On the need to control the state of the flowing media by the values of relaxation constants

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Abstract. The article substantiates the necessity of measuring the longitudinal $T_1$ and transverse $T_2$ relaxation times of the flowing media to control its state. For such measurements, a new method for measuring $T_1$ in a flowing fluid is proposed. Therefore, the results of experimental studies are presented. In addition, measured values of relaxation constants were compared to the data obtained on industrial devices was performed. The results of this comparison are also presented.

1. Introduction
Currently, the phenomenon of nuclear magnetic resonance (NMR) has many different applications. This includes scientific researches (determination of the composition or molecular structure of the media, etc.) and for monitoring the condition of condensed media in production, services, etc. [1–7]. Industrial devices, the principle of which is based on the phenomenon of nuclear magnetic resonance, are among the most accurate and reliable measuring devices [6–10]. They have several undeniable advantages over other devices. Their measurements do not cause irreversible changes in the physical structure and chemical composition of the medium under study [8–13], unlike optical, ultrasonic and other devices [14–20]. This makes it possible to use devices based on the NMR method in biology, medicine, etc.

The most difficult studies are studies of condensed media flow, especially turbulent flow [21–23]. When conducting various experiments with the use of such flow, in most cases it is necessary to control not only the flow of the medium, but also its state. The state of the flowing liquid medium also needs to be known in order to ensure the efficient functioning of various physical processes. This may be, for example, the heat exchange between the media in the different circuits of the nuclear reactor in power plants [24–26] or change of technological process of fuel combustion for higher heat output. One of the possible solutions to the problem of effective and reliable control of the flowing media is considered in this paper.

2. Peculiarities of flowing media state control by NMR
In practical applications of nuclear magnetic resonance (NMR), many methods have been developed for measuring the times of longitudinal $T_1$ and transverse $T_2$ relaxation of condensed media. It is assumed that these media are in a stationary state. The results of the measurements mentioned earlier are successfully used for express control of the state of media in solving various problems [3, 11, 12, 27-29]. This is because relaxation times $T_1$ and $T_2$ may change due to various reasons. These reasons include...
any changes in the molecular structure of the medium (ingress of impurities into it, a concentration change of the components, etc.), as well as a change in medium temperature. Knowing the values of $T_1$ and $T_2$ corresponding to the standard state of the medium, you can monitor its state at the place of sampling in real time [3, 11, 12, 27–32]. In most cases, when conducting research using a flowing liquid medium, it is necessary not only to monitor its state, but also to measure its flow rate $q$. The same applies to the control of technological processes in the production required to monitor its state. Many different NMR flowmeter models have now been developed [1, 2, 6, 21–26, 30–33]. A number of these devices are designed to measure the transversal relaxation time $T_2$. The results of the studies have shown that there are many cases, especially for liquid media mixtures, when the measurement of $T_2$ time alone is not enough to determine the state of the medium [2, 11, 12, 23, 27, 28]. Both relaxation constants must be measured for reliable and efficient monitoring of the flowing media. The same problem is relevant for express control of condensed medium by NMR [3, 4, 11–13].

There are many different impulse methods used to measure the values of $T_1$ and $T_2$ of a condensed medium in a stationary state. However, the results of our experiments have shown that it is extremely difficult to use these methods to measure the relaxation constants of the flowing medium. This is because the residence time of the liquid in the registration coil of the NMR flowmeter-relaxometer must be greater than the total time of a single measurement. This time consists of the durations of the pulses acting on the magnetized current fluid, as well as the duration of the intervals between them and the time of the registration of the free precession signal (its processing allows us to determine the relaxation constants). Considering that the possible range of changes in the values of $q$ and relaxation constants can be at least two orders of magnitude, the need to develop new methods for measuring $T_1$ and $T_2$ for NMR flowmeter-relaxometer is evident.

Figure 1 shows the scheme of the experimental setup developed by us for conducting research of flowing media by NMR method.

**Figure 1.** Structural scheme of experimental setup. 1 — magnet-polarizer; 2 — vessel-polarizer; 3 — nutation coil; 4 — modulation coils; 5, 6 — nutation and modulation coils generators; 7 — vessel-analyzer; 8 — magnet-analyzer field modulation coils; 9 — magnet-analyzer; 10 — NMR signal registration coil; 11 — NMR signal registration circuit; 12 — control and processing unit; 13 — electronic keys; 14 — RF generator; 15 — indication circuit; 16 — magnetic shield.
In contrast to the setup for the study of the stationery liquid medium, in this experimental setup the spatial separation of the zone of flowing liquid magnetization (magnet-polarizer 1) and the zone of NMR signal registration (magnet-analyzer 9) is performed. To measure the flow rate $q$ of a liquid medium, the effect of rotation of the magnetization vector [22, 23, 30, 34, 35] in the nutation coil 3 is used. Full inversion of magnetization (i.e. rotation of the magnetization vector by the angle $\varphi_n = 180^\circ$) occurs at the resonant frequency $f_n$ of the $\mathrm{H}_1$ field. To measure $q$, signals with and without magnetization inversion are used. Figure 2 shows, as an example, the registered NMR signals from feed water at $T = 299.3$ K, $f_m = 50$ Hz.

![Figure 2(a, b)](image)

**Figure 2(a, b).** NMR signal line shape for feed water (a) without magnetization inversion; (b) with magnetization inversion at $f_n = 1788204$ Hz, $H_1 = 15.2$ A/m.

Figure 2.a corresponds to $\varphi_n = 0$, while figure 2.b corresponds to $\varphi_n = 180^\circ$ (the NMR signal with the magnetization inversion). In case $\varphi_n = 90^\circ$; $270^\circ$ the magnetization vector components are equal to $M_z = M_x = M_y = 0$, so the NMR signal amplitude in the registration device is equal to zero. The obtained NMR signals have a high signal-to-noise ratio, which allows them to be used to measure relaxation constants (both the signal with and without magnetization inversion). The use of two signals to measure relaxation constants makes it possible to increase the accuracy of measurements compared to methods that use only one NMR signal (without inversion of magnetization).

It should be noted that due to the peculiarities of using NMR flowmeters-relaxometers, the registration of NMR signals in a wide range of liquid flow rates is possible only with the use of modulation technique. When using it, it is necessary to take into account the time $t_r$ when the flowing liquid is in the registration coil 10, as well as the modulation period (modulation frequency $f_m$) of the magnetic field $B_a$. The results of our studies allowed us to establish that in order to provide the maximum signal-to-noise ratio (S/N) and to obtain the recorded NMR signal in the form of "wiggles" (figure 2) the following ratio should be performed:

$$t_r > 2/f_m,$$

(1)

If ratio (1) is not met, the S/N ratio is reduced, and the shape of the recorded NMR signal is distorted. In several cases it creates insurmountable problems when measuring relaxation constants of the flowing medium.

3. Results of experimental studies and their discussion

The results of our research showed that the developed design of the experimental setup allows to register NMR signals from different nuclei of the flowing medium. This is a prerequisite for the use of NMR methods in various experiments with flowing media. Figure 3 shows, as an example, the registered NMR signals from the flowing aqueous solution of sodium hydroxide NaOH.
The registration was performed at resonance frequencies of protons $f_p = 19287097$ Hz (figure 3.a) and sodium nuclei $f_{Na} = 5108578$ Hz (figure 3.b) at optimal flow rate $q = 0.01 \text{ m}^3/\text{s}$, temperature $T = 292.4 \text{ K}$, and modulation frequency $f_m = 50 \text{ Hz}$. Fluid velocity in the connecting section of the pipeline is equal to $v = 3.538 \text{ m/s}$.

In the previously developed design of the NMR flowmeter-relaxometer [21-26, 31] the measurement of sodium hydroxide flow rate $q$ was possible only with the use of the NMR signal recorded at the resonant frequency of protons $f_p$. The analysis of the NMR signals presented in figure 3 shows that when registering the NMR signal at the resonant frequency of sodium nuclei $f_{Na}$, the ratio $S/N$ more than 100 without using the NMR signal accumulation scheme.

When using measuring devices, which have a structural scheme and the principle of NMR signal registration like the one we are considering, there are several difficulties in developing new methods for determining $T_1$ and $T_2$. This is especially true for measuring $T_1$. This is because NMR flowmeters-relaxometers use a modulation technique to register the NMR signal. The NMR waveform represents damped oscillations (figure 4), also known as “wiggles”. Figure 4.b shows the envelope of the NMR signal waveform, drawn by peaks of “wiggles”.

The shape of the recorded NMR signal at a single pass through the resonance can be approximated by the following dependence:

$$u(t) = U_0 \exp \left(-\frac{t}{T_2^*}\right) F(t),$$

Figure 3(a, b). NMR signal line shape for aqueous solution of sodium hydroxide. (a) signal at protons resonance frequency $f_p$; (b) signal at sodium resonance frequency $f_{Na}$.

Figure 4(a, b). NMR signal waveform. (a) corresponds to tap water at temperature $T = 276.3 \text{ K}$; (b) corresponds to tap water at temperature $T = 279.9 \text{ K}$.
where $F(t)$ is the function describing the harmonic nature of the recorded signal, $T_2^*$ is the effective time of transverse relaxation, $U_0$ is the maximum value of the amplitude of the recorded NMR signal.

Using the ratio (2), the effective transverse relaxation time $T_2^*$ is determined by the envelope decline. Relaxation time $T_2$ can be found from the $T_2^*$ time, using the value of the magnetic field heterogeneity in the placement zone of the registration coil.

Using Bloch’s phenomenological equations and theoretical postulates of the Julotto method for stationary condensed media, we studied the processes occurring in the experimental setup (figure 1). The results of these studies allowed to obtain the ratio for the change of magnetization $M$ in the flowing liquid in the registration coil 10 (figure 1). The recorded amplitude value of the NMR signal $U_0$ is proportional to the value of magnetization $M$, the change of which is determined by the following relationship:

$$M = M_0 \left(1 - \frac{1 - \exp\left(-\frac{\tau}{T_1}\right)}{1 + \exp\left(-\frac{\tau}{T_1}\right)}\right)$$

(3)

where $M_0$ is the magnetization of the liquid medium in the absence of modulation of the magnetic field.

It follows from (3) that to measure $T_1$, it is necessary to measure the amplitude of the NMR signal at two different modulation frequencies (i.e., for two different $\tau$), and then calculate the value $T_1$. Modulation frequencies must correspond to the ratio (1). It should be added that in order to obtain a reliable result and estimate the error in accordance with standard methods, it is desirable to carry out measurements at least 10 times.

For tap water at $T = 276.3$ K the measured values of relaxation times were $T_1 = 1.436 \pm 0.013$ s and $T_2 = 0.896 \pm 0.007$ s (measurements were made 10 times). A sample of this water was investigated at the same temperature on a stationary NMR relaxometer Minispec mq 20, the measured values were $T_1 = 1.4338 \pm 0.0028$ s and $T_2 = 0.8942 \pm 0.0028$ s. The obtained results of $T_1$ and $T_2$ values coincided within the limits of measurement error.

4. Conclusion
The experimental results obtained for the $T_1$ and $T_2$ values confirmed the possibility of monitoring the state of the flowing medium in real time by the proposed method in a wide range of flow rate $q$ changes. This significantly expands the possibilities of using NMR flowmeters-relaxometers both for scientific research and for industrial applications in power engineering, pharmacology, etc.

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References

[1] D’yachenko S V, Kondrashkova I S and Zhernovoi A I 2017 Technical Physics 62 1602–1604
[2] Kashaev R S and Gazizov E G 2010 Journal of Applied Spectroscopy 77 321–328
[3] Myazin N S, Neronov Yu I, Dudkin V I, Davydov V V and Yushkova V V 2018 MATEC Web of Conferences 245 11013
[4] Rykin E V, Moroz A V, Smirnov K J, Davydov V V and Yushkova V V 2018 MATEC Web of Conference 245 12002
[5] Davydov R V, Atonov V I and Moroz A V 2018 Proceedings of the 2018 IEEE International Conference on Electrical Engineering and Photonics, EExPolytech 2018 (Saint-Petersburg) 8564378 p. 236-239
[6] Marusina M Ya, Bazarov B A, Galaidin P A, Silaev A A, Marusin M P, Zakemoskya E Yu, Gilev A G and Alekseev A V 2014 Measurement Techniques 57 461
[7] Alexandrov A S, Archipov R V, Ivanov A A, Gnezdilov O I, Gafurov M R and V.D. Skirda V D 2014 Applied Magnetic Resonance 45 1275-1287
[8] Filippov A V, Artamonova M R, Rudakova M F, Gimatdinov R G and Skirda V D 2012 Magnetic Resonance in Chemistry 50 114 – 119
[9] Chizhik V I and Tagirov M S 2017 Applied Magnetic Resonance 48 621-623
[10] Alakshin E M, Gazizulin R R, Klochkov A V, Kuzmin V V, Sabitova A M, Safin T R and Tagirov M S 2013 Magnetic resonance in solid 15(1) 13104
[11] Myazin N S, Davydov V V, Yushkova V V, Davydova T I and Rud’ V Yu 2017 Journal of Physics: Conference Series 917(4) 042017
[12] 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
[13] Davydov V V, Dudkin V I, Petrov A A and Myazin N S 2016 Technical Physics Letters 42 692–696
[14] Nepomnyashchaya E K, Velichko E N and Aksenov E T 2016 Journal of Physics: Conference Series 769(4) 012025
[15] Nepomnyashchaya E K, Akenov E T, Bogomaz T A and Velichko E N 2015 Journal of Optical Technology (A Translation of Opticheskii Zhurnal) 82 162-165
[16] Nepomnyashchaya E K, Cheremiskina A V, Velichko E N, Aksenov E T and Bogomaz T A 2015 Journal of Physics: Conference Series 643(1) 012018
[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] Grebenikova N M, Smirnov K J, Davydov V V, Rud V Yu and Artemiev V V 2018 Journal of Physics: Conference Series 1135(1) 012055
[19] Grebenikova N M, Myazin N S, Rud V Y and Davydov R V 2018 Proceedings of the 2018 IEEE International Conference on Electrical Engineering and Photonics, EExPolytech 2018 (Saint-Petersburg) 856-4409 p. 295-297
[20] Grebenikova N M, Smirnov K J, Davydov V V and Rud V Y 2018 Journal of Physics: Conference Series 1124 (4) 041011
[21] Davydov V V, Dudkin V I, Velichko E N and Karseev A Yu 2015 Journal of Optical Technology (A Translation of Opticheckii Zhurnal) 82(3) 132-135
[22] Davydov V V, Dudkin V I and Karseev A Yu 2015 Russian Physics Journal 58 146 – 152
[23] Davydov V V 1999 Russian Physics Journal 42(9) 822-825
[24] Davydov V V, Dudkin V I and Karseev A Yu 2014 Optical Memory and Neural Networks (Information Optics) 23 170-176
[25] Davydov V V, Dudkin V I and Karseev A Yu 2014 Optical Memory and Neural Networks (Information Optics) 23 259-264
[26] Davydov V V, Dudkin V I and Karseev A U 2013 Optical Memory & Neural Networks (Information Optics) 22 112 – 117
[27] Myazin N S, Davydov V V, Yushkova V V and Rud V Yu 2018 Journal of Physics: Conference Series 1038 (1) 012088
[28] Davydov V V, Myazin N S and Velichko E N 2017 Technical Physics Letters 43 607-610
[29] Davydov V V, Myazin N S, Logunov S E and Fadeenko V B 2018 Russian Journal of Nondestructive Testing. 54(3) 213-221
[30] Davydov V V, Dudkin V I and Myazin N S 2016 Journal of Communications Technology and Electronics 61 1159–1165
[31] Davydov V V, Dudkin V I and Karseev A Yu 2014 Measurement Techniques 57(8) 912-918
[32] Marusina M Y, Bazarov B A, Galaidin P A, Marusin M P, Silaev A A, Zakemovskya E Y and Mustaev Y N 2014 Measurement Techniques 57(5) 580-586
[33] Davydov V V 2016 Optics and Spectroscopy (English translation of Optika i Spektroskopiya) 121(1) 18-24
[34] Davydov V V, Dudkin V I and Karseev A Yu 2015 Thechnical Physics 63 456-460
[35] Davydov V V, Dudkin V I, Velichko E N and Karseev A Yu 2015 Measurement Techniques 58(5) 556-561