Transient NMR Quantitative Measurements[1]

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ABSTRACT

The transient nuclear magnetic resonance technique is briefly described. Application of this technique allowed quantitative observation of the protons in the oil, water and solid material in a single corn kernel and on a corn kernel baked at 107 C. These results along with measurements on lyophilized foods are discussed.

INTRODUCTION

The transient NMR technique is a scheme for observing the nuclear magnetic resonance phenomena and is particularly suited for the measurement of the characteristic relaxation times T_1 and T_2. The theory governing the nuclear spin dynamics under transient conditions is found in several standard texts on magnetic resonance (1,2). Each relaxation time can be measured using several different pulse schemes depending on the particular requirements of the experiment. Through the determinations of these relaxation times, the interior of the bulk matter can be seen and the microscopic nuclear magnetic interactions can be related with the macroscopic sample properties.

In the present work only T_2 measurements are presented to identify the moisture and oil signals in foodstuffs. For very short T_2 values, the free induction decay after a single 90° pulse is used and for the longer values, the 90°-τ-180° pulse sequence is used.

TRANSIENT NMR MEASUREMENTS

The signals received after repeated application of a 90° pulse were followed by a 180° pulse (Fig. 1). If the time spacing between the 90° and 180° pulses is τ, after the 180° pulse, a nuclear spin echo will appear. The results of repeating the pulse sequence for different times, τ are presented. Echo amplitude typical of gases, liquids and some amorphous solids decreases with the characteristic time T_2, where T_2 usually lies in the range of a few milliseconds to seconds. For other, more tightly bonded solids, the spin-spin interactions are very strong so that T_2 has a value in the microsecond range (Fig. 2). Figure 2 shows the free decay signal following a 90° pulse from the hydrogen, in a kernel of corn dried at ambient temperatures.

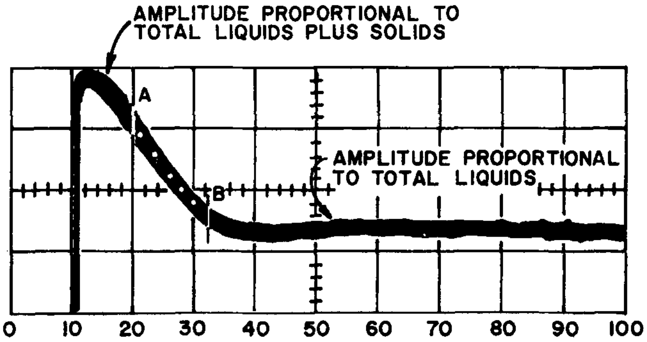

FIG. 2. Free-decay signal from one kernel of corn at 10 μsec/cm.

The amplitude of the total hydrogen signal from the corn kernel (oil plus water, starch, gluten, etc.) is proportional to the maximum value of free decay signal at 10 μsec, and at 60 μsec (Fig. 2) it is proportional to the total liquid signal (oil plus water). The complete free decay signal is limited by the inhomogeneity of the magnet (Fig. 3).

The free decay liquid signal at maximum magnet homogeneity is shown in Figure 4. The contribution of the water and oil is resolvable directly; however, the oil signal decay is limited by magnet inhomogeneity so that the 90°-τ-180° pulse sequence is needed to determine T_2 for oil.

Plots of the logarithm of the amplitude of the echo as a function of time show that the curve of Figure 5b is the same as curve a except that the time scale is expanded to 0.2 millisec per division. Since the plots are curves rather than straight lines, there are multiple values of T_2. The data is obtained by the equation:

$$A_o = \text{echo amplitude} = A_{21} \exp(-2\,\tau/T_{21}) + A_{22} \exp(-2\,\tau/T_{22})$$

where A_{21} is the amount with time constant T_{21}; A_{22}, amount with time constant T_{22}; T_{21}, shorter time constant; T_{22}, longer time constant; τ, time between the 90° and 180° pulses.

From the graphs of Figure 5, the values of the normalized amplitudes, A_{21}/A_o, and A_{22}/A_o, and the values of the corresponding time constants are: A_{21}/A_o, 77%; T_{21}, 0.92 millisec; A_{22}/A_o, 23%; T_{22}, 22 millisec, where $A_o = A_{21} + A_{22}$.

Comparison of these results with those of Figure 4 shows that A_{21} and T_{21} correspond to the water signal and

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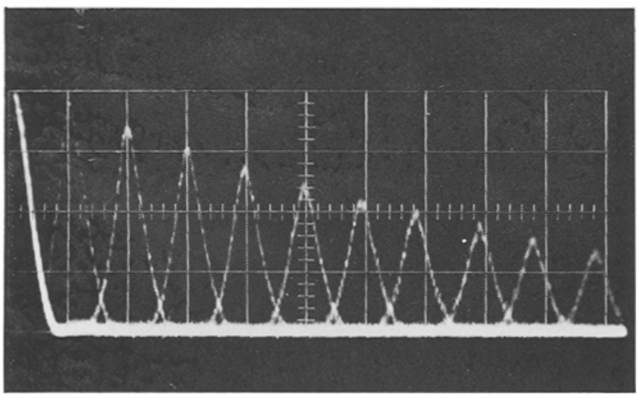

FIG. 1. Spin echoes.

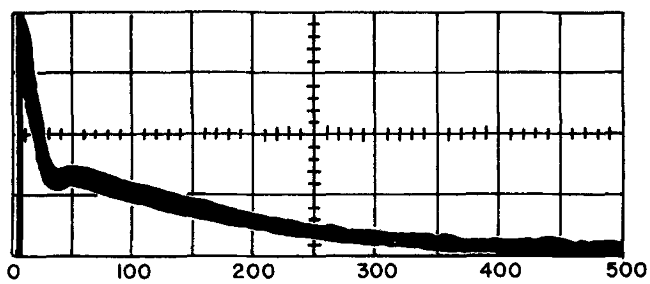

FIG. 3. Free-decay signal from one kernel of corn at 50 μsec/cm.

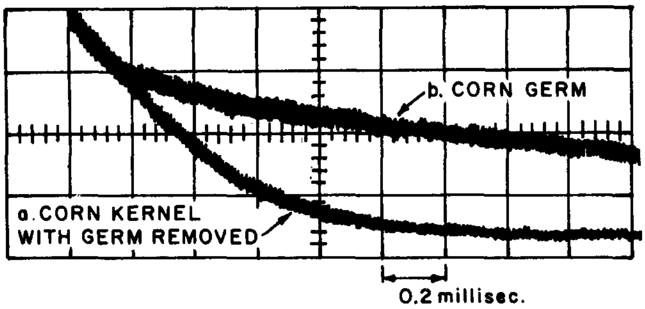

FIG. 4. Free-decay signals from one kernel of corn at 200 μsec/cm. (a) Corn kernel with the germ removed; (b) corn germ.

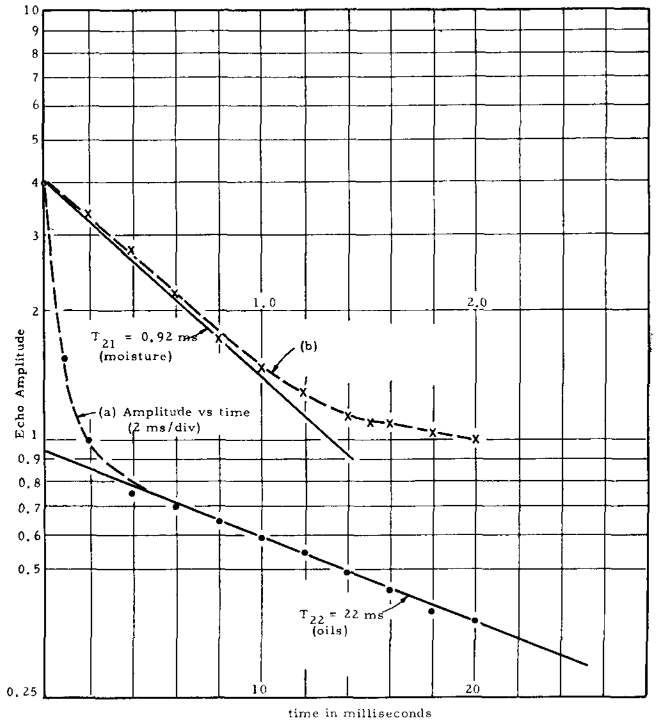

FIG. 5. Graph of the spin-echo amplitude as a function of time for a kernel of corn. (a) 2 millisec/division; (b) 0.2 millisec/division.

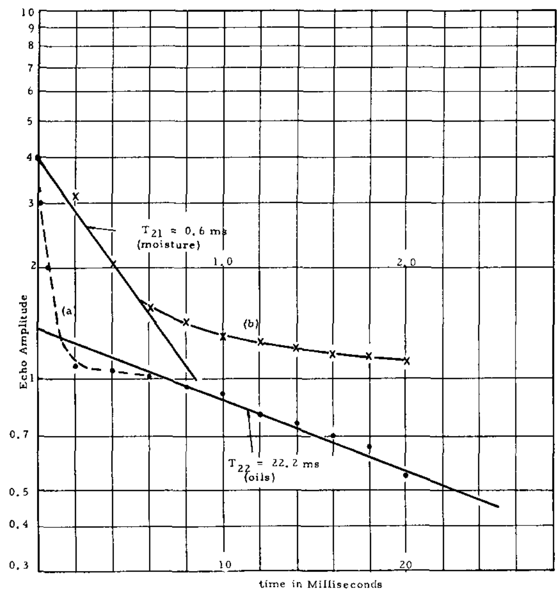

FIG. 6. Graph of the spin-echo amplitude as a function of time for a kernel of corn baked for 4.75 hr at 107 C. (a) 2 millisec/division. (b) 0.2 millisec/division.

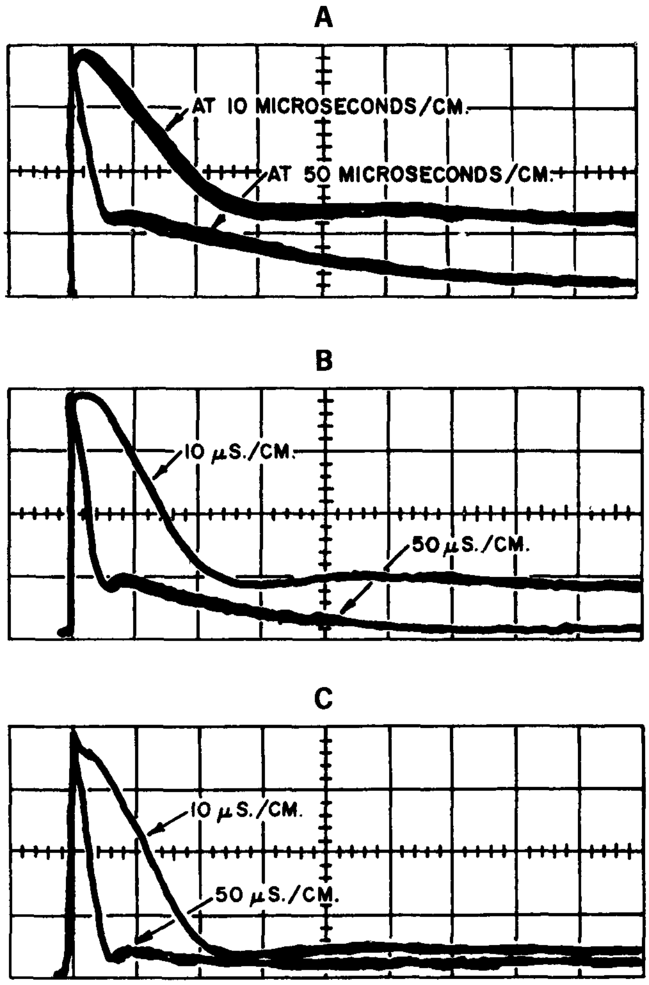

FIG. 7. Free-decay signals from one ground corn kernel. A. One ground kernel corn unbaked; B. 4 3/4 hr at 107 C; C. 20 hr at 107 C.

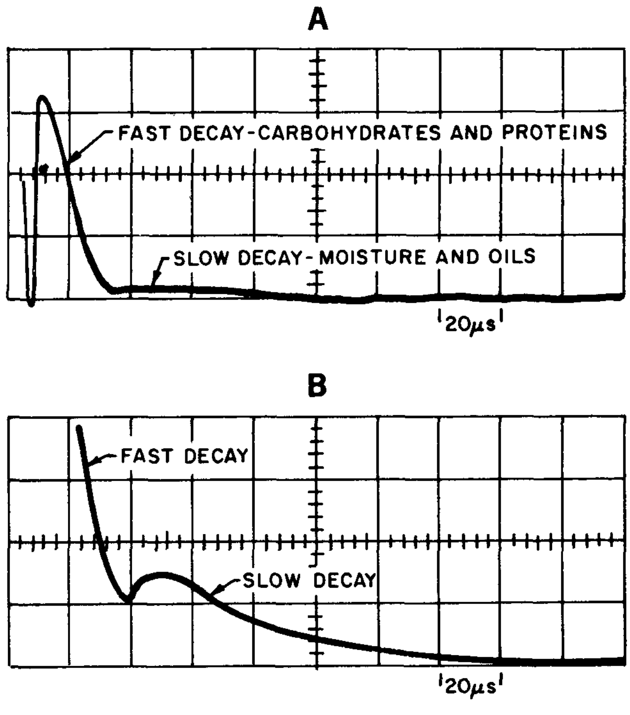

FIG. 8. Free-decay signals from lyophillized mashed potatoes. B. Gain x 10.

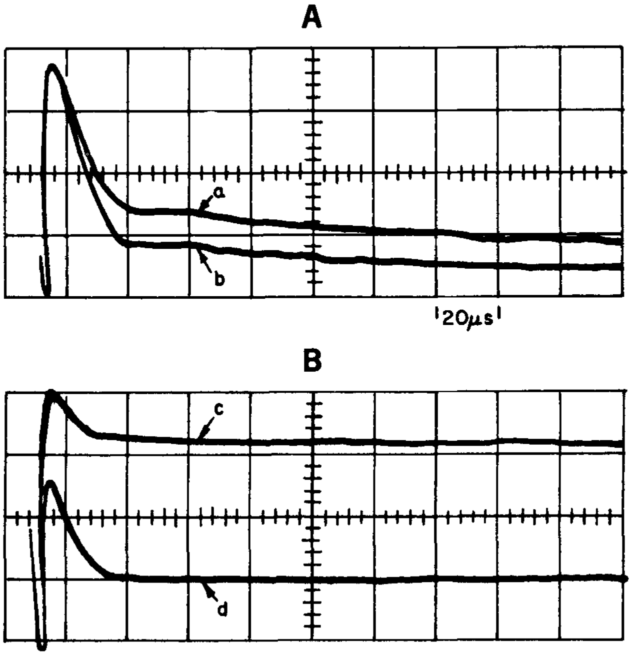

FIG. 9. Free-decay signals from lyophillized gravy and meat as taken from the package and equilibrated at 55% RH. (a) Upper trace, gravy equilibrated at average relative humidity of 55%; (b) lower trace, gravy as taken from sealed package. (c) upper trace, meat equilibrated at average relative humidity of 55%; (d) lower trace, meat as taken from sealed package.

A_{22} and T_{22} to the oil signal.

When the corn kernel was ground and baked at 107 C for 4.75 hr the spin-echo amplitude curve of Figure 6 was obtained. With this treatment both the oil and the water were reduced in amplitude and the total liquid signal contained 34% oil and 66% water. When the baking time was increased to 20 hr, the water was reduced so that in the total liquid signal 45% of it was oil and 55% water. The free decay signals obtained from this baking are shown in Figure 7. Figure 7a is the signal, with two horizontal sweep rates, from ground, unbaked kernel. The curves of Figure 7b were obtained after 4.75 hr of baking at 107 C. After 20 hr, the curves of Figure 7c were obtained.

The free decay obtained from the hydrogen nuclei in lyophilized mashed potatoes is shown in the oscilloscope photographs of Figure 8. The upper trace in Figure 8 is the oscilloscope presentation at a low gain so that all of the decay signal can be observed. The fast-decay signal from the hydrogen in the carbohydrate and protein has a relaxation time, T_{21} = 9.5 μsec. The slowly decaying signal is barely observed. The lower trace in Figure 8 is the same as the upper trace except that the gain has been increased by a factor of 10 to show the slowly decaying signal. When the slowly decaying signal is plotted on semilog paper the value of T_{22} is found to be 48 μsec.

Lyophilized gravy and Swiss steak were exposed to an atmosphere with a relative humidity of 55%. The gravy nearly doubled the amplitude of its long-decay component while the short-decay amplitude remained the same as shown in Figure 9a and b. The meat absorbed the most moisture from the 55% relative humidity atmosphere as shown in Figure 9c and 9d. In fact, it nearly tripled its moisture as noted by the increase in the amplitude of the long-decay component. This brief study indicates the differences in the hygroscopic properties of these samples and shows the useful data which may be obtained from a complete study involving measurements before, during and after the lyophilization process. The transient NMR method should also give information related to the long-range stability of the lyophilized foods, the effects of storage and storage conditions and deterioration.

REFERENCES

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