

110° C. and a few drops of cooked balsam are placed on the slide. When the slide has had sufficient time to reach thermoequilibrium with the hot plate, it is removed and placed on an asbestos pad, and the specimen, face down, is quickly placed over the balsam. Enough pressure should be exerted on the specimen to force excess balsam from between the specimen and the slide. After the slide has cooled, the excess balsam around the edge of the specimen is cut away with a razor blade. The exposed face of the mounted specimen is then ground to the required thickness by first using the paper with coarse abrasive (No. 120), then the intermediate (No. 400), and finally the fine (No. 600) abrasive. Careful manipulation of pressure with the fingers will facilitate removal of thick spots and procure a section with fairly uniform thickness. Final grinding of the specimen to the proper thickness and uniformity is determined by inspection for light transmittance under the microscope. It is usually desirable to grind the specimen to a thickness of 0.03 mm. or less.

**Applying Cover Glass.** A thin coating of flexible collodion (nitrocellulose dissolved in ether) is brushed over the exposed surface of the specimen with a

camel's-hair brush to prevent the particles from flowing or separating when the cover glass is applied. A cover glass, 22 mm. in diameter, is placed on the hot plate (100° to 110° C.) and a few drops of cooked balsam are placed on it. The slide with the mounted specimen is inverted and placed face down over the cover glass, then quickly placed on an asbestos pad, and pressure is applied to the cover glass to remove the excess balsam. It is advisable to warm the slide and specimen to approximately 70° C. before the cover glass is applied. This prevents the balsam from getting hard before the cover glass can be seated. Any excess balsam on the slide may be removed with acetone.

**Use of Thin Sections.** Figures 1 and 2 illustrate the usefulness of thin sections in the microscopic comparison of two triple superphosphates from different sources. The photographs were taken at a magnification of 450 times. Figure 1 shows a distinct crystal formation and a heterogeneous pore size and distribution within the particle, while Figure 2 indicates a lesser degree of crystal formation with relatively good homogeneity of pore size and distribution. Preliminary microscopic comparison of thin sections made in triplicate for each

of seven samples from different sources indicate that it may be possible to classify triple superphosphates on the basis of particle structure. Such a classification should be helpful in predicting their behavior in fertilizer processes such as ammoniation and granulation.

#### Acknowledgment

The authors are indebted to J. G. Cady and W. F. Holton, Soil Conservation Service, for valuable suggestions during this study.

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Received for review August 9, 1960. Accepted January 19, 1961. Division of Fertilizer and Soil Chemistry, 138th Meeting, ACS, New York, N. Y., September 1960.

## LIQUID FERTILIZER ACIDITY

### The Salt Effect in Measuring pH of Liquid Fertilizers with Color-Change Indicators

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The pH of an 8-24-0 liquid fertilizer must be controlled to prevent corrosion of storage facilities, ammonia loss, high salt-out temperatures, and an off-grade product. An inexpensive and convenient method of measuring the pH of a solution is with color-change indicators and commercially available indicator standards. At high salt concentration, as found in liquid fertilizers, a shift in the color-change interval of indicators is observed. This leads to a false measure of the pH of the solution. Theoretical and practical considerations of this indicator salt-effect are discussed.

THE LIQUID fertilizer manufacturer should be constantly concerned with the pH of the product. It is general practice to prepare an 8-24-0 liquid fertilizer by reacting ammonia with phosphoric acid. The pH of this product must be controlled so that the manufacturer can store it in mild steel tanks with a minimum of corrosion. The pH of the ammoniated phosphoric acid solution indicates the ratio of ammonia to phosphoric acid, a necessary bit of information to ensure that a final product is on-grade. A third factor to be considered is the pH-dependence of

the solubility of the ammonium phosphate salts in the 8-24-0 product.

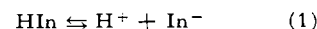
For these reasons, the pH of liquid fertilizers should be measured, especially if storage is contemplated. The least expensive method of measuring pH is by use of color-change indicators. It is the purpose of this paper to discuss the factors involved in this type of measurement and to indicate errors which can arise from them.

#### Theoretical Considerations

Color-change indicators, such as bro-

mothymol blue which is used extensively to measure the pH of liquid fertilizer solutions, are weak acids. Let HIn represent the form of the indicator molecule in acid solution and In<sup>-</sup>, the form in basic solution where the two forms have the characteristic color observed in acidic and basic media. For bromothymol blue, the color of HIn is yellow and In<sup>-</sup> blue.

The reversible dissociation of acid-base indicators is represented by the equation



**Table I. Spectrophotometric pH Determination**

Solution No.	8-24-0, Ml.	H <sub>2</sub> O, Ml.	Indicator, Ml.	A, 617 m $\mu$	pH Meter
1	5.0	...	0.2	0.018	7.20
2	4.5	0.5	0.2	0.051	7.20
3	4.0	1.0	0.2	0.080	7.22
4	3.0	2.0	0.2	0.180	7.22
5	2.0	3.0	0.2	0.349	7.25
6	1.0	4.0	0.2	0.400	7.25
7 <sup>a</sup>	...	5.0	0.2	0.946	Strongly basic
8 <sup>b</sup>	...	5.0	0.2	0.006	Strongly acidic

<sup>a</sup> All indicator in basic form to give total concentration of indicator. Dilute NaOH used.

<sup>b</sup> All indicator in acidic form to give total absorption correction at 617 m $\mu$ . Dilute HCl used.

This dissociation occurs so that the visual color change is over the so-called color-change interval of the indicator (pH 6.0 to 7.6 for bromothymol blue). At any pH value in this interval, there will exist both colored forms of the indicator so that the pH is determined by matching the color hue of the solution due to the indicator with any commercial color standard.

The thermodynamic equilibrium constant for Equation 1 is

$$K = \frac{a_h a_{in}}{a_{hin}} \quad (2)$$

where  $a_h$  is the activity of hydrogen ions in solution,  $a_{in}$  the activity of the basic form of the indicator and  $a_{hin}$  the activity of the acid form of the indicator. Rearranging Equation 2:

$$\frac{K}{a_h} = \frac{a_{in}}{a_{hin}} = \frac{f_{in}}{f_{hin}} \cdot \frac{c_{in}}{c_{hin}} \quad (3)$$

where  $f$  and  $c$  are activity coefficients and molal concentrations, respectively, of the solution species indicated by subscripts.

Since pH is defined by the expression  $\text{pH} = -\log a_h$ , at constant pH, the left-hand side of Equation 3 is constant. An 8-24-0 fertilizer solution is well buffered—i.e., its pH is insensitive to rather large changes in concentration—

so that upon dilution the factor  $\frac{K}{a_h}$  remains relatively constant. As a general rule, when a concentrated salt solution of the type found in liquid fertilizers is diluted, the mean activity coefficient of the solution decreases. When this happens, the function  $f_{in}$  decreases, while  $f_{hin}$  is relatively unaffected. So that the right-hand side of Equation 3 can remain constant as required by the condition of constant pH,  $c_{in}$  must increase at the expense of  $c_{hin}$ . This changes the ratio of the two colored forms of the indicator showing a false pH change.

A more detailed discussion of this "salt-effect" can be found in advanced texts on analytical chemistry (2, 5).

### Procedure

A stock solution which represented an overammoniated 8-24-0 liquid fertilizer was prepared by dissolving mono- and diammonium phosphates (c.p. grade) in water. The solution contained 30.9% of (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub> and 12.0% of NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> by weight. Measured with a Beckman Model G pH meter, its pH was 7.20 at 30° C. This pH is higher than that of an 8-24-0 solution, probably because of the difficulty in obtaining pure ammonium phosphates. The high pH solution was purposely used for this study because of its striking example of the salt effect in this type of measurement.

As indicator stock solution, a 0.5% bromothymol blue solution was prepared as recommended by Kolthoff and Rosenblum (3).

A series of solutions was prepared by diluting the 8-24-0 stock solution with water and adding 0.2 ml. of indicator stock solution to 5 ml. of diluted 8-24-0. The pH of each solution was determined with a pH meter and the absorbance of each solution ( $A$ ) was measured at 617 m $\mu$ , which is the absorption maximum for the basic form of bromothymol blue with a molar absorptivity of  $4.45 \times 10^4$  (7). A Bausch and Lomb Spectronic 20 spectrophotometer was used for spectrophotometric measurements. Solutions were measured in matched test tubes with a 1-cm. path length.

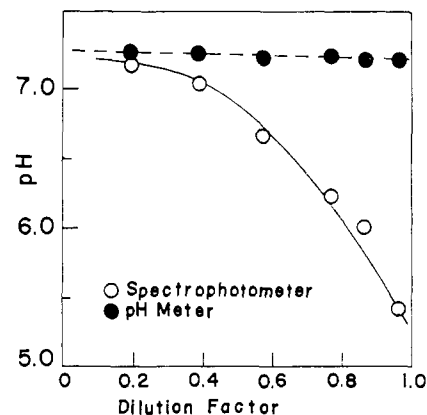
Table I summarizes spectrophotometric data.

### Discussion and Conclusions

Since absorptiometric measurements lead to the molar concentration of the absorbing species, Equation 2 can be written in terms of molar concentrations and not of the activities of the quantities concerned.

$$K = \frac{c_h c_{in}}{c_{hin}} \quad (4)$$

It may be expressed in the Henderson-Hasselbach form.



**Figure 1. Plot of pH vs. dilution factor for 8-24-0 liquid fertilizer**

$$\text{pH} = \text{pK} + \log \frac{c_{in}}{c_{hin}} \quad (5)$$

The pK of bromothymol blue is 7.30 (4). The ratio of the concentrations of the two forms of the indicator is determined visually by matching color hue to standard samples. An equivalent method for determining these concentrations is to measure light absorption. It was adopted in this study as a more accurate means of illustration.

Total concentration of indicator was calculated from absorbance of solution 7 using the equation

$$A = abc \quad (6)$$

where  $a$  is molar absorptivity,  $b$  solution path length in centimeters, and  $c$  molar concentration of the absorbing species. In a like manner concentration of the basic form,  $c_{in}$ , was calculated for solutions 1 through 6 and  $c_{hin}$  determined by difference. The apparent pH of each solution was then calculated using Equation 5.

Figure 1 summarizes these measurements. The true pH of each solution as measured with a pH meter is shown. The pH values determined by spectrophotometric measurements represent the apparent pH determined by visual color matching. These values are plotted against a dilution factor which is here taken as the volume of 8-24-0 solution divided by the total volume of liquids and solutions mixed to prepare each solution. For instance, solution 4 prepared by mixing 3 ml. of 8-24-0, 2 ml. of water, and 0.2 ml. of indicator solution has a dilution factor of  $3.0 / (3.0 + 2.0 + 0.2) = 0.58$ .

Figure 1 illustrates the large error introduced by using color-change indicators in solutions with a high salt concentration. If an 8-24-0 solution is used without dilution, an error of 2 pH units is introduced. Indeed, in this case the apparent pH indicated by the spectrophotometer is outside the range to which the eye is sensitive, since for visual

measurement bromothymol blue has a color-change interval of pH 6.0 to 7.6. At a dilution factor of 0.5 an error of 0.4 pH unit is shown. An experienced observer should be able to determine pH much closer than this with color standards. At a dilution factor of 0.2 this error is only 0.1 pH unit, which is well within the range of sensitivity of the visual method of measurement.

On the basis of these results, it is recommended that for measurement of the pH of an 8-24-0 liquid fertilizer with color-change indicators, the sample should be diluted with four volumes of distilled water. The buffer capacity of this system is sufficient to allow this degree of dilution as can be seen from true pH values of Figure 1. Of course,

for closest control of the product the use of a pH meter is recommended.

A current technical sales bulletin (6) recommends the use of universal indicator papers and dilution of the sample with an equal volume of distilled water. As shown above, this is insufficient dilution to overcome the salt effect. The error of 0.4 pH unit thus introduced could reduce solubility of the salts at 32° F. some 20% as shown elsewhere in the same bulletin (7).

#### Acknowledgment

The author gratefully acknowledges the assistance of Martha Shipley in performing spectrophotometric measurements for this study.

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Received for review September 12, 1960. Accepted February 14, 1961.

## GROWTH RETARDANTS AND PLANT VIGOR

# Increasing Tolerance of Soybean Plants to Some Soluble Salts through Application of Plant Growth-Retardant Chemicals

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Plants that were altered through the use of plant growth retardants, such as Amo-1618, phosfon, or CCC, were more tolerant to toxic levels of salts placed around their roots than were plants grown without retardants. Young soybean plants retarded chemically were able to withstand, without visible injury, amounts of commercial 5-10-5 fertilizer applied to the surface of the soil that killed comparable plants not treated with the retardants. Retarded plants that withstood excessive amounts of fertilizer produced viable seeds.

CONSIDERABLE INTEREST has been shown recently in plant-regulating chemicals that retard the height of plants without injurious effects. In 1949 Mitchell, Wirwille, and Weil (5) reported the growth-retarding effects of six related nicotinium compounds. In 1950, six quaternary ammonium compounds reported to be growth retardants for bean plants (10) were later found to be very active on several other plant species (4). The most promising compound, 2-isopropyl-4-dimethylamino-5-methylphenyl-1-piperidine carboxylate methyl chloride, was designated Amo-1618 and methods of synthesizing it and related retardants were recently published (2).

A new group of growth-retarding chemicals, the phosphoniums, was reported in 1958 by Preston and Link (6). One of these, tributyl-2,4-dichlorobenzyl phosphonium chloride (phosfon), affects some species of plants that do not respond to Amo-1618. Another group of growth retardants was reported more recently by Tolbert (9). One of these, (2-chloroethyl)-trimethyl ammonium chloride (CCC), is effective in retarding

some plants not affected by Amo-1618 or phosfon (7).

Interest in our laboratory has been directed toward other types of responses besides the dwarfing induced by these chemicals. For instance, the leaves of treated plants were usually thicker and greener and, in a number of experiments treated bean and chrysanthemum plants lived 40 to 60% longer than did untreated ones (4). When water was withheld from plants in other experiments, the untreated plants wilted more quickly and severely than did the treated ones (3). Recently, Teubner and O'Keefe (8) reported that certain varieties of potatoes were more resistant to heat after treatment with CCC or related compounds.

The purpose of the present study was to learn whether chemically retarded plants could withstand higher concentrations of salts in the soil than unretarded ones.

#### Methods

Seeds of soybean (Lee variety) were sown in composted soil in 3-inch clay

pots and allowed to germinate. The plants were thinned to two per pot and selected for uniformity when about 4 inches tall. In most instances the growth-regulating chemicals were applied when the primary leaves were almost fully expanded and the trifoliolate ones were about 1/2 inch long. One experiment was conducted with older plants 8 inches tall and with two sets of fully expanded trifoliolate leaves. Amo-1618 was applied either as an aqueous spray to the foliage or as a soil drench. Phosfon was applied as a soil drench to the roots, because it is known to be phytotoxic when applied to leaves. CCC also was applied to the soil, because it is not readily translocated out of leaves. No wetting agent was used in preparing the drenches, but all spray solutions contained 0.1% Tween 20. The drench was applied at the rate of 30 ml. per pot. This volume contained sufficient retardant to make the rate of application equivalent to 15 pounds per acre.

A commercial 5-10-5 fertilizer from a single lot was used throughout the experiments to make the soil-fertilizer mixtures. The nitrogen content of the