pH AND ETHYLENE MEASUREMENTS IN FLORIDA CITRUS PACKINGHOUSES

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pH

The measurement of pH in Florida citrus packinghouses is important for the proper adjustment of solutions with chlorine SOPP (see presentation by G. E. Brown in this Short Course), color-add, and until recently Benlate (no longer allowed for postharvest uses). Chlorine may be included in truck or bin drenchers as well as on the packinghouse line. SOPP is used at the time of washing, frequently as a part of soap formulation. Color-add is used only on oranges and tangelos after washing and before waxing. Improper pH can greatly reduce the effectiveness of the treatment, and in the case of SOPP result in fruit damage or in the case of chlorine result in excessive rust on the machinery.

Definitions

1. <u>Acid and Base</u> - The pH of a liquid is related to the ratio of hydrogen ions (H^+ to hydroxide ions (OH^- An acidic solution has a greater concentration of H^+ than OH^-, and conversely if a basic solution has more OH^- than H^+ present the material is a neutral salt.

2. <u>pH Scale</u> - The scale used to measure pH is based on a molar solution (molecular weight in grams in 1 liter of solution) and is expressed from 0 to 14 with 7 being neutral (Table 6). A molar solution of hydrochloric acid (HCl) is about a 3.6% acid solution and has a pH of 0. A molar solution of sodium hydroxide (NaOH) is about a 4% solution of

the base and has a pH of 14. The pH of some common foods and chemicals are shown in Figure 4.

Table 6. pH of various strong acid and base molar solutions

Acid		Base	
Molar	pH	Molar	pH
1.0	0	1.0	14
0.1	1	0.1	13
0.01	2	0.01	12
0.001	3	0.001	11
0.0001	4	0.0001	10
0.00001	5	0.00001	9
0.000001	6	0.000001	8
0.0000001	7	0.0000001	7

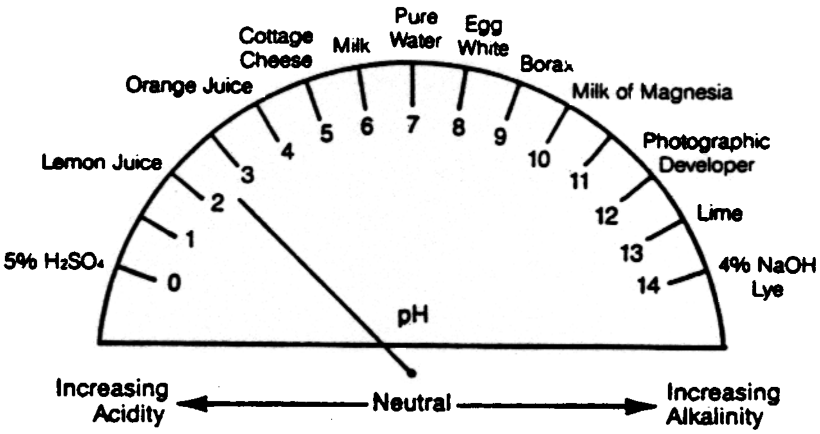

Figure 4. pH Values of common foods and chemicals. (Anonymous 1989).

If we dilute the acid with pH of 0 or the base with pH of 14 by 1/10 (one volume solution with nine volumes pure water) pH changes by a unit of one. The acid becomes pH 1, and the base becomes pH 13. It is helpful to remember that a unit change (e.g. 5 to 6) in pH represents a ten-fold change in acidity or alkalinity. Both solutions with a 1/10 dilution change from 1.0 molar to 0.1 molar. With each successive 1/10 dilution the pH changes by a unit of one until on the seventh dilution, the solutions are both 0.0000001 molar with a pH of 7 (Table 6)

To a chemist, the pH is a number that is the negative logarithm of the molar concentration of hydrogen ions Fortunately, we do not have to use the language of chemists this Short Course.

Using Table 6, if you combine equal amounts of acid and base on the same line (e.g., pH 3 + pH 11 or pH 5 + pH 9) the mixture would have a neutral pH 7. Equal amounts of H^+ and OH^- neutralize the solution.

3. <u>Weak vs. Strong Solutions</u> - All acids and bases do not act the same. The amount of H^+ and OH^- that are free in solution vary greatly. When strong acids or bases (e.g. of hydrochloric acid and sodium hydroxide) 100% release of the H^+ or OH^- occurs and are free in solution. Vinegar (acetic acid) is a weak acid and only about 1.3% of the H^+ are dissociated. Likewise household ammonia (ammonium hydroxide) is a weak base.

Measurements

1. Litmus Paper or pH Paper - Dyes sensitive to various pH levels can be impregnated on paper to give a color response to pH. This will give a general idea of the pH range, accuracy is sacrificed for convenience. There are two major drawbacks with the use of indicators. First is the difficulty of detection in highly colored or turbid solutions and second is chemical interferences with the indicator, invalidating the test

2. Dye Solutions - Phenolphthalein is used in the test rooms of citrus packinghouses to determine the total (titratable) acid in juice. Accurate measurements of juice and standard sodium hydroxide are used for this determination.

3. pH Meters

   a. Equipment - A pH meter includes a probe which is inserted in a liquid and produces a voltage related to the pH of the solution. The pH meter receives the electric impulse from the probe and translates it to a scale which reads pH directly. The reading may be on an old traditional dial or on a digital readout. The pH meter can be a bench model smaller portable, or even the pen like pocket models.

   b. Standard Solutions - It is a good idea to have standard buffered solutions near the pH of the solution ranges you expect to measure. Then you can check the accuracy of the pH meter against these standards to obtain correct readings.

c. Temperature Accurate pH readings temperature dependent. The temperature of a solution must be known and an adjustment made to obtain accurate pH readings.

d. Unknown Solution Readings - Turn on the pH meter and allow a few minutes warmup.

Set the temperature dial to the temperature of the sample (we will assume that the sample and buffers are at room temperature). Calibrate the pH meter as described in the instrument instruction manual. An example of instrument calibration is as follows:

> Place the pH probe in a 7.00 buffer and position the pointer with the Set knob for a reading of 7.00
>
> Remove the probe, rinse, wipe, and then immerse it in the unknown
>
> Note the reading. If it is near 7.00, record exact value and the measurement is complete.
>
> If it is below 6.00 or above 8.00, then select a buffer that is closest to the unknown. Place probe in this buffer after a rinse and wipe.
>
> the Set control to make the meter read exactly the value of the buffer.
>
> Remove the probe, rinse, wipe, and place in the unknown. Note the reading. The accuracy of this reading will depend primarily on the accuracy of the standard buffer. The closer the buffer value

to the unknown, the more accurate the reading. Note: If the unknown in this example had read a value above pH 12.00, you should substitute a special probe that is designed for pH measurement in highly alkaline solution. Most general purpose probes begin to lose accuracy above pH 12.00 due to sodium ion interference, termed sodium or alkaline error.

Ethylene

Most Florida citrus packers know ethylene as the gas used to degreen citrus. It is also used to ripen fruits like avocado, banana, honeydew melon, kiwi fruit, mango, papaya, pear, and tomato. Ethylene can also be detrimental for produce, including that which is ripened or colored with the use of ethylene. Too much citrus degreening time can result in increased decay (see presentation by G. E. Brown in this Short Course). For a more thorough discussion of degreening see Grierson et al. (1986).

Definitions

1. Ethylene Ethylene, a hydrocarbon gas, C_2H_4, is a plant hormone which is produced by all plants. It is colorless with a faint sweetish odor and acts as a plant growth regulator. The physical properties of ethylene are given in Table 7

2. Concentration Ethylene concentration is often expressed in parts per million (ppm) and the values are

Table 7. Physical properties of ethylene gas (Reid 1985)

Appearance	Colorless with a faint sweetish odor
Molecular weight	28.05
Boiling point:	
at 760 mm Hg	-103.7°C
at 300 mm Hg	-118°C
at 10 mm Hg	-153°C
b.p./ p at 750 to 770 mm Hg	0.022°C/mm Hg
Freezing point at saturation pressure (triple point)	-169.2°C
Surface tension at -103.7°C	16.4 dynes/cm
Flammable limits in air:[z]	
lower	3.1% by vol
upper	32% by vol

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[z] All compositions between the upper and lower limits are flammable and can be explosive.

extremely low. The Florida recommended degreening concentration is 5 ppm while the level at which some response on oranges can be expected is only 0.1 ppm (Table 8).

3. Occurrence

a. Plants - Ethylene is produced by all plants and in trace amounts interacts with other plant hormones to coordinate and regulate a wide variety of natural growth and developmental processes. The rate of production varies with type of tissue and stage of development. In general, citrus fruit produce very low amounts of ethylene, and their rates

Table 8. Threshold^z for ethylene action in various fruits (Reid 1985)

Fruit	Concentration (ppm)
Avocado (var. Choquette)	
Banana (var. Gros Michel	0.1 - 1
(var. Lacatan)	0.5
(var. Silk fig)	0.2 - 0.25
Cantaloupe (var. P.M.R. No. 45)	0.1 - 1
Honeydew melon	0.3 - 1
Lemon (var. Fort Meyers)	0.1
Mango (var. Kent)	0.04 - 0.4
Orange (var. Valencia)	
Tomato (var. VC-243-20)	

[z] Minimum levels to initiate desired effect. Optimum levels are commonly higher.

of production can be as much as 1,000 times less than a ripening apple or avocado (Table 9). However, when citrus fruit are invaded by decay organisms, the production of ethylene increases several-fold as a result of wounding of the tissue and production of ethylene by the pathogen itself.

Application of ethylene to the plant environment can result in a myriad of responses. Plant responses to ethylene include fruit ripening, abscission, breaking of dormancy, and chlorophyll destruction. The Florida citrus industry utilizes the latter response to initiate fruit degreening.

Table 9. Classification of horticultural commodities according to ethylene production rates (Kader 1985).

Class	Range at 20°C (68°F) (1 C_2H_4/Kg-hr)	Commodities
low	Less than 0.1	Artichoke, asparagus, cauliflower, cherry, citrus grape, jujube, strawberry, pomegrante, leafy vegetables, root vegetables, potato, most cut flowers
	0.1 - 1.0	Blueberry, cranberry, cucumber, eggplant, okra, olive, pepper, persimmon, pineapple, pumpkin, raspberry, tamarillo, watermelon
Moderate	1.0 - 10.0	Banana, fig, guava, honeydew melon, mango, plantain, tomato
High	10.0 - 100.0	Apple, apricot, avocado, cantaloupe, feijoa, kiwifruit, (ripe), nectarine, papaya, peach, pear, plum
Very High	More than 100.00	Cherimoya, mammee apple, passion fruit, sapote

John McPhee (1967) commented, "One McIntosh apple, puffing hard, can turn out enough ethylene to de-green a dozen oranges in a day or two." His statement summarizes some complex ideas into simple terms.

b. Chemical Companies - Ethylene may be produced as a breakdown product of ethyl alcohol as is done by generators commonly found in banana ripening rooms, frequently in tomato ripening rooms and occasionally in citrus degreening rooms. A second source used by most citrus packers is ethylene produced commercially for sale in gas cylinders.

Equipment

1. Gas Chromatograph Because of the low amounts in citrus fruits, ethylene was not detected until the use of gas chromatographs (Soule and Grierson 1986). Gas chromatography using a flame ionization detector is a common, highly sensitive system for the measurement of ethylene and other hydrocarbons up to C5. The ethylene in the gas sample is separated from the other gases on an alumina column; the separated ethylene emerging from the column is mixed with hydrogen, burnt in air, and the ions given off in the flame provide an electrical signal proportional to the amount of ethylene present in the gas sample. Commercial instruments vary widely in sophistication, but a single column, single detector, instrument is adequate for routine ethylene analysis. The more sophisticated research instruments can measure 0.001 microliters per liter ethylene in a 5 milliliter sample of air.

Other highly sensitive gas chromatograph detectors include the photo ionization detector. Carrier gas (usually nitrogen) only is required and the separated gases emerging from the column are fed directly to the detector. (Wills *et al*. 1989).

2. Portable Ethylene Analyzer A portable ethylene analyzer (Figure 5) is used by citrus packers to determine the ethylene concentration in degreening rooms. The most common one is a Kitagawa gas analyzer with low range ethylene tubes. A sealed glass tube is broken at both ends and a measured volume of degreening room air is drawn through the tube. A reaction with ethylene changes a portion of the tube contents from yellow to blue, with the amount of blue indicating the ethylene concentration.

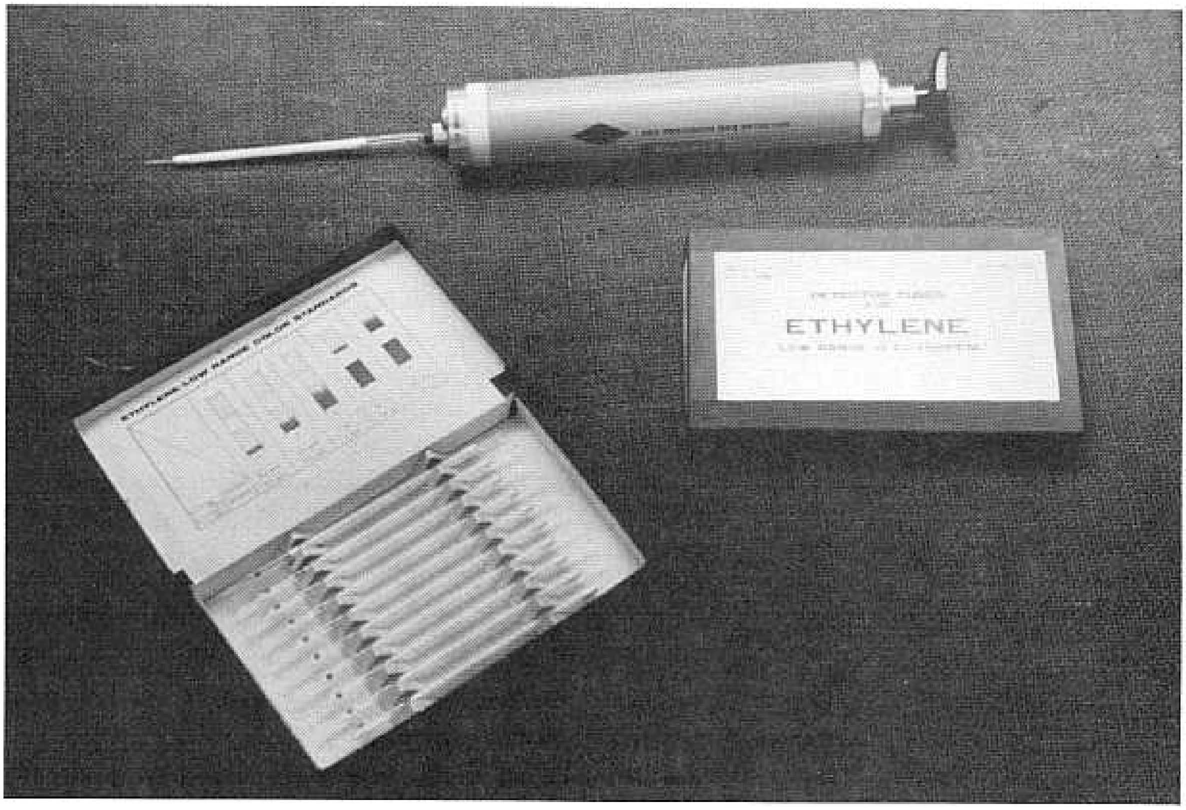

Figure 5. Ethylene analyzer commonly used by Florida citrus packers. (Wardowski 1989).

The ethylene tubes can be used beyond their expiration dates if they are stored in cool (refrigerator) temperatures. It is never good to store the tubes at high temperatures. A start of the season check of old ethylene tubes by comparison with new tubes is a good idea. Proper sampling within a degreening room is not usually a problem when there is good air circulation. Take samples for ethylene well into the room and away from doors or curtains.

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