Relations between Pulsed NMR, Wide-Line NMR, and Dilatometry

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ABSTRACT

Hitherto, solid fat contents often have been expressed as dilatations. Since the development of pulsed NMR into a quick and accurate method for the determination of the solid fat content, while wide-line NMR still is being used, accurate equations are needed to enable conversion from dilatations to NMR values and vice versa. The inaccuracies arising when NMR values are converted into dilatations are almost equal for the various NMR methods. The direct pulse method in which one mean solid fat factor f is used is the most attractive method to replace dilatometry. For further reduction of the standard deviation when converting NMR values into dilations and vice versa, it will be necessary to split up the fats into groups with similar compositions.

INTRODUCTION

Pulsed NMR has proved to be a good alternative for the laborious dilatometer technique (1,2). However, pulsed NMR instruments are expensive compared to dilatometers, and, therefore, dilatometry will continue to be used where pulsed NMR measurements are not justified economically (fewer than 10-15 determinations/day). For this reason and because, until now, process control and margarine blending often are based upon dilatation values, accurate conversion equations are needed to switch from dilatations to pulsed NMR values and vice versa.

Although pulsed NMR has essential advantages over wide-line NMR, for the time being, wide-line, as well as pulsed, NMR will be used, since small and cheap wide-line instruments were introduced on the market before pulsed NMR instruments became available. Therefore, accurate conversion factors also are needed for the conversion of wide-line into pulsed NMR values and dilatations.

EXPERIMENTAL PROCEDURES

Pulsed NMR measurements were performed as described before (1,2). For the wide-line NMR measurements, a Newport analyzer (3) operating at 2.7 MHz was used. All samples were stabilized and tempered in the same way (1,2). Dilatations and percentages of solids of 48 fats and fat mixtures were determined by wide-line and direct and indirect pulsed NMR.

RESULTS AND DISCUSSION

Direct Pulsed NMR

The direct pulse method is based upon the measurement of two signals after an rf pulse has been applied. The signal immediately after the pulse is proportional to the total amount of fat (solid plus liquid), while, 70 μs later, the signal is proportional to the amount of liquid fat. In view of the "dead time" of the receiver, it is impossible to measure the signal immediately after the pulse. The decrease caused by this time delay is indicated by the factor f. The direct pulse values are indicated by N^p_{dir}.

The solid fat factor f increases with the temperature (2). We were able to reduce the systematic errors considerably by using a mean f value for each temperature. This could be realized with an eight step correction function for f. Solid fat contents thus obtained are indicated by $N^p_{dir(8)}$. When this eight step function is used, f has to be adjusted manually at each temperature, which needs stand-by and may give rise to mistakes. As automation of this correction seemed rather complicated, we looked for an indirect way to correct. Since the solid fat content depends upon the temperature, we expect f to depend upon the solid fat content (Fig. 1). The solid fat content decreases with increasing temperature, and we expect f to increase with decreasing solid fat content for the following reasons: (A) components (saturated) melting at higher temperature often give rise to less imperfections than those (unsaturated) melting at lower temperature, and (B) less ordered crystals will melt at a lower temperature than the more ordered ones.

We have now developed an electronic device which largely corrects the value of the solid fat content automatically for the change in f using a three-step function (Fig. 1): $0 \leqslant$ % solids < 25 (f = 1.42), $25 \leqslant$ % solids < 40 (f = 1.36), and $40 \leqslant$ % solids $\leqslant 100$ (f = 1.34).

After starting the measurement, f is adjusted automatically. The signals of the first two 90° pulses are processed with a f value of 1.42 into the uncorrected percentage of solids. The output of the divider of the processing unit, which is proportional to the percentage of solids (1), then is fed into the correction unit which readjusts f according to the three step function. The percentage of solids then is recalculated with the new f value. Almost immediately after the third 90° pulse, the corrected percentage of solids ($N^p_{dir(3)}$) is shown by the digital voltmeter; total measuring time: 6 sec. Solid fat contents obtained with the use of a mean f (1.37) for all fats over the whole temperature range are indicated by $N^p_{dir(1)}$.

Reproducibility of Tempering Procedure

Even when the same tempering procedure is applied to all samples, it is still possible for small differences in temperature adjustment of the thermostats and crystallization behavior to occur. To investigate this, we measured the solid fat content of eight fats by the indirect method—this

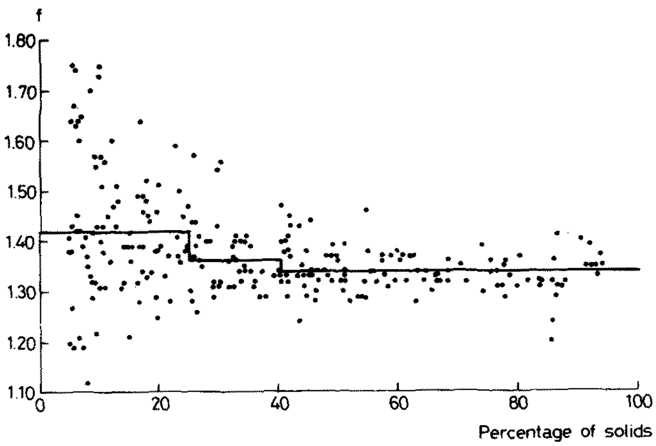

FIG. 1. Factor f as a function of the percentage of solids; dead time 7 μs.

TABLE I

Solid Fat Contents Measured in Duplicate[a] by Indirect Method

Fat	Solid fat (%)					
	10 C	15 C	20 C	25 C	30 C	35 C
Fractionated palm oil 36 C	78.4	65.2	51.8	34.2	20.6	9.8
	77.9	65.8	51.1	34.4	19.8	9.4
Hydrogenated palm oil 45 C	93.8	92.4	87.1	78.0	63.9	46.0
	93.5	92.2	86.7	78.0	62.2	45.3
Margarine A	22.2	15.3	9.7	5.4	2.2	0.5
	21.8	15.0	9.4	5.1	2.2	—
Margarine B	37.5	27.0	17.8	9.7	4.4	1.2
	36.8	26.3	16.7	8.8	3.8	0.2
Margarine C	52.8	31.5	14.3	6.9	2.4	0.3
	53.4	31.9	13.8	6.7	2.6	0.2
Margarine D	19.2	13.4	8.2	3.6	—	—
	19.7	14.2	8.8	4.2	—	—
Margarine E	8.4	6.8	5.1	3.7	1.5	0.5
	9.3	7.4	5.7	4.1	2.5	1.5
Margarine F	46.7	33.0	21.7	12.1	4.9	1.5
	46.4	32.6	21.2	12.0	5.1	0.8

[a]Measured in two different departments of the laboratory.

TABLE II

Regression Equations and Standard Deviations around Regression Lines[a]

Method	Regression equation	Standard deviation (%)		Systematic deviation (%)
$N^p_{ind} - N^p_{dir(1)}$	$N^p_{dir(1)} = 0.987 N^p_{ind} + 1.8$	0.74	0.85[b]	− 0.16
$N^p_{ind} - N^p_{dir(3)}$	$N^p_{dir(3)} = 1.000 N^p_{ind} + 0.1$	0.72	0.83[b]	− 0.07
$N^p_{ind} - N^p_{dir(8)}$	$N^p_{dir(8)} = 0.998 N^p_{ind} + 0.1$	0.50	0.65[b]	− 0.06
$N^p_{ind} - N^w$	$N^w = 0.988 N^p_{ind} + 0.8$		1.44	
$N^p_{dir(1)} - N^w$	$N^w = 0.978 N^p_{dir(1)} + 0.9$		1.45	
$N^p_{dir(8)} - N^w$	$N^w = 0.990 N^p_{dir(8)} + 0.7$		1.45	
$N^w - D$	$N^w = 100D/(62.6 + 1.06t) - 0.1$		1.9	
$N^p_{dir(1)} - D$	$N^p_{dir(1)} = 100D/(59.5 + 1.18t) - 0.7$		1.9	
$N^p_{dir(3)} - D$	$N^p_{dir(3)} = 100D/(60.2 + 1.19t) - 0.6$		1.8	
$N^p_{dir(8)} - D$	$N^p_{dir(8)} = 100D/(62.7 + 1.04t) - 0.6$		1.9	
$N^p_{ind} - D$	$N^p_{ind} = 100D/(62.1 + 1.06t) - 0.7$		1.8	

[a]See text for explanation of abbreviations.

[b]Corrected to values that would have applied had the direct values been obtained by again tempering the samples after the indirect measurements.

being the most accurate one—in two different departments of the laboratory. Thus, the tempering procedure was carried out by different people using different thermostats (Table I). The standard deviation was 0.28% solids. Some samples showed a systematic difference between the first and second measurement. The average difference between the solid fat contents of both series was 0.09% solids.

Regression Equations

NMR methods: The slopes of the regression lines representing the conversion of the indirect (N^p_{ind}) and direct pulse values are almost equal to 1 (Table II). The mean difference between direct and indirect values is less than 0.2% solids. The standard deviation around the regression line is smallest when the direct method with the eight step function is used and largest when a mean f value is taken; the improvement when use is made of the three step function is negligible. The agreement between the different pulsed NMR methods is satisfactory.

To compare the standard deviations of the pulse values with those of wide-line NMR (N^w) and dilatometry (D), the irreproducibility of the tempering procedure has been included in the standard deviations of the pulse values. To this end, the standard deviations of the pulse values were corrected to those that would have applied had the direct values been obtained by again tempering the samples after the indirect measurements. The capacity of the wide-line spectrometer was not sufficient to measure all samples on the same day. We, therefore, dividied the samples into three groups (one group a day). The mean differences between indirect pulse and wide-line values on the first, second, and third day were, respectively, −1.0, +0.2, and −0.6% solids.

Since the pulsed NMR values were obtained in one run, this systematic change must be due to temperature instability of the wide-line spectrometer. The standard deviations around the regression lines representing the conversion of wide-line into indirect and direct pulse values are almost equal, although considerable differences in precision between the various pulse methods were found. Systematic errors caused by long term instability of the wide-line spectrometer contribute considerably to the standard deviation. This standard deviation is somewhat better than that found in an interlaboratory test for wide-line spectrometers (4).

NMR vs Dilatometry

In our experiments, the standard deviations corresponding with a single dilatation determination were 1.8 dilatation units (ml/kg) over the whole range. To improve the accuracy all dilatation values were determined in duplicate. Moreover, those dilatations that deviated more than 1.6 dilatation units from their duplicates were rejected and measured again. This resulted in a standard deviation of 0.3 dilatation units, this being almost equal to that of a single pulse measurement. As explained earlier (2), the fan of lines representing the regression equations of the conversion of the wide-line and pulse values into dilatations does not pass through the origin (Table II). The standard deviations around the regression lines are considerably higher than would be expected on the grounds of the standard deviations in the dilatations and the NMR values. These rather large standard deviations must be ascribed to the dependence of the melting dilatation and the influence of the difference in expansion of liquid and solid on the fat composition and temperature (2). To improve the conversion accuracy, it will be necessary to split up the different fats into groups with similar fat compositions.

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