Albuquerque Bernalillo County
Water Utility Authority

COMPLIANCE DIVISION
4201 2ND STREET SW, ALBUQUERQUE, NEW MEXICO 87105

WATER QUALITY LABORATORY
STANDARD OPERATING PROCEDURE

WQL SOP ~~204~~ 203 pH 5/3/10

CURRENT VERSION # 07

Implementation Date: 2/24/2010

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Reason:

History of Revision This table lists the revision history and effective dates of this procedure.

Revision	Date	Description of Changes
06	08/22/08	Revised entire SOP to comply with SM 4500-H+ B Online Edition, added slope and temperature checks, revised form, addressed A2LA audit concerns.
07	1/25/10	Revised SOP to include use of new meter in place of old meter. Added capability to extend range by running buffer at pH 4 to check slope without recalibration.

1.0 SCOPE AND APPLICATION

1.1. This method is used to measure the pH of aqueous samples in pH units. As written, this method is capable of typically measuring pH between 4 and 7 pH units or between 7 and 10 pH units. If additional range is needed to measure the pH of a particular sample, calibration buffer solutions outside these ranges must be used. The pH 7 buffer is used to set the isopotential point for the calibration of the meter. The pH 4 or pH 10 buffer is then used to set the slope of the calibration for the meter and probe.

1.2. This method is applicable to drinking, surface, and saline waters and domestic and industrial wastes.

2.0 SUMMARY OF METHOD

2.1. Results for pH are acquired by measuring the electromotive force (emf) of solutions with a glass electrode. The emf of the glass electrode system varies linearly with pH. This linear relationship is described by plotting the measured electromotive force against the pH of different buffers. The pH is determined by extrapolation using the slope.

3.0 DEFINITION OF TERMS

3.1. QA SOP-007- Reference for general terms related to quality and technical procedures, which applies to all standard operating procedures within WQL.

4.0 INTERFERENCE

4.1. 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 $\geq$10. Reduce this error by using special "low sodium error" electrodes. Since this method is typically only applied to solutions with a pH less than 10, this interference is not significant.

4.2. 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. In the first instance, the slope increases with increasing temperature and electrodes take time to achieve thermal equilibrium. This can cause long-term drift in pH. Because chemical equilibrium affects pH, standard pH buffers have specified pH at indicated temperatures.

5.0 SAFETY

5.1. **Health Hazards**

5.1.1. For specific hazards, consult the MSDS for compounds listed in section 7.0 of this SOP [MSDS on file in WQL Conference Room].

5.1.2. Use, store, and dispose of chemicals in accordance with WQL Chemical Hygiene Plan (CHP).

5.2. **Protective Equipment**

5.2.1. Wear appropriate Personal Protective Equipment (PPE) in accordance with WQL CHP.

5.3. **Spills and Contamination**

5.3.1. Clean up spills immediately in accordance with WQL CHP.

6.0 APPARATUS AND EQUIPMENT

6.1. All analytical equipment requirements for availability, installation, out-of-service, and record keeping (identification, manufacture, serial #, model #, and date of purchase) will follow WQL Quality Assurance Manual (QAM) procedures (Section 5.5).

6.2. **pH Meter:** Thermo Scientific Orion Star Plus Series Meter, or equivalent.

6.3. **pH Probe:** ROSS Ultra Combination pH electrode, or equivalent.

6.4. **Temperature Probe:** Thermo Scientific Automatic Temperature Compensation (ATC) Probe or equivalent.

6.5. Magnetic stirrer with TFE-coated stirring bar or mechanical stirrer with inert plastic-coated impeller.

6.6. Sample containers (preferably polyethylene or TFE)

6.7. Calibrated Thermometer (capable of reading to 0.5 °C)

6.8. DI Water

7.0 REAGENTS AND STANDARDS

7.1. **Chemicals/Reagents** - All chemicals and reagents transport and storage requirements will follow WQL QAM procedures (Section 5.6.4).

7.2. **pH Buffers:** NIST traceable pH buffers for pH 4, 7, and 10. Follow manufacturer's recommendations for expiration dates and storage.

7.3. **CCVS pH buffers:** NIST traceable CCVS pH buffer solutions should be selected for the range of 4 to 7 pH units and 7 to 10 pH units. These buffers should be obtained from different sources than the ICAL buffers to act as checks on pH buffer stability. Follow manufacturer's recommendations for expiration dates and storage.

NOTE: A pH 7 buffer should not be used as the CCVS as this is the isopotential point and does not provide any check on the stability of the calibration slope.

7.4. **pH storage solution:** ROSS pH Electrode Storage Solution (Orion PN 910001) or use 200 mL pH 7 buffer solution with approximately 1gKCl added.

7.5. **pH electrode reference filling solution:** ROSS Reference Filling Solution (Orion PN 810007) or equivalent.

8.0 QUALITY ASSURANCE/ QUALITY CONTROL

8.1. **Analyst Training** - Analysts must follow the steps outlined in the DOC Training Program for WQL SOPs. Follow requirements in QA SOP-004.

8.2. **Quality Control Requirements** – Follow requirements in QA SOP-005. The Quality Control Requirements section covers the following topics: 1) Quality Control Limits 2) Quality Control - Instrument Performance 3) Laboratory (Method)

8.3. **Data Evaluation**- Follow requirements in QA SOP-005. The Data Evaluation section covers the following topics: 1) Internal Audits 2) Control Charts Procedures 3) Performance Audits 4) Method Detection Limit Procedures

9.0 PROCEDURE

9.1. **Sample Handling**

9.1.1. **Preservation** – Samples should not be preserved.

9.1.2. **Sample Holding Time** – Samples can be stored for up to 2 hours in tightly sealed containers. It is recommended that pH be tested immediately after collection.

9.1.3. **Storage** – Samples should be allowed to come to room temperature before analysis. Samples can be collected and stored in polyethylene or glass containers.

9.2. **pH Meter Calibration Procedure**

NOTE: These instructions are for operation of the Thermo Scientific Orion Star Plus Series Meter. If an equivalent meter is used, calibrate for temperature compensation and pH following the manufacturer's instructions using the buffers and QC requirements in this SOP.

9.2.1. Record analysis date and time, calibration date and time, instrument used, and analyst's initials on the logsheet.

9.2.2. Read temperature on calibrated thermometer in pH analysis area and record on logsheet

9.2.3. Pour pH 7 and either pH 10 or pH 4 buffer solution into separate containers, record the reference numbers of the ICAL1 and ICAL2 buffer solutions (located on the box of buffer solution) onto logsheet, and insert a clean TFE-coated stir bar into each.

NOTE: Select either the pH 4 buffer or the pH 10 buffer based on the expected pH of the samples to be analyzed. Make sure that the pH for all samples measured is bracketed by the ICAL1 solution and the ICAL2 solution selected.

9.2.4. Connect electrodes to meter, turn on, and make sure the meter is in pH mode (Press the select button to the right of the ▲▼to set in pH mode).

9.2.5. Press the **Calibrate** button on the meter (Cal. 1 should be displayed in the lower field).

9.2.6. Remove pH probe from storage solution, remove the cap from the temperature probe, and rinse both the pH and temperature probes with DI water. Blot the probes dry with a soft tissue.

9.2.7. Place pH 7 ICAL1 container on magnetic stirrer and ensure stir bar is spinning.

9.2.8. Place the temperature probe and pH probe into pH 7 ICAL1 buffer solution and wait for the **pH** icon in the top right corner to stop blinking. This is the temperature-corrected pH value for the buffer.

9.2.9. Record temperature of ICAL1 buffer. If the temperature recorded is greater than 0.2 °C different than the temperature recorded in 9.2.2 for the room, conduct the temperature calibration in Section 11.2, record this on the logsheet and start over with a new calibration on a new logsheet. This will document the temperature calibration conducted.

9.2.10. Record buffer pH for ICAL1 buffer at temperature measured on logsheet.

9.2.11. Press **Calibrate** again (Cal. 2 should be displayed in the lower field).

NOTE: The daily process samples and the majority of samples analyzed are between pH 7 and pH 10. The pH 4 to pH 7 calibration range is only used if samples are analyzed at pH values less than 7.0 and the low-range verification described in Section 9.4 fails to meet requirements.

9.2.12. Remove the probes from the ICAL1 solution and rinse with DI water. Blot the probes dry with a soft tissue.

9.2.13. Place ICAL2 container on magnetic stirrer and ensure stir bar is spinning.

9.2.14. Place the probes into the ICAL2 buffer for the two-point calibration.

NOTE: If there are samples with a pH outside of the range selected, for example the pH 10 ICAL2 is selected and a pH of 6.5 is measured, the calibration at this range must be checked using the Low Range Verification procedure, as indicated in Section 9.4. If the calibration check fails all samples measured outside the original calibration range must be reanalyzed on a new calibration that covers the pH range of the samples.

9.2.15. Wait for the **pH** icon in the top right corner to stop blinking. Record the pH (either 4 or 10) of the ICAL2 buffer selected on the logsheet.

9.2.16. Press the **Measure** button to save and end the calibration. The slope will automatically display, in percent, in the main field (SLP should be in the lower field).

9.2.17. Record the slope value on the logsheet. Slope should be in the range of 95 – 105% to comply with quality control. If the slope is not within this range, correct the situation and recalibrate. If the slope is not within the range of 85 – 115%, E107 appears. See meter error codes in the User Guide (p. EN-54) for instruction.

9.2.18. Press the **Measure** button to continue with sample pH readings.

9.2.19. Pour CCVS solution into a container, insert a clean TFE-coated stir bar, and record the reference number on the log sheet.

NOTE: Select another buffer for the CCVS solution. The buffer should be in the calibration range selected and should be within 1 to 2 pH units of the samples to be measured. A pH 7 buffer should not be used as the CCVS as this is the isopotential point and does not provide any check on the stability of the calibration slope.

9.2.20. Remove the probes from the ICAL2 solution and rinse with DI water. Blot the probes dry with a soft tissue.

9.2.21. Place CCVS solution container on magnetic stirrer and ensure stir bar is spinning.

9.2.22. Place the probes into the CCVS solution

9.2.23. Wait for the **pH** icon in the top right corner to stop blinking and record the pH for the CCVS on the logsheet.

9.2.24. The CCVS must be within 0.1 pH units of the given value for the CCVS at the measured temperature. If CCVS value is not within specification, stop the calibration and make appropriate corrections before recalibrating the pH meter and probe. See User Guide for further information.

9.2.25. Remove the probes from the CCVS solution and rinse with DI water. Blot the probes dry with a soft tissue.

9.2.26. The meter is now calibrated and ready to be used for analysis. Place either into storage solution or directly into the first sample for measurement.

9.3. **Sample Analysis**

9.3.1. If not already in Measure mode, press the **Measure** button.

9.3.2. Place sample on magnetic stirrer and ensure stir bar is spinning

9.3.3. Place probes into sample, wait for the **pH** icon in the top right corner to stop blinking and record the pH.

NOTE: For buffered samples or samples of high ionic strength, condition the probe by dipping it into an aliquot of the sample for 1 min. Blot the probe dry and place into a fresh portion of the sample for analysis.

9.3.4. Record time of measurement, analyst's initials, and the pH reading on the logsheet.

9.3.5. Remove the probes from the sample solution and rinse with DI water. Blot the probes dry with a soft tissue.

NOTE: If the sample result is less than pH 7.0 and the pH 7 to pH 10 calibration described in Section 9.2 was used, implement the low-range verification described in Section 9.4 before continuing sample analyses.

9.3.6. Repeat steps 9.3.1 through 9.3.4 for all samples listed on the logsheet. Include at least one duplicate sample analysis per batch of 20 samples. Record the duplicate difference for the duplicate analysis on the logsheet.

9.3.7. Analyze the CCVS listed on the logsheet following steps 9.3.1 through 9.3.4. If the CCVS does not meet the 0.1 pH unit requirement, initiate a corrective action. All sample analyses conducted from the last acceptable CCVS cannot be reported and must be reanalyzed.

9.4. **Low-Range Verification**

NOTE: Use for samples with a pH less than 7.0 pH units when the pH 7 to pH 10 calibration described in Section 9.2 is used to calibrate the meter for analysis.

9.4.1. Analyze the pH 4 ICAL solution following the sample analysis procedure in Section 9.3 and record the result as a sample on the logsheet. This is the low-range verification.

9.4.2. The result for the 4 ICAL solution must be 4.0 pH units ± 0.1 pH units for the low-range verification to be accepted.

9.4.3. If the low-range verification fails, continue with sample analysis for remaining samples. (All samples with results less than 7.0 pH units will need to be reanalyzed on a pH 4 to pH 7 calibration following Section 9.2).

9.4.4. If the low-range verification is accepted, record the 4 ICAL solution result as a sample on the logsheet.

9.4.5. Continue with sample analysis. The low-level CCVS will need to be run along with the high-level CCVS every 10 samples and at the end of the run. (The CCVS results should be within 0.1 pH units)

9.5. **Analysis completion**

9.5.1. After the final CCVS is analyzed, rinse the probes and place the pH probe into the probe storage solution and put the cap back on the temperature probe.

9.5.2. If no more analyses are to be conducted that day, complete the logsheet entries.

9.5.3. Calculate the duplicate results and record on the logsheet.

10.0 DATA REPORTING

10.1. **Calculations** –The only calculation is to calculate the differences between the results indicated on the logsheet. The calculations are as follows:

Duplicate difference = The absolute value of the first measurement of sample pH minus second measurement of sample pH

CCVS Difference = The absolute value of the CCVS known pH – CCVS measured pH

10.2. **Logsheet Data Entry** –Logsheet entry indicated in the procedure Record all pH values to two significant figures (method is limited to pH less than 10 due to interferences and calibration so results will all be entered as #.#). Enter the calculated values indicated in 10.1 upon completion of the analyses required for the calculation.

10.3. **Corrective Actions**- Follow requirements in QA SOP-003 and QA SOP-005. The Corrective Actions section covers the following topics: 1) Out of Control Data Procedures and 2) Corrective Action Logbooks.

10.4. **Data Assessments** – Follow requirements in QA SOP-005. The Data Assessments section covers the following topics: 1) Accuracy and Precision 2) Data Validation Procedures 3) Data Reporting Procedures.

10.5. **Data Entry** -- Enter results in SQL-LIMS as required.

11.0 MAINTENANCE

11.1. **Daily Maintenance**

11.1.1. Check reference electrode filling solution level in probe and add solution as necessary. To maintain an adequate flow rate, the level of filling solution must cover the end of the coil and be at least one inch above the sample level when immersed.

11.1.2. Check probe for any contamination such as oil and grease or membrane/junction deposits. Rinse electrode with DI water to remove any visible contamination. If DI water is insufficient to remove contamination, use mild detergent or a methanol solution to remove oil and grease. Soak in Orion Cleaner A to remove protein deposits or 0.1M tetrasodium EDTA to remove inorganic deposits

11.1.3. Check probe for scratches and cracks. Replace probe if cracked or if the scratches are affecting calibration or stability.

11.2. **Temperature Calibration**

11.2.1. Use a thermometer probe accurate to ± 0.1°C to determine the temperature of the solutions to be measured.

11.2.2. In the Measurement mode, press the select button to the right of the ▲▼ buttons to choose the top measurement line and press ▲▼ until the temperature is shown for the selected line.

11.2.3. Press the **Calibrate** button.

11.2.4. When the reading stabilizes, the arrow icon and the first digit will flash. Enter the temperature by pressing ▲▼ to adjust each digit and the select button to the left of the ▲▼ buttons to move to the next digit.

11.2.5. Press the **Calibrate** button to save and end the calibration.

12.0 TROUBLESHOOTING

12.1. See the User Guide for a Meter Self Test or General Troubleshooting (p. EN53)

13.0 WASTE DISPOSAL AND POLLUTION PREVENTION

13.1. All waste disposal procedures will follow the Water Quality Laboratory CHP. Disposal procedure is as follows:

13.1.1. Discard all remaining analyzed samples in an acid sink.

13.1.2. All sample labware must be washed with laboratory soap inside and out followed by multiple rinses with distilled or deionized water.

13.2. Pollution Prevention - Eliminate waste at the source and base the quantity of purchased reagents on expected usage during their shelf life.

14.0 REFERENCES

14.1. SM 4500-H+ B Online Edition, pH Electrometric Method.

14.2. Orion Research Incorporated. Orion Star Plus Meter, User Guide. Fort Collins, CO. 2008.