
NUCLEAR QUADRUPOLE RESONANCE (PAPER II)*Allen N. Garroway, Naval Research Laboratory¹*

INTRODUCTION: NUCLEAR QUADRUPOLE RESONANCE AT THE NAVAL RESEARCH LABORATORY

The Polymer Diagnostics Section (Code 6122) of the U.S. Naval Research Laboratory (NRL) has expertise in solid state nuclear magnetic resonance (NMR), magnetic resonance imaging (MRI), and nuclear quadrupole resonance (NQR). In 1983, NRL established an interagency agreement with the Federal Aviation Administration (FAA) to advise the FAA on NMR methods to detect explosives. We were aware of earlier work [1] on the use of NQR for explosives detection, and in 1987 we initiated a research program at NRL to explore NQR, with initial support of the FAA and Technical Support Working Group (Department of Defense). NQR explosives detection technologies, including methods applicable for landmine detection, have been developed and patented by NRL and have been licensed by the U.S. Navy to Quantum Magnetics (San Diego, Calif.), a subsidiary of InVision Technologies Inc.

PHYSICAL PRINCIPLES**Limitations of Conventional Detection Methods²**

The basic technology for both military and humanitarian mine detection is still the electromagnetic metal detector, a direct descen-

¹This work was prepared by a U.S. government employee as part of his official duties.

²This section is adapted from Garroway et al. [1].

dant of those used in World War II. Finding a metal-encased antitank mine (5–10 kg of explosive) buried 10 cm underground is trivial for such a device, but finding a “low-metal” antipersonnel mine (50–100 g of explosive, and perhaps 0.5 g of metal for the firing pin) below the surface is highly challenging. The electromagnetic return signal from the antipersonnel mine is much weaker, and so the operator must turn up the detector gain. At higher sensitivity, however, much more of the other metal detritus, such as nails and shell fragments, becomes visible to the detector. The operator is compelled to operate at very high sensitivity and to flag any alarm as a potential landmine. Unfortunately, the next step is the most difficult: One must then separate the landmines from the false alarms arising from this benign background of signals. Currently, that “resolution of false alarms” is still done by mechanical probing: The deminer or combat engineer performs very delicate archeology with a pointed stick to classify the source of the electromagnetic signal—a landmine, perhaps rigged with an antihandling device, or just a rusty nail. In that sense, finding landmines is easy; however, separating them from the clutter is tough—and extremely hazardous.

Why NQR? What is desired is a detector based on a signal that is specific to the landmine. Certainly a unique signature of the explosive would provide a way to reduce this clutter problem. Such arguments lead to chemical detection of the explosives in landmines. While dogs are being used to find landmines, their method of detection is still a subject of controversy and their efficiency is not high. The vapor pressure of the military explosives used in landmines is quite low, and commercially manufactured mines hermetically seal the explosives in a polymeric case. Further, as explosive vapors and particles are quite sticky, the transport of explosive from the main charge, through the case, and then through the ground is slow and inefficient. Vapor sensors have been explored for landmine detection, and there is a recent indication that, under some field conditions, exquisitely sensitive vapor detectors can detect the plume from a landmine [2].

But there is another method—NQR—that is specific to the chemistry of an explosive, regardless of how it is packaged.

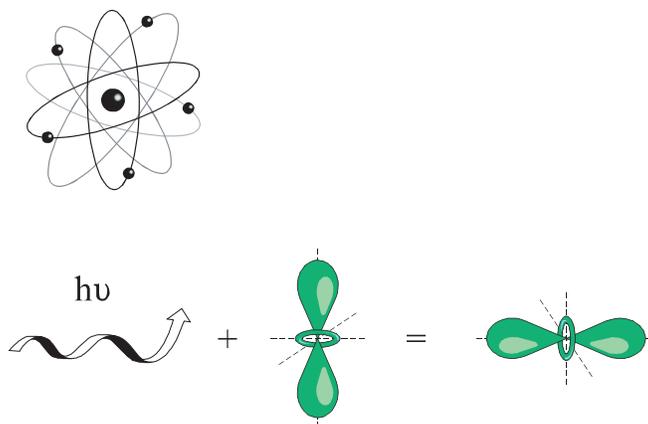
BASICS OF NQR

NQR [3] is a magnetic resonance phenomenon related to NMR and its offspring, MRI. In NMR and MRI, a large static magnetic field (0.05–20.00 T, 0.5–200.0 kG) orients the nuclei so that slightly more are in the low energy state (aligned parallel to the static field) than are in the higher state (opposed to the field). This population difference corresponds to a weak diamagnetism of the nuclear spins, with a classical magnetization vector aligned along the static magnetic field. The magnetic field corresponding to this nuclear diamagnetism can be observed by applying a resonant radio frequency (RF) pulse (at the Larmor frequency and at right angles to the static field), causing the magnetization to rotate away from the axis of the static magnetic field. The magnetization then precesses freely in the static field, at the Larmor frequency, and this time-dependent flux induces a weak voltage in an RF pickup coil perpendicular to the static field. This induced signal is the NMR signal.

Comparison to Nuclear Magnetic Resonance

NQR is similar to NMR but has some important distinctions. In NQR, the splitting of the nuclear spin states is determined by the electrostatic interaction of the nuclear charge density, $\rho(r)$, with the external electric potential, $V(r)$, of the surrounding electron cloud (see Figure K.1). A moment expansion of this electrostatic interaction shows that the important coupling is between the nuclear quadrupole moment, indicated schematically in Figure K.1, and the second derivative of the electric potential (equivalently, the gradient of the electric field). *This is a key result.* The quadrupole moment, nonzero only for nuclei with spin quantum number I greater than or equal to 1, is a nuclear physics parameter describing the distribution of charge in the nucleus. (For landmine applications, the primary nucleus of interest is ^{14}N , with I equal to 1.) The second term, the coupling to the electric field gradient of the valence electrons is largely based on chemistry, although the local crystal packing also plays a role.

Contrast the chemical specificity of NQR with that of NMR. While NMR provides highly detailed information about chemical structure, the range of “chemical shifts” is generally small. Hydrogens in any

NQR

NOTE: Applying a pulse of the correct frequency ν flips the nuclear spin and induces an NQR signal in a pickup coil.

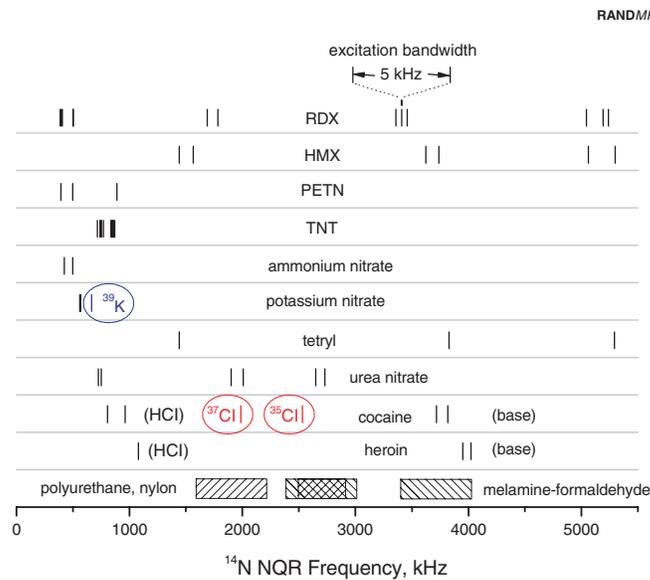
Figure K.1—A Quadrupolar Nucleus Slightly Aligned by the Electrostatic Interaction with the Valence Electrons

arbitrary organic structure differ by a range of about 10 ppm away from their nominal NMR frequency, e.g., a 6-kHz range of frequencies in a 600-MHz NMR spectrometer. However, for ^{14}N NQR, the NQR frequencies can range from *zero to 6 MHz*, depending on the symmetry of the molecule. Indeed, one of the difficulties of NQR is that it can be *too sensitive* to the chemistry of the compound of interest.

There are also some significant subtleties in NQR compared with NMR: For NQR the nuclear spin is greater than or equal to 1, and the spins are quantized along the principal axis system of the electric field gradient, rather than for the NMR or MRI case that (commonly) involves spin-1/2 nuclei quantized along the static magnetic field. For the present purpose, these distinctions are best overlooked, and, in a rough sense, it suffices to regard NQR as NMR without the magnet.

NQR as a Detector

One significant advantage of NQR is the absence of a magnet: Even if the NMR approach were thought to give some advantage to detecting explosives, projecting a large static magnetic field into the ground is difficult. But the main advantage is that NQR provides a highly specific and arguably unique frequency signature for the material of interest. Figure K.2 shows the NQR frequencies for a number of common explosives, as well as for some narcotics and other materials. Although the chemical structure of RDX (Figure K.3) indicates that the three ring nitrogens are chemically equivalent and hence would be expected to have identical NQR frequencies, in fact the crystal packing is sufficient to remove this degeneracy, and indeed the chemically equivalent ring nitrogens are separated by the order



NOTE: Unless otherwise indicated, the frequencies are for ^{14}N . Also shown are estimates for the general frequency bands expected for some commercial polymers.

Figure K.2—Representative NQR Frequencies for Some Explosives and Narcotics

RANDMR1608-K.3

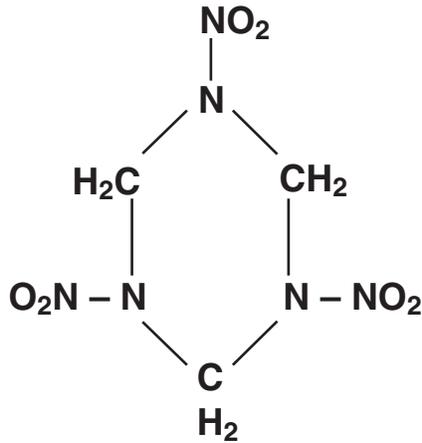


Figure K.3—Chemical Structure of RDX

of 100 kHz from one another (see Figure K.2). This demonstrates the specificity of NQR: Even such small effects from crystal packing are sufficient to resolve the NQR lines from nominally equivalent nitrogens. Because the bandwidth of excitation is only about 5 kHz for commercial NQR detectors, NQR lines more than 5 kHz away from the carrier will not be excited.

For landmine detection, TNT, RDX, and, to a lesser extent, tetryl are the most important explosives. The basic detection concept is particularly simple: Apply a pulse or series of RF pulses resonant at the appropriate NQR frequency of the explosives of interest, and look for the presence (or absence) of a return signal.

As discussed below, the intrinsic signal-to-noise ratio (SNR) (of the NQR signal to the random thermal noise, primarily Johnson noise from the detector coil) is inherently low, and much effort goes into designing effective RF pulse sequences and detector coil geometries that maximize the SNR per unit time. To the degree that the noise is completely random, the improvement in SNR increases with the square root of scan time. A major complication in landmine detection is that radio frequency interference (RFI) from far field sources,

such as AM radio transmitters, and near field sources, such as automobile ignitions and computers, creates substantial coherent noise that can be within the frequency regime of interest. Note (Figure K.2) that TNT frequencies are below 1 MHz, right in the AM band. Much effort has been devoted to reducing this problem—by coil design and by monitoring the RFI with a separate antenna and then subtracting the unwanted RFI signal. Nonetheless, the inherently weak NQR signals and the possible contamination by RFI dictate that *for present technology* it is not expected that the NQR detector will be satisfactory as a *primary* sensor for landmine detection in military applications. However, the exquisite selectivity suggests NQR is tailor-made as a *confirmation* sensor: e.g., when a primary sensor, such as an electromagnetic induction coil or ground-penetrating radar, indicates an anomaly, the NQR detector can be used as a confirmation tool to distinguish false alarms from landmines, without the need to mechanically probe the ground.

STATE OF DEVELOPMENT

In the United States there are presently two programs to develop prototype NQR landmine detectors, both executed by Quantum Magnetics (QM). The U.S. Army Mine Countermeasure Division at Fort Belvoir, Va., sponsors development of a vehicle-mounted prototype NQR detector, designed initially as a confirmation sensor to clear mines from roadways. Under support from the Office of Naval Research and the U.S. Marine Corps, QM is also developing a prototype handheld landmine confirmation detector for the U.S. Marine Corps Systems Command, Quantico, Va.

CURRENT CAPABILITIES

The prototype developments, above, represent the current capabilities. Both are for military applications, and development of an NQR detector for humanitarian purposes would use the basic technology but would take a somewhat different path—see below.

It is premature to report receiver operating characteristic curves.

KNOWN LIMITATIONS

Not all explosives exhibit an NQR signal. In particular, some landmines, such as the PFM-1, employ liquid explosives that are not expected to be detectable [4]. Of course, NQR requires that the RF field must penetrate to the explosive, and so no NQR signal is obtained from a metal-encased mine. However, metal mines are easily found by metal detectors, and indeed the NQR detector acts as a crude metal detector itself. If the RF flux is excluded from a conducting volume, the effective inductance of the NQR detector coil is reduced and the presence of the metal case is indicated by an inability to resonantly tune the coil within the range of the variable tuning capacitor.

Both the NQR frequency and the relevant NQR relaxation times T_1 and T_2 are functions of temperature. The relaxation time T_1 determines how rapidly the pulse sequence can be repeated, and T_2 restricts the maximum length of the “spin echo” sequence used for TNT and tetryl detection. Roughly speaking, an acquisition of length T_2 can be obtained every T_1 . Because the exact temperature of the mine is not known, one uses pulse sequence parameters that are broadly effective over a band of temperature. With some improvements, it is expected that estimating the approximate mine temperature to within 10–20°C should be adequate.

Detectability of RDX and tetryl is rather good by NQR, but for TNT the NQR relaxation times are less favorable, and the possible presence [5] of two crystalline polymorphs (monoclinic and orthorhombic) lead to weaker TNT signals. Finding small (50 g) antipersonnel TNT mines by NQR will be difficult, but is not ruled out. RDX and tetryl mines are much easier to find.

Most NQR detector coils use variants of a simple circular surface coil, for which the magnetic field intensity drops by about a factor of three at a distance of one coil radius along the coil axis. Beyond that distance, the field drops off more rapidly with distance, and so the detector coil radius determines the *approximate* useful depth of interrogation. A larger coil is an alternative, but more RF power is required for the transmitter, and because the “filling factor” (the volume fraction of the explosive divided by the effective volume irradiated by the coil) is reduced, the overall SNR can be reduced. Corre-

spondingly, a significant increase in the “standoff distance” of the coil above the ground will also reduce the SNR of the mine.

In general, soil characteristics do not play a significant role in NQR detection. At these NQR frequencies (1–5 MHz), the RF field is not significantly attenuated, even for rather wet soils. The decrease in the effective Q of the detector coil corresponding to this RF loss results in a rather insignificant deterioration in SNR.

POTENTIAL FOR IMPROVEMENT

Compared with combat engineering applications, there are some advantages to NQR for humanitarian demining. It is anticipated that increased scan time can be tolerated for humanitarian applications, especially if NQR is used as a confirmatory tool. For example, for TNT with a nominal T_1 relaxation time of 6 seconds at 20°C, two data acquisitions can be taken with a 6-second scan (using a delay of T_1 between acquisitions), but 51 acquisitions can be obtained in a 5-minute scan, giving an improvement of 5x in SNR. In other words, a 50-g mine would give the same SNR or detectability in 5 minutes as a 250-g mine in 6 seconds—an easy task for NQR. And, a 5-minute NQR scan sounds more appealing than digging by hand for 5 minutes.

Improvements in technology, especially the RF transmitter, and advanced NQR techniques such as “stochastic NQR” [6], should reduce the weight and the power requirements of the present military prototype detector and will be advantageous for humanitarian applications.

Other approaches that may be viable for humanitarian demining include combined NQR-NMR methods. For these a weak polarizing magnetic field is used, on the order of 10–100 G. Variants allow a cross relaxation between the nitrogen transitions and hydrogen NMR transitions, to either decrease the nitrogen T_1 relaxation time or to detect the nitrogen NQR transition as a perturbation on the much stronger proton NMR signal. These techniques have been explored to some extent in the laboratory for the past 50 years, and certain variants may be appropriate to humanitarian demining. See Nolte et al. [7] for a recent application, albeit one more suited to the laboratory.

Even with improvements, it is anticipated that NQR would still be integrated with some other detection method, such as electromagnetic metal detection.

R&D PROGRAM TO REALIZE THE POTENTIAL

As indicated, NQR landmine detection for military applications is still in the prototype stage, and substantial improvement in the technology is expected as experience is gained. Extension to humanitarian demining can build on this experience, but significant effort should be devoted to adapt NQR to humanitarian demining.

The current five-year program to develop a prototype handheld NQR detector represents a projected investment of about \$15 million for engineering and some science and technology (S&T). Further S&T work is necessary for the humanitarian approaches, perhaps \$3 million worth. A program funded at about \$1 million per year for research and development and \$5 million per year for engineering development over a three-year period should make real progress toward an NQR detector specialized for humanitarian applications.

In the near term, the military version of the handheld NQR detector should be available in about four years. One might use those detectors for humanitarian purposes, assuming that there is no difficulty in the “dual use” of this technology. However, this appears to be at best a short-term solution because humanitarian demining requirements are different than those of the combat engineer.

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