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Journal of Food Technology **16**, 67-72 (1981)

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### Abstract:

We have found a good correlation between the iodine number of maize oil and an empirical parameter related to the proton T1 relaxation time determined by means of low resolution pulsed nuclear magnetic resonance spectroscopy. This result opens a way to fast and reliable determination of the iodine number during oil hydrogenation.

Keywords: NMR, Pulsed NMR, Oil, Maize oil, Cracking, T1, Iodine number

## **Correlation between iodine number and proton relaxation times in maize oil**

E. BROSIO\*, F. CONTI\*, A. DI NOLA\* AND S. SYKORA†

### **Summary**

We have found a good correlation between the iodine number of maize oil and an empirical parameter-related to the proton  $T_1$  relaxation time determined by means of low resolution pulsed nuclear magnetic resonance spectroscopy. This result opens a way to fast and reliable determination of the iodine number during oil hydrogenation.

### **Introduction**

Pulsed low resolution nuclear magnetic resonance (NMR) is becoming a standard technique for determination of solid fat index (Van Putte & Van den Enden, 1973, 1974; Jansson & Andersson, 1976). A series of other applications has also been developed and found a positive response in the food industry; this includes studies of fat polymorphism (Brosio *et al.*, 1980), studies of fatty emulsions (Trumbetas, Fioriti & Sims, 1976), determination of oil content of seeds (Tiwari, Gambhir & Rajan, 1974), determination of humidity in a variety of foodstuffs (Hester & Quine, 1976; Brosio *et al.*, 1978; Brosio *et al.*, 1979), etc.

All these techniques are based exclusively on the analysis of the free induction decay (FID) after a single-pulse excitation and are possibly due to a marked difference between so-called transverse relaxation times ( $T_2$ ) of solids and liquids. It is, however, well known (Farrar & Becker, 1971) that certain NMR techniques based on two-pulse excitation provide a different parameter called the longitudinal relaxation time ( $T_1$ ). Like  $T_2$ , this parameter is also related to molecular mobility but in a quite different way.

In this paper we will show that  $T_1$  of maize oil varies considerably upon hydrogenation and the experimental  $T_1$  values correlate with the iodine number

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(NI) of the oil. Let us repeat that the iodine number is defined as the weight of iodine absorbed by 100 parts (by weight) of the sample and that it is a widely used measure of the degree of unsaturation. The determination of iodine number is today rarely made according to the original definition (the Wij's method).

A more common procedure is to calculate it from fatty acid composition of the oil as determined by gas chromatography after a hydrolysis. Even so, it is a rather lengthy process. The  $T_1$  values, on the other hand, can be measured in a matter of seconds, an important factor in industrial hydrogenation monitoring. The fact that the iodine number correlates with  $T_1$  is perhaps not too surprising considering the marked effect of hydrogenation upon the melting point of oils a clear indication that molecular mobility is affected.

It should be noted that the iodine number can be determined also by means of high resolution proton NMR (Johnson & Shoolery, 1962; Nielsen, 1976). The disadvantage is that automated (and therefore fast) high resolution spectrometers are currently much more expensive than the low resolution versions and require a trained operator.

## Experimental

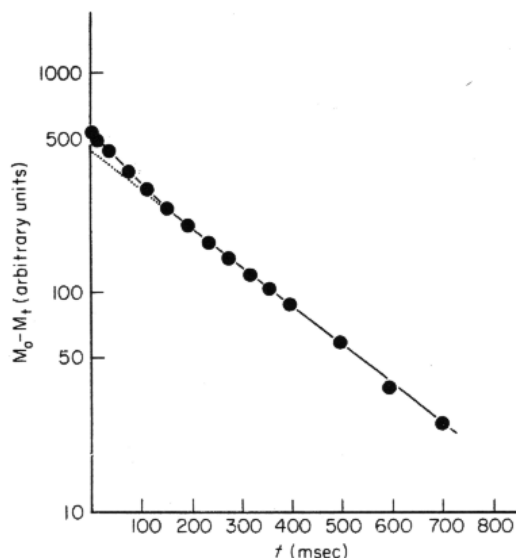
The measurements were made on a low resolution pulsed NMR instruments 'Minispec P20' produced by Bruker Analytische Messtechnik GmbH (Karlsruhe, Germany). The definition of the longitudinal relaxation time  $T_1$  and the various methods for its determination are described in the literature (Farrar & Becker, 1971) as well as in the company manual. We will only briefly summarize the principle of the method of inversion recovery which was employed in this study.

The sample, located within a permanent magnet, is first subject to a  $180^\circ$  RF pulse (i.e. a pulse which 'flips' the equilibrium nuclear magnetization  $M_0$  by  $180^\circ$  with respect to the magnetic field direction). After a variable delay  $t$ , a  $90^\circ$  RF pulse is applied which gives rise to a transverse nuclear magnetization with a component  $M_t$  detected in the direction of  $M_0$ , by the transmitter/receiver coil wound around the sample.  $T_1$  is then determined as the slope of the semi-logarithmic plot of  $(M_0 - M_t)$  against  $t$ . The  $90$  and  $180^\circ$  pulses are adjusted empirically by varying their respective widths (about  $4 \mu\text{sec}$  and  $8 \mu\text{sec}$  on our instrument).

The time delay  $t$  between the pulses was varied from 10 msec to 1000 msec. Each measurement was repeated 30 times, the time between two consecutive measurements was kept to 3–5 sec to allow the nuclear magnetization to return to its equilibrium value.

The oil samples were measured without any pretreatment in sample tubes of 10 mm external diameter.

During measurement the sample temperature was kept constant by means of



**Figure 1.** Longitudinal magnetization decay of a maize oil sample (iodine number = 123.2) measured at  $T = 41^\circ\text{C}$ .

a thermostated water bath with a precision of  $\pm 0.1^\circ\text{C}$ . Its absolute value was checked by a mercury thermometer.

The untreated and partially hydrogenated maize oil samples were kindly supplied by STAR S.p.A. (Agrate, Brianze, Italy).

## Results and discussion

Fig. 1 shows a typical 'decay' (i.e. return to equilibrium value) of the proton longitudinal magnetization of a maize oil sample (NI = 123.2) at the temperature  $T = 41^\circ\text{C}$ . Unfortunately, the semilogarithmic plot of  $(M_0 - M_t)$  against  $t$  does not yield a straight line. This can be caused by chemically distinct protons in the sample, which have different relaxation times  $T_1$ , due to different mobility of the double bond segments and the saturated chains.

The decay may be well approximated ('fitted') by a combination of two exponentials of the type

$$M_0 - M_t = C_1 \exp(-t/T_{1F}) + C_2 \exp(-t/T_{1S}), \quad (1)$$

$T_{1F}$  and  $T_{1S}$  are the relaxation times of a fast and a slow decaying component, respectively, while  $C_1$  and  $C_2$  are the relative concentration of the two components.

There is however no reason why only two components should be present; the curves may in fact be fitted by formulae similar to eqn (1), but with practically any number of terms.

Moreover, the uncertainties in the parameters derived by least square fitting of eqn (1) to the experimental curves are large enough to make the whole procedure questionable.

Rather than insisting on a detailed interpretation of the decay curves, we have therefore decided on a purely empirical parameter which would be related to overall decay rate.

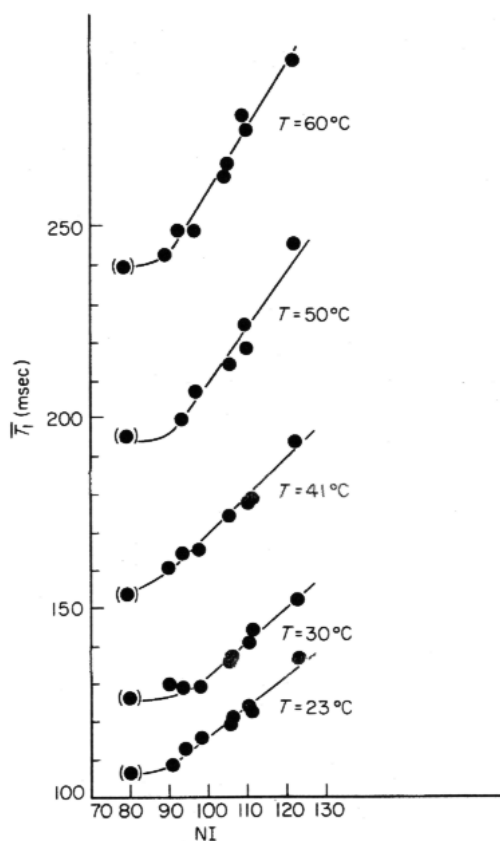
In order to be practical, such a parameter should also be easy to determine by means of only a few measurements and a simple calculation suitable for any programmable pocket calculator.

The parameter we have chosen is defined as

$$\bar{T}_1 = (t_2 - t_1) / \ln (M_t - M_{t_1}) / (M_t - M_{t_2}), \quad (2)$$

where  $t_1$  and  $t_2$  are fixed delays equal in our case to 10 and 200 msec., respectively, and  $t$  is long enough to insure that  $M_t$  is practically equal to  $M_0$  (in our case  $t = 2$  sec.).  $\bar{T}_1$  may therefore be calculated from only three measurements.

In Table 1 are reported  $\bar{T}_1$  values for maize oil samples with different iodine



**Figure 2.** Correlation between  $\bar{T}_1$  [see equation (2) in the text] and iodine number values at different temperatures. The experimental points in parenthesis have not been taken into account in the linear regression.

**Table 1.** Correlation between iodine number and  $\bar{T}_1$  values at different temperatures

NI	$\bar{T}_1 \pm 1.5$ (msec)				
	$T = 23^\circ\text{C}$	$T = 30^\circ\text{C}$	$T = 41^\circ\text{C}$	$T = 50^\circ\text{C}$	$T = 60^\circ\text{C}$
123.2	136	152	193	245	293
111.4	122	144	179	217	275
110.4	123	140	177	224	279
106.3	120	136	175	214	266
106.0	119	135	174	213	263
97.9	115	129	165	207	249
94.0	112	128	164	199	249
90.4	108	129	160	195	243
80.2	106	126	154	195	240
$r^2$	0.961*	0.969*	0.984*	0.951*	0.968*

\*excluding the sample with NI = 80.2

numbers measured at temperature  $T = 23, 30, 41, 50,$  and  $60^\circ\text{C}$ . The respective plots are presented in Fig. 2. It is apparent that there is a good linear relationship between  $\bar{T}_1$  and NI: the linearity breaks down only for the most hydrogenated sample (NI = 80.2) which is close to the liquid-to-solid transition.

The correlation coefficients reported in Table 1 were calculated excluding this particular sample. It must be pointed out, however, that there is no reason why the relationship between  $\bar{T}_1$  and NI should be linear. A non linearity also does not invalidate the practical value of this study as long as calibration curves can be prepared *a priori* for each type of oil.

We want to point out that the technique requires a good control of the sample temperature  $T$ .  $\bar{T}_1$  in fact depends quite strongly upon  $T$  and an error of  $1^\circ\text{C}$  in sample temperature would result in an error of about 3.5 in iodine number.

The present study indicates that the NMR phenomenon of longitudinal relaxation can be exploited for fast determination of the iodine number of partially hydrogenated oils. Further work is needed in order to see the behaviour of different types of oil. It is clear, however, that the method is viable and could become valuable for industrial production monitoring.

By automating the instruments, it is certainly possible both to increase the precision and to develop the method to a fully operator independent level.

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(Received 22 July 1980)