



22

chapter

pH and Titratable Acidity

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22.1 INTRODUCTION

There are two interrelated concepts in food analysis that deal with acidity: **pH** and **titratable acidity**. Each of these quantities is analytically determined in separate ways, and each provides its own particular insights on food quality.

Titratable acidity (also called **total acidity**) measures the **total acid concentration** in a food. This quantity is determined by exhaustive titration of intrinsic acids with a standard base. Titratable acidity is a better predictor of acid's impact on flavor than pH. However, total acidity does not give all relevant information on a food. For instance, the ability of a microorganism to grow in a specific food is more dependent on the concentration of free hydronium ions, H_3O^+ , than titratable acidity. In aqueous solution, these hydronium ions arise from the combination of water with hydrogen ions (H^+) dissociated from acids. The need to quantify only the free H_3O^+ concentration leads to the second major concept of acidity, that being pH (also called active acidity and discussed in Sect. 22.3). pH is defined as the negative log (base 10) of the hydrogen ion concentration and can span a range of 14 orders of magnitudes. In foods, it is not only a function of the type and concentrations of acids present, but also of the concentration of ionized acid counterparts (their conjugated bases). If present in similar amounts, the system can be described as a buffer (see Sect. 22.4.2.1 and Chap. 2 in Food Analysis laboratory manual).

For general and food-specific information on measuring pH and titratable acidity, see Refs. [1–16]. For the pH and titratable acidity of select foods, see Ref. [10].

22.2 CALCULATION AND CONVERSION FOR NEUTRALIZATION REACTIONS

22.2.1 Concentration Units

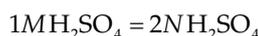
This chapter deals with the theory and practical application of titratable acidity calculation and pH determination. To quantitatively measure components of foods, solutions must be prepared to accurate concentrations and diluted into the desired working range (see Food Analysis Laboratory Manual, Chap. 3, Dilutions and Concentrations).

The common terms used for concentration in food analysis should be reviewed (see Food Analysis Laboratory Manual, Chap. 2, Preparation of Reagents and Buffers, Table 2.1). Molarity (M) and normality (N) are the most common SI (International Scientific) terms used in food analysis, but solutions also can be expressed as percentages. It is important that the analyst be able to convert between both systems.

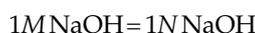
Molarity (M) is a concentration unit representing the number of moles of the solute per liter of solution.

Normality (N) is a concentration unit representing the number of equivalents (Eq) of a solute per liter of solution. In acid and base solutions, the normality represents the concentration or moles of H^+ or OH^- per liter that will be exchanged in a neutralization reaction when taken to completion. For oxidation-reduction reagents, the normality represents the concentration or moles of electrons per liter to be exchanged when the reaction is taken to completion. The following are some examples of molarity vs. normality (equivalents):

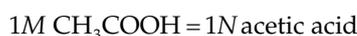
Acid-Base Reactions:



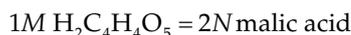
Two equivalents of H^+ per mol of acid



One equivalent of OH^- per mol of base

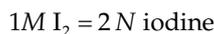
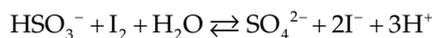


One equivalent of H^+ per mol of acid

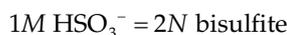


Two equivalents of H^+ per mol of acid

Oxidation-Reduction Reactions:



Two equivalents of electrons gained per mol of I_2



Two equivalents of electrons lost per mol of bisulfite

Many analytical determinations in food analysis use the concept of equivalents to measure the normality or equivalency of an unknown solution. Such tests use the stoichiometry or the whole number ratios of atoms that react to produce a particular product. Perhaps the most familiar of these is **acid-base reactions** in which hydrogen ions are exchanged and can be quantified through stoichiometric neutralization with a standard base. Examples for food analyses that use acid-base titration include nitrogen in the Kjeldahl protein determination (see Chap. 18, Sect. 18.2.1.3.4), benzoic acid in sodas, and determining percent titratable acidity. The concept of equivalents also is used in oxidation-reduction problems to quantify unknown analytes that are capable of direct electron transfer.

Equivalent weight can be defined as the molecular weight divided by the number of equivalents in the reactions. For example, the molecular weight of H_2SO_4 is 98.08 g. Since there are two equivalents per

22.1

table

Molecular and equivalent weights of common food acids

Acid	Chemical formula	Molecular weight	Equivalents per mole	Equivalent weight
Citric (anhydrous)	H ₃ C ₆ H ₅ O ₇	192.12	3	64.04
Citric (hydrous)	H ₃ C ₆ H ₅ O ₇ •H ₂ O	210.14	3	70.05
Acetic	HC ₂ H ₃ O ₂	60.06	1	60.05
Lactic	HC ₃ H ₅ O ₃	90.08	1	90.08
Malic	H ₂ C ₄ H ₄ O ₅	134.09	2	67.05
Oxalic	H ₂ C ₂ O ₄	90.04	2	45.02
Tartaric	H ₂ C ₄ H ₄ O ₆	150.09	2	75.05
Ascorbic	H ₂ C ₆ H ₆ O ₆	176.12	2	88.06
Hydrochloric	HCl	36.47	1	36.47
Sulfuric	H ₂ SO ₄	98.08	2	49.04
Phosphoric	H ₃ PO ₄	98.00	3	32.67
Potassium acid phthalate	KHC ₈ H ₄ O ₄	204.22	1	204.22

mole of H₂SO₄, the equivalent weight of H₂SO₄ is 49.04 g. Table 22.1 provides a list of molecular and equivalent weights for acids important in food analysis. In working with normality and milliliters, the term **milliequivalents** (mEq) is usually preferred. Milliequivalent weight is the equivalent weight divided by 1,000.

Percentage concentrations are the mass amount of solute or analyte per 100 mL or 100 g of material. Unlike molarity, normality, and equivalents, percent concentrations neither require nor provide insight into the stoichiometry of a reaction. Percentage can be expressed as volume of solution or for weight of solids and can be on a volume basis (v) or mass basis (w). Therefore the particular basis is normally stated. For example, 10% (w/v), 10% (v/v), and 10% (w/w) express different concentrations in all cases for which the specific gravities of the two components are not the same. When the percentage becomes a number less than 1%, **parts per million** (ppm), **parts per billion** (ppb), and even **parts per trillion** (ppt) usually are preferred. If percentage is defined as the mass of the solute or analyte per mass (or volume) of sample × 100, then ppm is simply the same ratio of mass of solute per mass of sample × 1,000,000 (see Food Analysis Laboratory Manual, Chap. 2, Table 2.2).

22.2.2 Equation for Neutralization and Dilution

There are some general rules in evaluating equilibrium reactions that are helpful in most situations. At full neutralization the equivalents of one reactant in the neutralization equal the equivalents of the other reactant. This can be expressed mathematically as:

$$(\text{vol of } X)(N \text{ of } X) = (\text{vol of } Y)(N \text{ of } Y) \quad (22.1)$$

Equation 22.1 also can be used to solve dilution problems where X represents the stock solution and Y rep-

resents the working solution. When Eq. 22.1 is used for dilution problems, any value of concentration (grams, moles, ppm, etc.) can be substituted for N. Units should be recorded with each number since cancellation of units provides a quick check on proper setup of the problem. (See Food Analysis Laboratory Manual, Chap. 2, Practice Problems 1–11.)

22.3 pH

22.3.1 Acid-Base Equilibria

The Brønsted-Lowry theory of neutralization is based upon the following definitions for acid and base:

Acid: A substance capable of donating protons. In food systems the only significant proton donor is the hydronium ion.

Base: A substance capable of accepting protons.

Neutralization is the reaction of an acid with a base to form a salt as shown below:



Acids form hydrated protons called **hydronium ions** (H₃O⁺), and bases form **hydroxide ions** (OH⁻) in aqueous solutions:



At any temperature, the product of the molar concentrations (moles/liter) of H₃O⁺ (note: molar concentrations are commonly signified by brackets) and OH⁻ is a constant referred to as the **ion product constant for water** (K_w):

$$[\text{H}_3\text{O}^+][\text{OH}^-] = K_w \quad (22.4)$$

K_w varies with the temperature. For example, at 25 °C, K_w = 1.04 × 10⁻¹⁴ but at 100 °C, K_w = 58.2 × 10⁻¹⁴.

The above concept of K_w leads to the question of what the $[\text{H}_3\text{O}^+]$ and $[\text{OH}^-]$ are in pure water. Experimentation has revealed that the $[\text{H}_3\text{O}^+]$ is approximately $1.0 \times 10^{-7} \text{ M}$, as is that of the $[\text{OH}^-]$ at 25 °C. Because the concentrations of these ions are equal, pure water is referred to as being **neutral**.

Suppose that a drop of acid is added to pure water. The $[\text{H}_3\text{O}^+]$ would increase. However, K_w would remain constant (1.0×10^{-14}), revealing a decrease in the $[\text{OH}^-]$. Conversely, if a drop of base is added to pure water, the $[\text{H}_3\text{O}^+]$ would decrease, while the $[\text{OH}^-]$ would increase, maintaining the K_w at 1.0×10^{-14} at 25 °C.

How did the term pH derive from the above considerations? In approaching the answer to this question, one must observe $[\text{H}_3\text{O}^+]$ and $[\text{OH}^-]$ in various foods, as shown in Table 22.2. The numerical values found in Table 22.2 for $[\text{H}_3\text{O}^+]$ and $[\text{OH}^-]$ are bulky and led a Swedish chemist, S.L.P. Sørensen, to develop the pH system in 1909.

pH is defined as the logarithm of the reciprocal of the hydrogen ion concentration, which is equal to the negative logarithm of the molar concentration of hydrogen ions.

$$\text{pH} = -\log[\text{H}^+] \quad (22.5)$$

Thus, a $[\text{H}_3\text{O}^+]$ of 1×10^{-6} is expressed simply as pH 6. The $[\text{OH}^-]$ is expressed as pOH and would be pOH 8 in this case, as shown in Table 22.3.

Calculation of $[\text{H}^+]$ of a beer with pH 4.30:

Step 1. Substitute numbers into the pH equation:

$$\begin{aligned} \text{pH} &= -\log[\text{H}^+] \\ 4.30 &= -\log[\text{H}^+] \\ -4.30 &= \log[\text{H}^+] \\ -4.30 &= 0.70 - 5 = \log[\text{H}^+] \end{aligned}$$

Step 2. Calculate the antilog of -4.30 : $[\text{H}^+] = 5.01 \times 10^{-5} \text{ M}$

22.2 table

Concentrations of H_3O^+ and OH^- in various foods at 25 °C

Food	$[\text{H}_3\text{O}^+]^a$	$[\text{OH}^-]^a$	K_w
Cola	2.24×10^{-3}	4.66×10^{-12}	1×10^{-14}
Grape juice	5.62×10^{-4}	1.78×10^{-11}	1×10^{-14}
Seven-Up	3.55×10^{-4}	2.82×10^{-11}	1×10^{-14}
Schlitz beer	7.95×10^{-5}	1.26×10^{-10}	1×10^{-14}
Pure water	1.00×10^{-7}	1.00×10^{-7}	1×10^{-14}
Tap water	4.78×10^{-9}	2.09×10^{-6}	1×10^{-14}
Milk of magnesia	7.94×10^{-11}	1.26×10^{-4}	1×10^{-14}

From Pecsok et al. [14], used with permission. Copyright 1971 American Chemical Society

^aMoles per liter

22.3 table

Relationship of $[\text{H}^+]$ vs. pH and $[\text{OH}^-]$ vs. pOH at 25 °C

$[\text{H}^+]^a$	pH	$[\text{OH}^-]^a$	pOH
1×10^0	0	1×10^{-14}	14
10^{-1}	1	10^{-13}	13
10^{-2}	2	10^{-12}	12
10^{-3}	3	10^{-11}	11
10^{-4}	4	10^{-10}	10
10^{-5}	5	10^{-9}	9
10^{-6}	6	10^{-8}	8
10^{-7}	7	10^{-7}	7
10^{-8}	8	10^{-6}	6
10^{-9}	9	10^{-5}	5
10^{-10}	10	10^{-4}	4
10^{-11}	11	10^{-3}	3
10^{-12}	12	10^{-2}	2
10^{-13}	13	10^{-1}	1
10^{-14}	14	10^0	0

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^aMoles per liter. Note that the product of $[\text{H}^+][\text{OH}^-]$ is always 1×10^{-14}

While the use of pH notation is simpler from the numerical standpoint, it is a confusing concept in the minds of many students. One must remember that it is a logarithmic value and that a change in 1 pH unit is actually a tenfold change in the $[\text{H}_3\text{O}^+]$.

It is important to understand that pH and titratable acidity are not the same. Strong acids such as hydrochloric, sulfuric, and nitric acids are almost fully dissociated at pH 1. Only a small percentage of food acid molecules (citric, malic, acetic, tartaric, etc.) dissociate in solution. This point may be illustrated by comparing the pH of 0.1 N solutions of hydrochloric and acetic acid.



The HCl almost fully dissociates in solution to produce a pH of 1.02 at 25 °C. By contrast, only about 1% of CH_3COOH is ionized at 25 °C, producing a significantly higher pH of 2.89. The calculation and significance of partial dissociation on pH is presented in more detail in Sect. 22.4.2.1.

22.3.2 pH Meter

22.3.2.1 Activity Versus Concentration

In using pH electrodes, the concept of activity vs. concentration must be considered. **Activity** is a measure of expressed chemical reactivity, while **concentration** is a measure of all forms (free and bound) of ions in solution. Because of the interactions of ions between themselves and with the solvent, the effective concentration or activity is, in general, lower than the actual concentration, although activity and concentration

tend to approach each other at infinite dilution. Activity and concentration are related by the following equation:

$$A = \gamma C \quad (22.8)$$

where:

A = activity
 γ = activity coefficient
 C = concentration

The **activity coefficient** is a function of ionic strength. Ionic strength is a function of the concentration of, and the charge on, all ions in solution. Activity issues can become significant for hydronium ions below pH 1 and for hydroxyl ions at pH 13 and above. While such extreme pH values are not commonly encountered in food science, ionic strengths may be high, and thus different calculations would need to be used (refer to relevant literature, e.g., Ref. [1]).

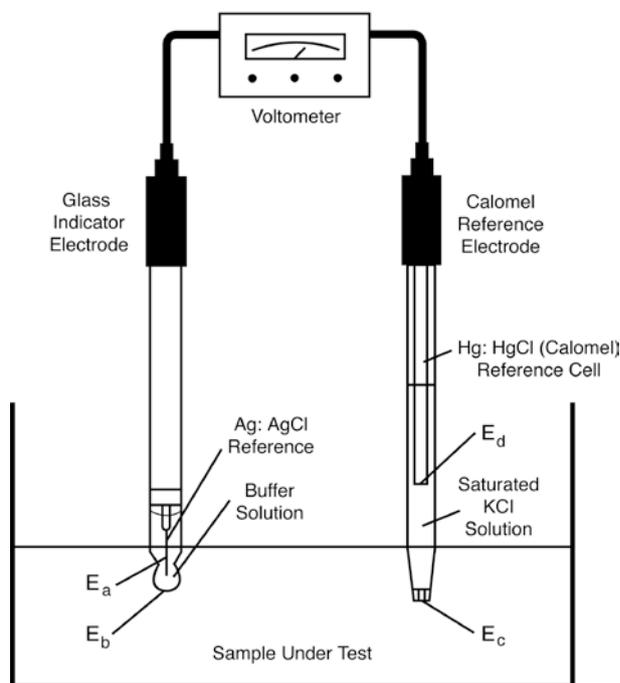
22.3.2.2 General Principles

The pH meter is a good example of a **potentiometer** (a device that measures voltage at infinitesimal current flow). The basic principle of **potentiometry** (an electrochemical method of voltammetry at zero current) involves the use of an electrolytic cell composed of two electrodes immersed into a test solution. A voltage develops, which is related to the ionic concentration of the solution. Since the presence of current could alter the concentration of surrounding ions or produce irreversible reactions, this voltage is measured under conditions such that infinitesimal current (10^{-12} amperes or less) is drawn.

Four major parts of the pH system are needed: (1) reference electrode, (2) indicator electrode (pH sensitive), (3) voltmeter or amplifier that is capable of measuring small voltage differences in a circuit of very high resistance, and (4) the sample being analyzed (Fig. 22.1). For convenience most contemporary pH electrodes combine the reference electrode and indicator electrode in a common housing (see Sect. 22.3.2.5).

Each of the two electrodes involved in the measurement is designed carefully to produce a constant, reproducible potential. Therefore, in the absence of other ions, the potential difference between the two electrodes is fixed and easily calculated. However, H_3O^+ ions in solution contribute a new potential across an ion-selective glass membrane built into the indicating electrode. This alters the potential difference between the two electrodes in a way that is proportional to H_3O^+ concentration. The new potential resulting from the combination of all individual potentials is called the **electrode potential** and is readily convertible into pH readings.

Hydrogen ion concentration (or more accurately, activity) is determined by the voltage that develops



22.1
figure

The measuring circuit of the potentiometric system. E_a , contact potential between Ag/AgCl electrode and inner liquid. E_a is independent of pH of the test solution but is temperature dependent. E_b , potential developed at the pH-sensitive glass membrane. E_b varies with the pH of the test solution and also with temperature. In addition to this potential, the glass electrode also develops an asymmetry potential, which depends upon the composition and shape of the glass membrane. It also changes as the electrode ages. E_c , diffusion potential between saturated KCl solution and test sample. E_c is essentially independent of the solution under test. E_d , contact potential between calomel portion of electrode and KCl salt bridge. E_d is independent of the solution under test but is temperature dependent (From Bergveld et al. [4], used with permission)

between the two electrodes. The **Nernst equation** relates the electrode response to the activity where:

$$E = E_o + 2.303 \frac{RT}{zF} \log A \quad (22.9)$$

where:

E = measured electrode potential
 E_o = standard electrode potential, a constant representing the sum of the individual potentials in the system at a standard temperature, ion concentration, and electrode composition

R = universal gas constant, $8.313 \left(\frac{J}{\text{mol K}} \right)$

F = Faraday constant, 96,490 coulombs (C) per mole $\left(\frac{C}{\text{mol}} \right)$

T = absolute temperature in Kelvin (K)

Z = number of charges on the ion

A = activity of the ion being measured

For monovalent ions (such as the hydronium ion) at 25 °C, the relationship of $2.303 RT/F$ is calculated to be 0.0591, as follows:

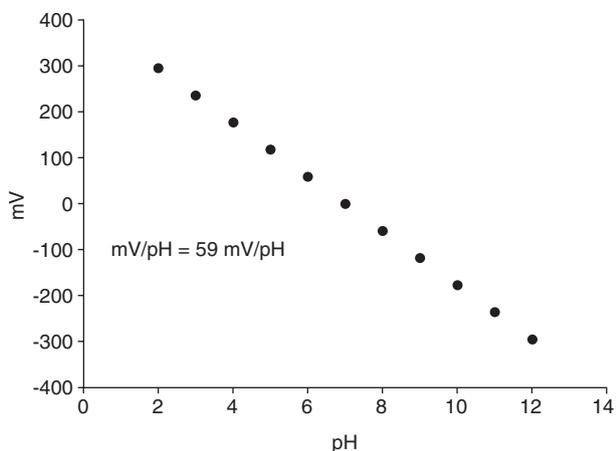
$$\frac{2.303 \times 8.316 \times 298}{96490} = 0.0591 \quad (22.10)$$

Thus, at 25 °C voltage produced by the electrode system is a linear function of the pH, the electrode potential being essentially +59 mV (0.059 V) for each change of 1 pH unit. At neutrality (pH 7), the electrode potential is 0 mV. At pH 6, the electrode potential is +59 mV, while at pH 4, the electrode potential is +177 mV. Conversely, at pH 8, the electrode potential is -59 mV (Fig. 22.2).

It must be emphasized that the above relationship between millivolts and pH exists only at 25 °C, and changes in temperature will alter the pH reading in accordance with Eq. 22.8. For example, at 0 °C, the electrode potential is 54 mV, while at 100 °C, it is 70 mV. Modern pH meters have a sensitive attenuator (temperature compensator) built into them in order to account for this effect of temperature.

22.3.2.3 Reference Electrode

The **reference electrode** is needed to complete the circuit in the pH system. This half-cell is one of the most troublesome parts of the pH meter. Problems in

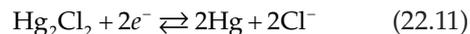


22.2
figure

Relationship between mV and pH for a monoprotic acid at 25 °C

obtaining pH measurements are often traced to a faulty reference electrode.

The **saturated calomel electrode** (Fig. 22.1) is the most common reference electrode. It is based upon the following reversible reaction:



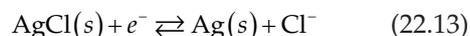
The $E_{0,25^\circ\text{C}}$ for the saturated KCl salt bridge is +0.2444 V vs. a standard hydrogen electrode; the Nernst equation for the reaction is as follows:

$$E = E_0 - 0.059 / 2 \log [\text{Cl}^-]^2 \quad (22.12)$$

Thus, one observes that the potential is dependent upon the chloride ion concentration, which is easily regulated by the use of saturated KCl solution in the electrode.

A calomel reference electrode has three principal parts: (1) a platinum wire covered with a mixture of calomel (Hg_2Cl_2), (2) a filling solution (saturated KCl), and (3) a permeable junction through which the filling solution slowly migrates into the sample being measured. Junctions are made of ceramic or fibrous material. These junctions tend to clog up, causing a slow, unstable response and inaccurate results.

A less widely used reference electrode is the **silver-silver chloride electrode**. Because the calomel electrode is unstable at high temperatures (80 °C) or in strongly basic samples (pH >9), a silver-silver chloride electrode must be used for such application. It is a very reproducible electrode based upon the following reaction:



The internal element is a silver-coated platinum wire, the surface silver being converted to silver chloride by hydrolysis in hydrochloric acid. The filling solution is a mixture of 4M KCl, saturated with AgCl that is used to prevent the AgCl surface of the internal element from dissolving. The permeable junction is usually of the porous ceramic type. Because of the relative insolubility of AgCl, this electrode tends to clog more readily than the calomel reference electrode. More commonly, a double-junction electrode configuration is used in which a separate inner body holds the Ag/AgCl internal element electrolyte and ceramic junction (see Sect. 22.3.2.5). An outer body containing a second electrolyte and junction isolates the inner body from the sample.

22.3.2.4 Indicator Electrode

The **indicator electrode** most commonly used in measuring pH today is referred to as the **glass electrode**. Like the reference electrode, the indicator electrode (Fig. 22.1) also has three principal parts: (1) a silver-silver chloride electrode with a mercury connection that is needed as a lead to the potentiometer; (2) a

buffer solution consisting of 0.01 N HCl, 0.09 N KCl, and acetate buffer used to maintain a constant pH (E_a); and (3) a small pH-sensitive glass membrane for which the potential (E_o) varies with the pH of the test solution. In using the glass electrode as an indicator electrode in pH measurements, the measured potential (measured against the calomel electrode) is directly proportional to the pH as discussed earlier, $E = E_o - 0.059 \text{ pH}$.

Conventional glass electrodes are suitable for measuring pH in the range of pH 1–9. However, this electrode is sensitive to higher pH, especially in the presence of sodium ions. Thus, equipment manufacturers have developed modern glass electrodes that are usable over the entire pH range of 0–14 and feature a very low sodium ion error, such as <0.01 pH at 25 °C.

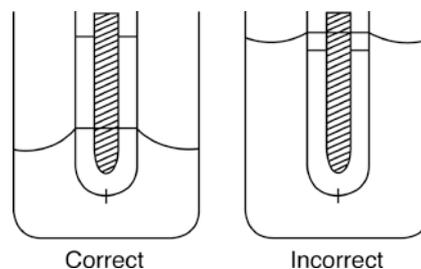
22.3.2.5 Combination Electrodes

Today, most food analysis laboratories use **combination electrodes** that combine both the pH and reference electrodes along with the temperature sensing probe in a single unit or probe. These combination electrodes are available in many sizes and shapes from very small microprobes to flat surface probes, from all glass to plastic, and from exposed electrode tip to jacketed electrode tips to prevent glass tip breakage. Microprobes may be used to measure pH of very small systems such as inside a cell or a solution on a microscope slide. Flat surface electrode probes can be used to measure pH of semisolid and high viscosity substances such as meat, cheese, and agar plates and small volumes as low as 10 μl .

22.3.2.6 Guidelines for Use of pH Meter

It is very important that the pH meter be operated and maintained properly. One should always follow the specific instructions provided by the manufacturer. For maximum accuracy, the meter should be standardized using at least two buffers (**two-point calibration**). Select two buffers of pH values about 3 pH units apart, bracketing that of the anticipated sample pH. The three standardization buffers used most widely in laboratories are a pH 4.0 buffer, a pH 7.0 buffer, and a pH 9.0 buffer (at 25 °C). These are the typical pink, yellow, and blue solutions found adjacent to pH meters in many laboratories.

When standardizing the pH electrode, follow manufacturer's instructions for **one-point calibration**; rinse thoroughly with distilled water and blot dry. Immerse electrode in the second buffer (e.g., pH 4) and perform a second standardization. This time, the pH meter slope control is used to adjust the reading to the correct value of the second buffer. Repeat these two steps, if necessary, until a value within 0.1 pH unit of the correct value of the second buffer is displayed. If this cannot be achieved, the instrument is not in good working condition. Electrodes should be checked,



22.3
figure

Correct and incorrect depth of calomel electrodes in solutions (Reprinted with permission from Pecsok et al. [14. Copyright 1971 American Chemical Society)

remembering that the reference electrode is more likely in need of attention. One should always follow the electrode manufacturer's specific directions for storage of a pH electrode. In this way, the pH meter is always ready to be used and the life of the electrodes is prolonged. One precaution that should be followed pertains to a calomel reference electrode. The storage solution level always should be at least 2 cm below the saturated KCl solution level in the electrode to prevent diffusion of storage solution into the electrode (Fig. 22.3).

22.4 TITRATABLE ACIDITY

22.4.1 Overview and Principle

The titratable acidity measures the total acid concentration in a food. Food acids are usually organic acids, with citric, malic, lactic, tartaric, and acetic acids being the most common. However, inorganic acids such as phosphoric and carbonic (arising from carbon dioxide in solution) acids often play an important and even predominant role in food acidulation. The organic acids present in foods influence the flavor (i.e., tartness), color (though their impact on anthocyanin and other pH-influenced pigments), microbial stability (via inherent pH-sensitivity characteristics of organisms), and keeping quality (arising from varying chemical sensitivities of food components to pH). The titratable acidity of fruits is used, along with sugar content, as an indicator of maturity (Sect. 22.4.6). While organic acids may be naturally present in the food, they also may be formed through fermentation, or they may be added as part of a specific food formulation.

Titratable acidity is determined by neutralizing the acid present in a known quantity (weight or volume) of food sample using a standard base. The endpoint for titration is usually either a target pH or the color change of a pH-sensitive dye, typically phenolphthalein. The volume of titrant used, along with the normality of the base and the volume (or weight)

of sample, is used to calculate the titratable acidity, expressed in terms of the predominant organic acid.

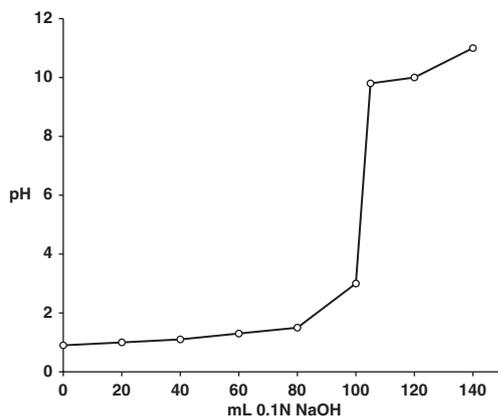
22.4.2 General Considerations

Many food properties correlate better with pH than with acid concentration. The pH is also used to determine the endpoint of an acid-base titration. The pH determination can be achieved directly with a pH meter, but more commonly using a pH-sensitive dye. In some cases, the way pH changes during titration can lead to subtle problems. Some background in acid theory is necessary to fully understand titration and to appreciate the occasional problems that might arise.

22.4.2.1 Buffering

Although pH can hypothetically range from -1 to 14 , pH readings below 1 are difficult to obtain due to incomplete dissociation of hydrogen ions at high acid concentrations. At $0.1N$, strong acids are assumed to be fully dissociated. Therefore, for titrations involving strong acids, fully dissociated acid is present at all titrant concentrations; the pH at any point in the titration is equal to the hydrogen ion concentration of the remaining acid (Fig. 22.4).

In contrast to strong acid titration, when weak acids are titrated with strong base, a mixture of this acid and its conjugated base is present in the system. This tends to cushion the solution from abrupt changes in pH. This property of a solution to resist change in pH is termed buffering. **Buffering** occurs in foods whenever a weak acid and its conjugated base are present in the same medium. Because of buffering, a graph of pH vs. titrant concentration is more complex for weak acids than strong acids. However, this



22.4
figure

Titration of a strong acid with strong base. The pH at any point in the titration is dictated by the hydrogen ion concentration of the acid remaining after partial neutralization with base

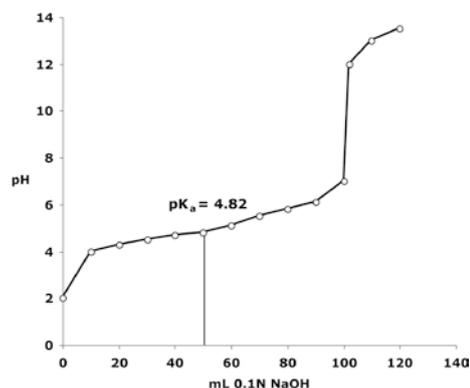
relationship can be estimated by the **Henderson-Hasselbalch equation**:

$$\text{pH} = \text{pK}_a + \log \frac{[A^-]}{[HA]} \quad (22.14)$$

[HA] represents the concentration of undissociated acid. $[A^-]$ represents the concentration of its **conjugated base**. The pK_a is the pH at which equal quantities of undissociated acid and conjugated base are present. The equation indicates that maximum buffering capacity will exist when the pH equals the pK_a . A graph showing the titration of $0.1N$ acetic acid with $0.1N$ NaOH illustrates this point (Fig. 22.5).

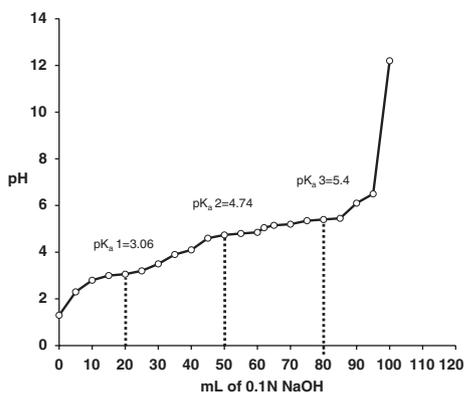
Di- and triprotic acids will have two and three buffering regions, respectively. A pH vs. titrant graph of citric acid is given in Fig. 22.6. If the pK_a steps in polyprotic acids differ by three or more pK_a units, then the Henderson-Hasselbalch equation can predict the plateau corresponding to each step. However, the transition region between steps is complicated by the presence of protons and conjugate bases arising from other dissociation state(s). Consequently, the Henderson-Hasselbalch equation breaks down near the equivalence point between two pK_a steps. However, the pH at the equivalence point is easily calculated. The pH is simply $(\text{pK}_{a1} + \text{pK}_{a2})/2$. Table 22.4 lists pK_a values of acids important in food analysis.

Precise prediction of pH by the Henderson-Hasselbalch equation requires that all components form ideal solutions. An approximation to ideal solutions occurs at infinite dilution for all active components. However, real solutions may not behave ideally. For such solutions, the Henderson-Hasselbalch equation may only provide a good estimate of pH. For more details about buffers, and for practice problems



22.5
figure

Titration of a weak monoprotic acid with a strong base. A buffering region is established around the pK_a (4.82). The pH at any point is described by the Henderson-Hasselbalch equation



22.6 figure

Titration of a weak polyprotic acid with a strong base. Buffering regions are established around each pK_a . The Henderson-Hasselbalch equation can predict the pH for each pK_a value if pK_a steps are separated by more than three units. However, complex transition mixtures between pK_a steps make simple calculations of transition pH values impossible

22.4 table

pK_a values for some acids important in food analysis^a

Acid	pK_{a1}	pK_{a2}	pK_{a3}
Oxalic	1.19	4.21	–
Phosphoric	2.12	7.21	12.30
Tartaric	3.02	4.54	–
Malic	3.40	5.05	–
Citric	3.06	4.74	5.40
Lactic	3.86	–	–
Ascorbic	4.10	11.79	–
Acetic	4.76	–	–
Potassium acid phthalate	5.40	–	–
Carbonic	6.10	10.25	–

^aNote that some values differ from those listed in Table 2.2 of the Food Analysis Laboratory Manual, Chap. 2. See that chapter for information on factors affecting dissociation constants

using the Henderson-Hasselbalch equation to prepare buffers and calculate pH, see the Food Analysis Laboratory Manual, Chap. 2.

22.4.2.2 Potentiometric Titration

At the **equivalence point** in a titration, the number of acid equivalents exactly equals the number of base equivalents, and total acid neutralization is achieved. As the equivalence point is approached, the denominator [HA] in the Henderson-Hasselbalch equation becomes insignificantly small, and the quotient $[A^-]/[HA]$ increases exponentially. As a result, the solution

pH rapidly increases and ultimately approaches the pH of the titrant. The exact equivalent point is the half-way mark on this slope of abrupt pH increase. The use of a pH meter to identify the endpoint is called the **potentiometric method** for determining titratable acidity. The advantage of determining the equivalence point potentiometrically is that the precise equivalence point is identified. Since a rapid change in pH (and not some final pH value per se) signals the end of titration, accurate calibration of the pH meter is not even essential. However, in order to identify the equivalence point, a careful record of pH vs. titrant must be kept. This and the physical constraints of pH probes and slow response with some electrodes make the potentiometric approach somewhat cumbersome.

22.4.2.3 Indicators

For simplicity in routine work, an indicator solution is often used to approximate the equivalence point. This approach tends to overshoot the equivalence point by a small amount. When indicators are used, the term **endpoint** or **colorimetric endpoint** is substituted for equivalence point. This emphasizes that the resulting values are approximate and dependent on the specific indicator. Phenolphthalein is the most common indicator for food use. It changes from clear to red in the pH region 8.0–9.6. Significant color change is usually present by pH 8.2. This pH is termed the **phenolphthalein endpoint**.

A review of pK_a values in Table 22.4 indicates that naturally occurring food acids do not buffer in the region of the phenolphthalein endpoint. However, phosphoric acid (used as an acidulant in some soft drinks) and carbonic acid (carbon dioxide in aqueous solution) do buffer at this pH. Consequently, taking the solution from the true equivalence point to the endpoint may require a large amount of titrant when quantifying these acids. Indistinct endpoints and erroneously large titration values may result. When these acids are titrated, potentiometric analysis is usually preferred. Interference by CO_2 can be removed by boiling the sample and titrating the remaining acidity to a phenolphthalein endpoint.

Deeply colored samples also present a problem for endpoint indicators. When colored solutions obscure the endpoint, a potentiometric method is normally used. For routine work, pH vs. titrant data are not plotted as shown in Figs. 22.5 and 22.6. Samples are simply titrated to pH 8.2 (the phenolphthalein endpoint). Even though this is a potentiometric method, the resulting value is an endpoint and not the true equivalence point, since it simply reflects the pH value for the conventional phenolphthalein endpoint which slightly overshoots the equivalence point.

A pH of 7 may seem to be a better target for a potentiometric endpoint than 8.2. This pH, after all, marks the

point of true neutrality on the pH scale. However, once all acid has been neutralized, the conjugate base remains. As a result, the pH at the equivalence point is often slightly greater than 7. Confusion also might arise if pH 7 was the target for colored samples and pH 8.2 was the target for noncolored samples.

Dilute acid solutions (e.g., vegetable extracts) require dilute solutions of standard base for optimal accuracy in titration. However, a significant volume of dilute alkali may be required to take a titration from the equivalence point to pH 8.2. Bromothymol blue is sometimes used as an alternative indicator in low-acid situations. It changes from yellow to blue in the pH range 6.0–7.6. The endpoint is usually a distinct green. However, endpoint identification is somewhat more subjective than the phenolphthalein endpoint.

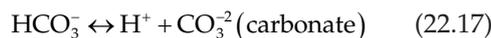
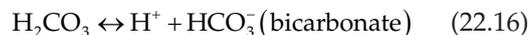
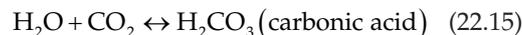
Indicator solutions rarely contain over a few tenths percent dye (w/v). All indicators are either weak acids or weak bases that tend to buffer in the region of their color change. If added too liberally, they can influence the titration by conferring their own buffering to the sample under analysis. Therefore, indicator solutions should be held to the minimum amount necessary to impart effective color. Typically, two to three drops of indicator are added to the solution to be titrated. The lower the indicator concentration, the sharper will be the endpoint.

22.4.3 Preparation of Reagents

22.4.3.1 Standard Alkali

Sodium hydroxide (NaOH) is the most commonly used base in titratable acidity determinations. In some ways, it appears to be a poor candidate for a **standard base**. Reagent grade NaOH is very hygroscopic and often contains significant quantities of insoluble sodium carbonate (Na_2CO_3). Consequently, the normality of working solutions is not precise, so each new batch of NaOH must be standardized against an acid of known normality. However, economy, availability, and long tradition of use for NaOH outweigh these shortcomings. Working solutions are normally made from a stock solution containing 50% sodium hydroxide in water (w/v). (See Food Analysis Laboratory Manual, Chap. 2, Preparation of Reagents and Buffers, and Chap. 21, Standard Solutions and Titratable Acidity.) Sodium carbonate is essentially insoluble in concentrated alkali and gradually precipitates out of solution over the first 10 days of storage.

The NaOH can react with dissolved and atmospheric CO_2 to produce new Na_2CO_3 . This reduces alkalinity and sets up a carbonate buffer that can obscure the true endpoint of a titration. Water and CO_2 alone can also react to form buffering compounds and generate hydrogen ions, as shown in the following equations:



Therefore, CO_2 should be removed from water prior to making the stock solution. This can be achieved by purging water with CO_2 -free gas for 24 h or by boiling distilled water for 20 min and allowing it to cool before use. During cooling and long-term storage, air (with accompanying CO_2) will be drawn back into the container. Carbon dioxide can be stripped from reentering air with a soda lime (20% NaOH, 65% CaO, 15% H_2O) or **ascarite trap** (NaOH-coated silica base). Air passed through these traps also can be used as purge gas to produce CO_2 -free water.

Stock alkali solution of 50% in water is approximately 18N. A working solution is made by diluting stock solution with **CO_2 -free water**. There is no ideal container for strong alkali solutions. Glass and plastic are both used, but each has its drawbacks. If a glass container is used, it should be closed with a rubber or thick plastic closure. Glass closures should be avoided since, over time, strong alkali dissolves glass, resulting in permanent fusion of the contact surfaces. Reaction with glass also lowers the normality of the alkali. These liabilities also are relevant to long-term storage of alkali in burettes. NaOH has a low surface tension. This predisposes to leakage around the stopcock. Stopcock leakage during titration will produce erroneously high acid values. Slow evaporation of titrating solution from the stopcock valve during long periods of nonuse also creates a localized region of high pH with ensuing opportunities for fusion between the stopcock and burette body. After periods of nonuse, burettes should be emptied, cleaned, and refilled with fresh working solution.

Long-term storage of alkali in plastic containers also requires special vigilance because CO_2 permeates freely through most common plastics. Despite this shortcoming, plastic containers are usually preferred for long-term storage of stock alkali solutions. Whether glass or plastic is used for storage, working solutions should be re-standardized weekly to correct for alkalinity losses arising from interactions with glass and CO_2 .

22.4.3.2 Standard Acid

The impurities and hygroscopic nature of NaOH make it unsuitable as a primary standard. Therefore, NaOH titrating solutions must be standardized against a **standard acid**. **Potassium acid phthalate (KHP)** is commonly used for this purpose.

KHP's single ionizable hydrogen ($\text{pK}_a = 5.4$) provides very little buffering at pH 8.2. It can be

manufactured in very pure form, it is relatively nonhygroscopic, and it can be dried at 120 °C without decomposition or volatilization. Its high molecular weight also favors accurate weighing.

KHP should be dried for 2 h at 120 °C and allowed to cool to room temperature in a desiccator immediately prior to use. An accurately measured quantity of KHP solution is titrated with a base of unknown normality. The base is always the titrant. CO₂ is relatively insoluble in acidic solutions. Consequently, stirring an acid sample to assist in mixing will not significantly alter the accuracy of the titration.

22.4.4 Sample Analysis

A number of official methods exist for determining titratable acidity in various foods [1]. However, determining titratable acidity on most samples is relatively routine, and various procedures share many common steps. An aliquot of sample (often 10 mL) is titrated with a standard alkali solution (often 0.1 N NaOH) to a phenolphthalein endpoint. Potentiometric endpoint determination is used when sample pigment makes use of a color indicator impractical.

Typical titration setups are illustrated in Fig. 22.7 for potentiometric and colorimetric endpoints. Erlenmeyer flasks are usually preferred for samples when endpoint indicators are used. A magnetic stirring bar may be used, but mixing the sample with hand swirling is usually adequate. When hand mixing is used, the sample flask is swirled with the right hand. The stopcock is positioned on the right side. Four fingers on the left hand are placed behind the stopcock

valve and the thumb is placed on the front of the valve. Titrant is dispensed at a slow, uniform rate until the endpoint is approached and then added dropwise until the endpoint does not fade after standing for some predetermined period of time, usually 5–10 s.

The bulkiness of the pH electrode usually demands that beakers be used instead of Erlenmeyer flasks when samples are analyzed potentiometrically. Mixing is almost always achieved through magnetic stirring, and loss of sample through splashing is more likely with beakers than Erlenmeyer flasks. Otherwise, titration practices are identical to those described previously for colorimetric endpoint titrations.

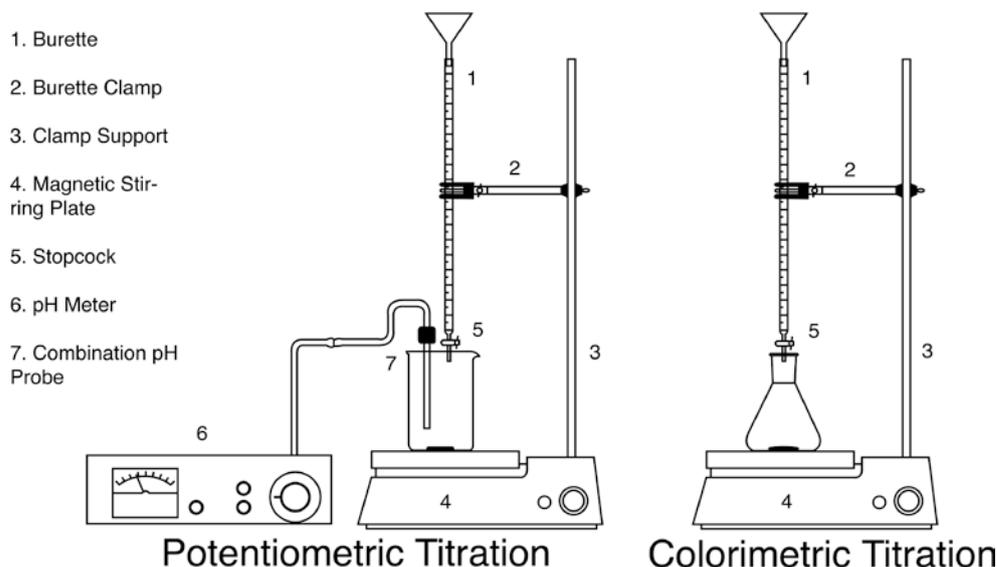
Problems may arise when concentrates, gels, or particulate-containing samples are titrated. These matrices prevent rapid diffusion of acid from densely packed portions of sample material. This slow diffusion process results in a fading endpoint. Concentrates can simply be diluted with CO₂-free water. Titration then is performed and the original acid content calculated from dilution data. Starch and similar weak gels often can be mixed with CO₂-free water, stirred vigorously, and titrated in a manner similar to concentrates. However, some pectin and food gum gels require mixing in a blender to adequately disrupt the gel matrix. Thick foams are occasionally formed in mixing. Antifoam or vacuum can be used to break the foams.

Immediately following processing, the pH values of particulate samples often vary from one particulate piece to another. Acid equilibration throughout the entire mass may require several months. As a result, particulate-containing foods should be liquified in a

22.7 figure

Titratable
acidity
apparatus

Titratable Acidity Apparatus



blender before titrating. The comminuting process may incorporate large quantities of air. Air entrapment makes the accuracy of volumetric measurements questionable. Aliquots often are weighed when air incorporation may be a problem.

22.4.5 Calculation of Titratable Acidity

In general chemistry, acid strength is frequently reported in normality (equivalents per liter) and can be calculated using Eq. 22.1. However, food acids are usually reported as percent of total sample weight. Thus, the equation for titratable acidity is as follows:

$$\% \text{ acid (wt / wt)} = \frac{N \times V \times \text{Eq wt}}{W \times 1000} \times 100 \quad (22.18)$$

where:

N = normality of titrant, usually NaOH (mEq/mL)

V = volume of titrant (mL)

Eq. wt. = equivalent weight of predominant acid (mg/mEq)

W = mass of sample (g)

1,000 = factor relating mg to grams (mg/g)
(1/10 = 100/1,000)

Note that the normality of the titrant is expressed in milliequivalents (mEq) per mL, which is a typical way of reporting normality for small volumes. This value is numerically the same as equivalents/liter. Also note that it is easier to report sample mass in grams instead of milligrams, so multiplying sample mass by the factor of 1,000 mg/g allows units to cancel.

For routine titration of fruit juices, milliliters can be substituted for sample weight in grams, as shown in Eqs. 21.18 and 22.19. Depending on the soluble solids content of the juice, the resulting acid values will be high by 1–6%. However, this is common practice:

$$\% \text{ acid (wt / vol)} = \frac{N \times V_1 \times \text{Eq wt}}{V_2 \times 1000} \times 100 \quad (22.19)$$

or

$$\% \text{ acid (wt / vol)} = \frac{N \times V_1 \times \text{Eq wt}}{V_2 \times 10} \quad (22.20)$$

where:

N = normality of titrant, usually NaOH (mEq/mL)

V_1 = volume of titrant (mL)

Eq. wt. = equivalent weight of predominant acid (mg/mEq)

V_2 = volume of sample (mL)

1,000 = factor relating mg to grams (mg/g)
(1/10 = 100/1,000)

For example, if it takes 17.5 mL of 0.085N NaOH to titrate a 15-mL sample of a juice, the total titratable acidity of that juice, expressed as percent citric acid (molecular weight = 192; equivalent weight = 64), would be 0.635%, wt/vol, citric acid:

$$\% \text{ acid (wt / vol)} = \frac{0.085 \times 17.5 \times 64}{15 \times 10} = 0.635\% \quad (22.21)$$

Notice that the equivalent weight of anhydrous (vs. hydrous) citric acid always is used in calculating and reporting the results of titration.

22.4.6 Acid Content in Food

Most foods are as chemically complex as life itself. As such, they contain the full complement of Krebs cycle acids (and their derivatives), fatty acids, and amino acids. Theoretically, all of these contribute to titratable acidity. Routine titration cannot differentiate between individual acids. Therefore, titratable acidity is usually stated in terms of the **predominant acid**. For most foods this is unambiguous. In some cases, two acids are present in large concentrations, and the predominant acid may change with maturity. In grapes, malic acid often predominates prior to maturity while tartaric acid typically predominates in the ripe fruit. A similar phenomenon is observed with malic and citric acids in pears. Fortunately, the equivalent weights of common food acids are fairly similar. Therefore, percent titratable acidity is not substantially affected by mixed predominance or incorrect selection of the predominant acid.

The range of acid concentrations in foods is very broad. Acids can exist at levels below detection limits or they can be the preeminent substance present in the food. The contribution of acids to food flavor and quality is not told by acid content alone. The tartness of acids is reduced by sugars. Consequently, the **Brix/acid ratio** (often simply called ratio) is usually a better predictor of an acid's flavor impact than Brix (i.e., percent sugar (w/w) in a medium; see Chap. 15, Sect. 15.2.5.3) or acid alone. Acids tend to decrease with the maturity of fruit while sugar content increases. Therefore, the Brix/acid ratio is often used as an index of fruit maturity. For mature fruit, this ratio also can be affected by climate, variety, and horticultural practices. Table 22.5 gives typical acid composition and sugar levels for many commercially important fruits at maturity. Citric and malic acids are the most common acids in fruits and most vegetables; however, leafy vegetables also may contain significant quantities of oxalic acid. Lactic acid is the most important acid in dairy foods for which titratable acidity is commonly used to monitor the progress of lactic acid fermentations in cheese and yogurt production [16].

Organic acids contribute to the refractometer reading of soluble solids. When foods are sold on the

22.5
 table

Acid composition and °Brix of some commercially important fruits

<i>Fruit</i>	<i>Principal acid</i>	<i>Typical percent acid</i>	<i>Typical °Brix</i>
Apples	Malic	0.27–1.02	9.12–13.5
Bananas	Malic/citric (3:1)	0.25	16.5–19.5
Cherries	Malic	0.47–1.86	13.4–18.0
Cranberries	Citric	0.9–1.36	12.9–14.2
	Malic	0.70–0.98	
Grapefruit	Citric	0.64–2.10	7–10
Grapes	Tartaric/malic (3:2)	0.84–1.16	13.3–14.4
Lemons	Citric	4.2–8.33	7.1–11.9
Limes	Citric	4.9–8.3	8.3–14.1
Oranges	Citric	0.68–1.20	9–14
Peaches	Citric	1–2	11.8–12.3
Pears	Malic/citric	0.34–0.45	11–12.3
Pineapples	Citric	0.78–0.84	12.3–16.8
Raspberries	Citric	1.57–2.23	9–11.1
Strawberries	Citric	0.95–1.18	8–10.1
Tomatoes	Citric	0.2–0.6	4

basis of pound solids, Brix readings are sometimes corrected for acid content. For citric acid, 0.20° Brix is added for each percent titratable acidity.

22.4.7 Volatile Acidity

In acetic acid fermentations, it is sometimes desirable to know how much acidity comes from the acetic acid and how much is contributed naturally by other acids in the product. This can be achieved by first performing an initial titration to measure **titratable acidity** as an indicator of total acidity. The acetic acid is then boiled off, the solution is allowed to cool, and a second titration is performed to determine the **fixed acidity**. The difference between fixed and total acidity is the **volatile acidity**. A similar practice is used sometimes in the brewing industry to separate acidity due to dissolved CO₂ from fixed acids. Fixed acids are titrated after CO₂ is removed by low heat (40 °C) and gentle agitation.

22.4.8 Other Methods

High-performance liquid chromatography (HPLC) (see Chap. 13) and electrochemistry both have been used to measure acids in food samples. Both methods allow identification of specific acids. HPLC uses refractive index, ultraviolet, or for some acids electrochemical detection. Ascorbic acid has a strong electrochemical signature and significant absorbance at 265 nm. Significant absorbance of other prominent acids does not occur until 200 nm or below.

Many acids can be measured with such electrochemical techniques as voltammetry and polarography. In ideal cases, the sensitivity and selectivity of electrochemical methods are exceptional. However, interfering compounds often reduce the practicality of electrochemical approaches.

Unlike titration, chromatographic and electrochemical techniques do not differentiate between an acid and its conjugate base. Both species inevitably exist side by side as part of the inherent food-buffer system. As a result, acids determined by instrumental methods may be 50% higher than values determined by titration. It follows that Brix/acid ratios can be based only on acid values determined by titration.

New pH probe designs use an ion-sensitive field-effect transistor (ISFET) to measure hydrogen ion concentration. These may use standard calomel or Ag/AgCl reference electrodes. However development of a silicon-based reference electrode has met with mounting success. ISFET electrodes have faster response times than traditional electrodes. Also, compact chip technology makes miniaturized probes possible. ISFET probes do not require a fluid medium, making possible direct pH measurement of gels, meats, cheeses, and other dense foods. The higher cost of a ISFET probe and some tendency for reference electrode drift keep it from replacing traditional pH electrodes for routine analysis.

22.5 SUMMARY

Organic acids have a pronounced impact on food flavor and quality. Unlike strong acids that are fully dissociated, food acids are only partially ionized. Some properties of foods are affected only by this ionized fraction of acid molecules, while other properties are affected by the total acid content. It is impractical to quantify only free hydronium ions in solution by titration. Once the free ions are removed by chemical reaction, others arise from previously undissociated molecules. Indicator dyes, which change color depending on the hydronium ion environment, exist, but they only identify when a certain pH threshold has been achieved and do not stoichiometrically quantify free hydronium ions. The best that can be done is to identify the secondary effect of the hydronium ion environment on some property of the system such as the color of the indicator dyes or the electrochemical potential of the medium. The pH meter measures the change in electrochemical potential established by the hydronium ion across a semipermeable glass membrane on an indicator electrode. The shift in the indicator electrode potential is indexed against the potential of a

reference electrode. The difference in millivolt reading between the two electrodes can be converted into pH using the Nernst equation. Indicator dyes are used commonly to identify the endpoint of acidity titrations although pH meters can be used in critical work or when sample color makes indicators impractical.

The hydronium ion concentration can be back-calculated from pH using the definition of pH as the negative log of hydrogen ion concentration. Buffer solutions of any pH can be created using the Henderson-Hasselbalch equation. However, the predictions of all these equations are somewhat approximate unless the activity of acids and conjugate bases is taken into account.

Titrateable acidity provides a simple estimate of the total acid content of a food. In most cases, it is only an estimate since foods often contain many acids that cannot be differentiated through titration. Titrateable acidity is not a good predictor of pH, since pH is a combined function of titrateable acid and conjugate base. Instrumental methods such as HPLC and electrochemical approaches measure acids and their conjugate bases as a single compound and, therefore, tend to produce acid contents that are higher than those determined by titration. Titrateable acidity, somewhat curiously, is a better predictor of tartness than the concentration of free hydronium ions as reflected by pH. The perception of tartness is strongly influenced by the presence of sugars.

22.6 STUDY QUESTIONS

1. Explain the theory of potentiometry and the Nernst equation as they relate to being able to use a pH meter to measure H^+ concentration.
2. Explain the difference between a saturated calomel electrode and a silver-silver chloride electrode; describe the construction of a glass electrode and a combination electrode.
3. You return from a 2-week vacation and ask your lab technician about the pH of the apple juice sample you gave him or her before you left. Having forgotten to do it before, the technician calibrates a pH meter with one standard buffer stored next to the meter and then reads the pH of the sample of unpasteurized apple juice immediately after removing it from the refrigerator (40 °F), where it has been stored for 2 weeks. Explain the reasons why this stated procedure could lead to inaccurate or misleading pH values.
4. For each of the food products listed below, what acid should be used to express titrateable acidity?

- (a) Orange juice
- (b) Yogurt
- (c) Apple juice
- (d) Grape juice

5. What is a "Brix/acid ratio," and why is it often used as an indicator of flavor quality for certain foods, rather than simply Brix or acid alone?
6. How would you recommend determining the endpoint in the titration of tomato juice to determine the titrateable acidity? Why?
7. The titrateable acidity was determined by titration to a phenolphthalein endpoint for a boiled and unboiled clear carbonated beverage. Which sample would you expect to have a higher calculated titrateable acidity? Why? Would you expect one of the samples to have a fading endpoint? Why?
8. Why and how is an ascariate trap used in the process of determining titrateable acidity?
9. Why is volatile acidity useful as a measure of quality for acetic acid fermentation products, and how is it determined?
10. Regarding the use of a standard acid to standardize a NaOH solution to determine titrateable acidity, what factors make (a) KHP a good choice and (b) HCl, HNO_3 , or H_2SO_4 a poor choice?
11. Could a sample that is determined to contain 1.5% acetic acid also be described as containing 1.5% citric acid? Why or why not?
12. An instructor was grading lab reports of students who had determined the titrateable acidity of grape juice. One student had written that the percent titrateable acidity was 7.6% citric acid. Give two reasons why the answer was marked wrong. What would have been a more reasonable answer?

22.7 PRACTICE PROBLEMS

1. You are performing a titration on duplicate samples and duplicate blanks that require 4 mL of 1 N NaOH per titration sample. The lab has 10% NaOH and saturated NaOH (assume 11.5 M). Choose one of these and describe how you would prepare the needed amount of NaOH solution.
2. You are performing duplicate titrations on five samples that require 15 mL of 6 N HCl each. How would you prepare the needed solution from reagent grade HCl?
3. What is the pH of a 0.057 M HCl solution?

- Vinegar has a $[H^+]$ of $1.77 \times 10^{-3} M$. What is the pH? What is the major acid found in vinegar, and what is its structure?
- Orange juice has a $[H^+]$ of $2.09 \times 10^{-4} M$. What is the pH? What is the major acid found in orange juice and what is its structure?
- A sample of vanilla yogurt has a pH of 3.59. What is the $[H^+]$? What is the major acid found in yogurt and what is its structure?
- An apple pectin gel has a pH of 3.30. What is the $[H^+]$? What is the major acid found in apples and what is its structure?
- How would you make 1 L of 0.1 N NaOH solution from an 18 N stock solution?
- A stock base solution assumed to be 18 N was diluted to 0.1 N. KHP standardization indicated the normality of the working solution was 0.088 N. What was the actual normality of the solution?
- A 20-mL sample of juice requires 25 mL of 0.1 N NaOH titrant. What would be the percent acid if the juice is (1) apple juice, (2) orange juice, and (3) grape juice?
- A lab analyzes a large number of orange juice samples. All juice samples will be 10 mL. It is decided that 5 mL of titrant should equal 1% citric acid. What base normality should be used?
- A lab wishes to analyze apple juice. They would like each milliliter of titrant to equal 0.1% malic acid. Sample aliquots will all be 10 mL. What base normality should be used?
- Using Table 22.2, calculate the pH of cola.

Answers

- Four titrations of 4 mL each will be performed requiring a total of about 16 mL of 1 N NaOH. For simplicity, 20 mL of 1 N NaOH can be prepared. Use Eq. 22.1 to solve for the mL of stock solution, e.g., for a 10% NaOH:

$$\begin{aligned} 10\text{gNaOH} / 100\text{mL} &= 100\text{gNaOH} / L \\ &= 2.5\text{NNaOH} \end{aligned}$$

$$\begin{aligned} (20\text{ mL})(1\text{NNaOH}) &= (x\text{ mL})(2.5\text{N}) \\ x\text{ mL} &= 8\text{ mL of } 10\% \text{ diluted to } 20\text{ mL} \\ &\text{with distilled water} \end{aligned}$$

If saturated NaOH is used, approximately 8.7 mL of saturated NaOH diluted to 100 mL yields 1.0 N. Therefore, 1.87 mL or 2 mL of saturated NaOH diluted to 20 mL with distilled water will yield about 1 N NaOH.

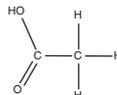
- A total of (5 samples)(2 duplicates)(15 mL) = 150 mL of 6 N HCl:

$$\begin{aligned} (150\text{ mL})(6\text{NHCl}) &= (x\text{ mL})(12\text{NHCl}) \\ x\text{ mL} &= 75\text{ mL concentrated HCl diluted with} \\ &\text{distilled water to } 150\text{ mL} \end{aligned}$$

- Since HCl is a strong acid, it will be almost completely dissociated. Therefore,

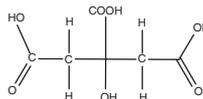
$$\begin{aligned} [\text{HCl}] &= [\text{H}^+] = [0.057] \\ \text{pH} &= -\log[0.057] = 1.24 \end{aligned}$$

- 2.75; acetic acid.

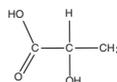


(Use Eq. 22.5, to solve Problems 14–17.)

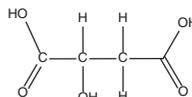
- 3.68; citric acid.



- $2.57 \times 10^{-4} M$; lactic acid.



- $5.0 \times 10^{-4} M$; malic acid.



- Using Eq. 22.1 and solving for volume of concentrate, we get

$$\begin{aligned} \text{mL concentrated solution} &= \frac{\text{final } N \times \text{final mL}}{\text{beginning } N} \\ &= \frac{0.1 \times 1000}{18} \\ &= 5.55\text{ mL} \end{aligned}$$

Consequently, 5.55 mL would be dispensed into a 1-L volumetric flask. The flask would then be filled to volume with distilled CO_2 -free water.

The normality of this solution will only be approximate since NaOH is not a primary standard. Standardization against a KHP solution or some other primary standards is essential. It is useful sometimes to back-calculate the true normality of the stock solution. Even under the best circumstances, the normality will decrease with time, but back-calculating will permit a closer approximation of the target normality the next time a working standard is prepared.

9. This answer is a simple ratio:

$$\frac{0.088}{0.100} \times 18 = 15.85 N$$

10. Table 22.5 indicates the principal acids in apple, orange, and grape juice are malic, citric, and tartaric acids, respectively. Table 22.1 indicates the equivalent weight of these acids are malic (67.05), citric (64.04), and tartaric (75.05). The N , v_1 and v_2 are given. Using Eq. 22.20, the percent acid for each of these juices would be:

$$\% \text{ malic acid} = \frac{0.1 \times 25 \times 67.05}{20 \times 10} = 0.84\%$$

$$\% \text{ citric acid} = \frac{0.1 \times 25 \times 64.04}{20 \times 10} = 0.80\%$$

$$\% \text{ tartaric acid} = \frac{0.1 \times 25 \times 75.05}{20 \times 10} = 0.94\%$$

11. Quality control laboratories often analyze a large number of samples having a specific type of acid. Speed and accuracy are increased if acid concentration can be read directly from the burette. It is possible to adjust the normality of the base to achieve this purpose by rearranging Eq. 22.20:

$$\% \text{ acid} = \frac{N \times V_1 \times \text{Eq wt}}{V_2 \times 10} \quad (22.20)$$

$$N = \frac{\% \text{ acid} \times V_2 \times 10}{V_1 \times \text{Eq wt}}$$

The desired % acids, v_1 , and v_2 are 1%, 5, and 10 mL, respectively. The equivalent weight of citric acid is 64.04 (see Table 22.2). Thus,

$$N = \frac{1 \times 10 \times 10}{5 \times 64.04} = 0.3123$$

In actuality, the standard alkali solution used universally by the Florida citrus industry is 0.3123 N.

12. This can be solved analogously to Problem 11. This time, % acid is 0.1, v_1 is 1 mL, and v_2 is 10 mL. The equivalent weight is 67.05. Therefore,

$$N = \frac{0.1 \times 10 \times 10}{1 \times 67.05} = 0.1491$$

13. Substitute the $[H^+]$ into Eq. 22.5:

$$\text{pH} = -\log[H^+]$$

$$\text{pH} = -\log[2.24 \times 10^{-3}]$$

There are now different ways to obtain the right answer:

- Type the concentration into a calculator, take the logarithm, and invert the sign.
- Use a computer program such as Excel (the corresponding formula in Excel would be “-LOG10(2.24*10^-3)”. While students may be more familiar with a calculator initially, saving results on the computer may be beneficial in the long run, e.g., if similar calculations such as for buffers need to be performed repeatedly. In this case, the same formula could be used, and only certain numbers would need to be changed.
- Separate 2.24×10^{-3} into two parts; determine the logarithm of each part:

$$\log 2.24 = 0.350$$

$$\log 10^{-3} = -3$$

Add the two logs together since adding logs is equivalent to multiplying the two numbers:

$$0.350 + (-3) = -2.65$$

Place the value into Eq. 22.1.

All three of these methods should lead to a pH of 2.65.

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