

# NORTH CAROLINA WASTEWATER/GROUNDWATER LABORATORY CERTIFICATION BRANCH

## APPROVED PROCEDURE FOR THE ANALYSIS OF pH

This document provides an approved procedure for the analysis of pH for compliance monitoring per 15A NCAC 02H .0805 (a) (7) and (g) (4).

pH is considered a method-defined parameter per the definition in the Code of Federal Regulations, Part 136.6, Section (a) (5). This means that the method may not be modified per Part 136.6, Section (b) (3).

### **HOLDING TIME:**

- Samples must be analyzed within 15 minutes of collection (40 CFR Part 136 Table II).

### **METER CALIBRATION:**

- Use a pH meter accurate and reproducible to 0.1 S.U. (as demonstrated daily by acceptable performance of a check standard buffer) with a range of 0 to 14 S.U. and equipped with temperature-compensation adjustment.
- Instruments are to be calibrated according to the manufacturer's calibration procedure prior to analysis of samples each day compliance monitoring is performed. Calibration must include at least two buffers (three preferred). The meter calibration must be verified with a third standard buffer solution (i.e., check buffer) prior to sample analysis. **The calibration and check standard buffers must bracket the range of the samples being analyzed.** A portion of the standard buffer is not to be used for more than one calibration. Discard any used buffer portions. Do not pour unused portions back into the original bottle.
- All check standard buffers must read within  $\pm 0.1$  S.U. to be acceptable. If the meter verification does not read within  $\pm 0.1$  S.U., corrective actions must be taken before any samples are analyzed. Possible corrective actions may be found at the end of this document.
- A post-analysis calibration verification must be performed at the end of the run any time the meter is transported by vehicle to another location after calibration. It is recommended that a mid-day check standard buffer be analyzed when samples are analyzed over an extended period of time. The post-analysis check standard buffer(s) must read within  $\pm 0.1$  S.U. or corrective actions must be taken. If recalibration is necessary, all samples analyzed since the last acceptable calibration verification must be reanalyzed, if possible. If samples cannot be reanalyzed, the data must be qualified.

### **GENERAL INFORMATION:**

- The pH probe must be stored and operated according to manufacturer's instructions (e.g., open or loosen the fill hole cap during measurement, ensure electrolyte fill solution is at the proper level, etc.). Change the storage solution regularly to avoid mold and bacterial growth, evaporation, and potential contamination. Keep electrodes wet by returning them to the storage solution whenever the meter is not in use.
- Samples shall be gently stirred during measurement or analyzed in-stream. The pH sensing portion and the reference junction must be completely immersed. Steps must be taken to eliminate cross contamination between measurements (e.g., rinsing and shaking gently or blotting the electrode dry, dipping the electrode in stream multiple times, etc.).
- Samples analyzed for pH cannot be diluted. If the value is outside the calibration range, recalibrate using a wider range of buffers or verify with a buffer that brackets the sample range. Alternatively, report the sample value and qualify it as being outside the calibration range.
- The units of measure for pH analyses are Standard Units (S.U.). It is recommended that pH be read and documented in one-hundredths (0.01). Values must be reported in tenths (0.1). It should be noted that Proficiency Testing (PT) providers require samples be reported to one-hundredths.
- Sample duplicates are not a required quality control element for Field parameters.
- If more than one pH concentration has been taken for a particular day, these values cannot be averaged due to the logarithmic nature of pH concentration. All values must be reported on the eDMR, either in the daily cell or the comments section. The following convention must be followed when deciding which value to report in the daily cell:
  - Any value in violation of permit limits must be reported in the daily cell. If multiple samples yielded noncompliant results, the most extreme noncompliant value must be reported in the daily cell.

- If all values taken during the day were compliant with the permit limits, the value closest to the bounds of the limit range (high or low) must be reported in the daily cell.

### **DOCUMENTATION:**

The following must be documented in indelible ink whenever sample analysis is performed:

1. Date and time of sample collection
2. Date and time of sample analysis to verify the 15-minute holding time is met. Alternatively, one time may be documented for collection and analysis with the notation that samples are measured *in situ* or immediately at the sample site
3. Permitted facility name or permit number, and sample site (ID or location)
4. Collector's/analyst's name or initials
5. Meter calibration and meter calibration time(s)
6. True values of buffers used for calibration
7. True value for the check standard buffer
8. Value obtained for the check standard buffer
9. Quality control assessments
10. True value and value obtained for the post-analysis calibration verification(s), where applicable
11. Indication of when the post-analysis calibration verification was performed (e.g., time of analysis, end-of-day analysis, etc.)
12. Final value to be reported
13. Units of measure
14. Report all data values to the nearest 0.1 S.U.
15. Traceability for chemicals, reagents, standards and consumables
16. Unique instrument identification (serial number preferred)
17. Parameter analyzed
18. Method reference or Standard Operating Procedure
19. Data qualifier(s), when applicable

Ref: Standard Methods 4500 H<sup>+</sup> B-2021 and SW-846 9040 C

### **TROUBLESHOOTING:**

If the check buffer does not read within  $\pm 0.1$  S.U., the lab should first try pouring a new aliquot of the check buffer and reading it again. If it still does not read within  $\pm 0.1$  S.U., the meter must be recalibrated. Possible corrective actions include: check the meter calibration procedure, refer to the trouble shooting section in the instrument manual, and check the buffers. If, after recalibration, the check buffer does not read within  $\pm 0.1$  S.U., the meter and/or probe operation may be suspect and may require servicing. If the laboratory does not have a back-up meter/electrode, or another meter/electrode cannot be procured, it is recommended that the lab report the measured pH results with a qualifier that indicates the value is estimated.

The true values of buffers are temperature dependent. Check the manufacturer's label on the bottle for the true value.

Refer to the NC DEQ WW/GW LCB website for additional resources.