Glycerin Analysis Committee Report*

Cooperative Investigation of Alleged Disagreement Between Acetin, Bichromate, and Specific Gravity Methods

By J. T. R. Andrews, *Chairman*

THE work of the Glycerin Analysis Committee this year has been confined to an investigation of the alleged disagreement between the acetin, bichromate and specific gravity methods of determining the apparent glycerol content of distilled glycerins, using the moisture determination as a check.

Preparation of Samples: "A" was a double-distilled C. P. or U. S. P. Glycerin. "B" consisted of "A" purified by a laboratory fractional distillation through a 48″ Vigreux column under 5-7 mm. pressure. The first and last portions of distillate (about one-third each) were rejected and the middle portion, which exhibited a very constant boiling point, was diluted with water to about 95% glycerol content before distribution. "C" was a double-distilled C. P. or U. S. Glycerin from a different producer. "D" was a single-distilled, carbon-bleached glycerin. All of the above glycerins presumably were made by the distillation of salt crudes.

Cooperative Analyses: Eleven laboratories determined apparent glycerol content by the acetin method; ten by the bichromate method. The specific gravity test was made by eleven laboratories and moisture determination by eight. In tabulating these figures it was thought advisable to exclude certain doubtful analyses from consideration in arriving at an "accepted value." Justification for such a procedure is found in Farnsworth's "Quantitative Analysis," p. 26. This author recommends rejection of any result whose deviation from the average, obtained by excluding the questionable value, exceeds four times the mean deviation from this average. Calculations of the probable errors of the accepted value and individual determinations were made by use of the formulæ given on pp. 523-24 of Mellor's "Higher Mathematics." The probable error of the accepted mean varies inversely as the square root of the number of cooperating laboratories and is a guide as to the reliance that may be placed upon the accepted value. The probable error of the individual determination is a measure of the reproducibility of the analytical method in the hands of different analysts and is of value as such. This error is not affected by increasing the number of analytical results.

Specific Gravity. Apparent specific gravity at 15°, 15.5°, 20° or 25° C. in terms of water at the same temperature was determined by eleven laboratories. All who described the method used employed a 10 cc., 25 cc. or 50 cc. pyknomèter generally of the Geissler type. Apparent glycerol content from sp. gr. was obtained by use of Bosart and Snoddy's table [I. and E. C. 19,506 (1927)]. For the sake of ready comparison specific gravities corrected to 25°/25° C. are tabulated.

Water: Eight laboratories determined moisture. Six employed vacuum desiccation methods and two the distillation method devised recently by Hoyt and Clark (*Oil and Fat Ind.*, Feb. 1931, pp. 59-61).

Laboratory No. 1 dried 1.5-2.0 gms. in a crystallizing dish over conc. H_2SO_4 under 1-2 mm. of Hg. pressure. The loss after three days was considered moisture, though further losses occurred on drying for six, nine and twelve days which must have represented volatilization of glycerol itself.

Laboratories 3, 4, 6, 10, and 11 dried on glass wool over P_2O_5 (Dupont's Modification of Rojahn's Method[1]). The loss after twenty-four hours under 12-18 mm. Hg. pressure was generally reported as moisture. Laboratory No. 4 found twenty-four hours drying insufficient but four days gave close to con-

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*Presented at Annual Meeting American Oil Chemists' Society, New Orleans, May 13-14.

[1] Lawrie—"Glycerol and the Glycols," P. 298.

stant weight. Laboratory No. 6 reported loss after twenty-four hours but noted additional losses on further exposure. Laboratory No. 10 dried under 20-23 inches vacuum to constant weight (time not stated). Laboratory No. 11 dried for forty-eight hours under 35 mm. pressure.

Laboratories 5 and 9 employed the distillation method of Hoyt and Clark. Laboratory No. 9 modified this method to the extent of using the bichromate method for estimation of glycerol in the aqueous distillate after previous dilution and boiling to expel toluene.

Apparent Glycerol by Acetin Method: The International Standard Method was employed by all laboratories, the figure reported being gross acetin uncorrected for acetylizable impurities in the residue. The precautions concerning carbonate-free NaOH, care in neutralizing prior to saponification and accurate standardization of acid seem to have been observed punctiliously. The following slight deviations from the standard method were reported: No. 5—(a) Sample not over 1.25 gms. (b) Acetylization time ninety minutes. (c) Saponification time twenty minutes. No. 10—Acetylization time two hours.

Apparent Glycerol by Bichromate Method: As was anticipated, the bichromate method was most productive of variation in the details of its application. Each chemist was requested to follow the procedure regularly used by his laboratory, or that modification of the standard method which seemed to him most suitable and accurate. The matter of purification with silver or lead was left open and only No. 7 carried it out using 0.2 the regular amount of silver carbonate and a reduced amount of basic lead acetate.

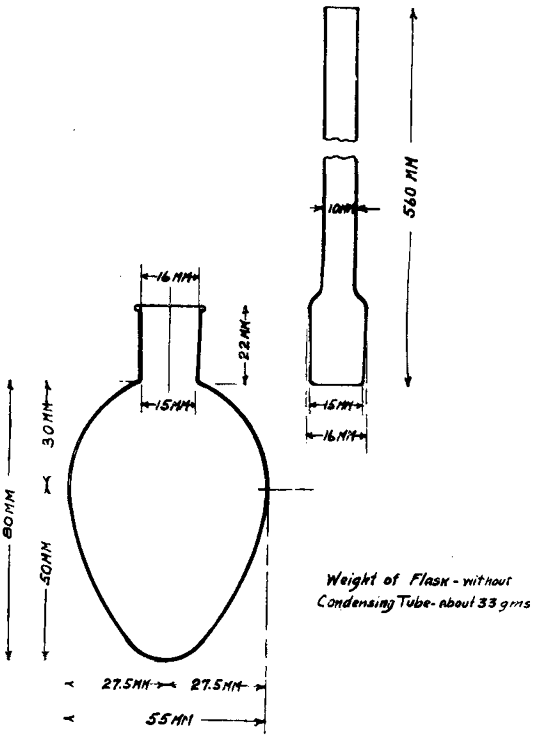
Ten laboratories reported results by the bichromate method. Several ingenious modifications are described:

Laboratory No. 1: 0.35-0.45 gm. in a 250 ml. beaker + 50 ml. $K_2Cr_2O_7$ sol'n (1 ml. = 0.01 gm. glycerol) + 25 ml. conc. H_2SO_4. Refluxed under stemless 3″ funnel and watch glass on steam bath for thirty minutes. Cooled and diluted to exactly 300 ml. This sol'n was used to titrate a standardized ferrous ammonium sulphate sol'n equivalent to 0.01 gm. glycerol (approx. 20 cc.) using diphenylamine indicator.

$$\% \text{ Glycerol} = \frac{50\,(T-6)}{T \times S}$$

Laboratory No. 2: Excess $K_2Cr_2O_7$ = 35-40%. H_2SO_4- 25cc. of 1:1 by volume in a total of 90 cc.; oxidation time three hours in a boiling water bath; $K_2Cr_2O_7$ standardized vs. Fe wire of known purity.

Laboratory No. 4: Standard method followed. $K_2Cr_2O_7$ added from weighing bottle. Ferrous salt used in sol'n as described under "Reagents." 1-2 cc. of this sol'n was added in excess and titrated back with dilute $K_2Cr_2O_7$ sol'n. Herner's old method yielded results 0.1-0.3% lower than the Standard Method which is the one reported.



Preferred Type of Acetylization Flask

Laboratory No. 5: $K_2Cr_2O_7$ sol'n = 74,552 gms./liter. Sample = 1.2-1.5 gms./500 cc. 50 cc. of this dilution + 25 cc. std. $K_2Cr_2O_7$ sol'n + 25 cc. conc. H_2SO_4 in 400 cc. beaker were covered with watch glass and immersed in steam bath for two hours. Cooled, diluted to 500 cc. exactly and a 50 cc. aliquot taken. Added 75 cc. water + 10 cc. 1:4 H_2SO_4 + 20 cc. 10% KI sol'n. Liberated iodine was titrated with 0.1 N thiosulfate.

Laboratory No. 6: Followed Bichromate International Method (Scott's "Standard Methods," 4th Ed. Vol. 2, p. 1755). Approx. 5 gms. was diluted to def. vol. and an aliquot of this sol'n containing 0.45-0.47 gm. glycerin, was used for oxidation.

Laboratory No. 7: Used International Standard Bichromate Method published in J. I. E. C. 3, 682 (1911). Purification was effected as noted above.

Laboratory No. 8: Presumably the Standard Method was used. No details given.

Laboratory No. 9: From a stoppered weighing bottle weighed 7-8 gms./2000 cc. 50 cc. aliquot = 0.175-0.200 gms. + 25 cc. standard bichromate sol'n (74.56 gms. C.P. $K_2Cr_2O_7$ + 150 cc. conc. H_2SO_4 per liter) + 15 cc. conc. H_2SO_4. This mixture, volume approx. 90 cc. and containing 18.75 cc. conc. H_2SO_4, was digested for two hours in a boiling water bath in a 250 cc. wide mouth Erlenmeyer covered with a watch glass. Cooled and titrated electrometrically with approx. 0.75 N. ferrous ammonium sulphate sol'n.

Laboratory No. 10: An aliquot corresponding to 0.1-0.15 gm. of glycerin, was added to 25 cc. of standard $K_2Cr_2O_7$ sol'n. (1 cc. = 0.01 gm. glycerol) + 15 cc. conc. H_2SO_4. Immersed in a boiling water bath for two hours, cooled and titrated with a standardized ferrous ammonium sulphate sol'n, using potassium ferricyanide indicator.

Laboratory No. 11: About 5 gms./1000 cc. 25 cc. aliquot + 25 cc. standard bichromate solution (74.56 gms. per liter) + 15 cc. conc. T_2SO_4. Heated on steam bath two hours and titrated with ferrous ammonium sulphate sol'n (240 gms./liter) using potassium ferricyanide indicator.

IT WILL be noted that a rigid uniformity of procedure prevailed only in the application of the International Acetin Method. Four distinct schemes for titrating the excess $K_2Cr_2O_7$ are represented in the bichromate methods; two general methods for water determination were employed with enough modifications of minor detail to increase this number to at least five or six. It is very doubtful if any two laboratories employed exactly the same technique in applying the specific gravity test. Keeping these facts in mind, the results, which at first glance appear very disappointing, are not at all bad and enable clearcut conclusions to be drawn.

1. Apparent glycerol content calculated from specific gravity using the Bosart and Snoddy table in excellent agreement with the water found.
2. Apparent glycerol content by bichromate oxidation is about 0.3% lower than apparent glycerol from specific gravity.
3. Apparent glycerol content by acetin method is about 0.8% lower than that by bichromate method and 1.1% lower than apparent glycerol from specific gravity.

These conclusions are the same whether drawn from averages of all four samples or from sample "B" which was purified by fractional vacuum distillation in a manner similar to that employed by Bosart and Snoddy. The probable errors attached to these accepted values are sufficient to account for most if not all of the discrepancy between bichromate and specific gravity but the errors attached to these analyses are not an adequate explanation for the wide disagreement between specific gravity and bichromate on the one hand and acetin on the other. This discrepancy, which was noted in the report of the Soap Section last year, is now considered proved. Its cause now becomes our active problem.

No claim is made for the absolute purity of sample "B" other than that it duplicates fairly closely the glycerol which Bosart and Snoddy regarded as pure. The impurities, other than water, which are most likely to be present are trimethylene glycol and polyglycerol ethers. Fractional vacuum distillation would eliminate the higher polymers so that the polyglycerol ethers in such a sample as "B" must be confined almost exclusively to diglycerol. The physical and chemical properties of trimethylen glycol and diglycerol are known and their apparent glycerol contents by bichromate and acetin methods are easily calculated. If a purified glycerine such as "B" is assumed to contain glycerol, trimethylene glycol, diglycerol ether, water and nothing else, its composition can be calculated from its specific gravity and apparent glycerol content by the bichromate and acetin methods if these methods really do yield the theoretical values and no change in volume takes place on mixing.

The following data on these substances are taken from Lawrie:

Substance	Specific Gravity 20°/20°C	% Apparent Glycerol	
		Bich.	Acetin
Glycerol	1.26362	100.00	100.00
Trimethylene Glycol	1.0554	138.33	80.69
Diglycerol Ether	1.3215†	110.84	73.90
Water	1.00000	0.00	0.00

Let:
X=% glycerol
Y=% trimethylene glycol
Z=% diglycerol ether
W=% water
And:
S=% Specific Gravity 20°/20° C
A=% App. Glyc. (Acetin)
B=% App. Glyc. (Bich.)
Then:
% Glycerol (X) = 2.9229 A — 1.6660 B — 97.48 (S — 1).
% Trimethylene Glycol (Y) = 0.9661 B — 0.2234 A — 281.72 (S — 1).
% Diglycerol Ether (Z) = 1.995 B — 2.3581 A + 439.51 (S — 1).
% Water (W) = 100.00 — 0.3414 A — 0.4996 B — 60.31 (S — 1) or
100.00 — (X + Y + Z).

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† As there are three possible isomers of diglycerol, this figure is a bit uncertain.

Glycerin Analysis Results of Cooperating Laboratories

Number of Coöperating Laboratory	Sample "A"					Sample "B"				
	Sp. Gr. at 25°/25° C	% Glycerol			%	Sp. Gr. at 25°/25° C	% Glycerol			
		From Sp.Gr.	Bich.	Acetin	Water		From Sp.Gr.	Bich.	Acetin	Water
1	1.2497	95.24	92.68*	94.17	5.44*	1.2495	95.16	94.33	93.91	5.15
2	1.24987	95.30	95.44	93.18*	——	1.24995	95.33	96.19	93.21	——
3	1.25000	95.35	——	93.23*	4.59	1.25013	95.40	——	94.00	4.52
4	1.24945	95.13	95.01	94.47	4.67	1.24925	95.06	94.93	94.53	4.78
5	1.24835*	94.72*	94.29	93.96	4.68	1.24969	95.23	94.42	94.96	4.96
6	1.24975	95.26	95.58	94.35	4.40	1.24945	95.14	95.65	94.32	4.38
7	1.2497	95.24	94.24	93.91	——	1.2498	95.27	94.73	93.95	——
8	1.2502	95.43	95.27	94.31	——	1.2505	95.55	95.45	93.68	——
9	1.2497	95.24	94.62	94.56	4.83	1.2496	95.20	95.17	94.41	4.84
10	1.2500	95.35	94.42	94.87	4.51	1.2499	95.31	94.52	94.26	4.54
11	1.2502	95.43	94.64	94.51	4.56	1.2496	95.20	94.64	94.29	4.71
Average (All included)	1.24972	95.24	94.64	94.14	4.71	1.24977	95.26	95.00	94.14	4.73
Average (accepted value)	1.24986	95.30	94.86	94.35	4.60	1.24977	95.26	95.00	94.14	4.73
Probable error of accepted value	0.00005	0.02	0.11	0.06	0.03	0.00007	0.03	0.13	0.09	0.06
Probable error of individual determination	0.00016	0.06	0.33	0.19	0.09	0.00023	0.09	0.40	0.31	0.17
Accepted Water + Accepted Glyc.		99.90 ± 0.05	99.46 ± 0.14	98.95 ± 0.09			99.99 ± 0.09	99.73 ± 0.19	98.67 ± 0.15	

Number of Coöperating Laboratory	Sample "C"					Sample "D"				
	Sp. Gr. at 25°/25°C	% Glycerol			%	Sp. Gr. at 25°/25°C	% Glycerol			%
		From Sp.Gr.	Bich.	Acetin	Water		From Sp.Gr.	Bich.	Acetin	Water
1	1.2491	95.00	93.34	93.78	5.24	1.2492	95.04	93.28*	93.56	5.24
2	1.2496	95.20	96.16	93.15	——	1.2494	95.12	96.38*	92.92	——
3	1.24948	95.15	——	93.67	4.70	1.24946	95.14	——	93.81	4.65
4	1.24885	94.91	94.79	94.43	4.95	1.24875	94.87	94.76	94.37	5.05
5	1.24905	94.98	94.19	94.51	4.60	1.24929	95.07	94.67	94.45	4.98
6	1.24955	95.18	95.56	94.19	4.35	1.24925	95.06	95.48	94.12	4.82
7	1.2494	95.12	94.15	93.82	——	1.2494	95.12	94.83	93.80	——
8	1.2494	95.12	95.16	93.98	——	1.2497	95.24	95.49	93.88	——
9	1.2492	95.04	94.87	94.59	4.80	1.2492	95.04	94.81	94.62	4.81
10	1.2492	95.04	93.78	94.28	4.62	1.2490	94.96	93.66*	94.82	4.65
11	1.2491	95.00	94.21	93.78	4.79	1.2492	95.04	94.50	93.25	4.78
Average (All included)	1.24935	95.10	94.62	94.01	4.75	1.24934	95.09	94.78	93.96	4.85
Average (accepted value)	1.24935	95.10	94.62	94.01	4.75	1.24934	95.09	94.94	93.96	4.85
Probable error of accepted value	0.00005	0.02	0.18	0.09	0.06	0.00005	0.02	0.10	0.12	0.06
Probable error of individual determination	0.00017	0.07	0.56	0.29	0.18	0.00017	0.07	0.26	0.39	0.18
Accepted Water + Accepted Glyc.		99.85 ± 0.08	99.37 ± 0.24	98.76 ± 0.15			99.92 ± 0.08	99.77 ± 0.16	98.79 ± 0.18	

* Values rejected by Farnsworth's method. See Farnsworth - "Quantitative Analysis", page 26 (1928)

Applying these formulæ to the accepted values of "B":

% Glycerol = 92.38
% Trimethylene Glycol =—0.09
% Diglycerol Ether = 2.48
% Water = 5.23

From theoretical considerations a mixture such as the above would have a specific gravity and would show bichromate and acetin analyses corresponding to those found. The water actually determined is, however, 0.50% lower than the theoretical. Furthermore a diglycerol content of 2.48% would surely yield a distinct organic residue at 160° C. Such was not the case, as the writer's laboratory found only 0.06% organic residue.

Reluctantly then, we are forced to the conclusion that one or more of these analyses is not yielding the theoretical value. The finger of suspicion points most directly at the acetin test and it is natural to investigate first that part of the International Acetin Method which is likely to be most productive of low results and in the performance of which the method itself urges particular care, viz: the saponification of the triacetin.

Lack of time prevented further cooperative work this year by the committee on such an investigation but a few experiments in the writer's laboratory point the way to interesting and necessary future cooperative work.

A sample of Eastman's Triacetin, No. 256, B.P. 152°-154°C./22 mm. was used for the purpose.

1. Two samples of about 2.25 gms. each were acetylized and analyzed for glycerol by the International Acetin Method.
(a) =42.08%; (b) =42.12%; Average=42.10%.
2. Two samples of about the same size were dissolved in 400 cc. cold CO_2—free water, neutralized to phenolphthalein (1 drop of N/I NaOH sufficient), saponified and glycerol calculated as above.
(c) =41.63%; (d) =41.70%; Average=41.67%.
3. Two similar samples were dissolved in about 300 cc. of cold CO_2—free water, 7.5 cc. glacial acetic acid and 3.0 gms. fused sodium acetate were added and the subsequent neutralization, saponification and titration made as in the I. A. M.
(e) =41.28%; (f) =41.20%; Average=41.24%.
4. Another sample was acetylized and analyzed according to the I. A. M. except that the alkali used for neutralization was run in rapidly without any agitation whatever until within about 20 cc. of the neutral point. From then on the analysis was performed in the usual manner.
(g) =40.85%.

Two blanks on reagents were carried out with each pair of samples. All of these analyses were performed by an experienced analyst and except where otherwise noted the neutralizations were made with unusual care to avoid local excess of alkali.

It is evident from the above analyses that this sample contained a small amount of free hydroxyl, probably present as di- or perhaps mono-acetin. The theoretical glycerol yield of triacetin is 42.21%; of diacetin is 52.28%, and of monoacetin is 68.66%. The loss of glycerol due to saponification during a careful neutralization amounts to 0.43% based on the eight of triacetin taken, but based on a 1.0 gm. sample of 95% glycerin yielding the same weight of pure glycerol, this loss figures 0.97% which is in close agreement with the observed discrepancy.

Conclusions: From its work on distilled glycerins your committee concludes that the discrepancy noted last year is a real one and that the acetin method itself is the primary cause. It is suggested that further cooperative work be done with the object of determining more accurately the factors causing this error with a view to its elimination if possible. It is suggested that any further work include, if possible, a distilled glycerin from a saponification crude.

Your committee further recommends that whenever the International Acetin Method is employed, the acetylization flask used be similar in size and shape to that shown in the drawing. The condenser tube should be water-jacketed as described in the I. A. M. This flask can be purchased with new interchangeable ground glass joints at separate prices on flask, condensing tube and a stopper for use while weighing.

In conclusion your chairman wishes to thank each member of the committee for his loyal support and fine spirit of cooperation during the performance of our task.

The roster of your committee is as follows:

W. H. Burkhardt, Gold Dust Corp., Holabird and Vail Sts., Baltimore, Md.; Chas. G. Gundel, Fels & Company, Philadelphia, Pa.; C. A. Woodbury, E. I. duPont de Nemours Co., Explosives Dept., Wilmington, Del.; Ralph W. Bailey, Stillwell & Gladding, Inc., New York, N. Y.; L. F. Hoyt, Larkin Co., Inc., Buffalo, N. Y.; A. K. Church, Lever Bros. Co., Cambridge, Mass.; James W. Lawrie, A. O. Smith Corp., Milwaukee, Wis.; V. K. Cassady, The Palmolive Co., Milwaukee, Wis.; W. J. Reese, Colgate-Palmolive-Peet Co., Kansas City, Kansas; Wm. A. Peterson, Kirkman & Son, Brooklyn, N. Y.; M. L. Sheely, Armour Soap Works, Chicago, Ill.; John Ornfelt, La France Mfg. Co., Philadelphia, Pa.; H. C. Bennett, Los Angeles Soap Co., Los Angeles, Calif.; J. T. R. Andrews, *Chairman,* Procter & Gamble Co., Ivorydale, Ohio.