Wide-Line NMR for Product and Process Control in Fat Industries[1]

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ABSTRACT

A modified method is described for the determination of the content of solid phase in fats at various temperatures using a Varian PA-7 wide line NMR instrument with temperature accessory. To avoid variations in instrument sensitivity a liquid soybean oil was used as reference. There was no need for corrections depending on the IV of the fat or the temperature. The optimal instrument settings were determined and the importance of a standardized temperature conditioning of the sample was confirmed. With the observance of proper conditions a standard deviation of 0.7% solid phase was obtained. Using this method a large number of samples can be examined with only a reasonable amount of work, but there is an increased demand for faster and more exact temperature conditioning of the samples, better stability and easier handling to fit more routine conditions. With these improvements the NMR method does offer some advantages for product control over solid fat index. However, for the time being the NMR method cannot be used for process control of hydrogenation because the need to condition the sample does not permit the determination of the result in less than 1 hr. On the other hand, a direct measurement of fat content of press-meal gave a standard deviation (1.3% fat) too large for satisfactory production control.

INTRODUCTION

Since Chapman and co-workers (1) introduced the wide line NMR technique for the determination of the amount of solid phase in fats, this method has been studied by various authors (2-8). However, since they all worked with the same type of instrument (Schlumberger NMR analyzer or Varian PA-7), they also come to more or less the same conclusions. Methods have also been investigated for the determination of the oil content of seeds (9-13; also, Riiner and Wettstrom, unpublished data). It was of interest, therefore, to investigate the use of the same instrument for both the determination of solid to liquid ratio and the oil content of the meal from pressed coconuts.

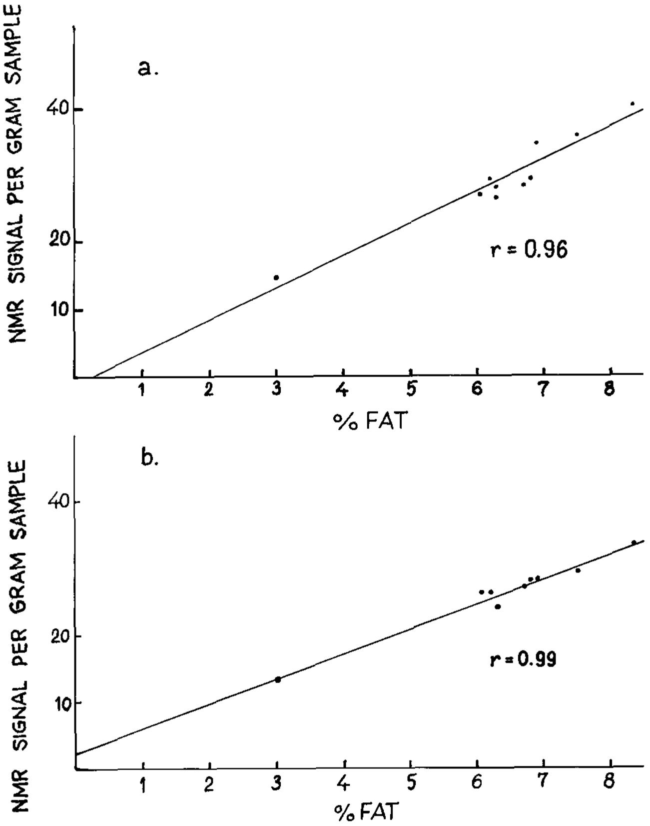

FIG. 1. Relation between NMR signal per gram of sample and amount of oil by extraction of coconut meal: a, NMR signal measured directly on the meal; b, NMR signal measured on carbon tetrachloride extract.

EXPERIMENTAL PROCEDURES

Apparatus

A Varian Model PA-7 wide line NMR spectrometer with a nominal field strength of 1715.5 gauss was used. The instrument was equipped with a model V 4221 integrator and a V 4220 variable temperature accessory. Sample size was about 2 ml. The NMR signal reported is the area under the pertinent differential curve normalized to a per gram basis (3) with the same sensitivity.

TABLE I

Standard Deviations of Alternative Parameter Settings

						Standard deviation, per cent solids		
Alternative	Time constant, sec.	Radio frequency, db	Sweep time, min	Sweep ampl. gauss	Modulation ampl. gauss	20 C	30 C	40 C
1	0.5	36	0.5	1	0.2	0.69	0.37	1.00
2	0.5	36	1.0	1	0.2	0.60	0.64	1.39
3	1.0	36	1.0	1	0.2	0.98	1.08	0.98
4	0.5	40	1.0	2	0.2	1.10	0.43	0.55

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

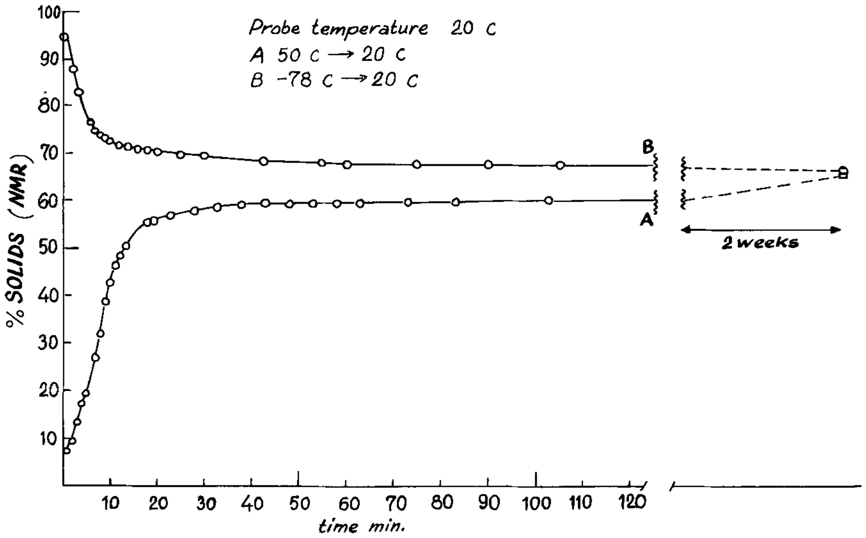

FIG. 2. Rate of reaching phase equilibration (Riiner and Wettstrom, unpublished data).

Determination of Fat in Meal

The fat content in 10 different samples of coconut meal was determined by extraction with petroleum ether according to AOCS Ba 3-38 method, (14) with the extraction time extended to 24 hr, and by comparison with results of NMR measurements.

The instrument parameters were: sweep time, min, 1; sweep amplitude, gauss, 1; modulation amplitude, gauss, 0.2; time constant, sec, 2; RF attenuation, db, 32.

In (a) about 1.5 g of the meal was weighed in a test tube, and in (b) 3 g of meal and 6 ml of carbon tetrachloride were mixed with an Ultra Turrax disintegrator for 3 min and then diluted to 10 ml. The test tube was filled with 2 ml of this solution. The results presented in Figure 1 show the correlation between the NMR signal and the fat content according to the AOCS method. By 10 independent measurements of the same meal the standard deviation for direct estimation of the meal was 1.3% fat and for the carbon tetrachloride method the standard deviation was 0.3% fat. This should be compared with the standard deviation of 0.03% fat for the extraction method.

Determination of Solid to Liquid Ratio

Samples. Ten hydrogenated fish oils with melting point from 30 C to 42 C were used to determine the optimal settings of the instrumental parameters and eight hydrogenated fish oils were used with melting point from 20 C to 42 C to determine precision and comparison with the solid fat index (15). Each sample was analyzed twice. Test tubes with a constant inner diameter of 9 mm were filled with a syringe of fixed volume. Twenty filled test tubes had an average oil weight of 1.56 g (standard deviation 0.0028 g). In this work all samples were weighed, but for normal routine analysis this is not necessary.

Sample Conditioning. The influence of conditioning is demonstrated by experiments with hydrogenated mustard seed oil of IV 64 (Riiner and Wettstrom, unpublished data). One sample was chilled at -78 C for 10 min and then put into the probe at 20 C. Another sample of the same oil was tempered at 50 C and the NMR signal was measured for 2 hr with a probe temperature of 20 C. The change in solid content with time is shown in Figure 2.

In this work the conditioning procedure proposed in previous work (4) was used, in which the sample is cooled from the melted state in a carbon dioxide bath for 10 min and then tempered at 10 C for 45 min followed by conditioning at 20, 30, 40 and 50 C for the same period of time. Pohle and Gregory (7) found that 30 min was sufficient while Bosin and Marmor (8) took 60 min for conditioning.

The tube was then put into the probe, where the temperature was maintained constant by a nitrogen gas flow. The dial calibration accuracy ±2 C was too broad. Normally 1 C gives about 3% too low solid content. The temperature of the gas flow in the probe was controlled with a mercury thermometer in the probe and adjusted within ±0.2 C of the desired temperature.

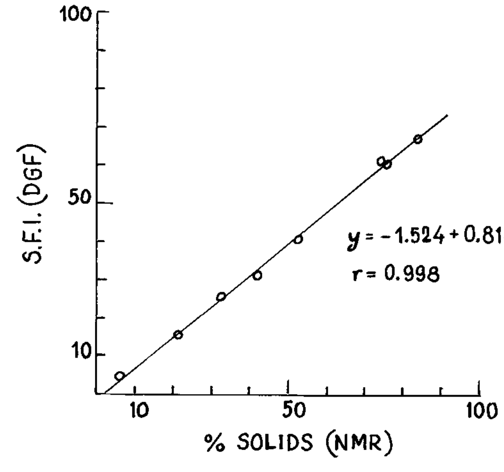

FIG. 3. Relation between solid fat index (15) and per cent solids by NMR at 20 C.

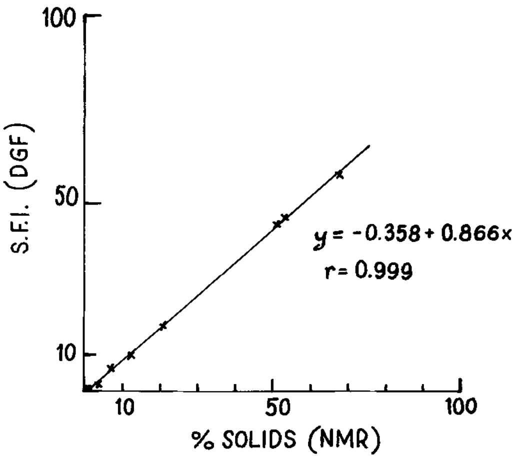

FIG. 4. Relation between solid fat index (15) and per cent solids by NMR at 30 C.

TABLE II

Duplicated Analysis of Per Cent Solids by NMR

	NMR, per cent solid					
	20 C		30 C		40 C	
Sample	1	2	1	2	1	2
1	4.9	6.2	0.1	0.0	0.4	0.0
2	21.0	21.4	3.2	3.3	0.4	2.0
3	31.6	32.9	7.0	6.7	2.3	0.0
4	52.2	52.7	20.4	20.9	2.0	2.4
5	40.9	42.1	12.7	12.7	0.9	2.0
6	75.8	75.7	51.2	50.1	10.6	11.4
7	83.1	84.7	68.1	67.0	26.2	27.5
8	74.6	74.1	52.8	53.1	13.8	13.4
S	0.71		0.49		0.86	

Measurements and Calculations

The stability of the instrument was rather poor, therefore all measurements had to be done on the same day. Besides the normal procedure to tune the probe and center the field some form of control of the NMR response per proton was necessary. A test tube containing 1.65 g of liquid soybean oil was used as reference. The reference tube was brought to the same temperature as the sample and the NMR signal of the sample was measured, immediately followed by the measurement of the NMR signal of the reference. The quotient of these readings at a specific temperature was compared with the quotient at 50 C where both the sample and reference are liquid. Hence the per cent solids could be calculated using the equation:

$$\text{Per cent solids at t°C} = 100 - \frac{\left\{\dfrac{\text{Sample signal}}{\text{Reference signal}}\right\}_{t\ °\mathrm{C}}}{\left\{\dfrac{\text{Sample signal}}{\text{Reference signal}}\right\}_{50\ °\mathrm{C}}}$$

Instrument Parameters

In a previous study different parameter settings were used. Four alternatives were chosen and for each of them the solid content of 10 different samples was determined at different temperatures (Table I).

Precision of NMR Value and Correlation With Solid Fat Index

Duplicated analysis of eight hydrogenated fish oils with melting points from 20 C to 42 C according to one of the four alternatives above showed an overall average standard deviation of ±0.7, thus giving a 95% confidence interval of ±1.5% solids (Table II).

The solid fat index was determined for the same samples by dividing the corresponding dilatation value (15) by 25. The relationship between SFI value and per cent solids by NMR has been plotted for 20 C and 30 C in Figures 3 and 4. The regression equations obtained with their regression coefficients were:

$$\mathrm{SFI} = -1.524 + 0.818\ (\%\ \text{solids}) \quad \text{at } 20\ \mathrm{C} \quad (r = 0.998)$$

$$\mathrm{SFI} = -0.358 + 0.866\ (\%\ \text{solids}) \quad \text{at } 30\ \mathrm{C} \quad (r = 0.999).$$

The overall regression equation was:

$$\mathrm{SFI} = -1.468 + 0.821 \quad (\%\ \text{solids}) \quad (r = 0.994).$$

DISCUSSION

The NMR technique for the determination of fat content in seeds has been shown by other authors (11,12) to give good results. To use the same technique for pressmeal is too unprecise to give satisfactory results. It would be better to measure the solid to liquid ratio. As shown in this study and by others (7,8) it is necessary to condition the sample for at least 0.5 hr; it seems that at least 45 min to 1 hr is needed for the determination of the solids content at a specific temperature too long a time for process control of the hydrogenation reaction. On the other hand many samples can be handled by one operator, which is economical for product control. The precision of the method is less than 1% solids (Table II). There is also a good correlation with the solid fat index for practical use. Experience in routine control has shown that the stability of the electronic part of the instrument used in this work is too poor for use as a control instrument. With an instrument which is more stable and easier to handle, the NMR method seems to be an adequate method for product control.

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