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To cite this article: N S Myazin et al 2018 J. Phys.: Conf. Ser. 1038 012088
On the possibility of recording absorption spectra in weak magnetic fields by the method of nuclear magnetic resonance

N S Myazin¹, V V Davydov¹,²,³, V V Yushkova², V Yu Rud*³

¹Higher School of applied physics and space technologies, Peter the Great Saint Petersburg Polytechnic University, Saint Petersburg 195251, Russia
²Department of photonics and communication lines, The Bonch-Bruevich Saint Petersburg State University of Telecommunications, Saint Petersburg 193232, Russia
³All-Russian Research Institute of Phytopathology, Moscow Region 143050, Russia
⁴Saint Petersburg University of Management Technologies and Economics, Saint Petersburg 190103, Russia

myazin.n@list.ru

Abstract. The new magnetic system construction and the registration circuit of the nuclear magnetic resonance signal in the weak magnetic field are considered. The new elaborated construction of the small nuclear magnetic spectrometer gives a possibility to register signals from different nuclei of investigated medium, having magnetic moment. That expands greatly the functional possibilities of the nuclear magnetic resonance in the investigation of media in the express-mode. The experiment investigation results for different media are represented.

1. Introduction

One of the urgent problems of applied physics today is the elaboration of high speed and reliable methods of express control of condensed media condition [1–5]. They are especially important for the medium condition control 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. [4–9]. A great number of devices using different physical phenomena are constructed for carrying out the medium investigation in the express mode [1–9].

Their technical characteristics analysis carried out by us, as well as analysis of data that we get while studying various media [4, 5, 7–10], showed that most of them can be used only for control of a small number of media or for the solution of narrow range of problems. For example, express analyzer “IT-1” for determination of the water percentage in engine or transformer oil and diesel fuel, the portable photometer pHotoFlex (for determination of the water condition and pH), the visible light portable spectrophotometer DR 190 manufactured by HACH-LANGE for the liquid media condition control with the turbidity not more than 10 FNU, etc.

Such devices are unsuitable for work in which it is proposed to study a wide range of substances with different physical characteristics (turbidity, viscosity), as well as containing various chemical elements (e.g. in environmental monitoring). Previous studies of condensed media using several models of these devices have confirmed this [3, 6, 10–12]. Therefore, as one of the solutions to this problem, it has been proposed to use the method of nuclear magnetic resonance to conduct studies of media in the express mode. In the proposed method, it was suggested to measure the relaxation constants $T_1$ and $T_2$ of the sample at the sampling site and, comparing them with the basic ones, corresponding to the standard state of the medium under study, instantly determine the degree of its deviation from the standard state [7, 9–12].
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.

In this situation, an important role will be played by a method that will allow us to determine the presence of the chemical elements considered above in the investigated medium. One of them can be nuclear magnetic resonance. The nuclei of these chemical elements (fluorine, potassium, etc.) have a magnetic moment, which makes it possible to record the NMR signal at their resonance frequencies in a magnetic field. 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 detect NMR signals at different resonant frequencies $f_{nmr}$ from nuclei with magnetic moments contained in the medium under study (like a spectrum in stationary high-resolution spectrometers). The implementation of this device in most cases will solve the problems discussed above, 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 Structural scheme of compact NMR spectrometer](image)

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 $d_m = 92$ mm and distance between them $d = 16$ mm to provide in the area of the registration coil 6 the inhomogeneity $0.5 \cdot 10^{-3}$ cm$^{-1}$ at the induction equal to $B_0 = 0.132$ T. The magnetic field modulation frequency can vary from 1 to 200 Hz. We have experimentally established that the optimal value is $f_{nm} = 50$, since it provides a high value of the signal noise ratio and at the same time allows to investigate a large number of media [12]. 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, 4, 6, 12]. 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, STM32F100RB76B). 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 H1), the modulation frequency fm and amplitude Hm of the B0 field.

Figure 2 shows, as an example, the registered NMR signals (the change in the voltage U8 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 fNa = 1488591 Hz.

![Figure 2](image_url)

*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 [4, 7, 9, 10] researchment of this media was possible only by using the NMR signal from protons registered at the resonant frequency fp. 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 fNa. This makes it possible to perform AFC fnmr on the resonance of sodium nuclei. However, measuring of the relaxation constants T1 and T2 with an error less than 1.0% (which allows us to uniquely determine the medium state [1–4, 6, 8]) 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 T1 and T2 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 VR and reduce the value of ΔB. At the same time, an optimum between the values of B0, ΔB and VR 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 at least 5 (figure 2.b). This makes it possible to measure T2 with an error not greater than 1.0% [1, 4–6, 9]. 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 [4, 7, 9, 10], was also retained.

In addition, in the developed 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 [4, 7, 9, 10].

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 [4, 7, 9].

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.

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