Structural and Functional Synthesis of the Radioelectronic Means of a Pulsed NQR

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***Abstract*—The principles of structural and functional synthesis of the radioelectronic means of a pulsed NQR are presented. To simulate signal transformations in the radio frequency paths of the spectrometer, an imitation model of the direct pulsed NQR observation method was developed in the MATLAB Simulink software. The feature of the proposed measuring setup is the implementation of all algorithms for digital processing and signal synthesis in the basis of one FPGA Cyclone IV. The NQR spectrum is reconstructed from the spin induction signal using the fast Fourier transform method.**

***Keywords*—nuclear imaging; chemical and biological sensors; computer simulation; fast Fourier transforms**

I. Introduction

The rapid development of integrated electronics and high-performance information message processing algorithms stimulates progress in the field of physical experiment. This is especially noticeable in the fields of radiophysics, chemistry, medicine, biology and others. The method of nuclear quadrupole resonance (NQR) allows us to study the distribution of electron density of materials which include atoms with quadrupole nuclei [1]. The analysis of existing experimental methods of observing NQR in the frequency range from ~2 to 1000 MHz has shown that promising in this direction is the development of cheap portable spectrometers with an integrated computational core based on the new algorithms of information transformations of the free induction decay (FID) signal into the transmitting and receiving path and visualization of NQR spectra [2].

The development of new methods for direct pulse detection generates considerable interest among scientists due to the achievement of the experiment sensitivity, comparable to that of the double resonance method while maintaining high accuracy and spectral informativeness [2]. In the process, considerable attention should be paid to increasing the signal-to-noise ratio which is provided by the spectrometer to the required level for error-free detection of the NQR signal in small-volume substances with masses ranging from tenths to several grams. Besides, methods of forming special multi-impulse sequences of nanosecond time intervals for the stochastic NQR technique have not been adequately studied.

High accuracy and informativeness of NQR method enables its effective implementation in various fields of science and technology - material science (research of symmetry, structure, phase transitions and analysis of crystal defects); solid state electronics (controlling the structure of semiconductors when creating radiation-resistant devices on their basis); the fight against terrorism and security (remote detection of explosives and narcotic substances) [3] - [7].

II. Concept of Nuclear Quadruple Resonance

The method of nuclear quadruple resonance is based on the energy absorption of radio waves due to a change in the orientation of quadrupole moments of atomic nuclei in the inhomogeneous electric field created by charges external to the nucleus. The levels of quadrupole energy in solids arise at the interaction of quadrupole moments and the inhomogeneous electric field with axial symmetry in the *z* direction at the location of the resonating core and are determined by equation:

$$E_{|m_I|} = \frac{e^2 Q q_{zz}\left[3m_I^2 - I(I+1)\right]}{4I(2I-1)}, \tag{1}$$

where eQq_{zz} – quadrupole interaction, m_I – magnetic quantum number which assumes the value $2I+1$, I – nuclear spin. NQR spectrum reflects the distribution of the electron density near a particular atom. This is the uniqueness of the NQR method in the study of subtle features of the structure of chemical compounds.

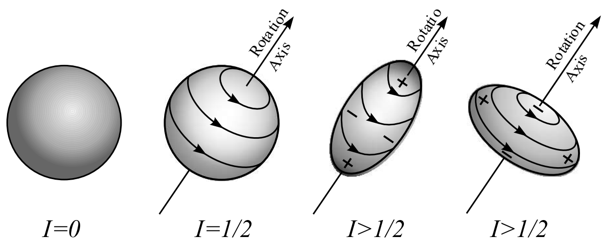


Fig. 1. Types of nuclei (I – spin the nucleus, μ – magnetic moment, Q – quadrupole moment): (a, b) – non-quadrupole nuclei; (c, d) – quadrupole nuclei with different sign of quadrupole moment and I > ½ [8].

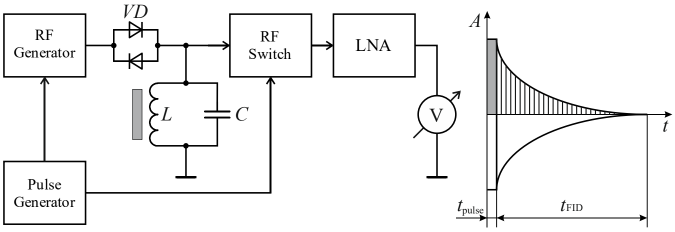


Fig. 2. Scheme of pulse experiment

The NQR pulse method lies in monitoring the response of a nuclear spin system (induction or echo signals) to a short and powerful radio frequency pulse or a series of pulses [1], [9] - [11]. The principles of constructing apparatus for observing the spin echo in the magnetic and quadrupole resonances differ little. Since the lines in the NQR are broader than the NMR lines in liquids, the apparatus for observing the quadrupole spin echo should provide more powerful radio-frequency pulses [11]. In addition, to search for weak signals of the quadrupole echo, it is necessary to have a receiver tunable over a wide range of frequencies. The principle of pulsed NQR observation is shown in Fig. 2. As a rule, to clarify the pattern of the phenomenon, it is believed that the axis of the coil with a radiofrequency field is oriented parallel to the *x* axis of the gradient electric field tensor. In real conditions, the axis of the coil is oriented arbitrarily concerning to the principal axes of the electric field gradient tensor. Then the effective radiofrequency field along the *x* axis will be:

$$H_x = H_1 \sin\theta\cos\varphi \,, \tag{2}$$

where θ – the angle between the direction H_1 and the axis z, φ – azimuth angle. Accordingly, the component of the radio frequency field along the y axis is equal to:

$$H_y = H_1 \sin\theta\sin\varphi \,. \tag{3}$$

These two components excite transitions between NQR levels. Therefore, formulae for the conditions of 90° pulses, in the general case, will include the angles θ and φ. If the sample is taken as a powder, these factors should be averaged over the sphere of an individual radius.

III. Software and Hardware Implementation of a NQR Radio Spectrometer

A. The simulation model of the NQR subsystem

To simulate signal transformations in the radio frequency paths of the spectrometer, an imitation model of the direct pulsed NQR observation method was developed in the MATLAB Simulink software [12]. A model that includes a high-frequency transmitter, a receiving path, and a measurement unit is based on the concept of implementing a single-coil coherent NQR radio spectrometer without conversion of the carrier frequency. To obtain a mathematical model of the spectrometer NQR-subsystem response in the form of a pulsed transient response, we represent the spin system of the nucleus as an oscillating link with the following transmitting characteristic [12]:

$$W(p) = \frac{k}{T^2 p^2 + 2\xi T p + 1} \,, \; 0 < \xi < 1 \,, \tag{4}$$

where k is dimensionless gain factor (in ideal case $k = 1$), T is time constant, ξ is damping factor.

A pulsed transient response is the system response to the ideal pulsed input influence, the mathematical model of which is a delta function $\delta(t) = x(t)$, then this transmitting function (4) must be transformed:

$$g(t) = L^{-1}\left\{ \frac{k}{T^2 p^2 + 2\xi T p + 1} \right\} = \frac{k}{\beta T^2} \cdot e^{-\alpha t} \sin\beta t \,. \tag{5}$$

In the case of studying samples with complex multiplet spectra, in the model of the NQR subsystem, the image of the response signal will be represented as:

$$Y(p) = Y_1(p) + Y_2(p) + \ldots + Y_n(p) \tag{6}$$

then the transmitting characteristic will describe the NQR subsystem of the spectrometer in the form of n oscillating links connected in parallel:

$$W(p) = \sum_{i=1}^{n} H_i(p) = \frac{Y_1(p) + Y_2(p) + \ldots + Y_n(p)}{X(p)} \,. \tag{7}$$

The simulation model of the NQR subsystem of the pulsed spectrometer corresponding to this mathematical model is depicted in Fig. 3. This figure depicts the *s*-model of the NQR subsystem of radio spectrometer in which the “Transfer Fcn0” unit simulates the response of the *LC* oscillating circuit, and the "Transfer Fcn1 - Transfer Fcn12" units simulate the response of spin oscillating systems of the NQR multiplet spectrum (FID signal). The “Band-Limited White Noise” unit serves as a model of the source of noise signals.

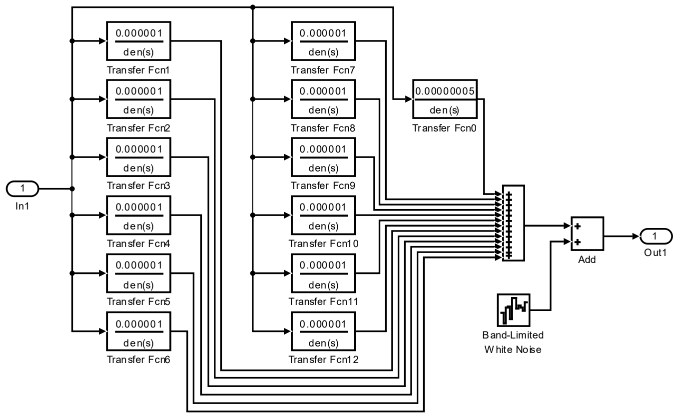


Fig. 3. The simulation model of the NQR subsystem of the pulsed spectrometer implemented in MATLAB Simulink software.

To verify the reliability of simulation results of signal transformations in a pulsed NQR-spectrometer, an indium selenide single crystal was chosen in which the complex broadband multiplet spectra of the NQR ^{115}In spectra are observed (Fig. 4 – Fig. 6) [12]. The simulation was carried out with the excitation of NQR by a probing pulse with duration of 10 μs and a power of 1000 W. The probing pulse frequency is set to 20 MHz.

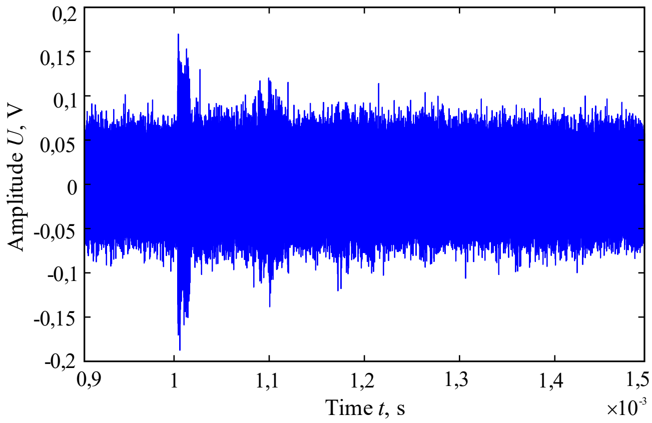


Fig. 4. The ^{115}In FID in *InSe* at the input of pulsed radio spectrometer.

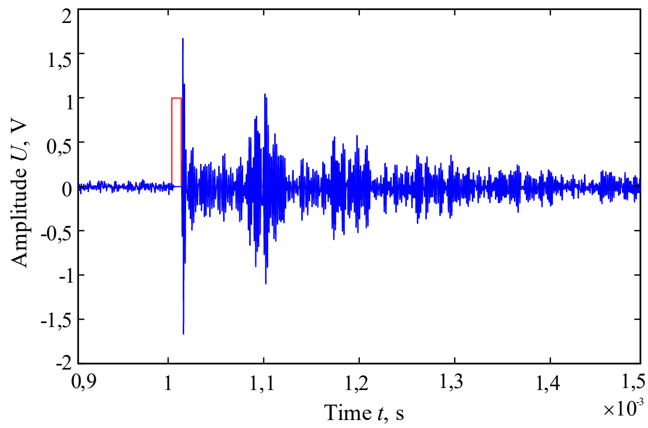


Fig. 5. FID after quadrature detection and filtration.

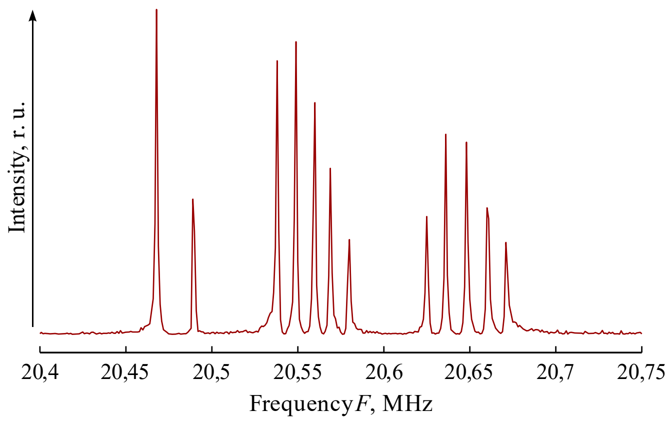


Fig. 6. NQR spectrum obtained with the use of fast Fourier transform of FID.

B. Input device of the NQR radio spectrometer

Let us consider the input block of the radio spectrometer shown on the Fig. 7. The input part of the spectrometer provides a feed for a time interval of 1 μs – 20 μs of a high-frequency radio pulse to the sample coil and the reception of the signal of the spin induction of quadrupole nuclei after the action of the pulse. The circuit is physically connected both with the pulse transmitter and the input part of the spectrometer. The intensity H_1 of RF field in the sample is expressed by the equation:

$$H_1 \approx 3\left(PQ/\nu_0 V\right)^{\frac{1}{2}} \approx 3{,}7\left(PT_r/V\right)^{\frac{1}{2}}, \qquad (8)$$

where P is transmitter power in watts, ν_0 is resonance frequency in MHz, V is coil volume in cubic centimeters, T_r is time of rise or fall of the envelope of the RF pulse in microseconds.

To obtain a strong RF field, the volume of the coil must be minimized, and the quality factor should be as high as possible. It is desirable that the transmitting coil, during the action of the excitation pulse, has a high resistance and a low inductance. But at the beginning and end of the pulse, it would be better to have a small Q, since the rise and fall time is related to the Q by the ratio:

$$Q \approx 1{,}5\nu_0 T_r. \qquad (9)$$

The signal/noise ratio in the pulse experiment depends on a number of parameters:

$$S/N \approx \zeta\gamma I\left(I+1\right)C\left(QV\nu_0 T_2/\beta T_1\right)^{\frac{1}{2}}, \qquad (10)$$

where ζ is filling factor of the receiving coil, γ is gyromagnetic ratio of the resonating nucleus, I is spin quantum number of the nucleus, C is a constant, T_1 and T_2 is spin-lattice and spin-spin relaxation times, β is bandwidth of the receiver-detector system.

For optimization of the signal/noise ratio it is desirable to have a large sample volume and a high Q-factor of the circuit.

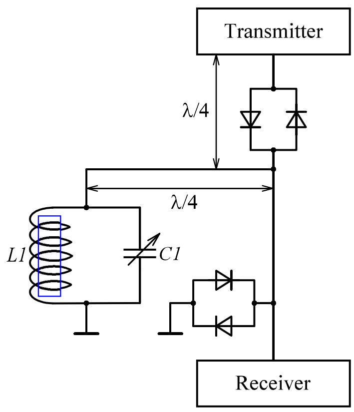


Fig. 7. NQR signal sensor

C. Pulse sequence shaper

Fig. 8 shows the proposed structural diagram of field-programmable gate array (FPGA), which is necessary for the development of pulse sequence shaper based on programmable frequency synthesizer [13]. The feature of the proposed method for forming a multi-pulse sequence is its implementation based on a multifunctional program-controlled digital frequency synthesizer with the possibility of high-speed frequency and phase modulations.

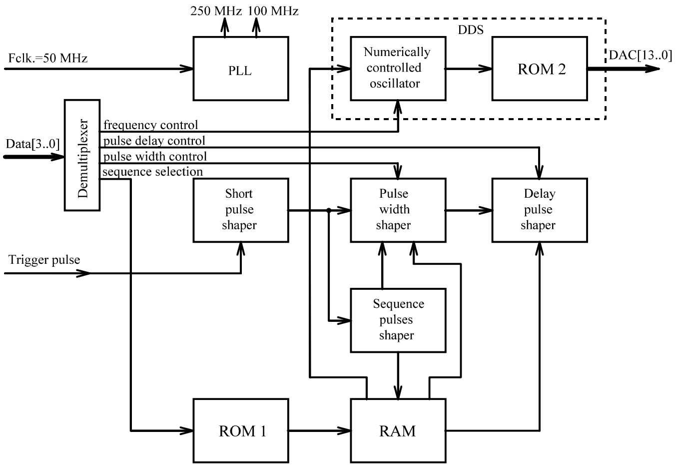


Fig. 8. Pulse sequence shaping diagram based on controlled synthesizer.

The basis for the proposed shaper is a 48-bit phase accumulator, which forms a sequence of codes of the instantaneous linearly-variable phase of the generated signal [13]. The values of the output signals of frequency synthesizer are recorded in the memory table – ROM2. The additional modules of the proposed structure serve to carry out phase manipulation of the carrier frequency of the original signal.

The sequence formation begins synchronously with the input sampling pulse at the "Trigger pulse" input. The value of carrier wave frequency, the 90º pulse duration, the duration of pause between the pulses, and the type of the sequence data come from the spectrometer control unit via the control bus. The 90º pulse duration is set in the range of 0.1 – 20 μs in increments of 0.1 μs. The interval between pulses is adjustable in the range of 0.1 μs – 1 s. Other time lengths, for example in the Carr-Purcell sequence, the length of 180º pulses and the intervals between them are set automatically, according to the selected program recorded in the ROM1 module. The number of pulses in the series is set within 1 – 30.

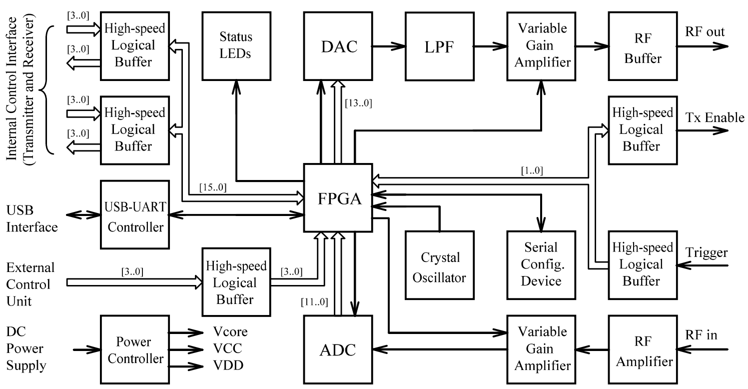
D. digital computational core

For the hardware implementation of the digital computational core of the pulsed NQR spectrometer, a motherboard (Fig. 9,a) was developed containing digital-to-analog and analog-to-digital converters, low frequency filters, matching and buffer amplifiers, configuration and power circuits, and other functional elements (see Fig. 9,b). The basis of the proposed development is FPGA EP4CE15E22C8. In the non-volatile memory of FPGA there are algorithms for the formation of thirty different types of pulse sequences, the application of which provides the implementation of a number of radio spectroscopic and relaxation techniques in NQR. The operation of the developed device was studied in single- and many-pulse modes.

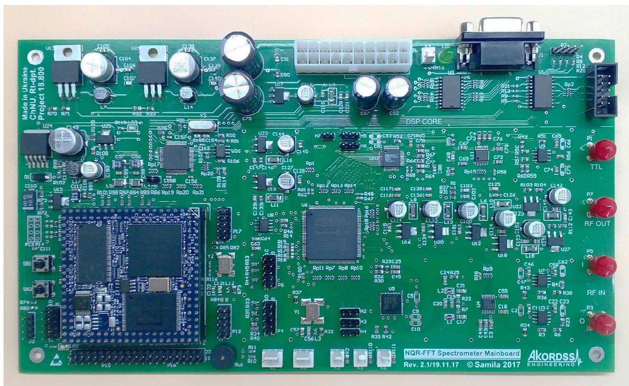
The radio spectrometer receiver was developed with Software Defined Radio technology using the Digital Down-Converter principle.

The task of visualization and processing of radiophysical experiment data was solved by creating software based on the National Instruments LabVIEW computer-aided design system [14]. The information transmitted by the FID signal can be accumulated. The presence of noise in the path of the spectrometer leads to a measurement error, which can be reduced by averaging a periodically repeating signal. Such a procedure is optimal for the maximum likelihood criterion in the event that a useful signal is received against the background of additive noise with a normal distribution. Time averaging can be done by the algorithms of the usual linear or normalized summation with a gradual output of results. The linear averaging algorithm has a significant disadvantage due to the presence of a constant component in the noise spectrum and the continuous movement of the baseline upward in intensity along with the useful signal.

The FID signal is digitized with a sampling frequency of 15 MHz, so the interval between N samples is about 6.67×10^{-8} s. At a constant sampling rate, the frequency interval Δf for 65536 points is 229 Hz and increases to 0.9 kHz with a decrease in the number of points to 16384 (the case of recording multiplet broadband NQR spectra, the duration of the FID is about 650 μs) [14].



a)



b)

Fig. 9. Block diagram (a) and the photo (b) of the NQR spectrometer motherboard.

IV. Comparison of NQR techniques

Based on the comparison of the resonant NQR spectra obtained by stationary and pulsed methods, conclusions were drawn about the expediency of the latter in the study of materials, the resonance spectra of which are complex and occupy a wide frequency range.

From the comparison of scaled-up fragments of the ^{14}N lines obtained by pulsed and continuous NQR methods (Fig. 10,a,b), it follows that there is line splitting (Fig. 10,a) due to the presence of non-equivalent groups of nitrogen in the hexamethylenetetramine $C_6H_{12}N_4$ molecule. Note that the registration time of the line obtained by the pulsed method was less than 1 min. To achieve the same signal/noise ratio when registering a line by continuous propagation, the registration time exceeded 10 minutes.

Thus, as compared to the continuous scanning method, pulsed Fourier spectroscopy offers the advantages of higher sensitivity, increased spectral resolution, much less distortion of the line shapes, a significant reduction of observation time, as well as the ability to quickly and accurately measure relaxation times.

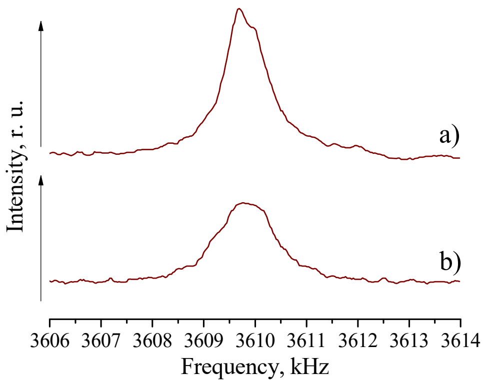


Fig. 10. NQR lines ^{14}N in the spectra $C_6H_{12}N_4$: obtained by pulse method (a), obtained by a continuous wave method with Zeeman modulation (b).

V. Conclusions

The principles of structural and functional synthesis of the radioelectronic means of a pulsed NQR are presented. The feature of the proposed measuring setup is the implementation of all algorithms for digital processing and signal synthesis in the basis of one statically-configured field-programmable gate array EP4CE15E22C8. The proposed means are distinguished by the minimum number of functional units while maintaining the sensitivity required for registration of the NQR spin induction signals. The digital 48-bit frequency synthesizer provides the formation of carrier frequency oscillations, which serve to fill the excitation pulses in the range of NQR frequencies 1 – 50 MHz. The radio spectrometer receiver was developed with Software Defined Radio technology using the Digital Down-Converter principle. The free induction decay signal after amplification in a pre-gated amplifier is fed to an analog-to-digital converter, and then to a digital quadrature detector. The high-frequency power amplifier develops an excitation pulse power in the receiving coil of about 1 kW. The NQR spectrum is reconstructed from the spin induction signal using the fast Fourier transform method.

The device was studied both in single-pulse mode and multi-pulse mode. The range of operating frequencies of the elaborated device was selected as 1 – 50 MHz, restricted to NQR frequencies of scientifically relevant isotope cores ^{14}N, ^{35}Cl, ^{63}Cu, ^{69}Ga, ^{71}Ga, ^{113}In, ^{115}In, etc.

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References

[1] V.S. Grechishkin, Yadernye kvadrupolnye vzaimodeystviya v tverdyh telah [Nuclear quadrupole interactions in solids]. Moscow: Nauka, 1973.

[2] O.Z. Hotra, A.P. Samila, H.M. Rozorinov, O.V. Hres, "Current status and development prospects of nuclear quadrupole resonance pulsed spectroscopy methods: A review," Telecommunications and Radio Engineering, vol. 78, pp. 1483-1496, 2019.

[3] V.P. Anferov, V.S. Grechiskin, N.Ya. Siniavsky Nuclear spin resonance. New methods. Leningrad: State University Publ., 1990.

[4] V.S. Grechishkin, N.Ya. Siniavsky, "Localnyi YKR v tverdykh telakh [Local NQR in solids]," Uspekhi Fizicheskikh Nauk - Physics Uspekhi, vol. 163(10), pp. 95-119, 1993.

[5] J.A.S. Smith , "Nitrogen-14 quadrupole resonance detection of RDX and HMX based explosives," Proceedings of European Convention on Security and Detection, pp. 288-292, 1995.

[6] V.S. Grechiskin, N.Ya. Siniavsky, "Novyie fizicheskiie tekhnologii: obnaruzheniie vzryvchatykh i narkoticheskikh veshchestv metodom yadernogo kvadrupolnogo resonansa [New physical technologies: detection of explosive and narcotic substances by nuclear quadrupole resonance method]," Uspekhi Fizicheskikh Nauk - Physics Uspekhi, vol. 167(4), pp. 413-427, 1997.

[7] T. Apih, B. Rameev, G. Mozzhukhin, J. Barras. Magnetic resonance detection of explosives and illicit materials, NATO Science for Peace and Security Series B: Physics and Biophysics. Springer, 2014.

[8] P.V. Vilkov, Yu.A. Pentin, Fizicheskiie metody issledovaniia v khimii. Resonansnyie i elektroopticheskiie metody [Physical research methods in chemistry]. Moscow: Vysshaya shkola, 1989.

[9] J.C. Harding, D.A. Wade, R.A. Marino, E.G. Sauer, S.M. Klainer, "A pulsed NQR-FFT spectrometer for nitrogen-14," Journal of Magnetic Resonance, vol. 36, pp. 21-33, 1979.

[10] P.M. Borodin (Ed.), Yadernyi magnitnyi resonans [Nuclear magnetic resonance]. Leningrad: Leningrad State University Publ., 1982.

[11] A. Samila, V. Khandozhko, L. Politansky, "Energy efficiency increase of NQR spectrometer transmitter at pulse resonance excitation with noise signals," Solid State Nucl. Magn. Reson., vol. 87, pp. 10-17, 2017.

[12] A. Samila, "Peculiarities of using s-simulation for parametric identification of multiplet 115In NQR spectra in InSe," Measurement, vol. 106, pp. 109-115, 2017.

[13] Yu. Bobalo, Z. Hotra, O. Hotra, L. Politans'kyy, A. Samila, "Pulse sequence shaper for radiospectroscopy and relaxation methods in NQR," Metrol. Meas. Syst., vol. 22, pp. 363-370, 2015.

[14] A. Samila, O. Hres, G. Rozorynov, "Hardware and software implementation of data acquisition system for pulsed NQR spectrometer," 14th International Conference on Advanced Trends in Radioelecrtronics, Telecommunications and Computer Engineering (TCSET), pp. 1166-1169, 2018.