Determination of the Solid Fat Content of Hard Confectionery Butters

J.C. VAN DEN ENDEN, J.B. ROSSELL[1], L.F. VERMAAS and D. WADDINGTON[2],
Unilever Research Laboratorium, Olivier van Noortlaan 120, postbus 114, Vlaardingen, The Netherlands

ABSTRACT

A method is described for the determination of the solid fat content in hard confectionery butters of the nonstabilized type, e.g., palm kernel sterine. The method is based on the technique of low-resolution pulsed nuclear magnetic resonance (pNMR) by means of which the solid fat content of a fat sample can be calculated directly from the relative intensity of signals arising from protons in both the liquid and solid phases. A measuring procedure is reported, based on the use of the Bruker Minispec p20i low-resolution pNMR spectrometer, and attention is drawn to the stabilization pretreatment to which the fat samples need to be subjected prior to measurement in the pNMR instrument. The entire procedure is straightforward to operate and ideally suited to the measurement of large numbers of samples. The relationship between the solids content (N-value) and dilatation (D-value) is discussed and an interconversion table is given. The accuracy and reproducibility of the method are indicated.

INTRODUCTION

The measurement of solid phase content in edible fats is of the utmost importance to the food industry. A number of methods for the determination of solids content in fats have been described, such as dye dilution (1), differential thermal analysis and differential scanning calorimetry (DTA an DSC) (2-4), various dilatometric methods (5-7), continuous wave, low-resolution nuclear magnetic resonance (CW-NMR) (8-11); and pulsed low-resolutuion nuclear magnetic resonance (pNMR) (12). Each of these techniques offers advantages and disadvantages.

The key difference between the thermal analysis and dilatometric techniques and the magnetic resonance approach lies in the fact that, in the first two techniques, the solid phase content is derived by inference using some related property. The magnetic resonance methods allow the observation of signals directly derived from solid or liquid fat (or both in the case of pNMR). This means that these NMR methods lead to results which are closer to the true solids content in the fat. The dye dilution method, which depends on the dilution of a marker by the liquid oil in the fat, can only be used with oils which are predominantly liquid and does not reveal the presence of oil occluded in the crystal interstices.

The DTA and DSC methods are generally imprecise for solids measurements and are unduly influenced by crystal defects, polymorphism and crystallization rate phenomena (13,14), and noncontinuous baselines (2). Since the specific heats of solid fat and liquid oil are different, the baselines before and after the melting peak can never be colinear. It is often not possible to determine the heats of fusion of the solid phase because the polymorphic forms present are unknown.

Dilatometry (5-7), which has become the most widespread technique to be used is empirical and there are several methods currently in use, each of which gives a different result. In principle, the dilatometry value (D-value) and the true solids content are related by the total melting dilatation (TMD) (15) but, because this varies among fats, confuion can arise if too great a reliance is placed on a comparison of D-values for different fats. Similarly, it cannot be assumed that D-values can be converted to true solids content by use of a single factor. The AOCS dilatation method (7) is officially not applicable to fats having a solid fat index (SFI) of greater than 50 at 10 C, which severely limits its reliable usage. This method can frequently lead to further confusion since it gives values which are often mistaken for true solids contents.

Continuous wave (low-resolution) NMR (9-11) leads to more meaningful results which have the added advantage of greater reproducibility. This technique depends on a comparison of signals arising from the protons of the liquid oil in the sample and that derived from a reference sample of a standardizing oil. However, at very low solids contents, the required result is derived from the small difference between two very large numbers, whereas at very high solids contents, the liquid signal is small and difficult to discriminate from the noise. At intermediate solids contents CW-NMR is satisfactory, but the relatively long period required for measurement necessitates thermostatic control of the sample holder during the measurement. This, in turn, leads to reduced operational flexibility (reduced throughput), and the possibility of accidental experimental error due to incorrectly correlated instrument and sample temperatures.

In contrast, it is felt that the present method of pNMR offers many advantages. It is faster than CW-NMR, does not need thermostating during measurement, and is more accurate at high and low solids content values. These techniques have been experimentally compared and reviewed by Walker and Bosin (16), and by van Putte et al. (17). Van Putte et al. concluded that pNMR offers the best method for solid phase determination, but decided that the fats need to be split into groups for the best accuracy.

Work has progressed within the Unilever laboratories on this topic, and it has been found to be convenient to split the fats into the same three groups as those chosen for dilatometric evaluations. These groupings are: group I—margarine fats and shortenings which are evaluated under the BSI system (5) by method Ib; group II—β' crystallizing, nonstabilized (18) confectionery fats, or hard butters, which are evaluated by method Ia; and group III—β' crystallizing, stabilized (18) confectionery fats such as cocoa butter, which are evaluated by method II. The IUPAC dilation procedure (6) is technically identical to the BSI system and uses the same groupings.

The terms "stabilized" and "nonstabilized" which have been used require clarification (18). A more accurate description of these two groups of confectionery fats would be "fats which require (or do not require) polymorphic stabilization" (1); but the classifications stabilized and nonstabilized are widely used and have become the accepted terms.

The pNMR technique for margarine fats has been developed and widely implemented within the Unilever labora-

[1]Formerly of Loders and Nucoline Limited, Cairn Mills, Silvertown, United Kingdom, and now at Food R.A., Randalls Road, Leatherhead.

[2]Now at Unilever Research Laboratory, Colworth House, Sharnbrook, Bedfordshire, United Kingdom. Please contact for further correspondence.

tories and factory quality control departments. It has been fully described and reported by Van den Enden et al. (19) in a paper which also describes the background to the topic and gives references to other work in this field.

It became appropriate to extend the application of pNMR to the more specialized fats used in the confectionery and allied trades, but problems were encountered which fell into two distinct areas, i.e., those associated with hard fats such as hydrogenated or fractionated lauric butters which crystallize in the β' polymorphic modification; (group II) and different problems associated with the 2-oleo disaturated fats, such as cocoa butter, which crystallize in the beta polymorphic modification (group III) (18). It turned out that the former of these was the easiest to solve and is the subject of this paper. Measurement of the solid content of fats such as cocoa butter by pNMR was a more difficult topic and is the subject of subsequent papers in this series. The successful outcome of a ring test, together with comparison measurements by CW-NMR showed the pNMR measurements are reliable.

Although it would be desirable for all who are concerned with the determination of solid fat content in confectionery fats to apply the same standardized method, it will take time for such a method to become generally accepted. Consequently, it was recognized at an early stage that it would be useful to produce conversion tables (at least for the most frequently used BSI/IUPAC dilatation procedures; the AOCS procedure is not applicable to these hard butters for the reasons stated) which would allow the interrelation of solids content measured by pNMR and dilatation (18,19). However, the dilatation conversion table established for margarine fats was shown to be inapplicable to hard butters, and it was realized that there are two reasons for this. First, these fats have different total melting dilatations compared to those of the predominantly softer oils used in margarine. This leads to slightly different relationships between dilatation and solids content for the two groups of fat. Second, further small differences result from the sample treatment involved in each case.

In dilatometry, it is convenient and practical to use a single dilatometer for each fat sample. This is stabilized at a series of temperatures during the dilatation measurements. The method is therefore described as a serial method. In the method commonly used in Europe (5,6), margarine fats are evaluated according to a long temperature range of e.g., 0, 10, 15, 20 C, whereas hard butters are evaluated by a short temperature range of, e.g., 0, 20, 25, 30 C. A consequence of the lack of stabilization at 10 and 15 C in the short range dilatation method is that different D-values are obtained at 20 C. In contrast, in pNMR it is convenient and practical to use subsamples, each of which is then stabilized in parallel at different temperatures. This method is described as a parallel method. The advantages of the parallel method are that any combination of temperatures can be used, and single, unambiguous, values are obtained. However, conversion of these unambiguous pNMR solids contents (N-values) into equivalent D-values requires both long- and short-range dilatation equivalents.

For these two reasons, it became important to establish two conversion tables, one for margarine fats (group I) and a second for nonstabilized confectionery fats (group II).

Fats were classified into the two groups (groups I and II) according to an easily remembered rule of thumb, i.e., that nonstabilized confectionery hard butters are fats which have over 25% solids at 20 C and less than 25% solids at 35 C, which do not need extended polymorphic stabilization, and which are not normally evaluated for solid fat content at temperatures below 20 C.

A range of 14 fats conforming to this definition were chosen and evaluated in duplicate by both dilatometry and pNMR. Statistical regression analysis of the resulting values led to the N-value to D-value conversion table presented in the final section of this paper. This table was then checked for accuracy by evaluation of a further 13 different confectionery fats and found to be of good reliability.

EXPERIMENTAL

Bruker Minispec p20i pulse NMR spectrometers were used at all sites, but some of the pNMR instruments had been modified slightly for the following reason. Work progressing on the development of methods for the evaluation of confectionery fats which crystallize in the β polymorphic modification had shown that magnetic saturation effects lead to incorrect results with trigger times of 5 sec or less. Some of the pNMR machines used in the present work were therefore adjusted to use the increased trigger time of 6 sec. A minor modification to the integrator circuitry within the instrument was then necessary in order to maintain optimal accuracy over this extended integration time (20). In order to retain the 6- sec measuring time used with margarine fats, and thus avoid the necessity for the thermostatic control of th sample during measurement, a single pulse is applied in this operational mode. This modified procedure leads to a slight reduction of instrumental accuracy, and hence an increase in the standard deviation for a series of fats, of from ca. 0.3% to ca. 0.4% solid, as mentioned earlier (19).

Fats were evaluated by the parallel procedure, essentially as described previously by van den Enden et al. (19), except that the temperatures used were 20, 25, 30, 32.5, 35, 37.5 and 40 C. (NOTE: while it has been shown (19) that introduction of lower temperature dilation measurements can change subsequent readings, the change is smaller at higher temperatures (e.g., about 1.2% at 20 C and 0.8% at 30 C). The introduction of the 32.5 and 37.5 C dilation measurements therefore gave no significant error in the 35 and 40 C readings, which were in any case quite small.)

All spectrometers were checked at least twice daily with calibration standards to ensure optimal accuracy and reliability. A constant f-factor was used throughout at each site in contrast to some earlier indications that this should be systematically changed (17,21), since experiments showed that systematic change of the f-factor could not be justified on the grounds of experimental accuracy.

The f-factor, which has been defined elsewhere (19), was not specifically selected and set on each Minispec but rather each instrument was calibrated using a series of stable reference standards whose solids content was accurately known. This procedure ensures that, despite small variations in f-factor among instruments, the reproducibility between sites was better than ± 0.3% solids over the solids content range. At any one site, the f-factor remains constant but variation of f-factor between instruments is usual since the f-factor value depends (in part) on the instrument. Unilever margarine factories have been successfully using this approach for calibration of their Minispec instruments for several years (19).

Dilatations were measured by the serial procedure in accordance with the method described in British Standard 684 (5), except that additional temperatures of 32.5 and 37.5 C were introduced. This did not alter the 35 C readings as the values were, in any case, quite small at this temperature (see notation in previous paragraph).

Typical fatty acid compositions of the commercially produced grades of fat used in the experimental work are shown in Table I, whereas physical properties are indicated in the subsequent tables. Fats 1-11 inclusive were used in the ring test, whereas the 14 fats corresponding to samples 1, 3 (2 different batches) 11, 12, 13, 14, 15 and 16 were

TABLE I

Typical Fatty Acid Compositions of Fat Grades Used in Experimental Work

Fatty acid	Trivial name	Sample nos. 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
		Weight percentages of fatty acid methyl esters																	
6:0	Caproic	–	0.1	tr[a]	0.6	–	tr	tr	–	tr	–	–	tr	0.1	0.1	0.1	0.1	tr	0.1
8:0	Caprylic	–	3.4	1.6	1.6	–	3.3	0.1	–	4.0	–	–	2.4	2.1	3.9	3.0	3.4	4.6	1.6
10:0	Capric	–	3.4	2.4	2.6	0.1	3.3	0.2	tr	3.7	–	0.1	3.0	2.9	4.8	3.2	3.3	3.5	2.0
12:0	Lauric	–	46.4	55.2	53.8	1.2	45.9	0.9	0.4	52.0	0.3	1.2	54.9	53.7	50.7	49.6	49.5	47.1	51.5
14:0	Myristic	0.6	15.5	24.1	21.6	1.0	13.3	2.8	0.3	20.0	0.2	1.2	21.4	22.1	23.2	16.9	16.5	14.9	30.2
14:1	(e.g., Myristoleic)	–	–	–	–	–	–	0.3	–	–	–	–	–	–	–	–	–	–	–
14:2		–	–	–	–	–	–	0.2	–	–	–	–	–	–	–	–	–	–	–
16:0	Palmitic	23.6	8.7	7.5	9.3	25.8	8.9	22.4	10.5	8.8	6.0	30.7	8.5	8.5	10.1	8.4	8.2	9.7	6.9
16:1	(e.g., Palmitoleic)	0.1	–	–	–	tr	–	3.2	–	–	–	–	–	–	–	–	–	–	–
16:2		–	–	–	–	–	–	1.7	–	–	–	–	–	–	–	–	–	–	–
18:0	Stearic	4.9	15.8	5.0	8.6	10.0	18.3	18.6	6.7	2.4	13.1	8.4	2.4	10.2	2.9	18.2	13.2	19.2	2.3
18:1	(e.g., Oleic)	65.5	6.8	4.2	1.8	58.0	6.8	44.3	73.0	7.5	70.2	54.7	6.4	0.1	3.5	0.4	5.6	1.0	4.5
18:2	(e.g., Linoleic)	5.0	–	–	–	3.3	–	2.7	8.8	1.4	3.4	3.3	0.8	–	0.7	–	–	–	0.8
18:3	(e.g., Linolenic)	–	–	–	–	0.2	–	–	–	–	–	tr	–	0.3	–	–	–	–	–
20:0	Arachidic	0.2	–	–	–	0.4	–	tr	0.3	0.0	2.6	0.5	0.1	–	0.1	0.2	0.2	–	–
20:1	(e.g., Gadoleic)	–	–	–	–	–	–	1.8	–	–	0.9	–	–	–	–	–	–	–	–
20:x	(Polyunsaturated)	–	–	–	–	–	–	0.4	–	–	22:0=1.2 21:1=1.9	–	–	–	–	–	–	–	–
Trans value (calculated as elaidic)		56.3	<5	<5	<5	48.2	<5	<5	69.1	<5	61.2	50.1	<5	<5	<5	<5	<5	<5	<5

[a]tr = trace.

TABLE II

***Ring Test* Results on 11 Fats Evaluated at Five Locations[a]**

Sample	Laboratory 1					Laboratory 2					Laboratory 3					Laboratory 4					Laboratory 5				
	Temperature (C)																								
	20	25	30	32.5	35	20	25	30	32.5	35	20	25	30	32.5	35	20	25	30	32.5	35	20	25	35	32.5	35
1	88.1	70.6	39.0	20.7	4.3	89.9	71.3	39.0	19.7	2.6	88.9	71.1	36.9	19.6	3.1	90.1	71.4	38.1	20.5	4.8	90.1	72.5	28.6	20.6	3.3
2	70.1	40.4	11.8	3.4	1.7	69.2	37.7	10.9	3.1	0.8	70.9	40.1	11.0	4.0	2.0	71.0	39.8	11.6	3.9	2.2	71.3	40.8	11.6	4.0	1.8
3	89.4	72.5	29.2	0.8	0.0	89.6	72.6	28.5	-0.1	-0.2	88.9	72.7	28.2	0.1	-0.5	90.4	72.5	28.9	1.2	-0.3	90.6	73.9	28.7	0.1	-0.3
4	94.0	80.6	38.5	11.5	2.0	94.0	80.3	37.2	11.3	2.7	93.3	80.1	36.7	12.2	3.5	93.6	80.5	38.1	12.6	3.8	94.2	81.1	36.5	12.0	3.4
5	58.3	42.3	24.3	15.9	7.1	58.2	41.5	23.3	14.8	7.7	58.1	41.4	22.1	14.2	7.2	59.0	41.5	23.6	15.5	8.2	59.6	42.7	23.6	15.2	8.2
6	60.6	32.3	10.3	6.2	3.4	58.9	29.3	8.6	4.8	3.7	59.3	30.4	8.7	4.9	3.1	60.5	30.6	9.4	5.6	3.0	60.8	31.5	9.3	5.0	2.7
7	18.8	12.4	7.3	4.8	3.4	18.0	11.3	7.3	5.0	4.0	18.1	11.3	7.2	5.3	3.4	18.6	12.3	7.5	5.5	3.8	19.9	12.2	7.3	5.8	4.2
8	47.4	29.0	10.2	2.9	-0.3	46.0	28.2	10.3	3.6	0.5	46.0	27.9	9.9	3.6	0.1	47.1	27.4	9.4	2.8	0.3	47.9	29.0	10.4	2.9	-0.1
9	63.4	36.7	-0.6	-0.6	0.5	61.9	34.5	-1.3	-0.6	-0.9	63.0	35.6	0.4	0.3	0.0	63.9	34.8	0.3	0.0	-0.2	64.7	36.8	-0.4	0.0	0.0
10	64.1	46.4	26.6	17.3	10.4	63.8	44.9	24.6	17.0	9.5	63.7	44.7	24.4	16.5	9.1	64.3	44.5	24.8	16.7	9.8	65.1	46.2	25.5	16.2	9.6
11	71.7	55.2	35.5	25.2	15.6	71.9	54.9	34.6	24.2	15.2	71.4	55.3	34.5	24.5	15.0	72.1	54.8	34.8	25.5	16.1	73.1	56.9	35.8	24.7	15.4
	Mean internal precision 0.5% solids					Mean internal precision 0.5% solids					Mean internal precision 0.4% solids					Mean internal precision 0.3% solids					Mean internal precision 0.3% solids				

[a]Mean values of duplicate results at each site.

used to construct the conversion table. The table was subsequently checked with five different commercially produced fats corresponding in composition to samples, 10, 11 (2 different samples), 17 and 18, together with samples of coconut oil, palm kernel oil, hydrogenated palm kernel oil (4 different samples), hydrogenated groundnut oil, and a hydrogenated liquid oil blend, giving 13 samples in all. For the ring test, duplicate samples of each fat were issued under different codings, whereas for the conversion table, the fats were analyzed in duplicate by both dilatometry and pNMR at a single location.

Thermometers used in thermostatic baths were carefully checked against officially certificated thermometers. Bath temperatures were checked regularly to ensure accuracy at all stages and were controlled to ± 0.1 C.

RESULTS

Collaborative Study

Twenty-two coded tins containing duplicate samples of each of the fats 1-11 inclusive shown in Table I were issued to five Unilever laboratories in Switzerland (1), The Netherlands (2), and the United Kingdom (2). The solid fat content was measured by pNMR at each location according to the method described earlier by Van den Enden et al. (19), except that the short temperature range was used, and that some instruments had been modified to give a single, 6-sec pulse, as described earlier. Samples were unthermostated during the 6-sec measuring time.

Results of the mean value obtained for each fat at each location are shown in Table II. These results were subjected to statistical analysis which gave a reproducibility of 0.7% solids. This standard deviation should be used when two single measurements from two different laboratories are compared. All different sources of variability are included in this value, i.e., variation due to the spectrometer, the ancillary equipment (e.g., thermostat baths) and possible variations in procedure. The mean internal precision of the laboratories was 0.4% solids ranging from 0.3 to 0.5% solids.

For comparison, the ring test carried out on the determination of the N-values of margarine fats on unmodified instruments showed a mean internal laboratory precision of 0.3% solids (19).

The reduced accuracy in the present work is probably due to the use of some of the instruments in the modified operating mode, an effect which is a direct consequence of the reduced number of individual measurements taken by the instrument during the 6-sec measuring period. It can therefore be alleviated by making three separate determinations at each temperature. No such efforts to increase the overall accuracy were made in the present work. (NOTE: Three determinations on the same sample would extend the measuring time to 18 sec and lead to temperature drift.)

The clear conclusion of this ring test is that the accuracy of the solid phase determinations is fully acceptable, and that measurement with three 2-sec pulses, or one 6-sec pulse, makes little difference to the precision of the method.

N-Value to Dilatation Conversion Table

The background and theoretical concepts underlying the preparation of N-value to D-value conversion tables have been discussed by Van den Enden et al. (19), and the same general concepts apply to the present conversion table for hard butters. Fourteen fats, having the previously indicated compositions, were evaluated in duplicate in one laboratory by both dilatometry and pNMR. These results were subjected to statistical analysis in much the same way as described previously (19), leading to the conversion table shown in Table III. It should be noted, as with the earlier table (19), that the correct use of this table is subject to the following restrictions.

(a) The table is valid for nonstabilized confectionery butters falling within the definition that they should have N20 values of over 25; N35 values of less than 25; should crystallize in the β' polymorphic form, and should (unlike cocoa butter) not need extended polymorphic stabilization.

(b) The dilatation values derived from this conversion table correspond to those which would be obtained by application of the short temperature range method in BS 684 (5) Section 1.12, Method 1 (a).

(c) The conversion table is only accurate for the ranges of values given. Extrapolation outside these ranges will lead to increasingly large conversion errors. (N-Values measured outside the ranges given in the table will, of course, still accord to the normal degree of accuracy, but any conversion of these N-values into dilatations will be erroneous. This normal degree of accuracy is much lower with N-values above 94% due to nonlinearity of the spectrometer at N-values in excess of 94.)

(d) The standard deviation of the dilatation values after conversion, averaged over all temperatures, is 29 dilatation units (mm^3/25 g). The magnitude of this standard deviation is mainly caused by differences in the total melting dilatation between different fats, but also includes other sources of experimental error, as with the ring test. This standard deviation is almost equal to the standard deviation of a single dilatation determination and is therefore acceptable for the conversion calculation.

(e) This conversion table should be used for quality control and research or development purposes alike. An advantage of using a single table for all users is that conversion is unambiguous, but it is known that some fats fall in a gray area where they may be alternatively described as margarine fats or confectionery hard butters. When dilatations derived from N-values are quoted, the table used for the conversion should also be given. Wherever possible, the original N-value should also be given.

(f) In cases where dilatation values of optimal reliability are needed, e.g., in connection with commercial contracts which specify properties in terms of dilatations, then actual dilatation measurements should be made.

Check on the Accuracy of Conversion

The number of fats used for the construction of the conversion table had been deliberately restricted to 14 in order to facilitate laboratory analytical requirements and planning. This enabled more systematic evaluation of the fat samples and helped to reduce accidental experimental errors, for example, in maintaining thermostat bath temperatures or any variation caused by deterioration of the fats during any lengthy storage. Nevertheless, this number of fats is small, much smaller than that used for the production of the margarine fats conversion table in which 46 different fats were used, and it was therefore appropriate to confirm the accuracy of the conversion table by the evaluation of a further batch of 13 different confectionery butters. Two of these corresponded to fats used for the construction of the table in that they were different batches of the same commercially produced fat grade.

The results of this evaluation are shown in Table IV. At each temperature, the N-value recorded has been converted into an equivalent D-value by use of the conversion table given as Table III (listed in the third column under the heading "Table D"). These latter values have been subtracted from an actually determined dilatation to give the differences listed in the fourth column. The values recorded

TABLE III

Conversion Table Pulse NMR Parallel versus Short-Range Dilatation Serial (Unstabilized Confectionery Fats)

Solids (%)	D 20	D 25	D 30	D 32.5	D 35	D 37.5	D 40
1			50	55	55	55	55
2			80	80	85	85	85
3			105	110	110	115	115
4			130	135	140	145	145
5			160	165	170	175	175
6			185	190	195	200	205
7			210	220	225	230	235
8			235	245	255	260	265
9			265	270	280	290	295
10			290	300	310	315	325
11		290	315	325	335	345	350
12		315	340	350	365	370	380
13		335	365	380	390	400	410
14		360	390	405	415	450	455
15		385	415	430	445	455	465
16		405	440	455	470	480	495
17		430	465	480	495	510	
18		455	490	510	525	535	
19		475	515	535	550	565	
20		500	540	560	575	590	
21		520	565	585	600		
22		545	590	610	625		
24		590	640	660	680		
25	550	610	660	685	705		
26	570	635	685	710			
27	590	655	710	730			
28	610	680	735	755			
29	635	700	755	780			
30	655	720	780	805			
31	675	745	805				
32	695	765	825				
33	715	785	850				
34	735	810	870				
35	750	830	895				
36	770	850	920				
37	790	875	940				
38	810	895	965				
39	830	915	985				
40	850	935	1005				
41	870	955	1030				
42	890	980	1050				
43	910	1000	1075				
44	930	1020	1095				
45	950	1040	1115				
46	960	1060	1140				
47	980	1080	1160				
48	1005	1100	1180				

Solids (%)	D 20	D 25	D 30	D 32.5	D 35	D 37.5	D 40
49	1025	1120	1200				
50	1045	1140	1225				
51	1065	1160					
52	1080	1185					
53	1100	1200					
54	1120	1220					
55	1140	1240					
56	1155	1260					
57	1175	1280					
58	1195	1300					
59	1215	1320					
60	1230	1340					
61	1250	1360					
62	1270	1380					
63	1285	1395					
64	1305	1415					
65	1325	1435					
66	1340	1456					
67	1360	1475					
68	1380	1490					
69	1395	1510					
70	1415	1530					
71	1430	1545					
72	1450	1565					
73	1470	1585					
75	1485	1600					
75	1505	1620					
76	1520	1640					
77	1540	1655					
78	1555	1675					
79	1575	1690					
80	1590	1710					
81	1610	1730					
82	1625	1745					
83	1645	1765					
84	1660	1780					
85	1680	1800					
86	1695	1815					
87	1715	1830					
88	1730	1850					
89	1750	1865					
90	1765	1885					
91	1780						
92	1800						
93	1815						
94	1835						

are within normal experimental error, bearing in mind that they contain all forms of error including, of course, errors contained in the actual dilatation value. It can therefore be concluded that the conversion table is fully satisfactory for the comparison of dilatometry and pNMR results.

DISCUSSION

It has been shown that the pNMR method for the evaluation of nonstabilized confectionery fats is fully reliable, giving repeatable and reproducible results in a ring test spanning five laboratories in three European countries. Some of the pNMR instruments had been modified slightly for evaluation of stabilized confectionery fats, but notwithstanding this modified procedure, the ring test showed good overall reproducibility of 0.7% solids. The mean internal precision of the laboratories was 0.4%, ranging from 0.3 to 0.5% solids.

The method described is therefore, in our view, preferred to those NMR techniques described elsewhere which are, in general, less well documented. Johanson, of Karlshamns Oljefabriker, Sweden (22), for example, describes a method in which five 2-sec pulses are used in a measuring time of 10 sec. Our experience has shown that measuring times of 10 sec are associated with errors due to temperature drift and changes in the actual solids contents, especially at temperatures significantly different from ambient, unless the sample is thermostated during the measurement. The reduced operational flexibility of a method which uses a thermostated instrument, and the added risk of accidental confusion of sample vs apparatus temperature, coupled with the technical difficulty of thermostating the instrument at 0, 10 or 15 C, for measurements on margarine fats and yet preventing condensation of atmospheric moisture in the instrument, has led us to adopt a systematic, nonthermostated measurement approach for the evaluation of all fats. The advantages of having related procedures for all three fat groupings and avoiding the need for a thermostat far outweigh the minor advantage of increased instrumental accuracy given by longer measuring times.

Several techniques which use comparisons of the NMR liquid signal have been suggested. Some of these use CW-NMR, whereas others use pNMR methodology. In both cases, the measurements suffer from somewhat reduced

TABLE IV

Comparison of N-Values, Dilatation Values and Values Taken from Table 3, for Various Confectionery Butters

Sample[a]	Temperature (C)																							
	20				25				30				32.5				35				37.5				40			
	N	D	Table D	diff	N	D	Table D	diff	N	D	Table D	diff	N	D	Table D	diff	N	D	Table D	diff	N	D	Table D	diff	N	D	Table D	diff
1	75.7	1555	1516	+39	59.8	1395	1336	+59	39.4	1025	993	+32	27.5	775	743	+32	16.7	510	488	+22	7.2	240	236	+4	0.3	25	17	+8
2	77.5	1595	1548	+47	61.7	1435	1374	-61	41.4	1050	1038	+12	28.8	785	775	+10	16.9	510	492	+18	7.1	225	233	-8	0.2	5	11	-6
3	81.3	1580	1615	-35	54.7	1175	1234	+59	26.1	660	688	-28	14.2	420	410	+10	8.8	270	275	-5	5.9	180	197	-17	2.6	100	103	-3
4	82.3	1615	1631	-16	57.1	1255	1282	-27	39.5	740	768	-28	17.9	500	507	-7	12.3	360	373	-13	9.2	275	295	-20	6.0	200	205	-5
5	84.4	1640	1668	-28	60.7	1310	1354	-44	33.0	795	850	-55	20.4	560	570	-10	13.0	370	390	-20	9.2	270	295	-25	6.4	195	217	-22
6	84.6	1660	1572	-12	63.1	1365	1397	-32	35.6	865	910	-45	23.4	630	645	-15	16.8	470	490	-20	13.0	380	400	-20	9.6	305	313	-8
7	83.5	1650	1653	-3	63.7	1375	1409	-34	39.4	970	993	-23	28.6	755	770	-15	23.6	650	668	-18	19.6	565	580	-15	15.9	480	492	-12
8	65.4	1350	1331	+19	45.6	1070	1052	+18	23.7	585	633	-48	13.3	340	388	-48	5.5	145	183	-38	0.3	20	17	+3	—	—	—	—
9	72.5	1490	1460	+30	56.6	1290	1272	+18	36.3	900	926	-26	25.8	650	705	-55	16.1	410	473	-63	8.0	220	260	-40	3.7	100	136	-36
11	94.3	1880	1841	+39	84.5	1785	1790	-5	36.8	945	936	+9	9.2	270	276	-6	3.5	115	125	-10	—	—	—	—	—	—	—	—
12	36.3	815	776	+39	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
13	44.3	940	936	+4	20.4	495	508	-13	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—

[a]1 and 2 correspond to sample 11, Table I; 3,4,5 and 6 = hydrogenated palm kernel oils; 7 = sample 17, Table I; 8 = hydrogenated groundnut oil; 9 = hydrogenated blend groundnut and soybean oils; 10 corresponds to sample 10, Table I; 11 = sample 18, Table I; 12 = coconut oil; 13 = palm kernel oil.

accuracy at both high and low solids contents compared to the present technique in which signals derived from both solid and liquid phases of the same sample are simultaneously measured. A criticism of the method may be that a constant f-factor is used throughout, and that this leads to errors of varying magnitude with different fats. However, our results have shown that these errors are quite small, and are within the normal limits of experimental accuracy.

New pNMR measurements will, of course, need to be related to earlier factory and laboratory information obtained using a traditional dilatation technique, and for this reason, a conversion table was prepared and shown to be within the normal requirements of experimental accuracy. It can be used only for conversion into D-values corresponding to the BSI/IUPAC method of determination (5,6).

Other methods, such as that used by the American Oil Chemists' Society (AOCS), give values expressed in different units using different experimental techniques. However, it has been considered acceptable in the past (as a rough approximation) to divide the BSI/IUPAC D-value by a factor of 25 to give an estimate of the AOCS solid fat index (SFI). This is not an exact procedure, but it will undoubtedly be found preferable to a simple interchange of SFI and N-values, as here, very great errors could be introduced. SFI of nonstabilized confectionery fats do not range from 0 to 100, expressing the true solid content of a fat, but instead range from 0 to about 80. Partly for this reason, the official AOCS method is only recommended for use with fats having SFI of less than 50 at 10 C.

It is hoped that all those working in the oils and fats field will adopt approaches such as the pNMR method which will give values very close to the true solids contents, and that conversion tables will no longer be necessary.

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Cyclopropenoid Fatty Acids in *Sterculia colorata* Seed Oil

C.D. DAULATABAD and **R.F. ANKALGI**, Department of Chemistry, Karnatak University, Dharwad-580 003, India.

ABSTRACT

Seed oil of *Sterculia colorata* is found to contain the following acids (wt %): sterculic (4.9%), malvalic (3.2%), myristic (0.3%), palmitic (29.4%), stearic (1.7%), oleic (56.6%), and linoleic (3.9%). The co-occurrence of malvalic and sterculic acids was established by gas liquid chromatography of the silver nitrate methanol-treated esters using *S. foetida* esters as reference standard.

INTRODUCTION

Sterculia colorata, Roxb, is a large tree with ash-colored bark. It has crowded leaves at the ends of the branches. The flowers are about 1 in. long and appear before the leaves. The tree is found throughout the Konkan and Deccan forests (1).

Although the fatty acid composition of some *Sterculia* oils have been determined (2), this paper contains the first report of fatty acid composition of *S. colorata* seed oil.

EXPERIMENTAL

The methyl esters were prepared (3) from *S. colorata* seed oil in the same way as for other *Sterculia* oils (2). Gas liquid chromatographic (GLC) analysis was done using a Hewlett-Packard Model 5730A with automatic integrator. The GLC unit was provided with flame ionization detector and 1.77 m x ¼ in. polyester column (polyethylene glycol, 5% succinate on Chromosorb W, 45-60 mesh). The temperatures at the injection port, detector block and column were 250, 300 and 220 C, respectively. The flow rate of nitrogen was 10-15 mL/min. The digital integrator calculated to obtain the peak area percentage. *S. foetida* seeds were analyzed for reference.

RESULTS AND DISCUSSION

The seed oil nD^{20} 1.4737, obtained from *S. colorata* seeds in 20.7% yield, contained 1.5% unsaponifiable matter. It responded to the Halphen test (4), indicating the presence of a cyclopropenoid functional group. The oil showed the typical nuclear magnetic resonance (NMR) signal at 9.2T for cyclopropene hydrogens and both the oil and the methyl esters of the oil had the characteristic infrared absorption at 1010 cm^{-1}. The quantitation of total cyclopropenoid fatty acids by the HBr titration method (5) indicated the presence of 8.6% by wt of cyclopropenoid acids.

The malvalate (3.2%) and sterculate (4.9%) were found by GLC analysis of the silver nitrate methanol-treated esters from *S. colorata* oil using the corresponding esters from *S. foetida* oil to identify the peaks. The major methyl esters present were oleate (56.6%) and palmitate (29.4%). Minor methyl esters detected were linoleate (3.9%), stearate (1.7%), and myristate (0.3%). The 8.1% total cyclopropenoid acids by GLC is in good agreement with HBr titration determination.

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ERRATUM

In the article "Measurement of Lipase Activity in Single Grains of Oat (*Avena sativa L.*)" appearing in the August issue of *JAOCS* (Sahasrabudhe 59: 354 [1982]), the following error was printed: under Results and Discussion, paragraph 2, the second line should read "16 hr after imbibition of buffer" and not "16 hr after inhibition of buffer."