Features of formation of structure of a nuclear magnetic resonance signal in weak magnetic field

N S Myazin¹, V V Davydov¹ ²

¹Higher School of applied physics and space technologies, Peter the Great St. Petersburg Polytechnic University, Saint Petersburg 195251, Russia
²All-Russian Research Institute of Phytopathology, Moscow Region 143050, Russia
myazin.n@list.ru

Abstract. The peculiarities of formation of the line structure of the detected signal of nuclear magnetic resonance in a weak field with use of the modulation technique are considered in the article. Relations are established that are mandatory for the registration of signals in a small-sized nuclear magnetic spectrometer to perform measurements with an error of less than 1%. The results of experimental studies of various media are presented.

1. Introduction

Currently, one of the tasks of applied physics is the development of various methods for real-time monitoring of the state of the liquid medium, both in the current and in the stationary state [1–4]. One of the most promising solutions to this problem is the use of devices whose principle of operation is based on the phenomenon of nuclear magnetic resonance (NMR) [1, 3, 5–7]. Such devices are used to study the flow structure of the liquid medium at various parameters to improve mathematical models describing the distribution of velocities in the flow [2, 3, 8]. Basically, these studies are carried out on laminar flows of the liquid medium. Therefore, for these studies, various NMR tomographs are used, by which the tomogram of the flow in a certain section of the pipeline is recorded, the longitudinal T₁ and transverse T₂ relaxation times of the liquid are measured, by which its state can be monitored [8]. But in the case of, for example, changes in the rate of fluid flow over a large range (more than two orders of magnitude) and the transition of fluid flow from laminar to turbulent, there are great difficulties with the registration of the NMR signal, as well as with the measurement of fluid flow q due to diffusion processes, etc. This circumstance made it impractical to use NMR tomographs to measure the flow rate of the liquid medium with simultaneous control of its state.

Flowmeters-relaxometers are used to measure q of the liquid medium and to control its state by relaxation constants in cooling systems of various power plants, in the production of alkalis and acids, as well as biological solutions [9–11]. The latest development of KROHNE Company, magnetic resonance multiphase flowmeters to control the flow rate q and the state (using T₂ constant) of oil and petroleum products, is actively introduced into production. In this device, it is possible to register the NMR signal only using the modulation technique. Other methods for recording the NMR signal, as shown by the experimental studies, are rather difficult to realize on fast fluid flows.

The modulation technique has proven to be a reliable method of recording the signal in the NMR magnetometer with the flowing sample. On the basis of these devices for many years in the USSR was in operation the primary standard of magnetic induction [12, 13]. Currently, two standards of magnetic induction are in operation in Russia [14, 15].

In order to ensure the highest signal-to-noise ratio (S/N) of the recorded NMR signal from the flowing medium over a range of variation of q by more than two orders of magnitude using a modulation technique, the circuit of the autodyne detector is adjusted to the absorption signal υ(t). In this case, the
autodyne detector operates on the oscillation failure mode. This mode is regulated by the value of the magnetic field strength $H_1$ [9, 11]. The other parameters in the NMR signal recording scheme are set taking into account certain ratios between the frequency and the value of the modulation field, as well as between the time of transverse relaxation of the current fluid and the magnitude and heterogeneity of the magnetic field at the placement zone of the registration coil. These ratios are discussed in more detail in [11]. The execution of these ratios provides a maximum value of S/N.

In the case of detecting the NMR signal in a weak magnetic field of a small-size NMR spectrometer [7, 16-18] using the modulation technique for solving the problems of express control, a number of difficulties arise. One of them is related to the peculiarities of the structure formation of the detected NMR signal in a weak field. This problem has not been considered before, since in the flowing liquid the NMR signal (absorption $\nu(t)$) is recorded using a modulation technique in fields with an induction $B_0$ of more than 0.5 T. In a weak magnetic field ($B_0 \leq 0.15$ T), it is extremely difficult to measure, for example, the relaxation constants $T_1$ and $T_2$, with an error of less than 1% without taking into account this feature of NMR signal recording. This is mainly due to the fact that at a low signal-to-noise ratio ($S/N \leq 1.3$), the operation of the NMR signal accumulation circuit becomes inefficient [16, 18, 19]. One of the possible solutions to this problem is considered in our work.

2. The structure of the detected NMR signal in a weak field

For studies of various media, we used the previously developed design of a small-sized NMR spectrometer (figure 1). “Neutral” means design of soft magnetic materials to attenuate the lines of the scattered magnetic field outside the zone of the interpolar space.

![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 studied medium; 8 — container with the studied medium; 9 — magnetic field modulation generator; 10 — registration scheme including RF autodyne generator; 11 — processing and control unit; 12 — oscilloscope](image-url)

The description of this structure and the principle of its operation are discussed in detail in [16, 18]. The design of small-sized NMR spectrometer developed by us allows to register on the resonant frequency of protons the NMR signals (absorption $\nu(t)$ and dispersion $u(t)$). As mentioned earlier, the autodyne detector operates on the oscillation failure mode to record the absorption signal $\nu(t)$. This mode can be set by the changing value of the magnetic field strength $H_1$. The dispersion signal $u(t)$ is recorded by synchronous detection of the recorded NMR signal with the phase of the modulation signal (the modulation signal is the reference for the synchronous detector).
The figure 2 shows as an example these signals from water at a temperature $T = 290.1$ K.

![Graph 1](image1.png)  ![Graph 2](image2.png)

**Figure 2.** Shape of the line of recorded NMR signal from water: (a) — absorption signal; (b) — dispersion signal

The analysis of the obtained results showed that the shape of absorption and dispersion lines are similar in appearance. At the same time, these signals differ in peak amplitude. In addition, they are obtained at different values of the field $H_1$. The comparison of the obtained results with the classical theory of NMR confirms the possibility of such a difference between the signals $\upsilon (t)$ and $u(t)$. The figure 3 shows, as an example, the calculated shapes of absorption and dispersion signals for proton medium using the dependences for $\upsilon (t)$ and $u(t)$ obtained in [20, 21].

![Graph 3](image3.png)

**Figure 3.** Shape of the line of recorded NMR signal from water: (a) — absorption signal; (b) — dispersion signal. Graphs 1, 2 and 3 correspond to the values $a^{1/2}T_2^*$: 0; 1; 2.

The analysis of the dependencies presented in figure 3 shows that it is impossible to obtain the simultaneous passage of the lines of absorption and dispersion signals $\upsilon (t)$ and $u(t)$ through zero. This means that the relations proposed in [20, 21] for the description of the lines of the recorded NMR signal do not allow to reproduce the experimental NMR signal line, the damped oscillations of which pass through 0 (both for the absorption signal and the dispersion signal). The obtained result shows that the proposed relations more correctly reproduce the absorption signal, since for it the theoretical calculation is similar to the experimental result. Such similarity is not observed for the dispersion signal. Therefore, in high-resolution NMR spectrometers ($B_0 > 10$ T), the absorption signal is mainly used to study condensed media. The dispersion signal is used for special studies.

To solve the problems of express control of the state of liquid media using a small-size NMR spectrometer, the values of $T_1$ and $T_2$ are mainly determined. As an example, let us consider the determination of $T_2$ using the signals $\upsilon (t)$ and $u(t)$, recorded in the weak field (figure 2).
It was established earlier [5, 7, 9-11, 16] that the value of the effective transverse relaxation time $T_2^*$ can be measured from the decay of the peak envelope of the detected NMR signal. Then the value of $T_2$ is determined from the following ratio [20, 21]:

$$\frac{1}{T_2} = \frac{1}{T_2^*} + \frac{\gamma H}{\pi}$$

(1)

where $\Delta H$ is the inhomogeneity of the magnetic field in the zone of placement of the NMR signal registration coil.

The obtained results showed that the value of $T_2 = 0.809 \pm 0.008$ ms obtained from the water absorption signal coincides within the error of measurement with the value $T_2 = 0.814 \pm 0.003$ ms, obtained on the NMR relaxometer Minispec mq 20 (BRUKER company). The value of $T_2 = 0.682 \pm 0.006$ ms determined from the signal $u(t)$ differs from the value of the transverse relaxation time obtained with the use of $v(t)$ by 16.2%. This once again shows that in a weak magnetic field it is impossible to use the shape of the dispersion signal line to measure $T_2$, since the lines do not pass through zero simultaneously (this leads to a large measurement error of more than 15%).

Our various studies of liquid media in the express mode showed that the use of absorption signal $u(t)$ is not effective for measurements in most cases. In the small-sized design of the NMR spectrometer, the NMR signal is registered from a small volume of the researched medium, in which the proton concentration can be low. Therefore, when the autodyne detector operates on the oscillation failure mode (which is the necessary condition for recording $u(t)$), the S/N ratio will be less than 1.3. Such a low S/N ratio does not allow the use of an accumulation scheme, and therefore all measurements will be carried out with a high error. In addition, in some cases, in order to make a reliable decision on the further use of the studied medium, it is necessary to register the NMR signal from some nuclei, for example, fluorine, phosphorus, potassium, etc. [18]. The nuclei of these chemical elements have a lower sensitivity to the NMR method than protons. If $H_1$ is low, it is extremely difficult to obtain $S/N > 1.3$ for these nuclei.

Therefore, during the express control of the medium, the $H_1$ value is set to the maximum S/N in the registering coil 6 (figure 1). In this case, the autodyne detector, which is an integral device, registers the total signal from $v(t)$ and $u(t)$. It is impossible to determine experimentally the relative contribution of these signals in the registered NMR signal at the moment. This is one of the main features of the formation of the structure of the NMR signal line in a weak field.

The second feature of the formation of the NMR signal line structure is the choice of modulation frequency $f_m$. In contrast to the NMR flowmeters, where the time of passage of the liquid through the NMR signal registration coil is the important characteristic, in a small-sized design of the spectrometer this time can be considered infinitely large. Therefore, the modulation period $T_m$ of the magnetic field $B_0$ in a small-sized NMR spectrometer is selected so that the following relation is satisfied:

$$T_m > 5T_2$$

(2)

The experiments have shown that the velocity of passage through the resonance $v_r$ has a significant influence on the structure formation of the registered NMR signal using the modulation technique. The value of $v_r$ is determined by the frequency $f_m$ and modulation field amplitude $H_m$. Modulation field frequency $f_m$ is limited by the ratio (2). Therefore, the main parameter that controls $v_r$ is the value of $H_m$. As a result of the experiments, it was established that in order to form the structure of the NMR signal during the time of passage through the resonance, which is detected by an autodyne detector, the following relation must be fulfilled:

$$\gamma H_m > 10\Delta f_{n,mr}$$

(3)

$$\Delta f_{n,mr} = 1/T_2$$

(4)

where $\Delta f_{n,mr}$ is the natural width of the NMR signal line.
This is another feature of the structure formation of the detected NMR signal in a weak field. The fulfillment of these features made it possible to register NMR signals during the express control of the state of liquid media not only at the resonance frequency of the protons.

3. The results of experimental studies and their discussion

The experience of express control of the state of liquid media using a small-sized NMR spectrometer showed that the greatest difficulties arise in the study of water and its solutions. Since it is necessary not only to determine the presence of a deviation from the standard state, but also the degree of danger of this medium for living organisms.

In accordance with sanitary and epidemiological norms, water must contain various chemical elements (e.g. phosphorus, fluorine, magnesium) in certain concentrations. If water does not meet these standards, it means that it is potentially dangerous. In environmental monitoring, the degree of environmental danger for living organisms is determined in a stationary laboratory using a biological test: bacteria are placed in the aqueous environment. The life time of these bacteria determine the degree of danger of the environment. In the conditions of express control, it is impossible to carry out these tests. However, since different impurities change the water relaxation times, it is theoretically possible to establish the presence of impurities by recording the NMR signal from the water and measuring the relaxation times.

Therefore, as an example, figure 4 shows the registered NMR signal from the aqueous solution of potassium nitrate at the resonant frequency of the potassium nuclei $f_k$.

![Figure 4. Shape of the line of recorded NMR signal from the aqueous solution of potassium nitrate at T = 293.3 K](image)

The shape of the registered NMR signal line allows determining the relaxation times $T_1$ and $T_2$. But experiments have shown that this information is not enough to make an informed decision about the degree of danger of the investigated medium. In some cases, the combination of different chemical elements in concentrations exceeding the norm in the aqueous medium creates relaxation times close to the standard state of water when there are no deviations from the norm. This environment is a potential danger for living organisms, but it seems safe according to the studied relaxation constants. A possible solution to this problem is to register the spectrum of the medium from nuclei that have magnetic moments and are contained in it [18].

The figure 5 shows, as an example, the registered spectrum of an aqueous solution of potassium nitrate (saltpeter) at $T = 293.4$ K.
Figure 5. Dependence of the amplitude of the NMR signal $U_s$ recorded from the aqueous solution of potassium nitrate on the frequency change of the autodyne detector $f_a$. Graph 1 corresponds to the detected NMR signal from potassium nuclei, graph 2 — from protons.

Calculations taking into account the different amplification factors of the recorded signal and the different sensitivity of potassium and proton nuclei to the NMR method show that the potassium content in saltpeter is $44.8\pm0.5\%$. These results are the same as the data declared by the manufacturer of saltpeter. This shows the possibility of using the proposed method to determine the concentrations of various substances with a generally accepted measurement error of less than 1%.

The analysis of the obtained results showed that the use of the recorded spectrum allows determining the relative concentrations of chemical elements from the nuclei of which these signals are recorded. This allows, in some cases, to determine the degree of danger of the medium under study during the express control of its state.

4. Conclusion
The experiments have shown that taking into account the peculiarities of formation of the NMR signal line structure established by us in the express control of the medium state makes it possible to exclude a significant part of the errors that have arisen, both in its research and in making decisions on further actions. In addition, in some cases, the obtained results allow to eliminate the revealed deviations in the studied environment at the place of sampling and to use it immediately for direct purpose, for example, chemical fertilizers in agriculture, etc. This is possible due to registration of the spectrum in a weak magnetic field.

5. References
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