The Determination of Water in Glycerols

*Describing An Adaptation of the Bidwell-Sterling Direct Distillation Method to Glycerine Analysis**

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SEVERAL methods for the estimation of water in glycerol have been proposed, the most convenient classifications of the methods being as follows:

I. Direct Drying Method.

LAWRIE in his book "Glycerol and the Glycols" (1928) p. 296 describes in detail the duPont company's modification of the Rojahn[1] method of drying a weighed sample of glycerol over phosphorus pentoxide under reduced pressure of 12 to 15 mm. On samples containing up to 5% water it is claimed that results accurate to within 0.05% absolute error may be obtained. This method is, however, time-consuming, requiring at least 24 hours elapsed time, and is rather cumbersome.

Note: This same method, given in Allen's Commercial Organic Analysis 5th ed. Vol. II, 721, was used by Mr. Church in the Analysis of the Standard A. O. C. S. Crude Glycerine.

II. Electrical Conductivity Methods

SCHMIDT and Jones[2] in 1920 proposed to determine the amount of water in glycerol by means of conductivity measurement of 3 electrolytes, LiBr, $CoCl_2$ and KI dissolved in the glycerol.

More recently Kameyama and Semba[3] worked out a formula by which the amount of water present in glycerol is determined by a single measurement of the specific conductance, at 25°C, of a solution of 471 mgs KCl in 100 cc of the glycerol sample, viz:

$K \times 10^5 = 2.24 + 0.38n + 0.0127n^2$
K=specific conductance at 25°C.
n=cc water per 100 cc of sample (i.e. % by volume)

III. Method Based on Chemical Reaction with the Water Present

LAWRIE p. 298 describes briefly such a method. Hulburd (*Thesis, Univ. of Vermont,* 1920) proposed to estimate the water in glycerol by measurement of the amount of acetylene generated when calcium carbide was caused to react with the glycerol sample.

IV. Distillation Methods

BERTH[4] in 1927 proposed a new method in which glycerol was distilled with tetrachlorethane, measuring the water to 0.01 cc Berth claimed that the addition of 2.5 grams of finely powdered silver nitrate to the distillation mixture of 150 cc tetrachlorethane and a 100-gram sample was necessary. The special apparatus used by Berth is that described by Tausz and Rumm, *Z.angew. Chem.* 39, 155 (1926) for the determination of water in a variety of products such as flours, breads, yeast, butter and petroleum. Berth claims the determination requires only 45 minutes. On dynamite glycerines claimed to contain from 0.4 to 1.3% moisture he obtained recoveries as follows:

0.7	—	found 0.63
0.4	—	found 0.48
1.3	—	found 1.36
0.6	—	found 0.51

Riesener and Kessen[5] investigated this method and claim that the addition of silver nitrate causes high results and that accurate and concordant results are obtained only when it is omitted.

The method used by the authors of this paper involves no new principles. It is merely an adaptation of the Bidwell and Sterling distillation method.[6] Bidwell and Sterling mention in their article that one of the disadvantages of their method is that substances miscible with water and volatile with steam such as glycerol, alcohol, acetone, etc. are liable to distill over and cause high results.

We have applied the Bidwell-Sterling method to the determination of water directly in sev-

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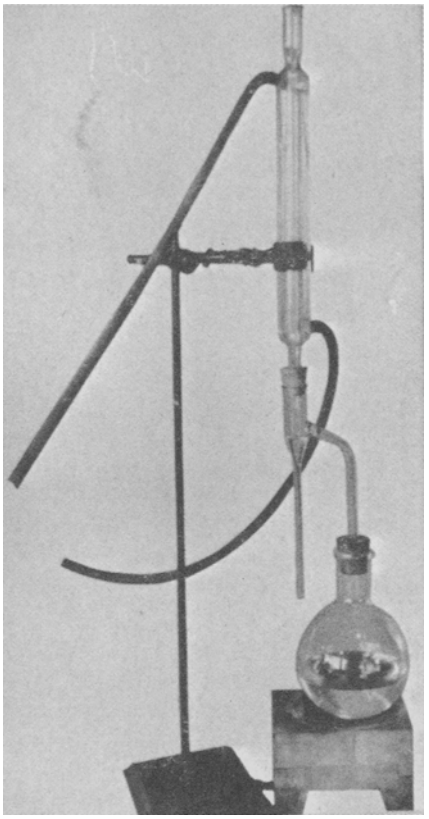
eral glycerols, using toluol as the boiling liquid, and have found that the amount of glycerol which distills over is very small; nearly within the limit of error of estimating the volume of water in the distillate.

(Note: In the Bidwell-Sterling distillation tubes as purchased the tube which projects into the boiling flask is cut off at an angle of about 45° sloping away from the graduated receiving tube. The result is that part of the liquid toluol refluxing back into the boiling flask is frequently caught and carried back up the tube by the vapors of the boiling toluol causing an accumulation of liquid in the condenser with resulting boil-over and the danger of a fire. If the 45° slope of the tube is reversed the liquid toluol has a much better chance to flow back into the flask and a more even distillation results.)

Table I shows the results of analyses by this distillation method.



Apparatus for the determination of water in glycerols

Procedure

IN analyzing dynamite glycerol use a sample of 50 grams or over; for C.P. and crude glycerols use 25 to 50 grams; for more dilute glycerols use a sample which will yield less than 5 cc water.

Weigh sample to .01 gm into a 1-liter round bottom Pyrex flask and add 300 cc toluol. Fill the graduated stem of the calibrated Bidwell-Sterling tube with water—saturated toluol, connect to condenser and distill with the aid of an electric flask heater until no more droplets of water come over, which usually requires about 1½ hours. Any droplets of water adhering to the condenser tube should be rinsed down with additional solvent, using a copper wire loop to aid in dislodging the droplets if necessary.

TABLE 1

Type Glycerol	Wt. of Sample	Volume Distillate	Apparent per cent Water	Grams Glycerol in distillate	Per cent water, corrected (a)	Non-volatile residue (b)	Glycerol, by Acetin Method (c)	Sum a+b+c
Dynamite	50.00 gm	0.17 cc	0.34%	0.009	0.33%	None	98.60%	98.93%
C.P.	50.65	2.75	5.44	0.029	5.38	None	93.46	98.84
C.P.	24.38	1.37	5.62	0.041	5.48	None	93.45	98.94
Composite Soap Lye Crude.	42.59	2.21	5.18	0.039	5.11	9.40%	84.15	98.66
*A.O.C.S. Standard Crude	48.90	2.50	5.11	0.064	*4.99	10.28	**83.33	98.60
Saponification Crude	28.78	2.10	7.30	0.012	7.26	2.55	89.89	99.70
Dynamite+	25.00 glyc	2.93	10.54	0.036	10.39			
added water	2.80 water							
(calc water content=10.37%)								
GPA—Radiator Glycerine	10.835	4.48	41.35	0.029	41.11	*None*	58.33	99.44
			Solvents other than Toluol					
C.P. (Xylol)	25.40	1.44	5.67	0.222	4.99			
C.P. (Isopropyl Ether)	24.26	1.85	7.63	0.002	7.63			
C.P. (Benzol)	25.69	1.25	4.87	0.005	4.87			

*On this Standard A.O.C.S. Crude Glycerine, Mr. Church in his letter to the Soap Section Committee of 2/28/30 reports that four laboratories reported 4.94—4.86—4.84—4.96% moisture or an average of 4.90%, by the P_2O_5—vacuum method.

**This value of 83.33% glycerol is the accepted average of the committee who analysed this sample.

Allow apparatus to cool and read volume of water.

$$\frac{\text{cc water in distillate}}{\text{wt. sample in grams}} \times 100 = \% \text{ water, by weight*}$$

*Note: Our results indicate that for C.P. and crude glycerols, containing about 5% water, this result uncorrected for glycerol which distills over will be about 0.1% high on the average. Where great accuracy is desired, separate the aqueous distillate from the solvent by rinsing the tube several times with distilled water into a separatory funnel. Draw off the water containing the glycerol into an acetylization flask, evaporate and determine glycerol by the acetin method. From the volume of the distillate and the grams of glycerol calculate the specific gravity of the distillate using the 20°C/20°C glycerol gravity tables. Then

calculate the weight of the distillate and deduct the weight of glycerol. The result will be the net weight of water in the distillate from which the corrected % water in the sample may be calculated.

Lack of time prevented us from attempting to apply the Kingman method[7] also to the direct determination of water in glycerols. It would be interesting to compare some chlorinated solvents including the official tetrachlorethane sp gr 1.582 b.p. 145°C, monochlorbenzol sp gr 1.113 b.p. 132°C and carbon tetrachloride sp gr 1.58 b.p. 77°C, using the Kingman method, with the results obtainable with a series of solvents of comparable boiling points using the Bidwell-Sterling method.

We did make three determinations of the moisture content of the C.P. glycerol by the Bidwell-Sterling method using first commercial isopropyl ether and later commercial benzol and xylol. The isopropyl ether used had a sp. gr. of 0.728 and a boiling range of 66-74°C. This solvent was entirely free from water yet the distillate obtained from a 25-gram sample of C.P. glycerol indicated 7.48% water, an impossibly high value. The aqueous distillate when analyzed for glycerol showed only 0.002 grams showing that very little glycerol is carried over by this low boiling solvent. The only apparently logical reason for the high moisture content obtained when using isopropyl ether as solvent is that perhaps a chemical reaction took place such as the dehydration of small amounts of isopropyl alcohol which may have been a minor constituent of this commercial solvent, thereby forming water. Commercial xylol, having a sp. gr. of 0.866 and a boiling range of 136 to 142° C when used as the solvent gave a value of 4.99% water in the C.P. glycerol. This solvent with its higher boiling point carried over a considerable quantity of glycerol—0.222 grams in a distillate of 1.44 cc.

It is an interesting fact that the time required to distill the water out of a sample of glycerol was practically the same for toluol and xylol. The bulk of the water comes over in the first half hour, while about 1½-2 hours are required to bring over the last traces. For rough control purposes the value after ½ hour distillation might be used, where toluol is the solvent. Commercial benzol boiling at 78-82°C gave a low result for moisture and required a longer distillation time. Of the four solvents tried, toluol only appears to give satisfactory results.

Summary

WATER in concentrated glycerols may be satisfactorily determined directly by the Bidwell-Sterling distillation method, using toluol as the boiling liquid. A variable but very small amount of glycerol is carried over with the water. In no case in our analyses did this glycerol carried over amount to as much as 0.10 gram, and the correction to the apparent per cent of water in the sample did not exceed 0.15% in any of the glycerols containing up to 10% of water.

The use of a solvent like xylol boiling appreciably above 100°C is not advisable since it causes considerably more glycerol to be carried over and does not markedly shorten the time of distillation. An analysis made by this method on a 25.00 gram sample of dynamite glycerol to which 2.80 grams of water was added, producing a sample containing 10.37% water, gave a recovery, corrected for .036 grams of glycerol carried over, of 10.39% water. On the A. O. C. S. Standard Crude Glycerine sample, Mr. Church reports that four laboratories found an average of 4.90% moisture by the P_2O_5-vacuum method. We found 4.99% moisture by direct distillation in this same sample.

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Whaling Companies to Restrict Killing

In a statement made at the annual meeting of the Hector Whaling Co. in London recently, it was indicated that in the future production of whale oil will be kept more closely in line with consumptive capacity. The company has rejected opportunities to secure interests in new expeditions. In the report the danger of promiscuous killing of whales is pointed out and doubts for the future of the industry are expressed. Representatives of the Norwegian whaling companies met with a number of representatives of foreign companies recently to consider the problem of limiting whale oil production to the demands of the markets.

Swift & Co., Chicago, elected Gustavus F. Swift president of the company to succeed Louis F. Swift who was recently made chairman of the board. Edward F. and Charles H. Swift, vice-presidents, have been made vice-chairmen of the board.