METHOD 9040C

pH ELECTROMETRIC MEASUREMENT

1.0 SCOPE AND APPLICATION

1.1   This method is used to measure the pH of aqueous wastes and those multiphase wastes where the aqueous phase constitutes at least 20% of the total volume of the waste.

1.2   The corrosivity of concentrated acids and bases, or of concentrated acids and bases mixed with inert substances, cannot be measured. The pH measurement requires some water content.

2.0 SUMMARY

2.1   The pH of the sample is determined electrometrically using either a glass electrode in combination with a reference potential or a combination electrode. The measuring device is calibrated using a series of standard solutions of known pH.

3.0 INTERFERENCES

3.1   The glass electrode, in general, is not subject to solution interferences from color, turbidity, colloidal matter, oxidants, reductants, or moderate (<0.1 molar solution) salinity.

3.2   Sodium error at pH levels >10 can be reduced or eliminated by using a low-sodium-error electrode.

3.3   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 rinsing with distilled water. An additional treatment with hydrochloric acid (1:10) may be necessary to remove any remaining film.

3.4   Temperature effects on the electrometric determination of pH arise from two sources. The first is caused by the change in electrode output at various temperatures. This interference should be controlled with instruments having temperature compensation or by calibrating the electrode-instrument system at the temperature of the samples. The second source of temperature effects is the change of pH due to changes in the sample as the temperature changes. 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.

4.0 APPARATUS AND MATERIALS

4.1   pH meter -- Laboratory or field model. Many instruments are commercially available with various specifications and optional equipment.

4.2   Glass electrode.

4.3   Reference electrode -- A silver-silver chloride or other reference electrode of constant potential may be used.

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

4.4   Magnetic stirrer and Teflon-coated stirring bar.

4.5   Thermometer and/or temperature sensor for automatic compensation.

5.0 REAGENTS

5.1   Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2   Primary standard buffer salts are available from the National Institute of Standards and Technology (NIST) and should be used in situations where extreme accuracy is necessary. Preparation of reference solutions from these salts requires some special precautions and handling, such as low-conductivity dilution water, drying ovens, and carbon-dioxide-free purge gas. These solutions should be replaced at least once each month.

5.3   Secondary standard buffers may be prepared from NIST salts or purchased as solutions from commercial vendors. These commercially available solutions have been validated by comparison with NIST standards and are recommended for routine use.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

Samples should be analyzed as soon as possible.

7.0 PROCEDURE

7.1   Calibration

7.1.1   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.

7.1.2   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. (For corrosivity characterization, the calibration of the pH meter should include a buffer of pH 2 for acidic wastes and a pH 12 buffer for caustic wastes; also, for corrosivity characterization, the sample must be measured at 25 ± 1 EC if the pH of the waste is above 12.0.) Various instrument designs may involve use of a dial (to "balance" or "standardize") or a slope adjustment, as outlined in the manufacturer's instructions. Repeat adjustments on successive portions of the two buffer solutions until readings are within 0.05 pH units of the buffer solution value.

7.2   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. If field measurements are being made, the electrodes may be immersed directly into the sample stream to an adequate depth and moved in a manner to ensure sufficient sample movement across the electrode-sensing element as indicated by drift-free readings (< 0.1 pH).

7.3   If the sample temperature differs by more than 2 ΕC 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.

7.4   Thoroughly rinse and gently wipe the electrodes prior to measuring pH of samples. Immerse the electrodes into the sample beaker or sample stream and gently stir at a constant rate to provide homogeneity and suspension of solids. Note and record sample pH and temperature. Repeat measurement on successive aliquots of sample until values differ by < 0.1 pH units. Two or three volume changes are usually sufficient.

8.0   QUALITY CONTROL

8.1   Refer to Chapter One for the appropriate QC protocols.

8.2   Electrodes must be thoroughly rinsed between samples.

9.0   METHOD PERFORMANCE

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

| | | Accuracy as | |
pH Units	Standard Deviation pH Units	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

10.0 REFERENCES

1.   National Bureau of Standards, Standard Reference Material Catalog 1986-87, Special
        Publication 260.

Start

7.1 Calibrate pH meter.

7.2 Place sample or buffer solution in glass beaker.

7.3 Does temperature differ by more than 2C from buffer?

Yes → 7.3 Correct measured pH values.

No

7.4 Immerce electrodes and measure pH of sample.

7.4 Note and record pH and temperature; repeat 2 or 3 times with different aliquots.

Stop