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Authors
Hirschfeld, T.
Klainer, S.M.

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T. Hirschfeld and S. M. Klainer

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SHORT RANGE REMOTE NQR MEASUREMENTS

T. Hirschfeld

Lawrence Livermore Laboratory, University of California, P. O. Box 808.

Livermore, California 94550 (U.S.A.).

S. M. Klainer

Geosciences Group, Lawrence Berkeley Laboratory, University of California,

One Cyclotron Road, Berkeley, California 94720* (U.S.A.)

ABSTRACT

Nuclear quadrupole resonance is both a highly specific detector of chemical compounds and a highly sensitive detector of details in their structure and of any alterations in these details. Given the high penetrating capability of radio frequency waves, its use as a remote chemical analyser for suitable target compounds would be obvious if it were not for NQR's well deserved reputation for insensitivity.

To meet a requirement for short range remote (external to the instrument) detection of some nitrogen-14 compounds, a new NQR instrument was built. Its pulsed Fourier transformer system uses a high power amplifier driving a large ribbon pancake coil with a nearly optimized winding profile with a high voltage pulse.

To obtain high sensitivity, the same coil is Q-switched to act as a low delay receiver, and fed through a Johnson noise limited amplifier to a Fourier transform data processor. An interlaced "skipping" scan using a frequency synthesizer was used to produce spectra, as was a special high repetition rate spin echo pulse train not constrained by T_1 limitations. The system is designed to operate at ranges up to 2-3 feet below the 1 foot sensing coil, with zeugmatographic range resolution in that interval.

Operating at 3 mHz, short range remote detection of the selected nitrogen-14 compound was accomplished.

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*When this study was performed both authors were employed at Block Engineering, Inc., Cambridge, Massachusetts.

INTRODUCTION

A number of military and industrial requirements exist for devices that can perform analyses of samples a short distance away from the measurement instrument. This includes cases where opaque materials may separate the sample from the instrument. Such applications include mine detectors, the detection of drugs and explosives in packages, quality analysis of solids in process streams, bulk solids analysis, explosives and propellant quality control in production and after installation in devices, salt bed rheology, measurement or rock properties, etc.

The location and accessibility of the sample rules out optical and most other methods of analysis. Radio frequency techniques at the longest (most penetrating) wavelength possible are most desirable. This leaves only EPR, NMR, and NQR as possible candidate methods.

It is possible to quickly discard EPR because of its specificity to free radicals/unpaired electrons, neither of which are associated, significantly, with the sample types of interest. NMR is, on the other hand, universal, selective, and sensitive but _needs_ an exceedingly constant strong magnetic field to resolve any spectral lines. The production of a strong uniform remote magnetic field, however, is not practical. NQR, unfortuneately is considered to have exceedingly low sensitivity. On comparison, however, the NQR method still has higher sensitivity than that provided by NMR under the specified conditions. This is because of the extremely small local region where a remotely generated strong magnetic field will be uniform and strong enough to provide data. The lack of uniformity means only small samples can be observed which decreases sensitivity. In addition the intensity of the magnetic field decreases as the square of the distance from the sample. When all factors are considered, therefore, remote NQR has the best sensivitity for the defined scenario. Furthermore, its specificity to given nuclei and the very narrow relative spectral linewidths make it very selective to each chemical grouping. For eaxample, in a remote land mine detector NQR system which is tuned to the $N^{14}O_2$ grouping it is possible to unambiguously detect TNT (trinitrotoluene) and RDX (hexahydro,1,3,5-trinitro,1,3,5-triazine) without any background contribution from the soil.

CONSIDERATIONS FOR A REMOTE NQR SPECTROMETER

While NQR is thus the "best game in town," it is admittedly a very poor one. Traditionally, NQR is so insensitive that often the problem is to find any signal at all in macroscopic samples placed within the instrument. This often happens even with the help of cryogenic sampling and shielded rooms. Clearly, order of magnitude improvements in signal are required for practical remote NQR even at short ranges (several tens of cm).

A number of facts and situations must be considered. if remote NQR is to be successful.

1. In many of the projected applications, samples larger than those used in the laboratory (>50 grams) are often available and a direct scale-up of the instrumentation is possible. For example, in a mine detector, quantities of the order of one pound must be detected, and larger systems can be used to advantage, up to the limit imposed by size, weight, and power constraints. In this application, for example, the scale-up in the likely amount of sample goes with the cube of the distance, largely canceling the range dependence of sensitivity.

2. Clearly, pulsed NQR techniques are required for high sensitivity, and a substantial degree of background (electrical noise, broadcasting signals, etc.) reduction (via time gating, bucking coils, etc.) is necessary. This is extremely important where nitrogen-14 NQR is concerned because many compounds resonate at broadcast frequencies. Sensitity can be further improved by spin echo techniques. Once again this is particularly important for nitrogen-14, whose lines occur at frequencies of a few MHz, which results in weak, easily saturated lines which must be measured against strong backgrounds.

3. It is absolutely necessary to efficiently use the available observation time. To do this multiple spin echo trains are used, and the pulse repetition rate optimized. This has been taken to its physical extreme in the SLSE technique, described elsewhere[1], where rapid pulse repetition rates are used continuously in disregard of T_1.

4. Frequency space should be effectively used by employing Fourier transform spectroscopy techniques and the specific resonance amplitude frequency isolated. Future improvements should include adaptive matched filtering (to counteract temperature induced line shifts) and correlation spectroscopy (for weighted coadding of multiple specific lines from a given compound). These improvements, which are currently being implemented, have not been used in the work described here.

5. Inasmuch as spin echo techniques require a specific value of the magnetic field intensity time product, field gradients at the samples must be reduced to fully exploit the large available sample quantities. This is of course helped by using a large coil, and also by winding a flat pancake coil rather than a solenoidal one. Furtheremore, the spatial variation of the coil's responsivity as a detector can be used to offset its spatial variation as an exciter. Finally, the coil's field is distorted to achieve higher uniformity at short ranges by an appropriate winding pattern. The use of ferrite field distorters to improve on this is under consideration but has not been incorporated in the experiments reported here.

6. It is important to consider that while enlarging the coil increases its field uniformity as a transmitter and its sensitivity as a receiver, it severely increases power requirements and lowers the self resonance wavelength. Detailed optimization of the coil design to: (a) optimize the self resonance, (b) achieve the required field intensity within a peak voltage constraint with the least possible power, and (c) have a good high Q for best detector sensitivity, will be described later. The trade-off includes the small losses in signal due to the finite pulse length arising from limited peak powers.

7. To allow for the largest possible coil size, the receiver and transmitter share a coil configuration, which for power economy and sensitivity is optimized for the maximum useable Q. It is necessary to avoid long ringdown times after the transmitted pulse so that the receiver can be operated. Q-switching is employed in the coils principally by using power dissipation diodes. In addition signal cancellation in the receiver coils is presently being considered.

8. For low noise data handling, a network matched, to a Johnson noise limited preamplifier is coupled to a digital signal processing computer system.

9. Background suppression coils of various types have been built to compensate out background electromagnetic radiation. Here use is made not only of frequency and time discrimination, but also of the much higher spatial dependence of the near field NQR compared to the far-field background interference.

SYSTEM DESIGN

The remote NQR spectrometer is a modification of a laboratory instrument described by Harding, et al.[2], Figure 1. The block diagram for this instrument is shown in Figure 2. The differences between the two instruments are primarily in the remote coil and its associated matching network. Both spectrometer configurations are primarily designed to maximize sensitivity while allowing automated operation.

The instrument is principally intended to operate as a Fourier transform nitrogen-14 spectrometer. It operates in the range 0.5 to 5 mHz and is capable of producing a rotating frame magnetic field H_1 of about 20 gauss in a cylindrical sample 2.5 cm in diameter and 8 cm long. In the remote system the solenoid coil and its associated matching network and preamplifier are replace by the remote coil with its special electronics package. The transmitter and receiver use a heterodyne configuration to eliminate the carrier feed-through problems present in autodyne NQR spectrometers. A matching network containing the transmit-receiver coil allows simultaneous tuning of both the transmitter and the receiver over a
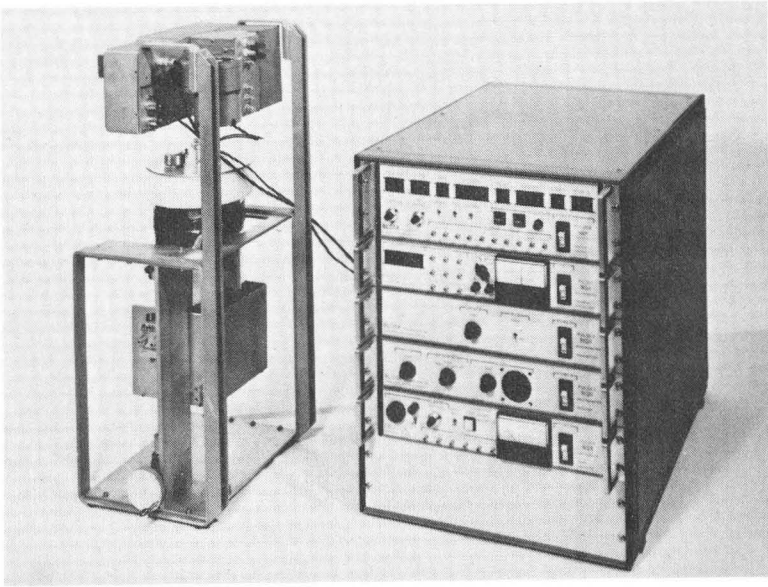
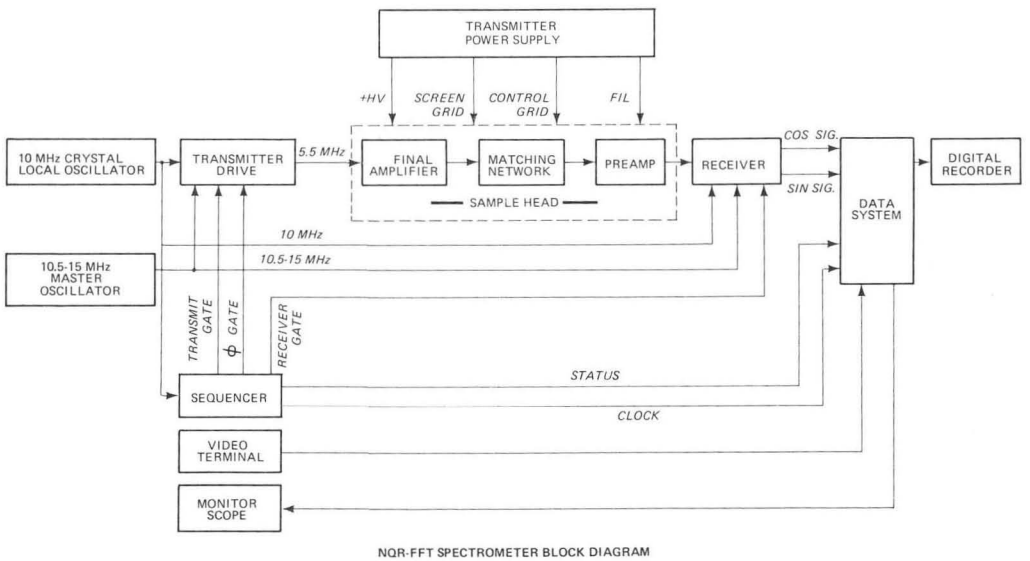Figure 1. NQR–FFT spectrometer (data system not shown).

NQR-FFT SPECTROMETER BLOCK DIAGRAM

Figure 2.

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two-to-one frequency range. Gating of the system is controlled by a pulse sequencer capable of generating Carr-Purcell, Meiboom-Gill modified Carr-Purcell, and Spin-Locked Spin-Echo sequences, as well as a sequence of $\pi/2$ pulses suitable for T_1 measurementss or collection of FID signals. The length of a "$\pi/2$" pulse for poly-crystalline samples is nominally 50 μsec. The sequencer also generates data collection control signals for the Fourier transform spectroscopy data system which includes real-time coadding.

SAMPLE HEAD

To maximize the sensitivity of the spectrometer, the coil, the matching network, and the preamplifier are built as a single unit in order to eliminate capacitive loading due to connecting lines between the coil and the preamplifier. This also provides signal amplification with a low impedance output to prevent interference pickup in the line between the preamplifier and receiver. This coupled with the design and shielding of the electronics allows a real time sensitivity within 12% (1dB) of the theoretical Johnson noise limit over the 0.5 to 5 MHz frequency range.

REMOTE COIL

The remote coil[3,4,5] used to obtain the data reported in this paper was not optimum. That is to say, the force field which reached the sample was neither uniform nor of optimum field intensity and the coil had limited sensitivity as a receiver. A pancake spinal wound ribbon conductor coil, 10 cm in diameter, having 10 turns of a 2.5 x 0.05 cm copper conductor insulated by 3.1 mm teflon spacers, was used both as transmitter and receiver[3,4,5]. This coil, shown in Figure 3, was used to produce the field pattern seen in Figure 4, which also shows its constant field amplitude contours.

MATCHING NETWORK

The impedance matching network allows simultaneous tuning of both the transmitter output and the receiver input by a single control over a full octave, an advantage when searching for unknown resonances. In addition, the network incorporates a Q switching device. During high voltage RF transmission the Q of the circuit is very low allowing transmit pulses with fast rise and fall times. On the other hand, in the observation intervals after RF pulses, the quality factor Q is as high as the coil itself. Further work presently in progress, programs the Q during the transmit pulse to minimize the required transmitter power and produces even faster coil "ringdown" of the transmitter pulse.

In order to futher increase the sensitivity of the remote NQR spectrometer, a more advanced matching network is in the design stages. This unit is specifically
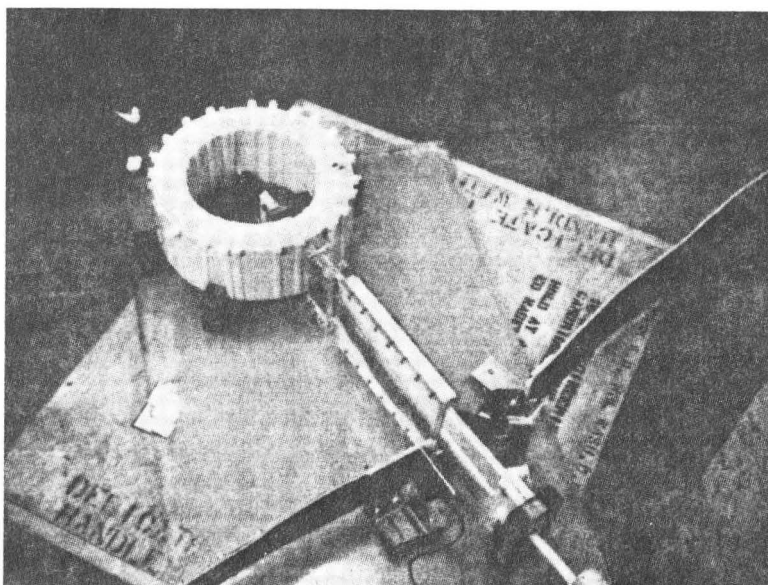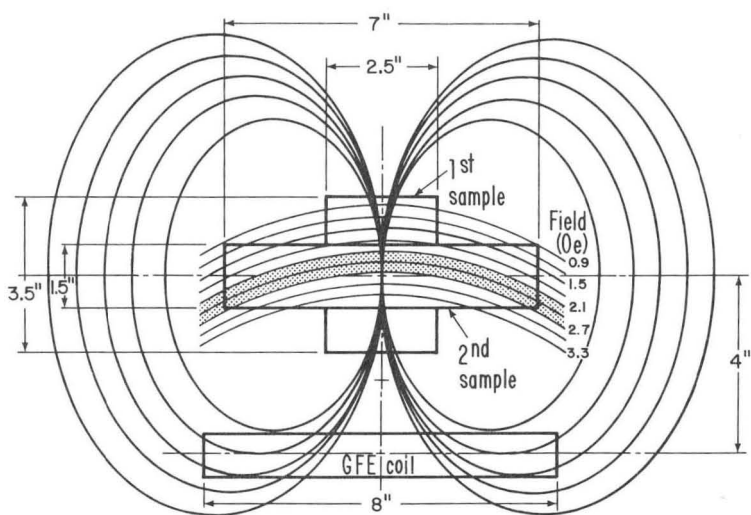
Figure 3. The initial remote NQR coil.

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Figure 4. Remote sampling geometry illustrating contours of constant field strength.

computer control, has been completed. It will provide up to one octave of unattended non-sequential scanning according to a preprogrammed frequency sequence. The parameters contributing to an optimized sequence are presently being analyzed. Using this technique areas of the frequency domain which are not in the excited state can be investigated while the others have time to decay. The data system then pieces the individual measurment outputs together into a standard frequency versus intensity spectrum.

TRANSMITTER SIGNAL CANCELLATION

High spectrometer sensitivity depends on the design and construction of an instrument which approaches the minimum theoretical noise, as already discussed and the development of a transmitter/receiver package with very small (microsecond) "ringdown" times. This later problem is presently being studied. Figure 5 represents the corresponding spectrometer block diagram based on the current radar techniques for coherent side lobe cancellation. Reduction of system recovery time when using high Q remote coils is essential if NQR techniques are to be applied to practical problems.
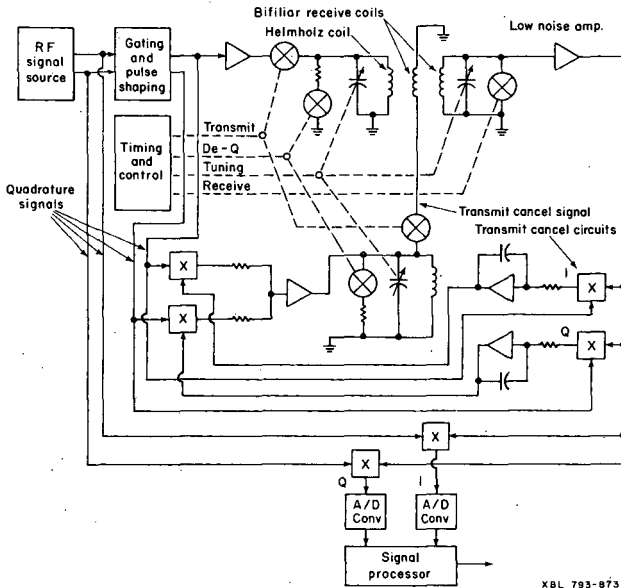

Figure 5. Block diagram of the NQR-FFT spectrometer with coherent side-lobe cancellation.

for to the detection of a predetermined compound whose resonance frequencies are accurately known. Here up to six resonances will be detected simultaneously and their intensities coadded.

PREAMPLIFIER

The preamplifier consists of two FET cascode gain stages coupled by an FET source follower, and an FET-bipolar transistor feedback compound that has a low impendance output to drive the twinax output cable. The cascade stages produce a gain of 40 dB from 0.5 to 5 MHz. In combination with the matching network, the preamplifier increases the Johnson noise of the coil by less than 10%. A pair of back-to-back diodes at the input protects the preamplifier from high RF voltages.

PULSE SEQUENCES

The spectrometer is capable of generating a number of sequences including single pulsed FID, Wahuha, Carr-Purcell, Meiboom and Gill, DEFT and spin lock-spin echo[1]. Multiple pulse sequences enhance sensitivity by recalling moments back into phase which extends effective lifetime and increases the integral signal magnitude. Accurate timing of the RF pulses and precise phase control results in a signal lifetime of up to several minutes.

DATA SYSTEMS

The data system serves many functions. It provides the fast Fourier transformation, instrument control functions, spectral storage and a variety of data processing techniques including spectral correlation.

The FFT capability assists greatly with resonant frequency location as it allows the bandwidth of the receiver to be opened so that a broad spectral range can be observed without deterioration in signal to noise. Typically, bandwidths of 10 kHz are used. Increases in system sensitivity are also obtained as it increases by the square root of the number of resolution elements in the frequency domain for a given observation time. The use of the Hilbert transform increases sensitivity by an additional 3dB while phase correction adds further 3dB improvement. Phase correction also make it possible to obtain true line shape information.

The basic components of the data system include a dedicated minicomputer with a 32K word core memory, a special interface (I/O) with 12 bit A/D converter and hardwired coadding capability at rates to 50 kHz, hardware multipy-divide, 256K disc memory, magnetic tape storage, digital plotter and video terminal. In addition an oscilloscope is used for output monitoring.

The NQR software system provides for data collection of a number of files with a total capacity of 128K points. Data may also be coadded into these files in

real time.   This mode is normally used to coadd successive FID's or echoes in order to improve the signal-to-noise ratio. Addition, subtraction, multiplication, or division of two files is also possible.   Data files are normally stored for future reference by the magnetic tape unit.   Software programs are also loaded by magnetic tape.

When using the FFT a four breakpoint apodization routine is used to minimize the sidelobes of the sampling interval transform and to zero any "ringdown" time transients at the beginning of the file. An FFT routine may be selected to perform amplitude only or real and imaginary transforms of a single receiver output channel. The FFT routine outputs to the monitor scope one point in frequency space for every point in the input file. A hardcopy plot of the lineshape with full annotation may then be made, or the transformed data may be stored along with the original data file on magnetic tape or on the disc if correlation techniques are to be utilized.   If both quadrature outputs of the receiver are alternately sampled, another FFT routine produces a single-sided frequency output with selection between upper or lower sideband. This routine is particularly valuable for analysis of wide lines or closely spaced multiple lines, but requires careful correction for amplitude and phase imbalances between the quadrature channels.

NEW AREAS OF DEVELOPMENT

The remote NQR spectrometer is presently undergoing major changes which are expected to further increase its utility and sensitivity.   These improvements are also valuable for laboratory studies.   Three of the more important projects are mentioned herein.

AUTOMATIC SCAN

The general problems associated with searching for unknown resonances fall basically into two catagories: the necessity of irradiating the sample at the exact frequency at which resonance occurs, and the requirement that the sample be in a non-excited state so that it can respond to the RF energy.   The first problem has been solved by use of the FFT technique which will respond to any resonance within a 10 kHz bandwidth.

The second area which needs attention is essentially limited by the spin lattice relaxation time, T_1. When T_1 is long (i.e., longer than the duration between RF pulses) then either the search speed must be reduced or the search cannot be done at sequential frequencies. An alternative scheme scans the spectrum by "slipping" through a set of widely spaced frequencies. This is repeated several times, at different offsets, until the entire frequency interval is filled.   In the present system concept non-sequential scan technqiues have been used manually.   The design of this accesory for doing this automatically, under

HIGH SENSITIVITY REMOTE COIL WITH BACKGROUND REJECTION

To optimize the coil, the ribbon height and winding spacing must be designed so that there is a high Q at the resonance line of interest while the peak voltage and transmitter power for a given field are maintained at reasonable levels. Figure 6 shows the present configuration of the remote coil.
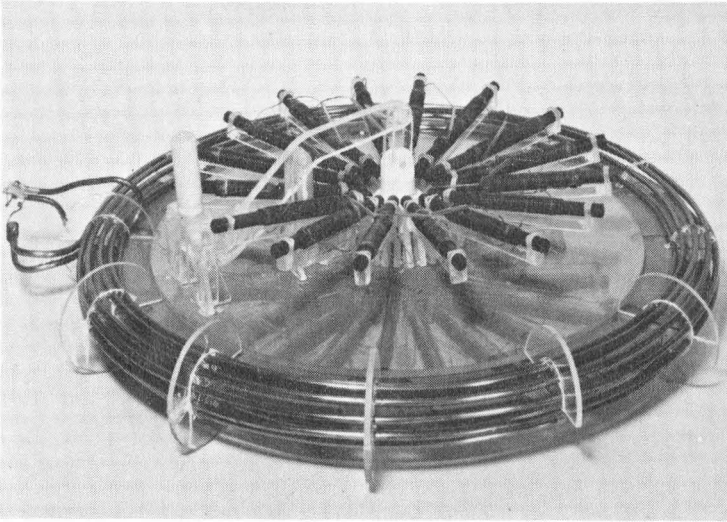

Figure 6.

The most updated design of the transmitter is two parallel fed multiturn coils. The spacing of the coil is such that the proximity effect, i.e., the non-uniformity distribution of the current caused by the close proximity of the turns, is minimized. Reducing this effect is most important because it increases the AC resistance and thus reduces the Q. This design is expected to result in uniform current distri- bution in a manner similar to that experienced with a large single turn conductor. Each conductor in the coaxial loop is in a uniform magnetic field in this con- figuration.

The receive coil consists of wire wrapped ferrite rods 1/2 inch in diameter. Fourteen of these rods are mounted flat inside the transmitter coil and in a radial position similar to the spokes on a wheel. The receiver is tuned by

moving the ferrites within their wire cores. This configuration also provides two other important functions: (a) cancelling external background fields and (b) intensifying fields emanating directly below the coil assembly.

The use of ferrites can also be used for field shaping and uniformization where a preselected operating distance is to be used.

EXPERIMENTAL RESULTS

Unfortunately a common situation in NQR, particularly for low frequency nuclei such as nitrogen-14, is that the lines manage to evade detection completely. This may be due not only to their weakness, but also to those having a T_2 too small for the instrument or T_1 too long to be compatible with tolerable scan speeds.

The high sensitivity and fast "ringdown" of the instrument described here addresses the first two problems while the third is handled by the nonsequential scan procedure. Under these circumstances, TNT (trinitrotoluene), a sample which normal NQR technques had failed to detect, gave a very satisfying 12 peak spectrum[6], as shown in Figure 7 and Table 1, and in detail for one peak in Figure 8. This work is still incomplete and R. A. Marino of Hunter College is presently continuing this research.

NQR SPECTRUM OF TNT (77K)
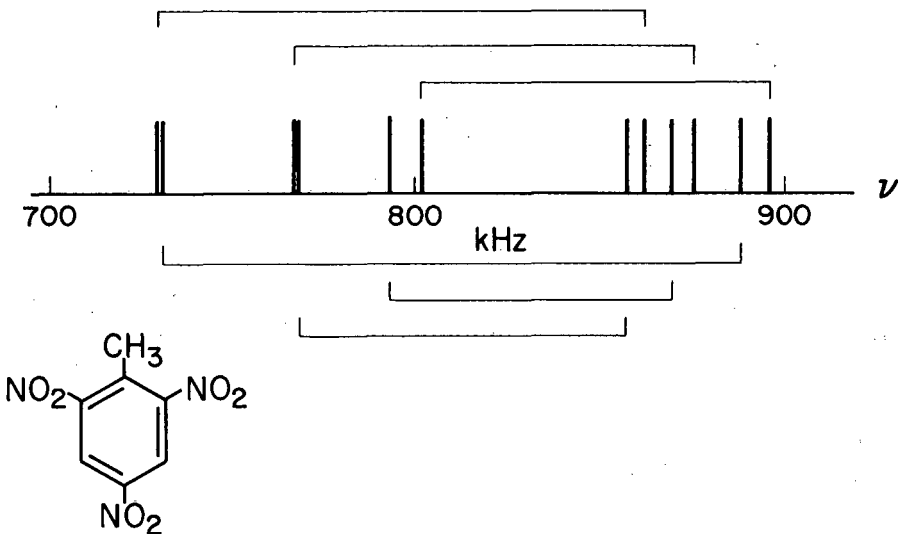
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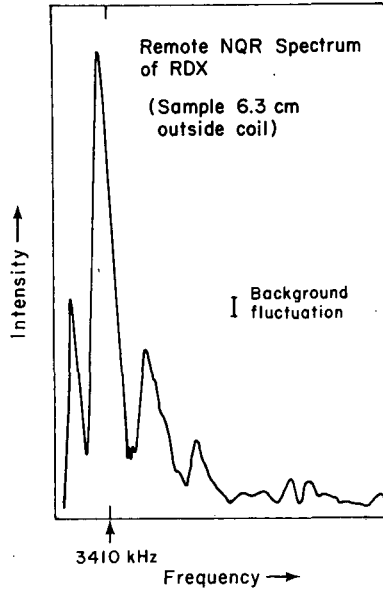
Figure 7.
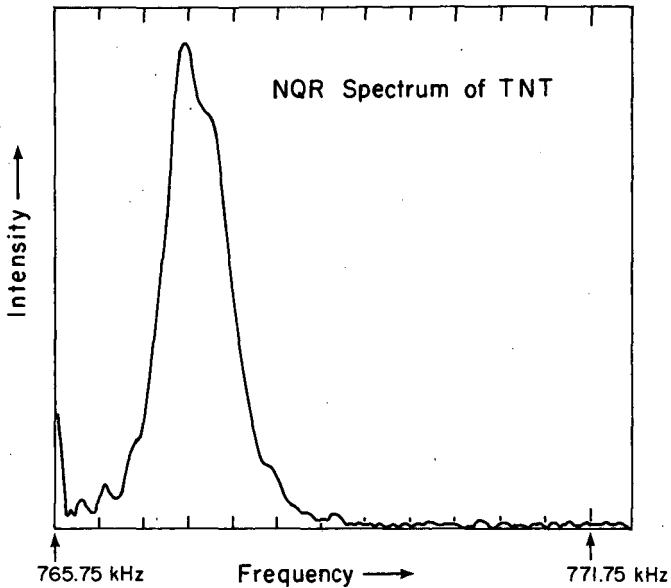
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Figure 8.

The first generation short range coil previously described then was used to measure a sample of RDX whose volume was 106 cm^3. Sampling was done at 50% efficiency. For safety reasons a slurry of RDX[3] in alcohol-water having 50 volume % RDX was used. This resulted in an effective sample weight of 50g.

Figures 9 and 10 show the sample spectral peak curves for the 3.410 MHz RDX peak for this sample at distances of 6 and 10 cm from the coil, respectively. The observation times were 12 seconds in each case. Unfortunately, a breakdown in the receiver electronics kept the signal to noise ratio at the 10 cm distance to just 7:1, and limited the largest distance at which the sample could be detected to 20 cm. The receiver electronics have been modified, but no new data taken.

DISCUSSION

The results shown here indicate that it is possible to detect samples by NQR in seconds at very short ranges outside the measurement coil. Transition to an optimized coil and improved electronics promises improvement, as does the simple method of scaling the transmitter coil. Fortunately, there are still many avenues open to improve system performance. Practical detection ranges, however, will

probably not exceed 50-80 cm for nitrogen-14 and a few times better for even the most favorable nuclei. These distances should be halved (giving an 8 fold signal to noise ratio gain) if quantification rather than simple detection is required.

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Figure 9.
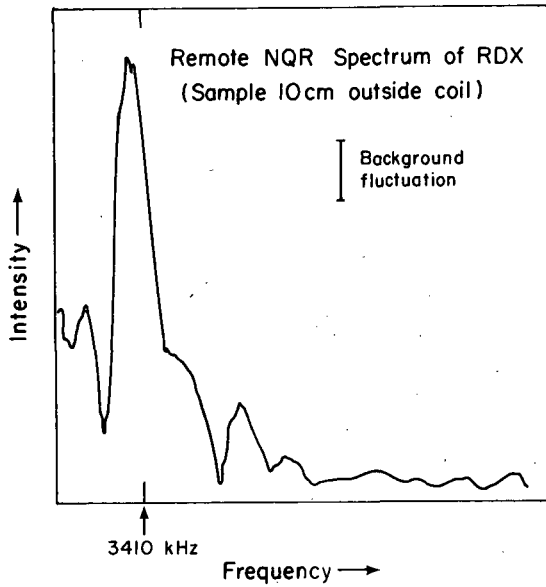
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Figure 10.

TABLE 1

Nitrogen-14 nuclear quadrupole resonant frequencies for TNT

Temperature	Site #	− kHz	+ kHz
77°	1	801.8	895.4
	2	730.1	888.1
	3	767.3	875.6
	4	792.1	869.4
	5	729.7	861.8
	6	767.7	857.0
16°	Unassigned	769	871.0
		752	860.4
		716·	845.0
		743	843.8
		(714)*	838.0

The reported measurements, while not very "remote," provide sufficient distance to put the sample definitely outside the instrument, and allow the many potential applications discussed in the introduction to be pursued. It is anticipated that such capabilities will eventually allow NQR to make the transition from an esoteric structural research technique (and one often used as a last resort) to a valuable tool for analysis and measurement. In this regard, the NQR research being performed at the Lawrence Berkeley and Lawrence Livermore Laboratories is oriented towards the solution of existing analytical problems which cannot be handled by other instrumental methods.

ACKNOWLEDGEMENT

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