A New Weak Field Double Resonance NMR Spectrometer *

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Weak field NMR and double resonance spectrometers are mostly homemade. In this work, some electronic units of such a spectrometer operating at 1.437 mT were designed and realized by including new integrated circuits: an audio generator, digital sweep generator, digital additional field and delay unit, Quartz generator, NMR detector(Q-meter), AF-narrowband amplifier, phase shifter and phase sensitive detector.

Introduction

Resonance spectra taken by continuous-wave weak field double resonance NMR spectrometers exhibit such a poor signal-to-noise ratio (S/N), that it is difficult to record a pure NMR signal, but there is a convenient S/N for enhanced signals. The phase sensitive (or lock-in) detection gives the derivative of the absorption signal of the sample and of the side-bands. The main field strength of the spectrometer is 1.437 mT, so the earths field can cause some distortion. The spatial homogeneity and the stability of the main field are very important to obtain a reasonable NMR signal. Our spectrometer is suitable for measurements of the dynamic nuclear polarization and of relaxation times in proton and fluorine containing solvents.

In the usual method, the magnetic field is slowly swept through the resonance line an x−y-recorder plots the spectrometer output as a function of the magnetic field. In this method, the NMR signal is very sensitive to the low-frequency noise (i.e. 1/f noise). To eliminate this noise, a three-channel integrator or a signal averager can be used.

Only the central bands of the slow-passage NMR u-mode signals obtained by the rapid modulation techniques are sufficient to evaluate the enhancement factors. The NMR frequency is 61.22 kHz for the spectrometer.

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Reprint requests to Prof. A. Yalçiner.

The Spectrometer

The block diagram of the continuous-wave weak field double resonance NMR spectrometer is shown in Figure 1. In principle it is a well known spectrometer designed in 1960 with electron tubes by Müller-Warmuth et al. [1–3]. The aim of this work is to design some electronic units of the spectrometer by using the latest analog and digital integrated circuits and printed circuit board techniques.

The Audio Frequency Generator

In the NMR spectrometer, the main field is modulated with an additional sinusoidal wave field. The modulation is done by Helmholtz coils fed by a sinusoidal wave generator [4, 5].

The sinusoidal wave generator shown in Fig. 2 is a Wien-Bridge type audio frequency generator. It works approximately at 90 Hz, which is the field modulation frequency. Two 1N4148 diodes serve as automatic amplitude control. The sinusoidal wave is taken out after a simple driver from point A, and the square wave from point B. The voltage-to-current converter is designed symmetrically. It can give a current of maximum 95 mA for the modulation field coils. The output is protected by two 1N4001 diodes which short-circuit to the ground the high voltage, which can be present on the inductive load.

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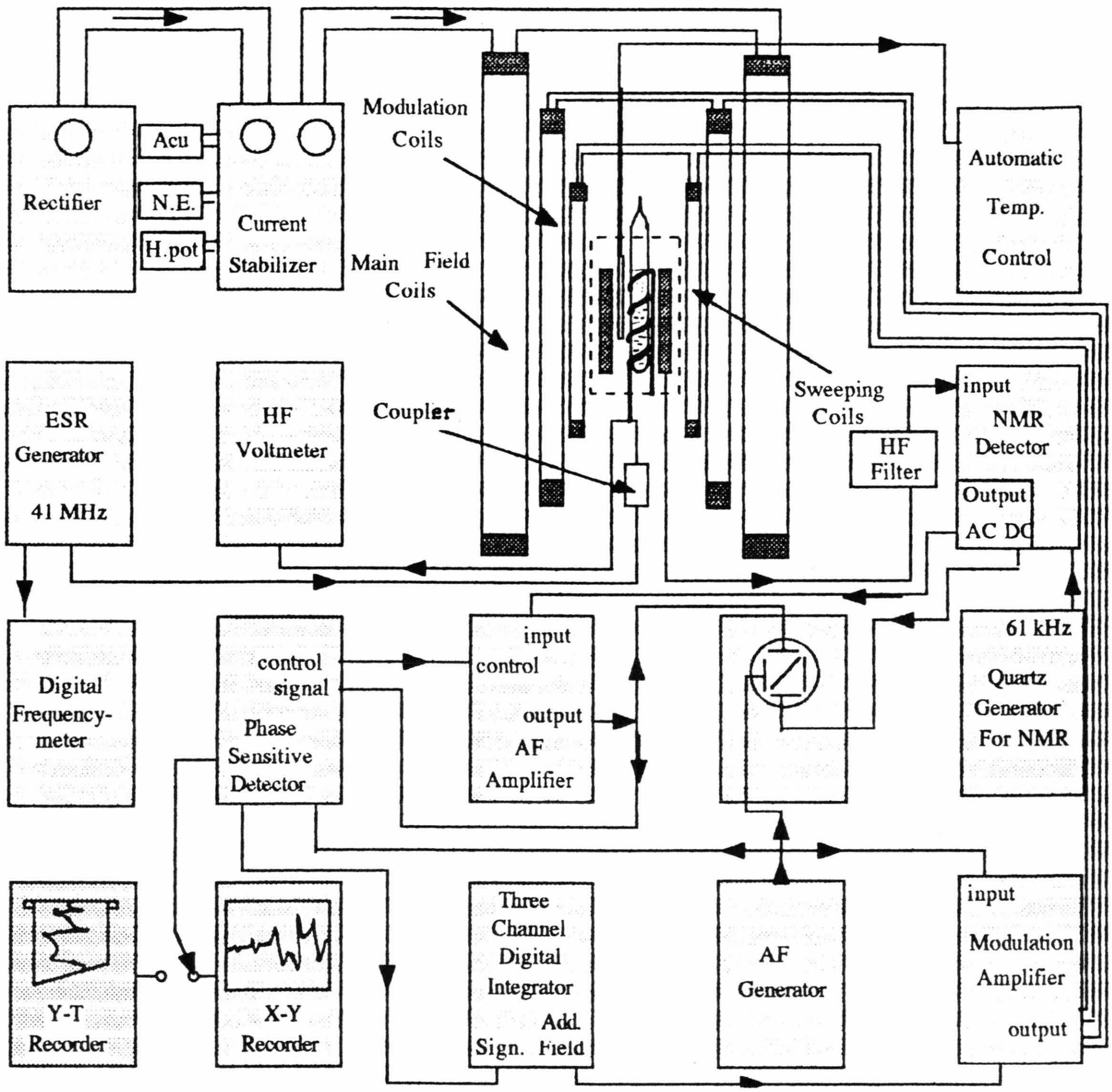


Fig. 1. Block diagram of the weak field double resonance NMR spectrometer.

Digital Sweep Generator

The main field of the spectrometer should be swept with an additional sawtooth field to obtain the resonance condition for the central-band and the side-bands. The digital sweep generator is shown in Figure 3 [6, 7].

A 555 timer works as an astable multivibrator. Its period can change from 5.037 ms to 1.478 s in 12 steps. A 4040 binary counter is used as an 8-bit counter. A DAC 0806 digital-to-analog converter has a current ramp at its output with 256 steps. A unit amplifier is used to process the current value as a voltage. This voltage can be symmetrized, and its level can be adjusted. The voltage-to-current converter and the transistor set can feed the sweeping coils from ± 0.6 mA to ± 12.2 mA. This can be achieved by switching R_f in 12 steps. The period of the ramp signal including the delay time can vary from 2.52 s to 753 s in 12 steps. Two 1N4001 diodes work as ground connections for the high voltage which can be present on the inductive load.

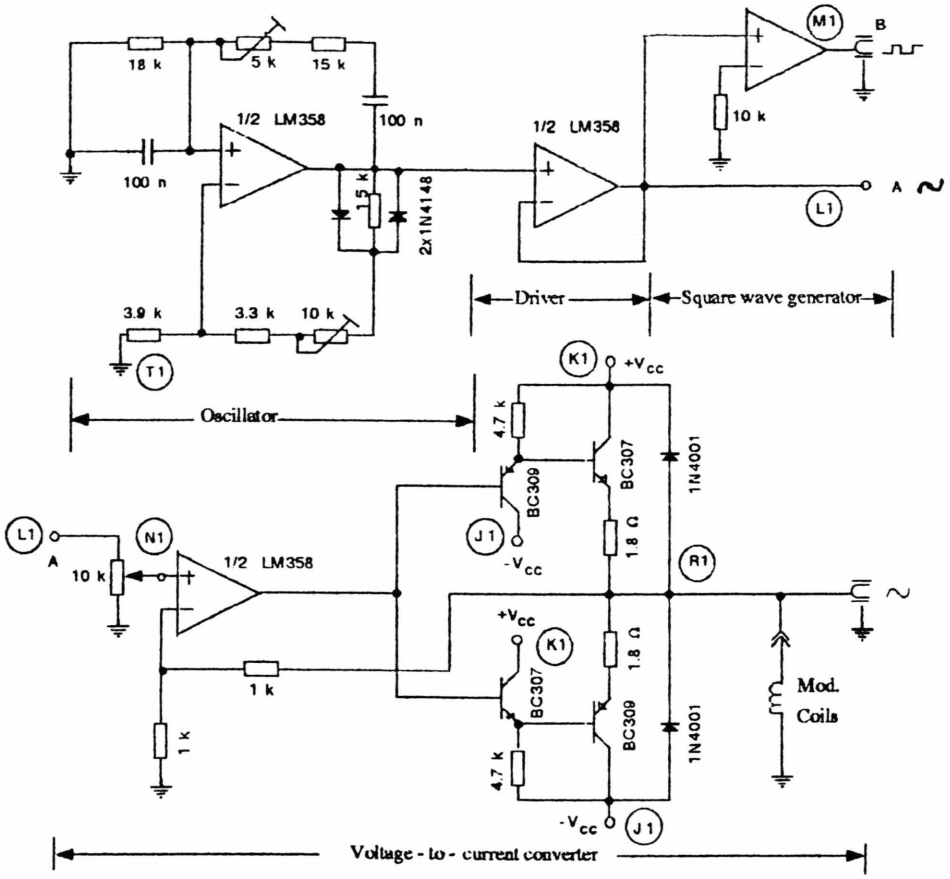


Fig. 2. The audio frequency generator.

Digital Additional Field and Delay Unit

In the spectrometer, sometimes a small DC field should be added to the main field and a convenient delay time is used before every field sweep. This unit is shown in Figure 4.

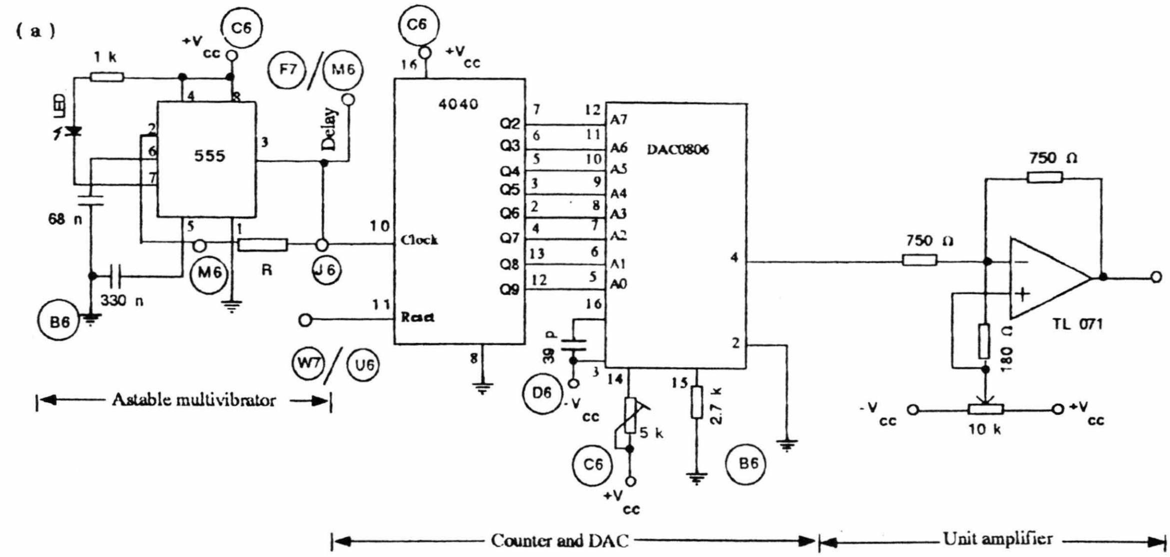
The asymmetric output of the astable multivibrator (555 timer of the digital sweep generator) can be symmetrized in the 4013 flip-flop integrated circuit. A 4040 binary counter is used as a 9-bit counter. The first 8 bits are treated in 4072 and 4071 gates and come to the trigger the input of the 555 timer. The ninth bit is inverted and comes to the reset input of the 555 timer. The A output of the 555 timer is used then as A or $\bar{A}$. The shape of A is shown in Figure 5.

The delay unit gives 1 or 0 to the reset input of the 4040 binary counter of the digital sweep generator. The inverted logic of the reset output will appear in the external trigger output. The LED will light when the reset output is 1 or the external trigger output is 0, showing the sweeping of the main field. The delay time can be choosen as 1/2, 1/4, 1/8 or 1/16 of the full sweeping time.

Quartz Generator

The quartz generator works with an NMR frequency of 61,220.7 Hz at the 1.437 mT for protons and the 1.529 mT for fluorines. It has a simple operational amplifier oscillator, a driver and an amplifier. The quartz generator is shown in Figure 6 [8].

The generator can produce very stable sinusoidal waves of (61,220.7 $\pm$ 0.1) Hz up to 18 V_{p-p}.



R (kΩ)	R_f (kΩ)
10.6	0.75
11.8	1.50
15.2	2.26
20.6	3.01
32.4	3.76
103	4.52
776	5.28
915	6.03
1102	6.78
1396	8.27
1995	9.75
3110	13.00

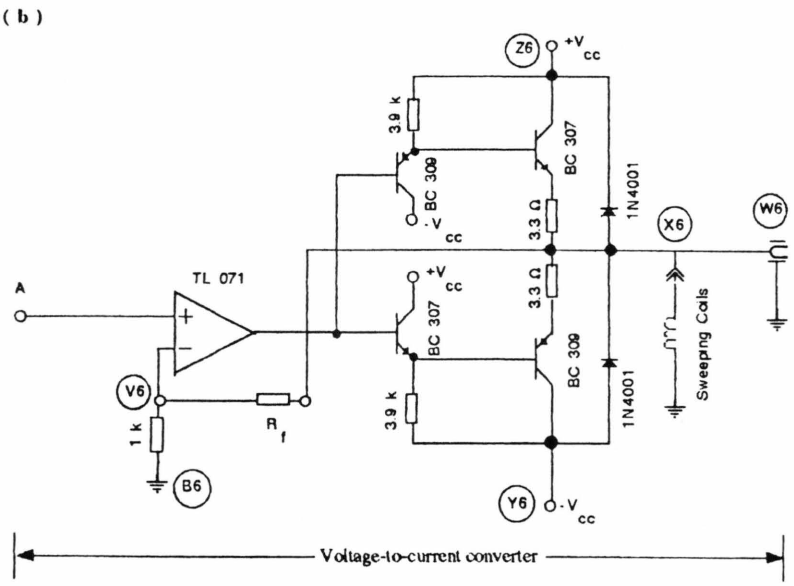


Fig. 3. a) Astable multivibrator, counter and DAC, and current-to-voltage converter of the digital sweep generator. b) Voltage-to-current converter of the digital sweep generator.

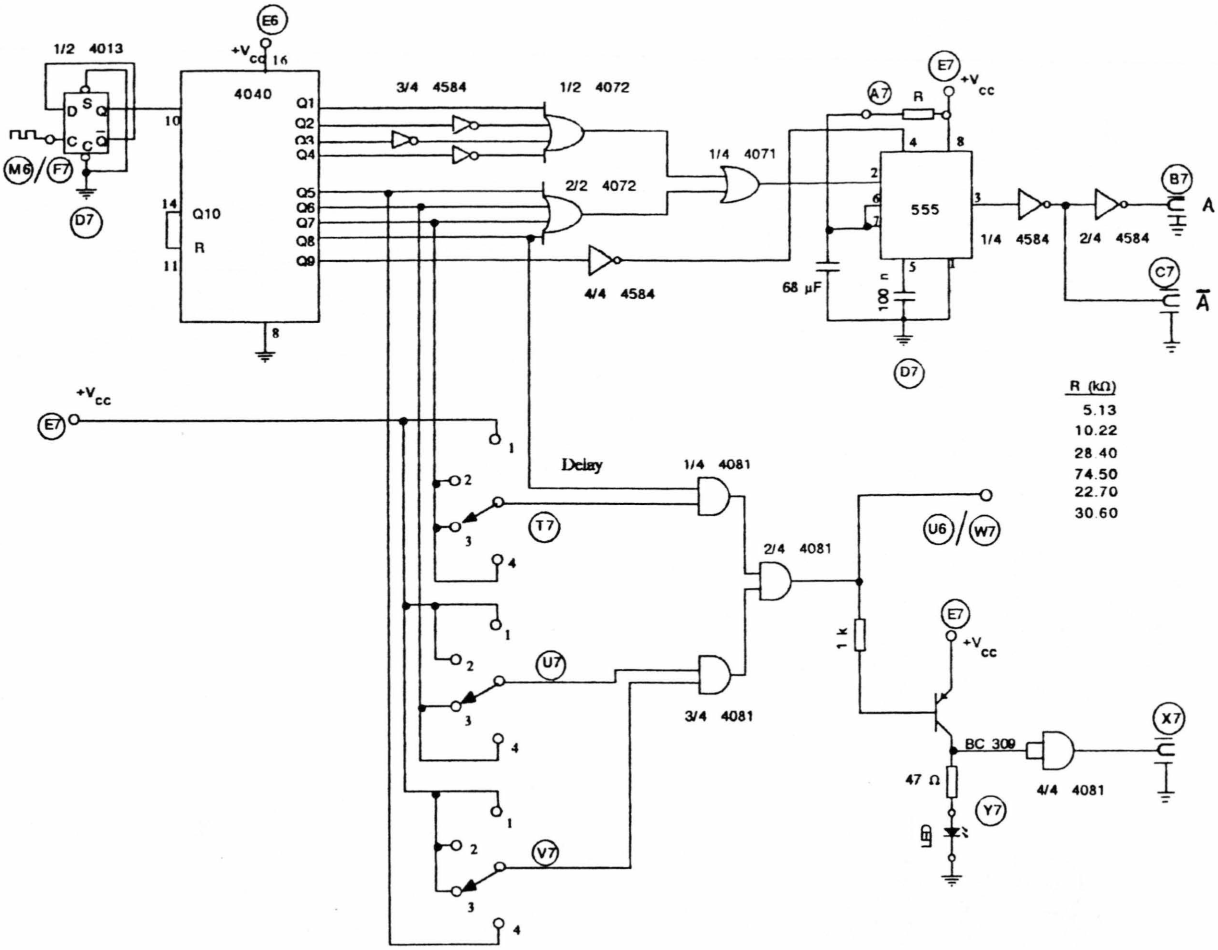


Fig. 4. Digital additional field and delay unit.

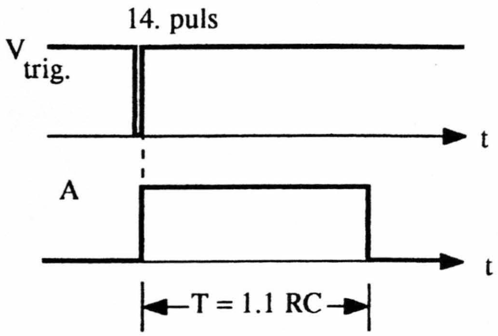


Fig. 5. Trigger input and A output of the 555 timer.

NMR Detector

The spectrometer should detect voltages in the order of microvolts of the e.m.f. present on the receiver coil. For this purpose an NMR detector is designed and shown in Figure 7. The L–C resonance circuit of the Q-meter is fed by a sinusoidal wave of 61.22 kHz, approximately 2.8 V_{p-p}.

The magnetic field being swept is modulated with a sinusoidal field of 90 Hz. The 90 Hz signal has an amplitude which is proportional to the slope of the Lorentz shaped resonance signal. It modulates the

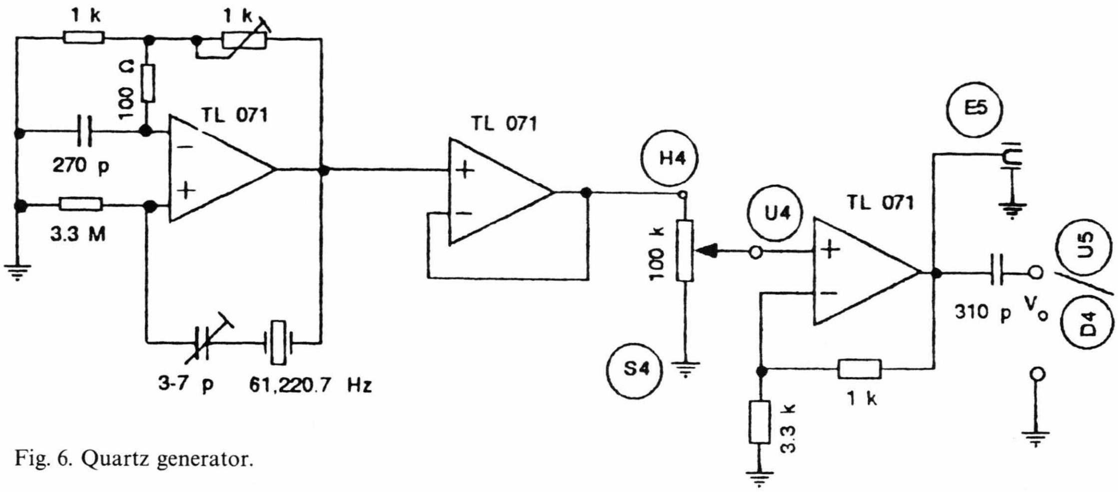


Fig. 6. Quartz generator.

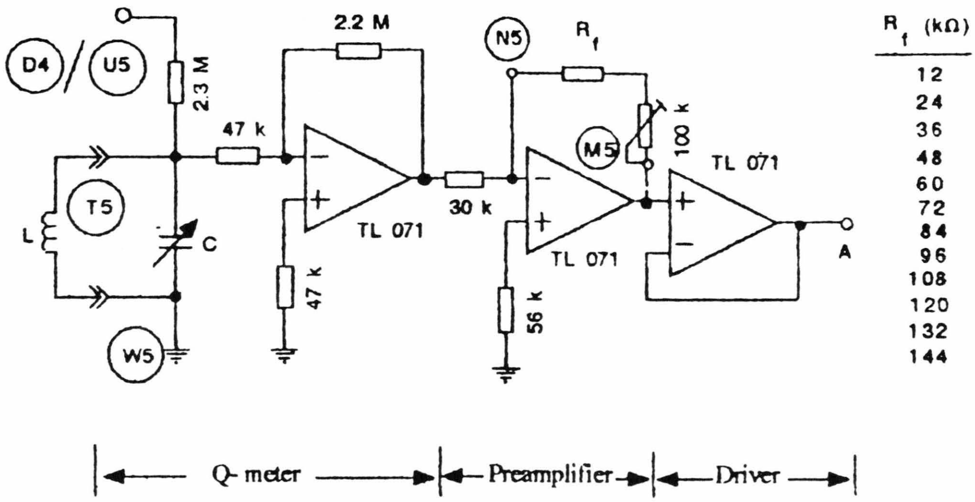


Fig. 7. a) Q-meter, preamplifier and driver of the NMR detector.

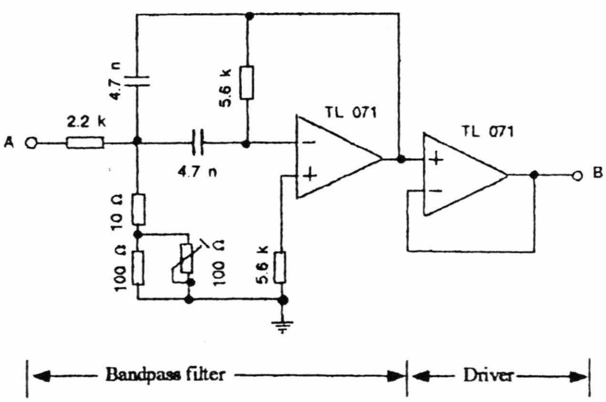


Fig. 7. b) Bandpass filter and driver of the NMR detector.

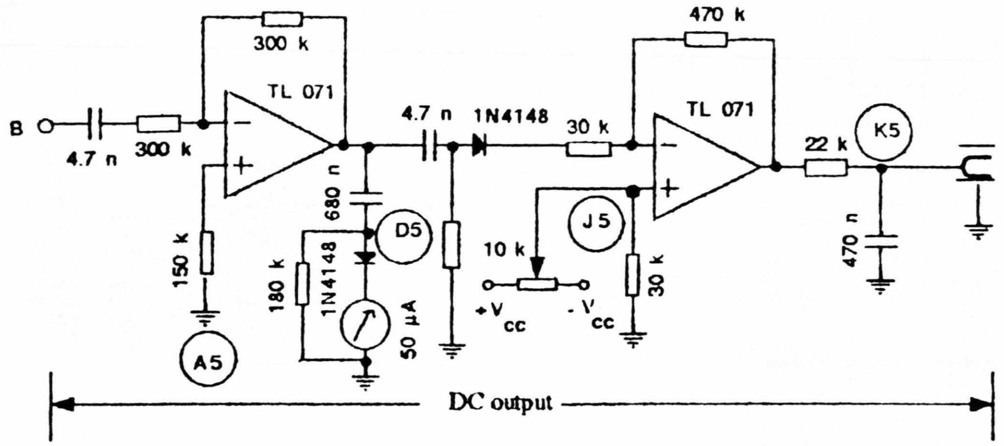


Fig. 7. c) DC output of the NMR detector.

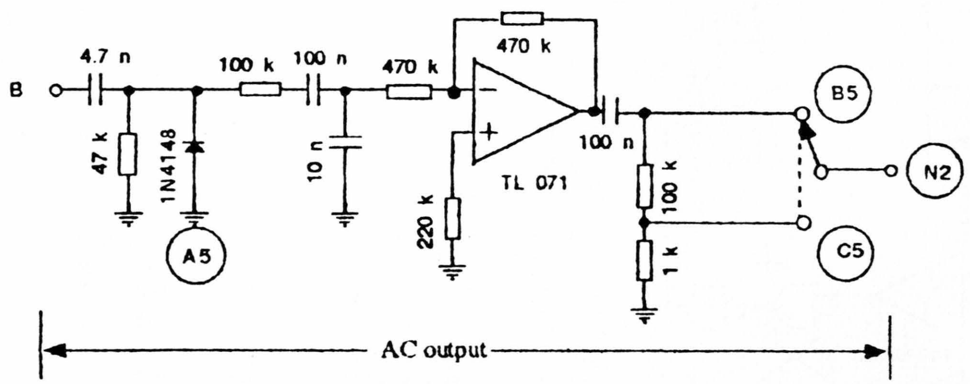


Fig. 7. d) AC output of the NMR detector.

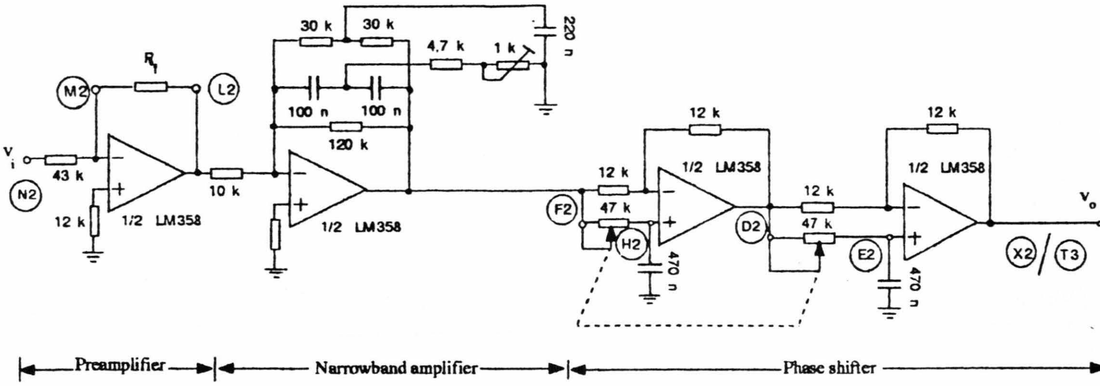
carrier signal of 61.22 kHz. This signal is amplified, the 61.22 kHz signal is filtered and the 90 Hz signal is taken from the AC output. The envelope of the 90 Hz signal is taken from the DC output of the NMR detector.

AF Narrowband Amplifier

The NMR signal is amplified by the preamplifier in 12 steps. The main amplifier has a double-T filter for the negative feed-back, so that only the 90 Hz signal can pass through with a bandwidth of 1 Hz. The phase of the signal can be changed (0°–360°) to obtain a good synchronization with the reference signal of the phase sensitive detector. The phase difference should be adjusted to 0° or 180°. The signal will be taken from the output of the phase shifter. The AF Narrowband Amplifier is shown in Figure 8 [9].

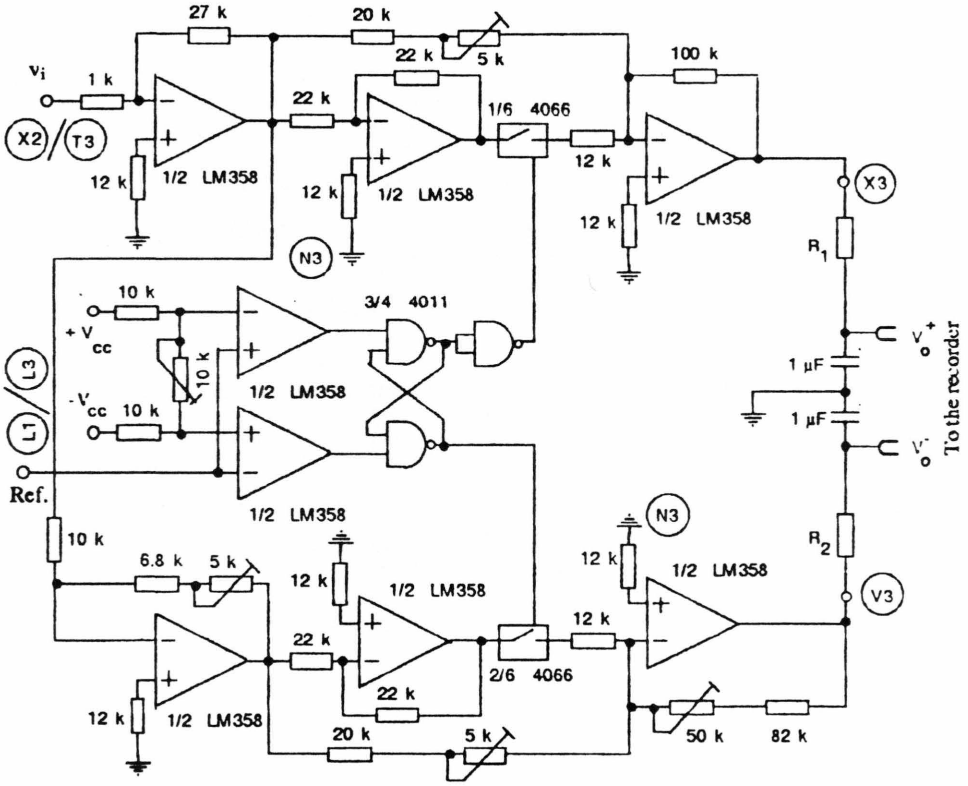
Phase Sensitive Detector

The amplified NMR signal is fed into the phase sensitive detector (see Fig. 9) [10]. A sinusoidal wave of 90 Hz is used as a reference signal. This signal is nanded in the primary flip-flop and used in the gates-relay. The detector has a positive DC output when the input and the reference signals are in phase and a negative DC output when they are in opposite phase. Due to the reduced bandwidth of the detector, the signal-to-noise ratio is extremely enhanced. A DC sig-



R_f (kΩ)
4.70
7.40
12.10
20.10
31.80
51.00
81.40
131.00
205.00
323.20
521.60
815.20

Fig. 8. AF narrowband amplifier.



R_1, R_2 (kΩ)
470
940
1410
1880
2350
2820

Fig. 9. Phase sensitive detector.

nal, proportional to the derivatives of the central-band and the side-bands, obtained from the amplitude modulation of the resonance curve, can be taken from the detector output.

Conclusions

A better S/N in a weak field NMR spectrometer has always been the dream of a physicist who works in this field. An appropriate electronic design could be the solution of this problem. The latest integrated circuits, a partly digital design and good grounding, homogeneity and stability of the main field is the solution.

In this work the idea is: "if a unit of the spectrometer can be digitally designed, it should be done". With these seven units, the spectrometer is accomplished, tested and works now better than the old one that was made with the technology of the sixties.

Acknowledgements

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[1] W. Müller-Warmuth, Z. Naturforsch. **15a,** 927 (1960).
[2] J. Haupt and W. Müller-Warmuth, Z. Naturforsch. **17a,** 1011 (1962).
[3] W. Müller-Warmuth and A. Yalçiner, Ber. Bunsenges. Phys. Chem. **75,** 763 (1971).
[4] J. Millman and C. Halkias, Integrated Electronics, Mc-Graw-Hill Corp., 1987.
[5] Linear Applications Handbook, National Semiconductor Corporation, 1986.
[6] Data Acquisition Linear Devices, National Semiconductor Corporation, 1989.
[7] CMOS Logic Databook, National Semiconductor Corporation, 1988.
[8] Ref. [4], Chapter 16.
[9] Ref. [4], Chapter 16.
[10] Ref. [5], Applications Notes 31, p. 91.