

condenser with about 100 cc. of purified petroleum benzine and add to the distillate. Now rinse the condenser well with 5 cc. of water and add to the distillate. Stopper the separatory funnel, shake well, and draw off the aqueous layer into a second separatory funnel. Extract the benzine oil solution three times with 5 cc. of water to completely remove the glycerin and add to the first extract. Shake the combined aqueous extracts with 30 cc. of petroleum benzine to remove traces of oil. Allow to stand one-half hour and draw off the aqueous layer into a tared four inch petrie dish. Rinse the separator with 5 cc. of water and add to the glycerin extract. Evaporate off most of the water at a low temperature (not over 50° C.) and de-hydrate in a vacuum dessicator over sulphuric acid for 24 hours or to constant weight. This anhydrous glycerin is very hygroscopic and must be weighed quickly. To convert to ordinary commercial glycerin divide the weight obtained by .97.

The distillation must be carried out cautiously at first to prevent bumping. After the water has passed over, the distillation proceeds quietly and can be carried out rapidly. A free flame should be used and this should be held in the hand and kept in constant rotation around the bottom of the flask.

In conclusion the writer wishes to express his thanks and indebtedness to Mr. W. B. Parker, who carried out the assays and did most of the experimental work in connection with this paper.

Scientific Department Parke, Davis & Co., August 26, 1914.

A SIMPLIFIED GLYCERIN ASSAY.

F. T. BRADT.

The object of this investigation has been to work out a simple, rapid, and accurate method of estimating the quantity of glycerin in a sample reasonably free from impurities.

The wide variation in results of assays in recent years was deemed of sufficient importance to warrant the appointment of committees in this country and Europe to study methods of analysis and recommend the ones that gave most satisfaction. As a result it was agreed that the acetin method should be the basis on which glycerin should be bought and sold, but that the dichromate method might continue to be used for technical purposes in a properly standardized form. The exact procedure to be followed in purification was described very minutely and also the actual process of assay. The dichromate method was substantially the same as that proposed by Hehner, using solid dichromate for oxidation, an excess of ferrous ammonium sulphate, and dilute dichromate solution to titrate the excess.

Many other methods, besides these two well-known ones, have been suggested for the assay of glycerin, and some of them are well worth a brief review.

In 1891 ¹Benedikt and Zsigmondy proposed to oxidize glycerin with potassium permanganate in alkaline sol. precipitate the manganese by treatment with H₂O₂,

¹ *Zeit. Angew. Chem.*, 1891, 400-401.

add sulphuric acid, and titrate the oxalic acid formed with volumetric permanganate. The advantage claimed for this method is that butyric acid, if present, does not interfere; chemically it is little different from the dichromate method, but is lacking in the simplicity of the latter.

Five years later ²Bordas suggested adding potassium dichromate (48 gm. per litre) to 5 cc. of a dilute glycerin solution until the color changed from a bluish green to a yellowish green. If the glycerin be either too dilute or too strong, difficulty will be experienced in detecting promptly the color change. Two years later Maurice Nicloux pointed out that the above method was based on the supposition that glycerin is oxidized to formic acid. He pointed out the fact that it was changed directly to CO₂ and water, giving as the equivalent 37.28 gms. per litre, and not 48 gms. as first proposed.

A method proposed by ³Simon Zeisel in 1902 is especially interesting. He proposed to distill the glycerin with 63 *per cent.* hydriodic acid in a current of carbon dioxide. The vapors, cooled to 60°, are passed through a small wash bottle containing amorphous phosphorus suspended in water to remove iodine or hydriodic acid fumes. The isopropyl iodide formed is then passed through a four *per cent.* alcoholic silver nitrate solution and the silver iodide collected and weighed. Schultze, in 1905, in a paper giving a comparison of results by various methods, insists that this is the only trustworthy estimation in many cases.

⁴Chaumeil, in 1902, suggested oxidizing glycerin with iodic acid in the presence of sulphuric acid and titrating the iodine liberated with thiosulphate. Chlorides, of course, will interfere, but by a preliminary estimation a correction may be made.

The specific gravity method is recommended by ⁵Stiepel, subtracting from the percentage found, the *per cent.* of ash multiplied by 3.33. This, of course, would only hold good in the presence of small amounts of salts. However, the method may be of marked value as a means of quick checking.

An extraction method is described by ⁶Schukoff in which he uses a sample containing about one gram of glycerin and evaporates to a syrupy consistency on a water bath. It is then mixed with twenty grams of anhydrous sodium sulphate, and extracted with anhydrous acetone in a Soxhlet apparatus. After evaporating the acetone the residue is weighed as glycerin.

A method which at first seems very simple and satisfactory is one proposed by ⁷Wagenaar in 1911. He precipitates copper by means of a fixed alkali in the presence of glycerin. The glycerin holds a quantity of copper in solution varying with certain physical constants. This is determined by causing liberation of an equivalent of iodine which is titrated with thiosulphate. In calculation of results an empirical table is used giving the quantity of glycerin equivalent to from one to thirty cc. of thiosulphate.

Three other methods may be just mentioned, (a) the litharge method which

² Compt. Rend., 1896, 1071-1072.

³ Chem. Centr., 1902, 1424-1425.

⁴ Bull. Soc. Chem., 1902, 629-634.

⁵ Chem. Centr., 1904, 1626-1627.

⁶ Zeit. Angew. Chem., 1905, 294-295.

⁷ Pharm. Weckblad, 1911, 497-502.

gives results neither theoretically correct nor in themselves concordant. (b) The oxidation with sulphuric acid and weighing of the glycerol carbon, and (c) treatment with excess of KOH and lime at 320° and collection of the hydrogen.

Recently a modification of ⁸Hehner's method has been proposed and highly recommended as being very practical for the ordinary laboratory routine. It is carried out something as follows:

Weigh accurately 5 gm. of glycerin and dilute with distilled water to 500 cc. Transfer 25 cc. of this solution into a 200 cc. beaker; add 40 cc. of a solution of dichromate (made by dissolving 74.615 gm. of potassium dichromate in 750 cc. of water, adding 150 cc. of sulphuric acid, and sufficient water to measure one litre at 25° C.), and 25 cc. of sulphuric acid. Cover the beaker and heat on the steam-bath two hours. Dilute the solution to 500 cc. and mix well. Remove 50 cc. to a 500 cc. flask, add 3 grams of potassium iodide and allow to stand five minutes. Dilute with 150 cc. of water and titrate the liberated iodine with N/10 sodium thiosulphate.

Each cubic centimetre of N/10 thiosulphate used indicates an excess of 0.0657 cc. of dichromate solution and each cubic centimetre of the dichromate solution is equivalent to 0.01 gm. of glycerin.

Several disadvantages have been found in working with this method. It seems to present many unnecessary complications. The number of dilutions necessary in carrying out the operation would seem to offer fertile ground for error. The use of such a concentrated solution of dichromate makes the temperature-factor very important, Hehner having shown that a variation of one degree causes an expansion of .05 *per cent.* Failure to recognize this fact might in itself introduce a very considerable error. Further, the solution used is stronger even than theory requires. Assuming that two and one-third molecules of dichromate are required to oxidize one of glycerin, then 74.5675 grams is the equivalent of 100 grams of glycerin and not 74.615 as proposed. Again, the time required for oxidation is longer than actual experiment shows to be necessary. In working with glycerin, slow oxidation would seem to indicate oxidation of impurities, which must be avoided as far as possible. Twenty minutes was found to be ample time to completely oxidize a sample of glycerin by this method. A further complication is introduced by the use of 50 cc. for the final titration when it is just as easy and satisfactory to use 32.88 cc. and avoid the use of a factor in the final calculation.

With these facts before us, then, we suggest a simple modification of the proposed dichromate method. The process is as follows:

Weigh out accurately 5 grams of glycerin, dilute to 100 cc. and take exactly five cc. (equivalent to 25 milligrams of the glycerin) for titration. Add 50 cc. of N/10 potassium dichromate solution, 25 cc. of sulphuric acid, and heat on a steam-bath for 20 minutes. Cool, add one gram of potassium iodide, and after standing 10 minutes, dilute with 150 cc. of water. Titrate the liberated iodine with N/10 sodium thiosulphate and calculate the percentage of glycerin.

Comparative results show this method to be very satisfactory. It is simple, rapid, and reasonably accurate. The dichromate solution is one that every laboratory uses constantly and so the making of new solutions is avoided. Although

⁸ Analyst, 1901.

the solution is much more dilute than the one proposed, still twenty minutes is ample time to completely oxidize the glycerin.

We tried checking our results by means of the specific gravity method and found that it may be feasible with certain cautions. First, there seems to be a surprising lack of complete glycerin specific gravity tables, and in those we have, there is a question concerning the accuracy of the expansion factor for dilute solution. On the other hand, if concentrated glycerin solutions are used, temperature becomes very important, an error of 0.1° in reading causing an error of nearly 0.15 *per cent.* in the amount of glycerin. But using a solution of from 60 to 80 *per cent.* glycerin and being very careful in reading the temperature a reasonably accurate check may be obtained for the oxidation method.

The following results give a fair comparison of the two methods, showing how they may be used as comparative methods.

SPECIFIC GRAVITY METHOD.

WATER	COMMERCIAL GLYCERIN	TEMPERATURE	CORRECTED SP. GR.	PERCENT OF GLYCERIN
14.8920 gms.	23.7315 gms.	80° F.	1.1526	95.08
20.1857 gms.	19.2522 gms.	82° F.	1.1194	95.14
20.0300 gms.	10.2064 gms.	82.7° F.	1.0809	95.02
.....	31.113 gms.	85.1° F.	1.2537	95.20
Average.....				95.11

DICHROMATE METHOD.

N/10 THIO. CORRECTED	N/10 DICHROMATE	PERCENT OF GLYCERIN
19.58 cc.	49.40 cc.	95.36
19.56 cc.	49.40 cc.	95.39
19.60+ cc.	49.40 cc.	95.23
19.53 cc.	49.40 cc.	95.49
Average		95.37%

DISCUSSION.

MR. VORISK:—I would like to ask the second speaker about the titration of that liquid after the oxidation has taken place,—What indicator is used?

MR. BRADT:—Simply use potassium iodide and the iodine liberated is titrated with thiosulphate, using starch as indicator. The color changes from blue to green.

THE NECESSITY OF A METHOD OF ESTIMATING THE INTRINSIC VALUE OR ESSENTIAL QUALITIES OF COFFEE.

L. E. SAYRE.



It has always seemed to the writer that the references in formularies, such as our National Formulary, in specifying the commercial or geographical brand of coffee, are made with a definiteness which is rather superfluous. To say, for example, that a coffee must come from Java and Mocha is a rather excessive discrimination. This will appear when it is shown that there are other brands than Java and Mocha (usually specified) which will give to coffee preparations equally fine flavor peculiar to the roasted berry. It is true that Mocha and Java coffees have a fine flavor widely esteemed, but Santos coffees for example, are immensely popular among American consumers and are