monthly check samples (cf. footnote,[c] Table II).

The application of the procedure for the determination of aluminum in wet-process phosphoric acid is shown in Table III. Duplicate determinations differed by 0.05% or less.

Acknowledgment

Grateful acknowledgment is made to Edward J. Fox for advice and guidance in this project, and to Milton A. Norland and Carl J. Erickson for assistance in the analytical work.

Literature Cited

(1) Assoc. Florida Mining Chemists, Florida Land Pebble Phosphate Industry, "Methods Used and Adopted," 1948.
(2) Atack, F. W., *J. Soc. Chem. Ind.* **34,** 936 (1915).
(3) Barton, C. J., *Anal. Chem.* **20,** 1068 (1948).
(4) Flagg, J. F., "Organic Reagents Used in Gravimetric and Volumetric Analysis," Vol. **4,** p. 133, Interscience, New York, 1948.
(5) Hillebrand, W. F., Lundell, G. E. F., "Applied Inorganic Analysis," 2nd ed., Wiley, New York, 1953.
(6) Jacob, K. D., *et al.*, U. S. Dept. Agr., Tech. Bull. **364** (1933).
(7) Sandell, E. B., "Colorimetric Determination of Traces of Metals," 2nd ed., pp. 142, 161, Interscience, New York, 1950.
(8) Sandell, E. B., Cummings, P. F., *Anal. Chem.* **21,** 1356 (1949).
(9) Strafford, N., Wyatt, P. F., *Analyst* **72,** 54 (1947).
(10) Yoe, J. H., Hill, W. L., *J. Am. Chem. Soc.* **50,** 748 (1928).

Received for review February 12, 1959. Accepted May 7, 1959.

WHISKEY AGING

Effects of Barreling Proof on the Aging of American Whiskeys

C. S. BORUFF and L. A. RITTSCHOF

Research Department, Hiram Walker & Sons, Inc., Peoria, Ill.

Three whiskey distillates were barreled for aging at 110 (control) and distillation proof. Experimental barreling proofs were 118, 127, and 154. During 8-year aging in new charred oak barrels the percentage losses of whiskeys barreled at proofs above 110 were slightly lower than the controls; the tendency was not statistically significant because of the relatively small number of experimental barrels. Chemical characteristics developed during aging of whiskeys barreled at 118 and 127 proofs fell within normal limits, but at 154 proof were lower than normal. Flavor after aging 8 years was normal in the whiskey barreled at 118 proof, slightly less mature at 127 proof and different at 154 proof because of a spicy green oak taste. An industry-wide experiment is now under way.

Traditionally, American distillers have barreled their whiskey distillates for aging at potable proof—i.e., about 100 to 102 proof (50 to 51% alcohol by volume). In other countries, distilled spirits are barreled for aging at proofs from 124 to 150 and more (*4, 12*).

In 1898, 31 U. S. distillers barreled their whiskeys between 100 and 104 proof (*3*); in 1929, 11 distilleries barreled their whiskeys between 100 and 102.6 proof (*13*), and in 1945, 13 distillers cooperating in an aging experiment barreled 16 whiskey distillates at proofs ranging from 101.1 to 110.0 (*8*).

Government regulations define straight whiskey as an alcoholic distillate from a fermented mash of grain distilled at not over 160 proof, barreled at not less than 80 nor more than 110 proof, and aged for not less than 24 months in charred new oak barrels (*10, 11*).

In the past, the barreling proof limitation on U. S. whiskeys was of little concern, but in recent years it has taken on greater importance. There are several obvious economic advantages in barreling whiskey at proofs higher than 110, if whiskey quality is not impaired and losses during aging are not excessive. These advantages have become increasingly pertinent recently because of the increasing high costs of new quarter-sawn white oak cooperage and warehouse aging facilities.

If whiskeys could be aged at higher proofs, more proof gallons per barrel would result and the number of proof gallons stored per warehouse would be increased. For example, a 50-gallon barrel filled with 102-proof whiskey contains 51 proof gallons. At 110 proof it would contain 55 proof gallons and at 130 proof, 65 proof gallons, resulting in gains of 7.8 and 27.4%, respectively. Very few U. S. whiskeys are distilled above 130 proof.

There have been no data published on the effects of aging U. S. whiskeys barreled at proofs above 110 on the losses experienced or the chemical and organoleptic quality. The data summarized below give the results of three typical experiments taken from a more extensive study on this subject, started in 1949 and concluded after an 8-year aging period.

Experimental

Distillates. Each experiment consisted of a typical whiskey distillate barreled at two proofs: 110 proof (control) and distillation proof. It had been established previously that barreling proofs of 102 and 110 give whiskeys of comparable quality after aging. Ever since 1944, the company's standard barreling proof has been 110 for American whiskeys.

The three distillates chosen for this report represent whiskeys distilled at high, low, and medium proofs: rye I, 154 proof; bourbon II, 118 proof; bourbon III, 127 proof. These distillates were from normal routine, full-scale commercial productions.

Cooperage. The barrels came from three carloads of routine receipts. Both experimental and control barrels for a single whiskey type came from a single carload of barrels. All barrels were charred new white oak barrels of approximately 50-gallon capacity, manufactured by the Hiram Walker Cooperage Division in accordance with the company's specifications. For each whiskey at each barreling proof, five barrels were chosen at random for the studies.

Warehousing. Experimental barrels were racked alternately with control barrels in a location considered normal

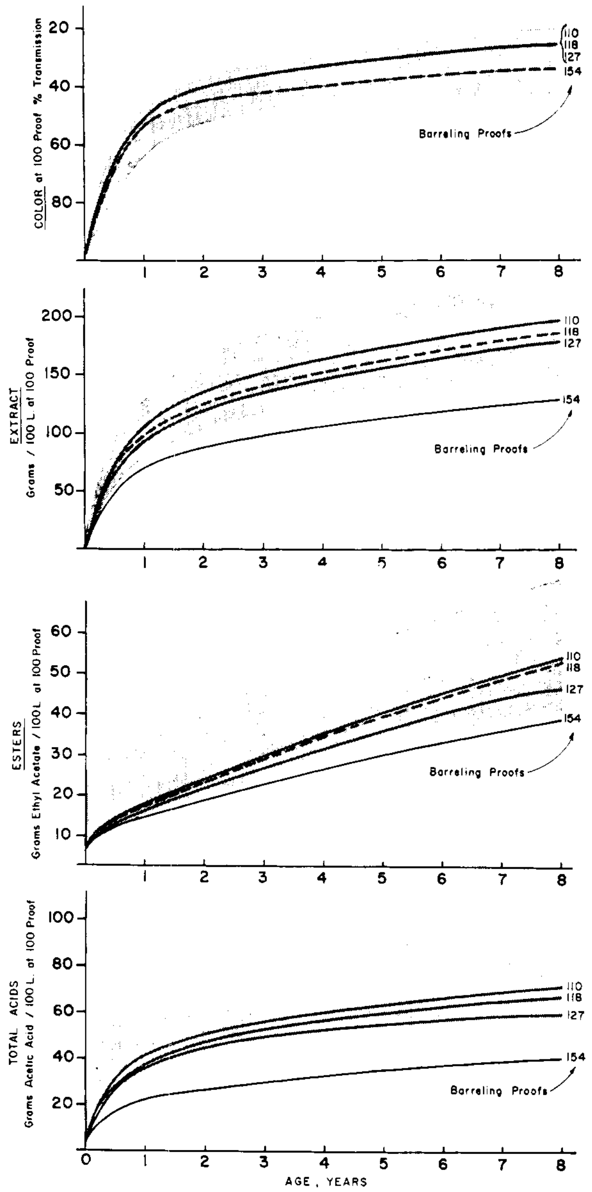

Figure 1. Effect of barreling proof on development of chemical characteristics in whiskey aged 8 years in new charred oak barrels

Shaded area shows dispersion of analytical values of 489 barrels of whiskey filled at 101.8 average proof

and average for the Peoria rack warehouses. Warehouses are of brick and concrete construction with solid concrete floors every 12 tiers and are equipped to give air circulation to facilitate temperature and humidity control (*5*). All barrels were listed with the Alcohol and Tobacco Tax Division, Internal Revenue Service, so that periodic samples could be taken under government supervision.

Losses. All barrels were weighed every 6 months and evaporation losses calculated. Losses were corrected for samples withdrawn. Total losses, including evaporation and soakage, were calculated at the end of 8 years of aging, when the barrels were withdrawn.

Sampling. At 6-month intervals, a half-pint sample was drawn from each barrel. The five samples from each group of barrels were composited in the laboratory. The composites were used for chemical analyses and flavor examinations.

Chemical Analyses. All analyses, except color and turbidity, were performed according to standard methods (*7*). Color was determined at 100 proof as per cent transmittance, with a Lumetron photoelectric colorimeter, in a 13-mm. cell, using a 490-mμ filter and setting the instrument at 100% transmittance with distilled water. Turbidity determinations were performed with a Model 7 Coleman Photo-Nephelometer calibrated against Nephelos standards supplied with the instrument.

Organoleptic Analyses. All taste and bouquet examinations were conducted by the expert organoleptic panel which is the Quality Committee for the distillery. This panel is composed of at least five examiners for every test. All 14 members of the panel were originally screened for acuity and trained. They have a background of many years of experience in flavor testing of whiskeys. Samples were examined in pairs: control *vs.* experimental. In instances where it appeared that there might be differences in flavor between samples, these differences were confirmed or rejected by means of the triangle test (*6*).

Results and Discussion

Loss Experience. The 8-year aging losses summarized in Table I show a slight tendency toward lower percentage losses at barreling proofs higher than 110. Evaporation losses at younger ages showed a similar trend. There are insufficient barrels in the experimental groups to make the data statistically significant. To bring the control group data to above the minimum of 30 to 40 barrels for statistical significance, 30 additional routine 110-proof barrelings were added to the 15 control barrels.

Chemical Quality. The changes occurring in whiskey during aging—that is, total solids, color, and constituents such as acids, aldehydes, esters, fusel oil, pH, tannins, and furfural—are fairly well known (*7*). These characteristics have been used for many years as a rough measure of quality, but they do not define all the flavor characters in whiskey. For example, the human senses of taste and smell can note a significant difference between a bourbon whiskey and a rye whiskey that appear to be identical according to ordinary chemical analyses.

The effect of barreling proof on the common characteristics of whiskey after 8 years of aging is shown in Table II. Congeners that come mainly from the charred oak barrel during aging, such as extract, acids, and tannins, do not reach levels, at the higher barreling proofs, quite as great as shown by the control whiskeys barreled at 110 proof. Esters and aldehydes show this tendency also; it is not so pronounced with color and furfural and is not evident with pH and fusel oil.

Graphs of the data accumulated from the chemical analyses for fusel oil and pH over the entire aging period show the normal increase with age, regardless of barreling proof, and need not be shown here. However, graphical illustration of how other congeners develop during aging are of interest, and examples are given in Figure 1.

Figure 1 shows how some of the chemical characteristics in whiskeys barreled at various proofs develop with age. The effects of barreling proof are pronounced, but not shown is the spread displayed by the values for the 110-proof controls and the experimental barrels. The single curves drawn for the control and experimental whiskeys are the lines that best fit all of the data in this study. There were some scattering of values, especially the ester determinations, and overlapping of data especially from the 110- and 118-proof barrelings.

Liebmann and Scherl (*7*), in an 8-year study of the changes occurring in 489 barrels of whiskey barreled at 101.8 average proof, calculated standard deviations for the various congeners in whiskey and plotted dispersion limits. The dispersion limits define the areas within which a whiskey from any barrel

Table I. Effect of Barreling Proof on Losses of Whiskeys Aged 8 Years in New Charred White Oak Cooperage

				Losses at 8 Years of Age[a]							
				Evaporation Losses				Total Losses			
				Leakers Not Included		Leakers Included		Leakers Not Included		Leakers Included	
Whiskey	Barreling Proof	Av. Final Proof	Av. Lb. Soakage	No. of bbls.	% loss	No. of bbls.	% loss	No. of bbls.	% loss	No. of bbls.	% loss
Controls[b]	110	112.8	22.6	32	20.33	45	21.43	32	26.35	45	27.46
Bourbon II	118	119.6	22.1	2	20.23	5	20.41	2	26.15	5	26.46
Bourbon III	127	128.1	22.8	5	19.60	5	19.60	5	25.84	5	25.84
Rye I	154	151.6	22.6	3	17.81	5	20.37	3	23.95	5	26.49

[a] Losses corrected for samples taken and expressed as % of original proof gallons. Total losses include soakage plus evaporation.
[b] 15 controls of this experiment plus 30 additional routine barrelings at 110 proof.

Table II. Effect of Barreling Proof on Chemical Analyses of Whiskeys Aged 8 Years in Charred New White Oak Cooperage

	Whiskey					
	Bourbon II		Bourbon III		Rye I	
Barreling Proof	110	118	110	127	110	154
Proof after 8 years	112.6	119.6	113.1	128.1	113.1	151.6
Color at 100 proof, % trans.	23.0	23.4	23.4	23.9	25.7	34.2
pH at 100 proof	4.00	4.00	4.02	4.03	4.03	4.02
	Grams per 100 Liters at 100 Proof					
Extract	200.4	187.2	201.3	179.8	191.5	127.6
Total acids as acetic	73.8	67.0	69.5	57.9	68.4	40.3
Fixed acids as acetic	16.0	15.0	17.1	15.9	16.0	11.8
Volatile acids as acetic	57.8	52.0	52.4	42.0	52.4	28.4
Esters as ethyl acetate	56.1	56.1	50.9	46.9	49.5	37.0
Aldehydes as acetaldehyde	10.2	9.3	8.1	6.8	9.5	5.5
Fusel oil as amyl alcohol	155.3	156.9	142.7	138.4	165.4	165.6
Furfural	2.1	2.0	2.3	1.9	2.1	1.6
Tannins	65.1	60.8	67.7	63.0	57.9	45.4

chosen at random will exhibit characteristics 95% of the time (shown as shaded in Figure 1). With only a minor exception, the whiskeys barreled at 110, 118, and 127 proof show normal chemical characteristics. The data for the whiskey barreled at 154 proof fall below the dispersion limits and therefore it may be considered different in chemical composition.

Organoleptic Quality. Taste and bouquet of whiskey are more important criteria of quality than the usual chemical analyses. Certainly, the consumers of distilled spirits use flavor as their most important measure of quality. For this reason, much emphasis was placed on conducting taste tests on the whiskeys in the most careful manner and under controlled conditions by the Quality Committee of expert tasters.

Samples of bourbon II, barreled at 110 and 118 proof, were always ranked the same in taste and bouquet over the entire 8-year aging period.

Differences in flavor due to barreling proof were noted in samples of bourbon III, barreled at 110 and 127 proof. For the first 2 years of aging, the whiskey barreled at 127 proof lagged behind its control in the development of mature flavor. From 30 to 66 months of age, both whiskeys tasted the same. Beginning at 72 months, the whiskey barreled at 127 proof was slightly lighter in bouquet. At 90 and 96 months, the experimental whiskey had a barely perceptible different kind of woody taste compared to the control. This taste, while not pronounced, was described as being like green oak wood and rather spicelike. As no perceptible different flavor developed in the whiskey barreled at 127 proof until it was almost 8 years old, the higher barreling proof had no commercial effect on whiskey quality at the currently common marketable ages.

Rye I, which was barreled at the highest proof, 154, showed rather significant flavor differences when compared to its control. It seemed to lag behind in development of mature flavor at all ages up to 72 months. At 78 months it was judged as fully mature as the control, but it contained a trace of a "different kind" of woody flavor, which increased slightly with age until the last samples were taken at 96 months. This different kind of woody flavor was definitely pleasant, slightly spicy, and similar to green oak wood. Hence, 154 barreling proof is undesirable because it resulted in slower development of mature flavor, and, at ages over 6 years, in a different flavor.

Whiskey Clarity. There is a slight tendency for aged whiskeys barreled at proofs higher than 110 to show higher turbidities when reduced to common bottling proofs (100, 90, and 86 proof) than the same whiskeys aged at 110 proof. This tendency is not significant for the 8-year whiskeys of 118 and 127 barreling proofs. However, for the whiskey barreled at 154 proof and aged for 8 years, the turbidities, when reduced to 100 and 86 proofs, are considerably higher than shown by its control. Table III summarizes the data.

Table III. Turbidities at Bottling Proofs of 8-Year Whiskeys Barreled at 110, 118, 127, and 154 Proof

		Turbidity, Nephelos Units	
Whiskey	Barreling Proof	At 86 proof	At 100 proof
Bourbon II	110	5.5	5.0
	118	5.5	5.0
Bourbon III	110	7.5	7.5
	127	9.0	7.5
Rye I	110	5.0	8.0
	154	18.0	14.0

Whiskeys that show a high turbidity when reduced to bottling proof will be more difficult to filter than whiskeys having a low turbidity when reduced to bottling proof. Therefore, one would expect little or no effect on filterability of aged whiskeys barreled at 118 or 127 proof, but would expect filtration difficulties for aged whiskey barreled at 154 proof.

Conclusions

The current U. S. legal maximum limit of 110 proof on barreling whiskeys could be increased to about 125 proof without affecting aging losses, quality, or filterability. Alternatively, the barreling proof portion of the regulations could be deleted, leaving the decision on entry proof to the distiller's discretion as it is in other countries.

As a result of a preliminary but more extensive report of 7-year data on this subject (*2*), the U. S. Treasury Department has made it possible recently (*9*) for each registered distillery to barrel, age, and use up to 1000 barrels of whiskey barreled at experimental proofs above 110. Many distillers are expected to participate in an industry-wide experiment. Final data will be summarized by both the participating distillers and the Treasury Department after an aging period of 4 to 8 years.

Acknowledgment

The authors are indebted to many colleagues at Hiram Walker & Sons, Inc., who contributed to this study, especially members of the Control Laboratory who performed most of the chemical analyses, members of the Quality Panel who conducted the taste tests, and members of the Maturing Division who made the loss determinations.

Literature Cited

(1) Assoc. Offic. Agr. Chemists, Official Methods of Analysis, 7th ed., p. 127, Chap. 9, 1950.
(2) Boruff, C. S., private communication, July 17, 1956, to Technical Committee, Distilled Spirits Institute, and to ATTD, Internal Revenue Service, U. S. Treasury Dept.
(3) Crampton, C. A., Tolman, L. M., *J. Am. Chem. Soc.* **30,** 98 (1908).
(4) Grossman, H. J., "Grossman's Guide to Wines, Spirits and Beers," rev. ed., p. 218, Charles Scribner's Sons, New York, 1955.
(5) *Heating, Piping & Air Conditioning* **26,** (1), 166 (1954).
(6) Helm, E., Trolle, B., *Wallerstein Lab. Communs.* **9,** 181 (1946).
(7) Liebmann, A. J., Scherl, B., *Ind. Eng. Chem.* **41,** 534 (1949).
(8) Schoeneman, R. L., U. S. Treasury Dept., Internal Revenue Service, Publ. **156** (1955).
(9) U. S. Treasury Dept., Internal Revenue Service, *Federal Register*, April 13, 1958, Amendment 220.548a, T. D. 6290.
(10) U. S. Treasury Dept., Internal Revenue Service, Regulations No. 5, Section 5.21 (b) (2).
(11) *Ibid.*, Section 5.1 (j).
(12) Valaer, P., *Ind. Eng. Chem.* **32,** 935 (1940).
(13) Valaer, P., Frazier, W. H., *Ibid.*, **28,** 92 (1936).

Received for review February 25, 1959. Accepted May 26, 1959.

MINERAL COMPOSITION OF VEGETABLES

Mineral Elements in Fresh Vegetables from Different Geographic Areas

HOMER HOPKINS and JACOB EISEN
Human Nutrition Research Division, Agricultural Research Service, U. S. Department of Agriculture, Beltsville, Md.

The concentration of ten elements in nine different fresh vegetables collected in the Washington, D. C., wholesale market is reported. Marked divergencies between different producing areas were found for the sodium content of lettuce and onions, and for manganese in carrots and celery, among others. Copper and manganese in sweet corn showed statistically significant differences between means for individual lots grown on the same farm and illustrate the problems inherent in reporting averages for highly variable elements for a given producing area.

With the introduction of new varieties and the use of different cultural practices in crop production during the last decade, there is interest among nutritionists and others regarding the nutrient content of present-day foods (*1, 10, 11*). This paper reports on the mineral composition of nine fresh vegetables grown in widely different sections of the United States during 1956 and 1957.

Materials and Methods

Among the 27 or more commercial fresh vegetables available to consumers in this country, nine were chosen for study: asparagus, snap beans, cabbage, carrots, pascal celery, yellow sweet corn, iceberg lettuce, dry yellow onions, and tomatoes. The selection was based on data from the Department of Agriculture's 1955 food consumption survey (*19*) which show these to be the vegetables, other than potatoes, consumed in the largest quantities by households in the United States. Market grades of all vegetables studied were designated as U. S. No. 1 or better.

Three or more lots of each vegetable were collected equally from major producing areas represented in the Washington, D. C., wholesale market during 1956 and 1957. By contacting as many as six wholesale merchants sufficiently in advance, it was possible to locate those who could furnish the needed vegetables. The producing areas for each vegetable studied in 1957 were chosen to account for 90% or more of the volume reaching the Washington wholesale market, except for sweet corn and tomatoes (*16*).

Most of the vegetables chosen for this study had a seasonal delivery pattern in the local market (*16*). Because of this, not more than five different vegetables made up each set collected in any one year. Difficulties in collection arose even with this small number, particularly for vegetables coming from a large number of producing areas.

Each lot collected came from a large population with respect to volume shipped into the Washington market. The smallest carrot population encountered in the wholesale market during 1957, among five carrot shipping areas, was 100,000 pounds shipped from Arizona, while the largest carrot population was 675,000 pounds shipped from Texas (*16, 18*).

In cases where the same shipper's label appeared during successive weeks of collecting the replicate lots, the wholesaler would make available other railway car or truck shipments from which it was possible to collect another lot. The shipper's name, railway car or truck number, name of wholesaler, date of collection, shipper's label on the carton, and other pertinent information were recorded on the receipt of each lot of vegetables. During 1957, much of this information was transferred to a postcard questionnaire and mailed to the various shippers and growers requesting more information on the origin of the samples.

Upon arrival of the vegetables in the laboratory, the entire sample was weighed to obtain the "as purchased" weight. Lot size for each vegetable corresponded to units normally found in the wholesale market, such as crates, cartons, or bushels. The entire lot or portion thereof was trimmed to the "edible portion," rinsed in demineralized water, and blotted with clean filter