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# Conversion of A-60 NMR Spectrometers to Fourier Transform Operation*

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## Abstract

A description of the instrumental modifications and additions required for the conversion of this class of field-swept, field-modulated 60-MHz NMR spectrometers is given. The radio frequency portions are straightforward adaptations of the single-coil sample circuit to pulsed operation. The standard instrument achieves field-frequency stabilization through use of a NMR sideband oscillator employing a separate sample. While such a configuration is adequate for the normal mode of operation, it does not provide sufficient absolute stability for the pulsed Fourier mode of operation. The requisite stability was achieved by phase-locking the sideband oscillation frequency to an external reference by forcing the radio frequency to change in accordance with the phase-lock error signal. Both analytical and control channels are driven by this common radio frequency source as is the reference signal to the analytical channel synchronous detector.

During a series of studies of chemically induced dynamic nuclear polarization (CIDNP) it became necessary to extend the sensitivity of our dowager Varian A-60 NMR spectrometer which had already been fitted with a light guide for eliciting photochemical reactions.[1] While conventional signal averaging techniques[2] could have been employed, the advantages of Fourier transform techniques for both signal enhancement[3] and relaxation rate measurements[4-6] dictated that the latter method would produce the greater benefits. We report our procedures for conversion of this class of spectrometers and comment on the performance.

This class of instruments achieves field-frequency stabilization by operation of the control channel as a NMR sideband oscillator.[7] In the A-60, the field modulation frequency is nominally 5 KHz. Instantaneous departures of the magnetic field from the correct value are compensated for by a corresponding change in the sideband oscillation frequency which also supplies the reference signal to the analytical channel signal phase detector. Longer term stabilization is achieved by routing a portion of this audio frequency to a 5-KHz discriminator and low pass filter whose output passes to a varicap diode in the 15-MHz crystal oscillator circuit. After quadrupling, the resultant 60-MHz signal drives both the control and analytical channels. During conventional CW operation the spectrum is scanned by applying a bias field sweep to one or the other of the two samples. With probes equipped for variable temperature operation the bias field is applied to the control sample, thus forcing the carrier frequency to change.

In Fourier operation with a single rf synchronous detector the pulsed rf field and the digital storage devices are employed most efficiently by positioning the carrier frequency at one or the other extremum of the spectral region of interest. Since in the sideband mode of operation the carrier frequency is effectively 5 KHz removed, it is necessary to (1) displace the analytical from the control transmitter frequency by this value, or (2) to displace the local Zeeman field between the two samples by an equivalent value in order to operate the analytical channel at the center band. In a preliminary series of experiments the fixed and selectable output of a frequency synthesizer were employed to achieve the first condition. As the synthesizer is occupied fully in other spectrometers and its cost mitigated against the acquisition of another to be devoted exclusively to the A-60, we elected the second approach.

Several benefits accrue from this choice aside from the obvious cost reduction. The integral transmitter, control receiver, and field modulation circuitry are used intact. The modifications to the analytical channel are minimized so that selection of conventional or pulsed operation is affected by a single switch. Figure 1 contains a composite diagram, both block and schematic, of those elements involved in the conversion.

The differential 5-KHz field offset is achieved by supplying current, obtained from the internal - 1.0 V power supply, through a current divider circuit to the sweep coils. This modification is shown in heavy lines in the upper right of Figure 1 where the series resistor and milliammeter are connected through RE-1 between the aforementioned supply and terminal 7 of TB-501. Since departures or fluctuations from the field-frequency relationship are no longer compensated for when the sideband oscillation frequency does not provide the reference signal to the analytical channel phase detector, it becomes mandatory to achieve the requisite stability in some other fashion. The most direct method is to phase lock the sideband oscillation frequency to a stable 5-KHz reference. This is achieved by taking a sample of the output of the field modulator and comparing it to the reference in a broadband synchronous detector and using the resulting error signal to vary the 60-MHz carrier frequency, which serves as both the excitation and homodyning reference signal, via the aforementioned varicap diode AFC circuitry. In the unmodified instrument a three-pole filter is inroporated between the varicap and the 5-KHz discriminator. We were unable to achieve stable operation by introducing our phase lock error signal at this same point. Instead, we introduced our error signal after the integral network. The connection is shown in heavy lines between the phase detector, shown on the lower left of Figure 1, and terminal 10 of the transmitter. The connection between terminal 10 and the varicap is our addition, as it does not exist in the original instrument. The network between the phase detector and the varicap was required to achieve a compromise between stability of the loop at low frequencies and minimization of 60-Hz modulation sidebands which arise from some component of field or frequency modulation at the line frequency. In the normal mode of operation such fluctuations are compensated for automatically.

Since the basic instrument operates as a single coil "Q-meter" circuit, the obvious choice for pulsed operation is also this configuration. A double pole-double throw coaxial relay, RE-1, is inserted in the cable which connects the probe to the analytical receiver-transmitter. One pole switches the probe between the internal and external circuitry. The second pole provides for switching the analytical transmitter port from the internal to the external circuitry where it provides the drive for the power amplifier, via gate and phase control circuitry, and also the reference signal to the 60-MHz synchronous detector via a continuously variable phase shifter.

In the pulsed mode the rf circuitry is patterned after that described by Clark.[8] The pre-amplifier is protected by shunt back-to-back diodes. Back-to-back diodes in series with the transmitter prevent leakage of low level signals into the probe-receiver circuitry. The probe contains a parallel resonance circuit with a capaciive divider proportioned to present an impedance of 100 ohms to a coaxial cable of like impedance. Since all of our external devices are designed for 50-ohm operation, we inserted a 2:1 impedance matching transformer between the internal and external elements.

Double balanced mixers are used as gates in both the transmitting and receiving circuits. The pulses are obtained from a pulse-sequence generator designed for this application. The preamplifier, which has been described by Leskovar,[9] drives a conventional IF amplifier, gates, and then a dual phase detector-video amplifier with selectable video bandwidths. The presence of the 5-KHz field modulation generates sidebands symmetrically disposed about the carrier frequency; these are discriminated against by setting the video bandwidth at 1 or 2 KHz. This is more than adequate for virtually all proton chemical shifts at 60 MHz.

The transmitter employed thus far is a wideband solid state 10-watt amplifier which derives adequate drive from the A-60 analytical transmitter when the output attenuator is set at minimum attenuation. With these settings a 90° pulse requires about 25 μsec. At higher power levels, as well as for very long pulses, we have observed some interaction between the pulsed analytical transmitter and the control channel, resulting in a momentary loss of the lock. Some improvement was achieved by enclosing both probe cables in separate braided shields. As a 25-μsec pulse represents a field in excess of two gauss in the rotating frame, we have not found it necessary to strive to attain higher power levels.

Figure 2 shows a representative Fourier spectrum of a 5% sample of ethyl benzene. The performance is as anticipated. We do not make a direct comparison between the normal and pulsed operation as there are sufficient differences in the preamplifiers to render such a comparison not very meaningful.

The data acquisition and Fourier transformation were executed in our laboratory-wide computer based system dubbed AQUIRE. This system is capable of taking data from many instruments concurrently in the foreground while simultaneously executing batch, display, teletype messages, and data manipulation tasks in background. A dialogue between computer and operator determines the number of passes and the number of spectra to be acquired and upon receipt of a start instruction *via* the teletype, the pulse programmer is started. Upon completion of the particular experiment, either the free induction decay signal or its Fourier transform is displayed on the storage oscilloscope together with an alpha-numeric description of the number of the spectrum and number of passes. The system details will be published elsewhere.

Use of appropriate pulse sequences permits measurements of relaxation rates in complex spectra. Fourier difference spectra between illuminated and unilluminated samples are obtained by a combination of hardware and software controls. Spectra obtained at varying times after sample illumination or sample mixing can also be recorded.

In sum, the conversion of the spectrometer when coupled with a suitable computer has rendered it a highly versatile instrument with sensitivity adequate for many purposes.

## Acknowledgments

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## Footnotes and References

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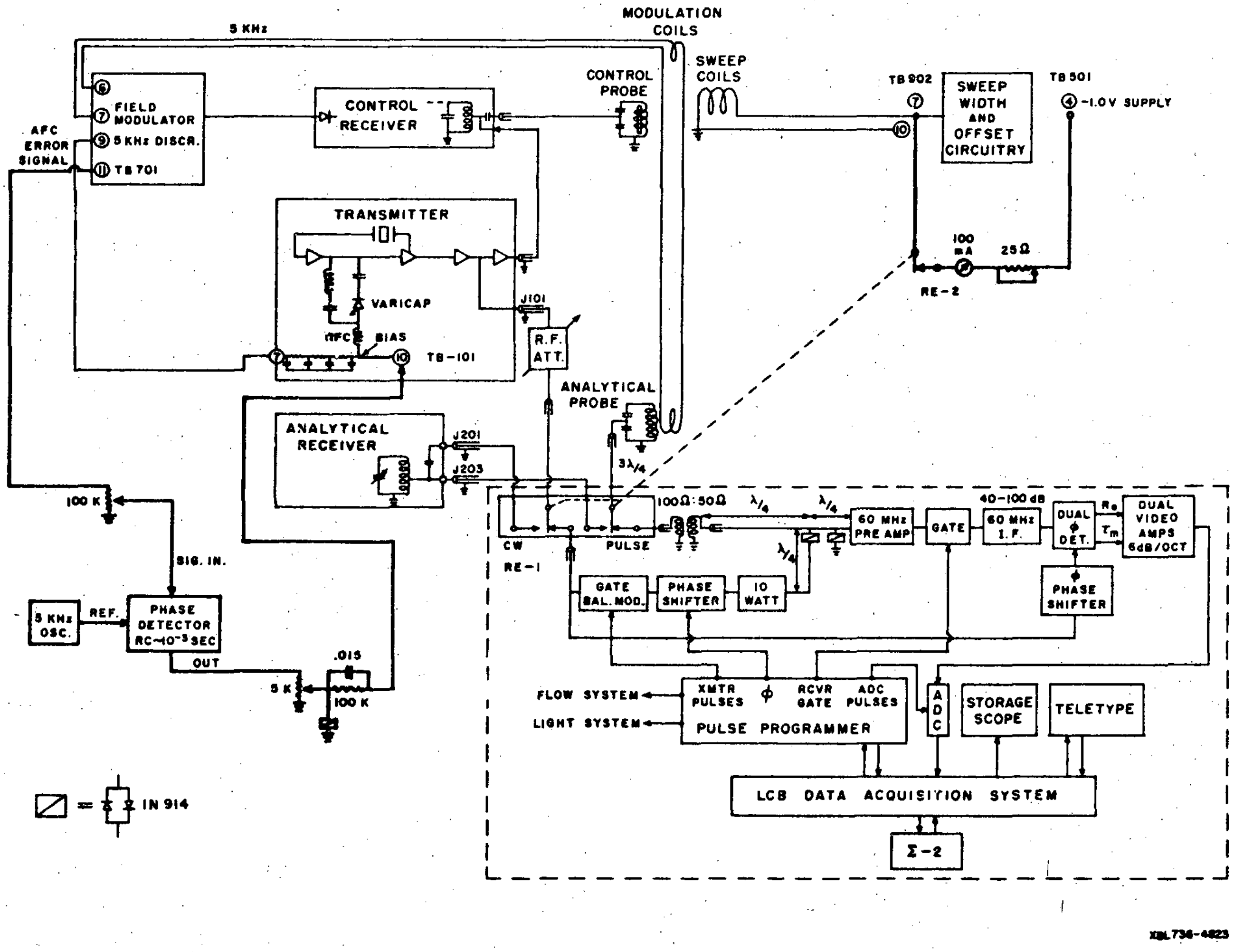
## Figure Captions

Figure 1. Diagram of elements involved in the conversion of an A-60 NMR spectrometer to Fourier transform operation. The components enclosed in the dashed lines are external additions concerned with the radio frequency circuitry, the digital conversion, data acquisition, and the Fourier transformation. RE-1 is a coaxial relay which switches the radio frequency elements from normal CW to pulsed operation. One pole is inserted into the probe circuitry while the other transfers the radio frequency drive between the internal and external circuitry. RE-2 connects additional bias current to the sweep coils to offset the Zeeman field at the analytical channel by 5 KHz, thus permitting operation at the "center band". The circuitry in heavy lines at the left is a phase-lock loop which compares a sample of the field modulation signal to that from a stable 5-KHz oscillator in a wideband synchronous detector and supplies an error signal to the varicap diode and provides field-frequency stabilization in both the CW and pulsed modes of operation. The connection between terminal 10 of TB-101 and the varicap circuitry was added during this conversion and does not exist in the standard instrument.

Figure 2. The NMR spectrum of a 5% solution of ethyl benzene obtained from the Fourier transformation of the free induction decay following a single 90° pulse.


5 KHz
MODULATION COILS
SWEEP COILS
CONTROL PROBE
FIELD MODULATOR
5 KHz DISCR.
TB 701
AFC ERROR SIGNAL
CONTROL RECEIVER
TRANSMITTER
VARICAP
RFC
BIAS
TB-101
J101
R.F. ATT.
ANALYTICAL PROBE
ANALYTICAL RECEIVER
J201
J203
TB 902
SWEEP WIDTH AND OFFSET CIRCUITRY
TB 501
-1.0V SUPPLY
100 mA
25Ω
RE-2
100 K
SIG. IN.
5 KHz OSC.
REF.
PHASE DETECTOR RC~10⁻³ SEC
OUT
.015
5 K
100 K
= IN 914
3λ/4
100Ω:50Ω
λ/4
λ/4
λ/4
CW
PULSE
RE-1
40-100 dB
60 MHz PRE AMP
GATE
60 MHz I.F.
DUAL ϕ DET.
Re
Im
DUAL VIDEO AMPS 6dB/OCT
ϕ PHASE SHIFTER
GATE BAL. MOD.
PHASE SHIFTER
10 WATT
FLOW SYSTEM
LIGHT SYSTEM
XMTR PULSES
ϕ
RCVR GATE
ADC PULSES
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ADC
STORAGE SCOPE
TELETYPE
LCB DATA ACQUISITION SYSTEM
Σ-2
XBL 736-4823

Fig. 1

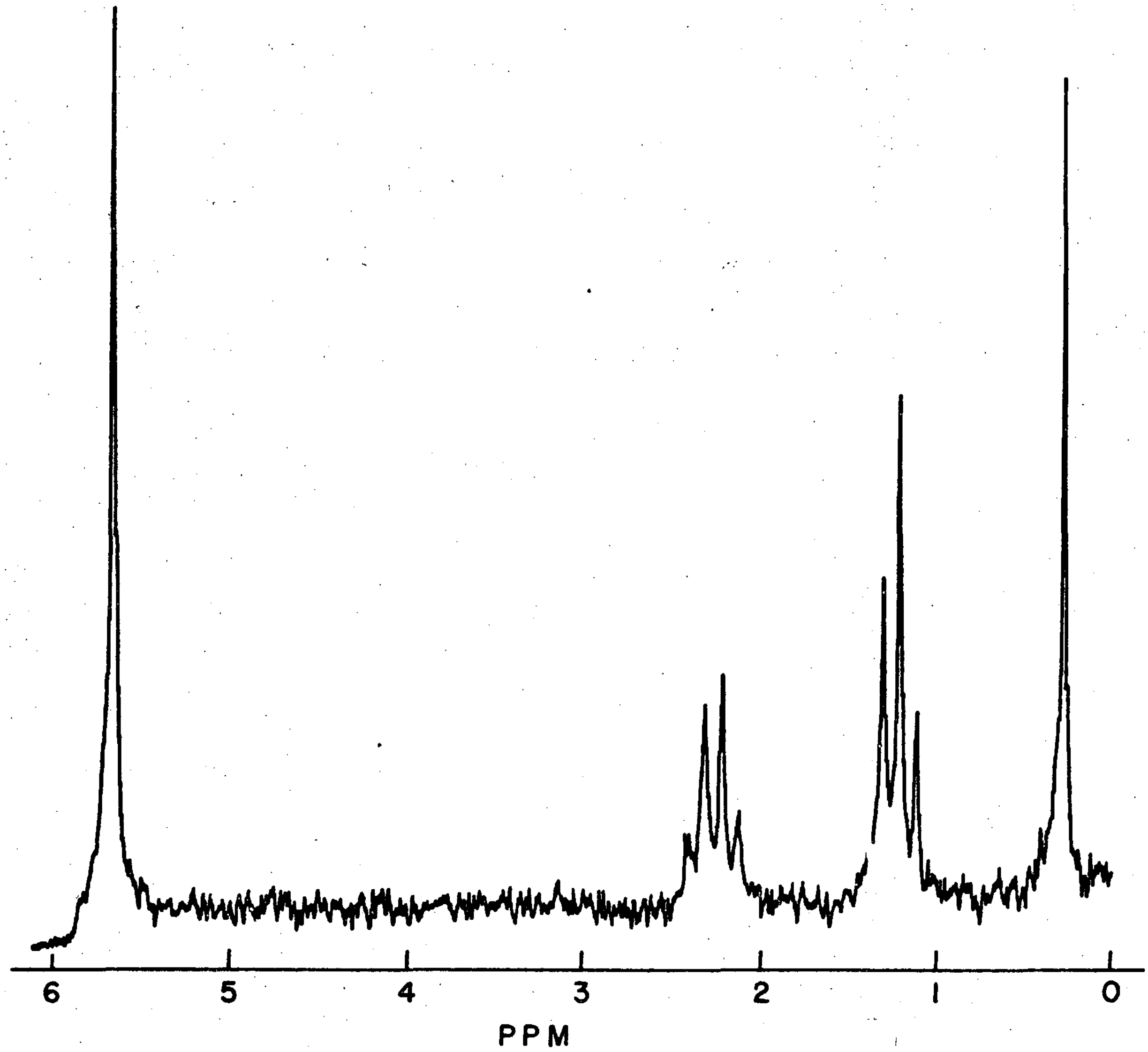

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Fig. 2

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