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A Low Frequency ^{1}H-NMR External Unit for the Analysis of Large Foodstuff Samples

Francesco Capozzi,* Mauro A. Cremonini,† Claudio Luchinat,‡ Giuseppe Placucci,§[,1] and Carlo Vignali¶

**Department of Chemistry, University of Calabria, 87036 Arcavacata di Rende, Cosenza, Italy; †Food Science and Technology Laboratory, University of Bologna, Via Ravennate 1020, 47023 Cesena, Italy; ‡Department of Soil Science and Plant Nutrition, University of Florence, Piazzale delle Cascine 28, 50144 Florence, Italy; §Department of Organic Chemistry "A. Mangini," University of Bologna, Viale Risorgimento 4, 40136 Bologna, Italy; and ¶Interfaculty Measure Center, University of Parma, Viale delle Scienze 23/A, 43100 Parma, Italy*

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An inexpensive external unit that allows the use of a commercial high-resolution NMR spectrometer as a very low frequency instrument is described. The external unit is phase coherent, the pulse timing being given by the parent spectrometer. With the exception of the probe, the external unit does not contain any tuned elements. This permits easy change of frequency in the range 100 kHz–1 MHz. The external unit may be appropriately employed in food science where, in several cases, low frequency is desirable. An application to hen shell eggs at the frequency of 700 kHz is described.

Key Words: **low field ^{1}H-NMR; foodstuff quality; shell eggs; relaxation times; external unit.**

INTRODUCTION

Relevant information about foodstuff quality can be obtained through the measurement of the longitudinal and transverse relaxation times of the bulk water in the sample (*1*). Often, such measurements are more sensitive to quality parameters when performed at low field. The general reason lies in the fact that water interacts with immobilized or slow-rotating tissue components. This interaction changes its spectral density in such a way that large relaxation can only be observed at relatively low field.

Low-field NMR spectrometers are far less expensive than their high-field counterparts. This fact, however, does not justify the purchase of a commercial low-field equipment for the sole purpose of testing the feasibility of a new application. Moreover, not every variety of low-frequency NMR spectrometer is commercially available. Fortunately, old NMR electromagnets are still available in many laboratories. A device of this type, together with a common high-resolution spectrometer, a homemade external unit, and a suitable probe, can be used to set up a versatile low-frequency apparatus at very low cost.

In this paper we describe the assembly of the external modules needed to permit the use of a Bruker CXP-200 spectrometer as a very low field NMR machine working in the 10^2–10^3 kHz frequency range. For the sake of clarity, we will refer to the setting-up of a 700 kHz prototype that we built to carry out a novel study on the aging process of shell eggs as studied by low-field NMR (*2*). Very few changes will be required to use the equipment at another frequency in the given range. The choice of specific commercial components was dictated by their availability and low price, and may therefore not always represent the *optimum* from a performance standpoint.

[1] To whom correspondence should be addressed.

EXTERNAL UNIT ARRANGEMENT

The block diagram of the whole external unit working at 700 kHz is shown in Fig. 1. Note that no 700 kHz signal is taken from the CXP console. In fact, the CXP pulse modulator cannot handle frequencies lower than 2 MHz. Consequently, the required frequency is obtained by mixing the CXP low-power transmitter output, set at 9.3 MHz, with the local oscillator provided by the CXP 10 MHz master oscillator signal, in such a way as to make the 700 kHz frequency available at the mixer output. The latter signal is amplified by an untuned cascade amplifier and delivered to a homemade probe through a passive diode switch. In this way, any phase cycle issued by a CXP pulse program can be safely transferred to the 700 kHz channel.

Similarly, the 700 kHz NMR signal from the probe is preamplified and back converted to 9.3 MHz by the same 10 MHz reference signal, before being applied to the CXP RF input. Phase coherence is achieved because the same 10 MHz reference is used for both the TX and RX circuits.

External Modules

Downconverter and RF amplifier. The downconverter and RF amplifier circuit are shown in Fig. 2. The TX mixer is a low-level and low-cost commercial double-balanced type. A first transistor low-level stage operates in class A, while the next MJ481 buffer amplifier and the MJ481 output amplifier

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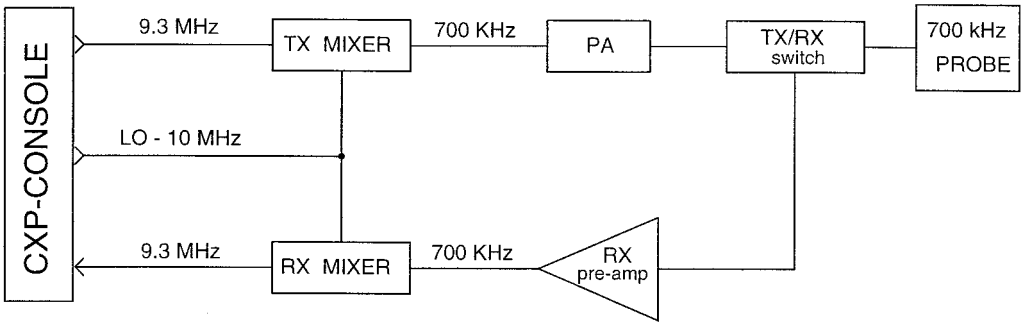

FIG. 1. Block diagram of the external unit. Because of the particular electronic configuration chosen, the 700 kHz NMR external unit appears to the CXP console as an heteronuclear probe tuned at 9.3 MHz. Here TX = transmitter, RX = receiver, PA = power amplifier, LO = local oscillator, pre-amp = preamplifier.

both operate in class C. By using class C the amplifier is automatically turned off when the unit switches to receiving mode, thus making gating circuits unnecessary. The relatively low frequency transistors used prevent the unwanted high frequencies present at the mixer output from being amplified. However, a high-pass filter (f_c = 100 kHz) is also necessary at the TX output to remove very low frequency noise and for proper impedance matching. No tuned circuits are used in the amplifier chain, so the amplifier is *flat* from 100 kHz to 1 MHz. The amplifier provides 20 W RF output power.

TX/RX switch, receiver preamplifier, and mixer. The general outline of the receiving part of the low-frequency NMR external unit is shown in Fig. 3. The NMR signal coming from the probe reaches the preamplifier input through a TX/RX switch. Diodes are employed on the transmitter and receiver arms for passive switching, i.e., switching is provided by the RF excitation itself (*3, 4*). A single stage FET preamplifier handles the 1 V overload appearing at the TX/RX switch output and applies a 10 dB gain to overcome the conversion loss of the following upconverter. The latter is a +17 dBm double balanced mixer whose local oscillator port is driven by the 10 MHz frequency available from the CXP master oscillator, thus providing a 9.3 MHz upconverted NMR signal. The local oscillator frequency is not gated, so the output is subjected to a residual 10 MHz signal that is filtered out by a very high *Q* crystal notch filter. A 30 pF variable capacitor permits fine notch tuning over a few kilohertz range around the nominal 10 MHz series resonance of the quartz crystal. The signal is coupled to the source follower BF245A to match the low input impedance of the following 50-ohm line that feeds the NMR signal to the CXP-200 standard preamplifier.

Probe. The prototype 700 kHz probe (Fig. 3) has been built large enough to contain a shell egg. The sample coil (L_1) is a simple solenoid wound around a common laboratory beaker and connected to a capacitor, to form a series resonant circuit with a *Q* of about 40. This relatively high value imposes a quite long pulse rise and fall time, of the order of 30 μs. Although the total dead time is even longer (about 200 μs), this is of no concern when samples with a sufficient long T_1 and T_2 (0.01–1 s) are dealt with. With the present probe configuration and the 20 W RF transmitter described above, a 60 μs 90 degree pulse and a 100 μs 180 degree pulse were obtained. The

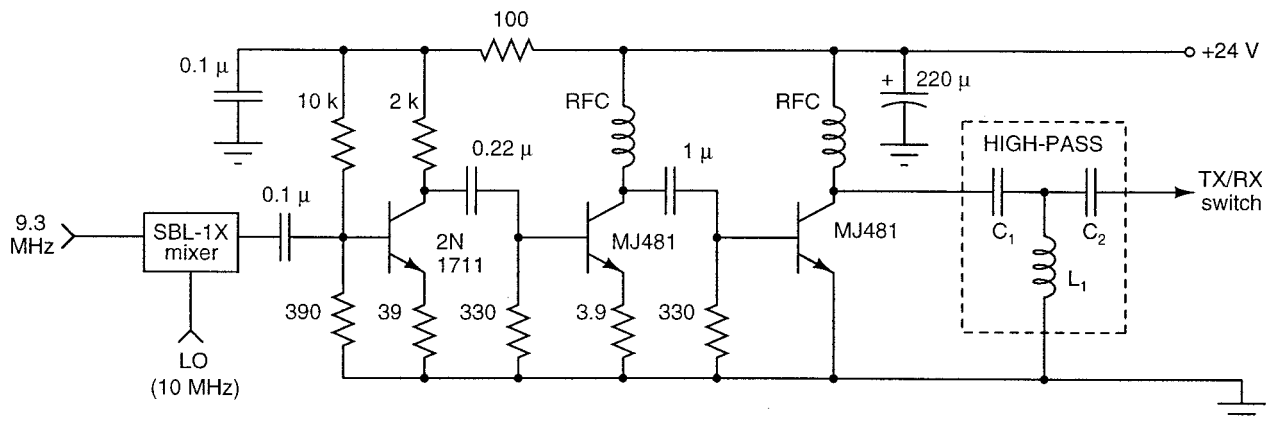

FIG. 2. Outline of the TX downconverter and power amplifier. The SBL-1X mixer is a Mini Circuits double balanced ring type. The high-pass filter components (f_c = 100 kHz) are $C_1 = C_2 = 15$ nF, $L_1 = 60$ μH.

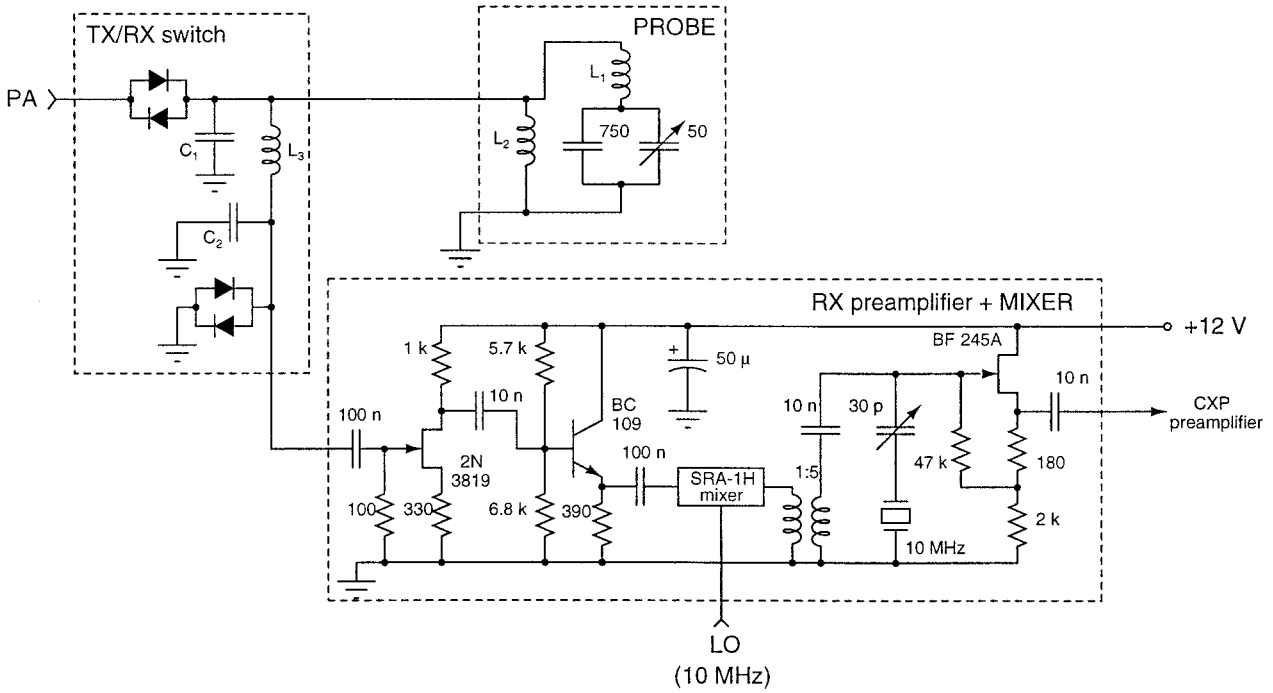

FIG. 3. Circuit diagram of the probe, TX/RX switch, and RX upconverter. *Probe:* The L_1 coil is made of 45 turns of 1 mm enameled copper wire wound around a 50 mm diameter pyrex beaker (about 67 μH). The circuit is tuned at 700 kHz by a 750 pF nonmagnetic high-Q capacitor and is finely tuned by a 50 pF variable capacitor, both working at 1 kV voltage. The series LC circuit is matched to 50 ohm by inductor L_2, a 20 mm diameter solenoid, about 45 mm long, consisting of 16 turns of self-supported 2 mm enameled copper wire. TX/RX switch: diodes are 1N4448 type. $C_1 = C_2 = 3.3$ nF, $L_3 = 15$ μH (at 700 KHz). RX upconverter: The SRA-1H is a Mini Circuits double balanced mixer. XTAL is a surplus 10 MHz series-resonance quartz crystal. T_1 is a toroidal transformer (grade F19 core): Primary has 6 turns and secondary has 30 turns of 0.5 mm enameled wire.

B_1 homogeneity has been measured by directly mapping the RF intensity within the probe and found to be within 95% for at least 90% of the volume, which is where the greatest part of a shell egg is actually placed.

The probe, together with the TX/RX switch, was contained in an aluminum box and inserted between the poles of an old Varian 12-inch electromagnet modified to a 74 mm gap. The electromagnet was driven to 0.0164 T by a 1 A current provided by a voltage supply set at about 1 V.

APPLICATION

NMR of Shell Eggs at 700 kHz

The 700 kHz frequency was chosen because preliminary field-cycling relaxometry experiments indicated that the process of egg aging is best mirrored into the albumen relaxation times at frequencies lower than ~1 MHz (*2*).

In the absence of any possibility of field shimming, and because of the large volume of the sample, the linewidth of the water protons of a shell egg is rather large (about 500–1000 Hz). This turns out to be not particularly annoying when both T_1 (inversion recovery) (*5*) and T_2 (spin-echo) (*6*) experiments are run. Besides, any unwanted magnetization due to the slight B_1 inhomogeneity can be successfully eliminated with simple phase cycles.

As an example, the longitudinal magnetization recovery and the transverse magnetization decay curves of a shell egg signal are shown in Fig. 4. They have been obtained by plotting the intensities of the Fourier transform of either the FIDs, in an inversion recovery, or the half-echo height in a spin-echo experiment. It is apparent that even at short times the experimental points are well behaved, the S/N ratio being quite high (better than 15 with a single scan). The clear at least (*7*) biexponential decay of both curves is actually the main subject of our future research: We have evidence that changes in the relaxation curves with time after laying could be used to infer the freshness of an egg (*2*). Further details are beyond the scope of this article and will be presented in a subsequent paper.

CONCLUSIONS

The inexpensive external unit presented in this paper has been used with a Bruker CXP-200 NMR spectrometer to determine T_1 and T_2 relaxation curves of a large food sample (a shell egg) at 700 kHz. Although our experience is limited to the CXP console, we believe that the same approach can be

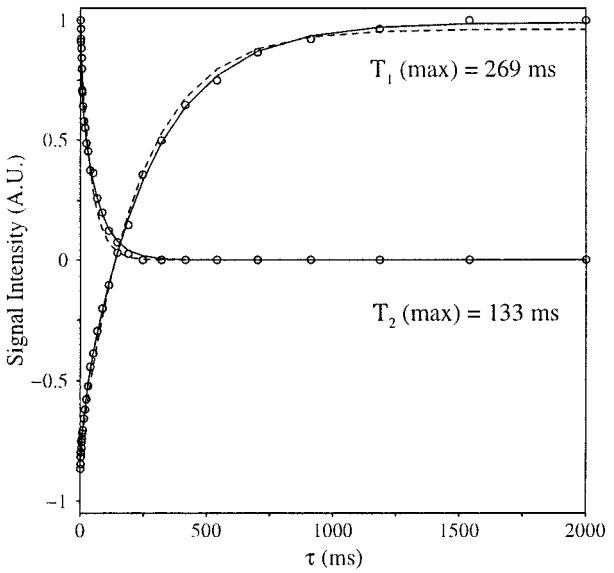

FIG. 4. Longitudinal magnetization recovery and transverse magnetization decay of the water proton signal of a shell egg at 700 kHz. Note that these curves cannot be fit with a single exponential function (dashed). A model based on the sum of two exponential functions, each having different weights and damping factors, is much more appropriate (solid), though not necessarily the best one (*7*). The relaxation time constants with the larger weight in the biexponential fit (more than 80%) are indicated.

followed with any other NMR console, provided a reference signal and a low-power transmitted output are available to the user.

The low resonance frequency allowed by the unit permits the easy construction of a probe capable of containing large samples, thus giving the possibility of performing nondestructive analyses of eggs. This feature, together with the fact that there is no risk of microbial sample contamination during the analysis, makes the approach suitable for on-line applications.

Even lower frequencies can be reached in a similar way by only modifying the probe and the C_1, L_3, C_2 network in the TX/RX unit (*4*), the only limitations being the dimension of the probe and, of course, the lower sensitivity.

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