Department of Environment & Conservation

DWR-NPDES-SOP-G-07-pH 4500-H B-01012024
pH, SM 4500-H+ B (2011) Electrometric Method

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1) **EFFECTIVE DATE: 01/01/2024**

2) **SIGNATURES:**

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Initial Demonstration of Capability (DOC)

- 4020 B.1.a. - Each analyst must run a known standard concentration at least four times and compare limits listed in the method
- **Summary: Each operator running this test needs to calibrate instrument and analyze four buffers at a pH of 7**
    - **Keep a folder for each analyst**
    - **Keep documentation (signed form) that analyst has read and understands all appropriate SOPs and Methods**
    - **A backup analyst should do the DOC once a year**
    - **The DOC is only good for that type of instrument you are using at that plant. If you have a backup instrument made by a different manufacturer or you work at another plant with a different make/model, you would need another DOC**
        - **DOCs demonstrate you are proficient with that one instrument**

Method Detection Limit (MDL)

- NONE

Initial Calibration Verification (ICV)

- 1020 B.11.b. – Perform initial calibration using at least three concentrations of standards for linear curves
- **Summary: calibrate daily with fresh buffers by following manufacturer's instructions**
- **Read 7 buffer after calibration daily (to evaluate accuracy)**

Method Blank (MB)

- NONE

Laboratory Fortified Blank (LFB)

- NONE

Duplicate

- 4020 B.2.f. – Randomly select routine samples to be analyzed twice
    - Process duplicate sample independently through the entire sample preparation and analysis
    - Include at least one duplicate for each matrix type daily or with each batch of 20 or fewer samples
- **Summary: on a 5% basis (one for every 20 samples or once per month, whichever is more frequent) analyze two samples for pH, after reading one, pour out sample and start with a fresh sample**
    - **Example, grab sample in bucket and dip pH probe in twice to get a duplicate reading**

Laboratory Fortified Matrix (LFM)/Laboratory Fortified Matrix Duplicate (LFMD)

- NONE

Continuing Calibration Verification (CCV)

- 1020 B.11.c. – Analysts periodically use a calibration standard to confirm that the instrument performance has not changed significantly since initial calibration
    - Verify calibration by analyzing one standard at a concentration near or at the mid-point of the calibration range
- 4020.B.2.b. – Verify calibration by periodically analyzing a calibration standard and calibration blank during a run – typically after each batch of 10 samples and at the end of the run
    - For the calibration verification to be valid, check standards must be within +/- 0.1 pH units of its true value, and calibration blank results must not be greater than one-half the reporting level
- **Summary: after calibration of the instrument and daily samples have been tested, reread the neutral 7.0 buffer (for accuracy). CCV must be within ± 0.1 of the 7.0 buffer to be considered valid**

Control Charts

- 1020 B.13.a. – The accuracy chart for QC samples is constructed from the average and standard deviation of a specified number of measurements of the analyte of interest. The accuracy chart includes upper and lower warning levels (WLs) and upper and lower control levels (CLs). Common practice is to use ±2*s* and ±3*s* limits for the WL and CL, respectively, where *s* represents standard deviation
- 1020 B.13.b. – The precision chart is also constructed from the average and standard deviation of a specified number of measurements [e.g., %RSD or relative percent difference (RPD)] for replicate or duplicate analyses of the analyte of interest... Perfect agreement between replicates or duplicates results in a difference of zero when the values are subtracted, so the baseline of the chart is zero. Therefore, for precision charts, only upper WLs and upper CLs are meaningful
- **Summary: Create and maintain control charts once you have 20-30 data points**

Corrective Action - 1020 B.5., B.8., & B.15.

QC Acceptance Criteria

- ICV/CCV within ± 0.1 s.u.
- Duplicates within ± 0.2 s.u.

Batch Size

- For samples that need to be analyzed on a 5% basis (1 for every 20 samples or once per month, whichever is more frequent) follow these criteria:

- If a permit stated that 3 analyses per week, we would allow for a duplicate to be analyzed at least once per month
  - Pick a date and be consistent, the 1st of every month or the 1st Thursday of every month. Mark your calendar!!
- If a permit stated 5 analyses per week, we would suggest twice a month.
  - Pick a date and be consistent, the 1st and 15th of every month or the 1st and 3rd Thursday of every month. Mark your calendar!!

Calculations

- None

Revision Number	Date	Brief Summary of Change
0	November 2013	Initial issuance of the Guidance
2	March 2019	Method editorial revision date changed from 200 to 2011, CCV and duplicate QC acceptance criteria changed from +/- 0.2 to +/- 0.1 s.u.
3	December 29, 2021	Added ICV requirement to read 7 daily, added ICV to QC acceptance criteria, duplicate QC acceptance criteria changed from +/- 0.1 to +/- 0.2 s.u., added control chart information
4	December 11, 2023	Added calculations information and definitions. Revised grammar and added effective date.