

The distiller should provide himself with a specific gravity apparatus calibrated at 25° C. The hydrometers now in general use throughout the distillation district are calibrated at 60° F. (15.5° C.), whereas they should be calibrated at 77° F. (25° C.). A distiller who tests his patron's oil at 60° F. and finds it just within the lower limit for specific gravity is much disgruntled when he discovers that the dealer or broker refuses to accept the oil, because it is not up to "gravity." As a matter of insurance to themselves brokers and dealers in volatile oils should see to it that the producer is equipped with proper instruments for testing his oils as they are distilled.

SUMMARY.

Producers of Oil of Wormseed, U. S. P., favor a change in the requirements of this oil, specifically a lowering of the minimum limit for specific gravity. Such a change is believed to be unwarranted, in view of the results herewith presented.

Oil of Wormseed can be produced that will meet all the U. S. P. requirements by distilling the herb with a large volume of steam during a relatively short period of time. It is recommended that with the apparatus now in use not less than 20 pounds of steam per minute be passed through the retort and that the distillation time does not exceed 15 minutes.

"Warming up" of the charge to be distilled is not necessary, in fact it is bad practice, and water should not be added to the retorts. These should be drained of condensed steam whenever necessary.

Changes in the present distilling outfits can be effected at small cost and without complicating the routine of distillation whatever.

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DETECTION OF DIETHYLPHTHALATE IN WHISKY.

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A special denatured alcohol (Formula 39 B) for use in perfumery is now obtainable at a moderate price, offering a new temptation to the bootlegging fraternity. A sample of whisky was recently brought to me for examination, said to have caused "sickness" in those who had sampled it. I examined it with reference to the presence of the usual denaturants. When tested for acetone in the usual manner with iodine and sodium hydroxide, distinct milkeness appeared in the solution tested within a minute at room temperature, increasing in density on shaking up to a certain point. The odor of iodoform was distinctly recognizable. After an hour or two the solution had become quite transparent, with a scanty, pale yellow deposit, which showed under the microscope hexagonal plates. The reaction was obtained both in the sample and in a distillate therefrom. It was also obtained from a dilute hydroalcoholic solution of diethylphthalate, and in denatured alcohol, Formula 39 B. From the scantiness of the precipitate in the latter cases, it may be inferred that the reaction is due to an impurity present only in small proportion and so has no practical importance.

A distillate from the sample was diluted with water and tested for methyl alcohol by the modified Hehner test, with unsatisfactory results. A color was produced, having a purplish shade, but the indications of the test were inconclusive, and further experiment showed that I was on the wrong track.

In distilling the diluted sample, it had been observed that the distillate, the first portion of which was quite clear, after a time became clouded, a behavior suggesting the presence of something soluble in alcohol but not in water. Could this be the new denaturant, diethylphthalate? The physical properties of that ester have become somewhat familiarly known to perfumers, who find it useful as a fixative for the more volatile of the essential oils, but chemical textbooks generally give no description of this interesting compound. It is easy, however, to procure the ester and so ascertain its physical properties.

It is a colorless, odorless liquid, oily in appearance and having a high specific gravity (about 1.117 apparent at 25° C.). It is readily miscible with alcohol, ether, chloroform and other solvents of like character. One is surprised to find that it has a most pronounced taste, with a characteristic pungency, producing a transient numbness of the tongue. Its most remarkable peculiarity is its very high boiling point—above 290° C. At ordinary temperatures it is almost wholly non-volatile. If, however, a solution in alcohol is distilled a notable quantity of the ester passes over with the alcohol vapor. The loss is almost negligible if an alcoholic solution is evaporated in a current of warm air.

Denatured alcohol, Formula 39 B, contains two percent of diethylphthalate, this being dissolved in U. S. P. alcohol. If 5 cc of it are evaporated in a current of warm air and the residual oily fluid dried 30 minutes at 60° C. the ester which remains should weigh close to 0.1117 Gm. One sample which I examined left a residue weighing 0.134 Gm. and the saponification test showed a corresponding excess of the ester. The quickest way to ascertain approximately whether the sample is of correct strength is to add to 5 cc of it, gradually, exactly 10 cc of distilled water; the temperature of the mixture is several degrees higher than that of the fluids before admixture. When cooled gradually, with shaking, the mixture becomes suddenly clouded. The temperature should be found to have fallen just below 21° C. If the proportion of ester is greater than 2 percent, the critical temperature will be higher than this. In case of a sample containing 2.5 percent of the ester, cloudiness appeared at 27.2° C.

It is possible, therefore, to determine with reasonable precision the quantity of ester present, provided the alcohol is of official strength. This may be ascertained by adding to 15 or 20 cc of the sample 0.250 Gm. of anhydrous potassium carbonate in powder. This will agglomerate or even become liquefied if the alcohol is not of full strength. If the alcohol is of official strength, and the critical temperature is found to be above 21° C., add to the mixture 1 cc of a mixture of alcohol 1 volume and distilled water 2 volumes, and determine the critical point. If this is still too high, add more of the diluted alcohol, and continue to do this until the critical temperature is brought to 21° C. If 4 cc of the dilute alcohol have been added, the total volume of the mixture will be 15 + 4 cc, and the percent of ester (x) will be found by the "rule of three" thus: 15 : 15 + 4 :: 2 : x , whence $15x = 38$ and $x = 38 \div 15$ or 2.53.

If the denatured alcohol contains less than 2 percent of the ester we may double its strength by cautious evaporation of 20 cc to a volume of 10 cc, proceeding then just as directed above, but the simpler plan in such case will be to determine the ester by evaporating off the solvent entirely and weighing the residue.

The principle, however, is one that admits of application in many similar cases, *e. g.*, in the testing of spirit of camphor. I am not aware that it has been heretofore employed in quantitative determinations. It may be designated as the method by critical temperature. Results are surprisingly exact and reached in a very few minutes. In the case of spirit of camphor we have heretofore been content with adding to 5 cc of the spirit, distilled water, drop by drop, until a permanent precipitate was produced. The directions given have been to conduct the test at a certain given temperature, but the attention was not called to the fact that mixing the spirit with water caused a rise of temperature. To maintain a constant temperature under such conditions is manifestly difficult. The expedient of adding the water in definite measure, greater than would be required if the temperature is kept constant and then cooling the mixture to a critical temperature, is certainly a capital improvement.

Whether or not the mixture of diethylphthalate, alcohol and water found to have a critical temperature of 21° C. will undergo gradually chemical change by which its critical temperature will be altered can be determined only by experiment. I have kept a sample for some weeks in a well-corked vial of white glass as a temperature indicator in a living room and thus far it has shown no change. It would be possible to construct a thermometer of limited range by filling a series of small vials with mixtures containing varying quantities of diethylphthalate, having critical temperatures, *e. g.*, of 18°, 19°, 20°, etc.

Quantitative determination of diethylphthalate in alcoholic solution may be made by diluting the solution with water and shaking out with successive portions of petroleum ether. Ordinary ether may be used, but this will carry with it some alcohol and a little water, so that this solvent is not to be recommended.

Of course the saponification method for determination of phthalic acid is that which is least open to fallacy.

Identification of diethylphthalate is easily made by causing the phthalic acid to react with resorcin, in the manner to be presently described, with formation of fluorescein.

ROUTINE PROCEDURE FOR DETECTION OF DENATURED ALCOHOL, FORMULA 39 B.

A preliminary distillation of the sample is not necessary or advisable. Proceed at once to a direct test for diethylphthalate.

To 5 cc of the sample in a separator add 5 cc of water and shake out with light petroleum ether 10, 10 and 5 cc. Evaporate the petroleum ether in a tared beaker at a temperature not above 45° C., by aid of a current of dry air. The diethylphthalate will remain in the form of oily drops, or of an oily film, which may be dried at 80° C., for 15 minutes with very slight loss of weight. If the weight of the residue is not over 25 mg., dissolve it in a few drops of alcohol and transfer the solution to a porcelain capsule. (If the weight is greater than 25 mg., dissolve it in a larger quantity of alcohol (*e. g.*, 2 cc) and use an aliquot part of the solution, representing about 25 mg., of the residue.) Add 2 drops of a 10% aqueous solution of potassium or sodium hydroxide. Evaporate by a gentle heat to dryness, add 2 or 3 drops of strong sulphuric acid (dropped from a 1-cc measuring pipette) followed by about 25 mg. of resorcin. Heat slowly over a small Bunsen flame until the brown or red color which at first appears gives place to an orange-yellow (in part at least). The temperature in this heating should reach 160° C. This is far below the temperature at which sulphuric acid fumes appear. When the capsule is cool add 25 cc of water and an excess of ammonia water, when an intense yellow-green fluorescence will appear if diethylphthalate is present.

A negative result does not prove that the sample did not contain alcohol denatured with diethylphthalate, since that ester is very easily saponified by alkalies. Proceed therefore to test for the product of such possible saponification, *i. e.*, an alkali phthalate. Evaporate to a volume of 2 or 3 cc the residue left after shaking out with petroleum ether. Transfer about 5 drops of the concentrated solution to a capsule, evaporate to dryness, add resorcin and sulphuric acid exactly as described above, phthalic acid being evidenced by the formation of the highly fluorescent fluorescein.

The probability is that the greater part of the ester originally present in the denatured spirit will be found to be in the form of an alkali phthalate. For approximate quantitative determination of the ester originally present, assuming that there has been no loss by side reactions, add to 10 cc of the sample, previously accurately neutralized if necessary, 5 cc of normal sodium hydroxide. Heat in a strong, well-stoppered bottle at 100° C. one hour. It will be well to make sure that saponification is complete, by making up the cooled solution with water to exactly 20 cc, and shaking out 10 cc of the solution (neutralized if necessary, but by no means rendered acid) with petroleum ether. No appreciable residue of diethylphthalate should be extracted. If necessary a new experiment must be made, using a stronger solution of sodium hydroxide, or increasing the time of cohobation.

When satisfied that saponification is practically complete, evaporate the solution, nearly neutralized with sulphuric acid, to a volume of about 5 cc, add excess of sulphuric acid and shake out the phthalic acid with repeated portions (15 cc) of ether. Wash the ether with water to remove traces of sulphuric acid, evaporate to a small volume, add 20 cc of distilled water (more if needed to insure complete solution of the phthalic acid), and titrate with decinormal alkali. Each cc of the volumetric solution corresponds with 8.3 mg. of phthalic acid or 11.11 mg. of diethylphthalate.

For the quantitative determination of diethylphthalate in alcoholic solution, *e. g.*, in denatured alcohol, Formula 39 B, place in a suitable flask a quantity of the alcoholic solution (which must be neutral in reaction) estimated to contain about 50 mg. of the ester. Add 1 cc of normal potassium or sodium hydroxide. Heat one hour under a reflux condenser (possibly experience will show that a longer time should be given). Add 1 cc of normal sulphuric acid and titrate the excess of acid, using phenolphthalein as indicator. Each cc of decinormal alkali required to restore neutrality corresponds with 11.11 mg. (0.009 cc) of diethylphthalate. (In the absence of other non-volatile substances an approximate determination is readily made by evaporating off the solvent, drying at a temperature not exceeding 60° C., and weighing the residue.)

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