Determination of Artificial Color in Whisky

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In the examination of whisky for color before the prohibition era, the principal test applied for caramel was straight amyl alcohol, which is not now considered a very satisfactory reagent in the light of present knowledge of color tests and reagents. The test was applied by putting about 10 cc. of whisky in a 6-inch (15-cm.) test tube, adding two or three times as much amyl alcohol, and shaking.

Amyl alcohol indicated practically all artificial color that was known at that time, giving a heavy test in the lower layer for coal-tar dyes and caramel, but showed a slightly positive reaction with aged whiskies when no artificial color was present. With the advent of the Marsh test or Marsh's reagent (amyl alcohol plus 3 per cent of phosphoric acid and 3 per cent of water) this reagent improved. It indicated caramel readily and gave a negative reaction for naturally aged whisky, although in some instances giving a very slight test with highly colored, naturally aged, very old whiskies, which experience has taught the analyst to consider as negative. Practically all coal-tar colors that produce a satisfactory brown color with whiskies are indicated positively by the amyl alcohol test, but usually show almost no color in the lower layer with the Marsh test. All coal-tar colored whiskies that have been analyzed in this laboratory gave a negative Marsh test, except that in some instances the lower layer was pinkish in color.

Various coal-tar dyes were mixed in the laboratory in order to produce a satisfactory whisky brown—for example, tartrazine and Bismarck brown. This combination imparted a yellowish brown color to proof alcohol which was Marsh-positive. When whisky is colored with coal-tar dye and the Marsh test is negative, amyl alcohol gives a positive test. When whisky is colored by quick-aging with either charred or uncharred chips, straight amyl alcohol gives a very strong positive test. The usual A. O. A. C. coal-tar double-dyeing tests (*2*) can be used to confirm coal tar, or its presence can be confirmed by drawing off the lower aqueous layer of the amyl alcohol test with the aid of a small separatory funnel into a white porcelain dish and treating with a few drops of strong hydrochloric acid. Usually this causes it to change to red or pink, which can be decolorized completely by a few drops of stannous chloride. Caramel or wood colors show no visible change with these last two reagents.

Zinc Acetate Test for Caramel

Through the use of numerous quick-aging processes, new colors have been developed, one of the most interesting being the reddish brown color extracted from uncharred white oak chips found in some well-known whiskies. This gives a positive reaction with Marsh's reagent, amyl alcohol, Williams' test (*4*) and other tests, including those outlined by the A. O. A. C. It became necessary for this laboratory to find some means of distinguishing this color from caramel. This most satisfactory test worked out in this laboratory, characterized as the zinc acetate test, is applied as follows:

Mark a 150-cc. beaker at 13-cc. and 25-cc. volume. Place in the beaker 25 cc. of spirits to be tested. Add 0.5 cc. of glacial acetic acid and mix, then add 0.75 gram of U. S. P. zinc acetate crystals. Mix, then heat rapidly over a strong flame to vigorous boiling until the volume is reduced to the 13-cc. mark, stirring to prevent spattering. Should the volume be reduced below 13 cc., make up to 13 cc. with water. Set aside to cool gradually. When cool, make up to the 25-cc. mark with 95 per cent alcohol, mix, and let stand several minutes. Then mix and pour through double 15-cm. folded filter paper into cylinder. Mix the filtrate, put 6 cc. into a 6-inch (15-cm.) test tube, and add 12 cc. of Marsh's reagent. Heavy precipitation takes place, but the precipitate will go back into solution if thoroughly mixed. Allow to separate thoroughly, pour off 4 cc. of the upper solution, and replace with 4 cc. of ethyl acetate, 88 per cent grade. Mix thoroughly and allow layers to separate.

The colored lower layer shows caramel or certain coal-tar dye material. If none is present, the lower layer is clear and colorless. Instructions must be followed as directed for the zinc acetate test, as oaks differ and this is the only combination of reagents which works under all conditions. If the test shows a strong positive indication (a reddish shade) and the original liquor gave a negative reaction with Marsh's reagent but was rather pinkish in the lower layer (and the straight amyl alcohol test gave a very heavy positive indication), coal-tar dye is likely to be present. This coal-tar color can be confirmed by adding a few drops of concentrated hydrochloric acid to some of the unused filtrate from the zinc acetate treatment in a small white porcelain dish. This will cause a deep pink color in the presence of certain coal-tar dyes, but by the further addition of stannous chloride the colors produced by the dyes are decolorized. In rare instances the pink color does not appear. In examining these reactions the best results are secured by using as a background the clear light of an open window.

Ferric Alum–Sodium Acetate Test

Another test for whisky that is suspected of being colored with uncharred chips or similar coloring matter is as follows:

To about 10 cc. of the whisky add 2 cc. of a ferric ammonium sulfate solution (1 per cent in water), followed by 5 grams of powdered sodium acetate. Mix, allow to stand for 10 minutes, and filter.

If the color is due to uncharred white oak chips, the solution becomes an intense blue-black on the addition of the ferric ammonium sulfate, but the filtrate is without color. Sometimes the filtrate is slightly bluish, becoming colorless on being warmed gently and poured through the filter several times.

If caramel is present, warming and refiltering does not affect the color. After the addition of ferric ammonium sulfate there is no color change or any pronounced change when 5 grams of sodium acetate are added, but the brown color of caramel comes through the filter paper in the usual manner. If the whisky was colored by quick-aging with charred or toasted oak chips, the filtrate is colored as in the case of caramel. If the color is due to natural aging in wood over a period of years, such as a sample of Bottled in Bond, the filtrate is colored.

Whiskies that are colored with uncharred white oak chips give a positive reaction with the A. O. A. C. paraldehyde test for caramel (*1*); they also give with the A. O. A. C. caramel test (*3*) a more positive reaction than when caramel is actually used to produce the same depth of color. This new form of color, which is easily extracted from white oak chips with hot or cold proof alcohol, is different from color produced by slow-aging in charred barrels or by ordinary quick-aging in the presence of toasted or charred chips. This extract has a reddish cast and with Marsh's reagent shows all the color in the lower aqueous layer. In order to prove that this color was not due to caramel, the following test was devised:

To 5 cc. of liquor add approximately 1 gram of calcium chloride and shake continuously until it has dissolved. Allow to cool, and then add Marsh's reagent in the same manner as in making the Marsh test. After shaking, allow to stand. The color which had been found in the lower aqueous layer lifts and forms a brown zone between the amyl alcohol and aqueous layer, leaving the bottom aqueous layer usually quite colorless.

A sample of uncharred white oak chips was found, the color of which it was difficult to remove with calcium chloride. For this reason this method has been abandoned in favor of the zinc acetate method outlined above, which has been proved the most satisfactory test for this purpose yet known. The calcium chloride test is retained for its value in indicating the quick-aging treatment. A heavy brown ring that settles between the amyl alcohol layer and the aqueous layer is formed with whiskies that have been treated with either charred or uncharred chips.

In testing for source of color in whisky, the following order is suggested:

1. Marsh test.
2. Amyl alcohol test.
3. If the Marsh test is positive, the zinc acetate test should also be applied; the lower layer will be colored if caramel or certain coal-tar dyes are present. Apply the simple coal-tar confirmatory test; if the color cannot be decolorized it is due to the caramel. If the lower layer is negative (colorless), the original color is due to uncharred or imperfectly charred wood.

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Melting Point Apparatus with Rapid Mechanical Stirring

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During the past several years the author has had occasion to make numerous determinations of the melting points of various organic compounds, especially higher paraffin hydrocarbons. In the course of these investigations certain discrepancies were noted in the values of the melting points taken with different types of melting point apparatus. For example, it was found during a thermal study of 3-phenyl-2,4-thiazolidione by means of heating and cooling curves that one form of the compound melted at 147° to 148° C., as determined by the capillary tube method employing an electrically heated air bath (*3*), whereas in the thermal apparatus (stirred oil bath, *1*) the product melted at 146° C. as measured with a thermocouple and 146° to 147° C. as measured with a thermometer. A similar discrepancy was noted in the melting points of *n*-nonacosane (*2*) determined in an electrically heated air bath (65.1° C.) and in an oil bath stirred at high speed (63.5° to 63.7° C.). These and other similar observations indicated that the melting points were influenced by the rate and mode of heat transfer within the apparatus. The melting points of a series of organic compounds were determined in a number of well recognized forms of melting point apparatus which differed principally in the manner of heat interchange. It was found, other conditions being the same, that unstirred air baths gave the highest, and high-speed mechanically stirred oil baths the lowest, values for the observed melting points, whereas intermediate stirring rates (hand-operated devices) gave intermediate values. All apparatus depending on air for the thermal conduction medium gave higher values than those employing a liquid medium.

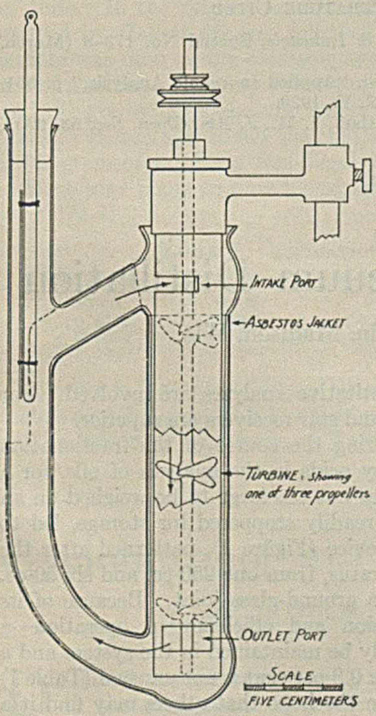

Figure 1. Modified Thiele Tube and Turbine Pump Assembly

During these studies a number of modifications of standard apparatus were devised with the view of attaining satisfactory high-speed stirring of the thermal conduction medium. The apparatus shown diagrammatically in Figure 1 was found to meet the requirements of accuracy, simplicity in construction, and ease of manipulation. The principle involved is that of the Thiele tube modified to permit high-speed stirring.

The Thiele tube of Pyrex glass consists of two arms of dissimilar size, both open at the top. The larger arm contains the pump and the smaller one the thermometer and sample. The pump is in reality a commercially available high-speed turbine stirrer, completely enclosed except for the inlet and outlet ports near the top and bottom. The larger arm of the Thiele tube is expanded to form a bulb at the bottom and an annulus at the top at the height of the upper inlet port of the pump. A thin film of oil separates the casing of the pump from the inside wall of the Thiele tube, thus insuring positive circulation through the arm containing the thermometer, immersed to bring the mercury bulb slightly below the bottom of the opening of the cross arm. With the use of a high-grade heavy petroleum oil, determinations of melting points up to 225° C. can be made. Melting point-bath wax may be used to attain temperatures up to 350° C., provided the Thiele tube is wound with sufficient asbestos-covered resistance wire to permit preliminary melting of the wax.

The apparatus holds approximately 250 ml. of oil which may be circulated at a maximum velocity of 5 liters per minute. Ordinarily, however, a pump speed of 1500 r. p. m. is sufficient to insure adequate circulation of the thermal conduction medium.

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