plate. Turn on stirrer to a moderate speed and immerse electrode into the sample. Note: If instrument goes into standby mode, press pH button to read pH.

10.8.2. Check that the temperature reading is adjusting. When the pH symbol stops blinking, record the pH reading on bench sheet. Note: Using the temperature reading on the pH meter, make sure to record the temperature of sample on the bench sheet.

10.8.3. If the pH value does not fall between 4.0 and 10.0 range, recalibrate the pH meter with appropriate buffers that will bracket the pH the sample pH. Then re-read the sample pH, record the reading and the temperature of the sample. See section 8.1 for appropriate buffers to use for your curve and section 8.3.2 for appropriate CCC buffer to use.

10.8.4. Rinse the electrode, stir bar, and beaker with reagent water and blot the electrode with tissue between samples. If the meter goes into standby mode, press the power button to turn it back on.

10.8.5. Store pH electrode in electrode storage solution when not in use and ensure the filling hole in the electrode is plugged.

10.8.6. Quarterly, compare temperature reading of pH probe against a NIST traceable thermometer. Record this result in the maintenance log. The temperatures should agree within 2 degrees. If not, then replace probe.

10.8.7. When replacing the pH probe, record the manufacturer, serial number and model number in the assigned maintenance log.

11. Calculations

11.1. The pH meter reads directly in pH units. pH is reported to the nearest 0.1 unit.

11.2. Quality Control Calculations

11.2.1. Duplicate Difference

$$\text{Duplicate Difference} = \left| R_{\text{sample}} - R_{\text{duplicate}} \right|$$

11.2.1.1. Where:

R_{sample} = pH result of the sample

$R_{\text{duplicate}}$ = pH result of the sample duplicate

11.2.2. Difference of ICV or CCC from Calibration

$$\text{ICV/CCC Difference} = \left| R_{\text{expected}} - R_{\text{actual}} \right|$$

11.2.2.1. Where:

R_{expected} = pH expected for the standard

R_{actual} = pH measured for the standard

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12. Waste Management

12.1. Refer to GA EPD Laboratory SOP- EPD Laboratory Waste Management SOP, SOP 6-015, online revision.

12.2. Buffer and samples with a pH less than 5.5 or greater than 10.5 must be neutralized before disposal in a lab sink drain.

13. References

13.1. Standard Method Online, SM4500-H+B-pH Electrometric Method 2000.

13.2. GA EPD Laboratory SOP's- Initial Demonstration of Capability SOP 6-001, online revision and Continuing Demonstration of Capability SOP 6-002, online revision.

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

13.4. GA EPD Laboratory SOP-EPD Laboratory Waste Management SOP, SOP 6-015, online revision.
13.5. GA EPD Laboratory – Laboratory Quality Assurance Plan, online revision.
13.6 GA EPD Laboratory SOP – Laboratory Safety/Chemical Hygiene Plan & Fire Safety Plan, online revision.
13.7 Manual for the Certification of Laboratories Analyzing Drinking Water, Criteria and Procedures Quality Assurance, EPA 815-R-05-004, Fifth Edition, January 2005 or later.

14. Reporting Limits (RLs), Precision and Accuracy Criteria, and Quality Control

Table 14. 1 RLs for Method SM4500-H+B

Parameter/Method	Analyte	Matrix (aqueous)	
		RL	Unit
SM4500-H+B	pH/Source pH	1.0	pH units

Table 14. 2 Acceptance Criteria for Method SM4500-H+B

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QC Type	Analyte	Accuracy Water (pH Units)	Precision Water (pH Units)
CCC(LCS)[1]	pH/Source pH	0.1	0.1
Sample Duplicate	pH/Source pH	NA	0.1

[1] LCS/LCSD for this analysis are essentially interchangeable with CCCs, therefore control limits are static.

Table 14. 3 Summary of Calibration and QC Procedures for Method SM4500-H+B

Method	Applicable Parameter	QC Check	Minimum Frequency	Acceptance criteria	Corrective Action	Flagging Criteria
SM4500-H+B	pH/Source pH	Initial Calibration	Initial calibration prior to sample analysis	pH slope of 92-102%	Correct problem then repeat initial calibration	
		Initial calibration verification (ICV)	Prior to every sample run	pH value must be within 0.1 pH units of expected value	Correct problem then repeat initial calibration verification	

Table 14. 3 Summary of Calibration and QC Procedures for Method SM4500-H+B

Method	Applicable Parameter	QC Check	Minimum Frequency	Acceptance criteria	Corrective Action	Flagging Criteria
SM4500-H+B	pH/Source pH	Initial Demonstration: Demonstrate ability to generate acceptable accuracy and precision using four analysis of a QC check sample, and a blind sample. In addition the analyst must perform an acceptable calibration	Once per analyst	QC Acceptance Criteria Table SOP 3-003 and Initial demonstration SOP (Reference 13.2)	Recalculate results: locate and fix problem with system and then rerun demonstration for those analytes that did not meet criteria	
		Continuing Demonstration: Demonstrate ability to generate acceptable accuracy and precision using a variety of analysis options of a QC sample(s)	Every 6 months	QC Acceptance Criteria Table SOP 3-003 and Continuing Demonstration of Capability SOP (Reference 13.2)	Continuing Demonstration: Demonstrate ability to generate acceptable accuracy and precision using a variety of analysis options of a QC sample(s)	
		Sample Duplicate	Minimum 10% of samples.	pH value must be within 0.1 units of expected value	Evaluation of out of control event and reanalyze sample	
		Continuing Calibration Check (CCC) CCCs are used for LCS/LCSD	After every 10 samples and at the end of the sample run.	pH value must be within 0.1 units of expected value	Correct Problem and reanalyze all samples associated with the out of control CCC.	
		Temperature Compensation Probe Verification	At least quarterly with NIST traceable thermometer	± 2ºC	Correct problem or replace probe	
		Record sample temperature	All samples	NA	Evaluate out of control event, reanalyze data	

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Updates to Previous Version:

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