COMPARISON OF PALM KERNEL STEARIN SFC MEASUREMENTS AT 30°C BY WIDELINE AND PULSE NMR

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The solid fat content (SFC) of palm kernel stearin was measured using both wideline and pulse nuclear magnetic resonance (NMR) spectrometers. For pulse NMR both the Direct Display Method and the Indirect Calculation Method were applied. The results obtained by the two methods showed large discrepancies at 30°C. The Direct Display Method consistently gave significantly lower values at the critical temperature of 30°C than did the Indirect Calculation Method, while the latter gave results comparable to those by the wideline NMR Method. There were no significant differences at other temperatures. It is recommended that either the Indirect Calculation Method of pulse NMR or wideline NMR be used in the measurement of the SFC of palm kernel stearin.

INTRODUCTION

Palm kernel stearin is an important material for producing cocoa butter substitutes. The solid fat content (SFC) profile of palm kernel stearin is an essential part of its commercial trading specifications (*Table 1*). It was brought to our attention by some of the producers that the SFC values obtained by pulse NMR were sometimes significantly lower than those determined by wideline NMR at the critical temperature of 30°C. There were, however, no significant differences at other temperatures.

SFC measurement by NMR has been in use since the 60s (Boisin and Marmor, 1968; Haighton *et al.*, 1971; Jacobsberg and Oh, 1976) and both wideline and pulse NMR are now widely used in the oils and fats industry in

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TABLE 1.
SOME COMMERCIAL SPECIFICATIONS OF PALM KERNEL STEARIN

		Specifications	
	(1)	**(2)**	**(3)**
Temperature (°C)		SFC (%)	
10	N.S.	N.S.	85-95
20	78 min	76 min	75-85
25	62 min	60 min	N.S.
30	29 min	21 min	30-40
35	2 max	1 max	1 max
		Iodine Value	
	7.0 max	8.5 max	6.0-8.0

Sources: (1) and (2) : Intercontinental Specialty Fats Sdn. Bhd. (3): Socoil Corporation Bhd.
N.S. = Not specified.

many countries (Timms, 1985). In 1986 Waddington gave a comprehensive treatment of the subject with an extensive list of references.

In the case of pulse NMR, there are two methods of measurement, the commonly used Direct Display Method, whereby the results are directly displayed on the computation unit, and the less common Indirect Calculation Method, whereby they are calculated from the liquid signal readings of the sample and reference. The Direct Display Method is based on signal readings of both the solid and the liquid protons and a correction factor (normally known as the f-factor) is required to correct for the dead time of the instrument in the measurement of the solid signals. An assumption is made in the pulse NMR Direct Display Method, *i.e.* that the f-factor used is suitable for the samples measured. However the f-factor is not the same for all samples at all the temperatures (van Putte, 1975; Waddington, 1986). The Indirect Calculation Method, on the other hand, does not make use of the f-factor because only the liquid signals of the samples are measured. This procedure is based on the same principle as the method of wideline NMR.

The present study was carried out to investigate the discrepancy in values of SFC at 30°C obtained by the two different NMR spectrometers under various conditions of measurement.

EXPERIMENTAL

A Bruker pulse NMR model PC 120/125/10 RTS was used, with a 10 mm routine temperature sample probe (PC PH20/10RTS-G25) and a variable temperature sample probe of the same diameter (PC PH20/10VTS) for the Direct Display Method. Using the factory-supplied calibration standards of 0%, 31.5% and 73.8% solids, the f-factor was found to be 1.12 and 1.25 for the routine temperature sample probe and the variable temperature sample probe respectively. The three standards were supplied in sealed NMR tubes and these are applicable only with the Bruker pulse NMR spectrometer.

A Newport Mark IIIA wideline NMR was also used. The instrument was set at: Gate-width 1.5 Gauss, RF Level 45 micro Amp, AF Gain 375 units and Integration Time 32 s.

Two refined and five crude commercial palm kernel stearin samples were studied. A set of tristearin-triolein mixtures with known amounts of solids was also prepared. The parallel (direct) tempering procedure (Oh, 1978) was followed. In this method the samples were melted at 70°C for 30 min, chilled at 0°C for 90 min and tempered at the measuring temperature(s) for 30 min prior to signal measurement. Depending on the different measuring temperatures required, a number of tubes were prepared for each sample and one tube was used for each temperature. This is the Standard PORIM Test Method and it is similar to the IUPAC SFC determination by the NMR Method 2.150 (Paquot and Hautfenne, 1987). The main difference is that the samples are kept for 90 min at 0°C in the PORIM Method as compared with 60 min at 0°C in IUPAC Method. The PORIM tempering procedure was adopted after detailed study (Oh and Berger, 1983) which revealed that 60 min of tempering at 0°C was not sufficient for palm products. The PORIM procedure is the same as that used by Jacobsberg and Oh in 1976 and it is in fact the same as the IUPAC tempering procedure for dilatation Method 2.141 (Paquot and Hautfenne, 1987). Hence in this study the palm kernel stearin samples were melted at 70°C for 30 min, chilled at 0°C for 90 min and tempered at 30 min before measurement.

Tristearin-triolein mixtures were melted at 80°C, tempered at 70°C for 30 min and then kept overnight at 30°C.

Four procedures of measurement were carried out with pulse NMR. These were: P1, by the Direct Display Method using the variable temperature sample probe with the probe-head kept at 40°C (the normal pulse NMR setting) P2, as in P1 but with the probe-head maintained at 30°C, by an external water circulating bath; P3, by the Direct Display Method using the routine temperature sample probe with the probe-head kept at the usual 40°C without external circulating water, and P4, as in P3 but by the Indirect Calculation Method. For palm kernel stearin samples, only procedures P3 and P4 were followed.

RESULTS AND DISCUSSION

In the Direct Display Method of pulse NMR the SFC values were shown directly on the digital display of the spectrometer. In the Indirect Calculation Method for both the pulse NMR and the wideline NMR, the SFC values were obtained by calculation according to the following equation:

$$\text{SFC } (\%) = 100\ (1 - R_{70}S_T/R_TS_{70})$$

where R_{70} is the signal of reference (winterized triolein) at 70°C; R_T is the signal of reference at the measuring temperature T°C; S_{70} is the signal of the sample at 70°C and S_T is the signal of the sample at the same measuring temperature, T°C.

As can be seen from *Table 1* palm kernel stearin melts sharply between 25°C and 35°C. Therefore, it was first considered that the lower values of SFC obtained by pulse NMR could be due to the use of the routine temperature sample probe which was fixed at the relatively high temperature of 40°C. The circulating water did not interfere with the measurement of the variable temperature probe-head and the results of procedures P1 and P2 (*Table 2*) showed that the effect of probe-head temperature was negligible.

Tristearin does not dissolve in triolein (Rossell, 1967) and the two do not form eutectic mixtures in the temperature range of interest. Mixtures of them may be used as standards for SFC measurement by NMR (Oh and Berger, 1983). The SFC values of the mixtures as determined by pulse NMR (Procedures P1 and P2) were consistently lower at both probe-head temperatures (40°C and 30°C) than the amounts of solid actually present (*Table 2*). Similar low SFC values were obtained in procedure P3. In all the three procedures the results were directly displayed. Since the displays made use of the correction f-factor to compensate for the dead-time of the instrument, the results suggested that the low SFC values obtained were due to the procedure of measurement and not to the intrinsic properties of the samples. This was clearly demonstrated to be the case by the results from the same instrument using procedure P4, which did not make use of the f-factor. The SFC values from both procedure P4 of pulse NMR and from wideline NMR were close to the actual amounts of solid present in the mixtures.

The SFC of the palm kernel stearin samples was subsequently measured by wideline NMR and by procedures P3 and P4 of pulse NMR. The Direct Display Method (procedure P3) of pulse NMR again gave lower SFC values at 30°C, but the results (*Table 3*) showed that there were no significant differences between wideline NMR and the Indirect Calculation Method (procedure P4) of pulse NMR. Hence the results showed that the three factor-supplied sealed calibration standards set an f-

TABLE 2.
SFC (%) OF MIXTURES OF TRISTEARIN IN TRIOLEIN BY PULSE AND WIDELINE NMR AT 30°C

	Pulse NMR				**Wideline NMR**
Probe-head	PC PH20/10VTS (Variable Temp)		PC PH20/10RTS-G25 (Routine Temp)		
Method	Direct Display	Direct Display	Direct Display	Indirect Calculation	
Procedure	P1	P2	P3	P4	
Probe-head temperature (°C)	40	30	40	40	30
Samples (solid %)					
A : Mixtures (% stearin)					
5	4.7	4.0	2.8	3.8	5.3
10	8.1	6.7	6.6	8.9	10.8
20	15.3	15.2	15.4	18.6	21.1
31.5	25.9	24.3	23.4	29.7	33.0
40	33.7	33.1	31.0	39.4	41.8
60	54.0	53.8	54.4	60.7	61.8
73.8	68.9	69.1	69.6	74.5	74.5
80	75.7	76.3	76.2	80.7	80.8
100	97.1	98.8	98.9	98.9	98.0
B: factory standards					
0	0.2	0.1	0.2	N.A.	N.A.
31.5	31.3	31.6	31.4	N.A.	N.A.
73.8	72.3	73.4	73.5	N.A	N.A.

Note: N.A. = Not applicable

TABLE 3.
SFC (%) OF PALM KERNEL STEARIN BY PULSE AND WIDELINE NMR AT 30°C

Method Procedure		Pulse NMR Direct Display P3	Pulse NMR Indirect Calculation P4	Wideline NMR
Samples[a]				
2258 R	(1)	24.1	27.4	28.3
	(2)	23.6	26.6	26.8
	(3)	24.7	25.9	26.9
Mean		24.1	26.6	27.3
2259 R	(1)	23.4	26.0	25.7
	(2)	23.8	26.1	25.4
	(3)	22.7	26.9	27.4
Mean		23.3	26.3	26.2
2260 C	(1)	22.8	26.0	25.7
	(2)	21.8	25.3	24.8
	(3)	23.0	25.1	24.5
Mean		22.5	25.5	25.0
2105 C	(1)	21.8	28.9	28.6
	(2)	21.5	28.7	27.0
	(3)	23.1	28.2	26.4
Mean		22.1	28.6	27.3
2265 C	(1)	24.3	30.1	27.8
	(2)	24.4	30.8	27.0
	(3)	25.0	31.0	30.6
Mean		24.6	30.6	28.5
2077 C	(1)	24.5	30.2	29.6
	(2)	25.2	30.0	28.4
	(3)	24.4	30.3	29.1
Mean		24.7	30.2	29.0
2062 C	(1)	26.5	33.6	33.1
	(2)	28.6	36.2	34.9
	(3)	27.2	33.6	34.6
Mean		27.4	34.5	34.2

[a] Note: C = crude, R = refined

factor which was suitable for routine use, but not for palm kernel stearin samples at 30°C. The Direct Display Method of pulse NMR was thus not appropriate. Either the wideline NMR method or the Indirect Calculation Method (Procedure P4) of pulse NMR should be used for measurement of the SFC of palm kernel stearin.

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REFERENCES

BOISIN, W A and MARMOR, R A (1968). The Determination of the Solids Contents of Fats and Oils by NMR. *J. Amer. Oil Chem. Soc. 45,* 335-337.

HAIGHTON, A J; VERMAAS, L F and DEN HOLLANDER, C (1971). Determination of the Solid-Liquid Ratio of Fats by Wideline NMR. *J. Amer. Oil Chem. Soc. 48,* 7-9.

JACOBSBERG, B and OH, F C H (1976). Studies in Palm Oil Crystallisation. *J. Amer. Oil Chem. Soc. 53,* 609-617.

OH, F C H (1978). Pulsed NMR for the determination of solid fat content in palm oil. *Proceedings of Seminar on Chemical Analysis: Malaysian requirements.* Organized and published by Institut Kimia Malaysia (Malaysian Institute of Chemistry), Kuala Lumpur, 1978, 137.

OH, F C H and BERGER, K G (1983). Determination of Solid Fat Content of Palm Oil by Wideline NMR. *The Palm Oil Product Technology in the Eighties.* E Pushparajah and M Rajadurai (eds.), Kuala Lumpur: Incorporated Society of Planters, p. 383.

PAQUOT, C and HAUTFENNE, A (1987). *Standard Methods for the Analysis of Oils, Fats and Derivatives.* 7th Revised and Enlarged Edition. Oxford: Blackwell Scientific Publications.

van PUTTE, K (1975). Pulsed NMR as a Routine Method in the Fat and Margarine Industry I, II and III. *Bruker Minispec Technical Bulletin.* Bruker Analytische Messtechnik GmbH.

ROSSELL, J B (1967). Phase diagrams of triglyceride systems. *Advances in Lipid Research Vol. 5,* 353-408.

TIMMS, R E (1985). Physical Properties of Oils and Mixtures of Oils. *J. Amer. Oil Chem. Soc. 62,* 241-248.

WADDINGTON, D (1986). Applications of Wide-line Nuclear Magnetic Resonance in the Oils and Fats Industry. *In Analysis of Oils and Fats.* R J Hamilton and J B Rossell (eds.), London and New York: Elsevier Applied Science Publishers.