Physics – Uspekhi **40** (4) 393 – 406 (1997)

INSTRUMENTS AND METHODS OF INVESTIGATION PACS numbers: **76.60.–k**, 76.60.Gv, 76.70.Fz, **81.70.–q**

New technologies: nuclear quadrupole resonance as an explosive and narcotic detection technique

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Abstract. Possibilities of detecting nuclear quadrupole resonance (NQR) signals in explosives and drugs are considered. Direct and indirect NQR techniques for searching substances are described and the potentialities of various experimental methods are compared.

1. Introduction

Nuclear-quadrupole-resonance (NQR) spectroscopy [1 – 5] is an area of radio-frequency spectroscopy which offers several special possibilities for the analytical detection of chemical substances in a solid phase. This relatively inexpensive method is harmless, provides a way for nondestructive quantitative analysis, makes it possible to analyze inhomogeneous mixtures in large volumes and perform express analysis without prior preparation of samples, and finally, can be used with no external magnetic field. The serious limitation for wide use of the NQR method is the need for sufficiently large amount of samples for detection (grams or tens of grams). Besides, in many cases there is little sense in using a direct detection procedure to search for unknown frequencies as this takes much time.

The stable nitrogen isotope ^{14}N has a natural abundance of 93.6% and a nuclear spin $I = 1$ with its associated nuclear electric quadrupole moment. The ^{14}N NQR transitions fall in the frequency range 0 to 6 MHz. The frequencies of NQR lines are determined predominantly by the electron distribution over chemical bonds about a nitrogen atom, i.e. by the tensor of the electric field gradient (EFG) at the nucleus. The electric quadrupole moment interacts with the electric field gradient having an asymmetry (defined by η parameter), which is caused by the local electron environment of the atom. The quadrupole coupling constant eQq_{zz} and the EFG-tensor asymmetry parameter η carry structural information on this environment. For nuclei of spin $I = 1$, in the general case there exist three resonance frequencies ν_+, ν_-, and ν_0 for transitions between quadrupole energy levels. For nuclei of spin $I = 3/2$, such as ^{37}Cl, NQR in a zero magnetic field reveals only one transition at the frequency ν_Q, and the conventional NQR experiment gives no way to evaluate the eQq_{zz} and η quantities. Notice that ^{35}Cl isotope, owing to its greater natural abundance (75.4%) and greater nuclear moment in comparison with ^{37}Cl, is better suited to the detection of chemical substances by the NQR method.

For the most part, drugs and explosives contain nitrogen or chlorine atoms, and this provides a promising way to detect these substances using NQR spectroscopy. In spite of the fact that the NQR frequencies of ^{14}N, ^{35}Cl, and ^{37}C fall in the low-frequency range resulting in a low sensitivity of the method, NQR spectroscopy is presently in serious competition with other methods.

Interest in the possibilities of NQR spectroscopy to detect explosives goes back to the 1960s, a period of the war in Vietnam. Initially the spectral parameters of NQR for some explosives were found from the line shape of nuclear magnetic resonance (NMR). In spite of an interest in solving the detection problem being shown by many governments and ministries, early attempts to use NQR for this purpose have been largely unsuccessful. Marino was the first who succeeded in observing ^{14}N resonances from cyclic nitrogen in hexogen with the stationary NQR method using a Robinson oscillator. By order of the Ministry of Defence, Bray and co-workers performed measurements of resonance frequencies in some other explosives [6, 7]. For clear reasons, only a few of the results of this investigations was reported. In the late 1970s Marino made the measurements of NQR frequencies in various crystalline modifications of trotyl using the pulse-sequence techniques — spin-locking signal echo (SLSE) and strong off-resonance pulses (SORC) — to acquire the ^{14}N NQR spectra [8].

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Received 19 November 1996, revised 12 December 1996
Uspekhi Fizicheskikh Nauk **167** (4) 413 – 427 (1997)
Translated by V M Matveev; edited by A Radzig

Beginning in 1970, a method for the detection of explosives during air-luggage control, based on the cross-relaxation spectroscopy of ^{14}N and ^{1}H nuclei was developed. Interest in the problem of detection of explosives and narcotics was stimulated by an increase in the number of acts of terrorism with great human cost as well as by a desire to prevent drug traffic.

A program to search for explosives in small items of mail was developed in the UK. This program was based on the use of double NQR-NMR resonance with a cycling magnetic field, proposed by Edmons.

In our country an NQR-based detector of explosives was developed by Prof. Grechishkin's research group in Kaliningrad and Novosibirsk, in 1978. The earliest paper [9] of the group was concerned with the investigation of explosive [Hexa (hexamethylene tetramine) $\cdot$ HNO_3] using NQR. In the first work on narcotics the NQR method was applied to the study of nicotine. This research group was engaged in investigations on double nuclear quadrupole resonance (DNQR), cross-relaxation spectroscopy, and the direct pulsed method with a large coil [11, 12]. Work on the detection of antitank mines and explosives in items of mail which had been progressing with much success was frozen upon the suspension of financing after the war in Afghanistan.

In the early 1990s Garroway and co-workers began to work on devising a large-volume NQR scanner for luggage control. In such a scanner, a radio-frequency power of several hundreds kilowatt is required for creation of the 90° pulses [13].

Maruizumi's research group started working on the exploration of the capabilities of a NQR scanner in Japan in 1990 [14]. Interest in the problem is also being shown in Poland and China.

2. Detection of explosives and drugs using NQR technique

2.1. Investigation of NQR spectra in explosives

The four basic explosives — trotyl, hexogen, octogen, and PETN – contain NO_2 groups. To date the ^{14}N NQR spectra for these nitrogroups has been investigated in only a few organic compounds [6, 15]. Unlike alkali-metal nitrites ($NaNO_2$, KNO_2, $CsNO_2$) involving an NO_2 ion and an atomic nitrogen sp^2-orbital occupied by a lone-electron pair [16], organic nitrocompounds contain an NO_2 group which makes up the σ type N – C bond through the same orbital. This involves a sharp decrease in the quadrupole coupling constant and the ^{14}N NQR frequencies. As a consequence, one observes a drastic decrease in the sensitivity of the direct-detection method and an increase in the adverse effects of radio-frequency interference, because in organic compounds the ^{14}N NQR frequencies for NO_2 groups fall in the range of medium-frequency broadcast stations.

In recent years the detection of ^{14}N NQR spectra of chemical substances involving N – C bonds has become important because of a direct relationship between these substances and narcotics and explosives [16].

From the viewpoint of searching for explosives via NO_2 groups, of great interest is the pulse direct-detection technique using the Fourier transform of time response to obtain the ^{14}N NQR spectrum. ^{14}N NQR spectra for these nitrogroups in trotyl have been obtained by this technique at temperatures of 77 K and 16 °C [15, 17]. A technique based on Fourier-transform NQR spectroscopy has been tested at the frequencies of trotyl NO_2 groups ($T = 77$ K) [8]. All the investigations were conducted on pure samples of either monoclinic or orthorombic form. These and some other spectra of NO_2 groups are shown in Fig. 1. Data on the investigation of industrially prepared samples of trotyl using double NQR-NMR resonance at a temperature of 120 K are presented in Refs [18, 19]. Also presented are the ^{14}N DNQR spectra of NO_2 groups in hexogen and octogen at 120 K. As a consequence of a large DNQR linewidth and a lowering of the method sensitivity because of the absence of direct nitrogen-hydrogen bonding in NO_2 groups, the DNQR spectra allow one to determine only the regions of location of the ^{14}N NQR lines without resolving closely-spaced lines.

The double NQR-NMR spectrum for a sample of trinitrotoluene from a German shell manufactured in 1944 is shown in Fig. 2. It was obtained at a temperature of 293 K. Analysis of this spectrum with the use of an NQR-data bank revealed that we clashed with a technological mixture and that the 260, 940, and 1200 kHz lines could be assigned to the

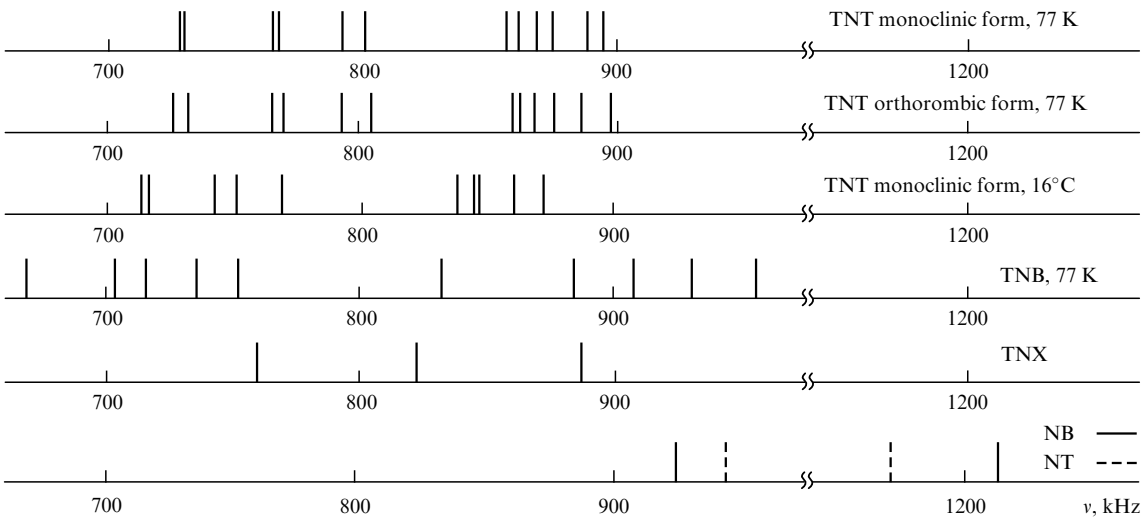


Figure 1. The ^{14}N NQR spectra of nitrogroups in trinitrotoluene (TNT), trinitrobenzene (TNB), trinitrohexane (TNX), nitrobenzene (NB), and nitrotoluene (NT) [20, 21].

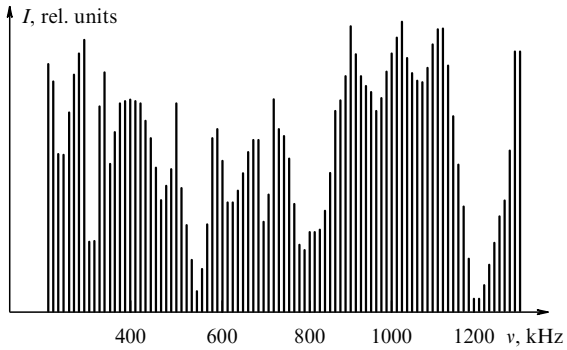


Figure 2. The ^{14}N-^{1}H DNQR spectrum of trotyl with impurities.

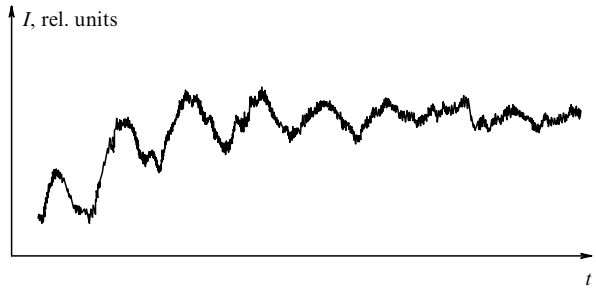


Figure 3. The ^{14}N NQR signal in $C_3H_6N_6O_6$ from the ν_0 line (1687 kHz) at $T = 300$ K, $T_{rep} = 4$ ms, $t_w = 90$ μs, number of records $N = 600$, horizontal record length is 2 ms.

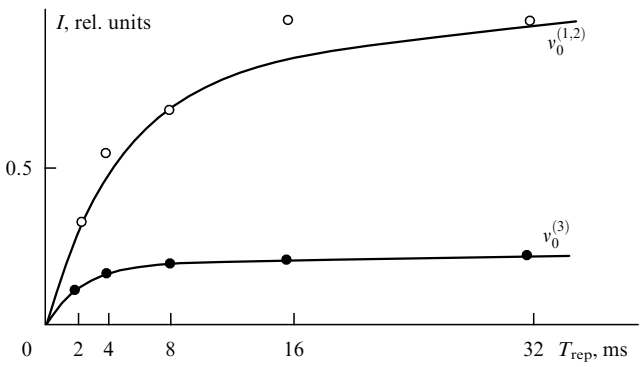


Figure 4. The T_{rep}-dependence of the NQR signal intensities for the $\nu_0^{(1,2)}$ and $\nu_0^{(3)}$ lines.

volatile substance n-$(CH)_3C_6H_4NO_2$ imparting a yellow colour to the sample, and the 350, 490, and 1200 kHz lines — to borax.

Adequate resolution of spectral lines is possible with the use of the direct-detection technique only. The double-resonance method was essentially improved by application of the selective-magnetic-field technique [22–24] that provides a sharp increase in sensitivity in the absence of direct bonds between a proton and a nitrogen nucleus. Subsequently, this allowed us to use the selective-magnetic-field technique for a prior search for the nitrogen NQR lines from NO_2 groups.

As already noted, it is a complicated problem to investigate NQR of nitrogen nuclei in nitrogroups and identify NQR spectral lines in these compounds, because NO_2 groups produce very weak NQR signals.

Even with the intensive development of NQR techniques for nitrogen nuclei in the last decade, there is only isolated evidence of successful detection of NQR signals from nitrogroups. The situation is complicated when a sample contains nuclei which are chemically nonequivalent or molecules which occupy crystallographically nonequivalent positions thus resulting in a multiplicity of lines [25–27].

To eliminate the ν_0 lines of cyclic nitrogen in hexogen from the spectrum of NO_2 groups and check the sensitivity of an NQR spectrometer for direct detection of ^{14}N NQR in the low-frequency range, we measured the parameters of these lines. The results obtained show that the intensity of the ν_0 lines in this compound is no worse than that of the relevant ν_- lines. The frequencies of the ^{14}N NQR lines from cyclic nitrogen (3 lines) at a temperature of 300 K were found to be $\nu_0^{(1,2)} = 1780.6 \pm 0.2$ kHz and $\nu_0^{(3)} = 1687.3 \pm 0.2$ kHz. The recorded signal of a free induction at a frequency $\nu_0 = 1687.3$ is shown in Fig. 3. For the linewidth factor and the spin-lattice relaxation time we obtained $T^{*(1,2)} = 1.1 \pm 0.1$ ms, $T^{*(3)} = 1.7 \pm 0.1$ ms and $T^{(1,2)} = 6 \pm 9$ ms, $T^{(3)} = 3 \pm 9$ ms, respectively. The measurements of free-induction signals were taken with a frequency separation $\Delta\nu \sim 4$ kHz from resonance. The $\nu_0^{(1,2)}$ line has a greater width as it actually consists of two unresolved lines (at 300 K). The experimentally obtained relationships between the signal intensity and the rf pulse-repetition time T_{rep} are presented in Fig. 4.

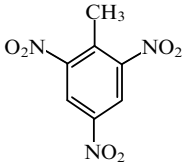
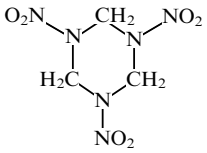
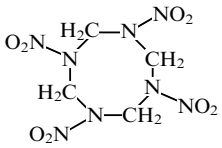
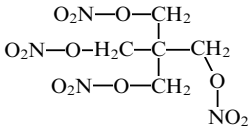
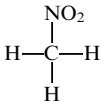
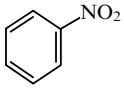
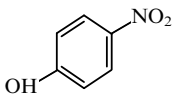
Observing the ^{14}N NQR lines from NO_2 groups in trotyl by the direct pulse method at $T = 77$ K presents no special problems. At room temperature, however, even with a long-period data collection from an industrially prepared sample of reasonable volume (a trotyl cartridge) we failed to observe these lines. This may be explained by the movement of NO_2 groups at room temperature (the melting point of industrially prepared trotyl does not exceed 80–85 °C) that results in a sharp broadening of NQR lines. Apart from various crystalline modifications of trotyl, an industrially prepared sample contains the compounds from which trotyl has been synthesized thus leading to a marked decrease in signal intensity.

In the case where a nitrogroup makes up strong hydrogen bonds with protons, its signals may be observed by the DNQR method since this procedure exhibits high sensitivity in the low-frequency range. In the explosives under investigation (see Table 1) there are no direct proton-nitrogroup bonds.

The results of detecting the NQR lines in explosives and the analysis (based on NQR data) of a double-bonding factor for chemical bonds holding a nitrogen atom to nitrocompounds were reported in Refs [26, 27].

To increase the sensitivity of the DNQR method when investigating weakly-protonated nuclei, the selective-magnetic-field technique was successfully used. Measurements were conducted at a temperature of 110 K using a modernized double-resonance spectrometer. The measuring-cycle time was determined by the spin-lattice relaxation time $T_{1\rho}$ of protons and chosen to be 30 s and 9 s for octogen and hexogen, respectively. In this case the irradiation time for the nuclear quadrupole system comprised 0.5 s. The selective-magnetic-field technique was combined with a low-frequency modulation of the quadrupole frequency ($\sim$ 25 kHz) to promote a search for NQR lines. Spectra were processed by averaging repeated records. The results of taking the NQR spectra of all the explosives that were investigated are presented in Table 2. The lines above 1300 kHz observed in

Table 1. Chemical formulae of explosives investigated by the NQR method.

Compound	Formula	
	general	structural
Trotyl (2, 4, 6 — trinitrotoluene)	$C_7H_5O_6N_3$	
Hexogen (cyclotrimethylene-trinitroamine)	$C_3H_6N_6O_6$	
Octogen (1, 3, 5, 7 — tetranitro-1, 3, 5, 7 — tetrazocyclooctane)	$C_4H_8N_8O_8$	
PETN (pentaerythrityl tetranitrate)	$C_5H_8N_4O_{12}$	
Nitromethane	CH_3NO_2	
Nitrobenzene	$C_6H_5NO_2$	
Nitrobenzonol	$C_6H_5O_3N$	

the ^{14}N DNQR spectrum of octogen belong to cyclic nitrogen (ν_0 lines).

When analyzing the ^{14}N NQR spectra in octogen and PETN, the identification of spectral lines can be accomplished by recognizing that NO_2 groups in both compounds are chemically equivalent (see Table 1). Thus, considering that the DNQR spectra contain a great many lines and assuming the samples to be free from nitrogen-containing impurities, one may conclude that there appear several nonequivalent crystallographic positions in these samples. In these cases the quadrupole coupling constants vary only slightly, whereas the asymmetry parameters may exhibit wide alterations.

For the spectra to be interpreted the spectral lines of fillers were eliminated. The ^{14}N NQR frequencies for the four basic military grade explosives measured by the direct and double NQR techniques [30] are summarized in Table 2.

Figure 5 presents the two-dimensional ^{14}N NQR spectrum in hexogen $(CH_2NNO_2)_3$. The diagonal section of the spectrum corresponds to a one-dimensional spectrum (ν_+ and ν_- lines). Because of the large scale, the triplet of closely-spaced lines associated with three nonequivalent sites occupied by nitrogen atoms does not resolve either in the basic resonance peaks or in the cross peaks. The cross-peak intensities depend on the exciting pulse width. The two-dimensional ^{14}N NQR spectra in the high-frequency range were obtained for the first time using a new method of detecting the two-dimensional spectra [31].

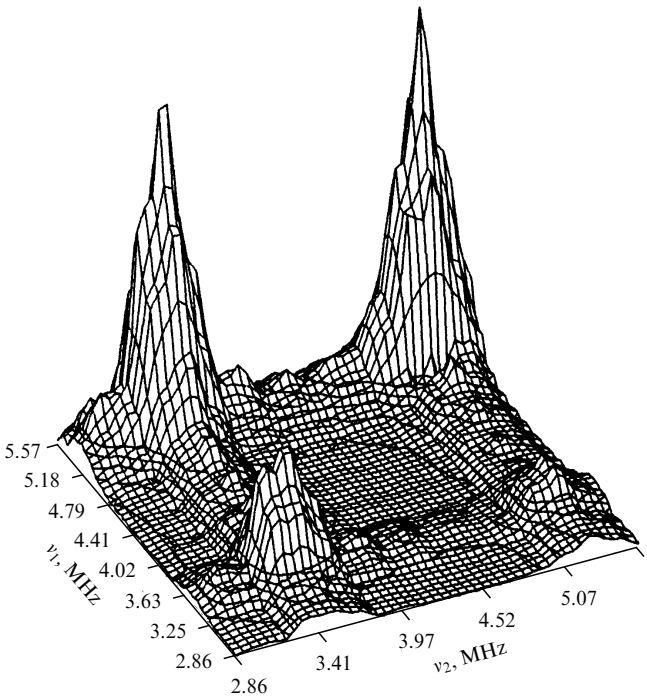


Figure 5. The two-dimensional ^{14}N NQR spectrum of hexogen.

To extend the detection time for weak ^{14}N NQR spectral lines, Marino and Klainer [8, 32] suggested multiple-pulse sequences of spin-locking signal echo (SLSE) and strong off-resonance chain (SORC) of pulses instead of the standard method of detecting the free-induction signal after a 90° pulse or a 90° and 180° two-pulse Hahn sequence. The SLSE sequence is essentially a modified Meiboom – Gill sequence in which all pulses (not just the first pulse) are 90° ones. If the time separation between the pulses is less than the spin-spin relaxation time, the spin-echo-sequence decay time after the second pulse will be determined by the spin-lattice relaxation time owing to the spin-locking effect. Such an echo sequence, upon analog-to-digital conversion, may be stored in real time, with a marked increase in a signal-to-noise ratio. The greater the spin-lattice relaxation time in comparison with the spin-spin relaxation time, the higher the efficiency of this method.

SORC is a sequence of pulses of the same width and phase. Here, a signal is built up in real time after each pulse under off-resonance conditions. The response of a nuclear spin $I = 1$ ensemble to such a sequence is analogous to the long-known (from NMR spectroscopy) response of a spin $I = 1/2$ ensemble to a strong stationary radio-frequency field with a frequency detuning from resonance. In this case the NQR-

Table 2. Resonance frequencies and spectral parameters of some explosives.

Compound	ν_+, kHz	ν_-, kHz	eQq_{zz}, kHz	η	Temperature, method
Trotyl	869	792	1107	0.1396	77 K,
$C_6H_2CH_3(NO_2)_3$	895	801	1131	0.1640	direct method and
	857	767	1083	0.1654	DNQR
	875	767	1095	0.1978	
	861	729	1061	0.2490	
	888	730	1078	0.2929	
Hexogen	5118	3394	5674	0.608	77 K,
$N_3(CH_2)_3(NO_2)_3$	5256	3413	5779	0.638	direct method;
	5319	3511	5887	0.614	DNQR at 110 K
	600	450	700	0.420	
Octogen	5063	3623	5457	0.497	300 K,
$N_4(CH_2)_4(NO_2)_4$	5300	3737	6027	0.516	direct method;
	720	540	840	0.42	DNQR at 110 K
	720	490	806	0.48	
PETN	1470	1170	1426	0.34	110 K,
$C_5H_8N_4O_{12}$	1300	1080	1586	0.27	DNQR
Hexa — nitric	3828.2	3585.1	4942.2	0.0984	300 K,
acid complex	3710.1	3468.2	4785.5	0.1011	direct method
$2HNO_3 \cdot (CH_2)_6N_4$					

signal amplitude is a complex function of the frequency offset, the pulse width, and the pulse separation in the train.

With the use of a series of identical off-resonance pulses without a priming pulse $(\tau - t_w - \tau)^n$, the urotropine — nitric acid complex $2HNO_3 \cdot C_6H_{12}N_4$ (being explosive as well) has been investigated at room temperature [33]. The spectrum of this complex exhibits greater values of the eQq_{zz} quantity compared to pure Hexa and modest values of the asymmetry parameter η. Also noteworthy is the high intensity of the ^{14}N NQR lines for this complex. With a series of identical pulses, NQR signals were easily observable on the oscilloscope screen. Figure 6 illustrates the time-dependent signals obtained in these experiments. Signals with an increasing amplitude prior to the start of the next pulse in turn can be easily seen on certain of these dependences.

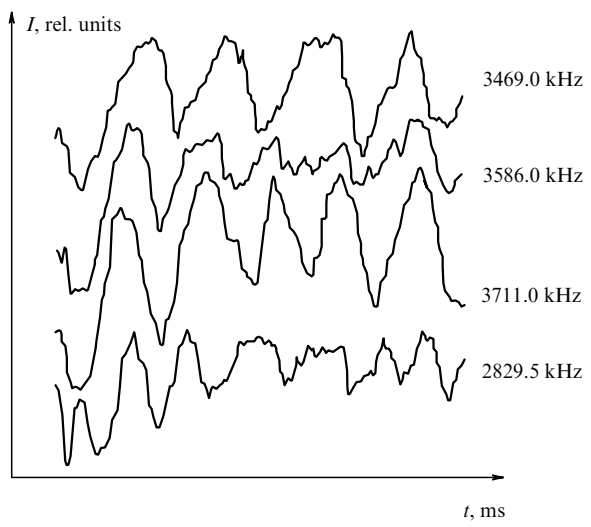


Figure 6. Free-induction signal records for $2HNO_3 \cdot C_6H_{12}N_4$ obtained with the use of an identical pulse train with a frequency offset and $t_w = 35$ μs, $T_{rep} = 16$ ms; horizontal sweep is 340 points ×20 μs, and $T = 300$ K.

The relationship between the intensity of a free-induction signal and the rf-pulse repetition time is presented in Fig. 7. The signal intensity rises both with increasing and decreasing the pulse-repetition time. The growth of intensity with an increase in the repetition time (region II) is caused by weakening the saturation effect, so that at $T_{rep} > T_2^*$ the spin-lattice relaxation time T_1 can be determined (saturation method). The increase of the induction-signal intensity with a decrease in the repetition time (region *I*) results from the pulse spin-locking effect arising at $T_{rep} < T_2^*$ and reducing the signal decay.

The spin-lattice relaxation time for all four lines was found to be about the same: $T_1 = 300 \pm 50$ ms. The

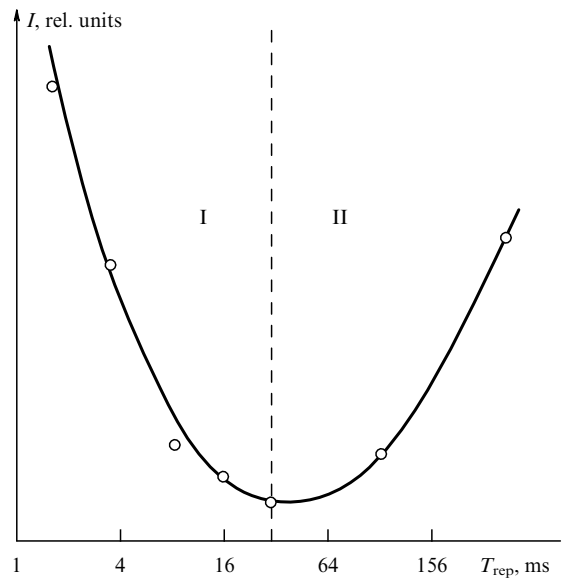


Figure 7. The relationship between the free-induction signal intensity of the $\nu_+^{(2)}$ line (3585.1 kHz) recorded in $2HNO_3 \cdot C_6H_{12}N_4$ and the pulse-repetition time.

relaxation time T_2^* was determined from the free-induction signal waveform and likewise was about the same for all four lines: $T_2^* = 6 \pm 3$ ms.

We have proposed a technique to improve the sensitivity of the local ^{14}N NQR method through the use of a two-frequency exposure and establishing a weak magnetic field [34]. Hexogen $N_3(CH_2)_3(NO_2)_3$ was adopted as the object of experimentation. In this sample at 300 K the strongest ^{14}N NQR lines were detected at frequencies $\nu_+ = 5192$ kHz, $\nu_- = 3410$ kHz, and $\nu_0 = 1782$ kHz [35, 36]. The saturation of the transition in hexogen at the frequency ν_0 with a radio-frequency pulse caused the ν_--signal intensity to increase [37]. The two-frequency exposure was conducted using a pulsed local-NQR spectrometer with two flat surface coils. The width of the radio-frequency saturating pulse at frequency ν_0 was chosen to be 1 ms with a pulse amplitude of 10 G. The duration of the reading pulse at frequency ν_- with a frequency offset of 0.25 kHz from resonance ranged up to 30 μs. The observation of the NQR signal at the frequency ν_+ (with a transverse relaxation time $T_2 = 1.5$ ms and longitudinal relaxation time $T_1 \approx 8$ ms at 300 K) made it possible to examine all the theoretical relationships for the two-frequency experiment [38].

The use of the two-frequency technique for changing the intensity of the signals relevant to an observed transition is mainly due to the relaxation time of the sample and the means of exciting the two-frequency signal. The process of excitation affects the relaxation characteristics of excited NQR transitions [38].

The observing conditions for local NQR can also be improved by establishing a weak magnetic field to the sample. This causes the relaxation time T_2 to increase. Figure 8 displays the ^{14}N NQR signals for $N_3(CH_2)_3(NO_2)_3$ in a magnetic field at 300 K obtained using a Fourier transform of the free-induction signal acquired after separate radio-frequency pulses. The magnetic field was applied perpendicularly to the axis of the radio-frequency coil. A comparison with the analogous experiment for $N_4(CH_2)_6$ shows that the sensitivity to an external magnetic field depends strongly on the asymmetry parameter η. In the field $B = 70$ G the ν_0 linewidth in hexogen increases approximately by a factor of two relative to that in a zero field (~ 0.3 kHz). At the same time, the doublet of spectral lines in Hexa (urotropine) transforms to a single line of width ~ 2 kHz in a much lower magnetic field (~ 1.4 G), and this line broadens asymmetrically due to line shifting to higher frequencies.

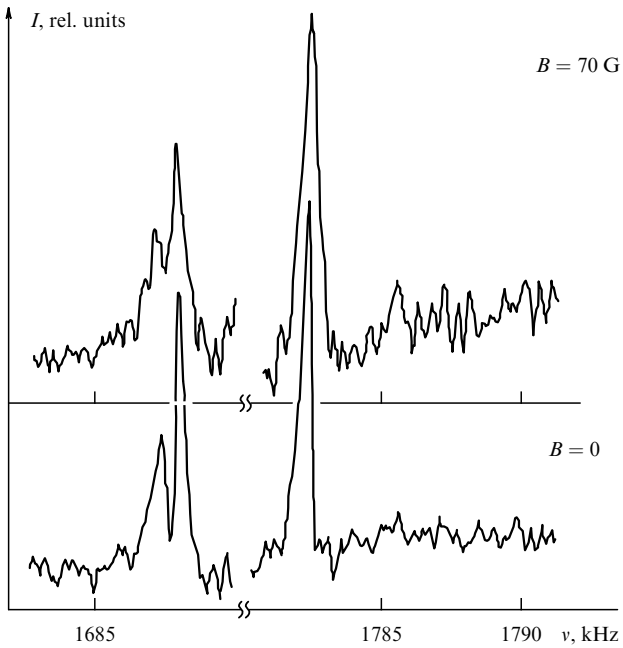


Figure 8. The ^{14}N NQR lines $\nu_0^{(1)} = 1688$ kHz, $\nu_0^{(2)} = 1689$ kHz, and $\nu_0^{(3)} = 1782$ kHz recorded in $C_3H_6N_6O_6$.

The ν_- line in hexogen $N_3(CH_2)_3(NO_2)_3$ depends on the magnetic field still more weakly. Figure 9 shows the angle-averaged external-magnetic-field (B_0) dependence of the quadrupole energy levels in hexogen powder obtained using computer calculations (25×10^3 points), where $R = 4\mu B_0/(eQq_{zz})$, μ is the nuclear magnetic moment of ^{14}N, and eQq_{zz} is the quadrupole coupling constant.

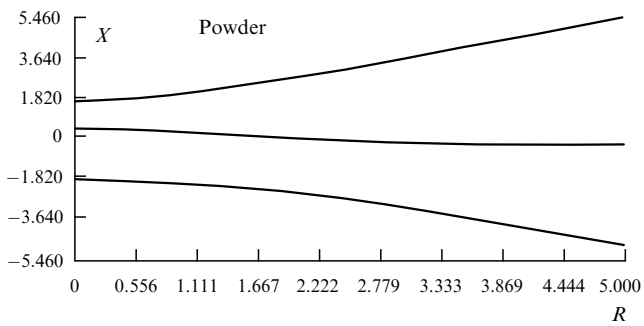


Figure 9. The dependence of the quadrupole energy levels for nuclei of spin $I = 1$ on a constant magnetic field ($R = 5000$, the asymmetry parameter $Z = 0.634$).

2.2. Local NQR and detection of plastic mines

Nuclear quadrupole resonance enables one to detect explosives at a distance from a detecting coil (antenna) [39–41]. Local NQR in a weak magnetic field and the optimal observing conditions for local NQR are discussed in Refs [42, 43]. If some explosive, say hexogen, is placed in a plastic container, then metal and radio-frequency detectors fail. The neutron detectors of explosives are ineffective because of low selectivity. A dog picks up primarily a smell of man. 'Electronic noses' based on mass spectrometry are also inefficient, because the diffusion of molecules to the container surface takes a very long time.

Hexogen $C_3H_6N_6O_6$ is a constituent of the plastic explosive PE-4. Most of the present antitank mines are made from a blend of trinitrotoluene and hexogen (PE-4 has the following composition: 80% hexogen, 20% plasticizer; the antitank mine ATM-62P2-2: 57.5% hexogen, 19% trotyl, 4.77% aluminium, 6.4% retarder; the TS-2.5 and TS-6 Italian antitank mines: 45% hexogen, 55% trotyl). Explosives present in the composition of these mines possess different melting points: from 80 °C (trotyl) to 204.1 °C (hexogen). In manufacturing the ammunition, hexogen is not brought to its melting point; otherwise a sharp increase in its impact and friction sensitivity is observed. Besides, hexogen is insoluble in toluol from which trotyl is obtained by nitration. All this results in the fact that in the trotyl — hexogen mixture one observes no shifting and broadening of the NQR lines of nitrogen nuclei as compared to pure $C_3H_6N_6O_6$.

All the ^{14}N NQR lines from cyclic nitrogen in hexogen, both ν_+, ν_- and ν_0, show a high intensity and can be detected in one measuring cycle (without data amassing) when measured with the use of a conventional cylindrical coil.

NQR-based detector of hidden layings of explosives exploring ^{14}N-nucleus lines is the only device which provides an unambiguous identification of a particular explosive. This fact is reflected in some author's certificates and papers [44–52]. An arrangement of the ^{14}N NQR spin locator and local NQR of ^{14}N, ^{81}Br, and ^{127}I nuclei in large volumes is discussed in Ref. [53] and Refs [54, 55], respectively.

Hexogen and most other explosives, including widely used trinitrotoluene ($C_7H_5O_6N_3$), contain NO_2 nitrogroups. To detect NQR signals from these nitrogroups is far more difficult than from cyclic nitrogen. The situation is further complicated if a sample contains nuclei which are chemically distinct. The chemical nonequivalence of various nuclei along with presence of the crystallographic nonequivalence resulting in multiplicity of lines (12 lines for trotyl) is also a complicative factor. Moreover, as already noted, NO_2 groups in compounds present in the composition of explosives seem to be able to rotate at room temperature which results in a broadening of the ^{14}N NQR lines.

For the practical implementation of a hexogen-responsive mine detector it is fortunate that the frequencies of the ^{14}N NQR lines in hexogen have only a weak temperature dependence in addition to a high line intensity for cyclic nitrogen. Besides, as already emphasized, the NQR lines of nitrogen show no broadening in a weak magnetic field owing to the large value of the EFG asymmetry parameter η in hexogen ($\sim 62\%$). This is also favourable for the observation of NQR signals from explosives in practice.

We have produced and tested an NQR plastic-encased mine detector [56]. This detector is based on a coherent pulsed NQR spectrometer with an irradiation-pulse power of up to 1 kW. A block diagram of this device is shown in Fig. 10. A master crystal-stabilized oscillator produces a reference frequency of 10384 kHz so that after dividing by 2 to obtain the ^{14}N NQR frequency in hexogen, $\nu_+ = 5192$ kHz, convenient for work at room temperature. The overall setup is operated by a programmer unit generating a repetitive spin-locking pulse sequence and gating pulses. The radio-frequency pulses are formed by a digital gate circuit. To store an NQR signal, a train of up to 10^4 pulses with a frequency detuning from exact resonance was used. The signal building up was carried out with the use of a computer. In a companion pickup connected by a 3 m cable to a measurement unit, a power-amplifier output stage, a receiver preamplifier, and a spiral surface coil of diameter 200 mm were located. The pickup was placed in a cylindrical brass shield of diameter 400 mm closed from below, on the side of a receiver-transmitter coil, by a plastic lid. The distance from the surface of the coil to the plastic lid (i.e. practically to the Earth's surface) was 2 cm, and this provided protection against the adverse effects of possible piezoresonances in soil fractions.

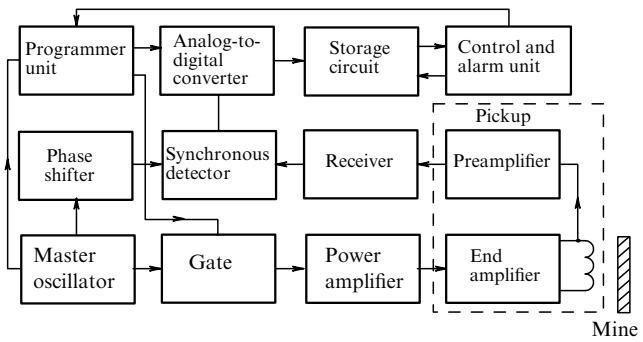


Figure 10. Block diagram of an NQR mine detector.

A spiral flat surface coil produced by printing technology from copper-clad textolite glass is placed above the region of the assumed location of a mine. Because of the nonuniformity of the radio-frequency field set up by such a coil, it receives an NQR signal originating from an area of explosive limited by the circumference of the coil and separated by the distance from its surface approximately equal to the radius of the coil [57]. To improve sensitivity as the distance to the explosive grows, it is expedient to increase the diameter of the flat coil, but this leads to problems in making and tuning large rf coils as well as protecting them against interference.

Experimental investigations were performed on the anti-tank Italian-made mines TS-2.5 and TS-6, the Russian-made mines ATM-62P2-2, and the plastic explosive PE-4. The investigations were conducted on mines buried in the earth at different depths with different types and humidity of soil. As expected, the intensity and shape of the ^{14}N NQR signal did not depend on whether a mine was covered by dry or humid soil or even by a layer of water. Just as when the distance from the coil to soil was varied, only a change in the resonant-circuit tuning was observed because of altering the equivalent capacitance of the resonant circuit. Thus, all one need do is tune automatically to the resonance frequency of this circuit.

The NQR-detector tests conducted with the Italian mines TS-2.5 and TS-6 showed the high efficiency of the NQR method in searching for hexogen-containing explosives in nonmetallic containers. With the above-described detector, the mine-detection time for mines buried in soil at a depth of 10 cm comprised 10 s. In such tests, the probability of reliable detection of a mine determined from 150 measurements was as great as $D = 0.97$. With a 4-channel detector, inspection of 1 m^2 area of soil for the presence of mines took 20 s. A strictly specified signal frequency unique to this type of explosive and its relaxation characteristics enables one to eliminate false signals. For the hexogen line with a frequency $\nu_+ = 5192$ kHz, taken as the operating frequency, the relaxation times at a temperature of 300 K were as follows: $T_2^* = 1.5$ ms, $T_1 \sim 8$ ms. The width of radio-frequency irradiation pulses in the series constituted 10 μs. The optimal value of the NQR-spectrometer frequency offset relative to the operating resonance line, depending on the strength of the radio-frequency field in the site where the explosive is located, was selected (~ 1 kHz) experimentally.

Analysis of the relationship between the ^{14}N NQR signal intensity, on the one hand, and the frequency detuning $\Delta\nu$ from the resonance, the radius R of the irradiating surface coil, and the distance h to the sample under investigation, on the other, allowed us to develop a procedure for determining the bedding depth and location of the explosive, based on finding an optimal frequency offset in the strong off-resonance pulse train [58].

The experimental results on the optimization of the multiple-pulse SLSE and SORC sequences are reported in Ref. [59]. The complicated dependences of the ^{14}N NQR signal intensity in hexogen and octogen on the number of

pulses in a sequence, the pulse width, the interval between pulses, and the frequency offset from resonance were obtained. The optimal number of pulses in the SLSE sequence for hexogen equaled 400, and an optimal ^{14}N NQR signal was obtained for unexpectedly short pulses (0.3 μs). Hence, to obtain an increase in sensitivity, the parameters of these multiple-pulse sequences should be optimized for every substance involved.

2.3. The NQR in cocaine, cocaine hydrochloride, heroin, and codeine. The NQR approach using a large coil

The ^{14}N frequencies in cocaine were measured by the direct NQR method at the temperatures 77 K and 295 K ($\nu = 3.740 \pm 0.001$ MHz, $\nu_+ = 3.829 \pm 0.001$ MHz and $\nu_- = 3.7176 \pm 0.0001$ MHz, $\nu_+ = 3.8186 \pm 0.0001$ MHz, respectively) [60]. For these measurements a Fourier-transform spectrometer with a coil over 60 mm in diameter and a 90° pulse width of 10 – 30 μs was employed. To eliminate piezoresonances, the sample was placed inside a copper shield. A sample with a mass of 150 g containing about 1% impurities and purified through recrystallization (12.9 g) was investigated.

The three practically equivalent nitrogen atoms in cocaine are characterized by a small value ($\sim 4\%$) of the asymmetry parameter. The width of the ^{14}N NQR lines for an unpurified sample was approximately three times greater (0.87 kHz) because of the random distribution of the electric field gradients on nuclei.

Cocaine is a handy substance from the viewpoint of its detection by means of the direct ^{14}N NQR method. The sensitivity of this technique is easily improved by increasing the number of scans (the gain in sensitivity is proportional to the square root of the storage number). Multiple-pulse sequences (spin-locking echoes, for example), being most effective for $\tau \ll T_2$, satisfy this condition in the case of cocaine and provide a considerable increase in sensitivity.

The ^{35}Cl NQR spectrum obtained from a 60 g sample of recrystallized cocaine hydrochloride at $T = 295$ K showed a broad ($\sim$ 20 kHz) resonance line at a frequency of 2.53 ± 0.01 MHz [60]. Attempts to observe NQR in this compound for the ^{37}Cl isotope employing the direct NQR method failed. Even with shortest intervals between pulses there is no way to use multiple-pulse sequences for increasing the sensitivity.

The ^{14}N NQR in cocaine ($C_{17}H_{21}NO_4$) was first investigated in works [12, 39]. Since the presence of an external magnetic field leads to a broadening of NQR lines, only one broad line of ^{14}N at a frequency $\nu_\pm = 4260$ kHz, coincident with the proton resonance frequency in cocaine, was observed in this compound. In this case the parameter $R = 1.6$, defined as

$$R = \frac{4\mu B_0}{eQq_{zz}} ,$$

where μ is the nuclear magnetic moment, B_0 is the induction of an external magnetic field, and eQq_{zz} is the quadrupole coupling constant. The DNQR spectrum of ^{14}N nuclei in cocaine at $T = 295$ K is shown in Fig. 11. For double-resonance-data processing with a correction for the presence of a constant magnetic field, an original computer program was in use [61]. With an allowance made for the magnetic field in cocaine (1040 G), these results are in good agreement with those obtained more recently by the direct ^{14}N NQR method [60].

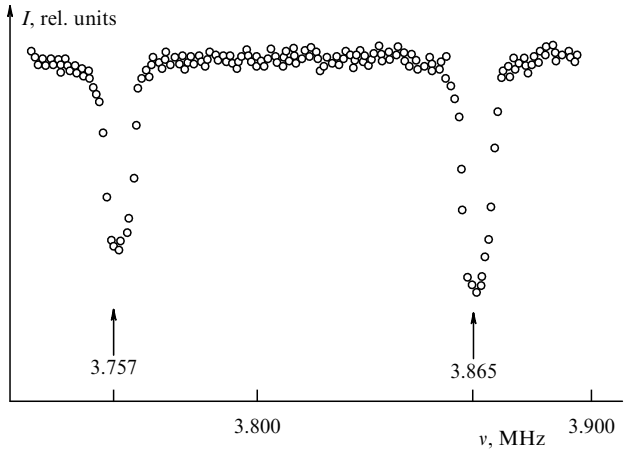


Figure 11. ^{14}N DNQR spectrum taken in cocaine.

For cocaine hydrochloride, cross-relaxation spectroscopy of ^{14}N NQR gives the following frequencies at room temperature: $\nu_+^{\rm H} = 1384$ kHz ($R = 1.63$) and $\nu^{\rm H} = 752$ kHz ($R = 1.3$). Computer extrapolation to a zero magnetic field yields $\nu_+ = 961$ kHz, $\nu_- = 806$ kHz, which correspond to $eQq_{zz} = 1178$ kHz and $\eta = 0.263$.

The ^{14}N NQR frequencies in heroin at $T = 295$ K were found to be $\nu_+ = 4026$ kHz and $\nu_- = 3950$ kHz, which gives the spectral parameters $eQq_{zz} = 5.31$ MHz and $\eta = 0.028$.

The weakest ^{14}N NQR signal was observed in codeine having a low-percentage content of nitrogen in a molecule. Here the resonance frequency in a magnetic field is close to that in cocaine (4.20 MHz) and easily detectable. The results of the investigations of ^{14}N NQR in drugs are summarized in Table 3.

Table 3. ^{14}N NQR in some drugs at $T = 295$ K.

Compound	ν_+, kHz	ν_-, kHz	eQq_{zz}, kHz	η
$C_{17}H_{21}NO_4$ (cocaine)	3865	3757	5081	0.043
$C_{17}H_{22}NO_4Cl$ (cocaine chloride)	960	809	1178	0.263
$C_{21}H_{22}NO_5$ (heroin)	4026	3950	5031	0.028
$C_{18}H_{21}NO_3 \cdot H_2O$ (codeine)	4028	3980	—	0.02
Hashish	Line series	—	—	—
Opium	3000 – 4000		—	—
$C_{18}H_{21}NO_3 \cdot H_3PO_4$ (codeine phosphate)	1017	785	1200	0.35

The direct NQR method is appropriate for detecting the ^{14}N nuclei in massive samples using a large coil with a volume of about 300 l [62]. This approach can also provide reliable information about the linewidths and the spin-spin (T_2) and spin-lattice (T_1) relaxation times of ^{14}N nuclei. This allows one to investigate the effect of sample impurities on these parameters.

The results of the measurements of NQR frequencies in pure narcotics and their salts show a number of remarkable distinctions between these two classes of compounds. For the quadrupole coupling constant and the asymmetry parameter of the EFG tensor we have $eQq_{zz} = 5.046$ MHz, $\eta = 0.039$ (at a temperature of $T = 295$ K) and $eQq_{zz} = 1.178$ MHz, $\eta = 0.263$ in cocaine and cocaine hydrochloride, respectively. Thus, the formation of salts of any acids is attended by a four-fold decrease in the ^{14}N NQR frequency and a six-fold increase in the asymmetry parameter. Such a sharp change in the NQR parameters may be due to the fact that the molecule of pure narcotic conforms from one chiral state to the other. The point is that molecules of morphine, cocaine, codeine and some other narcotics are not planar and may exist in two enantiomeric forms. In such compounds four different atoms or functional groups are arranged about a central sp^3-hybridized atom. The role of such a centre is played by a nitrogen atom and chemical groups bonded to it. In pure narcotics a nitrogen atom is trivalent. The reaction of salt formation comprises a proton transfer from acid to base, i.e. in these compounds a proton is transferred to the nitrogen. For salt formation it is necessary that nitrogen becomes pentavalent; chlorine and hydrogen atoms are added to it. The structure of a cocaine molecule $C_{17}H_{21}NO_4$ corresponds to the 'chair' conformation. On formation cocaine hydrochloride (chloride) $C_{17}H_{22}NO_4 \cdot HCl$, the cocaine molecule evidently changes to the 'bath' conformation.

The molecules of morphine and codeine come in the 'bath' conformation. Here the chiral centre is formed by carbon, nitrogen atoms and a CH_3 group bonded together. In this case the sp^3 hybridization occurs.

On formation of codeine phosphate $C_{18}H_{21}NO_3 \cdot H_3PO_4$, nitrogen becomes pentavalent and adds oxygen and hydrogen. It is likely that the molecule changes to the 'chair' conformation.

It has been possible to verify this presumption using the Hoffman MO-LCAO method. 28 π-electrons in cocaine and 32 in cocaine chloride were used in the calculations. The parameters of heteroatoms (Cl, O, N) were deduced from spectroscopic experiments. This calculation enabled the asymmetry parameter η for the molecules of cocaine, codeine and their salts to be found:

$$\eta = \frac{3}{2}\frac{eQq_0}{eQq_{zz}}\rho\,,$$

where $eQq_0 = 8400$ MHz is the quadrupole coupling constant per unbalanced p-electron of a nitrogen atom, ρ is the π-electron defect calculated from the formula

$$\rho = 2\sum_i C_i^2\,.$$

Here the summation is over all the unoccupied molecular i-orbitals, and C_i are the coefficients of the atomic nitrogen wave functions for unoccupied energy levels.

The ratios of the asymmetry parameters, first, for cocaine chloride and cocaine and, second, for codeine phosphate and codeine were found to be 4 and 10, respectively. Thus, the results of the calculations turned out to be close to the experimental ones. It follows that the 'bath-chair' transition provides an adequate explanation for the experimental findings.

Taking into consideration a lowering of the NQR frequency to sub-megahertz values under the 'bath-chair' transition, it may be concluded that the direct pulsed method of detecting these narcotics will lead to problems, so that it is advantageous to use the cross-relaxation and DNQR methods.

Since the NQR frequencies of narcotics and explosives can be divided into two groups: (1) trotyl and narcotic acid salts with frequencies of about 1 MHz, and (2) cocaine, heroine, codeine, hexogen, and opium with frequencies of 3.4–4.0 MHz, a two-channel control system can be employed [63, 64]. A large pickup coil makes it possible, when using a moving conveyer track, rapidly to detect these compounds in luggage. In this case there is little sense in using open resonant circuits as this results in a sharp limitation of the controlled volume and a lowering of sensitivity. Since the ^{14}N NQR frequencies of the main explosives and drugs fall within a narrow frequency range, only one programmed radio-frequency channel (Fig. 12) with time multiplexing can be used in the control device for the excitation of resonances (Fig. 13) [65, 66].

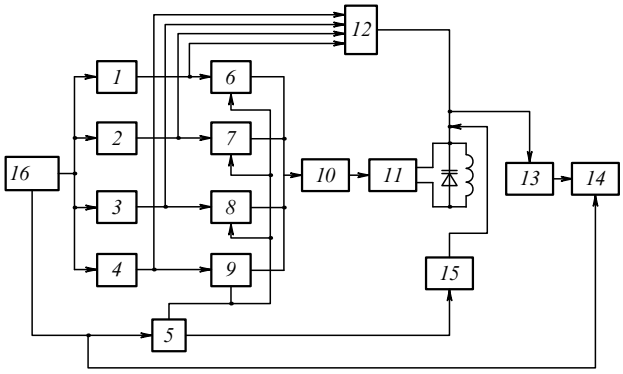


Figure 12. Block diagram of a control device for luggage checking on cocaine, heroin, hexogen, and octogen: *1–4* — frequency synthesizers, *5* — programmer unit, *6–9* — switches, *10* — OR gate, *11* — power amplifier, *12* — delay circuit, *13* — receiver, *14* — detector, *15* — shunt and varicap switching circuit, *16* — reference frequency source.

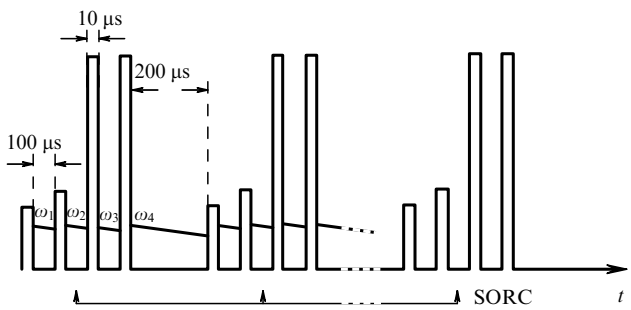


Figure 13. Time chart of detecting four different substances during customs control: ω_1 — hexogen, ω_2 — octogen, ω_3 — cocaine, and ω_4 — heroin.

There appeared information that the Quantum Magnetics Co. (USA) began manufacturing NQR devices with a coil volume of 170 l for the detection of explosives and drugs in frozen fish. An NQR spectrometer with a large coil for the detection of explosives in parcels is described in Ref. [67].

3. Double NQR – NMR resonance in codeine phosphate, opium, and hashish

The double-nuclear-quadrupole-resonance method is usually applied when the sensitivity of the direct NQR approaches is found to be inadequate because of the location of the absorption lines in the low-frequency range ($\sim$ 1 MHz) or the small concentration of quadrupolar nuclei in the compound involved [68, 69]. All modifications of the double resonance technique are based on the assumption that a sample contains two different spin subsystems: the spin subsystem A (with a strong nuclear-resonance signal) and the subsystem B (of the nuclei being investigated) which are coupled with each other by the dipole-dipole interactions. The weak signal of B nuclei is observed indirectly through the detection of variations in the resonance signal of A spins. The various DNQR techniques differ from each other predominantly in the conditions in which the energy transfer between the two subsystems takes place. The most universally used technique is based on DNQR in a weak magnetic field. This technique makes it possible to investigate both half-integer and integer spins in polycrystalline samples with high efficiency.

We adopted this technique for detecting the ^{14}N absorption lines in studies of narcotic compounds. As distinct from other DNQR techniques possessing low sensitivity for integer spins, the method under discussion takes advantage of an increase in the coupling of the A and B subsystems in some intermediate magnetic field $B_0 \gg B_{\rm loc}$, where the quantity $B_{\rm loc}$ specifies the level of the internal local magnetic fields [38].

An experimental cycle is accomplished as follows. A sample is exposed to a high stationary magnetic field B_0 where the A spins (proton spins in our case) are magnetized up to their steady-state values. Then the sample is mechanically moved from the magnet gap into the region of zero magnetic field in such a way as to keep constant the entropy of the A system and there exposed to radio-frequency irradiation up to its saturation. Thereafter the sample is returned to the original field B_0, and a signal on the proton NQR frequency is measured using a 90° pulse. A decrease in the induction signal amplitude for A spins indicates that the quadrupolar B nuclei have absorbed the radio-frequency energy. Such a process of momentary (compared to the spin-lattice relaxation time T_{1A} of the subsystem A) change of the external magnetic field B_0 is referred to as the adiabatic remagnetization of a sample. The contact of A and B spins takes place when one of the quadrupole frequencies coincides with the Zeeman splitting of the proton subsystem, i.e. at $\omega'_B = \gamma_A B'_0 = \omega'_A$. Equalization of the energy levels of the two subsystems causes a heat exchange between them via transitions induced by dipole-dipole interactions. Cross-relaxation (Fig. 14) occurs for a time $\tau_{\rm cr}$ when the condition $\omega'_A \approx \omega'_B$ is fulfilled. Since the rate of the adiabatic switching of the magnetic field B_0 must obey the inequality $\mathrm{d}B_0/\mathrm{d}t \ll \gamma_A B_{\rm loc}$, a limiting value of $\tau_{\rm cr}$ may not exceed $\Delta\omega_A/\omega_{A0}$, where $\omega_{A0} = \gamma_A B_0$. Multiple cross-relaxation is also possible for $n\omega'_B \cong m\omega'_A$, where n and m are integers, but the probability of such a process is considerably lower. At $n = m = 1$ we obtain $\tau_{\rm cr} \approx \Delta t\,(\Delta\omega_A/\omega_{A0})$, where Δt is the time taken for decreasing the frequency ω_{A0} to a value $\omega_{\rm d} = \gamma_A B_{\rm loc}$ corresponding to the frequency of magnetic dipole interactions. Energy-level crossing results in the equalization of spin temperatures of the A and B subsystems. For sufficiently large values of the relaxation times of

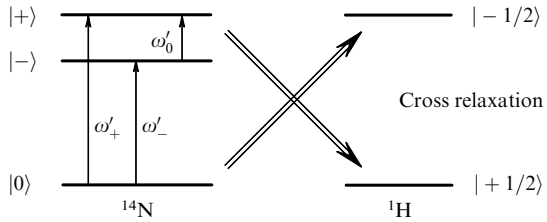


Figure 14. Energy-level diagram of ^{14}N($I = 1$) and ^{1}H ($I = 1/2$) quadrupole spins in a magnetic field $B'_0 = \omega'_+/\gamma_A$.

protons and quadrupolar nuclei, T_{1A} and T_{1B}, the level-crossing process may be repeated many times during one cycle of retuning the frequency ω_B, at which the B subsystem is saturated in a zero field. To accomplish this, an intermediate field B_0 in the form of a meander at a frequency of about 10 MHz was applied so that the condition $\omega_0 \approx \gamma_A (B_0^2 + B_{\rm loc}^2)^{1/2}$ was fulfilled, and the irradiation of the B subsystem by a radio-frequency field B_{1B} was conducted in the fields $B_{\rm loc}$ to avoid ω_B-line broadening and lowering of the method sensitivity.

The sensitivity of the method is defined by the expression: $S_B = S_A(\Delta M/M_0)$, where ΔM is the change of residual proton magnetization at the close of an experimental cycle, and M_0 is its steady-state value, and is typically two-three orders greater than the sensitivity of the direct NQR method. In addition, the S_B magnitudes are practically constant as the detected frequency decreases down to very low ω_B values. This makes possible the use of double level-crossing resonance (DLCR) for the investigation of quadrupolar nuclei in codeine phosphate, opium, and hashish. In fact, the sensitivity S_B depends on the relationship between T_{1B} and $T_{1\rm d}$ and on the concentrations ratio n_B/n_A (here $T_{1\rm d}$ is the spin-lattice relaxation time of the A subsystem in a local magnetic field) and has a maximum at $T_{1B} \gg \tau_{\rm irr}$, $T_{1\rm d} \ll \tau_{\rm irr}$, and a minimum at $T_{1B} \ll \tau_{\rm irr}$, where $\tau_{\rm irr}$ is the time of radio-frequency irradiation of the quadrupolar system.

The resolution of the method is determined by the resonance linewidth $\Delta\omega_B$ at a specified level of radio-frequency irradiation in a zero external magnetic field.

To extend the duration of the thermal contact between the A and B subsystems, a sample was held in a constant magnetic field $B'_0 = \omega_B/\gamma_A$ for a time $3T_{AB} \lesssim \Delta t \lesssim 5T_{AB}$ in each cycle of magnetic reversal. The magnetic induction B_0 of the field was retuned in synchronism with the irradiation frequency ω_B. In practice, such a procedure was realized with the use of an additional solenoid. During the mechanical movement of a sample from the field B_0 to the region of zero field, it travels through the solenoid.

The time T_{1A} features a complex temperature dependence, therefore a preliminary investigation of each sample was conducted with the goal of minimizing this time for deciding on a convenient duration of the DLCR cycle. The relation $t_{\rm c} \approx 3T_{1A}$ was taken as optimal. Correspondingly, the spin-lattice relaxation time $T_{1\rm d}$ in a zero external magnetic field at a given operating temperature may not be very short. If $T_{1\rm d} \leqslant \Delta t$, where Δt is the magnetic field (B_0) switching time for adiabatic remagnetization, then DNQR is impossible.

The times T_{1A} were measured by the saturation method. For the samples under investigation they were found at room temperature to be: 18 s in cocaine, 8 s in hashish, and 3 s in codeine phosphate. The values of $T_{1\rm d}$ were determined from

the experimental relationships between the induction signal amplitudes and the duration of stay of a sample in a zero field without irradiation. The following values of T_{1d} were obtained for narcotics: 1.6 s for cocaine, 3 s for hashish, and 1.8 s for codeine phosphate. The accuracy of the latter measurements was rather low because of the level-crossing influence on magnetization, therefore the result should be considered as an estimate. The data on measured relaxation times indicate that in the samples of interest the DNQR signals can be observed at room temperature.

The amount of substance used for the detection of DNQR signals was confined by a container of inner diameter 8 mm and volume 2 cm^3, which was moved inside irradiating coils in a constant magnetic field $B_0 = 0.47$ T and $B_0 = 0$. The sample weight was ~ 2 g.

The ^{14}N NQR signals in cocaine were detected with a signal-to-noise ratio of 6:1 (after 5 storages) that made it possible to acquire the spectrum without trouble (see Fig. 11). In codeine phosphate two lines of ^{14}N NQR lying in the low-frequency range were detected (Fig. 15). The use of an intermediate magnetic field B_0' for extending the duration of thermal contact enabled the acquisition of the spectrum after 5 measuring cycles.

For hashish in the form of a technological mixture, five pairs of lines with a signal-to-noise ratio of 2:1 (6 measuring cycles) were observed in the frequency range of 3.0 – 5.0 MHz. Clearly these lines may be attributed to nitrogen atoms in various components (Fig. 16). A search for spectral lines in the region of lower frequencies was not conducted, since the low intensity of NQR signals and difficulties associated with their identification for lack of a voluminous data bank of NQR frequencies made such a search unpromising.

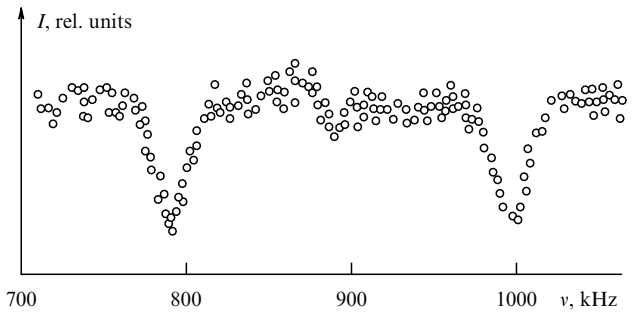


Figure 15. ^{14}N DNQR spectrum taken in codeine phosphate.

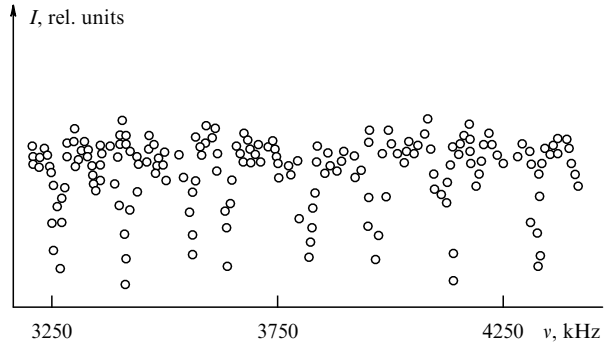


Figure 16. ^{14}N DNQR spectrum in the high-frequency range taken in hashish.

The ^{14}N NQR spectra for trinitrotoluene, opium, and hashish in the form of technological mixtures were first measured in Refs [70, 71]. An analysis of a trinitrotoluene technological mixture using a computer data bank is presented in [63, 72]. A program complex was developed which involves, apart from the NQR data bank, calculations of the asymmetry parameters and the resonance fields for basic narcotics and explosives as well as the determination of optimal conditions for local NQR observation.

4. Cross-relaxation spectroscopy of explosives

To improve the sensitivity of detecting the ^{14}N NQR signals from NO_2 groups associated with explosives, the cross-relaxation spectroscopy was used to advantage [73, 74]. True, this method results in a broadening of the nitrogen NQR lines because of the presence of a magnetic field as well as enhancing the harmonics of the basic frequency. However, when solving the problem of detection of substances involving NO_2 groups, the latter presents no serious problems. The advantage of the double-resonance method with the use of cross-relaxation is the possibility of working at room temperature without radio-frequency irradiation of the quadrupole system. The cross-relaxation line of an NQR spectrum is detected through slow variation of a weak magnetic field.

Of interest is the creation of a multi-purpose device based on the cross-relaxation approach to search instantaneously for several basic types of explosives in a nonmetallic container. This may be accomplished by varying a magnetic field in such a way (following a special program) as to create alternate cross-relaxation conditions for the ν_+, ν_- and ν_0 lines in the nitrogen NQR spectra of several basic explosives during one cycle of detection. Such a possibility may be realized without loss in sensitivity providing the large value of the spin-lattice relaxation time of the proton system in a constant magnetic field ($T_{1d} \sim 10$ s). In a zero magnetic field the time T_{1d} is about 0.2 s. In the case of trotyl (6 pairs of lines), to achieve greater degradation of the proton-system magnetization when it contacts the quadrupole spin system, and hence, to obtain an increase in sensitivity, a magnetic field may be varied in such a way as to accomplish energy-level crossing for all the ν_+ and ν_- lines of trotyl during the process of measurement. Here, the cross-relaxation conditions are fulfilled in one cycle of detection not for one NQR line but in turn for several lines of different explosives at once. To decrease the number of the 'steps' of the magnetic field in one measuring cycle, a search for explosives may be carried out using the ν_- lines only, because the shift and broadening of these lines in a constant magnetic field is the least [75].

A detector of explosives described in Ref. [76] contains a pulsed proton ^1_1H NQR spectrometer with an operating frequency of 2.5 MHz in a magnetic field $B_0 = 587$ G (Fig. 17). The essence of the method is illustrated in Fig. 18 where a time chart of the variation of the magnetic field in the cross-relaxation spectrometer is shown. The container being checked for the presence of explosives is placed in the search coil of the spectrometer (see Fig. 17). The variation of the magnetic field (Fig. 18) generated by an electromagnet, is performed to a program that provides the cross-relaxation conditions between the spin systems of ^{14}N nuclei and protons, in turn for various explosives (hexogen, PETN, trotyl). The detector is operated under the control of a

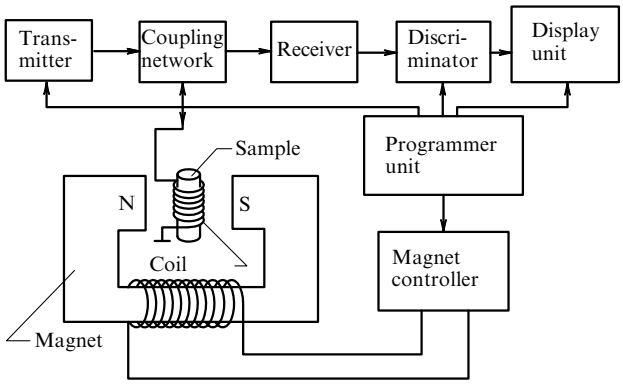


Figure 17. Block diagram of a cross-relaxation detector of explosives [76].

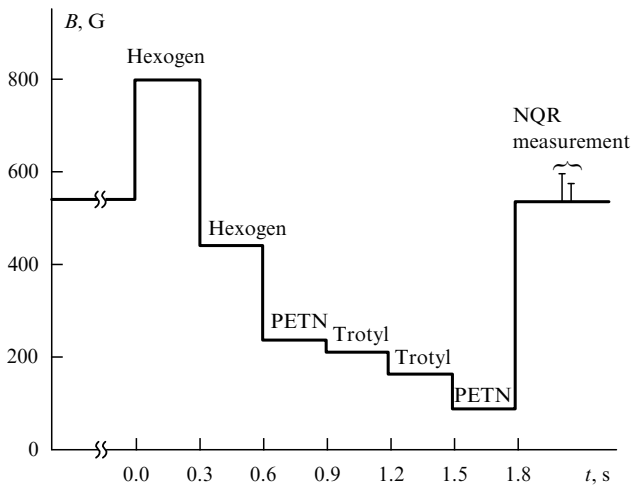


Figure 18. Time chart of the magnetic field variation in a cross-relaxation spectrometer [76].

programmer unit. A display signals the presence of any explosive. Equalization of the proton and quadrupole resonance frequencies, $\nu_P = \gamma B/(2\pi)$ and ν_Q, respectively, occurs sequentially with $\nu_Q = 5.2$, 3.4, 1.8 MHz (hexogen), 0.9, 0.5, 0.4 MHz (PETN), 0.87 MHz (trotyl), because the gyromagnetic ratios are as follows: $\gamma_H/(2\pi) = 4.25$ kHz/G and $\gamma_N/(2\pi) = 307$ Hz/G. Cross-relaxation between the energy levels of the proton system and the appropriate levels of the quadrupole system lead to a dip on the magnetization curve of the proton system. The change in magnetization with reference to its steady-state value is fixed by a 90° reading pulse after re-establishing the field B_0.

Preliminarily, the steady-state value of magnetization is also determined using a 90° pulse in the first half of the detection cycle when the field B_0 is constant. Change of the NQR-induction signal in the course of the measuring cycle upon exceeding a certain threshold value (to eliminate false changes of state) causes the alarm unit to switch-on.

Such a detector may be used to control items of mail (printed matter, parcels) and luggage for narcotics and explosives. The objects under investigation may be fed into the search coil by means of a conveyer. The time taken for the checking of an object for the presence of explosives will be about 10 s, and the minimum detectable mass of explosive may be of the order of 10 g.

5. Monitoring the explosives and narcotics with SQUID

Recently, systems based on SQUIDs (SQUID — superconducting quantum interference device) have found advantageous use as various magnetic-field sensors. They are used, for example, in apparatus for the study of biomagnetic fields (see Ref. [77]).

SQUID-based techniques, owing to their high sensitivity, make it possible to measure NQR transitions at low frequencies. Such measurements offer problems when performed by the direct pulse NQR method.

The sensitivity of an inductive coil used as a magnetic-field sensor is limited by noise in its winding. The spectral density of coil-voltage fluctuations is known to be $S_U^{1/2} = (4kTR)^{1/2}$, where R is the coil resistance. A magnetic field of induction B at a frequency ω induces in the coil a voltage $U = \omega GNB$, where N is the number of turns of the coil, and G is a form factor having dimension of area (equal to the winding area at $l \gg D$, where l is the winding length, D is the turn diametre) [77]. Thus, the spectral density of magnetic-field fluctuations can be expressed as $S_U^{1/2} \propto (4kTR)^{1/2}/(\omega NG)$. This implies that the minimal detectable field for a given inductive coil is proportional to $1/\omega$, i.e. it increases with decreasing frequency.

The advantage of SQUIDs over Faraday gages is most pronounced for frequencies below 100 kHz. With the use of a pulsed SQUID-based NQR spectrometer, the ^{35}Cl NQR signal in $NaClO_3$ from a sample with a volume of 0.32 cm^3 was detected at 4.7 K with a sensitivity of 2×10^{16} spins per cubic centimetre [78].

Figure 19 shows a block diagram of a SQUID-based NQR spectrometer [79]. A sample is placed in a half of the detecting coil; the other half of the coil is wound in the opposite direction to weaken the direct interference with pulses from the excitation system of the spectrometer. To minimize the coupling between the coil of the transmitting system and the operating circuit, a shield is used. The adjustment of the C_i capacitor is performed outside a cryostat, and R_i includes the leakage resistance of the capacitor and the contact resistance. A direct-current

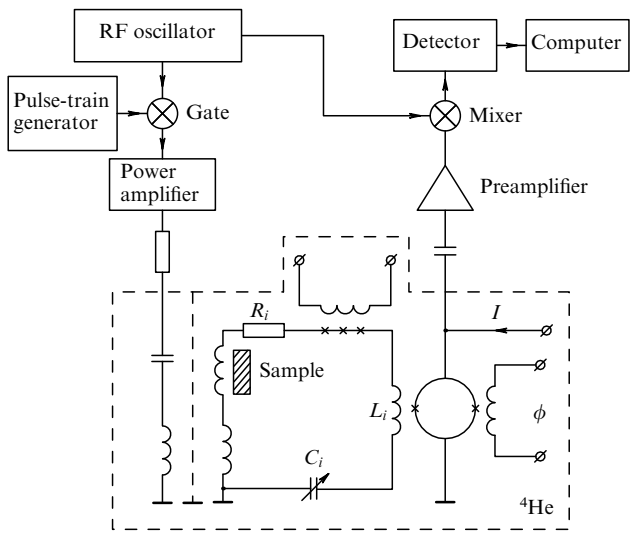


Figure 19. Block diagram of a SQUID-based NQR spectrometer [79].

SQUID is coupled with the operating circuit through the coil L_i. The SQUID output is connected through a coupling capacitor to a low-noise preamplifier operating at room temperature.

Owing to a low noise temperature of SQUIDs and the possibility of obtaining high Q-values, one observes a ten to one hundred-fold gain in voltage resolution as well as a decrease in the resonant-circuit 'ringing' time as the SQUID is switched synchronous with a radio-frequency pulse.

A SQUID, being an ultra-low-noise detector of a radio-frequency field, may be employed for the direct NQR detection in a zero magnetic field. Its high sensitivity obviates the need for using a strong polarizing field in such experiments. In this case, there is no need for shielding the SQUID from static magnetic field applied to the sample in the NQR experimentation.

A SQUID-based NQR spectrometer using a continuous frequency-detection procedure is described in Ref. [80]. This spectrometer affords a frequency range from 1 kHz to 100 MHz. To avoid pump saturation in a sample, a very weak radio-frequency field was used. A comparison between a SQUID-based sensor and a Robinson network shows that the SQUID has a great advantage over a field-effect transistor at frequencies below 100 kHz. Copper NQR signals were detected in a field of 0.67 mT. Resonance was observed at multiple frequencies as well.

The unprecedented sensitivity of SQUID, being of the order of 1 fT, highlights the fact that low-frequency fluctuations of the Earth's magnetic field are several orders greater. For protection against radio interference and fields of other origin, a good shielding is required. Thus, the main problem of practical implementation of this method is associated with parasitic detection of external interference which accompany any measurements carried out with the use of a highly sensitive detector. Nevertheless, the direct observations of the magnetization component of a sample in a zero magnetic field by means of SQUID were performed with much success [78, 79, 81].

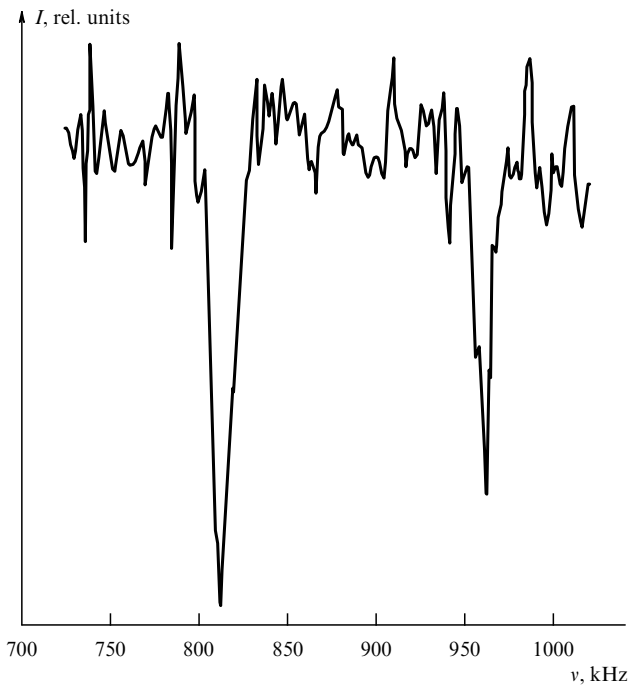


Figure 20. ^{14}N NQR spectrum for a 144 mg sample of cocaine hydrochloride taken with the use of a SQUID detector [60].

To protect SQUID and damp 'ringing' of the circuit after completion of each radio-frequency pulse, a Q-switch (spoiler) consisting of 20 Josephson junctions is used. The critical current of each junction is close to 4 μA and may be varied by applying a weak constant magnetic field (shielded from the sample) parallel to the spoiler layers. When the spoiler is OFF, $Q = 2500$; otherwise, $Q = 0.5$.

The stationary SQUID-based spectrometer [60] used to detect ^{14}N NQR in narcotics does not directly detect nitrogen transitions. The experiment was carried out in a weak magnetic field and detection was performed indirectly via protons coupled with the nitrogen nuclei through a dipole-dipole interaction. A frequency range of 250 kHz was scanned in 100 – 250 s. The saturation of one or two nitrogen transitions was used to increase the signal intensity and to assign spectral lines to one equivalent position of a nitrogen nucleus.

Figure 20 illustrates the ^{14}N NQR spectrum for 144 mg of purified (non-recrystallized) cocaine hydrochloride obtained using SQUID at 4.2 K [60]. In this sample an interesting temperature dependence of the spin-lattice relaxation time of ^{14}N nuclei came to light: T_1 reduces with decreasing temperature from room temperature to 77 K.

6. Conclusions

Cross-relaxation spectroscopy is the preferred method for the detection of narcotics. Future developments may also result in a practical implementation of the conventional local NQR method for samples of reasonable volumes (60 – 200 g) with a detection time of about 10 s at distances of 10 – 15 cm. However, at the present day such experimental data for narcotics are not available (in contrast with explosives). The identification of hashish- and opium-type mixtures will require large amounts of substance and a wealth of signal storages taking much experimental time and therefore seems to be problematic. Checking luggage for cocaine, heroin, and codeine can be accomplished with the use of a large detecting coil using both in the direct and cross-relaxation methods. The corresponding estimates for the remote detection of narcotic substances seem to be rather pessimistic, whereas the situation with explosives looks much better.

The first generation of inventions intended for detection of explosives have already found practical use in control devices. The high sensitivity and other advantages of these devices attract the attention of security services. Further improvement in sensitivity may be obtained with the use of SQUID detectors having an advantage over Faraday gages at frequencies below 1 MHz. Investigations in this direction have enabled the Quantum Magnetics Co. to manufacture the first commercial device for the detection of plastic explosives and narcotics in parcels and air-luggage. The NQR method, as follows from its nature, will be beyond comparison in creating the means of detection of explosives and narcotic substances.

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