Comparison of SFI, DSC and NMR Methods for Determining Solid-Liquid Ratios in Fats[1]

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ABSTRACT

Dilatometry (SFI) has gained wide acceptance for the characterization of solid-liquid contents of fats over approximately the past 15 years. In more recent times, wide-line nuclear magnetic resonance (NMR) has been used for this purpose. Still more recently the differential scanning calorimetry (DSC) technique has been used to determine solid-liquid contents. These three techniques were used to determine the properties of seven fats and oils which represent a cross section of commercially available materials. These products were blended into 14 different compositions and the solid-liquid contents were determined by the three methods. A comparison is made on the results obtained on the various samples by SFI, NMR and DSC techniques. The results of each procedure are compared according to fat composition.

INTRODUCTION

Solids in fats and oils have been characterized by several analytical procedures. Dilatometry is the basis of the most widely used method for solids measurement. The AOCS dilatometric solids fat index (SFI) determination (1) has been used extensively for quality specifications on fat and oil products. Procedures based upon nuclear magnetic resonance (NMR) have been reported by several authors including the work recently reported by Bosin and Marmor (2).

Denison and Justin (3), Bentz and Breidenbach (4) along with Miller et al. (5) have reported on the use of differential scanning calorimetry (DSC) for measurement of solids in fats and oils.

In the present work, solids results by SFI, NMR and DSC techniques are compared. Commercially available fats and blends made from these fats were examined by the three methods.

EXPERIMENTAL PROCEDURES

The AOCS SFI method (1) was used to determine solids by dilatometry. Single determinations were made on the samples examined.

The NMR technique used was that reported by Bosin and Marmor (2). A Varian Model PA-7 wide-line NMR spectrometer, equipped with an integrator and a variable temperature accessory, was used in this study. Duplicate determinations were made by NMR on the samples examined.

The DSC procedure used was that reported by Bentz and Breidenbach (4). A Perkin-Elmer DSC 1-B instrument was used. Duplicate DSC determinations were made on the samples studied. Calorimetric calibration was made using pure indium, while temperature calibration was done by use of lauric acid. The solids calculation based upon DSC response was made by use of 35 cal/g as the average heat of fusion for fat solids. If the actual heat of fusion differs from this, then the calculated value for DSC solids would be affected.

Materials for DSC analysis were transferred to aluminum sample pans from the melt by means of a 10 μliter micro-pipet. High melting samples were handled under an IR heat lamp to prevent crystallization. An empty sample pan containing approximately 7 mg of aluminum was used as the calorimeter reference. Liquid nitrogen was used as the coolant for the DSC work.

General test conditions were somewhat different for the three methods. Samples were tempered for the SFI and DSC methods, but not for the NMR procedure. Each method required a different sample weight. Approximate sample weights were: SFI, 9 g; DSC, 5 mg; and NMR, 2.2 g.

[1]One of 10 papers to be published from the Symposium "Wide-Line Nuclear Magnetic Resonance" presented at the AOCS Meeting, Minneapolis, October 1969.

TABLE I

Fatty Acid Composition (Wt %) of Fats Used to Prepare Blends

Fatty acid	Tallow (46.2 IV)[a]	Hydrogenated soybean oil-I (80.0 IV)[a]	Lard (64.8 IV)[a]	Palm kernel oil (23.2 IV)[a]	Hydrogenated soybean oil-II (72.0 IV)[a]	Safflower oil (137.9 IV)[a]	Hydrogenated tallow (5.4 IV)[a]
C6:0	---	---	---	Trace	---	---	---
C8:0	---	---	---	3.17	---	---	---
C10:0	0.06	---	0.08	3.94	---	---	0.06
C12:0	0.18	---	0.31	32.65	0.21	---	0.31
C14:0	3.05	0.15	1.45	20.42	0.18	0.13	3.74
C15:0	1.45	---	0.06	---	---	---	1.23
C15:1	---	---	---	---	---	---	0.22
C16:0	22.16	12.37	23.40	11.64	11.09	8.54	27.15
C16:1	3.51	0.20	2.77	---	0.20	0.15	0.92
C17:0	1.93	0.13	0.25	---	0.08	---	2.17
C17:1	0.95	---	0.28	---	0.09	---	---
C18:0	22.38	6.63	13.63	3.63	9.47	3.28	58.90
C18:1	40.65	66.57	44.03	22.13	73.05	15.77	4.08
C18:2	2.57	12.90	11.63	2.41	4.81	71.04	0.62
C18:3	1.01	0.40	1.48	---	0.26	0.46	---
C20:0	0.11	0.33	0.13	Trace	0.39	0.57	0.60
C20:2	---	---	0.43	---	---	---	---
?	---	---	0.09	---	---	---	---
C22:0	---	0.32	---	---	0.19	0.05	---

[a]Iodine value calculated from GLC fatty acid composition.

TABLE II

Comparison of SFI, DSC and NMR Solids Values on Blends of Tallow and 80.8 IV Soybean Oil

Composition, %			Temperature, F				
Tallow	SBO	Method	50	70	80	92	100
100	0	SFI	35.0	24.8	22.4	17.1	12.0
		DSC	25.0	20.8	19.3	16.9	12.5
		NMR	65.8	37.2	22.9	14.5	9.5
75	25	SFI	34.1	21.8	19.3	13.1	8.2
		DSC	22.3	18.7	15.9	13.1	8.8
		NMR	59.9	29.6	19.0	10.4	7.0
50	50	SFI	31.7	18.8	15.7	8.9	4.6
		DSC	23.9	18.7	12.9	9.3	4.9
		NMR	56.7	24.3	15.0	8.3	5.0
25	75	SFI	28.9	15.5	11.4	4.8	1.5
		DSC	30.8	14.5	9.8	5.2	1.1
		NMR	50.1	20.4	11.2	5.5	2.0
0	100	SFI	27.0	14.6	6.9	0.4	0.0
		DSC	32.4	14.2	6.3	0.6	0.0
		NMR	39.8	12.9	4.4	0.2	0.0

TABLE III

Comparison of SFI, DSC and NMR Solids Values on Blends of Tallow and Lard

Composition, %			Temperature, F				
Tallow	Lard	Method	50	70	80	92	100
100	0	SFI	35.0	24.8	22.4	17.1	12.0
		DSC	25.0	20.8	19.3	16.9	12.5
		NMR	65.1	36.7	23.9	14.4	9.8
75	25	SFI	34.4	21.9	18.4	13.0	8.6
		DSC	18.4	17.0	14.7	12.3	8.1
		NMR	64.0	32.9	20.4	12.4	7.6
50	50	SFI	41.6	23.0	15.8	10.4	7.3
		DSC	25.3	17.0	12.4	9.2	5.1
		NMR	61.9	30.9	16.3	9.4	6.6
25	75	SFI	35.3	21.5	14.2	7.3	4.8
		DSC	29.2	18.0	10.5	5.5	2.0
		NMR	50.7	25.3	13.2	7.2	4.6
0	100	SFI	28.2	20.7	14.2	4.5	2.9
		DSC	26.2	18.1	12.4	1.5	1.4
		NMR	34.0	20.8	12.6	4.1	3.4

TABLE IV

Comparison of SFI, DSC and NMR Solids Values on Blends of Palm Kernel Oil and 72.0 IV Soybean Oil

Composition, %			Temperature, F				
PKO	SBO	Method	50	70	80	92	100
100	0	SFI	48.2	32.2	12.3	0.0	0.0
		DSC	59.9	39.4	16.7	0.0	0.0
		NMR	72.1	34.3	9.5	0.0	0.0
75	25	SFI	44.5	21.6	2.4	0.2	0.0
		DSC	59.8	27.0	0.3	0.0	0.0
		NMR	67.2	19.8	1.2	0.0	0.0
50	50	SFI	39.6	16.1	3.0	0.0	0.0
		DSC	49.6	18.8	2.0	0.0	0.0
		NMR	64.4	15.4	2.7	0.3	0.0
25	75	SFI	37.3	14.2	7.5	1.2	0.0
		DSC	42.9	14.6	6.3	0.9	0.0
		NMR	63.2	15.2	6.4	1.8	0.0
0	100	SFI	41.8	24.8	17.4	4.8	0.0
		DSC	42.9	23.5	14.5	5.6	0.2
		NMR	69.7	30.1	15.2	3.3	0.4

TABLE V

Comparison of SFI, DSC and NMR Solids Values on Blends of Safflower Oil and 5.4 IV Tallow

Composition, %			Temperature, F				
SFO	Tallow	Method	50	70	80	92	100
70	30	SFI	30.5	31.6	31.8	31.8	30.9
		DSC	28.4	28.4	28.4	28.4	28.3
		NMR	33.1	30.4	28.8	26.7	25.2
50	50	SFI	47.3	49.3	50.3	50.9	50.6
		DSC	47.8	47.8	47.8	47.8	47.8
		NMR	53.5	50.6	48.8	45.7	43.7
30	70	SFI	---	---	---	---	---
		DSC	73.2	73.2	73.2	73.2	73.2
		NMR	76.5	73.7	71.6	68.9	66.9
10	90	SFI	---	---	---	---	---
		DSC	90.6	90.6	90.6	90.6	90.6
		NMR	93.7	92.5	91.1	89.2	87.4
0	100	SFI	---	---	---	---	---
		DSC	90.3	90.3	90.3	90.3	90.3
		NMR	98.3	98.0	97.8	97.5	97.4

The SFI and NMR values are obtained from measurements made under static conditions. DSC values result from a response obtained under programmed or dynamic conditions in which the heat of fusion vs. temperature is recorded continuously over the melting range. In the DSC test, solids values at any temperature up to the sample melting point can be calculated.

Results by the three methods were compared on 20 samples which had a wide range of solids. In addition, the effect of tempering on the NMR method was determined for several samples. Also, a DSC cooling temperature of -50 C was used for a few samples.

RESULTS AND DISCUSSION

Fatty acid composition analyses of the fats used to prepare blends in this study are listed in Table I.

Solids measurements by SFI, DSC and NMR techniques were compared on blends of tallow and 80.8 IV hydrogenated soybean oil. Table II shows the results obtained on the tallow-hydrogenated soybean oil blends.

Definite differences in results are seen at 50 and 70 F with the greatest differences evident at the higher levels of tallow. At these temperatures, the NMR values are higher than SFI and DSC solids for all compositions except 100% soybean oil at 70 F. The higher NMR results probably are due to lack of sample tempering. Any low melting components in a fat may crystallize on initial sample cooling but often will not recrystallize upon cooling after sample tempering. A sample of tempered fat and the same material untempered should have approximately the same amount of solids at the tempering temperature (80 F). At temperatures above 80 F, the untempered sample should have less solid fat than the tempered material. Low DSC values at 50, 70 and 80 F and with high tallow compositions may be caused by incomplete sample crystallization under DSC test conditions. DSC results are comparable with those of the other methods at 92 and 100 F for high tallow compositions. At lower levels of tallow, the DSC solids are less than those of the other methods at 92 and 100 F.

Blends of tallow and lard were then examined by the three methods. The results obtained on these blends are shown in Table III.

Differences between the results of the three methods are again obvious. NMR results are higher for most compositions up to the tempering temperature of 80 F. Differences between NMR and other methods at low temperatures are greater at higher concentrations of tallow. These differences should be reduced by tempering in the NMR method but the tempering effect would be influenced by oil composition. The smaller DSC values at low temperatures and high tallow compositions are probably influenced by incomplete crystallization.

Palm kernel oil and 72.0 IV soybean oil mixtures were compared next. The results are shown in Table IV.

The NMR levels at 50 F are higher than the other methods for all compositions. The effect of the tempering procedure to melt the low melting glycerides probably causes these differences. The DSC results are generally higher for the palm kernel oil-hydrogenated soybean oil blends than for the mixtures examined in Tables II and III. Two factors probably influence the DSC results shown in Table IV. First, the palm kernel oil has a high content of saturated fatty acids and glycerides of palm kernel oil and would have, as a consequence, higher heats of fusion than oils containing lesser amounts of saturated acids. Second, under the DSC test conditions, hydrogenated soybean oil apparently crystallizes to a greater degree than some of the other oils studied. The ease of hydrogenated soybean oil crystallization in the DSC method is also apparent from the DSC values obtained at low temperatures for 75% and 100% hydrogenated soybean oil compositions given in Table II.

Mixtures of safflower oil and 5.4 IV tallow were then examined by the SFI, DSC and NMR procedures. Results of the methods in Table V show that the NMR values are higher at low temperatures and lower at high temperatures than with the other methods.

The effects of tempering and incomplete crystallization are quite small for the safflower oil-tallow blends. The DSC response does not change between 90% and 100% tallow contents. Values for SFI could not be determined at tallow levels above 50%.

Data found for tallow-hydrogenated soybean oil, tallow-lard and palm kernel oil-hydrogenated soybean oil blends indicate that the amount of fat crystals developed is influenced by crystallization and tempering conditions used to form the fat crystals. The tempering conditions used in the AOCS SFI method were applied to the NMR method. The curves (Fig. 1) compare tempered and untempered NMR values on samples of lard and hydrogenated soybean oil.

The curves show significant differences between tem-

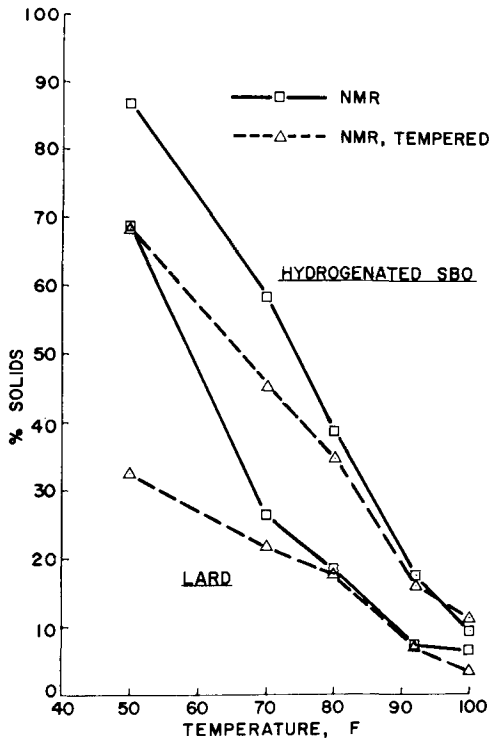

FIG. 1. Tempered and untempered NMR solids on lard and hydrogenated soybean oil.

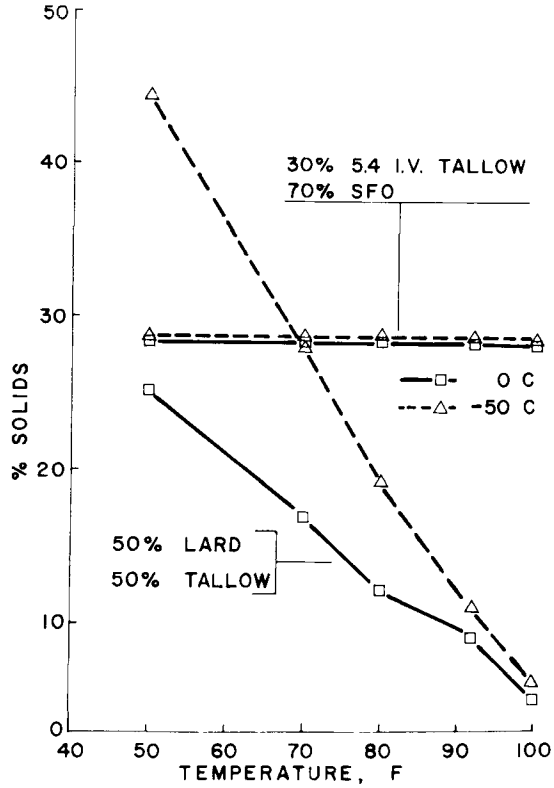

FIG. 2. Effect of cooling at 0 and -50 C on DSC solids.

pered and untempered samples at temperatures up to 80 F. Above this tempering point, the results are quite similar.

The effect of cooling temperatures on the DSC test is evaluated by comparing cooling at O and -50 C. The solids-temperature curves (Fig. 2) show that cooling at -50 C gave higher DSC response for a mixture of 50% lard and 50% tallow which indicates that this mixture was not completely solidified at 0 C.

DSC results on the easily crystallized mixture of 30% 5.4 IV tallow and 70% safflower oil show essentially no difference on the basis of cooling temperature.

The NMR and DSC data were examined statistically and the overall average standard deviation was 0.85 for the NMR method and 0.90 for the DSC method. SFI data were not evaluated statistically but precision information given in the AOCS procedure (1) indicates that SFI precision would be somewhat better than that found for the other procedures.

EVALUATION

The results of this work demonstrate the problems involved in obtaining exactly comparable values with the three solids measurement techniques. Differences in temperature equilibrium rates and in sample weights probably are involved in the variations observed.

The SFI method cooling time and temperature specifications combined with a larger sample weight probably do not allow complete crystallization of certain samples which have low melting components. The empirical nature of the SFI test leads one to expect that SFI values will not always be comparable to the results of the other methods.

In the sample tempering process used in the SFI and DSC methods, some low melting components are melted which do not recrystallize under conditions of the tests. The effect of tempering is to reduce the solids level below the tempering temperature. Sample tempering in the NMR method is expected to reduce differences among the methods at lower temperatures; however, this probably will not make the results of all methods exactly comparable because of differences in temperature equilibrium rates.

For some of the samples examined, particularly those with high amounts of tallow, higher DSC results at low temperatures should be obtained by use of -50 C as the cooling temperature. This cooling temperature will permit a more complete crystallization of the fat solids and should reduce differences found between DSC and the other methods. Again, differences probably will not be completely eliminated because of the problem of attaining temperature equilibrium in the SFI method.

At this time, the prospects seem remote for obtaining directly comparable solids results with the three techniques on a wide variety of fats and oils. It is worthwhile, therefore, to consider the merits of the instrumental NMR and DSC methods for solids measurement apart from the SFI method. The NMR and DSC methods do offer definite possibilities for improved characterization of the solid fat contents of fats and oils. Both methods are faster than the SFI method with the DSC technique possibly being fast enough for use as a control test in fat and oil processing. The DSC method also has the advantage of showing a continuous melting profile which can be used to determine the final melting transistion or melting point.

The SFI method has emerged as an accepted test primarily because of the work of an AOCS committee established to standardize the procedure. It is proposed that the NMR and DSC techniques be evaluated by a similar AOCS committee with the expectation that standardized tests using these techniques would be evolved to determine the solid fat content of fats and oils.

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REFERENCES

1. AOCS Tentative Method CD 10-57, Solids Fat Index.
2. Bosin, W.A., and R.A. Marmor, JAOCS 45:335-337 (1968).
3. Denison, Ruth C., and J.I. Justin, Presented at the AOCS Meeting, Philadelphia, October, 1966.
4. Bentz, A.P., and Barbara G. Breidenbach, JAOCS 46:60-63 (1969).
5. Miller, W.J., W.H. Koester and F.E. Freeberg, Ibid. 46:341-343 (1969).

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