



## TECHNICAL NOTE 4.

# UNDERSTANDING pH: THEORY, MEASUREMENT, APPLICATION

## 4.0 BACKGROUND

pH is one of the most commonly measured soil chemical properties. Technically, pH is a measure of hydrogen ion activity in a solution. pH is also called *soil reaction* which describes the acidity or alkalinity of the soil. Unfortunately, soil pH is an elusive, often misunderstood concept. This is due, in part, to the fact that pH measures something we cannot see. No human has ever seen a “hydrogen ion”, even with the most powerful microscope. We only understand the *effects* of hydrogen ions in solution. Because no one can see hydrogen ions, we must force our minds back to the fundamentals of atomic behavior for a systematic, logical way of reasoning. By grasping the fundamentals, our power to observe, measure, compare, and differentiate sharpens. When we *understand*, we can diagnose a problem more precisely.

## 4.1 ATOMS AND ELECTRONS: THE BASICS

Our modern idea of atomic structure is based on the nuclear *theory*. It’s called a theory because, as previously noted, no human has *seen* an atom to verify the details of its structure. The atomic theory holds that an atom is composed of a dense, central core called a nucleus containing *positively* charged **protons** surrounded by less dense *negatively* charged particles called **electrons**. The electrons are scattered in a very large space around the nucleus in *orbits* similar to the planets in our solar system. The positively charged nucleus and the negatively charged electrons are held together by a force of attraction similar to *gravity*. Now we must *understand* that this force does not *always* hold *all* of the electrons to the nucleus. Those electrons in the outer orbits of some elements are loosely held and are called “free electrons” (Figure 1). That is, they can move freely from one atom to another. They may wander about at random, or they may move over to a neighboring atom or molecule.

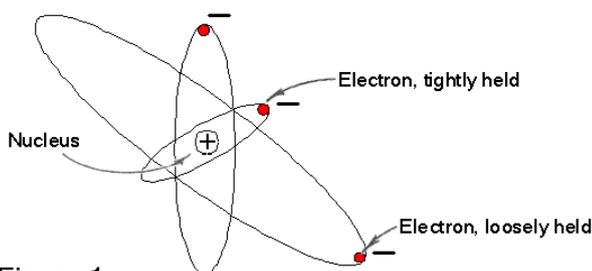


Figure 1.

The nucleus usually has a positive charge *equal* to the negative charge of all the electrons in its orbit. An atom in this state is said to be balanced, or *neutral* with respect to its charge. However, when electrons start to move away from the nucleus, the loss of electrons causes the atom to acquire a *net positive* charge. On the other hand, if a surplus of electrons moves into the orbit of an atom, the opposite thing happens. The atom acquires a *net negative* charge. When an atom gains or loses electrons, the atom is said to be an **ion** because it now has a net positive or negative charge. Keep this idea tucked away for the future. As it happens, our treatment of soil fertility will lean heavily on ions and ionic states of both atoms and molecules.

Hydrogen (chemical symbol **H**) is a very simple atom consisting only of one proton and one electron. The lone electron in its orbit is loosely held and free to wander about. Hydrogen ions are produced when an atom of hydrogen loses its electron, leaving the hydrogen atom in an *ionic state* with a net positive charge. We denote this net positive charge by writing  $H^+$ . These are the ions we measure in pH (conversely, a negative sign  $-$  is used to denote an atom having a surplus of electrons).

Another chemical concept we need to understand is **solution**. During this project we may be *making* solutions and *analyzing* solutions. We need to understand what this means so communications about the soil are understood by all. A solution exists in the soil by virtue of its water content. When we measure soil pH, we are measuring a chemical property of water plus ions, or **solutes** dissolved in that water. The solid phase of soil, consisting of sand, silt, clay, and organic matter is not directly involved. When we dissolve sodium chloride ( $NaCl$ , or table salt) in water the sodium and chloride dissociate as  $Na^+$  (a positively charged **cation**) and  $Cl^-$  (a negatively charged **anion**). The mixing of salt and water results in a **solution**. Thus we can speak of the *soil solution* as a mixture of water plus ions (and a few other molecules). Now that we *understand* how ions and solutions are formed, we can progress further to *understand* pH and its relationship to soil fertility.

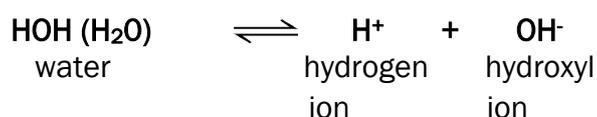
The pH of a solution is defined as  $-\log(H^+)$ , where  $(H^+)$  is the *active* concentration of hydrogen ions in the solution. *Ion activity* refers to chemical potential, or the “freedom” of ions to interact with other ions in solution. Active hydrogen ions are “free” in a sense that they may interact with other ions or molecules in a solution. In aqueous (water-based) solutions, there is good evidence to suggest that hydrogen ions do not exist as  $H^+$  but freely associate as hydronium ions,  $H_3O^+$ . Hence some ambiguity exists over how to write and speak of the “hydrogen ion”. When referring to the acidity of a solution, agronomists say “hydrogen ion activity” which is understood to mean free  $H^+$  that may produce acidity.

**Concentration** is the amount of a substance (ions or molecules) per unit volume of solution expressed as **moles per liter** (mol L<sup>-1</sup>). In dilute soil solutions the hydrogen ion activity (H<sup>+</sup>) is approximately equal to its concentration [H<sup>+</sup>] in mol L<sup>-1</sup>. Therefore we can write:

$$\text{pH defined } \approx -\log [\text{H}^+] \text{ or } \log 1/[\text{H}^+]$$

Note that we use parentheses ( ) to show activity and brackets [ ] to show concentration.

Water molecules have a natural tendency to split apart, or **dissociate**, releasing hydrogen and hydroxyl ions:



The **equilibrium constant**  $K_w$  is  $[\text{H}^+] \times [\text{OH}^-]$  and has a product of  $10^{-14}$  moles per liter at 25°C. In pure water  $[\text{H}^+] = [\text{OH}^-] = 10^{-7}$  mol L<sup>-1</sup> and the pH is 7 which is neutral. An input of acid (for example HNO<sub>3</sub>, nitric acid) raises the H<sup>+</sup> concentration, causes some association of H<sup>+</sup> and OH<sup>-</sup> to form water and leaves the [OH<sup>-</sup>] less than  $10^{-7}$ , [H<sup>+</sup>] greater than  $10^{-7}$ , and pH less than 7. The interesting thing is that regardless of the quantity of acid or base added to pure water, the product of  $[\text{OH}^-] \times [\text{H}^+]$  will always be  $1 \times 10^{-14}$ ! Because of this property, we can always calculate the [OH<sup>-</sup>] if we know [H<sup>+</sup>], and vice versa.

Using the “p” scale (negative logarithm) is a convenient way to express hydrogen ion concentration since the latter are very small numbers. The use of negative logarithms allows us to convert a negative power of ten into a small positive number. Thus solution pH is defined in terms of a **logarithmic** scale ranging from 0 to 14 (small positive numbers). This means that a solution with

pH 5.0 has a hydrogen ion concentration *ten times* greater than a solution at pH 6.0. Likewise, a solution with pH 4.0 has a hydrogen ion concentration *one hundred times* greater than a solution at pH 6.0. The range of pH in soil solutions varies from about 3 to 10 ( $10^{-3}$  –  $10^{-10}$  mol H<sup>+</sup> L<sup>-1</sup>). Table 1 shows the relationship between pH, concentration of H<sup>+</sup> and OH<sup>-</sup>, and scientific notation.

An *acid* is a substance that is a source of H<sup>+</sup> in solution, whereas a *base* is a substance that may combine with H<sup>+</sup>. If sodium hydroxide (NaOH, a strong base) is added to water to the extent that its final concentration is 0.01 mol L<sup>-1</sup>, the concentration of OH<sup>-</sup> is also 0.01 mol L<sup>-1</sup>, and the equilibrium concentration of H<sup>+</sup> is diminished according to the equation:

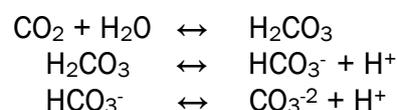
$$[\text{H}^+] = K_w/[\text{OH}^-] = 10^{-14}/10^{-2} = 10^{-12}$$

The pH of this solution is:

$$\text{pH} = -\log [10^{-12}] = 12.$$

This high pH indicates that the 0.01 M NaOH solution is strongly alkaline and the concentration of H<sup>+</sup> is very small.

Water will absorb CO<sub>2</sub> from the atmosphere which reacts to form carbonic acid, H<sub>2</sub>CO<sub>3</sub>. This is a weak acid and partially dissociates to release H<sup>+</sup>, HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup>:

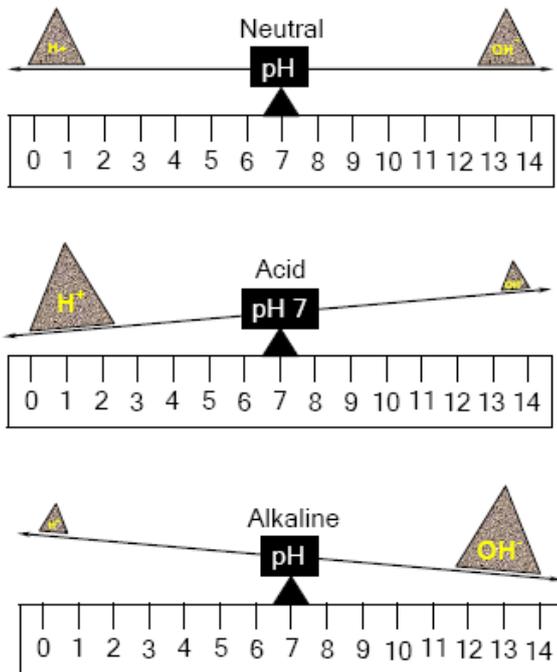


Pure water in equilibrium with CO<sub>2</sub> at the atmospheric concentration (0.03% v/v) has a pH of 5.6. A soil solution has a pH value lower or higher than 5.6 if the soil is acting as either an *acid* or a *base*.

Table 1.

pH	[H <sup>+</sup> ] decimal form	[H <sup>+</sup> ] scientific notation	[OH <sup>-</sup> ] decimal form	[OH <sup>-</sup> ] scientific notation	Degree of Acidity
0	1	1 x 10 <sup>0</sup>	0.000000000000001	1 x 10 <sup>14</sup>	extremely acidic
1	0.1	1 x 10 <sup>1</sup>	0.00000000000001	1 x 10 <sup>13</sup>	extremely acidic
2	0.01	1 x 10 <sup>2</sup>	0.0000000000001	1 x 10 <sup>12</sup>	acidic
3	0.001	1 x 10 <sup>3</sup>	0.000000000001	1 x 10 <sup>11</sup>	acidic
4	0.0001	1 x 10 <sup>4</sup>	0.0000000001	1 x 10 <sup>10</sup>	moderately acidic
5	0.00001	1 x 10 <sup>5</sup>	0.000000001	1 x 10 <sup>9</sup>	moderately acidic
6	0.000001	1 x 10 <sup>6</sup>	0.00000001	1 x 10 <sup>8</sup>	mildly acidic
7	0.0000001	1 x 10 <sup>7</sup>	0.0000001	1 x 10 <sup>7</sup>	neutral
8	0.00000001	1 x 10 <sup>8</sup>	0.000001	1 x 10 <sup>6</sup>	mildly basic
9	0.000000001	1 x 10 <sup>9</sup>	0.00001	1 x 10 <sup>5</sup>	moderately basic
10	0.0000000001	1 x 10 <sup>10</sup>	0.0001	1 x 10 <sup>4</sup>	moderately basic
11	0.00000000001	1 x 10 <sup>11</sup>	0.001	1 x 10 <sup>3</sup>	basic
12	0.000000000001	1 x 10 <sup>12</sup>	0.01	1 x 10 <sup>2</sup>	basic
13	0.0000000000001	1 x 10 <sup>13</sup>	0.1	1 x 10 <sup>1</sup>	extremely basic
14	0.00000000000001	1 x 10 <sup>14</sup>	1	1 x 10 <sup>0</sup>	extremely basic

A soil is said to be *acid* if it has an excess of  $H^+$  ions in solution or is capable of generating excess  $H^+$  ions. A *basic* soil has an excess of  $OH^-$  ions in solution or is capable of generating excess  $OH^-$  ions. A *neutral* soil has a balance of  $H^+$  and  $OH^-$  ions in solution and would have a pH near 7. When a soil is too acid or alkaline, some people speak of the pH being 'out of balance'. To balance a soil pH *does not* mean adjusting the pH to 7. Soils are not balanced with respect to pH; they are adjusted to "target" pH values determined by soil type and the specific crop being grown. Nevertheless, using the balance analogy we can figuratively represent pH as follows:



Soil *buffering capacity* is the ability of a soil to resist a change in pH when an acid or a base is added to soil. Adding acid or base to a poorly buffered soil causes a larger change in pH than adding the same acid or base to a highly buffered soil. Sandy soils are poorly buffered. The pH will drop after fertilization but will eventually take on the pH of the water surrounding the sand particles. Clayey soils and/or soils with high organic matter are strongly buffered and more resistant to influences that would tend to alter pH.

## 4.2 FACTORS AFFECTING SOIL pH

- The degree of soil acidity or basicity is influenced by the kinds of parent materials from which the soil was formed. Soils developed from basic rocks (e.g. basalt) generally have higher pH's than those formed from acid rock (e.g. granite).
- Rainfall also influences pH. Water passing through the soil leaches basic cations such as calcium (Ca) and magnesium (Mg) into drainage water. They are replaced by acidic elements such as hydrogen (H), manganese (Mn) and aluminum (Al). Soils formed in humid areas are more acid than those formed under dry conditions. In general, soils in the

eastern United States (where rainfall exceeds evaporation) are acid. A majority of soils in the drier western United States are alkaline.

- Soils formed under forest vegetation tend to be more acid than those developed under grassland. Evergreens (conifers) cause greater acidity than deciduous forests. Nutrient uptake by plants also contributes to soil acidification because cations absorbed by roots are balanced by an equivalent release of  $H^+$  by the roots.
- Soils become more acid as crops remove nutrient bases. Different crops remove different amounts of K, Ca and Mg. Legumes generally contain higher amounts of Ca and Mg than non-legumes. Calcium and magnesium content also varies in different parts of the plant.
- Acidity generally increases with soil depth and loss of topsoil by erosion and may increase acidity in the plow layer. As the depth of topsoil decreases, more subsoil is mixed in the plow layer.
- Fertilization, especially with ammonium-N fertilizers, increases acidity. On calcareous soils, the acidifying effects from fertilization can be beneficial.
- Nitrogen fixation by bacteria on legume roots contributes to soil acidification.
- Organic matter decomposition adds to soil acidity. One of the first products formed during the process of decomposition is ammonia. When ammonia is converted to nitrate, through the process of *nitrification*,  $H^+$  is released. This process is illustrated below (the effect from adding fertilizer ammonia is similar):



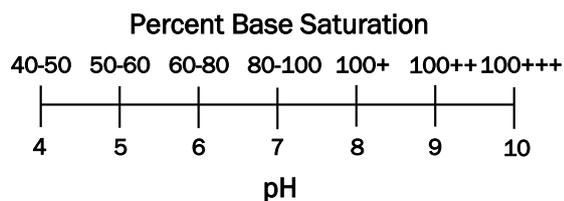
## 4.3 MEASURING ACIDITY

Two attributes of soil acidity can be measured. First is *active acidity* characterized by measurements of hydrogen ion activity and expressed as pH. Methods for measuring active acidity vary, but commonly involve mixing soil and water in a predetermined ratio and reading the results on a pH meter. Second is *exchangeable acidity* characterized by the presence of hydrogen and aluminum associated with the solid, or mineral phase of the soil. Methods for measuring exchangeable acidity also vary and may involve mixing soil in a solution of dilute  $CaCl_2$  (calcium chloride) or  $KCl$  (potassium chloride) or, may be determined analytically by measuring the quantity of alkali required to *titrate* soil to some predetermined endpoint. When soil is mixed with a solution of  $CaCl_2$  or  $KCl$ , the calcium and potassium exchange places with hydrogen and aluminum on *soil colloids*. The hydrogen ions are released in solution; the aluminum ions *hydrolyze* with water and release more hydrogen ions. When this exchange is

complete, the pH of the solution will be lower than when measured using a mixture of water and soil only. The quantity of exchangeable acidity is used to calculate the lime requirement of a soil, e.g. the quantity of lime needed to neutralize exchangeable acidity and adjust soil pH to its “target” value (see Technical Note 3). Measurements of hydrogen ion activity in a mixture of soil and water may express the soil’s need for lime, but cannot predict the number of pounds per acre to apply. Moreover, hydrogen ions alone do not manifest a direct toxic effect on plant growth unless soil pH drops below ~3. This rarely happens unless strong acids (usually man-made) are introduced to the soil. At this point you may be wondering, ‘why measure soil pH at all?’ But there’s more to the story...

Whether a soil is acid, basic or neutral has much to do with the *solubility* of plant nutrients, the proportion of nutrients bound to soil colloids in *exchangeable* form, the net charge (positive or negative) of certain soil colloids, and the activity of various microorganisms. As soil becomes more acid the following changes take place:

- The amounts of exchangeable  $K^+$ ,  $Ca^{2+}$  and  $Mg^{2+}$  decrease. These together with  $Na^{2+}$  and  $NH_4^+$  are known as *basic*, or *nonacid*, cations (a *cation* is an ion with net positive charge). The total amount of basic cations associated with soil solids (specifically, the *colloidal fraction*) is often expressed as a percentage of the *cation exchange capacity* of the soil which is termed the *percentage base saturation*. The percentage base saturation (% BS) indicates *how much* of the soil’s nutrient holding capacity is being utilized. There is a relationship between soil pH and percentage base saturation. As hydrogen ions increase the percent base saturation decreases, and vice-versa.



- The amount of exchangeable aluminum ( $Al^{3+}$ ) increases and is often expressed as the *percentage aluminum saturation*. Soluble  $Al^{3+}$  has a direct toxic effect on root growth and nutrient uptake.
- The negative charge on *humus* decreases and the positive charge on iron-enriched minerals (called sesquioxides) *increases*.
- The *solubility* of plant nutrients is altered. For example, the solubility of phosphorus is *decreased*.
- The solubility of elements such as aluminum and manganese is *increased* whereas, the solubility of zinc and copper is *decreased*.

- The activity of many soil organisms is *decreased*, resulting in reduced *mineralization* of organic matter, lower availability of nitrogen, phosphorus and sulfur.

Here we come upon a dilemma. While the *effects* of pH on soil fertility may be understood, it does not tell us what nutrients may be lacking, in adequate supply but unavailable, or in excess. The most we can say, at this point, is that pH is an *indirect* indicator of soil fertility status. We need a *quantitative* analysis of soil acidity, and nutrients, to determine what additions or subtractions might be needed to bring the soil into ‘balance’. Only a soil test can round out this piece of the puzzle.

There’s one more caveat. We measure soil pH using an instrument called a pH meter. The precise numerical values commonly obtained from pH meters convey the false idea that soils have characteristic pH values. In reality, a variety of pH values may be found for a given soil sample. Varying the soil/solution ratio, equilibration times, time of sampling, and addition of neutral salts such as  $CaCl_2$  or  $KCl$ , all tend to yield different results. Moreover, the presence of fertilizer salts in a soil sample will depress pH readings. Therefore it is essential to know where fertilizer bands are located in order to avoid acid-biased pH readings. Despite this complexity, interpretation of soil pH values can be justified on the basis of *uniform methods of sampling, measurement and correlation* with other soil properties.

#### 4.4 MEASURING pH

pH can be measured using an ion-sensitive *glass electrode*, a reference electrode and a pH meter which is a *millivoltmeter* (i.e. it measures very, very small voltages). Figure 2 shows a schematic of this arrangement. When there is a difference of pH between the solution inside and outside the bulb of the glass electrode, an electric *potential* develops across the glass membrane. The potential arises because of *ion exchange* between ions in the glass and  $H^+$  ions in the solution. This can only be measured relative to another potential and a calomel reference electrode containing a mixture of

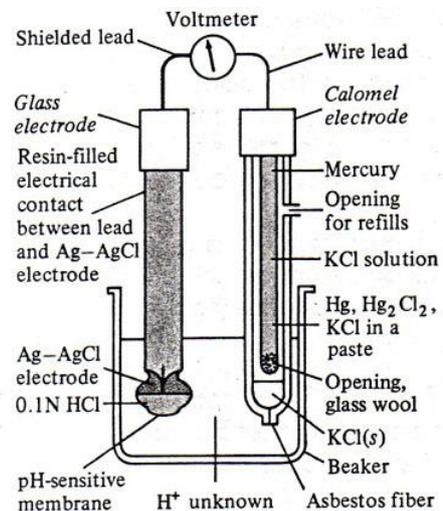


Figure 2. pH meter schematic.

mercury (Hg), mercurous chloride ( $\text{Hg}_2\text{Cl}_2$ , or 'calomel') and potassium chloride (KCl) is normally used. The potential difference between the electrodes is detected as a very small voltage which varies *linearly* with the pH of the solution. The meter is calibrated to give a pH reading. The two electrode half-cells are often manufactured as a single *combination* electrode (Figure 3).

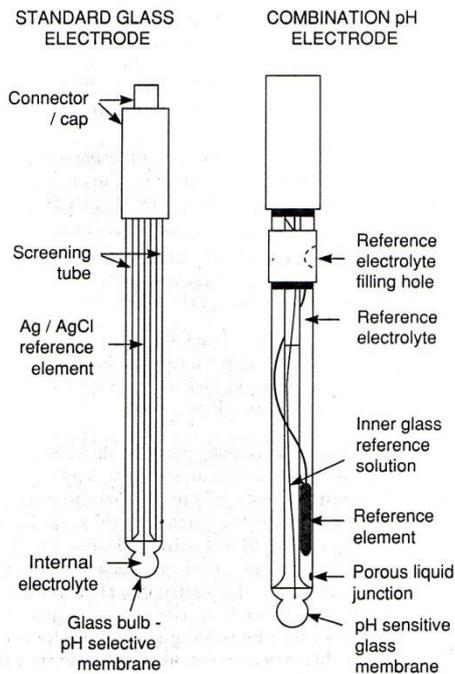


Figure 3. Standard and combination pH electrode.

The ion-sensitive half-cell includes a **buffer solution** with a fixed pH and ionic strength. A wire coated with silver chloride (AgCl) is immersed inside this internal solution, and establishes electrical contact between the solution and the meter. The voltage associated with this wire and the voltage associated with the pH of the internal solution and the inside wall of the  $\text{H}^+$  sensitive glass tip remain constant. Therefore changes in voltage from this electrode arise from the voltage developed between the solution and the outside of the glass tip. The wire dipping into the reference half-cell makes contact with the pH meter and current flows from the reference half-cell back to the test solution. Diffusion of KCl through the orifice of the reference half-cell makes contact with the test solution and completes the circuit. The potential of the reference electrode does not depend on pH and is assumed to be constant.

Since potentials in general are independent of the physical size of the electrodes, the electrode can be made quite small so that very small volumes of solution can be measured. Moreover, very small pH meters (so-called 'pocket' meters) are possible and have been introduced for field use.

Ambient temperature also affects the pH of a solution. At  $100^\circ\text{C}$  the pH of pure water is 6.0 and at  $0^\circ\text{C}$  is 7.5. The factory default setting on most pH meters is  $25^\circ\text{C}$ . If the test solution is not  $25^\circ\text{C}$  a temperature compensated probe (ATC) is required for accurate results. Some pH meters come with a separate probe, while others accept electrodes with a built-in ATC probe. Both Orion **290A** portable and **pHep** pocket pH testers have built-in temperature compensation (Figure 4). Check the manufacturer's spec sheet on temperature compensation if in doubt.

pH meters must be calibrated before use. The ability to calibrate a pH meter permits the meter to match the millivolt reading on the meter with the known pH value of a buffer solution, and display this millivolt reading as a pH value that we can interpret (we can't very well interpret millivolt readings!). For best accuracy, at least two buffer solutions bracketing the expected pH of the unknown test solution are required. A mathematical function is derived relating change in millivolts per unit change in pH. The *slope* of the function indicates how close the relationship is between expected voltage at the buffer pH and actual voltage. On pocket meters, slope output may not be noted visually. Laboratory grade pH meters may have a manual slope adjustment knob or automatic reading which is displayed after calibration. Most accurate readings of pH are obtained when the electrode slope is between 92-102%. Readings from an electrode operating outside these limits may be erroneous, although the electrode will continue to work.



Figure 4. Portable meters like the one shown here are invaluable for on-the-spot soil chemical properties determination.

Trouble shooting pH meters is beyond the scope of this technical note. However, most problems with pH meters are electrode-related. Failure of pH readings to stabilize usually means a mal-functioning electrode. The electrode should be inspected, the level of the reference solution checked, and the electrode cleaned thoroughly with distilled water. If the readings still don't stabilize, replace the electrode.

#### 4.5 KEY WORDS

**Anion:** A negatively charged ion, formed by addition of electrons to atoms or molecules. Denoted by a negative sign (-). The valence is indicated by a whole number either before or after the negative sign. For example,  $\text{NO}_3^-$  (nitrate ion) has a valence of 1;  $\text{SO}_4^{2-}$  (sulfate ion) has a valence of 2.

**Buffer Solution:** A solution that is formulated to resist change in pH.

**Cation:** A positively charged ion, formed by loss of electrons from atoms or molecules. Denoted by a positive (+) sign. The valence of a cation is indicated by a whole number either before or after the positive sign. For example,  $\text{Ca}^{+2}$  (calcium ion) has a valence of 2.

**Concentration:** The amount of a substance per unit volume in a solution.

**Dissociate:** The breakdown of one molecule into two molecules, atoms, radicals, or ions. The reaction is often reversible. A reversible chemical reaction is denoted by arrows pointing in two directions ( $\rightleftharpoons$ ).

**Electron:** An atomic particle of negative charge and negligible mass. Electrons are present in all atoms in shells, or orbits, around the nucleus.

**Electrode:** A solid electric conductor through which an electric current enters or leaves a medium such as an electrolyte, a non-metallic solid, a molten metal, a gas, or a vacuum.

**Equilibrium constant:** The equilibrium concentration of reactants and products in a reversible reaction. Given by the equation  $K = \frac{[R]^r [S]^s}{[A]^a [B]^b}$  where  $[R]$   $[S]$  and  $[A]$   $[B]$  is the product of the concentration in moles per liter of the products and reactants, respectively and raised to the power equal to their stoichiometric coefficients. Equilibrium constants are single values but may increase or decrease with changes in temperature and pressure.

**Humus:** The fraction of the soil organic matter remaining after the major portion of added residues has decomposed. Usually amorphous and dark colored.

**Hydrolyze:** A reaction between a compound and water in which the water molecule is split.

**Ion:** Atoms or groups of atoms that are electrically charged as a result of the loss of electrons (cations) or the gain of electrons (anions).

**Ion Exchange:** A process that takes place in certain soil solids such as clays and organic matter, which contain ions capable of exchanging with ions in the surrounding solution.

**Linear:** Directly proportional. For example, if height and weight were directly proportional, for every one inch increase in height there would be one pound increase in weight (or some other proportional unit).

**Mineralization:** The conversion of an element from an organic form to an inorganic form as a result of microbial decomposition.

**Moles per liter:** unit of concentration of a substance equal to the gram molecular weight of that substance dissolved in one liter of water. A centimole (cmol) is  $1/100^{\text{th}}$  of a mole and, when speaking of atoms in ionic state, is numerically equivalent to the older unit milliequivalent per liter (meq).

**Potential:** The energy of a particle or system of particles derived from position, rather than motion, with respect to a specified datum in a field of force.

**Proton:** A positively charged elementary particle found in the nucleus of an atom.

**Sesquioxide:** A term for minerals containing 1.5 atoms of oxygen per atom of metal. Aluminum and iron are common metal constituents of sesquioxides.

**Soil colloids:** A very finely divided particle forming a stable dispersed phase when dissolved in another continuous medium. Clay and organic matter are the colloidal fraction of the solid phase of soil. When clay is dispersed in water, it forms a stable suspension that does not settle out quickly.

**Solute:** A material that is dissolved in a solvent to form a solution. Table salt (NaCl) is the solute when it is dissolved in water (the solvent) to form a salt solution.

**Solution:** A liquid system of two or more substances that are intimately dispersed within each other at the molecular level.

**Titrate:** To find the concentration of an unknown substance by adding a known volume of another substance of known concentration until the equivalence point or end point of the titration is reached. Indicator dyes that change colors are used to determine the end point.

## FURTHER READING

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## PREPARED BY:

Robert Walters  
Department of Soil Science  
North Carolina State University  
101 Derieux St. CB 7619  
Raleigh, NC 27695

Email: waltersrobt@gmail.com