# 1933 Report of the Glycerine Analysis Committee

## Soap Section, American Oil Chemists' Society

J. T. R. Andrews, Chairman

Three years[1] ago the report of this committee called attention to low values obtained by the International Acetin Method and suggested that an invrestigation of the method be made. The following year[2] our work established beyond any reasonable doubt the existence of an error inherent in the method whereby results of the order of one per cent lower than the true glycerol content were obtained. Last year[3] it was shown that this error is a result of accidental saponification of triacetin during neutralization of the excess acetic acid. This year we have tried to devise a remedy.

Obviously the most satisfactory solution would be the elimination of the error by suitable modification of the existing method. A few preliminary experiments conducted by individuals in the direction of cooling and mechanical agitation of the solution during neutralization showed that such procedure is advisable yet wholly inadequate as a remedy. The suggestion of our German friends, Drs. Prager[3] and Berth, regarding the blank determination error in acetin analysis was tried using 5 c.c., 20 c.c., and 50 c.c. approximately normal NaOH for saponifying the acetylizable impurities in the acetic anhydride and sodium acetate of the blank. The apparent glycerol content of the reagents was found to be as follows:

| | | | | |
|---|---|---|---|---|
| C.c. N/1 NaOH | = | 5.0 | 20.0 | 50.0 |
| Gms. apparent glycerol | = | 0.0048 | 0.0079 | 0.0095 |

The increase in apparent acetylizable impurities of blank reagents with increase in excess NaOH for saponifying is clearly shown. The I.A.M., using 5.0 c.c. normal NaOH excess in the blank, does not really simulate the analysis of a sample using 50 c.c. normal NaOH with 17-18 c.c. remaining unused after saponification is complete. (Calculated from 1.000 gm. of absolute glycerol in sample.)

It is clean that apparent glycerol in the blank determinination increases with the amount of NaOH employed, the error being least with the 5.0 c.c. blank prescribed by the I.A.M. If 20 c.c. normal NaOH were used, in an effort to duplicate more closely the actual sample conditions, the sample would be found to contain 0.0031 gm. less glycerol and if a blank of 50.0 c.c. normal NaOH is used, 0.0047 gm. less glycerol will be found than in the I.S.M. In the case of a 1.25 gm. sample these amounts become, respectively, 0.25 per cent and 0.38 per cent. These experiments emphasize the necessity of adhering rigidly to the procedure indicated by the I.A.M. and the importance of avoiding carbonation of solutions during analysis.

Modification of the I.A.M. in such a way as to avoid the error due to inadvertent saponification seemed to be an extremely difficult problem and none too well suited to committee work. Accordingly we set about solving our problem by correcting for the error rather than attempting to eliminate it. This we have tried to do by use of a C.P. glycerol of known purity as an ultimate standard.

### Preparation of Cooperative Samples

A glycerol of very high purity was prepared by redistillation in vacuo of a high grade C.P. from salt crude rejecting the first and last portions of about 25 per cent each as described in our 1931 report.[2] The middle portion of the distillate, showing very constant boiling point, was diluted with distilled water to lessen hygroscopicity and bottled under the label "A.O.C.S. Standard G.P. Glycerin—1933."

A sample of salt crude glycerin of good commercial quality and quite free from suspended salts was bottled and labeled "A.O.C.S. Salt Crude Glycerin—1933."

The following analyses were requested:

### Standard C.P. Glycerin

1. Apparent specific gravity at one of the temperatures covered by the Bosart and Snoddy Table compared with water at the same temperature by pyknometer method reported to fourth decimal.
2. Per cent apparent glycerol by I.A.M. using a sample of 1.20-1.25 gms. (1.1 gms. absolute glycerol).
3. Per cent water, if possible, by any method preferred by the committee member.

### Salt Crude Glycerin

1. Per cent apparent glycerol by I.A.M. using a sample of about 1.35-1.40 gms. (1.1 gms. absolute glycerol). Both uncorrected (gross) and corrected acetin results to be reported.
2. Per cent ash.
3. Per cent total residue at 160° C.
4. Per cent glycerol value of acetylizable impurities in residue.
5. Per cent water, if possible, by any method preferred.

Samples wer sent to twelve laboratories but reports were received from only eight.

### Cooperative Analyses

Laboratory No. 1 determined water by drying for 24 hours over $P_2O_5$ under 12-15 mm. pressure. Analyst 2 of Laboratory No. 5 determined water by drying in an evacuated desiccator for five days. Pressure and dehydrating agent not stated. Analyst 1 of Laboratory No. 5 and all of the other laboratories which determined water used the toluene method of Hoyt and Clark.[4]

Presumably all acetin analyses were made at least in duplicate. Laboratory No. 7 reported the average of triplicate analyses. Laboratory No. 4 used approx. N/2 NaOH for neutralization. With these few notations it is believed that all analyses except specific gravity followed the International Methods.

Previous work of this committee has shown extremely good agreement between pyknometer specific gravity determinations. The glycerol content of the standard C.P. was determined by this method using the Bosart & Snoddy Table. Water was determined as a check but not for actual use in arriving at glycerol content. Since the size of sample was specified on both C.P. and salt crude at about 1.1 gms. of absolute glycerol it was thought that the difference between the apparent glycerol by acetin and specific gravity methods on the C.P. would serve as a directly additive "correction for acetin error" on the salt crude acetin analyses.

How well this objective was obtained is shown in the tabulated analyses. That acetin analyses are almost invariably low was again confirmed. Water determinations showed great variation and demonstrated the need of further standardization of method. It is interesting to note the general acceptance of the convenient toluene method of Hoyt and Clark. "True Glycerol" is 0.98% higher than the corrected acetin figures, a value which agrees well with that found in our previous work.

Contrary to expectation and hope, the agreement between laboratories after "correction for acetin error" is applied is no better than before. In the long run it would seem likely that such agreement would be improved, but the limited trial here made certainly is not impressive. The fact that summation figures for both C.P. and salt crude exceed 100% is an indication that our moisture determinations are probably a little high.

Your committee has been successful only in proving the existence of the error of the acetin method and locating its probable source. It has failed to find a remedy.

Mr. C. B. Cluff inquired whether some other method of analysis, as accurate as the acetin method, could not be used.

Mr. C. P. Long inquired whether the committee could not get away from working with acetic anhydride.

Mr. Andrews replied that the acetin method was as accurate as any. Other methods could be tried but to date had not been tried.

Mr. Andrews then asked that all the Glycerin Analysis Committee members meet with him during the session.

### Roster of Glycerin Analysis Committee, American Oil Chemists' Society—1933

Ralph W. Bailey, Stillwell & Gladding, Inc.; M. A. Beck, Van Camp Oil Co.; H. C. Bennett, Los Angeles Soap Co.; W. H. Burkhart, Gold Dust Corp.; A. K. Church, Lever Bros. Co.; W. H. Dickhart; Charles G. Gundel, Fels & Co.; L. F. Hoyt, Larkin Co., Inc.; James F. Lawrie, A. O. Smith Corp.; C. E. McLean, Arizona Testing Labs.; W. J. Reese, Colgate-Palmolive-Peet Co.; M. L. Sheely, Armour Soap Works; J. T. R. Andrews (chairman), The Procter & Gamble Co.

1. Oil & Fat Ind., Vol. 7, p. 299 (August, 1930).
2. Oil & Fat Ind., Vol. 8, p. 297 (August, 1931).
3. Oil & Soap, Vol. 10, p. 71 (April, 1933).
4. Oil & Fat Ind., Vol. 8, p. 59 (February, 1931).

### A.O.C.S. Standard C. P. Glycerin—1933

| Laboratory | Apparent Specific Gravity | Temp., ° C. | % Glycerol from Sp. Gr. (B. & S. Table) | % Glycerol by I.A.M. (uncorrected) | % Water by method preferred | % Glyc. (Sp.Gr.) — % Glyc. (I.A.M.) = "Correction for Acetin Error" Using Sp.Gr. Reported | Using Accepted Sp. Gr. |
|---|---|---|---|---|---|---|---|
| 1 | 1.2417 | 15.5/15.5 | 90.94 | 90.11 | 9.23 | 0.83 | 0.94 |
| 2 | 1.2391 | 25/25 | 91.23 | 88.27* | 8.45* | 2.96 | 2.78 |
| 3 | 1.23906 | 25/25 | 91.21 | 89.33 | 9.53 | 1.88 | 1.72 |
| 4 | 1.2387 | 25/25 | 91.98 | 90.41 | . . . | 0.67 | 0.64 |
| 1. | 1.2385 | | 91.00 | 90.32 | 9.00 | | |
| | | | | 90.09 | 9.11 | | |
| 5 | | 25/25 | | | | 0.69 | 0.74 |
| 2. | 1.2385 | | 91.00 | 90.48 | 10.16* | | |
| | | | | 90.36 | 10.31* | | |
| | 1.2420 | 15.5/15.5 | 91.06 | 90.79 | 9.25 | | |
| 6 | | | | 90.58 | 9.09 | 0.37 | 0.36 |
| | | | | | 9.43 | | |
| | | | | | 9.00 | | |
| 7 | 1.2382 | 25/25 | 90.89 | 89.78 | . . . | 1.11 | 1.27 |
| 8 | 1.2385 | 25/25 | 91.00 | 90.14 | 8.95 | 0.91 | 0.96 |
| | | | | 90.04 | | | |
| | Accepted Value | | 91.05 | 90.10 | 9.19 | Accepted Glyc. (Sp. Gr.) + Water = 100.24<br>Accepted Glyc. (I.A.M.) + Water = 99.29 | |

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* These figures were rejected in arriving at the "accepted values," as their deviation from the average exceeds four times the mean deviation from the average of the other results reported.

### A.O.C.S. Salt Crude Glycerin—1933

| Laboratory | % Glycerol I.A.M. uncorrected | % Ash | % Total Res. at 160° C. | % Org. Res. at 160° C. | % Glyc. Value of Res. | % Glycerol I.A.M. corrected | % Water by method preferred | % Glyc. (I.A.M. corrected) + "Correction for Acetin Error" = % "True Glycerol" Using C.P., Sp.Gr. Reported | Using Accepted C.P. Sp.Gr. |
|---|---|---|---|---|---|---|---|---|---|
| 1. | 82.41 | 9.40 | 11.06 | 1.66 | 0.40 | 82.01 | 6.19 | 82.84 | 82.95 |
| 2. | 81.20* | 9.12 | 11.30 | 2.18 | 0.62* | 80.58* | 7.30 | 83.54 | 83.36 |
| 3. | 82.01 | 8.82 | 10.41 | 1.59 | 0.00 | 82.01 | 6.73 | 83.89 | 83.73 |
| 4. | 82.40 | 9.26 | 10.75 | 1.49 | 0.24 | 82.16 | . . . | 82.83 | 82.80 |
| 1. | 82.88 | 9.13 | 10.81 | 1.68 | 0.38 | 82.50 | 6.24 | | |
| | 82.52 | | | | | 82.14 | 6.52 | | |
| 5. | | | | | | | | 83.04 | 83.09 |
| 2. | 82.86 | 9.08 | 10.80 | 1.72 | 0.30 | 82.56 | 5.88 | | |
| | 82.49 | | | | | 82.19 | 6.79 | | |
| | 82.47 | | | | | 82.16 | 6.41 | | |
| 6. | 82.36 | 9.00 | 10.54 | 1.54 | 0.31 | 82.05 | 6.06 | 82.48 | 82.47 |
| | | | | | | | 6.28 | | |
| | | | | | | | 6.26 | | |
| 7. | 82.23 | 9.31 | 10.61 | 1.30 | 0.23 | 82.00 | . . . | 83.11 | 83.27 |
| 8. | 82.37 | | 9.10* | | | 82.19 | | | |
| | 82.48 | 8.33* | 9.13* | 0.79* | 0.18 | 82.30 | 7.05 | 83.16 | 83.21 |
| Accepted Values | 82.37 | 9.15 | 10.78 | 1.63 | 0.24 | 82.13 | 6.65 | 83.11 | 83.11 |

Accepted % Glyc. (I.A.M. corrected) + Total Residue + % Water = 99.56
Accepted % "True Glycerol" + % Total Residue + % Water = 100.54

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* Values rejected as showing too great deviation from the mean.