METHOD FOR THE DETERMINATION OF THE FREEZING-POINT OF FATTY ACIDS.[1]

By F. Wolfbauer.

Translated and Abridged by S. S. Emery.

BY reason of the lack of agreement between different chemists in the determination of the freezing-point of a fat, and also because of the commercial importance of this determination as indicating the quality of fats, it seemed desirable that a standard method for this determination should be adopted.

Accordingly, my proposed method, after being carefully examined by Dr. R. Benedikt, Dr. von Perger, Dr. Ferd. Ulzer, and myself, was agreed upon by us as the method by which all future determinations of the freezing-point should be made.

The method is as follows:

One hundred and twenty grams of the fat is melted in a beaker at a temperature but slightly above its melting-point, mixed with forty-five cc. of caustic potash solution (1,250 grams of caustic potash in one liter of water[2]), and stirred until the fat is completely emulsified. It is then covered and kept at 100° C. for two hours, being occasionally stirred. A small portion is then tested by warming with alcohol (fifty per cent.) to ascertain whether saponification is complete, indicated by obtaining a clear solution; otherwise it must be replaced in the bath and there allowed to remain until this is accomplished.

The soap is now decomposed by boiling with 165 cc of dilute sulphuric acid (sp. gr. = 1.143 = 18° B.[3]), preferably done in a silver dish, and continued until the free fatty acid rises to the top as a perfectly clear oily layer.[4] The silver dish is then covered with an evaporating dish filled with cold water, to check the evaporation. The aqueous solution is then completely drawn off, and the fatty acid washed by boiling one-quarter of an hour

[1] From the Mittheilungen des Technologischen Gewerbmuseums, Wien, 1894.

[2] This solution should have a sp. gr. of 1.509, and contain forty-eight per cent. of potassium hydroxide.

[3] Or a mixture of twenty-two cc. concentrated sulphuric acid and 150 cc. water.

[4] If the size of the dish will permit of so doing, it is recommended to add (before decomposing) 150 cc. of boiling water, and allowing to stand ten minutes at 100° C.,—whereby the soap takes up water, rendering the subsequent decomposition more rapid

with dilute sulphuric acid (five cc. of concentrated sulphuric acid and 100 cc. of water). After settling and removing the dilute acid, it is boiled with 100 cc. of pure water,—this last being repeated should the washings taste distinctly acid. It is then dried in an open dish at 100° C. for two hours.

Only fatty acids obtained as above can be considered sufficiently pure and dry to be used for the determination of the freezing-point.

In the determination proper the following apparatus is employed: A thin-walled test-tube, three and one-half cm. by fifteen cm., is fixed by means of a cork in a suitable bottle A Centigrade thermometer, extending from 1° to 60°, and graduated in fifths of a degree, is fixed in the test-tube by a second cork, which must be sufficiently loose to permit of an easy stirring of the contents of the tube with the thermometer. As the thermometer should be as short as possible, its scale is shortened by an enlargement blown in the bore in the interval between 2° and 28°. The amount of mercury *above* the surface of the fatty acid is thus diminished and a very appreciable error (a lowering of the freezing-point) is consequently avoided.

To accomplish the determination the test-tube is filled to within one cm., or one and one-half cm., of the top with the melted fatty acid, the thermometer immersed in the liquid to about the 35° mark (when the instrument should clear the bottom of the tube by about four cm. or five cm.), and the liquid stirred until it becomes quite opaque, and partial solidification sets in. Care should be taken at this point that the thermometer be not more deeply immersed, and after stirring rapidly in a circle ten more times, the thermometer is allowed to stand. The mercury now begins to rise in consequence of the latent heat liberated from the solidifying fatty acid; the highest temperature noted may be taken as the freezing-point.

The reading of the thermometer should be corrected for its inherent errors, previously determined. Its zero point should also be redetermined from time to time.

Each freezing-point determination should be repeated, and the difference between the two should not exceed 0.1° C.; as a rule it will not exceed 0.05°.

The use of narrower test-tubes than above prescribed, as well as lack of attention to other details, generally leads to low results, as a so-called "over-cooling" always appears in the passage from the liquid to the solid state.

The experiments which justified the adoption of this method were carried out in the following lines:

I. The influence of the method of saponifying.

II. The influence of the length of time of saponifying.

III. The influence of the degree of dryness of the fatty acid.

IV. The influence of the size and shape of the vessel in which the freezing-point is determined.

V. The influence of a different length of thermometer.

I. The Effect of the Method of Saponifying.—The following determinations show that either an aqueous or an alcoholic solution of caustic potash may be used for the saponification:

	Freezing-point found by means of aqueous saponification.	alcoholic saponification.
Fatty acid I	43.00°	43.08°
Fatty acid II	43.49°	43.52°

It should be here remarked that, in the case of alcoholic saponification, a one and one-half hours' boiling of the soap solution diluted with one liter of water is necessary to completely remove the alcohol.

II. The Influence of the Length of Time of Saponifying.—The two following determinations were made on the same fat; in I the time of saponifying was limited to one and one-half hours, while in II it was prolonged to fully fifteen hours:

	Freezing-point.
Determination I	43.49°
Determination II	43.44°

It is therefore evident that a variation in the length of time of saponifying does not influence the final result.

Regarding the minimum length of time necessary, it varies with different fats,—slightly rancid fats requiring less than fresh fats, some of the former undergoing even spontaneous saponification on being mixed with the caustic potash. As a rule, however, for fresh fats two hours is amply sufficient, provided the fat was not melted at too high a temperature, and that, after

adding the caustic potash, a perfect emulsion was obtained by a vigorous stirring.

III. The Influence of the Degree of Dryness of the Fatty Acid.— Comparative tests have shown most conclusively that by increasing the amount of water in a fatty acid the freezing-point is lowered, and *vice versa*. Further, as the absorbent power of fatty acids for water is less in the cold than at a higher temperature, it follows that during the cooling of a fatty acid, saturated with the maximum amount of water, at a certain temperature a separation of water must take place, shown by the still liquid fatty acid becoming turbid. This turbidity naturally interferes with the detection of solidification, and consequently, determinations made on undried or partially dried fatty acids show much less agreement with each other than those made on the perfectly dried acid. In two determinations on the same fat, using the undried fatty acid, were obtained the

freezing-points	43.14°
and	42.86°
the freezing-points differing by	0.28°

If, after washing a fatty acid, a filtration be substituted for the drying, a partial removal of the water is thus effected. But as the freezing-point of a fatty acid so treated is 0.3°–0.4° lower than one similarly treated, but also dried, it appears that such a filtration is entirely superfluous.

As is shown in the following table, it makes no difference in the final result whether the fatty acid be dried only one and one-half hours or a much longer time. It is also immaterial whether the dried fatty acid be used immediately for the determination, or whether it be first allowed to solidify and to stand a long or short time, being subsequently remelted for the determination.

RESULTS OF A SERIES OF DETERMINATIONS OF THE FREEZING-POINT OF A FATTY ACID, BY AQUEOUS AND ALCOHOLIC SAPONIFICATION, AND USING THE DRIED FATTY ACID.

Determination. No	The saponification effected with	and continued.	Further treatment of the fatty acid.	Freezing-point found.	Difference from the average.
1.	Aqueous potash	15 hours	Dried 5 hours	44.44°	—0.02°
2.	"	1½ "	" 4 "	43.49°	+0.03°
3.	A mixture of the above two dried fatty acids, washed again with water, filtered, and then dried two hours.			43.35°	—0.11°

4.	The fatty acid from the above test after standing twelve hours in the solid state, and then heated one hour.			43.51°	+0.05°
5.	Alcoholic potash...	¾ hour.....	Filtered and dried one hour.	43.52°	+0.06°
6.	Aqueous " ...	3 hours....	Not filtered, dried two hours.	43.45°	—0.01°
7.	" " ...	The fatty acid from the above test after solidifying, immediately rinsed		43.46°	±0.00°
		Average		43.46°	

IV. The Influence of the Size and Shape of the Vessel in which the Freezing Point is Determined.—To ascertain what influence is exerted by the use of a narrower test-tube than prescribed, the freezing-point of two fatty acids was determined in a tube only two and one-half cm. in diameter, as well as in one of the usual diameter, three and one-half cm., with the following results:

	Freezing-point obtained in the wide tube.	in the narrow tube.	Difference.
Fatty acid I.....	43.52°	43.34°	0.18°
Fatty acid II....	42.88°	42.65°	0.23°
Average.....			0.20°

These results by no means fix the allowable minimum diameter of the tube, as, *a priori*, the possibility is not excluded of obtaining a still higher freezing-point by the use of a tube of still greater diameter.

Accordingly, the freezing-point of the same fatty acid was determined, first, in a test-tube of the usual diameter, three and one-half cm., and then in a similarly shaped vessel having a diameter of seven cm., making about four times as much fatty acid around the thermometer in the second case as in the first. The freezing-points obtained were as follows:

In tube three and one-half cm. in diameter..... 43.45°
" " seven cm. in diameter ..... 43.46°

which show that the diameter of the tube may be increased from three and one-half cm. without disturbing the ratio between the amount of heat radiating from the fatty acid through the walls of the tube and the amount of liberated latent heat.

Consequently a tube three and one-half cm. or more in diameter answers perfectly for the correct determination of the freez-

ing-point, but it is not permissible to use one appreciably narrower than this.

V. The Influence of the Length of the Thermometer.—In order to demonstrate and also to estimate the error (a too low result) caused by an incomplete immersion of the thermometer in the liquid, thus allowing a portion of the column of mercury to project above its surface, the shortened thermometer recommended above, and a long (normal) one were first tested by a complete immersion in a water-bath, when each registered exactly the same temperature (43°); after which they were simultaneously placed in the test-tube containing water at 43°. The shortened thermometer was immersed to the 35° mark, leaving but 8° of mercury above the surface of the water, while the long thermometer could be immersed to only its zero mark, leaving fully 43° of mercury exposed. The whole was then placed in an air-bath, kept at a temperature of 20° in order to avoid the error of radiation. The reading of the long thermometer was about 0.13° below that of the shorter one.

This error was now calculated for each thermometer, giving, theoretically, for the long

thermometer	0.15°
while for the shorter one, only	0.03°
the difference of	0.12°

being the theoretical error introduced by using a long (normal) thermometer, and agreeing closely with the experimental determination of the error (0.13°).

Though, of course, this error is not completely eliminated by using a shortened thermometer, still it is so reduced as to be of no practical importance.

RECENT WORK ON THE SUGARS.

By B. B. Ross.

(*Continued from page 553.*)

Received May 14, 1894.

DETERMINATION OF WATER IN SUGARS.

Herzfeld (*Ztschr. des Ver. f Rübenzucker*, **43**, 130, *Bull. Assoc. Chim. Belg.*, **6**, 267) reports the results of a large number of experiments in the determination of the amount of water in