Notes on the Determination of Glycerol in Soap Rapid Cerate Procedure

LOUIS SILVERMAN
5559 Hobart Street, Pittsburgh 17, Pa.

SOAP, manufactured by saponification of glycerides, will retain small amounts of glycerol. Glycerol analysis is made on kettle soap during the washing and settling operations and on the finished products. Certain soap specifications permit a maximum of 2% of glycerol. This paper applies the perchlorato-cerate procedure (5) to glycerol, in soap, and the speed and ease of operation invites its use. The soap is prepared for analysis by removing the fatty acids, proteins, and chlorides in the usual manner. An aliquot of the resulting solution is transferred to a dilute perchloric acid solution, an excess of cerate added, the reaction mix heated for 12 minutes and the excess of cerate titrated with oxalate solution.

G. F. Smith (5) pointed out the general uses of the perchlorato-cerate reactions, and in particular, the determination of glycerol in pure glycerol, glycerides, and soap lyes, but overlooked its advantages in soap making. Smith showed that the older dichromic acid procedure (1) requires two hours of boiling, as compared to a 12-minute reaction at 50°C.

Another procedure which might be used is the Malaprade (3) (6) reaction in which periodate converts glycerol into formic acid. The excess periodate is back titrated with arsenite and iodine solutions. A newer method which has possibilities is oxidation of the glycerol with periodate in neutral solution and alkalimetric titration of the formic acid product (2).

In the perchlorato-cerate procedure the reaction proceeds as follows:

$$\mathrm{CH_2OH\cdot CHOH\cdot CH_2OH + 8H_2Ce(ClO_4)_6 + 3H_2O \rightarrow}$$
$$\mathrm{3HCOOH + 8Ce(ClO_4)_3 + 24HClO_4}$$

It is evident from the equation that it is a perchlorato-cerate, and not a perchloric acid, reaction. An aqueous solution of perchloric acid is the medium and this is chosen because cerate has an oxidation potential of 1.71 volts in 4N perchloric acid. In comparison, the potential of a dichromate solution is 1.3 volts.

The equation also shows formic acid as a reaction product. Since cerate will oxidize formic acid to carbonic acid at higher temperatures and extended reaction times, the temperature is limited to 50°C. and the time to 15 minutes.

In addition, acetic acid is resistant to oxidation within the time-temperature conditions specified, and for this reason the acetates of lead and silver may be used; the lead and silver serve to remove proteins, chlorides, short chain organic acids, and long chain hydroxy-acids. Hydroxy-acids contain alcohol groups, and are subject to cerate oxidation.

After the cerate oxidation has been completed, the beaker is removed from the heat and an equal volume of water added. This reduces the acid concentration of the solution from 4N to 2N, and the beaker may be set aside for any convenient time to perform the back titration. The back titration is merely the addition of standard oxalate solution to the test solution (2N) in the presence of the indicator. The reaction is:

$$\mathrm{COOH\cdot COOH + 2H_2Ce(ClO_4)_6 = 2Ce(ClO_4)_3 + 6HClO_4 + 2CO_2}$$

The titration is made at room temperature. The indicator, nitro-ferroin, changes from blue, to colorless about 0.1 ml. before the end point, to pink. The color change is sharp.

Many interfering substances may be present in the soap. For example, ketones, higher alcohols, sugars, which were present in the fat or are added for technical reasons. Most of these are reacted upon by the active reagents of alternative procedures, but a difference will lie in the fact that the oxidation equations are not the same. This evidently occurs in the dichromate procedure, and check results will not be obtained when compared with cerate titrations. Since this paper is written to introduce the rapid cerate method for the control of glycerol content in soap making, analytical provisions for the presence of the adulterants, starch and sugar, are not made.

Precautions

This procedure is not a perchloric acid method, but one involving a characteristic oxidation potential of perchlorato-cerate in 4N perchloric acid. Therefore, the precautions concerning the addition of nitric acid (4) do not apply. If, however, the beaker be inadvertently *boiled*, any formic acid (perhaps 5 mg.) left after the boiling will be oxidized to carbon dioxide.

Reagents

Ultimate Standard. Dry Sodium Oxalate, Bureau of Standards. Weigh 13.412 grams and dilute to one liter with a 1:9 solution of 72% perchloric acid. This standard is 0.2N and one ml. is equivalent to 0.0023 gms. of glycerol in the perchlorato-cerate reaction. This solution will maintain its strength for six months. A working standard of c.p. sodium oxalate may be used for economy.

Ammonium perchlorato-cerate. This solution may be purchased from G. F. Smith Chemical Company, Columbus, Ohio, as 0.5N reagent in 6N perchloric acid. It may also be prepared in the laboratory (5). Standardize this reagent by pipetting 20 ml. into a solution of 75 ml. of water and 25 ml. of perchloric acid, adding two drops of nitro-ferroin indicator and titrating with sodium oxalate standard solution. Twenty ml. of this reagent are adequate for 75 mg. of glycerol. Excess cerate must always be present to insure complete oxidation of glycerol. The titer should be checked weekly.

Nitro-ferroin, ferrous sulfate complex with nitro-o-phenanthroline. The prepared indicator may be purchased.

Perchloric acid. Seventy-two per cent reagent grade.

Basic lead acetate. Ten per cent lead acetate solution which has been boiled with lead oxide.

TABLE I.
Determination of Glycerol in Soap.

No.	Glycerol by cerate %	Glycerol by dichromic acid %	Unsaponified and Unsaponifiable %	Alcohol Insoluble %	NaCl %	Titer of Acids °C.	Iodine No.	Color of Acids (F.A.C.)
1	2.1	2.0 2.2	1.05	.57	......	41.2	54.7	11b
2	2.5 2.6	2.2	.58	.47	.51	42.0	49.6	7
3	2.3	2.1	.71	.54	.85	39.7	60.5	21
4	3.87	3.97	1.07	.81	1.18	39.4	56.9	27
5	1.51 1.52	....	.77	.81	.68	42.0	52.1	11
6	2.01 2.03	....	.91	.31	.34	38.2	56.2	21
7	2.5 2.5	....	.41	.28	.48	42.2	51.3	17
8	4.85* 3.25* 2.21*	....	......	......	......	......	......	......

* Successive settling and washing tests on kettle soap.

Silver acetate or silver perchlorate. Laboratory reagents.

Proposed Procedure

Sample size. There are no rigid limits, but a convenient maximum is 0.050 g. glycerol, and a desirable amount is 0.010 to 0.030 g. of glycerol.

Soap sample. About 20 g. of sample (dry basis) are weighed, but an aliquot of 10% of the sample is used for the analysis.

Procedure. Weigh the sample (nearest 0.01 g.) and transfer to a 600-ml. beaker. Add about 300 ml. of hot distilled water and stir until the soap is in solution. Add one drop of methyl orange (do not use an indicator which has been dissolved in an alcohol) and carefully add (1:4) sulfuric acid until the solution is colored red. Add one ml. in excess. Maintain at 80°C. until the fatty acids gather at the surface and the solution clears. Cool the solution in a cold water bath until the fatty acids solidify. Filter the cold aqueous solution through a 15-cm. No. 40 Whatman paper into a 500-ml. volumetric flask. Wash the beaker, the acid cake, and the filter paper with cold water. Discard the paper and the acids.

To the volumetric flask add 10% basic lead acetate solution, in one-ml. portions until no further precipitation of proteins occurs. Add also about one ml. of 10% silver acetate or silver perchlorate solution to precipitate chlorides. Dilute the solution to the mark, mix well, and let settle until clear. Pipette 50 ml. (one-tenth of the weight of soap samples) into a 400-ml. beaker, and add 25 ml. of water and 25 ml. of 72% perchloric acid. This solution is approximately 4N in perchloric acid. Carefully pipette 20 ml. of 0.5N perchlorato-cerate into the solution, heat the solution to 50°C., and maintain at this temperature for 12 to 13 minutes, stirring occasionally. Each beaker should be provided with a thermometer. At the end of the reaction period, remove the beaker from the heat, add 100 ml. of water and let stand for five or more minutes to a convenient time for titration.

To titrate the excess cerate add two drops of the nitroferroin indicator and titrate slowly with standard 0.2N oxalate solution. The blue indicator becomes colorless about 0.1 ml. short of completion, then pink at the end point.

Calculation:

$$\%\,\text{Glycerol} = \frac{[(\text{ml. cerate} \times \text{N}) - (\text{ml. oxalate} \times \text{N})] \times 0.0023\ \text{gm.}}{\text{Weight of anhydrous sample, gm.}}$$

Results

In Table I are listed results obtained for routine analyses. When it was found that the cerate method gave results comparable to those of the dichromic acid method in much less time, the latter procedure was discontinued. Inaccuracies arising from small amounts of interfering substances are not considered, in the table. No. 8 lists three separate runs, showing decrease in glycerol content of a single batch of soap during settling and washing operations.

REFERENCES

1. American Society for Testing Materials, D460-44, p. 962 (1944).
2. Bradford, P., Pohle, W. D., Gunther, J. K., and Mehlenbacher, V. C., Oil and Soap, *19*, 189 (1942).
3. Malaprade, Bull. soc. chim., *43*, 683 (1928).
4. Silverman, Louis, J. American Oil Chemists' Society, *24*, 13 (1947).
5. Smith, G. F., "Cerate Oxidimetry," G. Frederick Smith Chemical Company, Columbus, Ohio (1942). A free publication.
6. Smith, G. F., and Duke, F. R., Ind. Eng. Chem., Anal. Ed., *15*, 120 (1943).