

pH (Hydrogen Ion)

AZPDES/APP Permit Field Method Training
Fall 2016



Approved Methods (In-line)

EPA 150.2

- Environmental Monitoring and Support Laboratory–Cincinnati, EPA, Pub. No. EPA-600/4-79-020, Methods for Chemical Analysis of Water and Wastes (rev. March 1983), available at <http://nepis.epa.gov/pubtitleord.htm>.



Approved Method (meter)

- SM 4500-H B (2011), 22nd edition

- American Public Health Association et al., Standard Methods for the Examination of Water and Wastewater (22th ed. 2012), available from American Public Health Association, 800 I St., NW, Washington, DC 20001.

Unacceptable Methods



Color Wheels



pH Paper

pH Calibration



- Temperature affects the value of the pH
 - Buffer temperatures and sample temperatures should be as close as possible
 - At $\pm 2^{\circ}$ C difference is suggested
 - Two affects – mechanical and chemical
 - Only one is compensated for with an automatic temperature control (ATC)

pH Calibration



- Ensure using the correct type of electrode for the measurement
- Electrodes come with a slope percent range of acceptance
 - Often 92 – 102%, but verify
- Check the electrode for at a minimum:
 - Storage solution – correct type, not dried, filled
 - Look for cracks, scratches
 - Do not use paper towels on electrode membrane

pH General



- Ensure meter is in
 - Calibration mode when calibrating
 - Read mode when analyzing samples
- Must be analyzed within 15 minutes

pH General



- Rinse electrode with deionized water between buffers and samples and blot dry (soft tissue)
- If using a bench meter with a magnetic stirrer, use small stir bars and stir slowly
 - This avoids bumping the electrode and potentially damaging it and to minimize carbon dioxide bubbles.

SM 4500-H B



• Calibration

- Minimum of 3 points for calibration
 - First buffer sets isopotential point
 - Second buffers at least two pH units of sample pH
 - 3rd buffer value on instrument must be within 0.1 pH units of true value
 - Recommend pH buffers 4.0, 7.0, and/or 10.0
- Record temperature of buffers
- Frequency
 - Each day of use for compliance testing

TABLE 4020:I. MINIMUM QUALITY CONTROL FOR METHODS IN PART 4000

Section	Method Blank	LFB*	LFM† & LFMD‡	Other	Section	Method Blank	LFB*	LFM† & LFMD‡	OTHER
4110B	×	×	×	1,3	4500-Cl B	×	×	-	2,3
4110C	×	×	×	1,3	4500-Cl C	×	×	-	2,3
4110D	×	×	×	1,3	4500-Cl D	×	×	-	2,3
4140	×	×	×	1,3	4500-Cl F	×	×	-	2,3
4500-B.B	×	×	×	3	4500-Cl G	×	×	-	2,3
4500-B.C	×	×	×	3	4500-Cl H	×	×	-	2,3
	×				4500-Cl I	×	×	-	2,3
4500-Br ⁻ B	×	×	×	3	4500-Cl ⁻ C	×	×	×	3
4500-Br ⁻ D	×	×	×	3	4500-Cl ⁻ D	×	×	×	3
					4500-Cl ⁻ E	×	×	×	3
4500-CO ₂ B	-	-	-	4	4500-Cl ⁻ G	×	×	×	3
4500-CO ₂ C	×	-	-	2	4500-ClO ₂ C	×	×	×	3
4500-CO ₂ D	×	-	-	2	4500-ClO ₂ E	×	×	×	3
4500-CN ⁻ C	×	×	×	3	4500-F ⁻ C	×	×	×	3
4500-CN ⁻ D	×	×	×	3	4500-F ⁻ D	×	×	×	3
4500-CN ⁻ E	×	×	×	3	4500-F ⁻ E	×	×	×	3
4500-CN ⁻ F	×	×	×	3	4500-F ⁻ G	×	×	×	3
4500-CN ⁻ G	×	×	×	3					
4500-CN ⁻ H	×	×	×	3	4500-H ⁺ B	-	-	-	2,5
4500-CN ⁻ I	×	×	×	3	4500-I B	×	×	×	3
4500-CN ⁻ J	×	×	×	3	4500-I C	×	×	×	3
4500-CN ⁻ L	×	×	×	3					
4500-CN ⁻ M	×	×	×	3	4500-I ⁻ B	×	×	×	3
4500-CN ⁻ N	×	×	×	3	4500-I ⁻ C	×	×	×	3
4500-CN ⁻ O	×	×	×	3	4500-I ⁻ D	×	×	×	3

* Laboratory-fortified blank.

† Laboratory-fortified matrix.

‡ Laboratory-fortified matrix duplicate.

× indicates that a QC type is mandatory for the method.

1. Additional QC guidelines in method.

2. Duplicates of the sample will be run. ←

3. Refer to 4020B for further QC requirements.

4. Compare to results from Section 4500-CO₂ 4500-CO₂.2.D.

5. Additional QC check with pH standard whose value is bracketed by calibration standards. ←

6. Zero check with zero oxygen sample.

SM 4500-H B



Quality Control and Reporting

- Duplicates: each matrix type daily or with each batch of 20 or fewer samples. Control limits per 1020B. (ADHS will accept ± 0.1 difference)
- QC Check: pH standard whose value is bracketed by calibration standards (± 0.1 recovery)

SM 4500-H B



Quality Control and Reporting

- Record temperature
 - Some meters have automatic temperature compensators (ATC) but still need to record temperature
- Report pH to nearest 0.1 unit and temperature to nearest degree °C

Field Video Demonstration

