METHOD #: 150.1   Approved for NPDES (Editorial Revision 1978, 1982)

TITLE: pH (Electrometric)

ANALYTE: pH

INSTRUMENTATION: pH Meter

STORET No.   Determined on site 00400
                              Laboratory 00403

1.0   Scope and Application

        1.1   This method is applicable to drinking, surface, and saline waters, domestic and
                industrial wastes and acid rain (atmospheric deposition).

2.0   Summary of Method

        2.1   The pH of a sample is determined electrometrically using either a glass
                electrode in combination with a reference potential or a combination electrode.

3.0   Sample Handling and Preservation

        3.1   Samples should be analyzed as soon as possible preferably in the field at the
                time of sampling.
        3.2   High-purity waters and waters not at equilibrium with the atmosphere are
                subject to changes when exposed to the atmosphere, therefore the sample
                containers should be filled completely and kept sealed prior to analysis.

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   Coatings of oily material or particulate matter can impair electrode response.
                These coatings can usually be removed by gentle wiping or detergent washing,
                followed by distilled water rinsing. An additional treatment with hydrochloric
                acid (1 + 9) may be necessary to remove any remaining film.
        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. 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 Meter-laboratory or field model. A wide variety of instruments are commercially available with various specifications and optional equipment.

    5.2   Glass electrode.

    5.3   Reference electrode-a calomel, silver-silver chloride or other reference electrode of constant potential may be used.
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   Magnetic stirrer and Teflon-coated stirring bar.

    5.5   Thermometer or temperature sensor for automatic compensation.

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 necessary.

        6.1.1   Preparation of reference solutions from these salts require some special precautions and handling[1] 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 standard buffers may be prepared from NBS salts or purchase as a solution from commercial vendors. Use of these commercially available solutions, that have been validated by comparison to NBS standards, are recommended for routine use.

7.0   Calibration

    7.1   Because of the wide variety of pH meters and accessories, detailed operating procedures cannot be incorporated into this method. Each analyst must be acquainted with the operation of each system and familiar with all instrument functions. Special attention to care of the electrodes is recommended.

    7.2   Each instrument/electrode system must be calibrated at a minimum of two points that bracket the expected pH of the samples and are approximately three pH units or more apart.

        7.2.1   Various instrument designs may involve use of a "balance" or "standardize" dial and/or a slope adjustment as outlined in the manufacturer's instructions. Repeat adjustments on successive portions of the two buffer solutions as outlined in procedure 8.2 until readings are within 0.05 pH units of the buffer solution value.

8.0   Procedure

    8.1   Standardize the meter and electrode system as outlined in Section 7.

    8.2   Place the sample or buffer solution in a clean glass beaker using a sufficient volume to cover the sensing elements of the electrodes and to give adequate clearance for the magnetic stirring bar.

        8.2.1   If field measurements are being made the electrodes may be immersed

directly in the sample stream to an adequate depth and moved in a manner to insure sufficient sample movement across the electrode sensing element as indicated by drift free (< 0.1 pH) readings.

8.3   If the sample temperature differs by more than 2°C from the buffer solution the measured pH values must be corrected. Instruments are equipped with automatic or manual compensators that electronically adjust for temperature differences. Refer to manufacturer's instructions.

8.4   After rinsing and gently wiping the electrodes, if necessary, immerse them into the sample beaker ar sample stream and stir at a constant rate to provide homogeneity and suspension of solids. Rate of stirring should minimize the air transfer rate at the air water interface of the sample. Note and record sample pH and temperature. Repeat measurement on successive volumes of sample until values differ by less than 0.1 pH units. Two or three volume changes are usually sufficient.

8.5   For acid rain samples it is most important that the magnetic stirrer is not used. Instead, swirl the sample gently for a few seconds after the introduction of the electrode(s). Allow the electrode(s) the equilibrate. The air-water interface should not be disturbed while measurement is being made. If the sample is not in equilibrium with the atmosphere, pH values will change as the dissolved gases are either absorbed or desorbed. Record sample pH and temperature.

9.0   Calculation

9.1   pH meters read directly in pH units. Report pH to the nearest 0.1 unit and temperature to the nearest degree °C.

10.0   Precision and Accuracy

10.1   Forty-four analysts in twenty laboratories analyzed six synthetic water samples containing exact increments of hydrogen-hydroxyl ions, with the following results:

pH Units	Standard Deviation pH Units	Accuracy as Bias, %	Bias, pH Units
3.5	0.10	-0.29	-0.01
3.5	0.11	-0.00	
7.1	0.20	+1.01	+0.07
7.2	0.18	-0.03	-0.002
8.0	0.13	-0.12	-0.01
8.0	0.12	+0.16	+0.01

(FWPCA Method Study 1, Mineral and Physical Analyses)

10.2   In a single laboratory (EMSL), using surface water samples at an average pH of 7.7, the standard deviation was± 0.1.

Bibliography

1.   Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 460, (1975).
2.   Annual Book of ASTM Standards, Part 31, "Water", Standard D1293-65, p 178 (1976).
3.   Peden, M. E. and Skowron, L. M., Ionic Stability of Precipitation Samples, Atmospheric Environment, Vol. 12, pp. 2343-2349, 1978.