



Standard Operating Procedure

pH

SOP # 618S

Revision 4

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STANDARD OPERATING PROCEDURES pH

METHOD: Electrometric, SM 4500-H⁺, EPA 150.1, SW-846 9040B, 9045C

HOLDING TIME: ASAP, <24 hr.

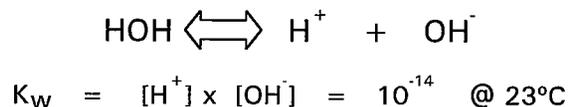
PRESERVATIVE: none

1.0 Scope and Application

pH is a measure of the hydrogen ion (H⁺) activity in solution and is defined as the negative logarithm (or the logarithm of the reciprocal) of that activity (roughly, it's molar concentration):

$$\text{pH} = -\text{Log} [\text{H}^+] = \text{Log} (1/[\text{H}^+])$$

pH is related to the dissociation of pure water and the ion product (K_w) for that dissociation:



The method described is applicable to most aqueous solutions. pH measurements for most types of samples should be conducted at the time of sample collection. Samples which are transported to the laboratory for analysis should be completely filled (no head space) and tightly sealed to prevent contact with the atmosphere. pH should be determined upon receipt in lab.

For soil and sediment samples, pH is determined using a 1:1, by weight, extraction ratio. Generally, extraction is done in DI water and measurement is made on the extraction slurry (SW-846 9045C).

2.0 Definitions

N/A

3.0 Supplies and Equipment

3.1. Equipment

pH meter, temperature compensating with auto-lock feature
combination electrode (Store in saturated potassium chloride solution)
beakers, 100 mL
magnetic stirrer and TFE stir bar

3.2. Reagents

3.2.1. Primary Standard buffers. pH4, pH7 and pH10. Use only certified, NIST traceable buffer solutions. Examples would be:

- pH 4 Potassium acid Phthalate Fisher SB98-500
- pH 7 Monobasic potassium phosphate + sodium hydroxide Fisher SB108-500
- pH 10 Potassium carbonate, borate, hydroxide. Fisher SB116-500

3.2.2. Potassium chloride (KCl), saturated solution.

4.0 Documentation

N/A

5.0 In-house Modifications from Referenced Method

N/A

6.0 Procedure

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6.1. Initial Calibration.

6.1.1. Calibrate the pH meter according to manufacturers instructions. Make sure the auto-temperature-compensating (ATC) probe is attached and use the procedure for automatic temperature compensation. All of our pH meters use 3-point calibration (pH of 7, 4 and 10) for "standard" and "slope" adjustments. Calibration pH should span the range of expected pH for the samples. Enter the calibration data into the "pH Calibration Logbook" each time a meter is calibrated.

6.1.2. Meters should be calibrated daily and verified prior to and immediately after each batch of samples analyzed. Aqueous samples for pH analysis will be accompanied by a "Critical.rpt" sheet. Record the date and time of last pH meter calibration on the "critical" sheet along with the pH reading for each buffer used in the calibration (available from the "pH Calibration Logbook"). The "critical" sheet contains space at the top and bottom right hand side for the entry of readings of a pH 7 verification buffer. Record the initial verification buffer reading at the top and the continuing verification buffer at the bottom of each page used. Date, time and initial each entry made into the "pH 7 Buffer" spaces. Each verification buffer should return a reading within 0.05 pH unit of its known value ("in-control" values). The verification buffer should be run after every 10 samples analyzed. Each batch of 10 or fewer samples must be bracketed by "in-control" pH verification readings.

6.2. Procedure, aqueous solutions

6.2.1. Aqueous samples for pH analysis will all be listed on the "Critical.rpt" sheet. As discussed above, this sheet contains space for calibration data entry and verification data entry. Samples values are entered directly onto this sheet. No other form is used for pH data entry.

6.2.2. Transfer to a clean 100mL beaker, an aliquot of sample sufficient to cover the sensing elements of the electrode (20-30 mL). Place beaker on magnetic stirrer and mix gently. Avoid excessive mixing to minimize atmospheric CO₂ exchange, this is particularly important for poorly buffered samples having pH values <7.

6.2.3. Insert the calibrated, temperature compensating electrode into the solution. Wait until meter achieves a stable pH and temperature reading.

6.2.4. Record the stable pH value and temperature of measurement (values should be temperature compensated automatically but record the value for future reference if questions should arise. Run a duplicate determination for every 20 client samples of equivalent matrix or more frequently as required by the client.

6.2.5. Make sure to thoroughly rinse the electrode with deionized water between successive samples.

6.3. Soil and Sediment. There is space on the "Soils Conductivity-pH" benchsheet for this entry. Open the computer and print a copy of the benchsheet. Use this for all raw handwritten data entry.

6.3.1. DI water extraction

6.3.1.1. Add 10 grams of solid sample to a 50 mL centrifuge tube. Add 10 mL of DI water solution and shake for 30 minutes.

6.3.1.2. Allow 30 - 60 minutes for settling of particulates. Decant the supernatant solution to a 50 mL beaker (or other appropriate container) for determination of pH as described above or measure the pH of the clarified extract directly in the extraction vessel. Prepare a duplicate extraction for every 20 client samples of equivalent matrix.

6.3.1.3. Record the actual weight of soil used, the volume of extract and the pH value on the benchsheet. The final report should read, "pH determined on 1:1 soil:water extracts"

7.0 Review

7.1. Supervisor reviews Service Request, enters information into the Conventionals database and assigns sample to the analyst.

- 7.2. Analyst verifies Service Request, reviews the SOP, obtains the appropriate benchsheet and proceeds with the analysis. A handwritten benchsheet is generated and the data are then entered into the computer for data reduction.
- 7.3. The final computer generated benchsheet is placed into the job folder. The handwritten benchsheet and a copy of the final benchsheet are placed into the method folder in chronological sequence.
- 7.4. The supervisor reviews the job folder for completeness of analysis (all requested parameters have been run) and sufficiency of Quality Control.
- 7.5. Completed analysis is given to the Data Section for final report preparation.
- 7.6. The final report is reviewed for accuracy and completeness and then signed by the Division Manager.

8.0 QC Limits

Each batch of 10 or fewer samples must be bracketed by the measurement of a pH 7 verification buffer. The recorded readings must be within 0.05 pH unit (6.95 - 7.05) of the known value.

Duplicate analyses should agree within 20% (Relative Percent Difference, RPD < 20.0)

9.0 Corrective Actions

If any verification standard does not return a value within 0.05 pH unit of its known value, you will first repeat the measurement to verify the "out-of-control" reading. If verified, you will re-calibrate the pH meter and repeat the verification process. All samples between the last in-control verification standard and the verified out-of-control standard must be re-analyzed.

If the duplicate RPD is greater than 20%, repeat the analysis one more time and report the triplicates and associated relative standard deviation (RSD).

10.0 Miscellaneous Notes and Precautions

Any sample showing extremes of pH (i.e. <3 or >10), particularly very extreme values, <2 or >12, is suspect and should be brought to the attention of your supervisor. Very extreme pH values may indicate a possible mix-up in sample containers (a preserved sample may have been miss-labeled) hence the identity of such samples should be confirmed prior to conducting any further analysis on any of the samples which may be associated with that suspect sample.

Alternative Extraction Procedure: Calcareous soils (CaCl₂ Extraction)

Note: This procedure is done upon client request ONLY!!

At one time, SW 846 9045A, called for a Calcium Chloride extraction procedure for calcareous sediment/soil sample pH determinations. This has since been revised and deleted in SW 846 9045C. As per client request, we are able to perform this procedure. The method calls for the use of a 0.01M calcium chloride solution for extraction of calcareous soils that pass an effervescence test.

Calcium Chloride (CaCl₂-2 H₂O) 0,01M. Dissolve 1.77 grams in 800 mL deionized water. Cool and dilute to 1000 mL. Adjust pH of the solution within the range of 5.0 to 6.5 using either calcium hydroxide or hydrochloric acid. The conductivity of this solution should be 2.32 mS ± 0.08.

Calcium Hydroxide, for pH adjustment. Dissolve approximately 2.0 gram into 800 mL deionized water. Dilute to 1000 mL.

Procedure:

Use an effervescence test to determine whether the sample is calcareous or non-calcareous. Place a small amount of sample (0.5 grams) on a piece of foil and add a few drops of 1:1

hydrochloric acid. If the sample bubbles or fizzes it is calcareous; if not, it is non-calcareous. The result of this test should be clearly noted on the benchsheet, along with the extraction method used (CaCl_2 or H_2O) which is determined by the effervescence test. Clearly identify on the benchsheet which extraction method is used.

Add 8 grams of calcareous sample to a 50 mL centrifuge tube. Add 40 mL of the 0.01M calcium chloride solution and shake gently for 30 minutes. Let the solids settle for an additional 30 minutes then follow the above procedure for water extractions for the pH determination.

Record the actual weight of soil used, the volume of extract, and the pH on the benchsheet. The final report should read, "pH determined in 0.01M CaCl_2 extracts."

11.0 Method References

Standard Methods for the Examination of Water and Wastewater. 18th ed. 1992.
Method Number 4500-H⁺

Methods for Chemical Analysis of Water and Wastes. EPA 600/4-79-020 (Rev March 1983). Method 150.1

Test Methods for Evaluating Solid Waste. SW-846. Methods 9040, 9045C

