an ammonium salt. This sublimes around 100°–25° and decomposes, when quickly heated, at 187°–8°. The latter salt can be changed by silver nitrate to a yellow silver salt. It also yields a yellow salt with a dilute hydrazine hydrate solution. All these salts form beautiful yellow crystals and are explosive when heated.

This acid oil, while itself nearly colorless and insoluble in water, colors the water an intense yellow green and stains the skin a permanent yellow, like picric acid. It decomposes suddenly when heated to 120°–130°, liberating red oxides of nitrogen.

The study of these acid oils, as well as of those formed in making ethyl mesoxolate, is under way and yielding interesting results.

One of us has also succeeded in preparing for the first time a perfectly pure *anhydrous* methyl oxomalonate. This substance has an unexpected intensity of reaction on the α-carbonyl group and a number of interesting addition products have already been made and studied.

URBANA, ILL., June 2, 1908.

NOTES ON THE ROESE METHOD FOR THE DETERMINATION OF FUSEL OIL, AND A COMPARISON OF RESULTS BY THE ALLEN-MARQUARDT METHOD.

BY WILLIAM L. DUDLEY.

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There has been considerable discussion in the Journals concerning the comparative merits of the Roese and the Allen-Marquardt methods for determining fusel oil in whiskies. For the past twelve months certain investigations have been made here which compelled a critical study of these methods, and our observations may be of service to others.

While these methods determine the higher alcohols, the results also include to some extent other constituents of the whiskey which with the higher alcohols have borne the name of "fused oil." This is especially true of the Roese method which doubtless determines many things beside the higher alcohols, and the results run much higher than those obtained by the Allen-Marquardt method, which in turn are probably somewhat low.

Discrepancies in results and many controversies which have arisen, are due in a measure to the variations in the technique practised by the analysts. Attention to minor details in these methods is absolutely necessary and the ordinary analytical procedure will not suffice. This is especially true of the Roese method. There is no description of this method given anywhere that we have seen which will give concordant results, if practised as an analyst would ordinarily follow a method. In fact, the Roese method if followed as described, is absolutely worthless. In this paper it will be our endeavor to point out the sources of error and to give the precautions which we have found necessary to obtain concordant results.

The Specific Gravity.—The Roese method requires that the distillate of the whiskey shall be diluted to *exactly* 30 per cent. by volume, which means that its specific gravity shall be 0.96541 at 15.6°. This is very important and it is needless to say that no hydrometer or usual form of pycnometer which has a stopper in contact with the liquid, can be used to determine the specific gravity of a volatile liquid with accuracy to the fifth decimal place. Nor will the ordinary precautions for filling and otherwise handling the instrument suffice, for we are dealing with two liquids in solution, one being much more volatile than the other.

The most satisfactory pycnometer is Reischauer's. It should be filled by means of a specially made pipette with a very narrow stem which will pass to the bottom of the bottle. This will obviate the flow of the stream of liquid through the air, which would introduce a very considerable error on account of evaporation. The diluted distillate should be drawn quickly into the pipette (its capacity being somewhat greater than that of the pycnometer) the liquid adhering to the outside of the stem of the pipette should be wiped off, and the pipette immediately introduced to the bottom of the pycnometer, which should be allowed to fill slowly to a point considerably above the mark on the neck into the enlargement at the top, care being taken to see that all air is forced out as the liquid rises. Care should also be taken in introducing the pipette to avoid getting any of the liquid on the inside of the neck of the pycnometer. The pipette should be thoroughly dried out before it is used again.

The pycnometer should be immersed at once up to the neck in a bath at 15.6° for 30 minutes, then the excess of liquid should be drawn out by means of rolls of filter paper until the meniscus is exactly at the mark. The stopper and its seat should at all times be kept perfectly dry, otherwise evaporation will take place, no matter how perfect the grinding may be. The stopper should be inserted tightly, the bottle wiped dry and weighed after it has reached room temperature. Correction should be made for the weight of the air displaced by the liquid in the bottle.

It is not sufficient to determine the specific gravity of the distillate and add the calculated amount of water in order to bring the solution to 30 per cent. The calculated amount of water should be added, but the specific gravity must be determined after dilution as described above and boiled distilled water or the distillate added as may be required to bring it to 30 per cent. The specific gravity should not vary more than 0.00002 either way from 0.96541 at 15.6°. It was found after many trials, exercising the greatest care to avoid unnecessary loss by evaporation that the actual specific gravity was higher than that calculated, frequently as much as 0.00008, which is far beyond the limit allowable. This part of the process is very tedious but it is absolutely essential for concordant results. Corrections which have been recommended for application to the chloroform volume reading in case of variation from the required specific gravity of the distillate, are of no value.

The Apparatus.—The Bromwell apparatus is usually recommended now, while the Hertzfeld is the older form. We have found the Bromwell apparatus unreliable because of the liability of leakage through the stop-cock. It is impossible to get a stop-cock perfectly tight when a film of liquid rests between it and its seat. Capillarity constantly takes place no matter how perfectly the stop-cock is ground nor how much pressure is exerted in closing it. This is very serious with a volatile liquid and fatal to accuracy in the Roese method. No dependance can be placed on the stop-cock in the Bromwell apparatus. It is intended merely to facilitate the adjustment of the quantity of chloroform in the apparatus after it has been cooled to 15.6°, but if the apparatus be removed from the bath in making this adjustment it will be inaccurate because the chloroform expands very greatly with a slight rise in temperature and a few seconds exposure to a higher temperature is sufficient to render the result worthless. In adjusting the volume of chloroform by means of the stop-cock, a film of chloroform will get between it and its seat and loss is sure to occur, slowly but continuously throughout the remainder of the process. Therefore, in using this apparatus, it is best to adjust the amount of chloroform, after cooling to 15.6°, by drawing it down to the mark with a small pipette, but even then you are menaced by a stop-cock, which is always uncertain.

We have found the Hertzfeld apparatus to be the best and with this apparatus only were we able to get concordant results. However the following details of procedure we found to be essential and unless the precautions mentioned are taken we believe the results by the Hertzfeld apparatus will be of little value.

The Hertzfeld tube is filled with chloroform to a point above the 20 cc. mark found to be necessary to give slightly more than 20 cc. when cooled to 15.6°. The apparatus is immersed in a shallow bath of water so as to completely surround the part filled with chloroform, cooled to 15.6° and allowed to remain twenty minutes. The chloroform is drawn down to the 20 cc. mark by means of a small glass tube attached to a suction pump, without removing the apparatus from the bath. This should be done as quickly as possible, the suction being controlled by pressure of the fingers on the rubber connecting tube so that no more air will be drawn out than just enough to suck up the necessary amount of chloroform. If air be drawn into the apparatus it will vitiate the result by depositing moisture. The alcoholic distillate diluted to 30 per cent. as previously described should be introduced by means of a 100 cc. pipette with a stem graduated to represent the volume for each degree from 15° to say 35°, so that the measurement can be made at room temperature. This pipette should be thoroughly dried out each time before use and the alcoholic distillate sucked up to the mark indicated by the room temperature. The alcohol from the pipette is introduced into the apparatus on top of the chloroform, so as not to get it on the sides above the level of the liquid as it rises. The stopper and its seat should be perfectly dry and firmly inserted. The apparatus is then inverted and shaken thoroughly to mix the alcohol and chloroform. Then it is placed in an upright position for a few minutes to permit the liquids to separate and the stopper carefully removed to relieve the pressure. The stopper and its seat are again wiped dry, the stopper inserted, covered with a rubber cap to avoid wetting, and the whole apparatus immersed in a bath of water at 15.4°. The stopper should not be removed again during the remainder of the process. After remaining in the bath fifteen minutes the apparatus should be removed, inverted and shaken three or four times vigorously. The shaking should be repeated every five minutes thereafter for thirty minutes. While in the bath and during the shaking the pressure in the apparatus is reduced and there will be no tendency of the stopper to lift from its seat.

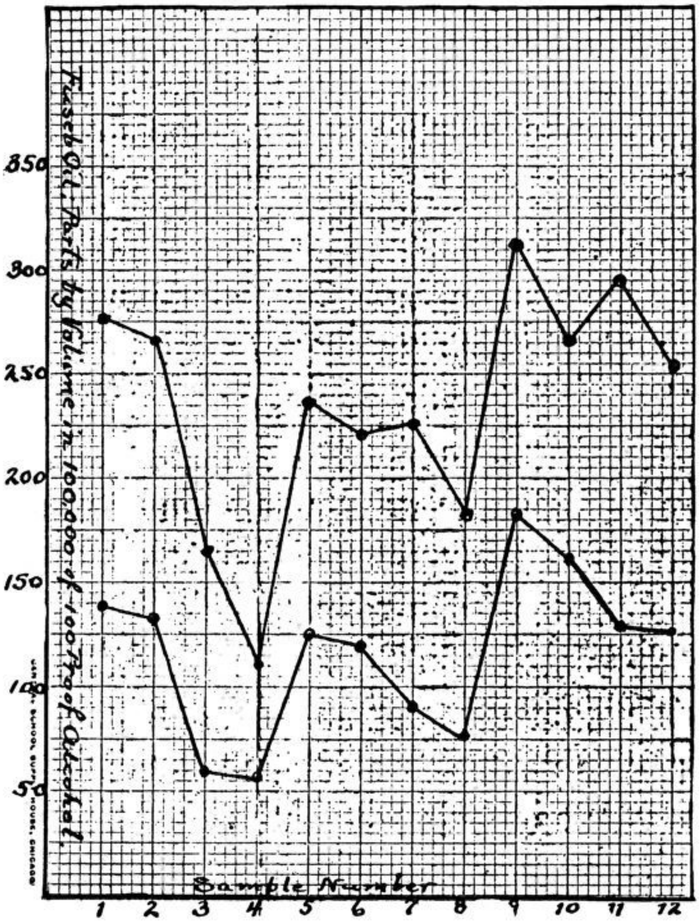
During the period of shaking the temperature of the bath is maintained at 15.4° because of the slight rise in the temperature of the apparatus during the brief period which it is out of the bath. As soon as the shaking period is over, the temperature of the bath should be brought up to 15.6°; the apparatus allowed to stand quietly in the bath for thirty minutes during which time the liquids will have completely separated. Then the reading is taken. The total time that the apparatus is in the bath is about one and a half hours.

Following the procedure given here an artificial whiskey 100 proof containing 290.2 parts by volume of amyl alcohol in 100,000 was analyzed with the following results. The determination was run in duplicate and the readings were identical.

		Parts of amyl alcohol by vol. in 100,000.		
		Actual amount.	Found.	Error.
Artificial whiskey	103.10 Proof	300.0	296.2	—3.8
Artificial whiskey	100.00 Proof	290.9	287.3	—3.6

In the Roese method for the determination of fusel oil in whiskey the result represents more than the content of amyl alcohol because other constituents are more or less soluble in chloroform and have an effect in increasing its volume. This is shown by the comparison of results with those of the Allen-Marquardt method given below.

Various samples of whiskey were analyzed according to the procedure given in this paper and a portion of each sample was sent to Dr. H. W. Wiley, Chief of the Bureau of Chemistry of the U. S. Department of Agriculture, and the fusel oil was determined under the direction of Mr. L. M. Tolman by his modification of the Allen-Marquardt method. The results were reported in "grams per 100 liters of 100 proof alcohol" and are given in the first column in the table below, but for comparison with the results by the Roese method the figures are reduced to volume by assuming them to represent amyl alcohol the specific gravity of which is taken at 0.815.



The following table shows that the results obtained by the Allen-Marquardt and the Roese methods with the same sample of whiskey are not comparable, but the accompanying curve shows a very marked relationship between the determinations made by the two methods. Samples Nos. 4, 6, 7 and 11 however show some discrepancy which cannot be accounted for except in the case of No. 6, which is low in esters and No. 7 which is high in esters.

If, in the Roese method, the esters be saponified previous to the distillation of the sample, the curve would be nearer that of the Allen-Marquardt, but the same tedious precautions as described in this paper would be necessary to obtain concordant results.

		Fuseloil: Parts per 100,000 in 100 proof alcohol.		
		Allen-Marquardt method.		Roese method.
No.	Sample of whiskey.	By weight.	By volume.	By volume.
1	Tennessee	113.0	138.6	276.2
2	''	108.3	132.9	265.2
3	Bourbon	48.5	59.5	165.7
4	''	46.1	56.6	111.6
5	''	101.5	124.5	237.6
6	''	97.5	119.6	221.0
7	Rye	74.0	90.8	226.5
8	''	62.0	76.0	182.3
9	''	149.0	182.8	314.8
10	''	131.0	160.7	265.2
11	Malt	105.1	128.9	296.3
12	''	104.5	128.2	254.1

This investigation leads me to the conclusion that the Allen-Marquardt method, is superior to the Roese method for the following reasons: First, it is more rapid; second, it possesses fewer sources of error, and third, it gives more nearly the amyl alcohol content.

The analytical results by the Roese method recorded in this paper were obtained by my assistant, Mr. Addison Cooper, Jr., to whom I desire to express my appreciation.

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THE ESTIMATION OF ALCOHOL IN FERMENTED LIQUIDS.

BY WM. ANTONI.

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Alcohol in fermented liquids is usually determined as follows: A certain amount of the liquid is measured in a flask, distilled, the distillate collected in the same flask and restored to the original volume. Then the specific gravity of the fluid is determined by means of an accurate pycnometer, and the amount of alcohol found by calculation. This method requires a number of adjustings at a constant temperature, which are tedious and productive of errors.

As the price of fortified wines depends largely on their alcoholic strength, determined to tenths of one per cent., and as often large quantities change hands at a time, it is of importance to have a way of determining alcohol, which combines speed with accuracy.

The following method has been found to comply with these requirements: The liquid is measured in a pycnometer of the Sprengel type, the distillate collected in it without the help of a second measuring flask, and weighed. The pycnometer (Fig. 1) has a capacity of about 50 cc. The body is cylindrical with a diameter of 3 cm. and a height of 7 cm. The tubes *a* and *b* are 8 cm. long and have a bore of about 1.5 and 0.75