

METHOD #: 150.2

Test Method (December 1982)

TITLE:

pH, Continuous Monitoring (Electrometric)

ANALYTE:

pH

INSTRUMENTATION:

pH Meter

1.0 Scope and Application

- 1.1 This method is applicable to the continuous pH measurement of drinking, surface, and saline waters, domestic and industrial waste waters.

2.0 Summary of Method

- 2.1 The pH of a sample is determined electrometrically using a glass electrode with a reference electrode or a single combination electrode.

3.0 Sample Handling and Preservation

- 3.1 The composition of the water or waste contacting the measuring electrode system must be representative of the total flow from the water body.

4.0 Interferences

- 4.1 The glass electrode, in general, is not subject to solution interferences from color, turbidity, colloidal matter, oxidants, reductants or high salinity.
- 4.2 Sodium error at pH levels greater than 10 can be reduced or eliminated by using a "low sodium error" electrode.
- 4.3 Manually inspect the conditions of the electrodes every 30 days for coating by oily materials or buildup of lime. If oil and grease and/or scale buildup are not present, this time interval may be extended.
 - 4.3.1 Coatings of oil, grease and very fine solids can impair electrode response. These can usually be removed by gentle wiping and detergent washing. The use of flowthrough electrode housings which provide higher flow velocity helps to prevent the coating action.
 - 4.3.2 Heavy particulate matter such as lime accumulation can be removed by careful scrubbing or immersion in dilute (1+9) hydrochloric acid. Continuous monitoring under these conditions benefits from ultrasonic or other in-line continuous cleaning methods.
- 4.4 Temperature effects on the electrometric measurement of pH arise from two sources. The first is caused by the change in electrode output at various temperatures. This interference can be controlled with instruments having temperature compensation or by calibrating the electrode-instrument system at the temperature of the samples. For best results, meters having automatic temperature compensation should be calibrated with solutions within 5°C of the temperature of the stream to be measured. The second source is the change of pH inherent in the sample at various temperatures. This error is sample

dependent and cannot be controlled, it should therefore be noted by reporting both the pH and temperature at the time of analysis.

5.0 Apparatus

- 5.1 pH Monitor - A wide variety of instruments are commercially available with various specifications and optional equipment. For unattended use, the monitor should be equipped with automatic or fixed temperature compensation and with a recorder or alarm function.
- 5.2 Glass electrode - with shielded cable between electrode and monitor unless preamplification is used.
- 5.3 Reference electrode - a reference electrode with a constant potential and with either a visible electrolyte or viscous gel fill.

NOTE 1: Combination electrodes incorporating both measuring and reference functions are convenient to use and are available with solid, gel-type filling materials that require minimal maintenance.

- 5.4 Temperature sensor - for automatic compensator covering general ambient temperature range.
- 5.5 Electrode mounting - to hold electrodes; may be flow through (for small flows), pipe mounted or immersion.

6.0 Reagents

- 6.1 Primary standard buffer salts are available from the National Bureau of Standards and should be used in situations where extreme accuracy is required.
 - 6.1.1 Preparation of reference solutions from these salts require some special precautions and handling¹ such as low conductivity dilution water, drying ovens, and carbon dioxide free purge gas. These solutions should be replaced at least once each month.
- 6.2 Secondary buffers may be prepared from NBS salts or purchased as a solution from commercial vendors. Use of these commercially available solutions, which have been validated by comparison to NBS standards, is recommended for routine operation. These buffers may be retained for at least six months if kept stoppered.

7.0 Calibration

- 7.1 Immersion type electrodes easily removed from mounting.
 - 7.1.1 The electrode should be calibrated at a minimum of two points that bracket the expected pH of the water/waste and are approximately three pH units or more apart.
 - 7.1.2 Repeat calibration adjustments on successive portions of the two buffer solutions until readings are within ± 0.05 pH units of the buffer value. If calibration problems occur, see 4.3.
 - 7.1.3 Because of the wide variety of instruments available, no detailed

¹ National Bureau of Standards Special Publication 260

operating instructions are provided. Instead, the analyst should refer to the particular manufacturer's instructions.

- 7.1.4 Calibration against two buffers should be carried out at least daily. If the pH of the fluid being measured fluctuates considerably, the calibration should be carried out more often. Calibration frequencies may be relaxed if historical data supports a longer period between calibration.
- 7.2 Immersion type electrodes not easily removed from mounting.
 - 7.2.1 Collect a grab sample of the flowing material from a point as close to the electrode as possible. Measure the pH of this grab sample as quickly as possible with a laboratory - type pH meter. Adjust the calibration control of the continuous monitor to the reading obtained.
 - 7.2.2 The temperature and condition of the grab sample must remain constant until its pH has been measured by the laboratory pH meter. The temperature of the sample should be measured and the temperature compensator of the laboratory pH meter adjusted.
 - 7.2.3 The laboratory - type pH meter should be calibrated prior to use against two buffers as outlined in 7.1.
 - 7.2.4 The continuous pH monitoring system should be initially calibrated against two buffers as outlined in 7.1 before being placed into service. Recalibration (every 30 days) at two points is recommended if at all possible to ensure the measuring electrode is in working order. If this is not possible, the use of electrode testing features for a broken or malfunctioning electrode should be considered when purchasing the equipment.
 - 7.2.5 The indirect calibration should be carried out at least once a day. If the pH of the fluid being measured fluctuates considerably, the calibration should be carried out more often. Calibration frequencies may be relaxed if historical data support a longer period between calibration.
 - 7.2.6 If the electrode can be removed from the system, but with difficulty, it should be directly calibrated as in 7.1 at least once a month.
- 7.3 Flow-through type electrode easily removed from its mounting.
 - 7.3.1 Calibrate using buffers as in 7.1. The buffers to be used may be the process stream itself as one buffer, and as a second buffer after adjustment of pH by addition of an acid or base. This will provide the larger volumes necessary to calibrate this type electrode.
 - 7.3.2 Since the velocity of sample flow-through a flow through electrode can produce an offset error in pH reading, the user must have data on hand to show that the offset is known and compensation has been accomplished.
- 7.4 Flow-through type electrode not easily removed from its mounting.
 - 7.4.1 Calibrate as in 7.2.
 - 7.4.2 Quality control data must be on hand to show the user is aware of possible sample flow velocity effects.

8.0 Procedure

- 8.1 Calibrate the monitor and electrode system as outlined in Section 7.
- 8.2 Follow the manufacturer's recommendation for operation and installation of the system.

- 8.3 In wastewaters, the electrode may require periodic cleaning. After manual cleaning, the electrode should be calibrated as in 7.1 or 7.2 before returning to service.
 - 8.4 The electrode must be placed so that the water or waste flowing past the electrode is representative of the system.
- 9.0 Calculations
- 9.1 pH meters read directly in pH units. Reports pH to the nearest 0.1 unit and temperature to the nearest °C.
- 10.0 Precision and Accuracy
- 10.1 Because of the wide variability of equipment and conditions and the changeable character of the pH of many process waters and wastes, the precision of this method is probably less than that of Method 150.1; however, a precision of 0.1 pH unit should be attainable in the range of pH 6.0 to 8.0. Accuracy data for continuous monitoring equipment are not available at this time.

Bibliography

- 1. Annual Book of ASTM Standards, Part 31, "Water" Standard 1293-78, Method D, p. 226 (1981).