By Martin S. Frant

The effect of temperature on pH measurements

IMAGINE THIS SCENE in the quality assurance (QA) laboratory of a food manufacturer. A worker comes in with a beaker containing hot strawberry jam and makes the following request: "Check the pH—it's got to be below 4.1!"

A technician quickly calibrates an electrode in two buffers (which are at room temperature) and places it in the molten jam. To correct for the temperature, either an automatic temperature compensator (ATC) probe is used or the temperature is measured manually and set into the instrument. The meter reads 4.00, and bottling can begin. A little later, walking past the packaging area, the technician picks up a now well-cooled bottle and brings it back to the laboratory. Will the pH reading be the same?

The answer is probably not. But by how much it will have changed is not an easy question to answer. There are at least five ways in which a change in temperature can affect the pH.

Slope changes

Measurements of pH by electrode obey the Nernst equation:

$$E_{\text{measured}} = E_{\text{ref}} + RT/F \log [\text{H}^+] \qquad (1)$$

where R, F, and E_{ref} are constants and T is the absolute temperature. A plot of the millivolt readings versus pH would have a slope of RT/F, or approximately 60 mV per decade change of H^+ at room temperature. Notice that the slope will vary directly with the absolute temperature. This means that the slope increases approximately 3.4% for a 10 °C increase in temperature, and if the room were at 25 °C and our jam were at 65 °C, the slope of the calibration curve in the instrument would have to change about 13%.

Such changes in temperature are accounted for in most pH meters, and the correction uses either a manually supplied temperature value or information from a temperature sensor. If this correction were not made, a 40° difference in temperature would result in a pH of 4.36 reading as pH 4.00, resulting in a batch of bad jam.

To make the change, the meter program must hold one point constant when it changes the slope and must swivel around that point. This means there is some point at which the pH calibration does not change with temperature. By common agreement, virtually all pH electrodes (and, therefore, meters) are designed so that the "isopotential" point is at pH 7. See *Figure 1.*

Slope correction by the meter generally works quite well, although there is evidence in the literature[1] that some manufacturers of electrodes do not set the isopotential point properly or consistently. (The location of the point can be checked by plotting multibuffer calibrations at two temperatures, as was done in Figure 1.)

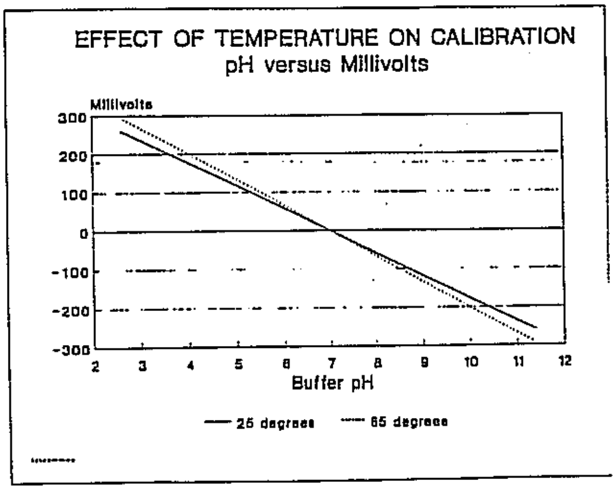

Figure 1 *Calibration curves for pH at 25 °C and 65 °C. The slope of the line increases with increasing temperature. By convention, electrodes are designed so that the lines cross at pH 7, and no change in reading occurs with a change in temperature. At pH 4, the change amounts to about 0.36 pH units.*

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ble 1

Changes in the assigned values of NIST buffers with temperature

ST buffers	25 °C	35 °C	Delta pH
thalate	4.008	4.024	+0.016
osphate	6.865	6.844	−0.021
rax	9.180	9.102	+0.078

ble 2

Changes in pH of 0.01 *M* acid from 50 °C to 25 °C

id	pH at 25 °C	pH at 50 °C	Delta pH
etic	3.387	3.402	−0.015
lic	3.555	3.580	−0.025
taric	3.197	3.209	−0.012
ric	3.224	3.266	−0.042

ffer changes

Ir [illegible] example of the food laboratory, the electrode s [illegible] rated by placing it in buffers at room tempera- e. [illegible] the temperature increases, the acids and bases ed to make buffers dissociate more, and the assigned values of the buffer will change slightly with temper- re. This information is built into most modern pH ters and is not a problem if the temperature is entered o those meters at the time of calibration. *Table 1* ows how the standard buffer values respond to a 10 °C nperature change.

mple changes

Not only do buffers change their pH with tempera- e, but samples do also, and in a much more unpredictable manner. Consider some of the common acids in foods, shown in *Table 2*. These results are for very simple, related acids. For more complex samples, such as wastewaters or plating baths, it is not possible to predict how the pH will change with temperature. This is why no meter will provide the pH value at 25 °C of a sample measured at some other temperature and why pH specifications should give the measurement temperature.

le 3

Changes in the neutral point of water with temperature

np. °C	Dissociation constant	−Log K	Neutral pH
0	1.15×10^{-15}	14.94	7.49
20	6.82×10^{-15}	14.17	7.09
25	1.10×10^{-14}	13.99	7.00 (6.995)
30	1.47×10^{-14}	13.83	6.92
40	2.95×10^{-14}	13.53	6.77
60	8.51×10^{-14}	13.02	6.51
70	1.58×10^{-13}	12.80	6.40

Neutral point changes

Less well-known is that the dissociation of water also varies with temperature. At 25 °C, the dissociation constant is about 10^{-14} and the neutral point of pure wa-

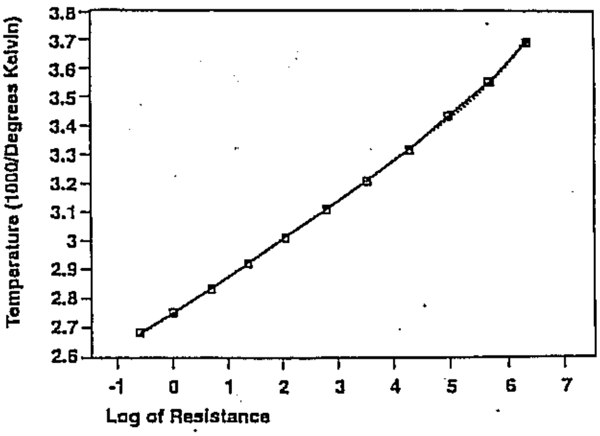

Figure 2 *The variation in the resistivity of a glass pH bulb with temperature, which gives an almost straight line when plotted as log resistivity versus 1/T. This information can be entered into meters using "Log R" technology to eliminate the need for a separate temperature sensor.*

Table 4

Change in solubility of silver chloride with temperature

Temperature °C	Approximate solubility, mg/L	Observed E_{ref} in mV
10	1	231.4
30	2.1	219.0
50	5	204.5
70	10	187.7
90	17	169.5

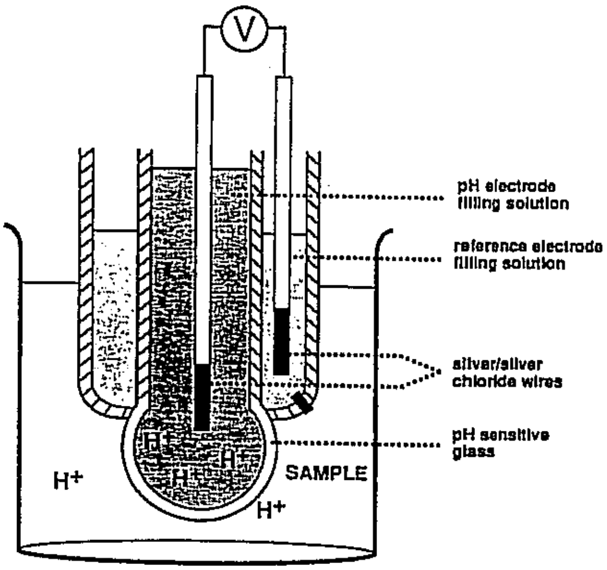

Figure 3 *Measuring circuit for pH. A voltage develops across the glass membrane that is proportional to the difference in pH inside and outside of the bulb. This voltage is measured by a pair of reference wires, one on each side of the bulb. To keep the sample from contaminating the outside reference wire, it is surrounded by a fixed solution and separated from the sample by a porous junction (the "reference electrode").*

ter is at pH 7, when there are 10^{-7} moles of hydroxide and 10^{-7} moles of hydrogen (or hydronium) ion. *Table 3* suggests that the neutral point of water at 65 °C is somewhere around pH 6.45. This could be a problem when adjusting a cosmetic, for example, to neutral pH while it is still hot.

A more subtle effect is that a fixed concentration of a strong base would give a different concentration of hydrogen ion as the temperature varied because of the different values of the dissociation constant. At 25 °C, a 0.001 *M* NaOH solution would be at about pH 11 (because $H^+ \times OH^-$ must equal 1×10^{-14} (or $10^{-3} \times 10^{-11}$). In the same solution at 70 °C, $10^{-3} \times$ the hydrogen ion concentration (assuming activities and concentrations to be the same) would have to equal 1.58×10^{-13}, and H^+ would equal 1.58×10^{-10}, or a pH of 9.8.

Temperature sensor errors

Thus far, we have assumed when making the measurement that everything was at the new temperature. But when pH and temperature sensors at room temperature are placed into hot jam (or any other hot solution), it takes several minutes for them to reach the new temperature. During this time, the readings will drift, which can be embarrassing if someone is watching and waiting for the results. Even if no one is watching, the delay results in lost time or errors if the reading is taken too soon.

There are two different sources of this drift. First, errors and drifting will occur if the temperature probe used for the meter correction of the slope is not at the same temperature as the sensing bulb. The most common method of temperature measurement is to use a separate probe, often encased in glass or epoxy. This probe may respond either faster or slower than the sensing electrode, depending on design and mass.

Thermistors have been placed inside pH electrodes, but these tend to lag behind the actual temperature. Thinly encapsulated thermistors placed very close to the pH bulbs are probably the best compromise approach when using external sensors.

An interesting alternative, the patented Orion PerpHecT meters ("digital LogR") (ATI Orion, Boston, MA), uses the inherent resistivity of the sensing glass, which varies in resistance with temperature according to the equation:

$$\text{Log resistivity} = a + (k/T) \qquad (2)$$

where T is in degrees Kelvin and k is a term related to the activation energy, which tends to be similar for many pH glasses. This approach should be the most reliable, because it is the Nernstian response across the glass membrane that is actually changing with temperature. What is required is a meter with a special circuit for measuring the resistance of the glass bulb simultaneously with the pH measurement. This approach is most precise if the meter has been calibrated for a particular type of glass or individual electrode. An additional advantage would occur with our example: A beaker of hot jam does not have a very uniform temperature for very long (in this case, the center will be warmer than the outside sections), and the thermometer or ATC probe could easily be placed where the temperature is not the same as at the pH bulb.

Reference element drift

The second major cause of drifting is the internal reference elements inside the pH and reference portions of the electrode (*Figure 2*). Most elements are made from mercury/mercurous chloride (calomel) or silver/silver chloride. Both depend on having a constant activity of a relatively insoluble chloride salt, but the solubility of both salts changes with temperature. Calomel-based reference electrodes often do not come back to the same reading after a large temperature variation and should not be used when temperature cycling is involved.[2] However, silver chloride solubility also changes markedly with temperature, as shown in *Table 4*.

This shift corresponds to about 60 mV, or a full pH unit between 10 and 90 °C. This could be quite serious, but electrode designers balance out this effect by using the same kind of reference element inside the pH bulb and the reference electrode, as show in *Figure 3*. Because the meter "sees" only the difference in voltage, if both reference elements change the same way, there is no net change.

However, when an electrode pair is placed into a hot solution, there will be a period during which the two internal elements are not at the same temperature, because they are in different locations, with different distances to the surface, or are in contact with different volumes of internal solution. During this period, drifting will occur.

A novel solution to this problem was invented by Dr. James Ross and is the basis for the Orion line of 81-series ROSS® pH electrodes. The reference element uses a completely water-soluble iodide/iodine couple in contact with a platinum wire. The composition of the solution was chosen to have an output that is independent of temperature. Not only do these electrodes eliminate a major source of drifting, but their use can result in significantly improved precision and accuracy.[3]

Summary

A change in the temperature of a solution causes changes in the slope of the pH electrode calibration, in the pH of the buffer or sample, and in the neutral pH point. Errors caused by the temperature change include a drift in readings until the electrode stabilizes at the new temperature and the possibility of uneven temperatures within the sample. These errors can be minimized by the use of new pH technology.

References

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3. Metcalf RC. Analyst 1987; 112:1573–7.