Solid Fatty Acids

*Their Determination by the Salt-Alcohol Method Using the Original Sample**

By Walter F. Baughman and George S. Jamieson

THE lead salt-alcohol method for the separation and determination of solid fatty acids, as described by Twitchell (*J. Ind. Eng. Chem. 13,* 806, 1921) is based upon the use of a weighed quantity of the total fatty acids instead of the original sample of fat or oil. It is often desirable to use this method without first preparing the anhydrous total fatty acids. Besides, the separation of the total fatty acids requires considerable time. For these reasons, it was of interest to determine the conditions under which the lead salt-alcohol method may be applied successfully to the oil or fat sample.

The first set of experiments was made with refined cottonseed oil. Portions of about 6 grams (accurately weighed) were saponified in Erlenmeyer flasks with excess of alcoholic potash. After the addition of glacial acetic acid, equivalent to the alkali used, a hot alcoholic solution of 1.5 g. of lead acetate, as specified by Twitchell (loc. cit.) was added to precipitate the solid fatty acids. This quantity of lead acetate is in excess of that equivalent to the solid acids but is less than the amount equivalent to the total fatty acids.

The precipitate was separated by filtration, washed, redissolved in 100 cc. boiling alcohol containing 0.5 cc. acetic acid and allowed to reprecipitate by cooling according to the Twitchell directions. The fatty acids were separated from the lead salts and weighed, but the results were lower than those obtained by the original Twitchell method, in which the total fatty acids were used for the working sample or by the lead salt-ether method. When only sufficient acetic acid to neutralize the alkali in excess of the amount equivalent to the total fatty acids in the sample was used, and the lead salts of the solid acids were precipitated as described above, the results were higher but were still too low. Increasing the amount of lead acetate used for the first precipitation, also caused higher results. It was also evident that in order to precipitate completely the solid acids as lead salts from an alcoholic solution containing the potassium salts of the solid and liquid fatty acids and potassium acetate, it was necessary to use an amount of lead acetate in excess of the amount equivalent to the total fatty acids.

Finally, the following directions for determining the percentage of solid fatty acids in an oil or fat were found to give satisfactory results. Weigh into a 300 cc. Erlenmeyer flask a quantity of the oil or fat that is estimated to contain (if possible) 1 to 1.5 g. of solid acids, in no case using more than a 6 g. sample. Saponify alcoholic potash solution prepared as directed in the A.O.A.C. method for determining the saponification number (40 g. potassium hydroxide dissolved in 1 liter pure 95 per cent ethyl alcohol). (*Official and Tentative Methods of Analysis of the Association of Official Agricultural Chemists.* Revised July 1, 1924. Page 288). Forty cc. of this solution are sufficient to saponify a 6 g. sample. After saponification add a few drops of phenolphthalein indicator, neutralize the excess potassium hydroxide with glacial acetic acid from a burette and add one drop of acid in excess. Add sufficient 95 per cent alcohol to bring the volume to 150 cc. Dissolve 5 g. of lead acetate in 50 cc. of alcohol. Heat both solutions to boiling and pour the lead acetate solution into the soap solution. Allow this to cool slowly to room temperature, and leave it over night in an ice box at approximately 15° C. Filter through an 11 cm. filter paper and wash the precipitate and flask with cold 95 per cent alcohol until a sample of the washings, diluted with water, remains clear. Wash the precipitate completely from the filter through a wide stem funnel back into the flask with about 100 cc. of alcohol, add 0.5 cc. glacial acetic acid and heat to boiling. The precipitate will slowly dissolve. Cool the solution slowly to room temperature and again allow to remain over night in the ice box at 15° C. Filter and wash with alcohol as before. Transfer the precipitate from the filter and flask into a 500 cc. separatory funnel with ethyl ether, add about 25 cc. hydrochloric acid (1-1) to decompose the lead salts and shake. Also decompose the small amount of lead salts adhering

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*(Contribution from Oil, Fat and Wax Laboratory, Bureau of Chemistry and Soils, U. S. Department of Agriculture).

to the sides of the flask with a little hydrochloric acid and wash into the separatory funnel with ether. Wash the ethereal solution of solid acids with water until the washings remain clear when tested with an aqueous silver nitrate solution. Dehydrate the ethereal solution with 6 or 7 g. anyhydrous sodium sulphate. Pour the solution through a 7 cm. filter into a weighed 200 cc. Erlenmeyer flask. Wash the separatory funnel and filter with several portions of ether. Distill off the ether, heat the flask in an oven at approximately 110° C. (in an atmosphere of CO_2 if iso-oleic acid is present) until the weight is constant, and obtain the weight of the solid fatty acids. Determine the iodine number of the solid fatty acids.

The figures in the first column of the accompanying table were obtained by following the foregoing directions. (The percentages in Column 3 were calculated from figures obtained by the original Twitchell method, with total fatty acid samples, and the calculations were made with the assumption that the oils or fats contained 95.5 per cent total fatty acids. The percentages of solid acids in Column 5 were determined by the lead salt-ether method and corrections were made for the small amount of unsaturated liquid acids that contaminates the solid acid fraction when this method is used (*J. Amer. Chem. Soc. 42,* 2398 (1920) ; *Cotton Oil Press,* Vol. 6, No. 1, p. 41 (1922). For samples 5 to 10 inclusive, the unsaturated acids are measured by the iodine numbers of the solid acid fractions. The solid acid fractions of the hydrogenated cottonseed oil samples contain iso-oleic acid, and therefore it is not possible to measure the contaminating unsaturated liquid acids by the iodine numbers.

From extensive experiences with the lead salt-ether method, it was assumed that the contaminating unsaturated liquid acids present are equivalent to an average iodine value of 5; consequently this figure has been deducted from the iodine numbers of the solid acid fractions (1 to 4 inclusive) so that the results by this procedure would be comparable with those by the lead salt-alcohol methods.

An examination of the table of results shows that the percentages of solid acids obtained by the lead salt-alcohol method applied to original oil samples agree favorably with the results obtained by the original Twitchell method and by the lead salt-ether method. Subtracting the figure 5 from each of the iodine values of the solid acid fractions separated by the lead salt-ether method from the four hydrogenated cottonseed oil samples, gave the following results:

Sample 1 — 29.5
Sample 2 — 17.7
Sample 3 — 14.6
Sample 4 — 33.2

These figures compare favorably with the iodine numbers of the solid acid fractions separated by the other two methods. This comparison indicates that each method gives a quantitative separation of the iso-oleic acids along with saturated acids.

PERCENTAGES OF SOLID FATTY ACIDS OBTAINED BY DIFFERENT METHODS

	Lead Salt-Alcohol Method Using Oil Instead of Total Fatty Acids		Original Twitchell Method Using Total Fatty Acids		Lead Salt-Ether Method
Sample	Solid Acids %	Iodine No. of Solid Acids	Solid Acids (Calculated to oil basis) %	Iodine No. of Solid Acids	Solid Acids % (corrected)
No. 1 Hydrogenated Cottonseed Oil	40.8	29.7	40.6	29.9	38.0
No. 2 " " "	35.3	16.2	34.8	16.3	36.3
No. 3 " " "	30.7	14.3	31.4	16.3	30.8
No. 4 " " "	37.6	31.3	—	—	36.5
No. 5 Cottonseed Oil (refined)	21.1	1.1	20.8	0.8	21.1
No. 6 Olive Oil	9.7	0.3	—	—	10.7
No. 7 Corn Oil (crude)	8.8	1.6	—	—	9.1
No. 8 Soy Bean Oil (refined)	11.2	1.7	—	—	11.2
No. 9 China Seed Oil[1]	8.2	3.1[2]	—	—	8.1
No. 10 Grape Fruit Seed Oil	25.3	0.3	—	—	26.5

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[1] *Oil and Fat Ind.* Vol. 6, No. 9, p. 15 (1929).

[2] The solid acids fraction contained considerable color. The coloring matter may have been responsible for this high iodine number.