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# Cross-polarisation method for improvement of $^{14}$N NQR signal detectability

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## Abstract

This is a study of the cross-polarization effects in the case of $^{14}$N quadrupolar spin-system with a long spin–lattice relaxation time. Two important benefits of the cross-polarization technique were demonstrated for PETN: (i) a polarization transfer resulting in increased NQR single shot signal response and (ii) a dynamic reduction in recovery time of the NQR system allowing scan repetition on a much shorter timescale. It was proved that this technique can reduce the optimal waiting time between pulse sequences up to 60 times through a significant reduction of the relaxation time of the quadrupolar spin-system. All experiments were carried out at room temperature using spin-locking multi-pulse sequences and small external magnetic field.

*Keywords:* Nuclear Quadrupole Resonance (NQR); Cross-polarization; Nitrogen-14; Free induction decay; Spin-echo

## 1. Introduction

As a radio-frequency spectroscopic technique, nuclear quadrupole resonance (NQR) is a powerful chemically specific method for the detection of illicit substances, such as explosives [1–3]. The NQR frequency of an explosive is very sensitive to its molecular environment and is therefore unique to each explosive chemical structure. Most explosives contain nitrogen-14 ($^{14}$N) nuclei whose spectral lines are usually located at low RF from 0.4 to 6 MHz. NQR signals are weak because of the small energy level separation and hence considerable effort is employed to optimally detect them. In order to improve sensitivity, it is common to employ a pulsed technique based on using special multi-pulse sequences [4–8]. However a long spin–lattice relaxation time ($T_1$) in some explosive types significantly reduces the efficiency of applied multi-pulse sequences. Examples of these explosives include PETN (pentaerythritol tetranitrate), Ammonium Nitrate (AN) and TNT (trinitrotoluene).

A quadrupolar spin-system once excited by an RF pulse or pulse sequence recovers to thermal equilibrium with the lattice in a time $T_1$. To take PETN as a specific example, a long $T_1$ time of about 32 s means that the $^{14}$N NQR signal which decays throughout the application of a first pulse sequence over a few seconds cannot be efficiently re-excited by the application of a second pulse sequence until around a $T_1$ time has elapsed. In most applications, this period is excessive and so detection results are generally based on the single application of a pulse sequence. Being able to effectively manipulate the recovery time allows a pulse sequence to be repeated on a much shorter timescale resulting in major improvements in the effectiveness of such techniques.

The cross-polarisation methods [9,10] can be used to reduce the recovery time after excitation of a quadrupole spin-system in hydrogen ($^1$H) containing solids. The recovery time reduction can be achieved by using contact between the proton and quadrupolar spin-systems, when the energy level separations in these systems are made the same and level crossings take place. According to the spin-temperature concept [11,12], for the technique to be effective the proton system should be much “cooler” than

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the RF pulse sequence "heated" quadrupolar spin-system. It is important to point out that efficiency of the method is not critically dependent on the uniformity of the magnetic field. Removing uniformity requirements lowers the hardware cost of generating a static magnetic field considerably and makes the use of these techniques over large inspection volumes or stand-off feasible.

This paper presents new results of applying the cross-polarisation technique for effective detection of plastic explosives with long $T_1$. The particular task of this work was to show an effectiveness of the method for the detection of PETN contained explosives, PETN being chosen because it posses very long $T_1$ and it is used in many plastic explosives throughout the world. In these experiments, we have used a relatively small magnetic field which can be easily provided by a permanent magnet or simple solenoid. We have proved that the cross-polarisation technique can reduce the optimal waiting time between pulse sequences up to 60 times demonstrating the significant reduction of the relaxation time of the quadrupolar spin-system. All experiments were carried out at room temperature using spin-locking multi-pulse sequences.

## 2. Background

Cross-polarisation is used to enhance the signal-to-noise ratio in both nuclear magnetic resonance (NMR) and NQR. In NMR experiments, the signal enhancement is normally achieved by transferring magnetisation from abundant spins like protons $^1$H to rare spins [9,10]. In the case of NQR, magnetisation is transferred to quadrupolar nuclei from $^1$H nuclei previously polarised in a reference magnetic field [13–17]. Two important benefits can be obtained (i) polarization transfer resulting in increased NQR single shot signal response and (ii) a dynamic reduction in recovery time of the NQR system allowing scan repetition on a much shorter timescale. Both enhancements offer a leap forward for QR explosive detection capability.

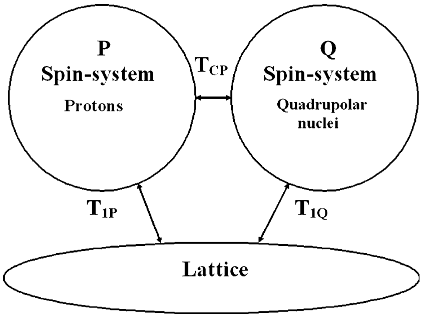

Fig. 1. Proton (P) spin-system, quadrupolar (Q) spin-system and lattice. Spin systems P and Q are connected with a lattice and this connection may be by the spin–lattice relaxation time $T_{1P}$ and $T_{1Q}$ accordingly. Connection between P and Q spin-systems via dipole–dipole interactions may be characterised by the cross-correlation time $T_{CP}$.

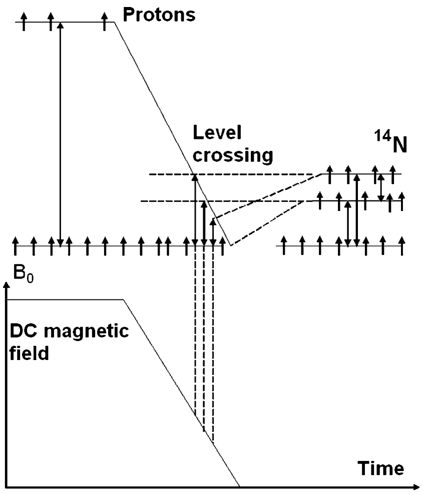

Fig. 2. Cross-polarizations NQR experiment. The static magnetic field initially polarizes the P spins using a static magnetic field so that the P energy levels have much greater energy separation than the Q levels. By reducing the external magnetic field adiabatically the P level splitting is reduced such that the proton and quadrupolar energy levels separations equalise allowing a transfer of polarisation.

Let us consider the sample containing two spin-systems, namely magnetic nuclei, usually protons (P) with spin–lattice relaxation time $T_{1P}$ and quadrupolar nuclei (Q) with spin–lattice relaxation time $T_{1Q}$ (Fig. 1). We assume that spin-systems P and Q are connected via dipole–dipole interactions and relaxation times $T_{1P}$ and $T_{1Q}$ are long enough for the experiment. The typical cross-polarisation experiment is clearly illustrated in Fig. 2. A basic approach of this sort of experiment is to initially polarize the P spins using a static magnetic field so that the P energy levels have much greater energy separation than the Q levels. Given time to equilibrate the P levels will have relative occupation numbers determined by the Boltzman distribution. Thus the relative population difference between the two P levels, hence polarisation, will correspondingly be much greater than the Q levels of interest. By reducing the external magnetic field adiabatically the P level splitting is reduced such that the proton and quadrupolar energy levels separations equalise allowing a transfer of polarisation. This results in a net polarisation flow from protons to the quadrupolar nuclei. This effect can also be explained through the concept of spin temperatures, where energy flows from the "hot" Q spin-system to the "cold" P spin-system "cooling" the Q spin-system. Applying conventional pulse detection techniques soon after removing the magnetic field, the NQR response can be improved according to the ratio of the proton NMR to NQR frequency [15]. Thus, the Q signal enhancement becomes greater the higher the initial polarization for P system. It should be noted that the efficiency of cross-polarisation also depends on the strength of the dipole–dipole interactions between the Q and P spins and the relaxation times $T_{1P}$ and $T_{1Q}$. An NQR signal increase by using level crossing technique was recently demonstrated for such explosives as TNT [16] and PETN [17].

The cross-polarisation method can be very efficient for reducing the relaxation time of Q spins previously excited (or "heated") by a sequence of RF pulses. In order to achieve the relaxation time reduction, the contact between the "cold" P spin-system and the "hot" Q spin-system can also be used. During the contact the Q spin-system mainly relaxes via a cross-polarisation "mechanism" described by a cross-polarisation time ($T_{\mathrm{CP}}$). During this time the P and Q spin-systems come to a common spin temperature. An important condition for the method to be effective is that $T_{\mathrm{CP}}$ must be much shorter than $T_{1\mathrm{P}}$ and $T_{1\mathrm{Q}}$ of the substance.

At contact or level crossing, the population differences between the P and Q levels are proportional to their inverse spin temperature $\beta$ and can be expressed as [9,12]

$$\begin{aligned}\tfrac{\mathrm{d}}{\mathrm{d}t}\beta_{\mathrm{P}} &= -\tfrac{\varepsilon}{T_{\mathrm{CP}}}(\beta_{\mathrm{P}}-\beta_{\mathrm{Q}}) - (\beta_{\mathrm{P}}-\beta_{\mathrm{L}})\tfrac{1}{T_{1\mathrm{P}}}\\ \tfrac{\mathrm{d}}{\mathrm{d}t}\beta_{\mathrm{Q}} &= -\tfrac{1}{T_{\mathrm{CP}}}(\beta_{\mathrm{Q}}-\beta_{\mathrm{P}}) - (\beta_{\mathrm{Q}}-\beta_{\mathrm{L}})\tfrac{1}{T_{1\mathrm{Q}}}\end{aligned} \tag{1}$$

where $\beta = \hbar/kT$ and $\beta_{\mathrm{P}}$, $\beta_{\mathrm{Q}}$ and $\beta_{\mathrm{L}}$ are the inverse spin temperatures of the P spin-system, Q spin-system and lattice, respectively. Taking into account the condition that $T_{\mathrm{CP}} \ll T_{1\mathrm{P}}, T_{1\mathrm{Q}}$ we can rewrite differential equations Eq. (1) in the simpler form

$$\frac{\mathrm{d}}{\mathrm{d}t}\beta_{\mathrm{P}} = -\frac{\varepsilon}{T_{\mathrm{CP}}}(\beta_{\mathrm{P}}-\beta_{\mathrm{Q}}) \tag{2a}$$

$$\frac{\mathrm{d}}{\mathrm{d}t}\beta_{\mathrm{Q}} = -\frac{1}{T_{\mathrm{CP}}}(\beta_{\mathrm{Q}}-\beta_{\mathrm{P}}) \tag{2b}$$

Subtracting Eq. (2b) from Eq. (2a) we find that

$$\frac{\mathrm{d}}{\mathrm{d}t}(\beta_{\mathrm{P}}-\beta_{\mathrm{Q}}) = -\frac{\varepsilon+1}{T_{\mathrm{CP}}}(\beta_{\mathrm{P}}-\beta_{\mathrm{Q}}) \tag{3}$$

This differential equation has the solution

$$\beta_{\mathrm{P}}-\beta_{\mathrm{Q}} = C\exp\left(-\frac{\varepsilon+1}{T_{\mathrm{CP}}}t\right) \tag{4}$$

where $C$ is a constant which is equal to $\beta_{\mathrm{P}}-\beta_{\mathrm{Q}}$ at $t = 0$. From Eq. (3), we can see that during the contact the inverse spin temperature difference $\beta_{\mathrm{P}}-\beta_{\mathrm{Q}}$ reduces with an effective relaxation time

$$T_{1\mathrm{eff}} = \frac{T_{\mathrm{CP}}}{\varepsilon+1} \tag{5}$$

It means that during the contact the Q spin-system which previously "heated" by RF pulses appears to relax with the time described by Eq. (4). Therefore, if $T_{\mathrm{CP}} \ll T_{1\mathrm{P}}, T_{1\mathrm{Q}}$ the cross-polarisation method can be very effective for reducing the effective relaxation time of quadrupolar spin systems.

## 3. Experimental details

The sample used in our experiments consisted of 220 g of the plastic explosive PRIMASHEET-1000 which contains of about 80% of PETN ($C_5H_8N_4O_{12}$). A transition frequency of $v_+ = 890$ kHz was used in all experiments. The spin–lattice relaxation time $T_1$ measured at room temperature (297 K) was about 32 s and the spin–spin relaxation time $T_2$ in the sample was about 52 ms. The relaxation time measurements are estimated to be accurate to within ±10%.

The experiments were carried out with the pulsed NQR spectrometer designed to operate in a low-frequency band (0.3–10 MHz). This instrument employs the TECMAG "Apollo" console for pulse generation and data collection, power amplifier (Model A150), preamplifier Miteq (Model AU-2A-0150-BNC) and laboratory probe. The resonant probe has a standard design containing essentially an electrically resonant solenoidal coil at the measurement frequency and matching elements. The sample to be investigated was contained in a 160 mm long plastic test-tube with a diameter of 80 mm placed in the centre of a 1 l RF solenoid coil. In our experiments, the duration of a single so-called "90°-pulse" was about 80 μs, where the maximum FID amplitude was observed. The delay between the end of an RF pulse and the beginning of acquisition time was 0.3 ms. In the experiments, we have measured the integral intensity of NQR signal in the "observation window" between RF pulses after FFT.

A permanent magnet and electromagnet were used as a source of external magnetic field. The permanent magnet had an internal volume of about 100 × 200 × 67 mm and created an average DC field of about 100 mT. The electromagnet was designed to create DC field up to 90 mT with homogeneity of about 15% for the sample. The magnet is a hand-wound solenoid with 85 mm internal diameter and 180 mm length. The 10 layer coil was air cored and air cooled. Air cooling was achieved through improving air circulation with fans. A DC Magnetometer made by Alpha Lab Inc was used for the field measurement. The field distribution from both pieces of equipment was not uniform, though the intensity at a point could be accurately measured in both systems. The solenoidal coil was used when making signal versus field intensity measurements, the sample always being paced in the same location within the coil.

In order to achieve the contact between the "cold" proton P spin-system and the "hot" quadrupolar Q spin-system, the magnetic field was reduced adiabatically by removing the sample from the DC magnetic field. A simple mechanical system with a minimal transfer time of 0.5 s was used.

The base multi-pulse sequence employed in the measurements was an SLMP sequence which can be written as

$$\theta^0_{90^\circ} - (\tau - \theta^1_{0^\circ} - \tau - )_N \tag{6}$$

where $\theta^0$ is the flipping angle of the preparatory pulse and $\theta^1$ is the flipping angle of the other $N$ pulses in the sequence phase shifted by 90° in relation to the preparatory pulse, $\tau$ and $2\tau$ are the time intervals between $\theta^0$ and $\theta^1$ pulses and between the other pulses accordingly.

## 4. Results and discussion

### 4.1. Signal enhancement

As was mentioned above, the cross-polarization method offers higher signal the greater the initial polarization of the P spins. The higher polarization is achieved by applying a strong magnetic field during the polarization time. The optimal time for this polarization depends on a number of conditions; in general it will be around $5T_{1P}$. In the present work, $T_{1P}$ in PETN was not measured directly but can be inferred from the data below.

A series of experiments were performed to determine the dependence of the $^{14}$N NQR signal intensity for a sample of PETN with the $^{1}$H polarization time. The results of these measurements are presented in Figs 3a and b. In these figures NQR signal intensities are plotted as a function of both the polarization time and applied DC magnetic field. Note that all these measurements commenced when Q spins were fully relaxed. Fig. 3a shows the dependence of $I_p/I$ on the polarization time for different values of $B$, where $I_p$ and $I$ is the total intensity of NQR signal obtained with and without the $^{1}$H polarization, respectively. This figure, in fact, demonstrates the enhancement of the $^{14}$N NQR signal in PETN which can be achieved by using the cross-polarization method. As we can see, it would be expected to enhance sensitivity in the detection of such explosives by a factor up to 4 for a magnetic field of less than 80 mT. Another plot presented in Fig. 3b is the dependence of $I_p - I$ on the same parameters as in Fig. 3a. Since $I_p - I$ is associated with the proton magnetization transferred the P spin-system to the Q spin-system, the curves in Fig. 3b can be used for indirect $T_{1P}$ evaluation. As expected, all curves in the figure are described by a single exponential function with the time constant $T_r$. In the condition $T_{CP} \ll T_{1P}, T_{1Q}$, it can be assumed that $T_{1P} \approx T_r$. The time constant $T_r$ for each curve in Fig. 3 was calculated and result is presented in Fig. 4. We can see that the time $T_{1P}$ in PETN is quite long so that the cross-polarization method is expected to be effective for reducing the recovery time after excitation of a quadrupole spin-system.

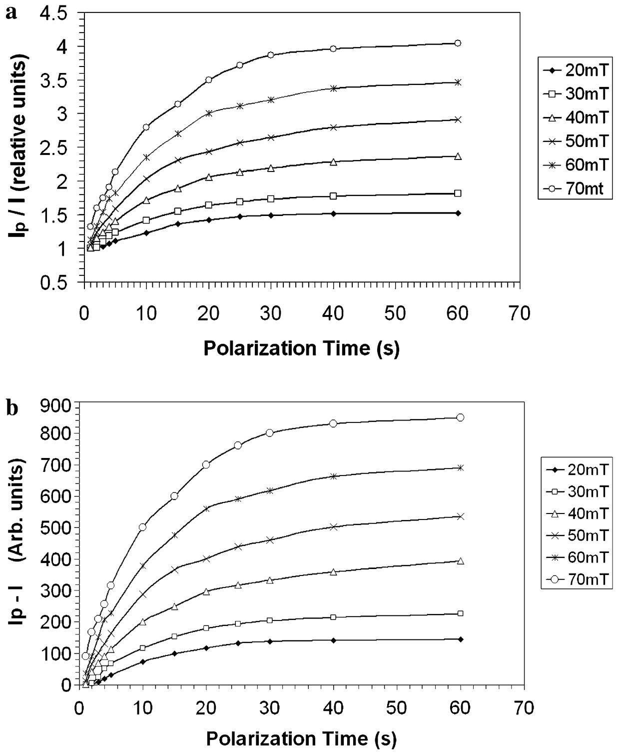

Fig. 3. The dependence of (a) $I_p/I$ and (b) $I_p - I$ on the polarization time for values of $B$. $I_p$ and $I$ is the total intensity of NQR signal in the PETN sample obtained with and without the $^{1}$H polarization accordingly.

Next, the dependence on magnetic field intensity was determined. The experiments were carried out placing the sample in a DC magnetic field for an extended period of time (60 s), greater than the inferred spin–lattice relaxation time of the proton system $T_{1P}$. After that time, the sample was transferred to the NQR measurement system in the same short time interval. The NQR detection pulse sequence Eq. (5) was used then used to read the NQR system intensity. Fig. 5 shows the dependence of NQR signal intensity in PETN on the magnetic field. As would be expected the trend is linear with field magnitude given the initial P spin level separation is greater than the Q spin level separation. It was demonstrated in [16] that the signal increases linearly with field but in fine detail the line changes slope at allowed NQR transitions. The PETN transitions match the proton frequency at static magnetic fields of 21, 12, and 9 mT so that we can expect to observe the similar effect in the range from 0 to 21 mT. The DC field step size in measurements shown in Fig. 5 is insufficient to show these changes conclusively. Finer stepped experiments are required in this range to see this effect.

## 4.2. Relaxation time reduction

Several experiments were performed in order to investigate the recovering process of NQR signals in the Q spin-system. The sample of PETN previously excited by the first pulse sequence was placed in magnetic field to polarize P spins. After polarisation the sample was moved back into the coil where NQR signal was detected using the second pulse sequence. Note that both pulse sequences used are the same (sequence Eq. (5)). The results of these experiments are presented in Fig. 6 and demonstrate the shortening of the signal recovery time. Fig. 6a shows the dependence of the signal intensity on the waiting or polarization time for different values of $B$. The dependence

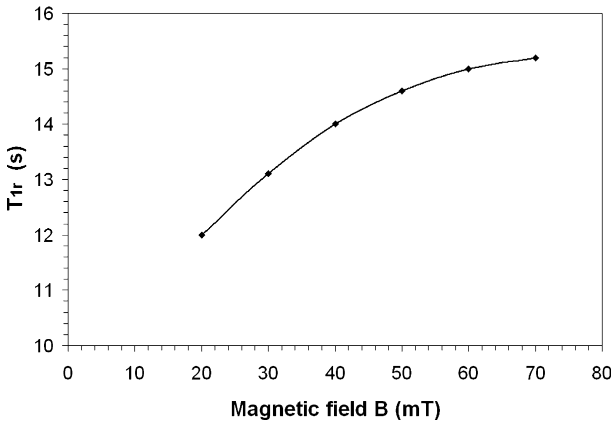

Fig. 4. The time constant $T_r$ with varying applied magnetic field intensity.

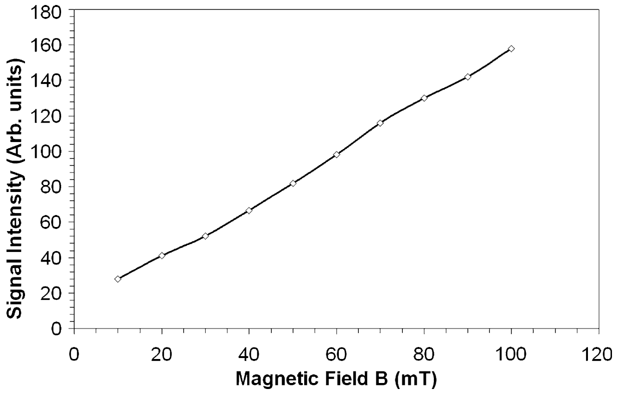

Fig. 5. The dependence of NQR signals intensity in the PETN sample on magnetic field *B*. The proton polarization time is 60 s.

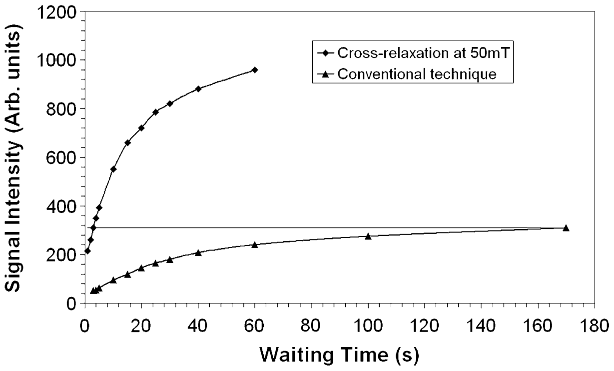

Fig. 7. Comparison of the cross-polarization (at 50 mT magnetic field) and conventional detection technique. In each case, the sequence is repeated twice with varying waiting times between each application. The intensity derived from second application sequence is shown.

of $I_p/I_0$ on the waiting time and *B*, where $I_0$ and $I_p$ is the total intensity of NQR signal obtained with first and second pulse sequence accordingly is shown in Fig. 6b. One can see that using cross-polarization method the waiting time between two pulse sequences to obtain the same intensity can be reduced considerably. This fact is clearly demonstrated in Fig. 7, where the cross-polarization detection technique is compared with the regular used technique. It can be seen that the cross-polarization method can effectively reduce the time between pulse sequences and in the case of PETN this reduction can be up to 60 times in this example using a small magnetic field.

It should be noted from Fig. 6 that the cross-relaxation effect similar to that discussed in [16] may take place in the case of PETN, but this effect is being overwhelmed by the cross-polarisation in this measurement.

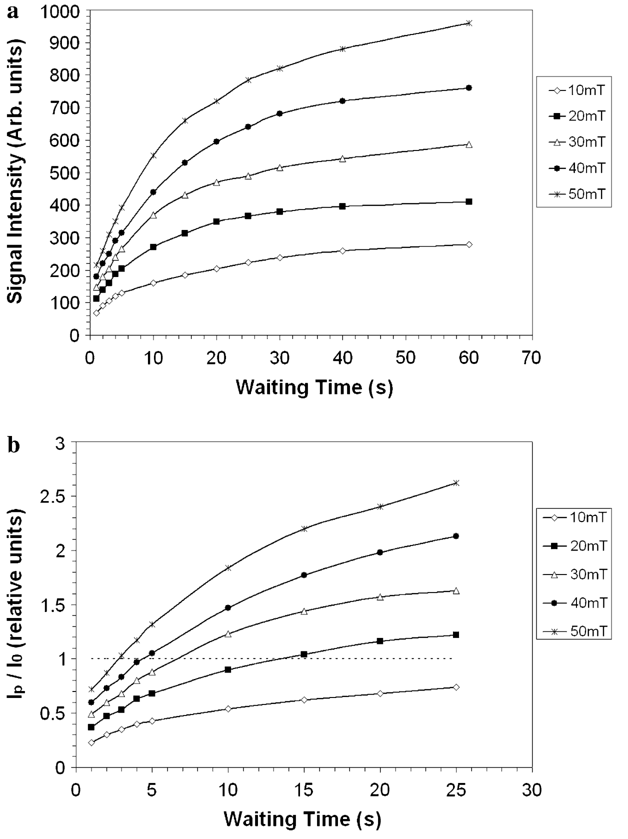

Fig. 6. The dependence of (a) NQR signals intensity and (b) $I_p/I_0$ in the PETN sample on the waiting (or polarization) time for different values of *B*. $I_0$ and $I_p$ is the total intensity of NQR signal obtained with first and second pulse sequence accordingly.

## 5. Conclusion

The use of the cross-polarisation effect between quadrupolar nuclei and protons has been shown to significantly enhance the NQR signal level using the same NQR pulse sequence for a long $T_1$ substance, PETN. The NQR signal from a SLMP was enhanced by allowing contact with a cooled proton system.

Further, when using an extended or repeating excitation sequence within a time interval, the NQR signal is superior than without the applied magnetic field, because of enhancement and the reduction in relaxation time. The outcomes are a result of the manipulated contact between the Q spin-system with the P spin-system and the transfer of ‘heat’ with characteristic time $T_{CR}$ (which is normally much shorter than $T_1$) for the substance. The cross-polarization concept for NQR has been shown to effectively lower the waiting time required between repeated pulse sequences. In this example explosive chemical, up to 60 times was demonstrated with a relatively small magnetic field.

The cross-polarisation method which we used does not require uniform external magnetic field and has great potential therefore in the use of large volume detection. This is a very useful aspect for explosive and drug detection, or any other field that requires efficient NQR detection. For explosive detection a better signal to noise ratio at comparable times would translate smaller sample detection than compared to non-polarised enhanced signals. Further the applied DC magnetic field could be used as a variable to potentially reduce false alarm rates, by correlating its expected effect on an analysed item. We propose to further explore cross-polarization methods with the intention of applying these principles and techniques to full scale NQR explosives detection systems.

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