Acid Content of Whisky

Variation with Age and Dilution

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Titration curves were obtained on different aged samples of the same whisky by means of a glass electrode potentiometric method using carbon-dioxide-free 0.046 *N* sodium hydroxide as titer. From the variation of the successive displacements of the curves as the age of the whisky increases, the conditions and environment of the storage warehouse can be predicted approximately.

The dissociation of the weak organic acids present in whisky is governed, to a considerable extent, by the concentration of ethyl alcohol and shows a marked change when the whisky is diluted with distilled water, 95 per cent ethyl alcohol, or a 50 per cent ethyl alcohol solution.

Similar variations were obtained when working with a synthetic whisky made by adding 0.5 ml. of glacial acetic acid to 1 liter of 100-proof ethyl alcohol solution.

The electromotive force of the cell or the pH values determined during the titrations are only relative to each other and are not the same as obtained on pure water solution, since the combined dissociation effect of the water and ethyl alcohol was not taken into account.

THE acids in whisky are determined according to the A. O. A. C. method and yield only the total amounts of titratable acids present. From these data it is concluded that the acid content of the whisky increases during aging and depends to some extent on the treatment and the storage environment. The acid content which is low in a new whisky increases rapidly at first and approaches asymptotically a constant concentration, indicating that the rate of increase of total acids decreases slowly with increased aging (*3*).

The method also suggests that the whisky, if dark, be diluted with water in order to decrease the color and make the end point or the phenolphthalein color change more perceptible. The results thus obtained are not corrected for dilution which, according to Acree and his associates (*1*) and to Kolthoff (*2*), affects the sensitivity of the phenolphthalein indicator and should accordingly alter the final value of the acid content of the whisky. For this reason it was decided to investigate the behavior of the acids in whisky during aging and on dilution with various solvents, by obtaining complete titration curves using a glass electrode potentiometric method. The changing alcoholic content makes the relations between hydrogen-ion concentration, undissociated acid, electromotive contact potential, salt errors, and color changes of indicators different from those of acetic and other acids in water, but the data can be used for comparative purposes.

Apparatus and Method

The determinations were made by pipetting 100 ml. of sample into a 150-ml. beaker in which dipped a glass and a calomel electrode. The solutions, which were stirred vigorously at all times to ensure rapid and complete equilibrium, were titrated with 0.046 *N* sodium hydroxide free of carbon dioxide. The change of the hydrogen-ion concentration during the titration was determined with a Leeds & Northrup potentiometer No. 7657, reading directly in pH units. The temperature was maintained within the range 30° to 31° C. during all of the experiments. The heat liberated during the dilution experiments was nullified by properly cooling the solvents prior to adding them to the whisky.

Description of Whisky

The whiskies for these experiments were those samples used in a previous investigation (*3*) and had stood in glass containers from the date of their removal from the barrel until the present time.

The whisky used in determining the variation of the acid content with dilution is a composite made of rye and bourbon of various ages. The average age of the composite is 2.5 years.

A sample of synthetic whisky was made by diluting absolute ethyl alcohol to 100 proof with distilled water and adding 0.5 ml. of glacial acetic acid and 1 ml. of phenolphthalein indicator solution to each liter of dilute alcohol solution. This simulated the composite whisky with respect to acid concentration, which is approximately 53 parts per hundred thousand, and allowed also the determination of the neutral point of the titration with respect to the color change of the indicator.

Results of Aging

Figure 1 gives the titration curves (pH versus volume of standard alkali) obtained on different aged samples of the same whisky (Serial No. 3630). Each curve represents the result obtained on a sample removed from the storage barrel at 6-month intervals, beginning on April 4, 1930. The rate of increase of the concentration of the acids, which is rapid at first, decreases as the aging proceeds, as shown by the gradual decrease in the displacement of the curves as the age of the whisky increases. However, the displacement of every curve is not a gradual decrease for each 6-month period but appears to be alternately periodic in nature. The age in years of the samples is given by the number above each curve. The increase in concentration of acids for the 6-month period from 3.5 to 4 years is less than that for the period from 4 to 4.5 years. We may predict from these periodic irregularities that, since the former period is from November to April and the latter period is from April to November, the whisky is stored in an unheated warehouse and the increase in acid

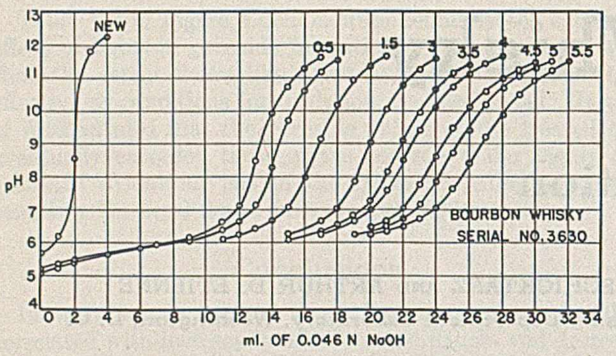

Figure 1. Titration Curves of Successive 6-Month-Old Samples of the Same Bourbon Whisky

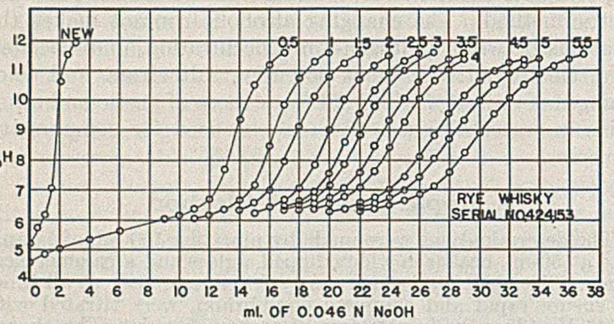

Figure 2. Titration Curves of Successive 6-Month-Old Samples of the Same Rye Whisky

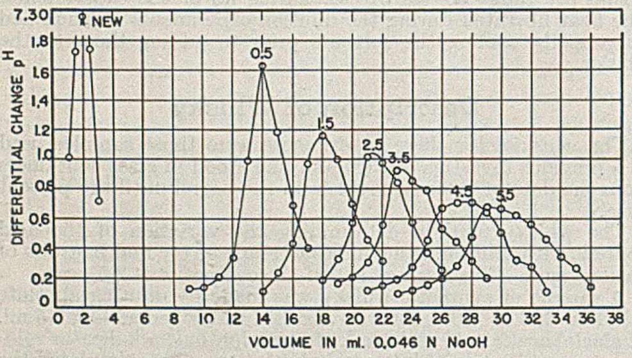

Figure 3. Change of $\Delta pH/V$ near the Neutral Point in the Titration of Different Aged Samples of the Same Whisky

concentration during the cold winter months is not as great as that during the hot summer months.

The newly made whisky, as shown by the first curve in Figure 1, contains only a small amount of acid. We may assume that the acid present belongs to the group of volatile acids, is paraffinic in nature, and has a dissociation constant approximating that of acetic acid, since the shape of the titration curve is similar in all respects to that of acetic acid. Figure 2 shows the titration curves obtained on a rye whisky (Serial No. 424,153) which was stored in a heated warehouse. It is concluded from the alternate periodic displacement of the curves that the warehouse was heated only during the winter months for the first 2.5 years and that the average temperature during this time was higher than during the summer months. At the end of the 2.5-year period the periodic displacement of the curves was reversed. It appeared, therefore, from then on, that the average temperature of the warehouse during the winter was lower than that during the summer months. (This was confirmed by a letter from the distillery stating that the experimental barrel of whisky, originally placed on the fourth floor of the warehouse and kept at an average temperature of 80° F., had been moved at the end of the 2.5-year period to the second floor, at a temperature of only 70° F.)

The shape of the curves also continues to change during aging, and the values of the tangents decrease between pH 8 and 10. This behavior is shown in Figure 3, in which the ratio of the rate of the change of pH to the volume of caustic is plotted against the volume of caustic added. The curve for the new whisky gives a sharp inflection point, which tends to smooth itself and broaden out as the age of the whisky increases, indicating a gradual change in the concentration and possibly the number of the weak acids, presumably being extracted from the barrel.

Results of Dilution

It was found that the shape of the titration curves was distorted and displaced considerably when the whisky was diluted and depended on the amount of dilution and the characteristics of the diluent.

Figure 4 shows the results obtained by titrating a 100-ml. sample of the composite whisky and 100 ml. of the whisky diluted to 400 ml. with distilled water, 50 per cent ethyl alcohol solution, and 95 per cent ethyl alcohol, respectively. The ethyl alcohol (U. S. P.) used for dilution was not neutralized.

Figure 5 shows the ratio of the rate of change of pH with volume of caustic plotted against the volume of caustic added for the four curves mentioned. The inflection, or neutral point, of the titrations of the 50 per cent alcohol

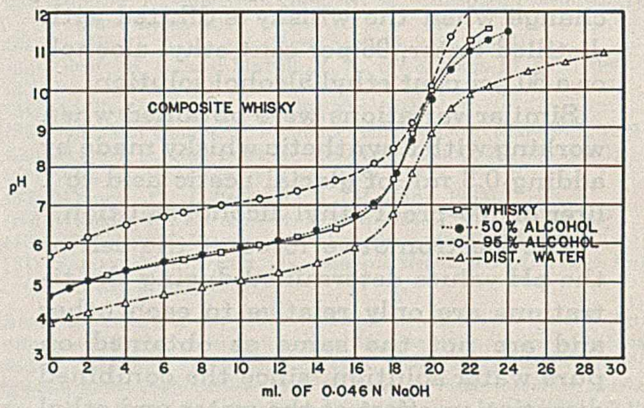

Figure 4. Variations in Shape and Position of Titration Curves of a Composite Whisky Diluted with Different Solvents

and the water dilution give the same total moles of acid present in the whisky, whereas the 95 per cent alcohol dilution indicates a greater amount of acid present. However, all three dilution curves yield results which are too high, as compared to the titration of the whisky itself. The percentage errors thus introduced are given in the third column of Table I.

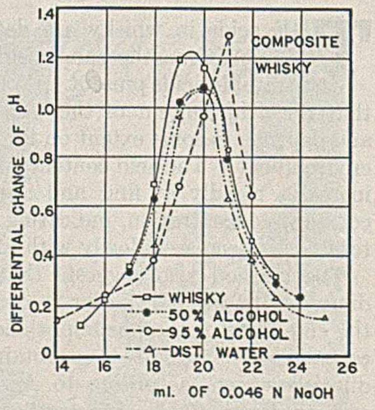

Figure 5. Change of $\Delta pH/V$ near the Neutral Point in the Titration of a Whisky Diluted with Various Solvents

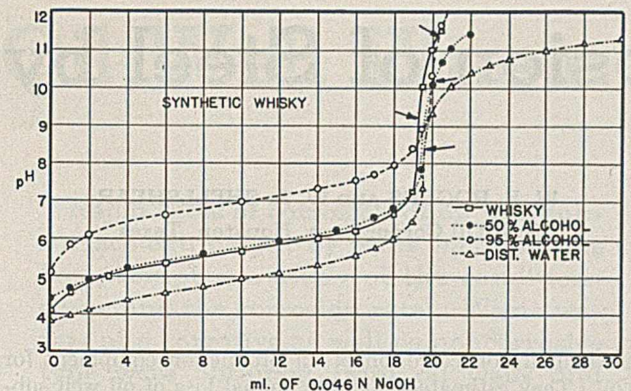

FIGURE 6. VARIATIONS IN SHAPE AND POSITION OF TITRATION CURVES OF A SYNTHETIC WHISKY DILUTED WITH DIFFERENT SOLVENTS

To investigate more fully this phenomenon, titration curves were obtained on a sample of synthetic whisky and on the various diluted solutions. The results of these determinations are given by the curves in Figure 6, which follow closely the results obtained on the composite whisky. The change of pH during the titration was followed with the glass electrode along with the phenolphthalein color change, which is indicated for each curve by an arrow and is given in the sixth column of Table I. The variation of the pH at which phenolphthalein changes color during titration is in agreement with the results obtained by Acree and his associates (*1*) and by Kolthoff (*2*). The sensitivity of the phenolphthalein depends on the concentration of the ethyl alcohol, and the pH at which the color change occurs increases with increasing concentrations of alcohol.

TABLE I. RELATION OF TOTAL TITRATABLE ACIDS TO DILUTION

Diluent	Inflection Point	Error	Phenolphthalein End Point	Error	pH of Phenolphthalein Color Change
	Mole acid/ 100 ml. whisky	*%*	*Mole acid/ 100 ml. whisky*	*%*	
Original whisky	0.000896	...	0.000887	...	9.15
Distd. water	0.000916	2.0	0.000896	1.0	8.35
50% alcohol	0.000916	2.0	0.000923	4.0	10.10
95% alcohol	0.000966	7.0	0.000970	9.0	11.40

There is a large difference between the end point as indicated by the change of color produced by the phenolphthalein, and that calculated from the titration curves. In the fifth column of Table I are given the errors introduced by dilution when the neutral points obtained by the change of color of the phenolphthalein for the synthetic whisky are used to determine the neutral points of the titration curves in Figure 5.

Figure 7 gives the curves showing the change of pH when 100 ml. of the composite whisky is diluted with distilled water, a 50 per cent ethyl alcohol solution, and 95 per cent ethyl alcohol, respectively. The pH remains fairly constant when the whisky is diluted with a 50 per cent ethyl alcohol solution, indicating that the buffer action of the acids and salts are fairly constant on dilution, as is usually the case. Since the whisky consists, approximately, of 50 per cent ethyl alcohol, we may assume that the dissociation of the acids is dependent largely on the concentration of the alcohol and only slightly on the dilution. When the whisky is diluted with distilled water, there is a noticeable decrease in pH or an increase in hydrogen-ion concentration, indicating that the dissociation of the acids is increasing because of the decrease in the concentration of alcohol and of an increase in the value of the dielectric constant of the solution. As should be expected from the previous dilution tests, the dissociation of the acids decreases when the whisky is diluted with 95 per cent ethyl alcohol.

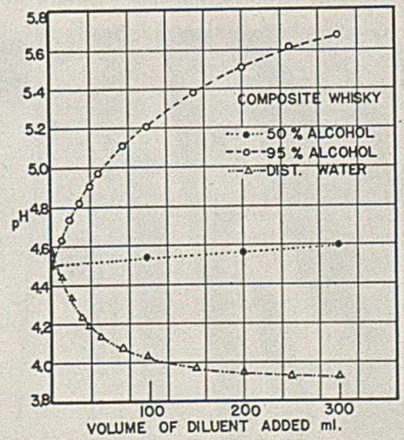

FIGURE 7. CHANGE OF pH OF A COMPOSITE WHISKY ON DILUTION

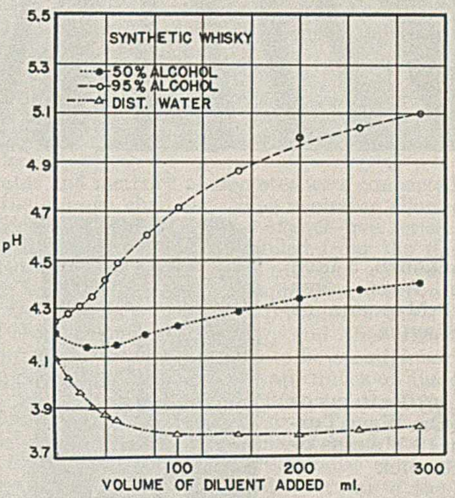

FIGURE 8. CHANGE OF pH OF A SYNTHETIC WHISKY ON DILUTION

Figure 8 shows the curves obtained when a 100-ml. sample of synthetic whisky is diluted with the respective diluents. These curves are similar in shape to those obtained from the composite whisky samples. The small increase in the initial pH of the 50 and 95 per cent ethyl alcohol dilutions was caused by a small amount of alkali remaining on the electrode from the water dilution determination. During the first part of the water dilution, the dissociation of the acid increases, owing to the decrease in concentration of the alcohol, and approaches a constant value at a dilution of about 2 parts of water and 1 of whisky. Upon further dilution, the pH of the solution increases, indicating that the dissociated acetic acid is now showing the normal effects of dilution. In other words, the increase in per cent of ionization of the weak acid by dilution is not sufficient to compensate for the decrease in concentration of the hydrogen ions on dilution, and hence a rise in pH.

Acknowledgment

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