are not conspicuous. On the other hand, the thiocyanogen-iodine numbers relationship suggests the presence of representatives of at least three types of unsaturation.

Separation of the unsaturated from the saturated acids was effected by the lead salt-alcohol method of Twitchell as modified by Baughman and Jamieson[4] and identification of the former by means of their bromo addition compounds and their separation by the use, in turn, of diethyl and petroleum ethers.[5] The identity of the components of this fraction was deduced from the following data: (1) linolenic acid from the corresponding, at —10°, ether-insoluble, hexabromo derivative (Br. 63.2 per cent, calculated 63.32 per cent; m.p. 179.3°, theoretical, 177°-181°); (2) linoleic acid from its (hot) petroleum ether-soluble tetrabromo derivative (Br 53.5 per cent, calculated 53.3 per cent; m.p. 113.7°, theoretical 114°); (3) oleic acid, in the residual fraction, through its soluble dibromo derivative (Br 35.85 per cent, calculated 36.18 per cent).

Confirmation of the foregoing identifications was subsequently obtained through the permanganate oxidation products of these acids which were removed from the resulting reaction mixture in the reverse order in which they are herein described. The isolation of linusic acid of melting point 203.5° theoretical 203°-205°) and carboxyl-hydroxyl ratio of 6:1 indicated the presence of a linolenic acid. Since repeated crystallizations did not yield any fraction of lower melting point than that originally found, it was concluded that no isomers of linolenic acid are present. A relatively larger quantity of sativic acid (m.p. 157.6°, COOH/OH = 4), indicative of the presence of a linoleic acid was obtained. In this case, too, replicated crystallizations did not produce an acid of different melting point. It was concluded, therefore, that linoleic acid does not occur in this oil in its two isomeric forms. The presence of oleic acid was confirmed in the formation of dihydroxystearic acid (m.p. 131.3°, theoretical 131°, COOH/OH = 2).

Using iodine and thiocyanogen numbers of the unsaturated acid fraction as a basis of calculation, it appears that this oil contains approximately 1.4 per cent oleic acid, 67.5 per cent linoleic acid and 20.8 per cent linolenic acid. These values are of the general order of magnitude of those which Jacobson and Holmes[2] found by the separation of the permanganate oxidation products of these acids. They are, in the order named, 3.30 per cent, 73.20 per cent and 23.50 per cent.

A report on the nature of the acids comprising the saturated group will be made at some future time after studies now in progress thereon will have been completed.

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ELECTROMETRIC TITRATION OF DICHROMATE GLYCEROL SAMPLES*

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Abstract

For routine control, glycerol is usually determined by oxidation of the sample with potassium dichromate in an excess of sulfuric acid with back titration of the excess dichromate solution after oxidation with ferrous sulfate solution. The usual procedure is to use potassium ferricyanide as an external indicator on a spot plate. The use of an electrometric titration apparatus with platinum and tungsten electrodes as an internal indicator is described. The apparatus is very easily constructed and gives rapid and accurate results with a sharp endpoint under all kinds of lighting conditions by any analyst who can read a buret—even by one who is color blind.

FOR control purposes in soap and glycerol manufacture glycerol is usually determined through the oxidation of a prepared sample by an excess of potassium dichromate in the presence of an excess of sulfuric acid. The most common procedure is to titrate the excess of the dichromate solution, after oxidation is completed, with ferrous sulfate solution using potassium ferricyanide as an external indicator on a spot plate. Randa (5) has recently described a method in which the dichromate solution after oxidation is made to volume and used to titrate standard ferrous sulfate solution, using diphenylamine as internal indicator.

For a number of years in the Procter & Gamble laboratories, the excess dichromate after oxidation has been titrated in the oxidation flask without any transfer or further treatment other than cooling. Ferrous sulfate is used for the titration with an electrometric setup as internal indicator. As far as the authors have been able to learn, the electrometric method has not been used in other laboratories for the titration of the excess dichromate

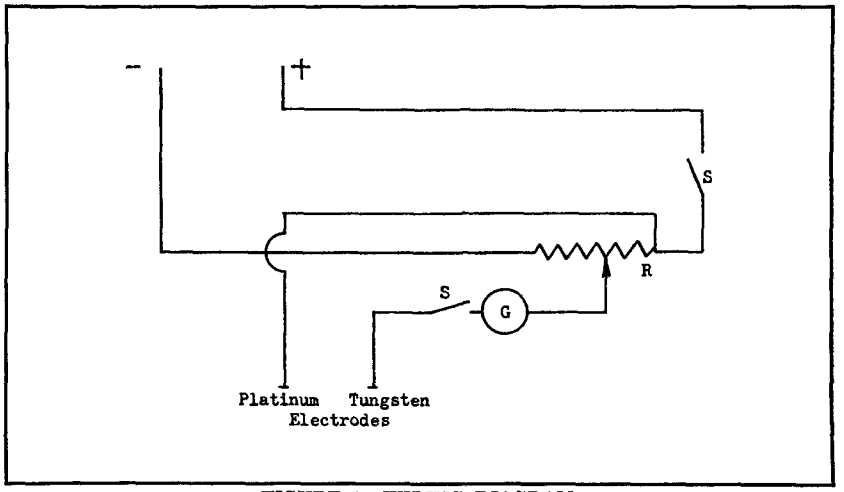

FIGURE 1. WIRING DIAGRAM.
S. Double-pole, single-throw switch. *R.* Potentiometer.
G. Galvanometer. Batteries (4 dry cells in series).

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in glycerol determinations, although such a setup has been in use for dichromate-ferrous sulfate titration in other laboratories, such as some of those of the steel industry (2).

In 1922 electrometric titration of practically all routine glycerol samples replaced the use of the spot plate in one of the company laboratries. In the first setup a platinum electrode and calomel half-cell were used with *N* potassium chloride. The ferricyanide spot plate was used only for checkup. In 1935 a bimetallic electrode setup was placed in use in one of the laboratories and the calomel cell was eliminated. Platinum and nickel electrodes (1) were used. The nickel electrode was changed monthly, and a few months later was replaced by a tungsten electrode (6, 7).

The platinum-tungsten setup is now in use in practically all of the company laboratories and an electrometric apparatus in all. Figures 1 and 2 show the photograph and the wiring diagram of the preferred bimetallic electrode apparatus.

The cabinet is of oak with a black Formica base, and is closed at the back with double wooden doors. The lines for ferrous sulfate solution, distilled water, and motor are carried through the back of the cabinet. All exposed metal clips and parts are chromium plated. The motor and the ring supporting the flask are carried on a rod in the interior of the cabinet. At the upper left (Figure 2) is the Weston galvanometer, model 699, sensitivity 2 microamperes per scale division. Below the galvanometer is the adjusting knob of the potentiometer, Yaxley Manufacturing Company, 1000 ohms. The knob below the potentiometer controls a three-armed distilled water spray for washing the eleetrodes and stirrer. The support for the flask is movable, so that the flask may be raised or lowered from position. In some installations the support is attached to the water valves, so that the spray operates when the ring is pushed to the left. The toggle switches are shown at the lower left: a single-pole single-throw at the left for the motor, and a double-pole single throw for the galvanometer circuit. The funnel, stainless steel or Monel, is connected to the drain. The electrodes are 20-gage platinum or tungsten wire sealed into glass tubing. The exposed electrode wires are approximately 5 mm. The tubing of the electrode is mercury-filled. The stirrer is made of a glass rod and fastened in a chuck on the motor shaft. The motor is model 3 (Eastern Engineering Corporation) with rheostat for regulating the speed.

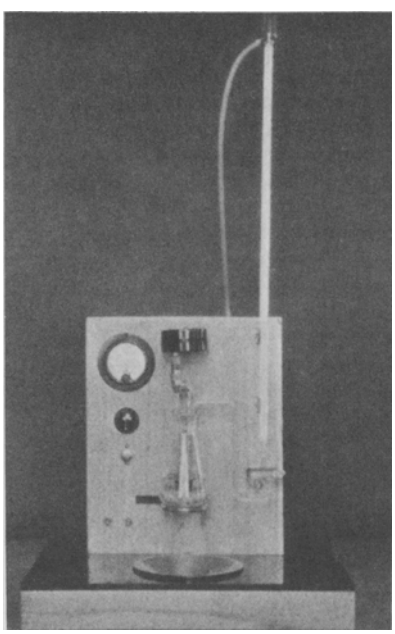

FIGURE 2. PHOTOGRAPH OF APPARATUS

Procedure

While the general procedure of the dichromate oxidation of glycerol is well known, an outline of the preparation of the solutions and details of oxidation and titration may be desirable.

Standard Dichromate Solution.—The dichromate solution is pipetted into the oxidation flasks with a 25-ml. Lowy automatic pipet (or for special samples a 10-ml. Lowy automatic pipet holding exactly two-fifths as much as the 25-ml. pipet). The strength of the dichromate solution is made so that the 25-ml. pipet will deliver 1.864 (4) grams of $K_2Cr_2O_7$, which is equivalent to 0.25 gram of glycerol. The weight of potassium dichromate in grams required for 1 liter at 25° C. is determined by multiplying 74.56 by the ratio of 25 to the volume delivered by the pipet at 25° C. The dichromate is dissolved in distilled water, 150 ml. of concentrated sulfuric acid are added, and the solution is made to 1 liter at 25° C. The strength of the solution is checked against standard dry powdered dichromate by weighing 1.864 grams of the latter, and dissolving in 75 ml. of distilled water and 15 ml. of concentrated sulfuric acid. The ferrous sulfate titrations of a pipetful of the dichromate solution and of the standard dichromate must check within 0.05 ml. of ferrous sulfate solution or the dichromate solution must be adjusted.

Ferrous Sulfate Solution.—Five kilograms of reagent grade ferrous ammonium sulfate are dissolved in about 10 liters of distilled water, 1,800 ml. of concentrated sulfuric acid are added, and the volume when cooled to room temperature is made up to 16 to 17 liters.

Details of Analysis of a Sample

The details described in the following paragraphs apply to a sample of C. P. glycerol requiring no preliminary purification. The procedures of oxidation and titration are identical for other samples.

Make a 2 ± 0.001-gram sample to volume in a 500-ml. flask. Pipet a 50-ml. aliquot into a 250-ml. wide-mouthed Erlenmeyer flask containing a 25-ml. pipetful (at 25° ± 0.5° C.) of the standard dichromate solution. Add 15 ± 1 ml. of concentrated sulfuric acid. Cover the flask at once with a watch glass.

The samples are usually handled in batches. With each batch prepare at least two blanks by using the same amounts of dichromate solution, sulfuric acid, and water as for the samples. Titrate one blank before and the second after the samples. Use the average of the blank titrations in calculating the glycerol content. Immerse the flasks containing the samples and blanks in a steam bath and hold them at a temperature of 90° to 100° C. for two hours. At the end of two hours cool the flasks and contents by immersion in cold water until a temperature of 25° to 40° C. is reached.

Remove the watch glass from a flask and place the flask in position on the apparatus with both electrodes and stirrer in the solution and the tip of the buret extending well into the neck of the flask. Close the circuits and bring the galvanometer reading to zero by adjustment of the rheostat. Begin titration slowly with ferrous sulfate solution and observe the galvanometer needle closely. When within 1 to 2 ml. of the end point the needle is deflected sharply to one side, but immediately returns to the zero position. Add the ferrous solution more slowly. When almost at the end point, a short time should be allowed after each addition to allow the needle to move back. At the end point the needle swings over to the side of the scale and remains there. Open the circuits, read the buret, and remove the flask for the next titration. Press the button and flush the electrodes and stirrer as the flask is being removed. After the final titration wash off the elec-

trodes and stirrer and allow the electrodes to stand in distilled water. The glycerol content of the sample is calculated from the difference between blank and sample titrations.

The tungsten electrode should be cleaned about every 6 weeks by dipping for a few seconds into fused sodium nitrite held just slightly above its fusion temperature.

Care must be taken to use sufficient sulfuric acid to give an equivalent of, at least, 1.230 specific gravity (3). The excess of dichromate after heating must be such that a back-titration of at least 9 ml. of ferrous sulfate solution is obtained. For some samples of low glycerol content, a 100-ml. aliquot, 30 ml. of sulfuric acid, and 10 ml. of dichromate are used.

Summary

The method is very rapid and accurate with a sharp, positive end point, and can readily be operated under varying conditions of lighting by any analyst who can read a buret —even by one who is color-blind.

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Stability Of Fats Used For Deep Fat Frying

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Abstract

This paper presents the results of some commercial doughnut frying tests using types of shortening available to the baker. The broad conclusion is that, from the stability viewpoint, the difference in shortening when used for deep fat frying is exaggerated.

AN inspection of the convention programs of the A.O.C.S. for the past few years reveals the fact that very few papers have been presented to this society upon the uses of edible fats and oils and how they react when used. This is due, no doubt, to the fact that the majority of chemists in the fat and oil industry are concerned primarily with the prepartaion and manufacture and not with the consumption of the products. For this reason some information regarding the way the finished products perform should be of interest.

Up to the present time, chemists have been striving to prepare edible fats and oils having various supposedly desirable characteristics such as low free fatty acid, low color reading, a high smoke point, high stability as considered from the standpoint of resistance to rancidity, etc.

In considering these factors from the standpoint of the consumer, specifically the baker, it is questionable whether or not he derives as much benefit as is supposed by obtaining fats and oils having these characteristics, and also, whether or not he actually needs them.

The demand for shortenings which are practically neutral, of a chalky white appearance and high smoke point, appears to have been brought about by competition of the advertising departments in the various companies, many of whom make absurd claims for their products with respect to the appearance, purity, stability, and smoke point. Those familiar with the bakery trade journals have seen many shortening advertisements with such indefinite wording as: it's whiter; it's purer; higher smoke point; will not break down; withstands high heat, etc. As chemists, you know many such statements to be preposterous, but a baker, without technical training, does not know what to believe, and is thus led to demand shortenings which may or may not be to his best advantage. This reference to advertising is not to be construed as a criticism of the advertising, but to illustrate the fact that the consumer is led to believe that he is getting fats which will remain stable under working conditions.

One of the most severe uses which is made of edible fats and oils is deep fat frying in the preparation of doughnuts, nuts, potato chips, and in the new type of frying equipment used by restaurants for the deep fat frying of chicken, oysters, French fried potatoes, and clams. In all of these operations the fat is held at a temperature of 350°-400° F., sometimes for a long period of time.

To obtain accurate information regarding the behavior and breakdown of fats subjected to high temperatures, a doughnut frying test was planned and conducted on a commercial scale and of such scope that there could be no doubt concerning the accuracy of the results.

Arrangements were made to run the test in a commercial shop using approximately 600 pounds of shortening per day for frying alone. Two automatic doughnut machines, made by the same manufacturer, were used. Five different shortenings were tested. Three were all-hydrogenated shortenings, the other two were blended or compound shortenings containing about 80 per cent refined, bleached and deordized cottonseed oil. The analyses of samples representing the shortening were as given on Chart No. 1.

SAMPLE	FREE FATTY ACIDS (AS OLEIC)	COLOR READING (LOVIBOND) YELLOW	RED	SMOKE POINT (A.S.T.M. OPEN CUP) °F
FAT #1 BLENDED	0.05	17	1.3	420
FAT # ALL HYDROGENATED	0.02	11	1.2	430
" 3 " "	0.03	18	1.3	430
" 4 " "	0.03	15	1.1	430
" 5 BLENDED	0.05	22	3.5	420

CHART NO. I

Ten drums, about 3,800 or 4,000 pounds, of each shortening were used in the test. In order to eliminate any partiality on the part of the operators, all brands, marks, and names were removed from the drums, with the exception of the