Free Glycerol in Soap

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THE conventional method for the determination of free glycerol in soap is a tedious and time-consuming procedure (2). It is altogether too slow for plant control purposes. A multiplicity of operations is involved, including acidification and splitting, solidification and separation of the fat acids, precipitation of salt and water-soluble acids and, finally, oxidation of the glycerol with potassium dichromate. The last step alone requires three hours. Silverman has suggested an improvement by utilizing a cerate oxidation which reduces the oxidation period to 12 to 15 minutes (6). However, time and temperature are critical and must be accurately controlled in this method.

Obviously the determination of glycerol in soap could be simplified if it were unnecessary to remove the fat acids or if they could be removed by extraction with an organic solvent. Since fat acids, salt, soap builders, and certain fat solvents do not interfere with the reaction between periodic acid and glycerol, an investigation was made to see if an improved method might be evolved. The reaction between glycerol and periodic acid is rapid and proceeds at room temperature without secondary reactions. Also, periodic acid reacts only with compounds having two or more adjacent hydroxyl groups.

The use of periodic acid in glycerol analysis has been reported in several previous papers (1, 3, 4, 5). The equation for the reaction of periodic acid with glycerol is given below:

$$C_3H_5(OH)_3 + 2\ H_5IO_6 \rightarrow 2HCHO + HCOOH + 2HIO_3 + 5H_2O$$

The glycerol can be determined after reacting with periodic acid in either of two ways: 1. from iodimetric titrations of the periodic acid reagent before and after reaction with the glycerol, or 2. by an acidimetric titration of the formic acid which is formed by reaction of periodic acid with glycerol. The former is a very satisfactory procedure, providing there is nothing present other than glycerol to react with the periodic acid. When substances such as propylene glycol are present, the acidimetric titration of formic acid should be used because such substances do not interfere with this test.

Experimental

Known quantities of glycerol were added to pure sodium palmitate prepared from distilled fat acids which were free from any constituent that reacts with periodic acid. The purity of glycerol was established by its specific gravity and confirmed by the periodic acid method (3). Sodium palmitate-glycerol mixtures were prepared containing known quantities of the usual variety of soap builders.*

The glycerol in these samples was then determined by dissolving samples in water, adding an excess of periodic acid, and titrating this excess iodimetrically. This method is designated hereafter as the direct-iodimetric method. The results are tabulated in Table I.

It is obvious from these data that the results were accurate if the sample size did not exceed 0.5 gram. Ordinary soap builders did not interfere. However, the accuracy and precision were somewhat less than desired when the glycerol content was below 1%. Furthermore, it was known that there was no interfering substance present, which would not normally be the case when working with samples of unknown history and composition.

* Alkaline inorganic salts added to soap to increase detergent action.

TABLE I

Analysis of known mixtures by Direct Method

Soap, g.	Salt, g.	Builders, g.	Grams of Glycerol Present	Glycerol % Present	Glycerol % Found
0.500	.....	.....	0.00	0.00	0.02
0.500	.....	.....	0.0201	4.02	4.00
1.000	.....	.....	0.0205	2.05	1.57
2.000	.....	.....	0.0210	1.05	0.57
0.500	.....	.....	.....	4.02	3.98
0.500	.....	.....	.....	2.04	2.07
0.500	.....	.....	.....	1.04	1.07
0.500	.....	.....	.....	0.21	0.23
0.500	.....	0.5 [1]	.....	4.19	4.15
0.500	.....	1.0 [1]	.....	4.02	3.85
0.500	.....	1.6 [1]	.....	0.00	0.07
0.500	.....	1.6 [2]	.....	0.00	0.05
0.500	0.05	.....	.....	0.00	0.02
0.500	0.10	.....	.....	0.00	0.02
0.500 [3]	.....	.....	.....	0.00	0.07

[1] Equal quantities of each Na_2SiO_3; $Na_2B_4O_7$; Na_3PO_4; Na_2CO_3; NaOH.
[2] Equal quantities of each Na_2SiO_3; $Na_2B_4O_7$; Na_3PO_4; $NaHCO_3$.
[3] 0.02 g. gelatin.

The procedure utilizing the acidimetric titration of the formic acid produced by the reaction between glycerol and periodic acid (4) was tried next because it is more specific for determining glycerol. To apply this procedure it was necessary to split the soap and to remove the fat acids. A simple and rapid separation was effected by adding 200 ml. of chloroform and 200 ml. of diluted sulfuric acid (25 ml. conc. H_2SO_4 per liter) to the sample and then shaking until all the soap was split, the fat acid separated, and the aqueous layer was clear. The fat acids went into the chloroform and the glycerol into the aqueous acid layer. Aliquots of the acid layer were used for determination of the glycerol by both the acidimetric and iodimetric procedures. Results of the tests on known mixtures of sodium palmitate, glycerol, and builders are given in Table II.

TABLE II

Analyses of Known Mixtures by Extraction Method

Soap in aliquot tested, g.	Builder in aliquot tested, g.	Glycerol, % Present	Glycerol, % Found by acidimetric titration	Glycerol, % Found by iodimetric titration
10	.....	0.00	0.00	0.00
10	.....	0.07	0.05	0.07
10	.....	0.13	0.11	0.13
10	.....	1.31	1.31	.....
10	3 [1]	0.13	0.05	0.13
10	3 [1]	1.31	0.61	1.28
5	1.5 [2]	2.61	2.65	2.63
5	.....[3]	2.61	2.7	.....

[1] 1 g. each of Na_3PO_4; Na_2SiO_3; $Na_2B_4O_7$.
[2] 0.5 g. each of Na_3PO_4; Na_2SiO_3; $Na_2B_4O_7$.
[3] 0.5 g. NaCl.

These data show that builders can interfere with the acidimetric procedure because of their buffer action in the titration. However, accurate results were obtained when the portion tested contained less than 1.5 grams of builders. The builders did not interfere with the iodimetric method. These two pro-

cedures are designated hereafter in this paper as the extraction-acidimetric and extraction-iodimetric methods.

A group of commercial soaps and soap products were analyzed by the methods discussed. These soaps were made from different types of soapstock, and some contained large amounts of builders. The results obtained by the extraction-acidimetric and extraction-iodimetric methods are summarized in Table III:

TABLE III

Analyses of Soap Products by Extraction Methods

Sample	Glycerol, % (Sample Basis)	
	Extraction-Acidimetric Method	Extraction-Iodimetric Method
Soap Chips (tallow)	0.76	0.77
Toilet Soap	0.88	0.94
Soap Powder (grease base)	0.00	0.02
Soap Flakes (tallow and grease base)	0.38	0.45
Soap Powder (Vegt. Oil Foots base)	0.18	0.21
Soap Flakes (Red Oil Base)	0.00	0.02
Soap Flakes (unknown base)	0.59	0.64
Sodium Oleate (Merck & Co.)	.....	0.91
Sodium Palmitate (Distilled fatty acids)	.....	0.00

The results by both methods are in good agreement, but it must be remembered that although the acidimetric method is more specific, it is not reliable when the portion tested contains more than 1.5 grams of builders. The iodimetric procedure is preferable because it is accurate, rapid, simple, and not affected by the presence of builders.

The soap products mentioned above were further tested by the direct-iodimetric method and the results compared with those obtained by the extraction-iodimetric method; see Table IV:

TABLE IV

Comparison of Analyses by Direct-Iodimetric Method and Extraction-Iodimetric Method

Sample	Direct-Iodimetric Method Glycerol, %	Extraction-Iodimetric Method Glycerol, %	Periodic Acid reducing material in $CHCl_3$ phase, calculated as Glycerol, %
Soap Chips (tallow)	0.85	0.77	0.08
Toilet Soap	1.03	0.94	0.10
Soap Powder (grease base)	0.10	0.02	0.10
Soap Flakes (tallow and grease base)	0.87	0.45	0.09
Soap Powder (Vegetable Oil Foots base)	0.50	0.21	0.56
Soap Flakes (Red Oil Base)	0.92	0.02	0.27
Soap Flakes (unknown base)	0.73	0.64	0.32
Sodium Oleate (Merck & Co.)	1.14	0.91	0.17
Sodium Palmitate (Distilled fatty acids)	0.03	0.00	0.01

Results obtained by the direct-iodimetric method were consistently higher than those obtained by the extraction-iodimetric procedure; however, the differences were small in most cases so that the direct method may be employed for plant control purposes when the composition of the soap and the deviations are known. These differences between the two methods are due to the presence of fatty products which react with periodic acid and are calculated as glycerol in the direct procedure but which are separated from the glycerol in the extraction method. An indication of the amount of these reactive fatty products was obtained by testing the chloroform solution from the extraction method. The behavior of these constituents was quite variable in products made from Red Oil and low grade greases.

Some of the samples tested were not readily split with sulfuric acid solution. An acetic acid solution (1 part glacial acetic acid and 9 parts distilled water) was found to be more effective and rapid and had no effect on the final results by the iodimetric method. Sulfuric acid is preferred when the glycerol is to be determined acidimetrically.

METHODS

Extraction-Iodimetric Titration Method

REAGENTS:

Periodic Acid Solution: Dissolve 5.4 g. of periodic acid in 100 ml. of distilled H_2O and then add 1,900 ml. glacial acetic acid and mix thoroughly. Store in a dark glass-stoppered bottle or store in the dark in a clear glass-stoppered bottle.

Sodium Triosulfate Solution 0.1 N: Dissolve 24.8 g. of sodium thiosulfate in distilled H_2O and dilute to 1 liter. Standardize against potassium dichromate. A.O.C.S. Method Cd 1-25.

Potassium Iodine Solution: Dissolve 150 g. of KI in distilled H_2O and dilute to 1 liter.

Starch Indicator Solution: Make a homogeneous paste of 10 g. of soluble starch in cold distilled H_2O and add 1 liter of boiling distilled H_2O. Stir rapidly and cool.

Acetic Acid Solution: Add 100 ml. of glacial acetic acid to 900 ml. distilled H_2O and mix thoroughly.

Chloroform U.S.P.: Run a blank test using 200 ml. of $CHCl_3$ and 200 ml. of acetic acid solution in the same manner as a sample. The titration of this test should agree with a blank test on 50 ml. distilled H_2O within 0.5 ml. 0.1 *N* thiosulfate. If not, the $CHCl_3$ must not be used.

PROCEDURE:

Weigh 20 $\pm$ 0.05 gm. of the sample into a 500 ml. glass-stoppered flask. Add 200 ml. $CHCl_3$ and 200 $\pm$ 2 ml. of acetic acid solution. Shake until soap is split. The flask may be warmed if the soap does not readily react with the acid. If the solution is alkaline due to large amounts of builders, add conc. H_2SO_4 in 0.5 ml. increments until the aqueous phase is acid to litmus. Allow to stand until the contents of the flask separate into two phases and the acid layer is practically clear.

Pipette 50 ml. of the aqueous phase into a 400 ml. beaker and add 50 ml. of the periodic acid reagent using a volumetric pipette and mix by gentle shaking. Cover the beaker with a watch glass and allow to stand at room temperature for 30 minutes. Prepare two blanks using 50 ml. of acetic acid solution in place of the aqueous phase and handle exactly as the sample.

Add 20 ml. of the KI solution, mix by gentle shaking, and allow to stand at least one minute, but not more than five minutes. Add 100 ml. of distilled H_2O and titrate with 0.1 *N* $Na_2S_2O_3$. Titrate to the disappearance of the brown iodine color and then add 2 ml. of the starch indicator solution. Continue the titration to the disappearance of the blue iodo-starch color. If the titration of the sample is less than 0.8 times the titration of the blank, repeat the determination using a smaller aliquot or a smaller sample.

CALCULATION:

$$\text{Free glycerol, \%} = \frac{(B - S) \times N \times 2.302}{W}$$

B = Titration of blank; average of 2
S = Titration of sample
N = Normality of $Na_2S_2O_3$
W = Weight of sample represented by aliquot tested.
2.302 = Mol. wt. of glycerol (92.09) divided by 40. Calculate to the nearest 0.01%.

Direct Iodimetric Method

This is used for routine testing where some accuracy can be sacrificed in the interest of time and simplicity and where the periodic reducing constituents of the sample, other than glycerol, are not large enough to interfere with the results.

PROCEDURE:

Weigh 0.5 ± 0.002 g. of the sample into a 400 ml. beaker. If the glycerol content is above 4.0%, use 0.25 ± 0.001 g. sample. Add 100 ml. distilled H_2O and heat if necessary to effect solution. Cool to room temperature and pipette 50 ml. of the periodic acid reagent into the solution of the sample and rotate gently to mix thoroughly. Cover the beaker with a watch glass and allow to stand 30 minutes. Prepare two blanks using 100 ml. of distilled H_2O in place of the sample. Proceed as directed in the extraction iodimetric titration method beginning with "Add 20 ml. KI soln." Calculate free glycerol to the nearest 0.1%.

Summary

The determination of free glycerol in soap has been improved and shortened.

1. When it is known that there are no substances which interfere with periodic acid reaction, the direct-iodimetric method is applicable. However, if the glycerol content is below 1%, the accuracy and precision are only fair.

2. The extraction-iodimetric method is applicable when the sample contains no periodic acid reducing substance other than glycerol or when such substances are soluble in chloroform.

3. The extraction-acidimetric method is preferable when the sample contains periodic acid reducing substances other than glycerol and which are soluble in the aqueous acid solution along with the glycerol.

REFERENCES

1. Allen, Carbonnier, and Coleman Anal. Ed. Ind. & Chem. Eng. *12*, 384 (1940).
2. Am. Oil Chemists' Soc. Official and Tentative Methods Da 23-42.
3. Am. Oil Chemists' Soc. Official and Tentative Methods Ea 6-46.
4. Bradford, Pohle, Gunther, and Mehlenbacher, Oil & Soap, *19*, 189 (1942).
5. Hoepe and Treadwell Helv. Chim. Acta, *25*, 353 (1942).
6. Silverman, J. Am. Oil Chemists' Soc., *24*, 410 (1947).

☆ ☆ ☆ ABSTRACTS ☆ ☆ ☆

Oils and Fats

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COMMERCIAL EXTRACTION OF SOYBEAN OIL USING NON-INFLAMMABLE SOLVENTS. E. G. Hollowell. *Iowa State Coll. J. Sci. 23*, 41-3(1948). A system for extracting oil from flakes moved countercurrent to trichloroethylene was put into successful operation in a commercial plant. Soybeans (moisture content up to 14%) were cracked, rolled into flakes 0.01 in. thick, heated to 140-150°, and with a 20-min. extraction time, reduced to 0.8% oil content. The oil was far above commercial requirements. About 0.05% of the beans were fines. Some corrosion occurred where solvent and water condensed. The solvent loss was 8-10 lb. per ton of beans processed. Other materials were tried. Milk-weed seeds were reduced from 23 to 5% oil in 15 minutes; cottonseed from 35 to 2% in 30 minutes; oatmeal from 6.5 to 1%; corn germs from 50 to 3%. The cottonseed oil was not good. (*Chem. Abs. 43*, 1581.)

HYDROGENATED WHALE OIL. ITS INDUSTRIAL EMPLOYMENT. P. Merat. *Oleagineux 4*, 203-12(1949).

RECENT DEVELOPMENTS IN CONTINUOUS FAT-SPLITTING. J. Seaman. *Soap, Perfumery & Cosmetics 22*, 384-5, 395(1949).

CHEMISTRY OF THE OXIDATION OF OLEFINIC FATS. K. Täufel and H. Rothe. *Angew. Chem. 61*, 84-9 (1949). A review from 52 references.

DEODORIZATION OF SHARK-LIVER OIL. P. K. Mathew, P. V. Nair, T. A. Ramakrishnan, and H. Sreemulanathan. *Nature 162*, 494(1948). Shark-liver oil can be deodorized by steam treatment, agitation with fermenting milk or toddy, or by catalytic hydrogenation with Ni catalyst. The first of these methods gives only temporary deodorization for several days, while treatment by the second gives an oil that remains bland for several months, with little change in physical constants or vitamin A potency. (*Chem. Abs. 43*, 1531.)

DETERMINATION OF SAPONIFICATION NUMBER. D. T. Englis and J. E. Reinschreiber (Univ. Illinois, Urbana). *Anal. Chem. 21*, 602-5 (1949). The reaction of KOH with HCl in solutions of varied proportions of ethanol and water, and in the presence and absence of soap, has been followed potentiometrically with special reference to its significance to the determination of the saponification number of oils and fats. In the usual saponification procedure the final ethanol content of the solution may be as low as 35%, yet the hydrolysis of the soap does not interfere seriously with the end-point detection at the proper stage of the reaction. The change in the pK value for phenolphthalein with change in solvent composition does not detract from the use of this indicator for the determination. The directions in the official method are properly prescribed. A series of analyses showing the effect of absorption of CO_2 under ordinary operating conditions was performed and results are reported.

SPOILAGE OF FATS AND OILS. II. E. Iselin. *Mitt. Gebiete Lebensm. Hyg. 39*, 310-36(1948). The process of spoilage of veal, mutton, beef, and pork fat is discussed. The fats were exposed for 2 to 3 years to diffuse daylight and the progress of oxidation was