Moisture determination in starch-rich food products by pulsed nuclear magnetic resonance

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Abstract:

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Keywords: NMR, Pulsed NMR, Food, Starch, Humidity

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Moisture determination in starch-rich food products by pulsed nuclear magnetic resonance

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Summary

The possibility of applying the low resolution pulsed NMR technique to moisture determination in starch-rich low-fat food products is described. The water content of the samples is measured from the liquid to solid ratio. The evaluation of the ratio depends upon the way of extrapolating the free induction decay (FID). The values of the extrapolation coefficients for the liquid and solid phases are measured and their dependence upon the sample water content is given. The method of standard addition for converting the percentage of moisture obtained in terms of hydrogen content to percentage in weight is described. The error statistical analysis is also reported.

Introduction

The technique of pulsed low-resolution nuclear magnetic resonance (NMR) can be used conveniently to distinguish between liquid and solid phases in a variety of samples (Van Putte & Van den Enden, 1973, 1974; Hester & Quine, 1976). The main advantages of the technique are the rapidity of the determination, the possibility of automation and, mainly, the fact of being non-destructive.

The purpose of the present paper is to show the applicability of the method to moisture determination in a variety of foodstuffs, rich in starch but very low in fat content. In particular, the following samples were studied: wheat flour, durum wheat semolina, corn flour, rice flour, ground whole rice, ground barley, potato starch, ground beans, ground and whole lentils, pasta made from 100% semolina and from 100% flour, gluten enriched pasta, and different types of bread.

For detailed information about the technique of pulsed NMR, the reader is

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referred to specialized literature, e.g. Farrar & Becker (1971); only its most relevant aspects will be summarized below.

The NMR signal is due to the magnetic moments of the protons present in sample. The protons are excited by a very short pulse of radiofrequency (RF). After the end of the pulse, the protons give rise to a decaying signal, called the free-induction decay (FID), the duration of which varies from a few tens of microseconds for solids to a few milliseconds (limited by the homogeneity of the magnetic field) for liquids. The total signal, just at the end of the pulse, is proportional to the number of protons in the measured volume. As an example, Fig. 1 shows the FID of a sample of flour. At the time $t = 0$, a trigger starts the experiment. After a certain instrumentally-fixed delay, δ, the RF pulse, of an adjustable duration p, begins. Typically, p is 4–5 μsec. After the pulse, the receiver is always inhibited for a certain period of time d, usually called dead-time. Therefore, the signal can be registered only subsequent to a time $t = \delta + p + d$. Since it is rather rare and impractical to digitize the whole FID, given the enormous difference in the decay rates between the solid and liquid signal, it is customary to sample the signal only at two points, placed

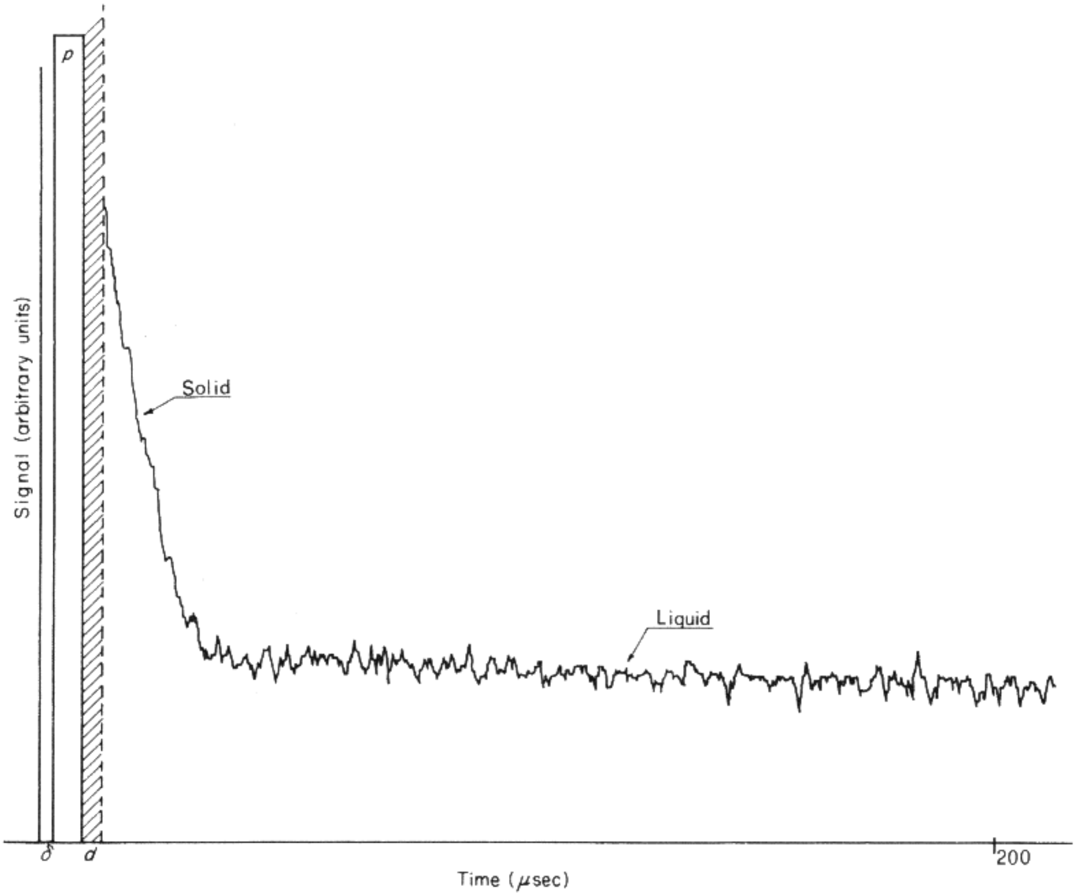

Figure 1. Free induction decay of (FID) of a flour sample.

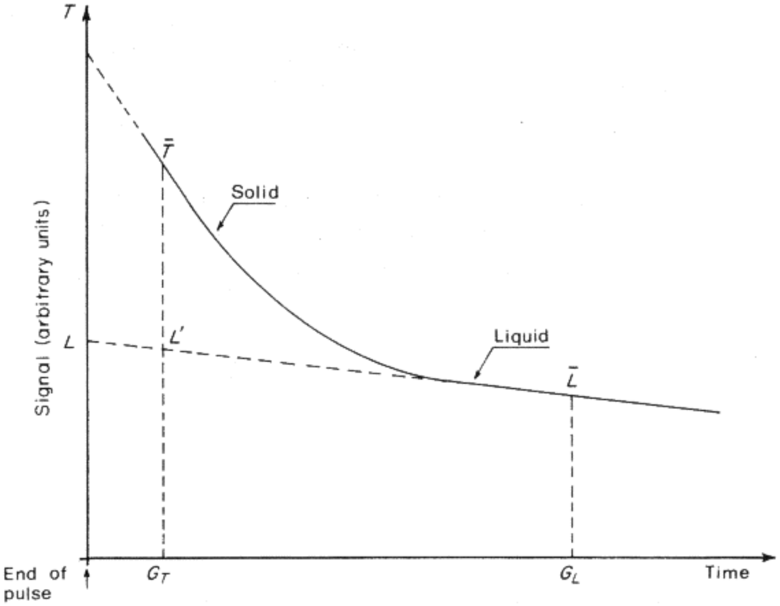

Figure 2. Schematic representation of the FID due to a solid phase and a liquid phase rapidly decaying.

at times G_T and G_L. This is accomplished by electronic sample-and-hold circuits piloted by DC pulses positioned at the desired times.

The signal $\bar{T}$, sampled at time G_T, (see Fig. 2) however does not coincide with the total signal T at the end of the pulse. The value of T can be obtained either by extrapolation based on the two digitized FID or by a semi-empirical extrapolation based on the two values L and $\bar{T}$, as described below. Once T is known, the relative amount of the liquid phase, measured in terms of hydrogen content, is simply L/T. Since the differences $\bar{S} = \bar{T} - L$ and $S = T - L$ are both proportional to the content of the solid phase, it is possible to write

$$S = f_s \bar{S} \tag{1}$$

where f_s is an empirical coefficient. Obviously, f_s depends upon the nature of the solid phase (i.e. the rate at which the solid phase signal decays) and on the position of the gate G_T. Taking into account eqn (1), the percentage of the liquid in the sample is

$$X = L/\,[L + f_s(\bar{T} - L)]\,. \tag{2}$$

This formula has been used for the determination of solid to liquid ratios in fats (Van Putte & Van den Enden, 1973, 1974).

In the present work the situation encountered is somewhat different. In starch-rich foods, the signal due to water decays unusually fast, indicating a dramatically reduced mobility of the water bound to the carbohydrates. In fact, in our case the decay is determined by the transverse relaxation time T_2 rather than by magnetic field inhomogeneity. It is therefore advisable to extrapolate also the signal due to the liquid phase. Denoting $\bar{L}$ the signal at the time G_L, consequently we have $L = f_l \bar{L}$, where f_l is an extrapolation coefficient. Denoting L' the signal of the liquid phase extrapolated to the time G_T, we have (see Fig. 2)

$$L' = \bar{L} + (L - \bar{L})(G_L - G_T)/G_L . \tag{3}$$

Notice that the quantity $(G_L - G_T)/G_L$ is a readily and accurately measureable instrumental constant. The quantity proportional to the solid phase content is then $\bar{S} = \bar{T} - L'$, with eqn (1) remaining valid. Combining all these equations, we have

$$X = f_l \bar{L} / [f_l \bar{L} + f_s(\bar{T} - L')] . \tag{4}$$

Experimental

FID values were measured on a pulsed low-resolution NMR spectrometer (20 MHz, model Minispec P20, Bruker Spectrospin). The temperature was 25 or 40°C; no significant difference was observed in relation to the temperature. When needed, the FIDs were digitized by a Bruker fast digitizer (model B-C104) and plotted on a Hewlett-Packard X–Y recorder. Measurements of $\bar{T}$ and $\bar{L}$ were carried out by means of a Bruker double-channel digitizer and analog computer B-AC5. In all cases, 90° pulse (pulse width about 5 μsec) and the phase detection mode were used. The centres of the gates G_T and G_L were placed at 9 μsec and 90 μsec from the end of the RF pulse, respectively. The width of the gates was in both cases 2 μsec. The relative gain in the two channels was made equal by adjusting the apparent solid content to 0% for a completely liquid, slowly decaying sample (oil). The samples were prepared and measured in 10 mm tubes (external diameter). The repetition rate between successive pulses was 1 sec; averages of ten measurements were taken for all digital values.

Results

Extrapolation coefficients

The coefficients f_s and f_l were obtained by a graphical extrapolation of digitized FIDs. In fact, this is the most reliable method. The results for a variety of food products of varying moisture content are reported in Fig. 3. There seems to be no significant difference between the products examined. It turns out that both coefficients depend somewhat on the water content. This dependence has been fitted by a second degree polynomial using the least squares technique. It is important to keep in mind that the extrapolation coefficients f_s and f_l depend on the distance between the end of the pulse and the gates G_T and G_L. The interpolation polynomials for different values of G_T and G_L are listed in Table 1.

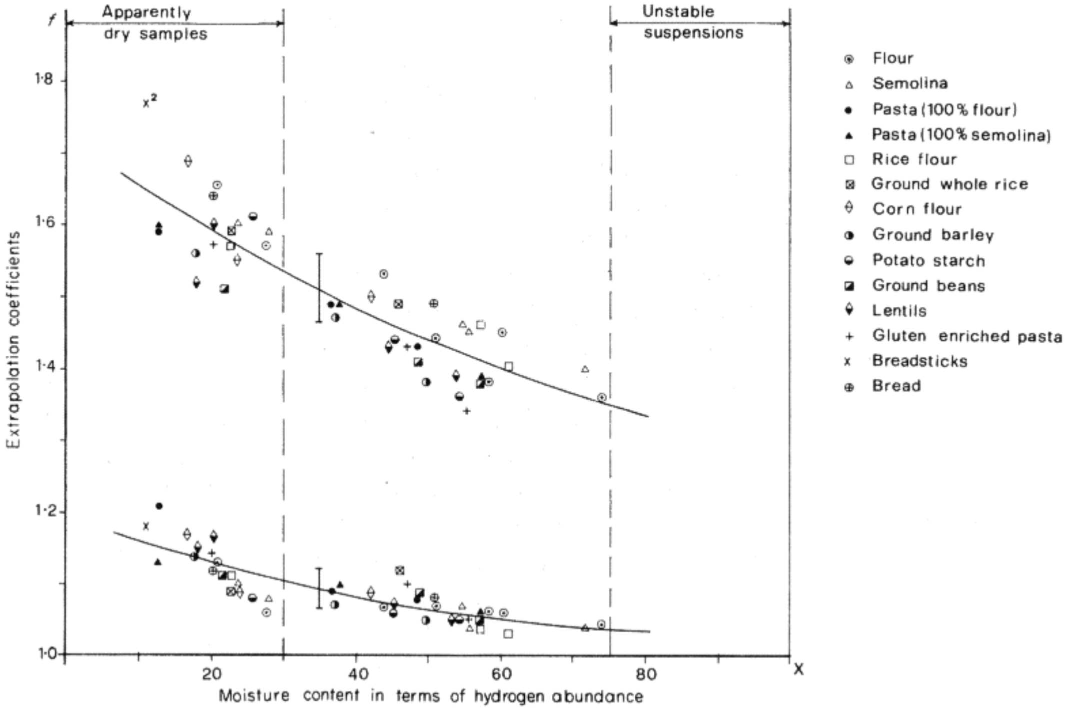

Figure 3. Dependency of f_s and f_1 coefficients on moisture content in a variety of samples. Solid lines represent the fitting of the experimental points by a second degree polynomial $f = a + bx + cx^2$ for $G_T = 9$ μsec and $G_L = 90$ μsec; bars represent mean square deviations.

Table 1. Least squares fits of the extrapolation coefficients f_s and f_1 by a quadratic function for different gate times G_T and G_L (measured from the end of the pulse)

G_T (μsec)	$f_s = a + bx + cx^2 \pm e$			
	a	b	c	e
5	1.335	– 0.447	0.340	0.0271*
7	1.487	– 0.445	0.165	0.0052
9	1.725	– 0.710	0.283	0.0068
11	2.086	– 1.411	0.806	0.0114

G_L (μsec)	$f_1 = a + bx + cx^2 \pm e$			
	a	b	c	e
50	1.066	0.032	– 0.178	0.0005†
70	1.159	– 0.352	0.261	0.0023
90	1.196	– 0.363	0.202	0.0035
110	1.233	– 0.352	0.098	0.0064

* Measurements impaired because of dead-time limitations.

† Anomaly due to the (sin At)/t beat observable in the solid phase part of FID.

Using Table 1, the practical determination of X can be carried out as follows: the values $\bar{T}$ and $\bar{L}$ are measured by a two-channel digitizer. Assuming any initial value of X, the coefficients f_s and f_l are calculated and a new value of X is determined from eqn (3) and (4). The coefficients f_s and f_l are then recalculated and the whole process is repeated until self-consistency is achieved. In practice, one or two repetitions are fully sufficient.

At $G_T = 9$ μsec and $G_L = 90$ μsec, the mean square deviations were 0.046 and 0.026 for f_s and f_l, respectively. These values, which are relatively large, are due partially to the low signal-to-noise ratios, typical for powdered samples, and partially to the variations in composition of the samples. Especially in the case of moistened samples, it is very difficult to ensure complete homogeneity. In order to reduce these problems, it would be preferable to use larger sample holders. This usually means lower homogeneity of the magnetic field and, therefore, faster decay of the liquid phase signal. In the particular case of moisture determination in starch-rich products, the latter disadvantage is of less importance, since the water signal decays rather fast anyway, while the advantages, due to the higher signal-to-noise ratio and to the better averaging of sample inhomogeneity, might be quite pronounced.

Determination of the liquid phase content by weight

So far, we have been considering only the X values, representing the relative content of the liquid phase in terms of hydrogen abundance. The quantity of more general interest is however the relative content of the liquid phase by weight, denoted as W.

Suppose two phases A (liquid) and B (solid) are present in the sample (the symbols A and B will be used also to indicate the respective absolute quantities in grams). Further suppose that the relative abundance of hydrogen in A and B is α and β, respectively. Then

$$X = \alpha A/(\alpha A + \beta B) \text{ and } W = A/(A+B). \tag{5}$$

A simple calculation shows that

$$W = X/[X + \mathrm{k}\,(1-X)] \tag{6}$$

where $\mathrm{k} = \alpha/\beta$ is a constant. Equation (6) can be rewritten also in the form

$$1/W = \mathrm{k}(1/X) + (1-\mathrm{k}) \tag{7}$$

showing that there is a linear relationship between $1/W$ and $1/X$. This can be used for calibration purposes if the values of W are available by means of another independent method.

Notice that it is common in the literature to apply linear regression to the $W(X)$ relationship, which is obviously incorrect.

When W cannot be determined independently, indirect methods for determining k must be found. One of the possibilities is the use of the 'standard addition' method. The only condition of its applicability is that it must be possible to homogenize the two phases after addition of the liquid phase A.

Suppose that a quantity a of phase A has been added to the total quantity $(A + B)$ of the sample and that the new value of X, called X', has been measured. We have

$$W' = X' / [X' + \mathrm{k}(1 - X')] \tag{8a}$$

and

$$W' = (A + a) / (A + B + a). \tag{8b}$$

A somewhat complicated but straightforward calculation based on the above equation shows that

$$\mathrm{k} = \frac{1}{m} \left[\frac{1}{1 - X'} - \frac{1 + mX}{1 - X}\right] \tag{9}$$

where $m = a/(A + B)$.

Determination of k

A theoretical estimate of k can be made considering the chemical structure of starch. Assuming that the liquid phase consists of pure water, we have $\alpha = 2/18 = 0.111$. The monomeric unit of starch has a molecular weight of 162, of which 10 is due to hydrogen. Hence, $\beta = 10/162 = 0.062$ and $\mathrm{k} = \alpha/\beta$ is 1.79. However, three of the ten hydrogens may be undergoing a rapid exchange with the hydrogens in the liquid phase. In this case, these hydrogens would contribute to the liquid phase signal better than to the solid phase, so that $\beta = 7/162 = 0.043$ and $\mathrm{k} = 2.58$.

An empirical determination of k, based on the method of standard addition as described above, should be guided by an estimate of the error involved. Assuming realistically that m can be set very accurately (only weighing and pipetting is involved), eqn (9) leads to the approximate formula

$$\sigma_{\mathrm{k}}^2 = \left(\frac{\delta \mathrm{k}}{\delta x}\right)^2 \sigma_x^2 + \left(\frac{\delta \mathrm{k}}{\delta x'}\right)^2 \sigma_{x'}^2 = m^{-2} [(1 + m)^2 (1 - x)^{-4} \sigma_x^2 + (1 - x')^{-4} \sigma_{x'}^2] \tag{10}$$

where δ_x, $\delta_{x'}$, and δ_{k} are the variances of x, x' and k, respectively.

Considering that a typical value of x in 'dry' substances is 0.2, assuming that $\mathrm{k} \approx 2.5$, and expressing x' in terms of x, k and m, σ_{k} can be calculated as a function of m, σ_x and $\sigma_{x'}$. Numerical analysis shows that σ_{k} increases very fast when m becomes smaller than 0.2, while for higher values of m it varies very little and has a shallow minimum around $m = 0.5$. Its value is almost entirely contributed by $\sigma_{x'}$, while the variance of x is of much less importance; for $0.3 \leqslant m \leqslant 1.0$ the ratio $\sigma_{\mathrm{k}}/\sigma_{x'}$ lies between 13 and 16, regardless of σ_x.

Table 2. Determination of k and true water content in 'dry' starch-rich substances

Sample	§	$\bar{T}$*	$\bar{L}$†	X	k	W‡
Barley flour						
	0.0	483	196	0.200		0.092
	0.5	589	394	0.625	2.60	
Beans						
	0.0	518	157	0.245		0.118
	0.5	454	311	0.643	2.63	
	0.0	469	138	0.237		0.114
	0.7	333	244	0.698	2.55	
Corn flour						
	0.0	604	178	0.238		0.114
	0.5	619	416	0.628	2.44	
	0.0	415	122	0.237		0.114
	0.7	414	279	0.630	1.68	
	0.0	427	123	0.232		0.111
	0.7	472	328	0.654	1.97	
Lentils						
	0.0	569	144	0.200		0.094
	0.5	574	386	0.629	2.64	
	0.0	427	104	0.192		0.089
	0.7	375	268	0.677	2.42	
	0.0	407	83	0.157		0.071
	0.7	388	282	0.691	2.74	
Pasta						
100% flour						
	0.0	421	108	0.203		0.095
	0.7	404	293	0.690	2.56	
	0.0	405	74	0.140		0.063
	1.0	386	304	0.764	2.91	
100% semolina						
	0.0	393	69	0.134		0.060
	0.7	359	249	0.653	2.31	
	0.0	404	76	0.144		0.065
	1.0	308	246	0.777	3.15	
Gluten enriched						
	0.0	416	112	0.215		0.102
	0.7	377	271	0.682	2.40	
	0.0	583	153	0.208		0.098
	0.5	623	445	0.677	3.40	
Potato starch						
	0.0	639	234	0.305		0.154
	0.5	707	476	0.629	2.07	
Rice flour						
	0.0	653	188	0.231		0.110
	0.5	724	428	0.615	2.29	
	0.0	557	163	0.236		0.113
	0.7	519	356	0.644	1.83	
Wheat flour						
	0.0	418	82	0.151		0.068
	0.5	489	369	0.724	2.27	
	0.0	293	58	0.152		0.069
	0.7	453	314	0.652	2.24	
	0.0	349	68	0.150		0.068
	0.7	381	259	0.637	2.08	

Table 2 – *continued*

Sample	§	$\bar{T}$*	$\bar{L}$†	X	k	W‡
Wheat semolina						
	0.0	334	67	0.155		0.070
	0.7	478	333	0.656	2.30	
	0.0	405	82	0.156		0.071
	0.7	465	321	0.649	2.19	
	0.0	564	169	0.242		0.117
	1.0	454	360	0.770	2.71	
	0.0	389	77	0.152		0.069
	0.7	495	342	0.650	2.22	

Mean value of k = 2.42 ± 0.08; variance $\sigma_k = 0.388$.

* Measured 9 μsec after the end of the pulse.

† Measured 90 μsec after the end of the pulse.

‡ Calculated with the mean value of k = 2.42.

§ Represents the value of the 'standard addition' of water in grams.

A number of measurements aiming at the determination of k is reported in Table 2. The resulting mean value k = 2.42 ± 0.08, corresponds very well to the theoretical estimate under the assumption that most of the exchangeable hydrogens in starch contribute to the liquid phase signal (fast exchange model). The fact that k is somewhat smaller than the theoretical value of 2.58 corresponding to this situation may be due to two factors: (i) the water phase containing a certain amount of dissolved organic matter, such as saccharides, which lowers its hydrogen content, and/or (ii) some exchangeable hydrogens are bound so strongly in hydrogen bonds within the solid matrix that they are not available for the exchange process with protons in the liquid phase.

The variance of k was $\sigma_k = 0.39$, which would correspond to $\sigma_{x'} = 0.026$. In reality, the experimental error in determining x' is smaller (definitely less than ± 0.01). The discrepancy arises from the difficulties in sample preparation (homogenization) which have been mentioned before.

Conclusions

The possibility of determining the moisture content of a large group of nutritionally important substances by pulsed NMR has been demonstrated. The determination is based on two values, $\bar{T}$ and $\bar{L}$, of the FID signal measured at two suitably chosen times, G_T and G_L, after the pulse. It is very fast; one determination takes about 10 sec to collect the data and 20 sec to evaluate them, provided a programmed pocket calculator is available. The evaluation is done in steps. First, the moisture is determined in terms of relative hydrogen content using eqn (4) and the extrapolation coefficients reported in Table 1; the iterative procedure reported in the third section is of interest in this step.

Secondly, eqn (6) is applied in order to obtain the liquid phase content by weight. The value of k is 2.42 ± 0.08. The overall error of a single measurement is about ± 0.01.

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