Glycerin Analysis Committee, Soap Section, American Oil Chemists' Society 1932 Annual Report

By J. T. R. Andrews, Chairman

LAST year[1] our work showed that, even in the hands of skilled analysts using all reasonable care in operation, the International Acetin Method yields figures on an average more than one per cent lower than the true glycerol content. This year we have followed a program suggested by a few preliminary experiments recorded in our 1931 report and have located the probable cause of this error in the accidental saponification of triacetin during neutralization. This error is apparently inherent in the method itself and cannot be eliminated without a radical alteration of the prescribed procedure.

Preparation of Samples:

Eastman's Triacetin p-256 was redistilled through an efficient fractionating column under a pressure of 7 mm. The first and last portions, representing about one-half the total were rejected and the middle fraction, boiling at 130°-135° C. (mostly 132°-133° C.), was collected. Contrary to expectation, this sample contained considerable diacetin (or monoacetin) which may be explained by the narrow range in boiling point of the acetins. Though this fact was known from its low saponification value of about 747, the sample was used as a cooperative sample in the hope that interesting information might be obtained regarding the relative ease of saponification of the acetins. This sample was designated "Purified Triacetin No. 1."

Pure triacetin was prepared in the following manner. One kilogram of Eastman's p-256 was refluxed for three hours with 350 grams of Eastman's 99% acetic anhydride and the excess anhydride and acetic acid removed by distillation under 7 mm. pressure through a fractionating column. Most of the anhydride and acid distilled off at 35°-40° C., while the triacetin distilled at 130°-135° C. A second distillation, rejecting first and last portions effected completed purification. The product was neutral and had a saponification value of about 772 compared with the theoretical value of 771.8 which corresponds to 42.21% glycerol yield. This sample was designated "Specially Purified Triacetin No. 2."

A quantity of high grade saponification crude glycerin, supplied by Mr. H. C. Bennett of the Los Angeles Soap Co., was mixed and bottled for distribution as "Saponification Crude Glycerin No. 1."

Cooperative Analyses:

The following analyses were requested on both triacetin samples:

A. Acetylize and analyze for apparent gross glycerol content by the International Acetin Method. Samples of about 2.25 grams are recommended.

B. Dissolve samples of similar size in about 400 cc. cold, CO_2-free water, neutralize to phenolphthalein (probably one drop of N/1 NaOH will be sufficient), saponify and calculate apparent gross glycerol content according to the I. A. M.

C. Dissolve samples of similar size in about 50 cc. CO_2-free water at room temperature. Add 3.0 grams fused sodium acetate, 7.5 cc. glacial acetic acid, filter and wash in the usual manner. Complete the analysis according to the I. A. M., observing the usual care in neutralization, and calculate apparent gross glycerol content.

Suitable blanks should accompany each of the above experiments and it is desirable that each analysis be made at least in duplicate. The object is, of course, to ascertain the extent of saponification of the triacetin prior to and during neutralization.

The following analyses were requested on the sample of saponification crude:

A. % Apparent gross glycerol by I. A. M.
B. % Total residue at 160° C. by I. A. M.
C. Acetin value of residue in terms of glycerol by I. A. M.
D. % Corrected glycerol content.
E. % Water by the method you consider most suitable. Please indicate briefly the method used.

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

Analysis of Saponification Crude:

Table 1 shows the analytical results reported. Though there is considerable variation in the apparent gross glycerol and residue figures, we do not feel that the number of cooperating laboratories is large enough to warrant rejection as questionable of any except the extremely low acetin analysis reported by No. 8.

Laboratory No. 2 determined moisture by drying to constant weight a sample of glycerin on asbestos in a vacuum desiccator over concentrated sulphuric acid. Nos. 3 and 8 used the Hoyt and Clark[2] method. No. 4 used the Hoyt and Clark method modified by use of the bichromate oxidation method to estimate glycerol in the water recovered by toluene distillation. No. 5 obtained moisture by drying in an evacuated desiccator for five days, the dehydrating agent being sulphuric acid. No. 6 determined water by allowing the glycerin to remain 24 hours in a vacuum desiccator over P_2O_5 at 12-13 mm. pressure.

These moisture figures are in considerable disagreement, those obtained by dehydration over sulphuric acid being considerably higher than the others. We are inclined to reject the average 9.16% reported by Laboratory No. 5 as outside the limit of probable experimental error and wish to recall that last year's report shows determinations made over sulphuric acid were from 0.4 to 0.5 per cent higher than the accepted values. With these few rather justifiable exclusions, the accepted values are:

% Apparent gross glycerol.......	=	90.65
% Total residue at 160° C.......	=	0.97
Acetin value of residue	=	0.13
% Corrected glycerol content.....	=	90.52
% Moisture	=	7.56

The sum of the total residue, corrected glycerol and moisture values is 99.05 per cent, leaving 0.95% un-

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[1] See Oil & Fat Ind. August 1931, pp. 297-301.

accounted for. This total could be raised by excluding the three lowest values for corrected glycerol content but we would still have about 0.6% unaccounted for and we are forced to conclude from the meager data here presented that the acetin method on saponification crude glycerin yields low results, though perhaps somewhat higher than on other glycerol solutions. This fact has been noted by many observers, e. g., Hoyt & Clark[2], who, by an analysis similar to ours, accounted for all but 0.3% of a saponification crude but failed by an average of 1.1% in their analyses of dynamite, C.P., salt crude and radiator glycerins.

An experiment performed in the writer's laboratory may throw some light on this situation. Using the method of Stillman & Reed[3], carbonyl values were obtained upon Saponification Crude Glycerin No. 1 and last year's cooperative sample "B". An average of several values for the former was 8.2, corresponding to about 1.3% glyceric aldehyde; for the latter the average carbonyl value was 0.2. Aldehydes in general are known to react with acetic anhydride to form diacetates[4] and one case in particular, that of citronellal, has been extensively studied by Reclaire & Spoelstra[5], who showed that the diacetate may thus be formed in almost the theoretical amount. It would seem that this is a sufficient explanation for the exceptionally satisfactory analyses by the acetin method which are obtained on saponification crudes.

TABLE 1

Saponification Crude Glycerin No. 1

Analyses by International Standard Methods

Laboratory	% Apparent Gross Glycerol by I. A. M.	% Total Residue at 160° C.	Acetin Value of Residue	% Corrected or True Glycerol	% Water by Method preferred by Analyst
1......	90.45	0.89	0.25	90.20	....
2......	90.28	0.60	0.15	90.13	8.11
3......	90.82	0.85	0.0	90.88	7.01
	90.95	0.95			
4......	90.96	1.18	0.0	90.92	7.59
	90.88				7.70
5......	90.28	1.20	0.30	89.91	8.89*
	90.12	1.23	0.28		9.43*
	90.99	0.77	0.09		7.45
	91.02	0.82	0.09		7.45
6......	91.14	0.94	0.06	91.00	7.54
	91.16	0.95	0.07		7.46
					7.35
7......	90.71	0.91	0.12	90.59	
8......	89.41*	1.35	0.18	89.23*	7.58
Accepted Average..	90.65	0.97	0.13	90.52	7.56

Total of accepted values for total residue,
corrected glycerol and water = 99.05%
Unaccounted for .... = 0.95%
*These values were excluded from accepted average.

Analysis of Triacetin Samples:

Tables 2 and 3 show the analytical results reported on the triacetin samples. The work on Purified Triacetin No. 1 requires little attention, as it obviously contains far too much diacetin or monoacetin to be typical of the product obtained by complete acetylization under the conditions prescribed by the I. A. M. These impurities are sufficient to account adequately for the high figures obtained by method "A" and the low results by methods "B" and "C". The difference "B-C" indicates that considerable inadvertent saponification of ester occurs during neutralization, though a comparison of these figures with the corresponding ones obtained on the completely acetylized triacetin No. 2 indicates mono- or diacetin is quite as stable during this process as triacetin itself. In general, the average value of 0.39 for "B-C" agrees quite well with the figure 0.43 given in last year's report, which was obtained by one laboratory only upon a sample of triacetin which was shown to contain appreciable amounts of these impurities.

TABLE 2

Purified Triacetin No. 1

Laboratory	Test A	Test B	Test C	B —A	B — C
1............	42.46	40.51	40.31	.....	0.20
3............	43.09	41.32	40.88*	.....	0.44
	43.22	41.25	40.81*		
4............	43.24	41.26	40.71*	.....	0.55
	43.19	41.28	40.72*		
5............	42.53	41.03	40.69*	.....	0.43
	42.58	41.14	40.63*		
	42.96	40.82	40.83		
6............	43.02	41.06	40.90	.....	0.07
	43.10	40.83	40.86		
	43.13	41.07	40.91		
7............	42.94	41.19	40.59	.....	0.60
8............	42.59	41.08	40.66	.....	0.42

Accepted average for "B — C" = 0.39%.
*By error acetic anhydride instead of acetic acid was used in these tests.

TABLE 3

Specially Purified Triacetin No. 2

Laboratory	Test A	Test B	Test C	B —A	B — C
1............	41.07	41.65	41.11	0.58	0.54
2............	41.39	41.97	41.45	0.58	0.52
3............	41.51	42.45	41.42*	1.04	0.92
	41.31	42.45	41.64*	....	
4............	41.84	42.30	41.56*	0.42	0.69
	41.81	42.19	41.55*	....	
5............	41.17	41.95	41.63*	0.99	0.40
	40.94	42.15	41.66*	....	
	41.49	42.24	41.71		
6............	41.54	42.33	41.73	0.64	0.48
	41.61	42.11	41.71		
	41.64	42.14	41.77		
7............	41.57	42.11	41.54	0.54	0.57
8............	41.07	42.25	42.14	1.18	0.11

Accepted average for "B — A" = 0.75%.
Accepted average for "B — C" = 0.53%.
*By error acetic anhydride instead of acetic acid was used in these tests.

On the other hand, the analyses made upon Specially Purified Triacetin No. 2 have even surpassed our expectations. It should be pointed out that absolute agreement between the different laboratories in columns A, B and C is relatively unimportant, as such agreement depends to some extent upon absolute accuracy of standard

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[2] Oil & Fat Ind. Vol. 8, No. 2, pp. 59-61.

[3] Perf. & Ess. Oil Record, August 1932, pp. 278-286.

[4] Bernthsen-Sudborough "Organic Chemistry." 1931, p. 132.

[5] Perf. & Ess. Oil Record, April 1927, pp. 130-132.

solutions, etc., which is of little consequence in these experiments. The vitally important figures are those obtained by the differences "B-A" and "B-C" and the excellent agreement here is both satisfying and conclusive. The extent of saponification of triacetin in a careful neutralization by method "A", *which is the I. A. M.*, or by method "C", which is an attempted simulation of the I. A. M., beginning at a point directly after completion of acetylization, is quite ample to account for the low acetin results which were demonstrated by our work last year. This error, in fact, amounts to about 1.5% of the actual glycerol involved, which is somewhat higher than the discrepancies noted during all of the previous work of the Glycerin Analysis Committee.

Cooperation with Prüfungsstation Darmstadt:

A portion of last year's sample "B" was sent to the Prüfungsstation Darmstadt at the request of its director, Dr. W. Prager. Dr. Prager reports that two analysts found 94.92, 95.36, 95.42 and 95.45% apparent gross glycerol by I. A. M., an average of 95.29% against our accepted figure of 95.26% from specific gravity. Their only deviations from the I. A. M. are in the use of 8.0 cc. of acetic anhydride instead of 7.5 cc. and the use of flat bottomed Erlenmeyer flasks instead of round bottomed flasks for acetylization. The first point seems trivial and the option as to choice of flasks is permitted by the I. A. M., yet Dr. Prager attributes our accepted acetin value of 94.14%, which is 1.15% lower than his and 1.12% lower than that from specific gravity, to the use of round bottomed flasks. At first we suspected that he was following the English practice of standardizing against a glycerol of known purity but, in reply to this inquiry, he assures us that his ultimate standard is sodium carbonate. Dr. Prager admits, however, that the Prüfungsstation "in dealing with the glycerin industry of France and the Netherlands is accustomed to the reproach that their figures are considerably higher than those arrived at in the laboratories of the said countries."

Sample "B" was also analyzed by the N. V. Chemische Fabriek of Naarden, Holland, who reported, through Dr. Prager, 94.99 and 95.15% apparent glycerol by the I. A. M. These results also are considerably higher than those obtained by American chemists.

In accepting his kind offer of further cooperation, a portion of Specially Purified Triacetin No. 2 was sent to the Prüfungsstation with a request for analyses by methods A, B and C. The following results were reported:

A	B	C
42.45	42.24	42.14
42.00	42.16	

B — A = —0.02. B — C = 0.06

These differences are negligible compared with those noted by us and all of the results are close to the theoretical glycerol yield of pure triacetin. Dr. Prager suggests that the quantity of NaOH used in the blank determination has an important bearing upon the analysis and cites articles on this subject by Berth in Chem. Umschau[6] 10, 129-31 (1927) and Chemiker Zeitung[7] 61, 597-98 (1928). The I. A. M. prescribes 5cc. of N/1 NaOH for saponifying impurities in the blank reagents, but Dr. Prager concludes that, in order to simulate more closely the actual conditions of the analysis itself, a larger amount is necessary so that the excess caustic of the blank will be subject to the same atmospheric carbonation as that of the sample. For the experiments on Triacetin No. 2, 18 cc. N/1 NaOH were used, this amount being practically identical with that remaining in the samples after saponification of the triacetin was complete. Furthermore, the carbonate content of the NaOH solution exerts a profound influence and this effect was entirely obviated by use of the new and absolutely carbonate-free N/1 NaOH solution obtained from the German firm of E. Merck.

These points are certainly most pertinent and indicate a line of further investigation which must be followed in any future program.

Conclusions:

While the conclusion expressed in the opening paragraph of this report represents adequately our position at this stage of the investigation, future constructive effort seems advisable in either or both of these directions:

1. If possible, improve the present method so as to eliminate the existing error. The suggestions of Drs. Berth and Prager should receive careful consideration.
2. Consider the adoption of a specially purified glycerol of known purity as an ultimate standard for analyses by the acetin method. This has been the accepted practice among English chemists for nearly twenty years.

At this time, your chairman wishes to thank each member of the committee for his cordial cooperation and helpful suggestions. To Dr. Prager and his associates, we wish to express our most sincere appreciation and gratitude for their interest and assistance in this work.

J. T. R. Andrews, *Chairman,*
Glycerin Analysis Committee.

The roster of the Glycerin Analysis Committee is as follows:

Ralph W. Bailey, Stillwell & Gladding, Inc., New York, N. Y.
H. C. Bennett, Los Angeles Soap Co., Los Angeles, Cal.
W. H. Burkhart, Gold Dust Corporation, Holabird & Vail Sts., Baltimore, Md.
V. K. Cassady, The Palmolive Co., Milwaukee, Wis.
A. K. Church, Lever Bros. Company, Cambridge, Mass.
Chas. G. Gundel, Fels & Company, Philadelphia, Pa.
L. F. Hoyt, Larkin Company, Inc., Buffalo, N. Y.
James W. Lawrie, A. O. Smith Corp., Milwaukee, Wis.
W. J Reese, Colgate-Palmolive Peet Co., Kansas City, Kans.
M. L. Sheely, Armour Soap Works, Chicago, Ill.
J. T. R. Andrews, Procter & Gamble Co., Ivorydale, Ohio.

Announcement

The convention fare arrangement has been completed and it will be one and one-third fare for the round trip. You may leave for the convention any time between May 8th and May 15th and remain for thirty days in beautiful New Orleans. Certificate and full information will be sent by Secretary Helm within a few days. Be sure to take advantage of the low return fare and join your fellow members at New Orleans for the convention.

Chemicals—Condition in the French Industry

The French chemical industry in 1932 was probably in a better condition than many other French industries and than those industries in many other countries. The set-up of the chemical industry showed little change in 1932, and the situation remained about the same as during the past few years.

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[6] C. A. 21, 2391 (1928).
[7] C. A. 23, 2124 (1929).