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Development of a small-sized NMR relaxometer for express monitoring of the state of the liquid medium

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Abstract. The necessity of developing devices for express monitoring of the state of the liquid medium at the sampling site is substantiated. The criteria for express control methods are substantiated. A design of a small-sized NMR relaxometer for express monitoring of the state of the medium has been developed. Experimental data are presented. The results obtained on the proposed small-sized NMR relaxometer were compared with the values obtained on an industrial NMR relaxometer.

Keywords: express control, NMR, nuclear magnetic resonance, instrumentation, relaxometer, NMR relaxometer, measuring equipment

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Материалы конференции
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Разработка малогабаритного ЯМР-релаксометра для экспресс-контроля состояния жидкой среды

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Аннотация. Обоснована необходимость разработки приборов экспресс-контроля состояния жидкой среды на месте забора пробы. Обоснованы критерии, предъявляемые к методам экспресс-контроля. Разработана принципиальная схема малогабаритного ЯМР-релаксометра для экспресс-контроля состояния среды. Приведены экспериментальные данные. Полученные результаты на предложенном малогабаритном ЯМР-релаксометре были сравнены со значениями, получаемыми на промышленном ЯМР-релаксометре.

Ключевые слова: экспресс-контроль, ЯМР, ядерно-магнитный резонанс, приборостроение, релаксометр, ЯМР-релаксометр, измерительная техника

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Introduction

Currently, there are many tasks in industrial production, in ecology, in physical and chemical experiments to control the state of the environment under study [1–8]. In some cases, the possibility of express monitoring of the state of the environment at the required time in difficult conditions is of particular importance [3, 6, 8, 9–11]. In most cases, the task of express control is only to establish whether there is a deviation from the standard state of the environment.

Therefore, increased requirements are imposed on the methods of measuring physical parameters during express control. It is necessary that the changes carried out do not make irreversible changes to the composition and structure of the environment under study [6, 8, 12–14]. This makes it possible, when detecting deviations from the standard state, to carry out further studies of the environment in stationary laboratories. Studies of various media using the phenomenon of nuclear magnetic resonance do not make irreversible changes to the medium, which allows this sample to be used for research on other devices [3, 6, 8, 14–18].

Modulation measurement technique and block diagram of NMR relaxometer

It is very difficult to register the NMR signal spectrum in a weak magnetic field [3, 6, 8, 18–20]. This problem can be solved by using a modulation technique to register the NMR signal. Monitoring of the state of the liquid medium is carried out by measuring the longitudinal T1 and T2 transverse relaxation times. According to the deviation of T_1 and T_2 from the standard, the presence of impurities in the medium is determined.

In the device developed by us, the NMR signal is obtained at the resonant frequency of protons. The Bloch equations are used in this case to describe the process of obtaining a signal at a resonant frequency. Figure 1 shows the developed design of the device.

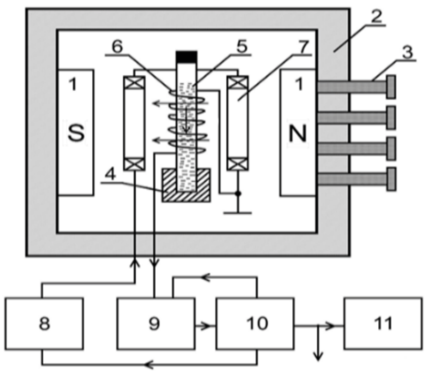

Fig. 1. Design of the NMR relaxometer: 1 – magnet, 2 – neutral for placing and centering magnets, 3 – adjusting screws, 4 – fixing device for the container with the test medium, 5 – container with the investigated medium, 6 – NMR signal registration coil, 7 – modulation coils, 8 – radio frequency generator, 9 – autodyne detector, 10 -processing and control device, 11 - oscilloscope

In the NMR signal registration coil of the relaxometer, the recorded signal from the medium under study is formed when the longitudinal and transverse components of the magnetization vector move, which are described by the Bloch equations [20–22]:

The results of the experiments performed show that in a small-sized NMR relaxometer, for any values of magnetic fields and modulation frequency f_m that satisfy the registration of an NMR signal in a weak field, it is impossible to ensure the fulfillment of the conditions for fast adiabatic passage through resonance [21, 22]. Therefore, to describe the line shape of the NMR resonance signal, taking into account the results of previous experiments and the identified features when using the modulation technique in a weak magnetic field [3, 6, 12, 20], it is proposed to introduce new coefficients into the Bloch equations. When using the modulation technique for recording the NMR signal, the magnetic field in the system of Bloch equations must be taken into account in accordance with the following relationship:

$$H = H_0 + H_m \sin(\omega_m t), \tag{1}$$

where H_0 is constant magnetic field, H_m is field created by the modulation coil, ω_m is modulation frequency.

One of the features of NMR signal registration in a weak magnetic field using the modulation technique is that it should be performed only at the resonance frequency ($\omega_{nmr} = \omega_0 = \gamma\, H_0$).

For most of the studied media, in the case of a detuning of the NMR signal detection frequency ω_{nmr} from the resonance frequency ω_0, the signal-to-noise ratio (SNR) can become less than 1.3 [3, 6, 11, 20-22]. At such a value of SNR, the operation of the NMR signal accumulation circuit in small-sized NMR relaxometers becomes inefficient [3, 6, 11, 20]. This does not allow performing various measurements with an error of no more than 1.5%. Considering this circumstance, frequency detuning is transformed into the following function:

$$\Delta\omega = \gamma H_m \sin(\omega_m t). \tag{2}$$

Relationship (2) is the new coefficient for the system of the Bloch equations. Another new coefficient, which is introduced in the Bloch equations, relates to the need to take into account the modulation of the weak magnetic field H_0 in the magnetization of the investigated medium M. The new relation for M, which is substituted into Bloch equations, must be written in the following form:

$$M = \chi_0(H_0 + H_m \sin(\omega_m t)). \tag{3}$$

After substituting new coefficients (2) and (3) into the Bloch equations, they take the following form:

$$\begin{gathered}
\frac{du(t)}{dt} + \frac{u(t)}{T_2} + \gamma H_m \sin(\omega_m t)\upsilon(t) = 0, \\
\frac{d\upsilon(t)}{dt} + \frac{\upsilon(t)}{T_2} - \gamma H_m \sin(\omega_m t)u(t) + \gamma H_1 M_z(t) = 0, \\
\frac{dM_z(t)}{dt} + \frac{M_z(t)}{T_1} - \frac{M}{T_1} - \gamma H_1 \upsilon(t) = 0.
\end{gathered} \tag{4}$$

The system of equations (4) is solved with respect to the components $\nu(t)$, $u(t)$ and $M_z(t)$, taking into account the initial conditions $M_z(0) = \chi_0 H_0$, $\nu(0) = 0$, $u(0) = 0$.

A feature of NMR signal registration in a weak magnetic field using the modulation technique is the need to fulfill the relation [3, 6, 18, 20]:

$$\gamma H_m > 10\Delta f_{nmr} \tag{5}$$

where H_m is magnitude of modulation field, Δf_{nmr} is natural line bandwidth of the NMR signal spectrum.

In weak magnetic fields with a high degree of uniformity, the value of Δf_{nmr} is determined by the relation [21, 22]:

$$\Delta f_{nmr} = \frac{1}{T_2}. \tag{6}$$

In turn, to measure the transverse relaxation time T_2 in a small-sized NMR relaxometer by the decay of the envelope of the registered NMR signal with an error of less than 1.0 %, the modulation field period T_m is subjected to the condition [3, 6, 18, 20]:

$$T_m > 5T_2 \tag{7}$$

We have found that a decrease in the frequency of the modulation field $f_m = 1 / T_m$ to fulfill condition (7) leads to a deterioration in the SNR due to a decrease in the accumulation rate. This deterioration due to the requirement of small dimensions for the NMR relaxometer cannot be fully compensated by an increase in H_1 and H_m.

We found that in the case of applying the modulation technique in weak fields, in addition to fulfilling conditions (5) and (7), it is necessary to consider the complex nature of the dependence of the SNR on the amplitude of the modulation field H_m. It is necessary to set the amplitude of the modulation field to the maximum of the SNR.

To analytically determine the given value of the amplitude of the modulation field, it is necessary to obtain an analytical solution of the system (4).

Experimental results

In Figure 2 shows the registered NMR signal in a weak magnetic field of 60 mT using the modulation technique at the resonant frequency of lithium nuclei at a temperature T=295.4 K.

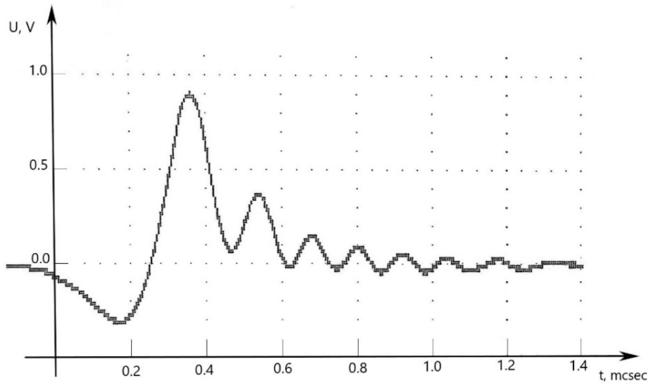

Fig. 2. Form of NMR signal obtained in a weak magnetic field of 60 mT using the modulation technique and accumulation when working with lithium nuclei.

The result obtained shows that the recorded NMR signal can be used to measure the relaxation times. For this medium T_1 = 24.872 ± 0.532 ms, T_2 = 0.160 ± 0.005 ms.

Table 1

Relaxation constant of liquid media

Medium	Small-sized NMR relaxometer		Industrial NMR relaxometer Minispec mq 20	
	T_1, s	T_2, ms	T_1, s	T_2, ms
Soviet Petrol standard A – 76	1.432 ± 0.007	146.05 ± 0.73	1.4266 ± 0.0029	145.35 ± 0.29
Soviet Petrol standard “Nefras C2-80/120”	1.333 ± 0.00	207.51 ± 1.04	1.3403 ± 0.0027	206.38 ± 0.42

Table 1 shows an example of the operation of a small-sized NMR relaxometer for express control of the state performed for the hydrocarbon medium. Table 1 presents the results of measurements of the longitudinal relaxation time T_1 and transverse relaxation time T_2 at a temperature of T = 291 K. In Table 1 also presents the results of measurements of the relaxation times of these media obtained using an industrial NMR relaxometer Minispec mq 20.

Analysis of the measurement results of T_1 and T_2 shows that they match within the measurement error. The measurement error of T_1 and T_2 using the device developed by us is less than 1.0%. This value of the measurement error satisfies the requirements for devices for express control.

Conclusion

The obtained results of studies of the state of various media and their comparison with the results of measurements obtained using instruments of higher accuracy confirm the possibility of using the developed small-sized NMR relaxometer for express control. Further improvement of the accuracy characteristics of a small-sized NMR relaxometer with a modulation technique for recording the NMR signal is planned to be carried out using new data that will be obtained after obtaining an analytical solution of the equations (4).

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