Determination of Free Alkali in Soaps

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THIS relatively simple determination is fraught with difficulty when only small amounts of free alkali are present as is usually the case in modern soaps.

The accepted A.S.T.M. standards for free alkali are not more than 0.1% as sodium hydroxide for toilet soaps and not more than 0.2% as sodium hydroxide for chip and powdered soaps. On a 5 gram sample these maximum percentages would require only 1.25 ml. and 2.50 ml. of tenth normal acid.

The method of determination which is recommended by the A.O.C.S. is to dissolve 2 to 10 grams of the soap in 200 ml. of freshly boiled ethyl alcohol, filter through a filter paper neutral to phenolphthalein or through a Gooch crucible with suction, protecting the solution from carbon dioxide and other acid fumes during the operation by covering with a watch glass. The paper or Gooch is washed with hot neutral alcohol until free from soap and the filtrate and washings heated to incipient boiling and titrated with standard acid after the addition of 0.5 ml. of a 1 per cent solution of phenolphthalein.

Considerable experience has shown that much depends on the neutrality to phenolphthalein of the filter paper and on how well the whole is protected from carbon dioxide and other acid fumes.

The first requirement may be met by previously washing the filter paper with alcohol which has a faint pink coloration after being titrated to just on the alkaline side using phenolphthalein as indicator. As filter paper apparently adsorbs alkali to an extent that is very considerable when compared to the small amounts present in good soaps, it will be necessary to wash the filter paper with sufficient slightly alkaline alcohol until the filtrate is the same tint of pink as the wash alcohol. A final washing with neutral alcohol is then needed. Alternatively the filter paper may be washed with definitely alkaline alcohol and finally with neutral alcohol until colorless.

In either case this procedure is tedious and somewhat indefinite.

The second requirement—to protect the whole from carbon dioxide and other acid fumes—is not easy to accomplish and at best is not 100 per cent effective.

A simple technic which obviates both of these difficulties consists in dissolving the soap in hot neutral alcohol and at once centrifuging until the alcohol solution is clear, which is readily accomplished. For most purposes the alcohol solution may then be decanted without disturbing the precipitate, heated to conform with the standard method and titrated. In general the titration is so small that it is unnecessary to wash the precipitate with neutral alcohol and centrifuge. However, for extreme accuracy this may be done.

Report of the Glycerin Analysis Committee American Oil Chemists' Society 1939-40

OUR last report (1) indicated that the Bertram-Rutgers method (2) of analysis for glycerin appeared to be more of "a principle than a method of analysis." The interest of our committee in this rather novel procedure has been sufficient to motivate further attempts to improve the method and its precision. After studying the results obtained by our committee, Dr. Bertram has made several valuable suggestions. Careful experiments have been conducted by a number of our committee (in particular by Dr. A. F. Nelson of the Lever Brothers Company at Cambridge) which have enabled the formulation of a workable procedure. This method has been applied to the "A.O.C.S. Standard Crude Glycerin" and to other selected samples.

While results by the revised method show a great improvement over those obtained by the original procedure, it is obvious that the precision is still considerably short of that demanded by commercial transactions or cost accounting. Your committee is unanimous in this opinion and accordingly the procedure is *not* recommended for adoption as a tentative method of the Society. The improved procedure, however, does afford a rapid and easy means of determining the approximate glycerin content of materials which are grossly contaminated with substances which seriously interfere with the standard acetin and bichromate procedures. Among these may be mentioned sugars; trimethylene and diethylene glycol; the glycol ethers, such as cellosolve, carbitol, etc.; hydroxy-acids, such as tartaric and citric; and oxalic acid. None of these substances shows as much as one per cent apparent glycerol. Ethylene glycol, propylene glycol and the hexahydric alcohols, such as mannitol and sorbitol, show apparent glycerol from two to five per cent. Polyglycerol ethers and the alkanol-amines are interfering substances. Ammonia, present in amount not exceeding about one gram of NH_3, shows no interference. Above this rather sharply-defined "threshold" a soluble cuprammonium compound is readily formed.

One of our members obtained results which led him to conclude that the glycerol percentage is dependent upon the size of sample used for analysis. This conclusion could not be substantiated by other members of the committee.

The simplicity, ease and speed of the improved

(1) Oil & Soap *16*, 19-20 (1939).
(2) Rec. trav. chim. *57*, 681-87 (1938).

method and its comparative freedom from the interference of common impurities, commend its use as a tool in appraising the value of low grade process materials and certain complex mixtures which would ordinarily require a tedious purification before application of the usual methods of analysis. For these reasons your committee recommends publication of the revised and improved Bertram-Rutgers method in Oil & Soap. The chemist is cautioned against the use of this method in analyses involving commercial transactions.

Revised and Improved Bertram-Rutgers Method

From the aqueous, glycerin solution a quantity not exceeding 10 ml. and containing not more than 0.8 gram of pure glycerol, *is weighed* into a calibrated 100 ml. volumetric flask and sufficient distilled water is added to bring the volume to 10 ml. Now 10 ml. of an aqueous solution of NaOH (30 grams/100 ml.) is added, followed immediately by 60 ml. 95%, by volume ethyl alcohol. (Formulas 30 or 3A may be used.) After mixing, an alcoholic solution of $CuCl_2$ (10 grams $CuCl_2.2H_2O$/100 ml.) is added from a burette, a few drops at a time, with thorough shaking between additions, until a clearly visible, permanently undissolved precipitate of $Cu(OH)_2$ is formed. Then 0.5 ml. excess alcoholic $CuCl_2$ solution is added, the flask is filled to the mark with alcohol, the stopper is inserted and its contents are shaken vigorously for at least one minute. All of these operations are performed with the *solution at a temperature of 20°C.*, using a cooling bath if necessary, to maintain the volumetric flask and its contents at that temperature.

At least 60 ml. of the well mixed solution from the volumetric flask is centrifuged in a clean, dry, stoppered tube or bottle at about 1300 r.p.m. for about 10 minutes. A higher rate of speed or longer time should be employed if the supernatant liquid is not *perfectly clear.* The tube or bottle is then placed in the 20°C. bath for a sufficient time to permit its contents to reach that temperature and 50 ml. of the clear, decanted solution is transferred with a calibrated pipette to a 300 ml. Erlenmeyer flask.

To the Erlenmeyer flask are added first, 100 ml. distilled water, then from a burette, glacial acetic acid just to an acid reaction, plus 2 ml. in excess. The change from an alkaline to acid reaction may be judged by the change in color from deep blue to light green. The solution is cooled in ice water for a few minutes, 10 grams KI is added and the iodine liberated on agitation is titrated immediately with 0.1 normal thiosulfate solution, which has been carefully standardized in any approved manner. A more dilute thiosulfate solution may be used if desired. Starch indicator is added after most of the iodine is titrated and just before the end-point is reached 2 grams of NH_4SCN is added and agitated thoroughly. The titration, near the end, should proceed slowly and with vigorous agitation.

Along with the samples blank determinations are conducted in every way the same except for the presence of glycerol. If the value of the blank titration is found to be quite constant, as would be expected due to the extremely slight solubility of the $Cu(OH)_2$, blanks need not be included with every batch of samples.

$$\% \text{ Glycerol} = \frac{(T - B) \times N \times 18.41}{S}$$

In which T = Sample titration
B = Blank titration
N = Normality of thiosulfate
S = Weight of sample taken.

For very accurate work the volume of the precipitate in the volumetric flask may be taken into account by measuring the volume of the precipitate in the centrifuge tube and considering the true volume of the solid phase as 50% its apparent volume. Particular attention must be paid to thorough shaking before pouring the entire contents of flask into the centrifuge tube, in order to secure an even distribution of the precipitate in the solution. If correction for volume of precipitate is made, the factor 18.41 will become:

$$9.205 \times \frac{100.00 - 0.5\ V}{50}$$

In which V = Apparent volume of precipitate in ml.

Notes:

1. If correction for volume of precipitate is to be made, the *entire contents* of flask must be poured into the centrifuge tube so that the precipitate measured may represent all of the precipitate in the 100 ml. of solution. Report should state whether correction for volume of precipitate has been made.

2. In some cases, with certain samples, there may be present in the volumetric flask, before the alcoholic $CuCl_2$ solution is added, a slight precipitate which may obscure that due to formation of $Cu(OH)_2$. Since it is necessary to add an excess of the alcoholic $CuCl_2$ solution, so that after thorough shaking a small but definite precipitate of $Cu(OH)_2$ will remain undissolved, every effort must be made to secure this end. A knowledge of the approximate weight of pure glycerol present may be of help in these doubtful cases, since the amount of $CuCl_2$ solution required may be roughly calculated on the basis that 1 ml. alcoholic $CuCl_2$ solution = 0.054 gm. glycerol.

A.O.C.S. Standard Crude Glycerin

ACCEPTED ANALYSIS

% Total Apparent Glycerol (Acetin)	=	83.81
% Apparent Glycerol in Residue	=	0.48
% True Glycerol	=	83.33
% Organic Residue at 160° C.	=	1.52

COMMITTEE ANALYSES

J. E. DOHERTY:

83.98 — 84.59 — 84.65 — 84.19
84.41 — 84.62 — 84.89 — 85.05
Average = 84.55

Ppt. correction applied. Approx. 0.8 gm. glycerol taken.

B. S. VAN ZILE:

Wt.	%	Wt.	%
.0575	68.34	.4546	79.82
.1120	76.08	.5155	82.84
.2397	79.46	.8061	82.80
.2572	80.44	.9111	80.54

Average = 78.79

Ppt. correction applied.

J. T. R. ANDREWS:

Wt.	%				
0.800	83.8	84.0	84.0	84.0	84.3
0.500	84.6	84.6	84.9		
0.200	84.4	84.4	85.1		

Ppt. correction applied. Average = 84.4

M. L. SHEELEY:

Wt.	Min. centrifuged	%
.8091	10	84.2
.5285	10	87.6
.6356	10	87.0
.7110	15	83.6
.5630	15	83.9
.6348	15	83.7
.5960	15*	85.3
.6232	15*	85.3
.4224	10	83.9
.4224	10	85.4
.8448	10	84.6
.8448	10	85.0
1.2673	10	84.2
1.2673	10	84.4
1.6897	10	85.9

* Centrifuged 8 min., stopped 2 min., then centrifuged for 7 more min.
No correction for ppt. volume. Average = 84.9

H. C. BENNETT:

83.96 — 82.06 — 83.98 — 84.16
84.42 — 82.31 — 83.54
All samples = 0.9 gm. Average = 83.49
82.44 — 83.31 — 82.26 — 82.66
Volumetric solution aliquots = 0.9 gm.
Average = 82.67
Ppt. correction applied.

W. J. REESE:

Wt.	%	Wt.	%
.8809	86.50	.8647	85.04
.9284	86.45	.6178	84.85
.9037	85.89	.4862	85.15
.9013	87.22	.3468	87.61
.9007	82.56	.9069	88.60
		.9166	88.65

Average = 86.23
Ppt. correction applied.

A Typical Soap Lye Crude
% Glycerol = 85.0 (Acetin)

Wt.	Min. centrifuged	%
.7005	10	86.8
1.1414	10	86.5
.6112	10	86.5
.3502	10	87.5

No correction for ppt. volume. Average = 86.8

A.O.C.S. GLYCERIN ANALYSIS COMMITTEE—(1939-1940)

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Quality Changes in the Industrial Storage of Crude and Refined Cottonseed Oil

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INTRODUCTION

Fats and oils are known to deteriorate to a certain extent on age, depending upon the conditions of storage. Rancidity and other off quality developments on ageing various animal and vegetable oils and fats have been discussed rather widely in the past years, and such factors as light, heat, presence of moisture, auto-oxidation, contact with air, and contact with various metals, have been shown to be the primary causes of these quality changes.

Investigators have shown that crude vegetable oils have certain anti-oxidants naturally present which are largely removed in caustic refining. This finding has led to the conclusion by some persons that when vegetable oils must necessarily be stored, it is more advisable to store them in the crude state rather than as refined, or further processed. On the other hand, others much prefer to store oil as refined rather than as crude, because of previous unsatisfactory experience in storing crude. This latter opinion seems to be the most prevalent.

The present work is divided into two parts: namely, the quality changes in crude and refined cottonseed oil on age, stored under normal atmospheric conditions in (1) small 4 lb. pails and (2) large industrial storage tanks. The various oils used in these tests represent normal receipts of crude cottonseed oil from Texas, Oklahoma, Louisiana, and Arkansas, during the 1939-40 season. Atmospheric and plant conditions of storage represent a normal North Texas Year from September to September.

It is not the purpose of this work to theorize or explain the quality changes shown, but merely to report these changes under the practical conditions of storage encountered, and to discuss the results as applied to manufacturing operations.

SMALL SAMPLE STORAGE PROCEDURE

Four-pound samples of freshly received crude, together with four-pound samples of the corresponding laboratory refined oil from the respective crudes, were stored in four-pound tin pails. The lids of these pails were punched with small holes for normal aeration, covered with inverted 100 lb. cans to exclude light and to minimize daily temperature changes, and stored on the roof of a building.

The crude oil stored represented "as is" samples from tank cars. The refined oil was refined from this crude by the official N.C.P.A. method, and stored after filter paper filtration.

Four sets of samples representing new crop crude were stored in this manner from September 1, to April 1, (7 months). Three other sets of samples representing end of season crude were stored similarly from February 1 to August 1 (6 months).

After these respective storage periods the crude oil was laboratory refined in the same manner in which the stored refined oil was produced. Then all refined oils were laboratory bleached using the official N.C.P.A. procedure, except using 2% of natural Texas fuller's earth. These bleached samples were used for the stability tests shown. Conventional or official laboratory procedure was used throughout.

SMALL SAMPLE STORAGE RESULTS

The following results are shown in the data of Table I regarding the relative merits of storing crude vs. refined cottonseed oil:

1.) The average F.F.A. on the stored crude rose .2% while the rise on the stored refined oil was almost negligible, except in one unexplainable case