where pH_s is the pH of the standard buffer solution, E_s is the voltage at pH_s, and E is the voltage of an unknown solution or suspension (Peech, 1965). This assumes that the junction potential will not change from the standard buffer to a soil suspension which, of course, it will as has been discussed earlier.

Equation [10] signifies that, in practical terms, the voltage change for 1 pH unit is 0.0591 V (or 59.1 mV) at 25°C, and all commercial pH meters are calibrated on this basis.

ELECTROMETRIC MEASUREMENT OF SOIL pH

Equipment

There is currently such a proliferation of equipment for determining soil pH that it is impractical to discuss them all. In general, the electrometer itself varies in quality with price and the cheaper electrometers cannot be used for readings more precise than ±0.1 pH unit. For field work they are entirely adequate. For more precise laboratory work they probably are not.

Combination electrodes, which usually have a Ag-AgCl reference rather than the usual calomel reference electrode, do not give results as accurate as those obtained with the standard two-electrode system. Nevertheless, for field work the combination electrodes may be preferable because they are easier to use. Similarly, plastic-encased electrodes are clearly preferable for field use because they resist breakage. On the other hand, standard glass electrodes are much easier to clean between samples and should be more useful in laboratory applications, unless careless operators are a problem. The new "Ross" electrodes which use a platinum wire and a redox filler solution to replace the traditional Ag-AgCl and $Hg\text{-}HgCl_2/KCl$ systems have the advantage that the reference is not sensitive to temperature changes and readings can be made much more quickly. Their disadvantage is that they cost two to three times as much as conventional electrodes.

Although digital readout is now much more common than the traditional analog and has many advantages, particularly with indecisive operators, the latter has the advantage of visually determining the approach of pH to an equilibrium value. This can be a very useful feature in certain kinds of studies, such as titrations.

It should be stated, in general, that the move to solid-state instruments has eliminated many of the problems of the older machines. On the other hand, many of those problems (shielding, grounding) could be handled by an experienced operator. When the new machines fail, they tend to fail completely a require a return trip to the manufacturer.

Standardization of the Meter

Most modern pH meters are equipped with a meter testing program to check the meter separately. This is done with a shorting plug installed to determine whether the meter is stable internally. Having done this check-up according to the operating manual, the meter and electrodes may be standardized.

For soils, a two-buffer standardization, at pH 7 and pH 4, should be performed. This will determine whether the electrodes are working properly and also will store the slope value (0.0591 V per unit of pH) in the memory of the electrometer.

In general, with solid-state pH meters, the procedure is to use a buffer of pH 7.0 and allow the machine to display the number. If the number is 7.0, the value is approved by pressing the yes button and the electrodes are cleaned and placed in the pH 4.0 buffer. The second buffer reading should be very close to 4.0. If it is, that number also can be approved by pressing the "yes" button and the pH meter and electrodes are now ready for use. If the meter cannot be standardized, it indicates electrode problems which are covered in the next section.

On older pH meters without programmed check sequences and without automatic temperature compensation (ATC), the procedure for standardization is as follows: the pH 7 buffer is introduced, the manual temperature control is set to the temperature of the buffer and the meter is set at 7.0. The electrodes are rinsed and blotted and the pH 4.0 buffer is introduced. If the buffer value reads 4.0 ± 0.1, the instrument is now ready for use. If not, adjust the reading to pH 4.0 using the temperature compensation knob. Repeat this with the pH 7.0 buffer and again with the pH 4.0 buffer until both readings are satisfactory. If this cannot be done, one or both electrodes probably are faulty.

Electrode Problems

Glass used in the H^+-sensitive electrode is characterized by low electrical resistance, low melting point, and high Na content (Dole, 1941). In addition, the glass must have the tendency to hydrate easily if it is to be predictably related to the activity of H^+. That the adsorption of water by the pH-sensitive glass was of overwhelming importance was known as early as the 1920s (Dole, 1941).

The most common problems with electrodes are caused by allowing them to dry out. In the case of the glass electrode, there is a hydrated layer of glass which facilitates the movement of H^+ (Westcott, 1978). Hydration does not occur immediately when the glass electrode is placed in water or dilute acids so that there will be a delay of some hours as proper hydration occurs. In addition, the surface of the electrode, upon drying, may become coated with carbonates or other compounds, rendering it somewhat impermeable to H^+. The electrode should be given alternate 5-min soakings in 0.1 *M* HCl followed by 0.1 *M* NaOH and finally in 0.1 *M* HCl again prior to use. This treatment will do a good job of removing any accumulated carbonates which restrict operation of the glass electrode.

If the rejuvenation procedure outlined above does not resolve the problem, the electrode may be lightly etched in 20% ammonium fluoride solution for 10 to 30 sec and then rinsed in water. This is a "last resort" treatment that cannot be repeated regularly because the glass is already very thin.

The calomel reference electrode also suffers from drying but the cause of potential problems is not due to the glass but, rather, the lack of flow of internal filling solution from inside the electrode to the soil suspension. The electrode should be full of solution before use and the vent cap should be open so that flow can occur. For soils measurements, it usually is preferred to have relatively slow leakage to minimize contamination of the soil suspension. However if leakage is too slow, the reading will be in error. The asbestos or glass fiber, or ceramic opening in the reference electrode (all three are used) may be plugged by KCl crystals (usually from inside the electrode) or by soil particles on the outside. It is necessary that some measurable flow occur. This can be checked by filling and cleaning the electrode and checking that slight wetting occurs.

PROCEDURE FOR SOIL pH MEASUREMENT

Equipment and Reagents

1. pH meter equipped with glass and reference electrode, or combination electrode.
2. 50- or 100-mL beakers.
3. Pipet or automatic pipet of 10 mL.
4. Standard buffers, pH 7 and pH 4.
5. Deionized water.
6. 0.01 *M* $CaCl_2$ solution.
7. 1 *M* KCl solution.

Determination—pH in water

1. Weigh out 10 g of air-dry soil in a 50- or 100-mL beaker.
2. Add 10 mL of deionized water to the soil in the beaker and mix well. A stirring stick, or stirring machine can be used but care should be exercised to minimize contamination. (For large-scale determinations, a shaking machine can be employed as is done in most soil testing laboratories.)
3. Let stand for 10 min.
4. Swirl the suspension in the beaker and insert the electrodes into the suspension. Electrodes may be placed in the clear supernatant above the soil, directly in the sedimented soil, or the entire suspension may be stirred during the pH determination. The *important* thing is that the measurements be carried out ina consistent way. In water pH determination, values taken in the supernatant generally will be slightly higher than in the stirred suspension. With a salt pH, the differences between the three techniques practically disappear. For exposed glass electrodes, it is useful to have a stop of some type so that the bulb will not contact the bottom of the beaker. McLean (1982) suggested a glass rod, slightly longer than the electrode, mounted on the electrode holder that makes contact with the beaker before the electrode does.
5. Read pH and record as pH_W.
6. Between pH readings, rinse the electrodes with distilled water. Blotting is not necessary.

pH in One-One Hundredth Molar Calcium Chloride

1. Repeat the above procedure (1–4) but use 0.01 *M* $CaCl_2$ instead of water to make the soil suspension.
2. Read pH and record as pH_{CaCl_2}.

pH in One Molar Potassium Chloride

1. Repeat steps 1 to 4 but use 1 *M* KCl instead of water to make the soil suspensions.
2. Read pH and record as pH_{KCl}.

ALTERNATIVE METHODS FOR pH MEASUREMENT

Use of Microelectrodes

The possibility of taking microsite pH values in intact soil systems has been facilitated by the use of microprocedures in plant cells (Felle & Bertl, 1986). Conkling and Blanchar (1989) have used homemade microelectrodes for this purpose and have obtained relatively stable and reproducible results. It is not yet clear, however, that startling new findings about the variability of pH in a soil matrix will be forthcoming.

Basically, the technique of Conkling and Blanchar, (1989) is to melt a small cap of pulled H^+ ion-sensitive glass over a pulled glass capillary, to install a silver wire, coated with AgCl and to fill it with a solution. This requires microscopic observation and manipulation and must be thought of as tedious work.

The reference electrode is a calomel electrode connected to a gel-filled KCl salt bridge to assure that a complete circuit is made. Readings on suspensions have shown close to 1:1 slopes with conventional electrodes so it is clear that the microelectrodes have some promise.

It is quite interesting to note that the pioneers of microelectrodes are following the path of the earlier pioneers (Sharp & Hoagland, 1919), making the equipment as they go.

Use of Test Kits

Test kits have always suffered somewhat by comparison with electrodes because (i) there are only certain pH values where ionic dyes change, and (ii) the color of the soil somewhat obscures those colors. Summing up (i) and (ii), it is clear that using kits is partly an art and depends considerably on the pair of eyes that is observing the color. Mason and Obenshain (1939) found good agreement between colorimeters and electrode pH values, but agreement was in the range of 0.3 to 0.4 pH units which is not very satisfactory for many applications.

Certainly, in many cases, these field kits can be useful in roughtly determining soil pH categories but they are more time-consuming than a portable pH meter and, probably, more expensive in the long run, and not as good.

pH Papers

The newer pH papers are reasonably useful for field work is accuracy of closer than 0.5 pH units is not critical. These papers have maximum practical use as a first approximation in the field when no pH meter is available. As such they are helpful in progressive soil mapping programs or in trouble-shooting situations. Nevertheless, the values usually have to be rechecked using a pH meter before complete confidence in the results can be attained.

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