Measuring the pH of Photographic Processing Solutions

Kodak

WHAT IS pH?

pH is the most common chemical measurement. It expresses the acidity or alkalinity of a substance. pH has an enormous effect on our environment and our lives. Plants require soil with a particular acidity or alkalinity, depending on the species. Animals, including human beings, can die if their blood pH is wrong. Milk turns sour at a pH of 6, jelly will not jell at a pH above 4, and sewage treatment plants cannot operate if the pH of what they are treating is too high or too low.

The correct pH is important in photographic processing too, because the solutions must remain within a specified pH range to produce good results. Because pH is so important to good processing, we've provided this publication to help you make accurate pH readings of your solutions.

THE pH SCALE

There are hundreds of acids—strong acids like sulfuric acid, which can dissolve steel nails—and weak acids like boric acid, which is safe enough to use as eyewash. There are also many alkaline solutions, called "bases"—mild alkaline solutions like milk-of-magnesia that soothes upset stomachs—and strong alkaline solutions like lye and sodium hydroxide, which dissolve human hair.

Acids and bases have a characteristic that lets us tell them apart and that we can measure—the concentration of hydrogen ions. Strong acids have high concentrations of hydrogen ions; weak acids have low concentrations. A unique numerical scale ranging from 0 to 14 is used to measure pH.

Numbers from 0 to 7 on the scale indicate acid solutions; 7 to 14 indicate alkaline solutions. The more acid a substance is, the closer its pH will be to 0. The more alkaline a substance is, the closer its pH will be to 14. Some photographic solutions are neither highly acidic nor highly alkaline but are closer to the neutral point, pH 7—the pH of tap water. Developer solutions measure on the alkaline portion of the pH scale, typically ranging from pH 9 to 12. Stop baths measure on the opposite end of the scale because they contain large amounts of acid; they typically have pH values of 1 to 3.

HOW IS pH MEASURED?

The most accurate and commonly used method for measuring pH is by using a pH meter and either a pair of electrodes, or a "combination electrode" (see below). A pH meter is basically a very sensitive voltmeter. The electrodes connected to it will generate an electrical current when they are immersed in solutions.

Two types of electrodes are used to measure pH, and each electrode has a specific purpose. The "glass" electrode has a bulb made of special composition glass that is very selective and sensitive to hydrogen ions. When this glass bulb is immersed in a solution, the voltage generated at the bulb's surface is related to the pH of the solution.

The other electrode is called the "reference electrode"; it provides a stable and reproducible voltage when it is immersed in a solution. When the two electrodes are connected to a pH meter, the voltage difference is amplified and displayed on an analog or digital meter. An electrode that combines both the pH-sensitive glass bulb and reference cell in one electrode body is called a "combination electrode," it is used in the same way as an electrode pair.

For accuracy and consistency, the meter must be standardized with solutions with known pH values called "buffers." A buffer is a specially prepared solution with two important qualities; it resists changes in pH, and it has a specific pH value at a specific temperature. The pH meter and the electrodes must be properly maintained and calibrated often for reliable pH readings. The solutions must also be measured at the correct temperature with the proper technique.

WHAT YOU WILL NEED:

pH Meter

The pH meter must be capable of two-point calibrations with either an adjustable slope control or readout of slope values. Readability to 0.001-pH unit and accuracy to ±0.002 are required.

The Corning 350 pH meter, or equivalent, is a satisfactory single-channel meter. This meter accommodates one electrode pair. However, you can upgrade it with accessories to accommodate multiple pairs of electrodes. The Orion EA 940 pH meter, or equivalent, is a satisfactory dual-channel meter. Two pairs of electrodes can be attached simultaneously.

Electrodes

We recommend the use of the Thermo/Orion, Ross Sure Flow Combination pH Electrode, part number 8172BNWP.

Because of the effect of the complex matrices of photo processing solutions on the glass membranes of pH electrodes, we have observed a significant difference between different manufacturers' pH sensing glasses. We use the Ross Sure Flow 8172BNWP for our processing solutions.

Note: The Ross Sure Flow Combination Electrode has replaced the Corning Combination pH Electrode, part number 476146, as the primary electrode for use in this method. The Corning Combination pH Electrode can be applied if it becomes necessary to use an alternate electrode. Theoretically, there is no reason why other combination electrodes cannot be used for this method, and they are continually tested for their precision relative to a standard electrode.

Temperature Equilibration

The primary recommendation for controlling the temperature of your sample is to use a temperature controlled water bath. Circulate tempered water around the sample containers to equilibrate all samples and buffer solutions. Maintain the sample and buffer temperature at 25 ± 0.25°C (77 ± 0.5°F) for 15 minutes before making the measurement.

Careful control of temperature is essential for precise and accurate measurement of pH. A change in temperature of 1°C (2°F) produces a change of 0.015 to 0.020 pH units in measurements of carbonate-buffered developers of about pH 10.

Note: Some pH meters have a temperature adjustment probe that does not require the use of a tempered water bath to control the temperature of the samples and buffers. The probe will adjust the pH reading to the actual temperature of the sample, trying to match it to a reading taken at 25 ± 0.25°C (77 ± 0.5°F). Although temperature adjustment probes can be used, they can produce further variability that could affect the precision and accuracy of the reading. Therefore, the method of taking a pH reading described in this publication will only include the use of a tempered water bath to stabilize the temperature of the samples and buffers.

Stirring

For greatest precision, stir solutions during both meter calibration and sample pH measurement. Stir the sample moderately during measurement so that the electrodes are exposed to a uniform sample. Avoid vigorous stirring that draws a large amount of air into the solution and can oxidize the solution. Use air-, water-, or electrically driven magnetic stirrers that can be immersed in the water baths.

Sample and Buffer Containers

You can use wide-mouthed jars with caps (8-ounce size) to hold buffers and sample solutions. Cover the sample solutions and buffers while bringing them to equilibrium temperature.

Reagents and Materials

Buffers can change with age or storage conditions. See the manufacturer’s literature for the expiration dates of individual solutions. When possible, store the buffers in their original container. Replace the buffers used for meter calibration at least once each 8-hour shift or work day; replace more often with frequent use. Change the buffers if you have difficulty to calibrating the meter.

See Appendix A for the recommended buffer solutions.

METHOD FOR MEASURING THE pH OF PHOTOGRAPHIC SOLUTIONS

You can use the following method to measure the pH of photographic processing solutions.

1) SETUP

- Equilibrate the fresh buffers and the solutions being measured to a temperature of 25°C ± 0.2°C (77°F ± 0.5°F). For photographic solutions of pH 7 to 14, use pH 7 and 10 buffers (for high-range pH meter calibration).

  For photographic solutions of pH 0 to7, use pH 4 and 7 buffers (for low-range pH meter calibration).

  For more information on buffers, see Appendix A.
- Change the reference-electrode fill solutions as described in Appendix B, and attach the electrodes to the meter.

Set the pH meter temperature compensator to 25°C (77°F). Adjust the manual control to this value, or if the meter is controlled by a microprocessor, input the value through the keypad. See the meter instruction manual for specific instructions on meter calibration.

2) CALIBRATING THE pH METER

High-Range pH Meter Calibration

1. Rinse the electrode with distilled water; *blot* excess water from the tips of the electrodes (and any protective assemblies) with a soft tissue. DO NOT rub the electrode membrane with the tissue; hold the tissue near the electrode surface and allow it to draw off the water.
2. Immerse the electrode in pH 7 calibrating buffer stirred with a Teflon-coated stirring bar and magnetic stirrer or a paddle-type stirrer rinsed with distilled water.
3. Wait 30 seconds for the electrode to equilibrate and meter reading to stabilize. If the meter does not display the pH value given by the manufacturer for the pH 7 calibrating buffer for 25°C (77°F), set the *calibration* control to the correct value.
4. Rinse the electrodes with distilled water, blot as in step 1, and immerse the electrode in the pH 10 calibrating buffer (stirred as step 1).
5. Wait 30 seconds for the electrodes to reach equilibrate and meter reading to stabilize. At the end of the 30 seconds, if the meter does not display the pH value given by the manufacturer for the pH 10 calibrating buffer for 25°C (77°F), set the *slope* control to the correct value.
6. Repeat Steps 1 through 5 until the meter displays the manufacturers stated pH values of the calibrating buffers within ± 0.005 pH units.
7. Read the slope value. If it is not within 98 to 102 percent of optimum electrode response, go back to Step 1, and redo the calibration. If the slope is still out of range, try another electrode.

Low-Range pH Meter Calibration

1. Rinse the electrode with distilled water; *blot* excess water from the tips of the electrodes (and any protective assemblies) with a soft tissue. DO NOT rub the electrode membrane with the tissue; hold the tissue near the electrode surface and allow it to draw off the water.
2. Immerse the electrode in pH 7 calibrating buffer stirred with a Teflon-coated stirring bar and magnetic stirrer or a paddle-type stirrer rinsed with distilled water.
3. Wait 30 seconds for the electrode to equilibrate and meter reading to stabilize. If the meter does not display the pH value given by the manufacturer for the pH 7 calibrating buffer for 25°C (77°F), set the *calibration* control to the correct value.
4. Rinse the electrodes with distilled water, blot as in step 1, and immerse the electrode in the pH 4 calibrating buffer (stirred as step 1).
5. Wait 30 seconds for the electrodes to reach equilibrate and meter reading to stabilize. At the end of the 30 seconds, if the meter does not display the pH value given by the manufacturer for the pH 4 calibrating buffer for 25°C (77°F), set the *slope* control to the correct value.
6. Repeat Steps 1 through 5 until the meter displays the manufacturers stated pH values of the calibrating buffers within ± 0.005 pH units.
7. Read the slope value. If it is not within 98 to 102 percent of optimum electrode response, go back to Step 1, and redo the calibration. If the slope is still out of range, try another electrode.

3) SAMPLE PREPARATION

The only preparation required is to equilibrate the sample to 25°C (77°F). A sample of 80 to 120 mL is adequate. You can use an 8-ounce (approximately 250 mL) wide-mouth jar as a sample container.

4) MEASURING THE pH OF YOUR SOLUTIONS

After calibrating the meter for the required pH range and temperature of the sample, follow these steps.

1. Verify that the sample temperature is 25°C ± 0.2°C (77°F ± 0.5°F).
2. Rinse the electrodes with distilled water, blot them, and immerse them in the sample while it is being stirred.
3. Wait 30 seconds for the electrodes to equilibrate and meter reading to stabilize.
4. Read and record the pH value to 0.01 pH unit.
5. Recalibrate the meter between sample measurements if possible.

If you measure several samples of similar pH, do no more than three measurements; measuring more samples without calibration may increase variability of the system. If you measure samples of widely differing pH (e.g., 7.5 and 12), recalibrate between samples.

If you measure more than one sample, always calibrate the meter after the final sample to check that no malfunction occurred during measurement. If you have difficulty calibrating the meter or if the slope tolerance is not met, remeasure any samples read since the last calibration.

APPENDIX A

Calibrating Buffers

Buffer	Manufacturer*
pH 10.000 ± 0.005 at 25°C (77°F)	VWR International http://www.vwrsp.com **Catalog Number(s):** RC160216 **Supplier:** Ricca Chemical **Description:** pH Buffer 10.000. Reference standard, pH 10.000 ±0.005 at 25°C. Meets USP requirements. Color-coded blue. Compared against and certified traceable to NIST Standard Reference Materials. Temperature/pH reference chart on label. Packaged in plastic container. 500mL
pH 7.000 ± 0.001 at 25°C (77°F)	VWR International http://www.vwrsp.com **Catalog Number(s):** RC1552-16 **Supplier:** Ricca Chemical **Description:** pH Buffer 7.000. Reference standard, pH 7.000 ±0.001 at 25°C. Meets USP requirements. Color-coded yellow. Compared against and certified traceable to NIST Standard Reference Materials. Temperature/pH reference chart available with certificate of analysis. Packaged in plastic container. 500mL
pH 4.000 ± 0.02 at 25°C (77°F)	VWR International http://www.vwrsp.com **Catalog Number(s):** RC1502-16 **Supplier:** Ricca Chemical **Description:** pH Buffer 4.000. Reference standard, pH 4.000 ±0.002 at 25°C. Meets USP requirements. Color-coded red. Compared against and certified traceable to NIST Standard Reference Materials. Temperature - pH reference chart available on label. Packaged in plastic container. 500mL.

Electrode Storage Buffer (0.1 M Potassium Chloride in pH 7 Buffer)

Add 2.5 mL of 4 M (saturated) potassium chloride solution to a 100-mL volumetric flask. Add pH 7 calibrating buffer to bring the solution to 100mL. This solution is stable for 6 months.

Glass-Electrode Storage Buffer

Use the pH 7 electrode storage buffer (described above) to store glass pH electrodes.

APPENDIX B

Electrode Care

Follow the manufacturer's recommendations for electrode care. Use 3.0 M potassium chloride solution for combo-electrode storage. For temporary storage of the electrode between measurements, use the pH 7 storage buffer (0.1 M potassium chloride in pH 7 buffer).

Electrode Preconditioning/Rejuvenation

Follow the manufacturer's recommendations for preconditioning glass pH electrodes. A minimum soaking time of 2 hours in pH 7 calibrating buffer is recommended before use for pH measurement; overnight soaking is better.

Reference Electrodes–Care/Rejuvenation

It is preferable to use the manufacturer's recommendations for rejuvenation of the glass pH electrodes. A rejuvenation procedure for the glass pH electrodes should be done only when accuracy and precision of pH readings become compromised or biased. In these cases, it is often necessary to replace the electrodes. However, if recommendations from the manufacturer do not exist, then try the following procedure.

Sleeve-type junction reference electrodes are the most accurate. However, due to the high flow rate of filling solution, close attention is required to insure that the electrode has adequate filling solution, and that the electrolyte does not drain completely into the sample being measured. This is necessary for proper electrode performance and to avoid sample contamination. Before installing a new reference electrode, withdraw the filling solution and refill the electrode with 3.5 M potassium chloride solution. At the beginning of each shift or day, withdraw the potassium chloride filling solution with a fine-tipped eyedropper and refill the electrode with fresh 3.5 M potassium chloride solution.

If substituting a new glass electrode does not improve the performance of the pH system, reference-electrode junction clogging may be the problem, especially when the pH readings are unsteady or inaccurate. If the filling solution has become contaminated, refill the electrode with fresh solution and recheck the system. Check frit-type junctions for flow by *gently* pressing the tip of the reference electrode against a paper towel several times. A small wet spot will be visible if the junction is flowing.

Clear a clogged calomel reference electrode by soaking the electrode junction for 1⁄2 hour in a warm solution (not above 50°C [122°F]) of 3.5 M potassium chloride diluted 1:9 with distilled water. Drain the electrolyte and replace the solution with fresh 3.5 M potassium chloride solution. Retest the electrode.

For clogged Ag/AgCI reference electrodes, use a 10-minute soak in 10 percent ammonium hydroxide solution to remove precipitated silver chloride from the junction. The electrode must contain filling solution during this procedure.

Do not use higher concentrations of ammonium hydroxide solution or longer periods of soaking, because you may damage the reference element in some types of Ag/AgCI reference electrodes.

As with glass electrodes, more severe rejuvenation procedures are not recommended because they are costly, and may result in more electrode damage than improvement in performance.

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