Compact nuclear magnetic spectrometer for non-destructive condition testing of biological objects

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Abstract. Paper discusses the express control technique based on the phenomenon of nuclear magnetic resonance (NMR). For a small-sized NMR spectrometer, a new magnetic system and a signal registration circuit have been developed, which makes it possible to detect the NMR signal at different frequencies from different nuclei in biological media, thus registering the spectrum of this media. In addition, this design also allows measuring the longitudinal and transverse relaxation times of the medium. With the help of the proposed technique, studies of a media have been carried out; the results of these studies are presented.

1. Introduction

Currently, nuclear magnetic resonance is one of the most accurate and reliable methods for various studies of condensed matter, as well as the measurement of various physical quantities (for example, magnetic field induction, etc. [1–9]). A large number of different models of NMR spectrometers and relaxometers have been developed to study the media. The greatest difficulties arise during the express control of the state of condensed media at sampling site. Such studies are most in demand to control the medium condition before carrying out different physical and chemical experiments (in particular after long their storage, container changing or transportation). Also this is suitable during ecological monitoring of difficult to access places of water objects and their coastal zones, during quality control of production, etc. [8–13].

Unlike other methods, studies using NMR do not cause changes in the physical structure and chemical composition of the condensed medium. The only condition for their implementation is the presence of nuclei with magnetic moment in the studied medium. Almost all existing environments have these nuclei, but signals from most of these nuclei can be registered only in strong homogenous magnetic fields with induction of more than 10 T. These fields can only be created in stationary superconducting solenoids that require a specialized cooling system. In accordance with the international standards for express control devices, their total weight with batteries should not exceed 10 kg. Therefore, we have developed small-sized designs of NMR-relaxometers [11, 13-16], in which the NMR signal was recorded in a weak magnetic field using a modulation technique. The signal was recorded at the resonance frequency of protons. To determine the state of the condensed medium, we used a technique based on measuring the time of longitudinal T₁ and transverse T₂ relaxation. The measured values T₁ and T₂ were compared with the standard values, and then the presence of impurities in the test medium was determined using the proposed mathematical model.

However, experience with the operation of a small-sized NMR relaxometer has shown that during environmental monitoring this may not be enough to make a decision at the measurement site for the further use of the investigated medium. The conducted experiments showed that the aqueous media, depending on the natural conditions, might contain chemical elements (for example, fluorine, potassium,
etc.) that are harmless in small quantities for living organisms. Their effect on the shape of the NMR signal is difficult to predict: these elements cause significant changes in $T_1$ and $T_2$. For this reason, after measuring $T_1$ and $T_2$, it may be concluded that the researched medium represents a potential hazard. Thus, it is possible to make wrong further decisions, which leads to additional spending on researching samples of this medium.

One of the solutions to this problem is to register the NMR signal on the nuclei of the elements mentioned earlier. Registration of NMR signal on fluorine nuclei is not very difficult (since fluorine has a sensitivity comparable in order of magnitude with protons and their resonant frequencies are close enough), but other nuclei have a lower sensitivity to NMR method than protons and a lower gyromagnetic ratio. In a compact magnetic system, it is extremely difficult to change magnetic field induction during media express control. Therefore, it became necessary to develop a small-size NMR spectrometer, in which the frequency of the NMR signal detection $f_{nmr}$ varies widely. This makes it possible to record the NMR signals at different resonant frequencies $f_{nmr}$ from nuclei mentioned above. The implementation of this device will solve the problems discussed above in most cases, which arise when investigating media with a compact NMR relaxometer in the express mode.

2. Design of a compact NMR spectrometer

Figure 1 shows the structural diagram of a compact NMR spectrometer with the new construction elements developed by us.

![Figure 1](image.png)

**Figure 1** Structural scheme of compact NMR spectrometer: 1 — permanent magnet; 2 — inserts; 3 — neutral for the placement and alignment of the magnets; 4 — adjusting screws; 5 — modulation coil; 6 — NMR signal registration coil; 7 — locking device for the container with the researched medium; 8 — container with the researched medium; 9 — magnetic field modulation generator; 10 — registration scheme including RF autodyne generator; 11 — processing and control unit; 12 — oscilloscope

The small-sized magnetic system was made of the material NdFeB in the form of a disk 1 with a large residual induction. This allowed at the diameter of the magnet 1 poles $d_m = 92 \text{ mm}$ and distance between them $d_1 = 16 \text{ mm}$ to provide in the area of the registration coil 6 the inhomogeneity $0.5 \cdot 10^{-3} \text{ cm}^{-1}$ at the induction equal to $B_0 = 0.132 \text{ T}$. The magnetic field modulation frequency can vary from 1 to 200 Hz. We have experimentally established that the optimal value is $f_m = 50$, since it provides a high value of the signal noise ratio and at the same time allows to investigate a large number of media [1]. The weight of the new developed magnetic system together with the coils of modulation 5 and registration 6, and the locking device of the container 7 appeared to be equal to about 3.2 kg.

To register NMR signals in weak magnetic field from nuclei with low sensitivity to the NMR method, a new scheme of a weak oscillation generator (an autodyne detector) was developed [1, 5, 8, 10]. This scheme is assembled on the basis of an amplifying cascade with drain detection of the NMR signal and its subsequent amplification using modern planar field-effect transistors. Such construction of the circuit allows to create a minimum level of oscillations in the receiver-transmission loop of the autodyne
detector, in which the sample with the investigated medium is placed, to obtain the greatest sensitivity (the ratio of the generation amplitude in the loop to the change in its Q) for NMR signal registering.

In the new design of the compact NMR spectrometer, the scheme of AFC on a resonance is based on the STM32 microcontroller (ARM Cortex M3, STM32F100RBT6B). In addition, on its basis, we have created an accumulation scheme and the new auto-tuning circuits to the maximum S/N ratio for the generation level of the autodyne detector (field $H_1$), the modulation frequency $f_m$ and amplitude $H_m$ of the $B_0$ field.

Figure 2 shows, as an example, the registered NMR signals (the change in the voltage $U_S$ at the output of the autodyne detector 10 from the time $t$) from the aqueous solution of sodium hydroxide NaOH at the resonance frequency of the sodium nuclei $f_{Na} = 1488591$ Hz.

![Figure 2](image)

**Figure 2** The registered NMR signal from sodium hydroxide at $T = 291.3$ K: a) without accumulation; b) output of accumulation scheme

In the earlier developed design of a compact NMR relaxometer [8, 11, 13, 14] researchment of this media was possible only by using the NMR signal from protons registered at the resonant frequency $f_p$. Analysis of the presented on figure 2 NMR signals shows that ratio S/N > 1.3 while registering signals on the sodium nuclei resonant frequency $f_{Na}$. This makes it possible to perform AFC $f_{nmr}$ on the resonance of sodium nuclei. However, measuring of the relaxation constants $T_1$ and $T_2$ with an error less than 1.0% (which allows us to uniquely determine the medium state [5–8, 10, 12]) impossible without using accumulation scheme since the ratio S/N < 3.0 (figure 2.a). In addition, there are noises at the peaks of the NMR signal. The subsequent accumulation of the NMR signal allows us to obtain a ratio S/N> 10.0 (figure 2.b), ensuring the measurement of $T_1$ and $T_2$ with the required accuracy.

Nevertheless, when investigating media for the presence of nuclei with low sensitivity to the NMR method, a situation may occur when the S/N of the detected signal is less than 1.3. In this case, the operation of the auto-tuning circuit will be impossible, and the signal cannot be registered. Therefore, in order to increase the S/N ratio in the new developed compact magnetic system, we proposed a new technical solution to the problem posed to increase the volume of researched medium $V_R$ and reduce the value of $\Delta B$. At the same time, an optimum between the values of $B_0$, $\Delta B$ and $V_R$ was achieved, which makes it possible to obtain S/N > 1.3 of the detected signal from different nuclei of the investigated medium with low sensitivity to the NMR method. In addition, this allows measuring the number of peaks (“wiggles”) in the NMR signal of at least 5 (figure 2.b). This makes it possible to measure $T_2$ with an error not greater than 1.0% [5, 8–10, 13]. Reduction in the degree of inhomogeneity of the magnetic field was achieved by placing inserts 2 (figure 1) at the poles of the magnets in the form of steps (shims) of soft magnetic material (ARMCO iron). The inserts that we have developed are disks with a diameter of 92 mm, a thickness of 8 mm. From the edge of the disc, along its diameter, two strips were made in the form of steps with a recess to the center (the width of each step is 3 mm and a height is 2 mm). As a result, inside of each of the inserts 2 (figure 1) was formed a free space along the axis of action of the field $B_0$ in the form of hollows (of cylindrical shape with a depth of 4 mm and a diameter of 80 mm),
where we have put carcasses with modulation coils. Therefore, to accommodate the manufactured inserts, the distance $d_z$ between the poles of the magnets 1 was increased by only 10 mm compared to the original ($d_z = 16$ mm), the new value $d_z = 26$ mm. In the newly developed design of the magnetic system, the possibility of mechanical alignment of the mutual arrangement of the magnet poles, previously used in [8, 11, 13, 14], was also retained.

In addition, in the developed new design of a compact NMR spectrometer we can measure amplitude change $U_S$ of the detected NMR signal by changing the frequency of NMR signal detection (autodyne detector 10) at a constant value of the magnetic field induction $B_0$. This allows us to register the absorption spectrum of the investigated medium using nuclei with magnetic moments. Figure 3–5 shows, as an example, the dependence of the amplitude $U_S$ of the detected NMR signal on the frequency $f_{nmr}$ at $B_0 = 0.132$ T and at temperature $T = 293.3$ K.

**Figure 3** The absorption spectrum of an aqueous solution of sodium hydroxide. Graph 1 corresponds to the detected NMR signal from sodium nuclei, graph 2 — from protons

**Figure 4** The absorption spectrum of sodium chloride. Graph 1 corresponds to the NMR absorption signal on chlorine nuclei, graph 2 — from sodium
Figure 5 The absorption spectrum of sodium chloride. Graph 1 corresponds to the NMR absorption signal on chlorine nuclei, graph 2 — from protons.

Using the dependence of $U_s$ on $f_{nmr}$ (absorption spectrum) obtained in figures 3–5 it is possible to determine which nuclei with magnetic moments are present in the investigated medium, their relative concentrations, acidity of the medium (pH), etc. Similar dependences are obtained in stationary high-resolution NMR spectrometers while studying various mediums.

3. Conclusion

The obtained experimental results have shown that the small-size NMR spectrometer developed by us makes it possible to carry out express control over the state of a much larger number of media than the previously considered instruments in \[8, 11, 13, 14\]. For the first time, the possibility of registering NMR signals in a weak field from a large number of nuclei with magnetic moments in the investigated medium (except for carbon, nitrogen and sulfur nuclei) was realized for a frequency tuning $f_{nmr}$ with its automatic tuning to resonance. This allows us to consider this device as a small-sized NMR spectrometer, since it differs from the NMR relaxometers considered in \[8, 11, 13, 16\].

In the future, our researches will be aimed at increasing the sensitivity of the autodyne detector circuit. This is necessary to solve the problem of registering the NMR signal from the nuclei of chemical elements that are not very sensitive to the NMR method (for example, calcium, etc.) but cause significant changes in medium’s $T_1$ and $T_2$ even at their small concentrations \[13, 15–19\].

References

[1] Davydov V V, Myazin N S and Velichko E N 2017 *Technical Physics Letters* **43** 607–610
[2] Davydov V V, Dudkin V I, Petrov A A and Myazin N S 2016 *Technical Physics Letters* **42** 692–696
[3] Davydov V V, Dudkin V I and Karseev A Y 2015 *Instruments and Experimental Techniques* **58** 787–793
[4] Neronov Yu I and Seregin N N 2012 *Journal of Experimental and Theoretical Physics* **115** 777-781
[5] Arkhipov V V 2012 *Instruments and Experimental Techniques* **55** 692–695
[6] Kashaev R S and Gazizov E G 2010 *Journal of Applied Spectroscopy* **77** 321–328
[7] Mussil V V, Plipenko V V, Lemeshevskaya E T and Keremzhanov K D 2011 *Instruments and Experimental Techniques* **54** 397–399
[8] Karseev A Yu, Cheremiskina A V, Davydov V V and Velichko E N 2014 J. of Physics: Conference Series 541(1) 012006
[9] Alexandrov A S, Archipov R V, Ivanov A A, Gnezdilov O I, Gafurov M R and Skirda V D 2014 Applied Magnetic Resonance 45 1275–1287
[10] Filippov A V, Artamonova M R, Rudakova M F, Gimatdinov R G and Skirda V D 2012 Magnetic Resonance in Chemistry 50 114–119
[11] Karseev A Yu, Vologdin V A and Davydov V V 2015 Journal of Physics: Conference Series 643(1) 012108
[12] Zaporozhets O V, Shkurtda V F, Peregu dov O N and Zaporozhets V K 2010 Instruments and Experimental Techniques 53 718–722
[13] Davydov V V, Velichko E N, Dudkin V I and Karseev A Yu 2015 Instruments and Experimental Techniques 58 234–238
[14] Davydov V V, Dudkin V I and Karseev A Yu 2014 Measurement Techniques 57 912
[15] Davydov V V and Myazin N S 2017 Measurement Techniques 60 183–189
[16] Myazin N S, Logunov S E, Davydov V V, Rud’ V Yu, Grebenikova N M and Yushkova V V 2017 Journal of Physics: Conference Series 929(1) 012064
[17] Grebenikova N M, Smirnov K J, Artemiev V V, Davydov V V and Kruzhalov S V 2018 Journal of Physics: Conference Series 1038(1) 012089
[18] Myazin N S, Davydov V V, Yushkova V V and Rud’ V Yu 2018 Journal of Physics: Conference Series 1038(1) 012088
[19] Davydov V V, Kruzhalov S V, Grebenikova N M and Smirnov K J 2018 Measurement Techniques 61 365–372