

A Continuous, Automatic Device for Alkalinity Measurement and Control

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WHILE THERE is certainly not universal agreement among sugar processors on the point, it is the belief of the Spreckels Sugar Company that the most important controlling variable in the first-carbonation process is the alkalinity of the filtered juice. This belief is based on several years' work with a bench-scale carbonation apparatus, some of the results of which have been published (1).²

If it is agreed that the alkalinity offers the best method of carbonation control, then the usefulness of an apparatus which will automatically and continuously measure the alkalinity is apparent. If this apparatus can also control the carbonation process, its value will be further enhanced. We have developed such an automatic device and have used it for several years at the carbonation station in our Woodland factory.

General Method of Operation of the Alkalimeter

The determination of alkalinity is simply a titration of an alkaline solution with an acid solution. The filtered first-carbonation juice is the alkaline solution and 0.0357 normal sulfuric acid is the acid solution. The strength of the acid is so chosen that when a 10-milliliter sample of the filtered juice is taken, the volume of acid required for neutralization divided by 100 is the numerical measure of the alkalinity. Furthermore, the alkalinity equals the number of grams of calcium oxide per 100 milliliters of juice, assuming that calcium hydroxide is the only alkali present in the juice.

First-carbonation control depends primarily upon the determination of the alkalinity which is made manually by the carbonation operator. Thus, the operator takes a sample of first-carbonation juice from the carbonation tanks, filters the juice and titrates a 10-milliliter sample of the filtrate with 0.0357 normal sulfuric acid, using phenolphthalein as a color indicator. If the measured alkalinity of the juice varies from the desired figure, the addition of milk of lime or carbon dioxide gas is changed so as to obtain the desired figure.

Approximate alkalinity control is frequently obtained by the use of intermediary devices such as pH or conductivity controllers. The principal objection to these devices is that other factors such as temperature or percentage of lime may alter the relationship between alkalinity and pH or alkalinity and conductivity.

Inasmuch as the determination of alkalinity is simply an acid-base titration, it is clear that an alkalimeter must automatically perform this

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²The numbers in parentheses refer to literature cited.

titration, plus the added step of preparing the first carbonation juice for titration. First, the juice must be filtered and cooled and delivered to a mixing chamber at a uniform rate. Inasmuch as the alkalinity will vary while the flow is constant, the number of equivalents of base delivered per minute will vary.

The dilute sulfuric acid will incompletely, exactly or more than completely neutralize the base present in the filtered Dorr feed, depending on the flow and the concentration of the acid. As it is not practical to vary the concentration of the acid, the state of neutrality must be reached by varying the flow. Thus, a unit is needed to detect the acid-base unbalance and actuate a device which will vary the flow of acid. This flow-controller must also incorporate a flow indicator, which of course is also an alkalinity indicator. And, if possible, the alkalinity indicator should be capable of exercising control over factory carbonation so that it may be carried out at any desired point.

Fortunately, the acid-base unbalance can be detected by any of various pH measuring devices. These devices can in turn be made to operate electrical and mechanical equipment to vary the flow of acid either directly by operating a valve or changing the static head involved or indirectly by any of more or less complex devices.

The whole problem of development, then, resolves itself into finding that combination of pieces of apparatus which will best carry out this automatic titration.

Nature of the Alkalinity Titration Curve

Automatic control of the acid-juice titration depends to a large extent on the nature of the titration curve. Figure 1 shows the results obtained in titrating four samples of filtered first-carbonation juice with factory acid, using glass and calomel electrodes to measure the pH at 25° C. The third curve was obtained by titrating a dilute solution of sodium hydroxide which contained some sodium carbonate. Nitric acid gives practically identical curves. It is evident that the solutions are quite strongly buffered. The true neutrality point in an acid-base titration is taken as the point of greatest slope in the titration curve. It was found that the pH end-point was the same in solutions ranging from 0.060 to 0.155 in alkalinity, namely $7.08 \pm .06$ for the four runs. In the case of curve three, two additional inflectional points were noted at the bicarbonate and carbonic acid end-points.

Due to the fact that the curves are not precipitous in the immediate vicinity of the end-point, the use of phenolphthalein introduces an error in the determination of alkalinity. It was found by measurement of the neutralized solution with a glass electrode that the pH of juice titrated using phenolphthalein as an indicator was about 7.9. This titration was carried out in the manner in common use at Woodland, using a considerable excess of the indicator. Such a method reduces the error due to the natural coloring matter of the juice. From the curves in figure 1, it is seen that the measured alkalinity when using phenolphthalein is about 0.0035 too low. If the alka-

linity is to be correct within ± 0.0025 , the pH at the end-point must be held within about ± 0.7 . It should be noted that this refers to the juice titration and not to first-carbonation control where the alkalinity-pH coefficient is much greater.

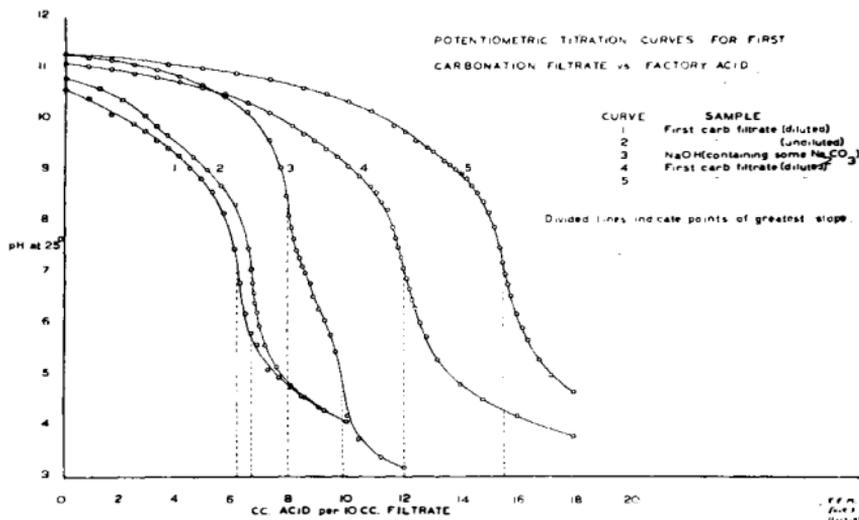


Figure 1.—Titration curves for first-carbonation juice.

General Description of Apparatus and Method of Operation

Figure 2 is a schematic diagram of the alkalimeter to which reference may be made in following the description of its operation.

The juice sample is taken from the recirculation line of the first-carbonation tanks, on the pressure side of the recirculation pump. It flows into a filtration pot in which are placed two Oliver-Borden type filters, which are connected through a reciprocating valve to sources of air pressure and vacuum. Sixteen-ounce duck cloth is used as the filtering medium and the filter cycle is set at 3 inches of vacuum for 17 seconds and 1 pound per square inch pressure for 7 seconds. For a more nearly continuous supply of juice, it is best to use two filters. Each filter must be connected to a separate filtrate receiver, but both receivers discharge through check valves into the same supply tank.

The filtered juice is next cooled and run into a miniature constant level tank from which it flows through a tube and out a glass capillary tip. The capillary tip is used so that a reasonably high static head may be employed and yet the flow rate will be a reasonably small value. This permits accurate adjustment of the constant juice flow.

The flow of filtered juice is easily controlled inasmuch as it is constant. The requirements for constant flow are (a) constant static head, (b) constant temperature, (c) constant orifice diameter and (d) constant composition of juice. Requirement (a) is easily satisfied and the heat exchanger in the filter system maintains the juice temperature within a few degrees. The juice composition should not vary sufficiently to affect the flow appreciably. The variation in factor (c) is not as easily estimated because scaling might cause a reduction in the orifice diameter. Tests to date have shown that this scaling effect is negligible over a period of 1 or 2 days. It may become serious, however, in a longer run, but an acid rinse will quickly dissolve the scale.

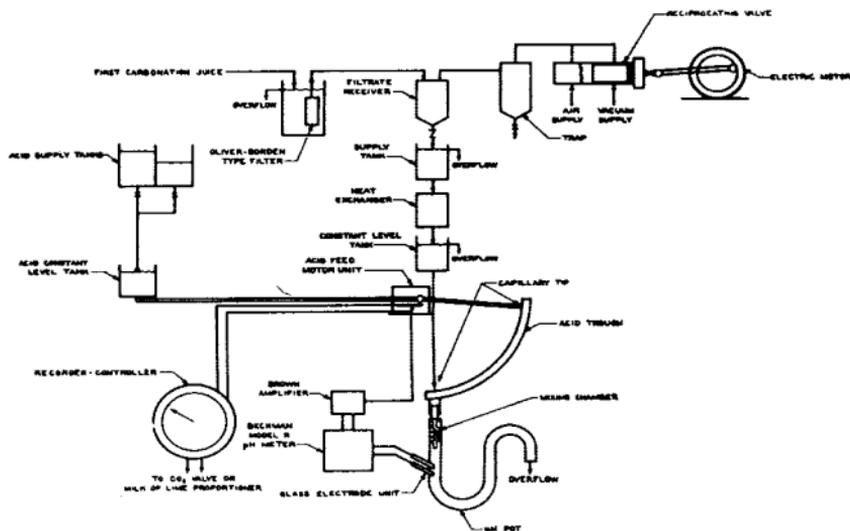


Figure 2. Schematic diagram of the alkalimeter.

The acid is stored in two large stainless steel tanks, one of which is in use while fresh acid is prepared in the other. From the storage tank the acid flows to a constant level tank, in which the level is controlled by a glass float valve. From this tank the acid flows through another tube and out a glass capillary tip. In this case the static head is variable, as will be explained later. Provisions are included to thermostat the acid.

The acid and juice are mixed intimately and passed by or through a detecting element which determines whether equivalent amounts of acid and alkali are present. This detecting element may be an optical system composed of a light source, color filters and a photo-electric cell. In such a case an indicator must be mixed with the acid. It may also be a set of electrodes to measure the electrical conductivity of the solution. Any of a number of different galvanic cells may be used to measure the hydrogen ion

activity in the solution. Examples of these cells are the antimony-calomel cells and the glass electrode-calomel cells. Inasmuch as the hydrogen ion activity is the most direct and exact measure of the degree of neutralization, we use a galvanic cell composed of a glass electrode and a saturated calomel electrode as the detecting element. Within 5 seconds after a change in the flow of acid, there should be an indicated change in the pH of the mixture in the pH pot.

The pH electrodes are connected to a Beckman Model R pH meter which is so adjusted that no current actuates the indicating milliammeter when equivalent amounts of acid and base are flowing through the pH pot. This has been shown to be the case when the pH is 7.08 at 25° C.

Now let us suppose that the alkalinity of the juice increases slightly. Since the flow rate of the juice is constant, the number of equivalents of alkali flowing per minute increases. This causes the pH of the acid-juice mixture to rise and current flows through the Beckman instrument milliammeter. Similarly, if the juice alkalinity decreases, the pH falls and current flows through the milliammeter in the opposite direction, i.e., the needle drops below the zero mark.

The change in pH must be made to cause a change in the flow of acid so as to restore the pH to 7.08. This is done by amplifying the small unbalance current from the pH meter with a Brown Instrument Company amplifier which in turn drives a reversible split phase motor. This motor is mounted in a Leeds and Northrup motor drive unit which also incorporates a gear train, output shaft and limit switches. The tube through which the acid flows is attached to the output shaft so that the capillary discharge tip can be moved in either a clockwise or counter-clockwise direction so as to dispense the acid into a circularly shaped trough. If the pH is above the control valve, the reversible motor will operate so as to rotate the acid dispensing tube in a clockwise direction and increase the flow of acid. As the pH approaches 7.08, the rate of rotation of the dispensing tube decreases and stops at the control point. The advantage of the Brown amplifier unit over a more conventional relay system is that the rate of operation is high when far away from the control point and becomes progressively slower as the control point is neared. This is highly desirable from a control standpoint. It is apparent that the acid dispensing tube will always move so as to restore the chemical balance in the mixture of juice and acid.

For any given juice alkalinity, there will be one and only one position of the acid dispensing tube which will produce a chemically neutral mixture. Hence the position of the tube is a measure of the alkalinity. The tube position may be indicated and recorded readily by connecting a resistance measuring instrument to the variable resistance which is an integral part of the Leeds and Northrup motor unit.

The alkalinity recorder must be calibrated under the conditions which will be used in actual operation. We use 75.0 milliliters of first-carbonation juice per minute and the strength of the nitric acid is 0.0250 normal

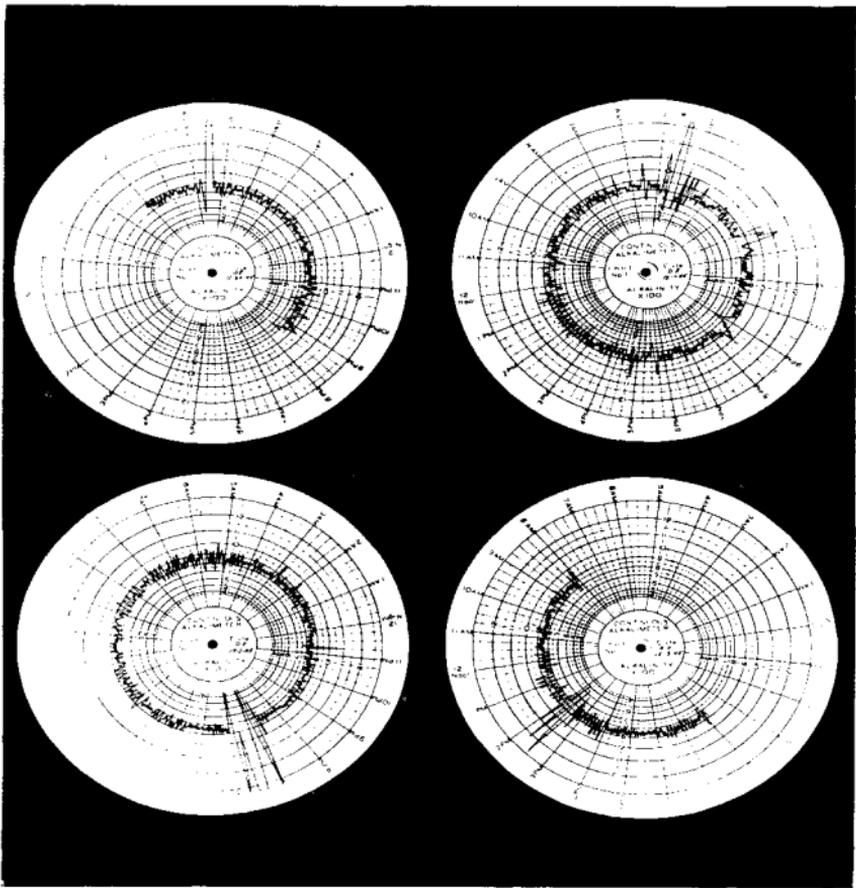


Figure 3.—Sample records of first-carbonation alkalinity control.

It is readily possible to use a recorder-controller in place of just an alkalinity recorder. In the installation at Woodland, the controller is used to position the kiln gas valve. In cases where control is effected by changing the milk of lime or saccharate milk flow, the alkalinity controller may be used for that.

Comparison of Alkalinity Determined by Alkalimeter and by Manual Titration

Many measurements have been made on various samples of juice to check the accuracy of the alkalinity as determined by the automatic titrator. Rather than include a lengthy table, only average values will be given. For

67 measurements, the average alkalinity determined by the alkalimeter was 0.0841 and that determined on 67 samples of juice titrated by hand was 0.0807. The average difference of 0.0034 is due to the fact that the pH end-point used in the phenolphthalein titration is not the true end-point, as was pointed out previously. The difference which one would expect from the titration curves (figure 1) is 0.0035. It is to be noted that the alkalimeter can be adjusted to titrate to any desired pH end-point.

Automatic Control of Alkalinity

As an illustration of the sort of control which has been obtained with the alkalimeter, we refer to figure 3, which shows the charts obtained in a 72-hour run during which rather complete data were taken on most of the variables affecting the process. The average alkalinity was 0.0856, which is quite close to the control value of 0.0850. At four different times, control was apparently lost; however, it was shown that these upsets were due to beet-end operating difficulties such as a plugged saccharate milk line to the carbonation station. At another time, the carbonation operator increased the saccharate milk flow by a large amount and considerable deviation occurred before control was again established.

The persistent cycling which was noted at times was due to an insufficiently wide throttling range. Little could be done about this point, however, as the control instrument was set at its lowest sensitivity.

Conclusion

An automatic alkalimeter can be used solely as a recording instrument and is of most value in such an application as a means of determining what aberrations in beet-end control are responsible for imperfect first-carbonation control. When these secondary variables have been placed under good control then the alkalimeter becomes of most value as a recorder-controller, giving the best possible alkalinity control. It is not recommended, however, that an alkalimeter be installed unless the secondary variables in carbonation such as first-carbonation temperature, raw juice density and flow, milk of lime flow and lime content, kiln gas pressure and carbon dioxide content are well controlled.

Literature Cited

- (1) SKAAR, K. S. AND MCGINNIS, R. A.
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