

content of the peanuts being somewhat higher than the moisture determined by analysis.

The yields of oil and meal which were obtained have been compared with the yields predicted on the basis of chemical analysis. Under the conditions of processing of this test run no so-called *invisible oil loss* was observed.

Acknowledgment

The authors are indebted to G. E. Mann for the refining loss determinations reported on the oil.

REFERENCES

1. War Food Order No. 100, 9 Federal Register 4974, 10446, 12609 (1944); 10 Federal Register 7, 103, 1428 (1945).

2. Weekly Peanut Report XXVI, No. 29, July 19, 1944. War Food Administration, Office of Distribution, Processed.

3. Report of the Peanut Committee—1939-40. Oil and Soap 17, 133-4 (1940).

4. Official and Tentative Methods of the American Oil Chemists' Society, pp. 10c-10d.

5. Rules Governing Transactions Between Members of the National Cottonseed Products Association 1942-3. Rule 270 C, Peanuts, pp. 133-6, (1942).

6. Magne Sethne, Zur Frage Der Ausbeutedifferenzen in Ölmühlensbetrieb, Eine Betriebstechnische Untersuchung. Kgl. Norske Videnskabers Selskabs Skrifter 1939, No. 3, pp. 1-150, Trondheim 1939.

7. Gerritz, H. W., Potassium in Fruits and Fruit Products, Volumetric Chloroplatinate Method. J. Assoc. Official Agri. Chem. 25, 232-238 (1942).

8. Official and Tentative Methods of Analysis of the Association of Official Agricultural Chemists, 1940.

9. Hoffpauir, Carroll L., Determination of Moisture in Peanut Kernels, Oil and Soap, 22, 283-6 (1945).

Comparison of Methods for the Determination of Glycerol by Acetylation

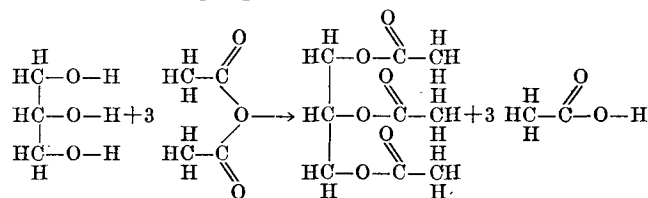
W. D. POHLE and V. C. MEHLENBACHER

Swift and Company, Chicago, Ill.

THE acetin method (3) is the accepted procedure for the determination of glycerol by acetylation although results by this method are usually considerably lower than the true value (2). In the past numerous attempts have been made to increase the accuracy of this method, but none has led to any fundamental improvement so the method remains as it was originally written.

The method to be presented in this paper was not the result of an investigation for the improvement of the acetin method but the by-product of a study of procedures for measuring the hydroxyl content of organic compounds. In the course of this investigation we found that the method of West, Hoagland, and Curtis (4) for the determination of hydroxyl groups was quantitative for glycerol. This acetylation procedure proved to be more accurate, more rapid and simpler than the conventional acetin method.

Acetic anhydride reacts with glycerol as indicated in the following equation:



One mol. of glycerol reacts with 3 mols. of acetic acid, thus the glycerol in a sample can be calculated from the amount of acetic acid combined with the glycerol. In the following procedure the acetic acid combined with the glycerol is calculated from the difference between the amount of standardized alcoholic potassium hydroxide required to titrate the acetylating reagent before and after reaction with the sample.

Experimental

The preliminary tests were made with the acetic anhydride-pyridine reagent (1 vol. acetic anhydride and 7 vol. pyridine) used by West, Hoagland and Curtis (5), but in later experiments, and in the

method finally adopted the concentration of acetic anhydride was increased by changing the ratio to 1 to 6. This provided an additional excess of acetic anhydride and permitted a greater variation in the size of sample without jeopardizing the accuracy of the method.

The conditions necessary for quantitative results were determined by analysis of a C. P. glycerin that contained 95.0% glycerol. The composition of the glycerin was established from specific gravity and refractive index measurements, analysis by the periodic acid (1) method and by subtracting the moisture determined by the Fischer Volumetric Method from 100.

The time required for complete reaction between the sample and acetylating reagent was established by analyzing samples after heating for varying periods on the steam bath. The results are given in Table I.

TABLE I
Relation Between Time Allowed for Reaction on the Steam Bath and the Analyses

Time allowed for reaction on the steam bath, minutes	Glycerol found by analysis, %
15.....	94.8
25.....	95.3
30.....	95.1, 94.9
60.....	95.0, 95.0
120.....	94.5, 95.5
240.....	95.0

The reaction between the sample and acetic anhydride proceeded to completion in a very short time, and no additional reactions occurred when the heating period was extended well beyond that required for quantitative results. Thirty to forty minutes was selected as the time the sample and reagent should be heated on the steam bath in order to insure complete reaction. Since the reaction proceeded so rapidly at steam bath temperatures some tests were made at room temperature. Under these conditions the reaction was not complete even after 24 hours for the analysis indicated only 94.1% glycerol. Quantitative results can be obtained at room temperature by increasing the reaction time to two to four days,

but such conditions are not practical for a routine laboratory test.

The excess reagent needed for quantitative results was determined by analyzing increasing amounts of C. P. glycerin while keeping the quantity of acetylating reagent constant. The results of these tests are shown graphically in Figure 1.

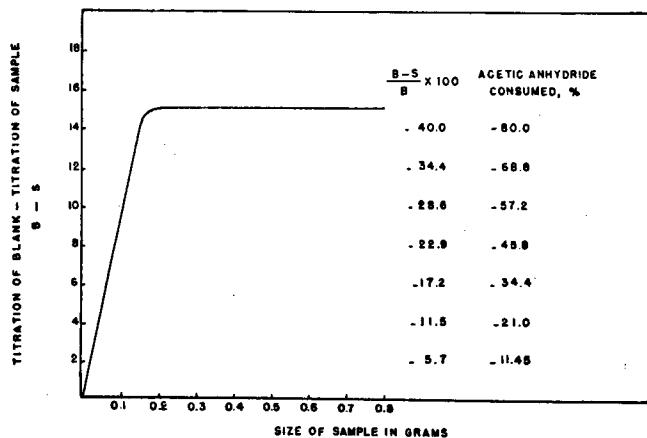


Fig. 1. Relation between reaction of acetylating reagent and size of sample.

The reaction between the sample and acetic anhydride was quantitative up to the point where 70% of the acetic anhydride was consumed by the sample. It must be remembered that the water in glycerin also reacts with the acetic anhydride and thus reduces its effective concentration. This method is intended only for glycerins containing less than 20% water. However, a crude glycerin containing 60% glycerol, prepared by diluting an 82% crude with water, was analyzed correctly. This showed that samples with less than 80% glycerol may be analyzed if the water content is not too high.

Tests have shown that Barrett's 2A-refined pyridine or Eastman Kodak Company pyridine 214, b. p. 113.5°-115.5°C. can be used in the acetylating reagent without the treatment specified by West, Hoagland and Curtis (4). The reagent will become colored on standing and should not be used after it has turned yellow. Analyses of four samples of glycerin using yellow colored reagent three weeks old were approximately 0.3% lower than those obtained when the solution was fresh. Our experience indicates the acetic anhydride-pyridine solution can be used after standing for two weeks at room temperature, but it is best not to use that which has stood longer.

A comparison of results obtained by several methods on C. P., high gravity C. P., dynamite, and crude glycerin is shown in Table II. The data in Table II indicates that the acetic anhydride-pyridine procedure is more accurate than the conventional acetin method. The acetic anhydride-pyridine procedure, like the acetin method, does not give accurate results when the sample contains compounds like trimethylene glycol which are also acetylated. However, the difference between the results by this method and those by the periodic acid procedure will give an indication of the amount of hydroxy compounds other than glycerol, when such compounds are present. The presence of acetyltable material other than glycerol is clearly indicated by the analyses of crude glycerins 7 and 8 in Table II.

TABLE II

Analyses of C. P., High Gravity C. P., Dynamite and Crude Glycerin

Sample	Glycerol Determined by				100-% water by Fischer volumetric method
	Acetic anhydride-pyridine procedure	Sp. Gr.	Periodic acid method	Acetin method	
C. P. Glycerin					
No. 1.....	95.7	95.4	95.5	93.8	
No. 2.....	95.0	95.3	95.3	93.7	
No. 3.....	95.3	95.5	95.2	93.5	
No. 4.....	94.7	95.0	94.8	93.4	
No. 5.....	95.5	95.3	94.7	93.6	
No. 6.....	95.2	95.2			
No. 7.....	95.3	95.0			
No. 8.....	95.1	95.4			
No. 9.....	95.2	94.9			
No. 10.....	94.6	94.4			
High Gravity C. P. Glycerin					
No. 1.....	99.9	99.8	99.5	98.2	
No. 2.....	99.4	99.2			
No. 3.....	98.5	99.0			
No. 4.....	99.5	99.0			
No. 5.....	98.7	99.0			
Dynamite Glycerin					
No. 1.....	98.8	98.7			99.0
No. 2.....	99.2	99.5			99.4
No. 3.....	99.1	99.2			99.1
No. 4.....	98.3	98.2			98.1
No. 5.....	98.8	98.7			98.8
Crude Glycerin					
No. 1.....	90.8		90.6	89.8	
No. 2.....	83.6		83.8	83.0	
No. 3.....	81.3		81.1	80.2	
No. 4.....	79.8		80.2	78.2	
No. 5.....	84.6		84.3	82.9	
No. 6.....	79.7		79.3	78.6	
No. 7.....	87.2		85.6	84.1	
No. 8.....	84.2		82.7	81.9	
No. 9.....	81.8		81.6	80.2	
No. 10.....	81.9		81.6	80.8	

The standard deviation for 17 analyses of a C. P. glycerin containing 95.0% glycerol was calculated in order to determine the precision of the method. The average of the 17 analyses was 94.97% glycerol and the standard deviation was $\pm 0.3\%$.

Method

Apparatus:

Glass stoppered flasks, 300-ml.
Buret, 50-ml., accurately calibrated.
Pipet, 5-ml.
Graduated cylinder, 25-ml.

Reagents:

Acetic anhydride-pyridine reagent, 1 volume of reagent quality acetic anhydride (assay minimum 95%) and 6 volumes of pyridine, Barrett's 2A-refined or Eastman Kodak Company, 214, b. p. 113.5°-115.5°C.

Alcoholic potassium hydroxide solution, 0.32 N to 0.35 N, U.S.S.D. Alcohol Formula No. 30 is satisfactory.

Isobutyl alcohol, reagent quality.

Phenolphthalein indicator solution, 1.0% in 95% alcohol.

Procedure:

Weigh accurately into a 300-ml. glass stoppered Erlenmeyer flask 0.10 to 0.15 gm. of samples containing ca 95% glycerol or 0.12 to 0.18 gm. of samples containing ca 80% glycerol. Add 5 ml. of acetic anhydride-pyridine reagent with a pipet. Prepare and conduct a blank determination simultaneously with the sample. The blank is not heated on the steam bath. Moisten the stopper with pyridine, place loosely in the flask and set the flask on a well-fitting hole on a steam bath. Loosen the stopper two or three times during the first three or four minutes the flask is on the steam bath so as to relieve the pressure. Then insert the stopper tightly and heat for 30 to 40 minutes. Remove the flask from the steam bath, cool at room temperature for one to three minutes and then add 5 ml. of distilled water. Let the water run down over the stopper and sides of the flask. Replace the stopper and heat on the steam bath for one to two minutes. Remove the flask from the steam bath, cool at room temperature for 10 to 15 minutes and add 25 ml. of isobutyl alcohol, allowing the alcohol to wash down the stopper and sides of the flask. Titrate with the alcoholic potassium hydroxide using 0.5 ml. of phenolphthalein indicator solution.

Calculations:

$$\% \text{ glycerol} = \frac{(B-S) \times N \times 3.07}{W}$$

B = ml. of alcoholic potassium hydroxide required to titrate blank.

S = ml. of alcoholic potassium hydroxide required to titrate sample.

N = Normality of alcoholic potassium hydroxide.

W = Weight of sample in gm.

Summary

A method for the determination of glycerol has been presented in which the acetylation is performed

with a reagent consisting of acetic anhydride in pyridine. Typical data obtained by this procedure and other accepted methods are shown. The proposed procedure is simpler, more rapid, and more accurate than the conventional acetin method.

REFERENCES

1. Bradford, Pohle, Gunther, and Mehlenbacher, *Oil & Soap* 19, 189, (1942).
2. Glycerin Analysis Committee, Am. Oil Chemists' Soc. Report, *Oil & Soap*, 10, 71, (1933); 11, 53, (1934).
3. Official and Tentative Methods of the Am. Oil Chemists' Soc., page D-3, (1938).
4. West, Hoagland, and Curtis, *J. Bio. Chem.*, 104, 627, (1934).

Determination of Borax in Soap and Synthetic Detergents*

E. W. BLANK and A. TROY
Colgate-Palmolive-Peet Company
Jersey City, N. J.

THE usual method employed for the determination of borax in soap and soap products is that described by Poetschke (1, 2). The procedure is accurate but tedious. It includes a lengthy fusion that requires constant attention and care. In addition, repeated operations of filtration and refluxing are required to remove, respectively, the excess of calcium carbonate over that required to neutralize the solution prior to titration of the boric acid and the carbon dioxide liberated during neutralization. The presence of calcium carbonate during the final titration, as recommended in the method, tends to obscure the phenolphthalein endpoint.

Scott (3) describes a method for the determination of borax in soap in which the soap is acidified, the fatty acids removed by filtration, and the boric acid titrated with normal sodium hydroxide solution in the presence of mannitol. The excess of acid remaining from splitting the soap is previously neutralized to methyl orange with sodium hydroxide. If silicate is present, it is removed by dehydration with concentrated hydrochloric acid employing a distillation flask and collecting the volatile boric acid in a receiving flask. If phosphates are present, a correction must be applied to the titration since a portion of the phosphate titrates as borate.

The method described in this paper is both accurate and rapid. The presence of phosphate or silicate does not interfere with the determination. Carbonates are destroyed during the course of the procedure.

Principle of the Method

The method to be described is based upon the fact that soluble silicates, carbonates, and orthophosphates can be quantitatively precipitated by strontium chloride whereas strontium metaborate is soluble in an excess of strontium chloride solution. After the insoluble strontium salts are removed by filtration, the strontium metaborate is converted into boric acid by acidification with hydrochloric acid, and the boric acid titrated in the usual manner in the presence of mannitol.

The solubility of strontium carbonate (SrCO_3) is given as 0.0011 grams per 100 ml. of water at 18°C. and 0.065 grams per 100 ml. of water at 100°C. (4). The same source lists strontium metasilicate (SrSiO_3) and strontium orthophosphate (SrHPO_4) as insoluble. It has been found by experiment that meta- or pyrophosphates do not interfere in the determination.

Borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) is slightly soluble in ethyl alcohol. For this reason determined values for borax in the alcohol insoluble material obtained from the original sample tend to run low. In the procedure described in this paper the borax is determined on the original sample to avoid errors due to the solubility of borax in ethyl alcohol.

Solubility of Boric Acid in Ethyl Ether and Petroleum Ether

During the development of the method the question arose as to the degree of solubility of boric acid in ethyl ether and petroleum ether. This question merits consideration since in the procedure to be described the fatty acids are normally removed from the sample solution by use of petroleum ether. The solubilities were determined by employing a modification of the apparatus devised by Bahr (5). Figure 1 shows the constructional details of the modified apparatus. The apparatus was maintained at $25 \pm 0.01^\circ\text{C}$. by immersion in a thermostatically controlled water bath.

The method of procedure was essentially as follows: Boric acid was placed in contact with the ether and stirred by a stream of dry nitrogen for six hours. Nitrogen was passed through the ether by closing stopcock B and opening stopcocks A and C. Stopcock D was oriented in such a manner as to permit passage of the nitrogen while sealing off the measuring pipet. A slight amount of refluxing took place in the condenser. Some ether was lost by volatilization. Due to the latter loss the solubility is determined in a solution that is being slowly concentrated. Super-saturation is prevented due to the agitation of the solution by the stream of nitrogen. The nitrogen was dried by passage over anhydrous calcium sulfate.

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