The Determination of Free Fatty Acids in the Oil Extracted From Cottonseed

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The determination of the free fatty acids in the oil extracted from cottonseed meats offers certain difficulties even though about 40 grams of the sample are taken and the percentages are usually small. In general, the higher the free fatty acid content, the greater will be the differences among chemists. For example, No. 2 of the 1942-43 series sent out by the Referee Board of the American Oil Chemists' Society contained 3.4% free fatty acid. The results of 53% of all collaborators and 56% of the licensed chemists group were outside the tolerance limit, while on sample No. 9 with only 0.5% free fatty acid, slightly less than 6% of the collaborators were outside the allowed tolerance.

The average percent of free fatty acid of the entire ten-sample series was 2.09%, and the average percentage of collaborators outside the tolerance limit was 22%.

With such a very low free fatty acid content, it would appear that results should be much closer. The titration is extremely simple. The differences seem to occur mainly in carrying out details of procedure in making the extraction. Rapid percolation of the petroleum ether affords less extraction of oil than slow percolation. In this connection, the method of the American Oil Chemists' Society, that of the National Cottonseed Products Association, and that of the Department of Agriculture, all specify the use of a filter bed consisting of a layer of asbestos over a perforated disc (as used in a Knorr extraction tube) using a Butt tube. The author's experience is that this affords quicker percolation, and therefore is not as satisfactory as when cotton is properly inserted in the stem of the tube and spread in a thin layer over the bottom surface of the tube. The recovered oil must be clear in all cases, since any residual colloidal matter combines with caustic soda in the titration.

The presence of a considerable number of hulls in the cottonseed meats has a tendency to cause variation in the extraction, since they may result in the formation of fissures through which some petroleum ether may pass without properly extracting the oil. The excess hulls may be easily removed by putting the meats in a circular dish or similar container and giving a rotary whirl, after which the hulls will mat together and rise to the surface.

The addition of 10 ml. of neutral petroleum ether to the recovered oil before the addition of the neutralized alcohol greatly facilitates the titration which may then be made simply while whirling the flask. When petroleum ether is not used a stopper has to be inserted and the flask shaken rather vigorously at intervals before the end point is reached. Whether the flask is shaken vigorously or not has an effect on the result due to the presence of carbon dioxide, for phenolphthalein is very sensitive to carbon dioxide. Obviously, violent shaking increases the contact between the indicator and carbon dioxide. The author's experience has been that isopropyl alcohol furnishes a medium that is far less sensitive to carbon dioxide than Formula No. 30 denatured alcohol. Further, the end-point appears more definite when isopropyl alcohol is used.

Interest in this subject has led the author to try a beaker extraction method on a number of current samples by the following procedure:

Place approximately 40 grams of ground cottonseed meats prepared according to the regular AOCS method in a 250 ml. beaker and add 110 ml. of petroleum ether; stir with a stirring rod and cover the beaker. Let stand for 30 minutes, stirring at five minute intervals. Filter, using S&S No. 597 Filter Paper (18.5 cm. size) and pouring some of the meats from the beaker on the paper to help form a filter bed. Wash three times with a small amount of petroleum ether, place on an evaporating bath and then follow the regular procedure for free fatty acid determination.

This method extracts approximately the same amount of oil as the regular method, amounting to about 8 grams. The results obtained are identical in 75% of the cases with those obtained by the official method of extraction, even though the free fatty acid is very high in some cases.

Beaker Method Pct.	Official Method Pct.
2.8	2.8
2.4	2.6
1.3	1.3
1.5	1.5
2.6	2.6
0.9	0.9
6.4 (Report 6.5)	6.2 (Report 6.0)
8.0	8.0

It is seen that results are in extremely close harmony, which in the light of the experiments eliminates any difficulty in the percolation method of extraction.

It should be mentioned that in the case of the last two samples, which had a pronounced dark reddish tinge, methyl blue instead of phenolphthalein was used as the indicator. Results would hardly have been so close on these dark oils by the use of the latter. Ten ml. of petroleum ether were used in each case just before adding the neutralized alcohol, and the alcohol was not added until just before titration to lessen the action of carbon dioxide. Titrating with accurately standardized N/10 alkali instead of N/4 would tend toward greater accuracy.

The author is interested in seeing all collaborators in the AOCS check seed series obtain closer results and believes that progress is being made in this direction. Through the visits of Mr. R. T. Doughtie, Jr., to commercial laboratories much constructive work has been accomplished. Mr. Doughtie's advice has

been helpful to the author and it therefore appears advisable that such visits be extended if possible to all collaborators, since the accepted averages of the Society are based on the collaborators as a whole.

It is recommended that the Society take some action in further standardizing a method embracing the points discussed above, as well as any others which may have a tendency to affect results.

Abstracts

Oils and Fats

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STEARIC ACID, RED OIL, AND GLYCERINE. A CHEM. AND MET. FLOW SHEET. *Chem. Met. Eng. 50,* No. 9, 132-5 (1943).

METHODS OF SPLITTING FATS AND OILS WITH REFERENCE TO THEIR EFFICIENCY. Kurt Lindner. *Fette u. Seifen 49,* 862-8 (1942). A review.

THE REACTION OF TETRANITROMETHANE WITH FAT ACIDS AND FATS. Hans Paul Kaufmann. *Ber. 75B,* 1201-14 (1942). Tetranitromethane (I) reacts with unsatd. fats and fat acids in $CHCl_3$ or CCl_4 soln. to yield a yellow to a dark red color depending on the amt. of unsatn. When read with a Pulfrich photometer the intensity of the color rose with the I no. of the test sample. I nos. detd. by this method checked within 5 of those detd. bromometrically. One per cent of I was a good elaidinization catalyst when tried on oleic acid, erucic acid, and olive oil. Elaidinization takes place on standing 1-2 days. On long standing linoleic and linolenic acids with 10% I yield a mass that is difficultly sol. in CCl_4 or $CHCl_3$. Marine liver and chaulmoogra oils polymerize to a gel under these conditions. A cod liver oil with 10% I increased in viscosity (20°) from 86-681 centipoise in 168 hrs. The use of I for oxidizing compds. to det. structure after analysis of the products was demonstrated with results on elaidic acid, erucic acid and stilbene. For the oxidation 1 part of the sample was reflux with about ⅔ part of I and ½ to ⅚ part of CCl_4 for several hrs. There are 21 references. This report also includes the work of collaborators Bao Wei King and Lan-Sun Huang. *(Chem. Abs.)*

COMPARISON OF THE IODOMETRIC AND ALKALIMETRIC ACID DETERMINATION FOR MARGARINE. H. Schmalfuss and U. Stadie. *Fette u. Seifen 49,* 779-80 (1942). The alkali method is simple and faster.

CHANGES IN THE OIL DURING GERMINATION OF LINSEEDS. Karl Schmalfuss. *Fette u. Seifen 49,* 773-4 (1942). Results of analyses on 0, 3d, 6th, and 9th days of germination at 20° were: fat based on original amt. present 100, 75.9, 51.8 and 28.7, fat I. no. 172, 172, 164.6 and 154.8, (SCN) no. 106.9, 110.9, 109.4, 100.3, solid satd. acids 8.9, 9.4, 10.3, and 10.8%, oleic acid 106.4, 85.4, 63.8 and 29.4%, linoleic acid 42.9, 33.2, 27.1, 36.3, linolenic acid 32.3, 37.4, 36.6 and 26.6. The Ivanow postulations that the highly unsatd. acids are first attacked was distinctly evident.

VITAMIN A AND LIVER FAT. H. W. Sachs. *Arch. Path. Anal.* (Virchows) *309,* 712-25 (1942). The vitamin A (1) content of the liver was detd. by its fluorescence in ultraviolet light. It is increased whenever its fat content is normally increased whereas in fatty degenerative processes I is diminished. Fatty infiltration of the reticulo-endothelial cells is a normal process. Examn. with ultraviolet light reveals that the central peribiliary fatty infilitrations consists of pigment lipide of lipofuscin. *(Chem. Abs.)*

DESPITE ITS USE IN EXPLOSIVES THERE ARE NEW USES OF GLYCERINE IN CONFECTIONERY. G. Leffingwell and M. A. Lesser. *Manufg. Confectioner 23,* No. 9, 15-7 (1943).

EDIBLE FATS AND OILS. TWO CHEMICAL CHARACTERISTICS. G. E. Vail and R. Hilton. *J. Home Econ. 35,* 43-46 (1943). The smoking temp. in this study ranged from a high of 245° C. to a low of 190° C. for the 17 vegetable fats and oils from 234° C. to 174° C. for the 8 animal fats. The 2 combination vegetable and animal fats smoked at 209° C. and 170° C. There was an av. drop of 2.2° C. in the decompn. points when the fats were heated in a 6-in. frying pan. The fuchsin bisulfite test for aldehydes resulted in still lower smoking pts. averaging 24.6° C. lower than those obtained when the visual method was used. The percentages of free fatty acids before and after heating showed a wide range. The percentage of free fatty acids, as oleic, in fats tended to be inversely proportional to the smoking point.

THE EFFECT OF CERTAIN DIETARY INGREDIENTS OF THE KEEPING QUALITY OF BODY FAT. R. H. Barnes, W. O. Lundberg, H. T. Hanson, and G. O. Burr. *J. Biol. Chem. 149,* 313-22 (1943). The natural stability of body fat from rats receiving a normal diet can be increased but this increase has been found to be relatively small and it is probably due to changes in both glyceride composition and antioxidant content brought about by alterations in the diet. Dietary supplements of lettuce, avenex, rice bran, yeast, casein, hydroquinone, mixed tocopherols, or wheat germ oil do not increase the keeping time of body fat which already possesses a normal stability. The keeping time of body fat of the rat is markedly reduced by the continued ingestion of a diet which is free of vitamin E and other sources of fat-soluble antioxidants. It is proposed that, in the rat, antioxidants of the body fat are derived solely from the diet. The ingestion of certain antioxidant substances such as yeast and hydroquinone does not restore the normal stability to body fat from vitamin E-deficient rats, but *a*-tocopherol effects such a restoration. Pro-oxidants of rancid fat are not stored in the fat depots, but if such fat is ingested throughout the growing period of a rat, body fat stability is reduced, presumably owing to destruction of the dietary antioxidants. Naturally occurring antioxidants in the fat depots do not require frequent replenishment from the diet, but are stored for relatively long periods.

NUTRITIVE VALUE OF BUTTERFAT. *Nutrition Revs. 1,* 358-61 (1943).

DIGESTIBILITY OF CERTAIN HIGHER SATURATED FATTY ACIDS AND TRIGLYCERIDES. R. Hoagland and G. G. Snider. *J. Nutrition 26,* 219-25 (1943). Expts. were conducted with mature male rats to det. the digestibility of pure stearic, palmitic, myristic and lauric