It will be noted that in but three cases out of the forty-five last stated does the difference between the two methods exceed 0.05, which is certainly as close as one can expect ordinary technical work to be done, and as between two samples is undoubtedly within the limits of accuracy of sampling large lots.

A still further test of the method was given by making a gliadin determination upon a gluten flour in which the Kjeldahl method showed 3.32 per cent. of gliadin nitrogen. The polariscopic method showed 3.45 per cent.

Considerable difficulty was experienced at the outset in securing a clean solution for filtration, but this was finally overcome by avoiding excessive agitation.

Snyder remarks that in the case of flours analyzed by him, and probably grown in the middle west, '' the combined alcohol soluble carbohydrates and non-gliadin proteins of the alcoholic solution affect the polarization to only a slight extent,'' and states that after the gliadin protein was precipitated the non-gliadin rotary bodies showed a reading of less than 0.20 on the sugar scale.

In our experience with the method it was always found necessary to make two polarization determinations, the first of the original solution, and the second after separating the protein bodies by the use of a concentrated solution of mercuric nitrate, and then making the required correction to give the true gliadin reading.

This was particularly true in the case of wheat meals where the average difference between the two polariscope readings was 1.05 on the sugar scale corresponding to 0.21 per cent. on the gliadin scale, the range of differences on the sugar scale being from 0.08 to 2.75. In the case of flours, unless extreme accuracy is required, the correction could be neglected inasmuch as the error is much less, not exceeding 0.04 per cent. of the gliadin scale.

The writer is strongly impressed with the idea that the method is worthy of a much more extended use than it has so far had, and that if precautions are taken to correct for the effect of other optically active bodies, there are fewer opportunities for error than with the ordinary method of nitrogen determination.

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THE SOLUBILITY OF STEARIC ACID IN ETHYL ALCOHOL AT ZERO.

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In some work on the determination of stearic acid by the method of Hehner and Mitchell,[1] difficulty was experienced in obtaining a definite

[1] Analyst, 21, 316; also This Journal, 19, 32 (1897) and Lewkowitsch, Oils, Fats and Waxes, 3rd edition, p. 355.

saturated solution of stearic acid. As the preparation of a solution which shall be saturated under the conditions of the determination is essential to the accuracy of the method, it was decided to study the solubility of stearic acid in ethyl alcohol at 0°.

Kreis and Hafner found[1] the solubilities of both stearic and palmitic acids much lower than had been previously given by Hehner and Mitchell. They also found that small amounts of stearic acid, below about 0.1 grm., form highly supersaturated solutions, and that very small amounts will not crystallize at all from a saturated solution, even though treated with a crystal of the acid and allowed to stand indefinitely, a fact with which I had also met.

The first step in the work was the preparation of a pure stearic acid. The melting point of the acid has been variously given from 68.5° to 71.5°. As a starting point a special stearic acid from Kahlbaum was used. The melting point was determined carefully using a thermometer standardized at the Reichsanstalt, graduated to $1/5°$, and the usual small melting tubes. The melting point was found 66.6°-68.3° (corr.). The range was observed from the first indication of change, marked by a shrinking of the test, to complete liquefaction, with very slow rise in temperature, about 0.1° per minute. The acid was then crystallized repeatedly from alcohol of about 95 per cent., noting the melting point from time to time. At the eighth crystallization it melted at 69.1°-69.4° (corr.) and further crystallization did not raise the melting point. Slight fluctuations of temperature due to irregularity of stirring were observed This melting point agrees best with that of de Visser, 69.32°.

The alcohol used was the "95 per cent." alcohol of commerce distilled from potassium hydroxide, 50 cc. left 0.2 mg. residue on evaporation. The specific gravities were determined by weighing in a picnometer provided with a thermometer and capillary side tube. The weighings were reduced to a vacuum. Essentially the same apparatus was used as recommended by Hehner and Mitchell in determining stearic acid except that one limb of the filtering tube was prolonged so as to form a siphon. To prevent unnecessary access of atmospheric moisture, which it was feared might condense in the cold flask and cause dilution of the alcohol, the crystalliz-ing and receiving flasks were closed with two hole rubber stoppers, the siphoning apparatus passing through one hole in each, and the other closed by capillary (thermometer) tubing. The method of procedure was generally to dissolve the acid in 100 cc. of alcohol in a tightly stop-pered flask, place both in the ice over night, shake in the morning, allow to stand four hours in the ice, then siphon off, using the pump to start the siphon. The alcoholic solution was then weighed, evaporated, and from the weight of the residue the solubility determined. The residue

in the crystallizing flask was dissolved again, followed by recrystallization in the ice bath, filtration, etc. This was repeated as often as desired. After the first solution, 50 cc. was generally used for resolution—sometimes 100 cc. throughout.

Some preliminary experiments showed that the solubility remained nearly constant as long as a considerable excess of stearic acid was present.

The following series was made with alcohol, specific gravity 0.81577, at 14.7°—about 95.1 per cent. by volume. Two tests were made at the same time and the table gives the parallel and successive solubilities expressed in grms. per 100 cc. at 0°.

TABLE 1.

Stearic Acid. 0.793 grms. Solubility	Vol. Alcoho	Stearic Acid. 0.775 grms. Solubility
a 0.1135	100 cc.	a′ 0.1144
b 0.1139	50 "	b′ 0.1134
c 0.1158	" "	c′ 0.1213
d 0.1164	" "	d′ 0.1164
e 0.1215	" "	e′ 0.1221
f 0.1241	" "	f′ 0.1257
g 0.1339	" "	g′ 0.1408

Previous to the solution for the test c′, the residual alcohol of the preceding test, (between 5 and 10 cc.) had been evaporated on the water bath.

At the test e, where the solubility began to increase rapidly it was estimated by weighing the residue and calculating back that 0.45 grm. of acid was present, and at e′ 0.43 grm. The exact amount could not be determined owing to uncertainty as to the loss due to solution remaining in the tube, and acid adhering to the filtering tube. These results indicate that supersaturation occurs with a much larger amount of acid present than was found by Kreis and Hafner.

The next series was made to try the effect of varying several conditions. Alcohol—specific gravity 0.80706 at 22.2°, about 95.7 per cent. by volume.

TABLE 2.

Stearic Acid. 0.742 grms. Solubility	Volume of Alcohol	Stearic Acid. 0.699 grms. Solubility
a 0.1234	100 cc.	a′ 0.1251
b 0.1250	50 "	b′ 0.1280
c 0.1282	" "	c′ 0.1284
d 0.1242	" "	d′ 0.1253
e 0.1280	" "	e′ 0.1309
	" "	f′ 0.1427

For b, the residual alcohol of the previous test was evaporated over sulphuric acid in a vacuum desiccator, and the acid redissolved without heating. For b′, the residual alcohol was evaporated on the steam bath,

and the acid redissolved without heat. For c and c', the alcohol was evaporated on the steam bath, and for c redissolved with a small flame and for c' on the steam bath. In redissolving with heat the solution as a whole was not allowed to become appreciably warm to the hand.

Apparently the only factor, other than the amount of acid, which appreciably affected the solubility was evaporation on the steam bath with alcohol. The amounts of acid present at e and e', when the solubility began to rise, were estimated to be 0.43 grm. and 0.39 grm. respectively.

The next test was made to see if supersaturation set in with a larger amount of acid present, when using a larger volume of alcohol, so 100 cc. was used throughout. It had been found that 0.7 grm. did not give a supersaturated solution with 100 cc. alcohol.

Alcohol, 0.80766 at 22.1°—about 95.5 per cent.

TABLE 3.

Stearic Acid. 0.782 grms. Solubility	Vol. Alcohol	Stearic Acid. 0.711 grms. Solubility
a 0.1217	100 cc.	a′ 0.1229
b 0.1268	"	b′ 0.1296
c 0.1462	"	c′ 0.1516

Supersaturation set in for b with 0.64 grm. acid present and b' with 0.57 grm. c' was allowed to stay in the ice bath over 40 hrs. with occasional shaking, which did not apparently overcome the supersaturation to any extent.

There was some evidence that supersaturation set in later, $i.\ e.$ with a smaller amount of acid present with more dilute alcohol—so the following test was made:

Alcohol, 0.80869 at 25.6°—about 94.5 per cent.

TABLE 4.

Stearic Acid. 0.525 grms. Solubility	Vol. Alcohol	Stearic Acid. 0.429 grms. Solubility
a 0.1037	50 cc.	a′ 0.1033
b 0.1052	"	b′ 0.1073
c 0.1083	"	c′ 0.1144

For c and b' the amounts of acid were 0.39 and 0.36 respectively. Comparing with Table 2 we see that the difference is slight if any, with this variation in specific gravity—c' was allowed to stand for over 40 hrs. in the ice bath with occasional shaking.

In the preceding determinations, while the solubilities were nearly constant with stearic acid above a certain amount, yet a slight irregular increase is noticeable. It was thought that this might be due to evaporating the succeeding solutions in the flask with the stearic acid from the preceding determinations. Some trials showed that there was a slight increase in weight on evaporating stearic acid with alcohol.

In order to determine if there is a slight increase in solubility, preced-

ing the rapid increase supposed to be due to supersaturation, the following test was made:—

Alcohol, 0.81228 at 22.2°—about 94.3 per cent.

TABLE 5.

Stearic Acid	Vol. Alcohol	Solubility
2.09	100	0.0954
1.89	"	0.0986
1.4	"	0.1001
0.97	"	0.0996

The first three results suggest a progressive increase in solubility. On the other hand there is only a variation of about 1 per cent. in solubility between the 2nd and 4th tests with a variation of 1 grm. of acid, and this variation is probably within the limits of error of the determinations. For use in Hehner and Mitchell's method, therefore, the solubility may be considered as practically constant for quite a wide range in the amount of stearic acid, when above about 0.7 grm. using 100 cc. of alcohol of 94 to 95 per cent., and when above about 0.5 grm. using 50 cc. of alcohol.

The solubilities found within this range and already given are here summarized :—

TABLE 6.

Specific gravity of alcohol at 0°	Approximate strength of alcohol by volume	Amount dissolved in 100 cc. at 0°
0.82650	95.7 %	0.1246 grms.
0.82715	95.5	0.1223 "
0.82871	95.1	0.1139 "
0.83126	94.5	0.1035 "
0.83183	94.3	0.0996 "

The specific gravities were reduced to 0° assuming 0.00088 as the change of specific gravity per degree. The solubility was determined as already stated by evaporating the alcohol and weighing the residue, and as this gives a slight increase in weight to the acid, the above values should be somewhat too high. This error is however of little importance as the other errors of the determination are much larger, probably about 1 per cent. Hehner and Mitchell found the solubility to be 0.15 grm. in 100 cc. of 94.4 per cent. alcohol. Kreis and Hafner found a much lower value 0.1249 in 95 per cent. alcohol. Calculations from the results above, give 0.1123 grm. as the solubility, in 95 per cent. alcohol, about 10 per cent. lower than the result of Kreis and Hafner. If they were using about 0.5 grm. in their solubility determinations, as seems probable from their article, then the explanation of the difference might be that they were working just within the range of supersaturation. The rather wide variations in their individual results, 0.1220 to 0.1310, would also imply this.

Hehner and Mitchell give the weights of acid used in their solubility determinations as 0.2 to 0.5 grm. per 100 cc. of alcohol. Their value for the solubility should therefore have been too high, as seems to have been

the case. At the same time they found nearly identical values for the varying amounts of acid, which does not agree with the results presented above, as, under the conditions given, there was invariably a steady increase in solubility after the acid had fallen below about 0.7 grm. using 100 cc. alcohol.

Some further tests were made bearing on the increased solubility due to evaporation with alcohol.

1.272 grms. of the acid were evaporated on the steam bath with 50 cc. of 94.3 per cent. alcohol which had been distilled from potassium hydroxide. The solubility was then determined using 100 cc. and found to be 0.1196 grm. The normal solubility for this alcohol was about 0.1000 grm., deducting this from that found, leaves 0.0196 grm. excess soluble matter, or 1.54 per cent. of the acid used.

Since the lower fatty acids in general give esters when heated with alcohol, it was perhaps to have been expected that ethyl stearate would be formed here, thus increasing the apparent solubility. However, considering the high molecular weight of the acid, the brief time of the action, and the hydrolysis due to the considerable proportion of water, this was thought at least doubtful. Another possible explanation of the increased solubility was that the alcohol contained some foreign substance of a basic nature, perhaps alkaloids. Some alcohol was therefore prepared by distillation from stearic acid, followed by distillation with potassium hydroxide and again with stearic acid. 1.713 grms. of acid were evaporated with 50 cc. of this alcohol and the solubility determined. The result showed an excess solubility of 0.0245 grm. per 100 cc. or 1.43 per cent. of the acid used, differing but little from the above. If due to the ester, it was thought that its amount would be increased by evaporating with absolute alcohol, thus partly avoiding the hydrolytic action of the water. So 1.048 grm. of acid were evaporated with 50 cc. of a 99 per cent. alcohol. The excess solubility was 0.0132 grm., 1.26 per cent. of the acid used—somewhat less than with alcohol of 94.3 per cent. Evaporation with 80 per cent. alcohol gave an excess of 1.1 per cent. of the acid. Finally a solution of the acid in alcohol was allowed to stand five days at temperatures mostly from 25° to 30° and the solubility determined in comparison with a freshly dissolved sample under otherwise identical conditions. The former showed a solubility of 0.1007, the latter 0.0983—a difference somewhat more than the probable error of experiment.

So far as could be ascertained from the literature available the formation of the ester under these conditions had not been noted, and it is intended to investigate this point further.

From the above it appears that in order to determine small amounts of stearic acid accurately it will be necessary to add a weighed amount of

pure acid sufficient to bring the total up to about 0.7 g. for 100 cc. of alcohol or 0.5 grm. for 50 cc. of alcohol. The "saturated" solution used can be tested for supersaturation by evaporating a portion of it and comparing with the solubilities of Table 6, provided the acid has been treated so as to avoid the action of the alcohol on it. It would seem necessary also to keep in mind this action between the alcohol and acid in determining stearic acid in mixtures which have been recovered from alcoholic solution.   W. H. EMERSON.

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THE APPLICATION TO SOLID FATS OF RENARD'S TEST FOR PEANUT OIL.

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Tolman's modification of Renard's test for peanut oil[1] is the best method in use for the purpose and is generally employed in testing edible oils for adulteration. Briefly this method is carried out as follows: The sample is saponified with alcoholic potash and treated with lead acetate, the lead soap being treated with ether, which dissolves the lead oleate, linoleate, etc. leaving the lead stearate, palmitate and arachidate as a residue. The precipitate is treated with hydrochloric acid and the liberated fatty acids freed, separated and dried. They are then dissolved in 90 per cent. alcohol and cooled to 15°, when the arachidic acid crystallizes out, is weighed and the melting point taken. Twenty times the amount of arachidic acid gives the approximate amount of peanut oil present.

In connection with this method, however, Tolman and Munson say[2] "Twenty grams of the oil to be tested should be taken so that enough of the arachidic acid can be separated to make the melting point which should be determined in every case, as some oils, such as cottonseed and lard, will give a precipitate which resembles arachidic acid except that it has a lower melting point."

In working with mixtures of solid fats with cottonseed oil, the writer, in nearly every case in which a test was made has obtained a precipitate at the point where arachidic acid should come down, although this precipitate was very often gelatinous in appearance, whereas the arachidic acid is crystalline.

The following table shows comparative results obtained with oleostearin,

[1] Bulletin 65, Bureau of Chemistry, U. S. Department of Agriculture.

[2] Olive Oil and its Substitutes; Bulletin 77, Bureau of Chemistry, U. S. Department of Agriculture, p. 35.