NORTH CAROLINA WASTEWATER/GROUNDWATER LABORATORY CERTIFICATION BRANCH

APPROVED PROCEDURE FOR THE ANALYSIS OF VECTOR ATTRACTION REDUCTION (VAR): OPTION 6 – Addition of Alkali

This document provides an approved procedure for the analysis of VAR: Option 6 for compliance monitoring per 15A NCAC 2H .0805 (a) (7) and (g) (4).

Holding Time:

- Analyze samples as soon as possible according to SW-846 9045 D.

General Information:

- If samples are not analyzed at 25 °C, the results must be adjusted based on the sample temperature (rounding to whole numbers is recommended) and the following calculation is applied (a quick reference for correction factors can be found in Attachment A):

$$\text{Correction Factor} = \frac{0.03 \text{ pH units} \times (T_{meas} - 25°C)}{1.0°C}$$

Actual pH = Measured pH +/- the Correction Factor

Where T_{meas} is the temperature of the slurry or sludge.

Note: Temperature compensation devices on pH meters correct only for variations in the conductance of pH probes, and not for the variability in solution concentration. Therefore, the temperature correction noted above must be applied to pH measurements, even though a pH meter with temperature compensation is used.

- Alkali is sometimes added to liquid sludge and sometimes to dewatered sludge. The pH requirements apply in the same way for both liquid and dewatered sludge.
- The pH measurement is made with a pH meter equipped with a temperature compensation adjustment. A low-sodium glass electrode is recommended to prevent low-biased results.
- For the measurement of pH in liquid sludge initially and 2 hours after addition of alkali, it is assumed that the alkali and the sludge have been mixed together for a sufficient time to reach equilibrium. Consequently, the pH measurement can be made directly in the liquid sludge.
- The measurement is made again 24 hours after addition of alkali. If the sludge is still in the liquid state, the pH measurement is made in the same fashion. However, if the process includes a dewatering step immediately following the alkali addition and the sludge is now a dewatered cake, the cake must be made into a slurry for the pH measurement.
- Dewatered cakes must be turned into a slurry for pH measurement by adding 20 mL of distilled water (containing 0.01 M $CaCl_2$) to 10 g of sludge cake and mixing occasionally for half an hour while waiting for the sample to clarify, if necessary. The important step is the mixing step that allows the alkali-treated dewatered cake to come into equilibrium with the added water. See Section 10.12 of Pathogens and Vector Attraction in Sewage Sludge, EPA/600/R-22/194, (January 2023) for directions about making a slurry.
- The temperature of the sample must be analyzed with an NIST verified temperature-measuring device.
- Refer to the NC Wastewater/Groundwater Laboratory Certification Branch (NC WW/GW LCB) Approved Procedure for the Analysis of Temperature for temperature-measuring device verification requirements.
- Sample duplicates are not a required quality control element for Field parameters.

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. A low-sodium glass electrode is recommended to prevent low-biased results.

- The pH meter must be calibrated each day of analysis. Calibration must include at least two buffers. 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 (i.e., 12 ± 0.5 S.U.). 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.

  Note: High pH buffers absorb CO_2 and acidic vapors from the atmosphere which lowers the pH. Ensure high pH buffers are within expiration and stored with minimal headspace.

- All check buffers (pre- and post-analysis) must read within ±0.1 S.U. to be acceptable. If the meter verification does not read within ±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 using the check standard buffer must be analyzed 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 ±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.

Procedure:

- Alkali is added to sludge to raise the pH to at least 12 S.U. A representative sample is analyzed for pH and Temperature to verify the temperature-corrected pH is ≥12 S.U.
- The pH and Temperature are measured again after 2 hours to assure it is still ≥ 12 S.U. without the addition of more alkali.
- If after 2 hours the temperature-corrected pH of the sample is <12 S.U., alkali must be added to the sludge to bring the pH back up to at least 12 S.U. and the process repeated.
- The pH and Temperature are measured after an additional 22 hours and the temperature-corrected pH must be ≥ 11.5 S.U.
- If after 22 hours the temperature-corrected pH of the sample is <11.5 S.U., alkali must be added to the sludge to bring the pH back up to at least 12 S.U. and the 24-hour process repeated.

Documentation:

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

1. Date and time of sample collection. If pH measurement is made *in situ*, it must be notated.
2. Date and time of sample analysis
3. Facility name or permit number, and sample site (ID or location)
4. Collector's/analyst's name or initials
5. Meter calibration time
6. True value of the buffers used for calibration
7. True value of the buffer check standard
8. Value obtained for the buffer check standard
9. True value and value obtained for the post-analysis calibration verification, if applicable
10. Indication of when the post-analysis calibration verification was performed (e.g., time of analysis, end-of-day analysis, etc.), if applicable
11. Acceptance criterion for check buffers (i.e., ± 0.1 S.U.)
12. Evaluation of the check buffers (check box acknowledging that it passed is acceptable)

13. Temperature of sample
14. pH of sample, as measured
15. Temperature-corrected (Reported) pH if not analyzed at 25 °C
16. Units of measure
17. Traceability for chemicals, reagents, standards and consumables
18. Instrument identification (serial number preferred)
19. Parameter analyzed
20. Method reference or Standard Operating Procedure
21. Data qualifiers, when necessary
22. Equipment maintenance (recommended)

Refer to https://www.deq.nc.gov/about/divisions/water-resources/water-sciences/chemistry-laboratory/laboratory-certification-branch/field-approved-procedures-and-technical-assistance for additional quality assurance and quality control requirements.

Ref: Pathogens and Vector Attraction in Sewage Sludge, EPA/600/R-22/194, (January 2023) and SW-846 9045 D.

TROUBLESHOOTING:

If the check buffer does not read within ±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 ±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 ±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.

Attachment A: pH Temperature Correction Factors at Varying Temperatures from Standard (25°C)

Temp (°C)	Correction Factor (S.U.)
40	Plus 0.45
39	Plus 0.42
38	Plus 0.39
37	Plus 0.36
36	Plus 0.33
35	Plus 0.30
34	Plus 0.27
33	Plus 0.24
32	Plus 0.21
31	Plus 0.18
30	Plus 0.15
29	Plus 0.12
28	Plus 0.09
27	Plus 0.06
26	Plus 0.03
25	0.00
24	Minus 0.03
23	Minus 0.06
22	Minus 0.09
21	Minus 0.12
20	Minus 0.15
19	Minus 0.18
18	Minus 0.21
17	Minus 0.24
16	Minus 0.27
15	Minus 0.30
14	Minus 0.33
13	Minus 0.36
12	Minus 0.39
11	Minus 0.42
10	Minus 0.45

Reported pH = Measured pH +/- the Correction Factor at the Measured Temperature