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Features of the study of condensed matter using the nuclear magnetic resonance method based on relaxation times T_1 and T_2

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The features of determining the longitudinal T_1 and transverse T_2 relaxation times in NMR relaxometer designs for measuring the parameters of condensed matter for various applications, including biology and medicine, which are both in a stationary and current state, are considered. The advantages of using the modulation technique for recording the NMR signal for flow NMR flowmeters-relaxometers and small-sized NMR relaxometers for express monitoring of condensed matter in comparison with other methods and techniques are noted. It has been experimentally proven that the resulting relationship from the Bloch equations using approximations for determining T_1 from the results of two measurements of NMR signal amplitudes or resonant frequencies has a number of restrictions on application for both flowing and stationary condensed matter. These limitations are associated both with the technique of recording the NMR signal and with the ability to generate NMR signals for different modulation frequencies of the H_0 field, the amplitudes of which will differ from each other beyond the measurement error. The reasons that led to this discrepancy in the ratio for determining T_1 and the limits of applicability of this ratio are determined. Based on experimental data, a study of the relationship for determining T_1 was carried out and it was proven that for a number of cases using it is impossible to obtain the T_1 value. In this case, NMR signals from a condensed medium are recorded in these cases, and the medium itself has relaxation times T_1 and T_2 . The results we obtained make it possible to eliminate errors when conducting experiments when studying condensed matter using the NMR method, this is especially important in biology and medicine, where the requirements for measurement accuracy are increased.

Keywords: nuclear magnetic resonance, liquid, condensed matter, modulation technique, NMR signal, nuclear magnetic flow meter-relaxometer, Bloch equations, relaxation times T_1 and T_2 , modulation frequency, measurement error.

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Introduction

Currently, the nuclear magnetic resonance (NMR) method is one of the main methods of studying condensed media, especially those in the liquid state [1–4]. The scientific result in biology and medicine is considered to be reliable only in rare exceptions in case of study of liquid media without using the NMR method. Various methods for recording the NMR signal have been developed for the practical implementation of the NMR method in industrial and laboratory devices [2,3,5,6–10]. The spectrum of [3,4,6,11–13] is recorded in most studies conducted using NMR. Designs of spectrometers with different operating frequencies of the magnetic field are used for recording the NMR spectrum (ranging from desktop NMR spectrometers with an operating frequency of 80 MHz to high-resolution spectrometers with the operating frequency of 1.8 GHz and higher). In a number of cases, recording of the NMR spectrum in the study of condensed media is complicated,

especially in a flowing liquid or during express control in weak fields. In this situation, the tasks of studying liquid media, as well as determining their state, are solved based on measurements of the longitudinal T_1 and transverse T_2 relaxation time [14–19].

The greatest preference is given to pulsed methods when measuring the values of T_1 and T_2 in liquid media that are in a stationary state [7,8,10–13,20,21], with the exception of weak magnetic fields [22,23]. It is extremely difficult to use pulse methods for conducting studies in a flowing liquid, especially for cases where the flow velocity changes by an order of magnitude or more. Therefore, a special place among the methods of recording the NMR signal is occupied by the modulation technique [9,14–17,22,23], which allows recording the NMR signal both in a weak field and from a liquid flow in a large range of changes in its flow rate q .

The NMR signal is recorded in the form of non-periodic damped oscillations („wiggles“) in case of usage of the

modulation technique. Relaxation times T_1 and T_2 are measured using NMR signals that are recorded at the resonant frequency of protons (^1H). This is due to the fact that protons have the highest sensitivity to the NMR method [2–8,11–14,22–26] and are part of 99.8% of liquid media and their mixtures [18–27]. In rare cases, the NMR signal recording frequency is tuned to the resonant frequencies of other nuclei (for example, lithium, fluorine, phosphorus, boron, and others). Based on the results of this tuning, a spectrum is formed that can determine the presence of these nuclei in the medium under study and their relative concentrations. In these cases, the concentration of these nuclei in the medium and the induction of the magnetic field should provide a certain signal-to-noise ratio (S/N) when registering the NMR signal. S/N > 1.3 for stationary media in weak fields, S/N > 2.5 for current media. The recording of the NMR spectrum refers mainly to the cases of the study of acids, alkalis, as well as, for example, perfumes (toothpaste and others).

One of the problems that currently arises when monitoring the state of a condensed medium using an NMR signal recorded using a modulation technique is the lack of a universal measurement method T_1 for both flowing and stationary liquids. The formulas currently used to determine T_1 do not allow in some cases determining the value of T_1 in the presence of a recorded NMR signal at a certain ratio between frequencies f_m of field H_m modulating a constant magnetic field H_0 . The values of T_1 for condensed media are successfully determined using the same formulas with other ratios between the values of f_m (the measured values of T_1 coincide with the measurement results of T_1 on an industrial NMR relaxometer Minispec mq 20M, which confirms the reliability of the measurements). The presence of the phenomenon noted by us significantly limits the possibilities of using NMR flowmeters-relaxometers and small-sized NMR relaxometers for conducting studies of condensed media and solving a number of technical problems, especially when working with biological solutions in their current state. Therefore, the purpose of this paper is to study in detail the causes of this physical phenomenon, as well as to determine the conditions under which it is possible to determine the values T_1 of condensed matter in the implementation of their studies and control of flow parameters.

1. Modulation technique for recording NMR signals from current and stationary condensed matter

The motion of the components of the magnetization vector during signal recording using various methods is described in NMR theory by the phenomenological Bloch equations [27–29]. A transition to a rotating coordinate system is performed using the Vagness method to describe the signals of absorption $v(t)$ and dispersion $u(t)$ in case of usage of the modulation technique to record the NMR signal [27,29]. It should also be noted that the peculiarity

of using the modulation technique, unlike other methods, is that the NMR signal is recorded at the resonant frequency of protons or other nuclei ($\Delta\omega = 0$). The system of Bloch equations in a rotating coordinate system has the following form taking into account this feature:

$$\begin{aligned} \frac{du(t)}{dt} + \frac{u(t)}{T_2} + \gamma H_m \sin(\omega_m t) v(t) &= 0, \\ \frac{dv(t)}{dt} + \frac{v(t)}{T_2} - \gamma H_m \sin(\omega_m t) u(t) + \gamma H_1 M_z(t) &= 0, \\ \frac{dM_z(t)}{dt} + \frac{M_z(t)}{T_1} - \frac{\chi(H_0 + H_m \sin(\omega_m t))}{T_1} - \gamma H_1 v(t) &= 0, \end{aligned} \quad (1)$$

where ω_m — field modulation frequency H_0 , H_m — modulation field amplitude H_0 , H_1 — radio frequency amplitude the field that is formed in the NMR signal recording coil, χ_0 — static magnetic susceptibility, t — current time.

Structural diagrams of laboratory layouts of an NMR relaxometer (the condensed medium is in a stationary state) and an NMR flowmeter relaxometer are presented as an example in Fig. 1,2 where magnetic fields and their directions are indicated in case of recording of an NMR signal using a modulation technique [1,9,17,22,23].

A comparison of the two designs of NMR signal recording systems (Fig. 1,2) shows a large number of coincidences in them both in the direction of the magnetic fields and in the identical location relative to the magnetic fields of the NMR signal recording coils 6 (Fig. 1) and 10 (Fig. 2) with condensed medium. NMR signals from a condensed medium (in two states) are recorded in the form of non-periodic damped oscillations (Fig. 3,4).

The differences in the recording of NMR signals for the two media states are that the segment of the magnetized flowing liquid from which the NMR signal is recorded is located in the recording coil 10 (Fig. 2) for a certain time t_p . The ratio $t_p > 1/f_m$ should be fulfilled at the same time. The pipeline in the recording coil area 10 is expanded in 2–2.5 times for increasing t_p (vessel—analyzer 7). This leads to the fact that the value H_0 decreases, this decrease can only be compensated by increasing the size of the magnetic system (increasing the size of the poles of the magnet) or using another magnetic material. This will lead to an increase of the weight of the entire measuring device structure. Therefore, the sizes of magnetic systems in flow-through NMR flowmeters-relaxometers are much larger than in stationary NMR relaxometers. It should be noted that the value of t_p depends on the flow rate of the flowing condensed medium q and varies within two orders of magnitude (operating conditions of flowmeters of various types [15,19,24]). Therefore, it is extremely difficult to apply the Fourier transform to solve the system (1).

The measurements of relaxation times T_1 and T_2 in these devices are currently implemented as follows. The time T_2 is determined by the decay of the envelope constructed from the peaks of the recorded NMR signal (Fig. 3). The number

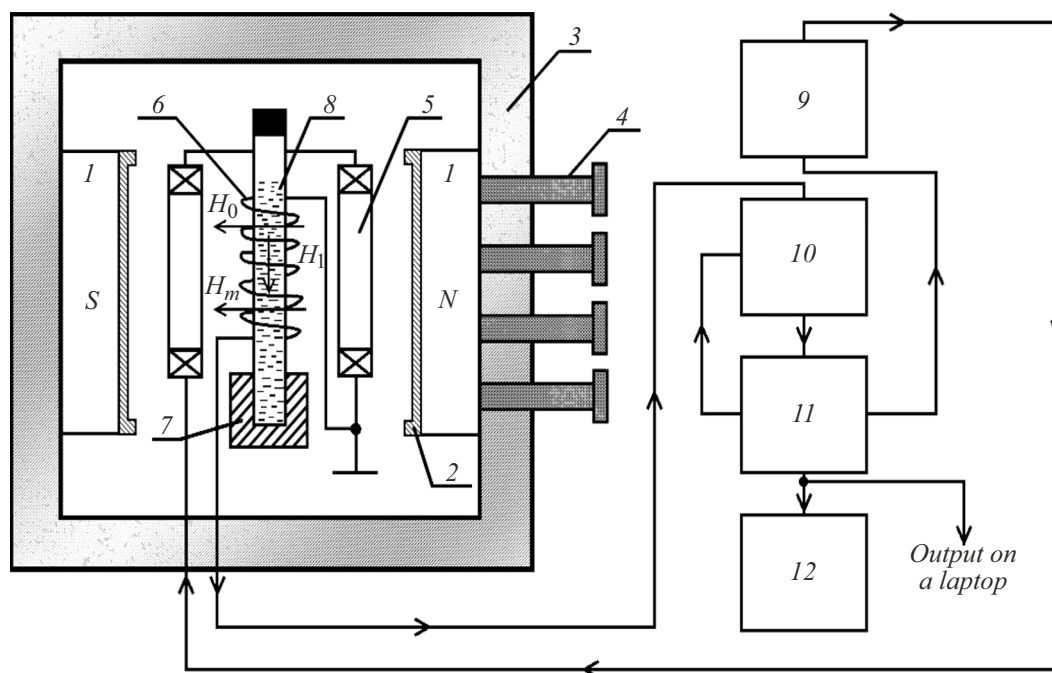


Figure 1. Block diagram of a small-sized mobile NMR relaxometer: 1 — permanent magnet; 2 — special buses; 3 — neutral for placement and adjustment of the position of magnets; 4 — adjustment screws; 5 — modulation coil; 6 — NMR signal recording coil; 7 — „tank“ for container with studied medium; 8 — a container with the studied medium; 9 — a magnetic field modulation generator; 10 — a recording circuit including an RF autodyne generator; 11 — a processing and control unit; 12 — display device.

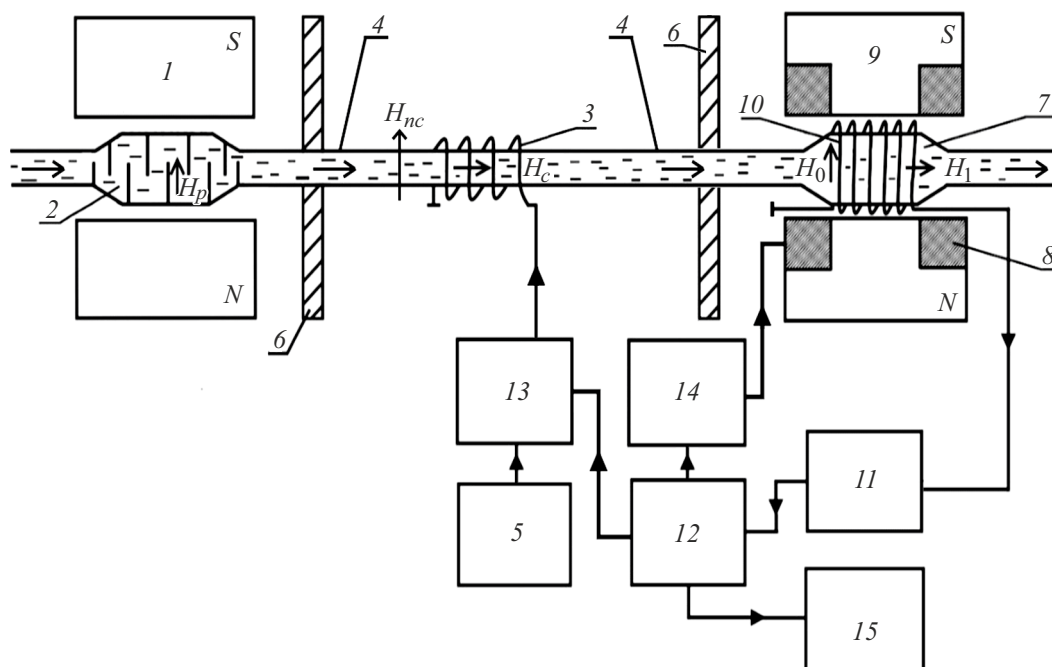


Figure 2. Structural diagram of the NMR flowmeter relaxometer: 1 — magnet polarizer; 2 — volume polarizer; 3 — nutation coil; 4 — connecting section of the pipeline; 5 — radio frequency generator; 6 — magnetic shield; 7 — polarizer vessel; 8 — field modulation coils H_0 ; 9 — electromagnet; 10 — NMR signal recording coil; 11 — NMR signal recording device; 12 — processing and control device; 13 — electronic key; 14 — low frequency generator; 15 — display device.

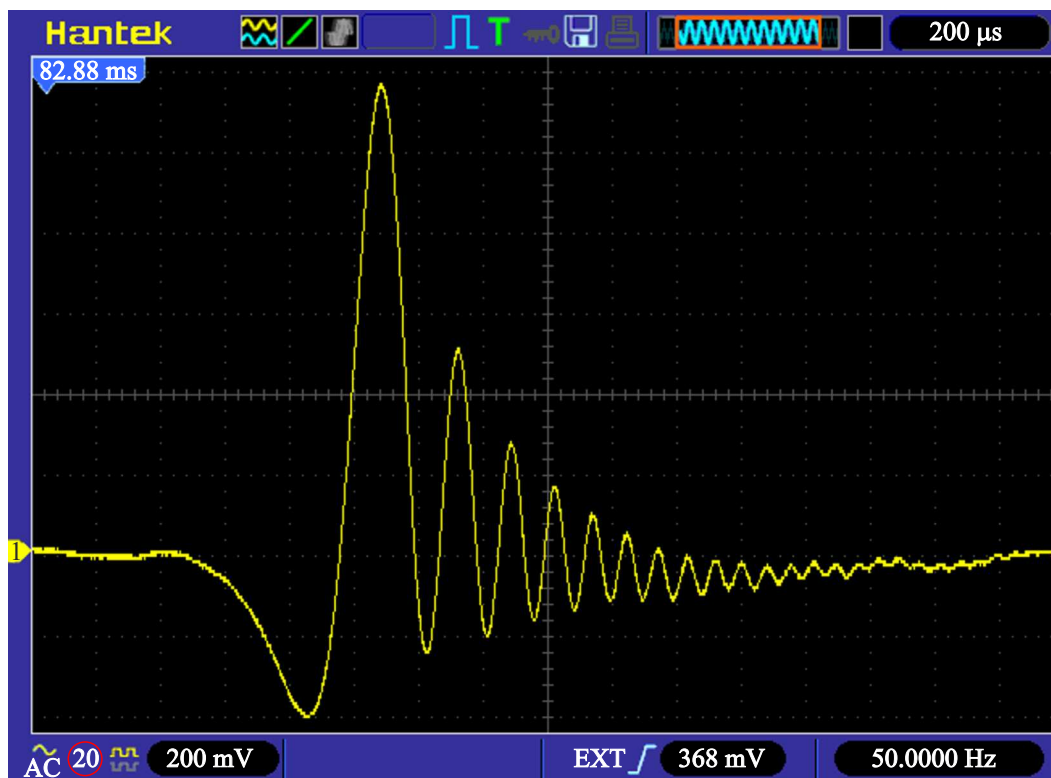


Figure 3. NMR signal from tap water at temperature of $T = 289.4$ K, recorded in a small-sized NMR relaxometer.

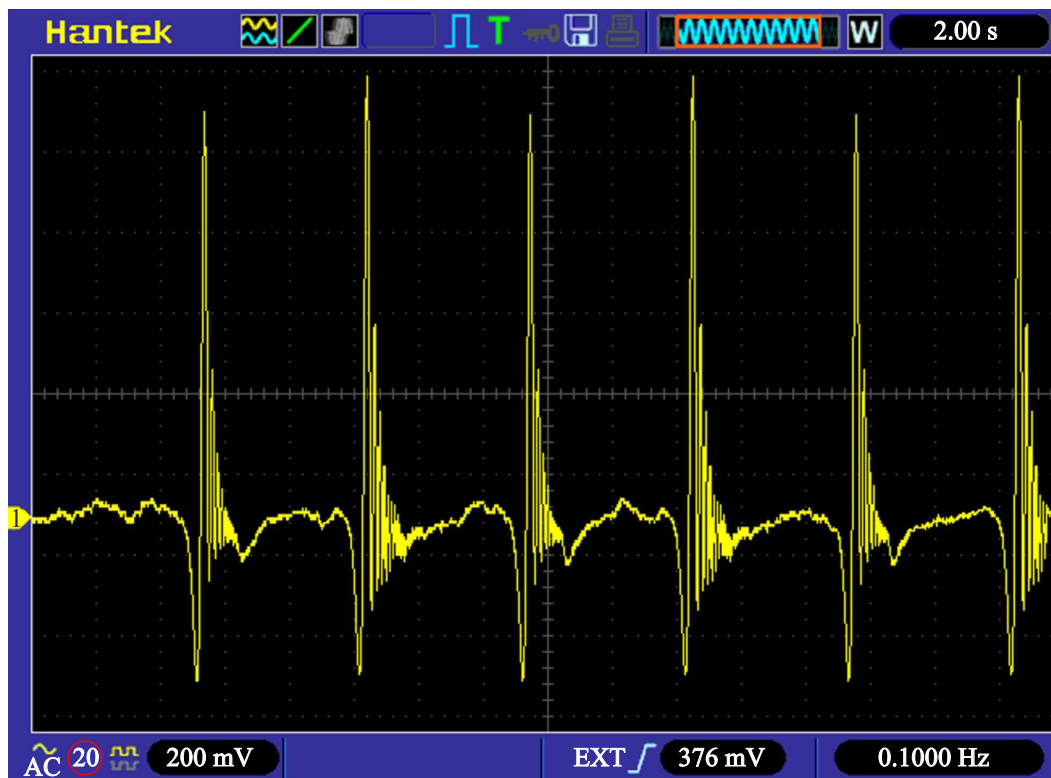


Figure 4. NMR signal from the current liquid medium (aqueous solution ($\text{H}_2\text{O}+\text{H}_3\text{BO}_3$) with nitride-plutonium filler) at temperature $T = 333.1$ K.

Table 1. The results of measuring relaxation times T_1 and T_2 of aqueous solution ($H_2O+H_3BO_3$) with filler made of plutonium nitride at different temperatures T by two devices

T, K	Small-sized NMR relaxometer		Industrial NMR relaxometer Minispec mq 20M	
	T_1, s	T_2, s	T_1, s	T_2, s
288.1	1.029 ± 0.009	0.655 ± 0.006	1.0284 ± 0.0031	0.6536 ± 0.0018
293.2	1.064 ± 0.009	0.661 ± 0.006	1.0627 ± 0.0032	0.6585 ± 0.0018
303.2	1.139 ± 0.010	0.675 ± 0.006	1.1402 ± 0.0034	0.6731 ± 0.0019
317.6	1.213 ± 0.011	0.684 ± 0.006	1.2118 ± 0.0036	0.6824 ± 0.0020
323.2	1.252 ± 0.011	0.694 ± 0.006	1.2514 ± 0.0037	0.6951 ± 0.0021
333.5	1.343 ± 0.012	0.716 ± 0.006	1.3443 ± 0.0040	0.7143 ± 0.0021
338.6	1.387 ± 0.012	0.730 ± 0.007	1.3869 ± 0.0041	0.7284 ± 0.0022
343.4	1.445 ± 0.013	0.746 ± 0.007	1.4443 ± 0.0043	0.7474 ± 0.0022
348.2	1.621 ± 0.014	0.766 ± 0.007	1.6225 ± 0.0048	0.7646 ± 0.0023

of peaks and the nature of changes in their amplitude are determined by the uniformity of the magnetic field in the area of the recording coil 6 (fig. 1) or 10 (Fig. 2).

Problems arise when measuring the longitudinal relaxation time T_1 . It is difficult to implement the classical measurement of T_1 using the frequency measurements of the Julotto method [27,30] in the design of a small-sized NMR relaxometer and an on-line NMR flowmeter relaxometer. The resonant frequencies differ from each other by fractions of a hertz in a weak magnetic field H_0 (Fig. 1) when the frequency of modulation of the magnetic field H_0 changes. The recording of such frequencies requires high precision of resonance tuning, which can only be achieved by measurements in laboratory conditions. It is extremely difficult to implement such a measurement mode in the case of usage of the device in the field conditions. In addition, the formula for determining T_1 in the Julotto method [30] was obtained from the Bloch equations without taking into account the peculiarities of NMR signal recording in a weak magnetic field using a modulation technique [1]. Also, its output did not take into account the features of the NMR signal recording in the flowing liquid, which are associated with the time of the liquid in the recording coil t_p and the modulation frequency f_m . Therefore, the following formula was derived for the case of equality of two relaxation times T_1 and T_2 , as well as for the assumption that the amplitude of the recorded NMR signal is maximum (a magnetized liquid with a maximum value of M_z enters the recording coil, which allows in the equations (1) consider $dM_z/dt = 0$) and taking into account the thermal equilibrium factor for different field modulation frequencies H_0 , when the magnetization value does not have time to recover after external action:

$$M = M_0[1 - (1 - \exp(-\tau/T_1))/(1 + \exp(-\tau/T_1))], \quad (2)$$

where M_0 — the magnetization of the medium under study before exposure to the modulation field, M — the magnetization of the medium under study at which the NMR signal is recorded.

As in the Julotto frequency method for determining T_1 using the ratio (2) it is necessary to measure the amplitudes of the NMR signal U_s at two times τ , which are determined through the modulation frequency $\tau = 1/f_m$ and to determine T_1 through the ratio of two amplitudes U_s which are proportional to M . The developed experimental setup (Fig. 1, 2) was used to check the ratio (2) for an aqueous solution ($H_2O+H_3BO_3$) with a nitride-plutonium filler (this solution is used in chemistry, biology with other fillers and cooling systems) for different temperatures T . Additionally, the change in the value T_2 of this solution was studied. Relaxation times are measured 10 times, then the average values for T_1 and T_2 , deviations from the mean and standard errors of measurement are calculated. Next, random errors are calculated for T_1 and T_2 with a confidence probability of 0.95, which is commonly used in technical measurements.

The results of measurement of the values T_1 and T_2 were compared with the results of measurement using industrial NMR relaxometer Minispec mq 20M (BRUKER, Germany). The data obtained are listed in Table 1.

T_1 was measured at two times τ , which differed by at least an order of magnitude. The analysis of the obtained results showed that they coincide within the measurement error.

On the other hand, it was experimentally found that the ratio (2) does not allow determining the value of T_1 for the case when the difference between the modulation frequencies of the field H_0 is less than one order of magnitude. This situation for the ratio (2) needs a more detailed study.

2. Research results and discussion

Fig. 5, 6 show the recorded NMR signals from an aqueous solution with fluorine ions (the NMR signal is recorded at the resonant frequency of fluorine ^{19}F).

The green line in Fig. 6 in the recorded NMR signal shows the peak decay envelope (it is used to measure T_2).

Table 2. The results of measurement of relaxation times T_1 and T_2 of an aqueous solution ($H_2About+H_3BO_3$) with filler made of plutonium nitride at different temperatures T by two devices

T, K	Laboratory NMR flow meter-relaxometer		Industrial NMR relaxometer Minispec mq 20M	
	T_1, s	T_2, s	T_1, s	T_2, s
288.2	1.032 ± 0.009	0.658 ± 0.006	1.0284 ± 0.0031	0.6536 ± 0.0018
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303.2	1.141 ± 0.010	0.678 ± 0.006	1.1402 ± 0.0034	0.6731 ± 0.0019
317.5	1.215 ± 0.011	0.686 ± 0.006	1.2118 ± 0.0036	0.6824 ± 0.0020
323.1	1.255 ± 0.011	0.698 ± 0.006	1.2514 ± 0.0037	0.6951 ± 0.0021
333.6	1.348 ± 0.012	0.719 ± 0.006	1.3443 ± 0.0040	0.7143 ± 0.0021
338.5	1.392 ± 0.012	0.735 ± 0.007	1.3869 ± 0.0041	0.7284 ± 0.0022
343.5	1.451 ± 0.013	0.750 ± 0.007	1.4443 ± 0.0043	0.7474 ± 0.0022
348.1	1.627 ± 0.014	0.771 ± 0.007	1.6225 ± 0.0048	0.7646 ± 0.0023

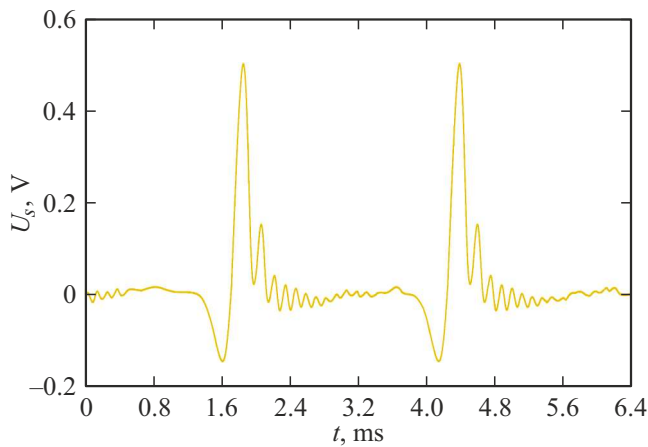


Figure 5. NMR signal from aqueous solution with fluorine ions at temperature $T = 294.8 K$, $f_m = 393.0 Hz$.

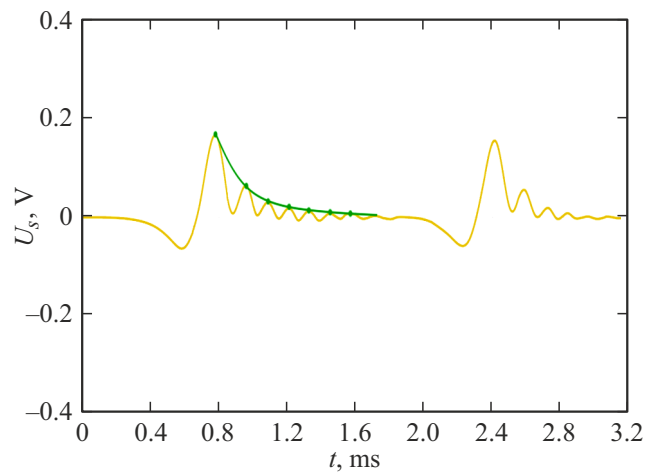


Figure 6. NMR signal from aqueous solution with fluorine ions at temperature $T = 294.8 K$, $f_m = 702.0 Hz$.

The modulation frequencies at which the NMR signal is recorded (Fig. 5,6) differ from each other by less than two times. The amplitude of the recorded signal decreases by more than 2 times with an increase of frequency f_m . All this shows that NMR signals actually exist with real relaxation times. The measurements of the values T_2 using two signals (Fig. 5,6) showed that these values coincide within the measurement error with measurements made using industrial NMR relaxometer Minispec mq 20M. On the other hand, it is impossible to determine the values of T_1 using (2). Let's prove mathematically that this is the case. Consider the ratio (2) in more detail to do this. Let us perform some transformations in the ratio (2). Let's bring the fraction on the right side to the common denominator. The following ratio is obtained after the conversion:

$$M = M_0 \left(1 - \frac{1 - e^{-\frac{t}{T_1}}}{1 + e^{-\frac{t}{T_1}}} \right) = M_0 \frac{2e^{-\frac{t}{T_1}}}{1 + e^{-\frac{t}{T_1}}} = M_0 \frac{2}{1 + e^{\frac{t}{T_1}}} \tag{3}$$

Next, let us introduce additional notation and substitute A_1 and A_2 in (3):

$$A_1 = M_0 \frac{2}{1 + e^{\frac{t}{T_1}}}, A_2 = M_0 \frac{2}{1 + e^{-\frac{t}{T_1}}}, \frac{A_1}{A_2} = \frac{1 + e^{-\frac{t}{T_1}}}{1 + e^{\frac{t}{T_1}}}$$

The following ratio is obtained after substituting and multiplying by the denominator of the right side:

$$\frac{A_1}{A_2} + \frac{A_1}{A_2} e^{\frac{t}{T_1}} = 1 + e^{-\frac{t}{T_1}} \tag{4}$$

Let us introduce additional notation for the transformation (4):

$$k = \frac{A_1}{A_2}, \quad e^{\frac{t}{T_1}} = x, \quad x > 0.$$

As a result, (4) is transformed into an equation of the form $f(x) = 0$, where the function $f(x)$:

$$f(x) = kx^{T_1} - x^{T_2} + k - 1. \tag{5}$$

Next, let us consider the case when $\tau_2 < \tau_1$. Since $k > 0$, the graph of the function $f(x)$ has no horizontal asymptote

$$f(x) \xrightarrow{x \rightarrow +\infty} +\infty.$$

Next, it is necessary to determine the intervals of increase and decrease of the function, let us find its critical points for this purpose. $f'(x) = 0$ is calculated for this purpose.

$$f'(x) = k\tau_1 x^{\tau_1-1} - \tau_2 x^{\tau_2-1} = 0,$$

$$x_0 = \left(\frac{\tau_2}{k\tau_1}\right)^{\frac{1}{\tau_1-\tau_2}} \text{ is a critical point.}$$

$x_0 > 0$ taking into account the previously set condition. Let us consider two gaps for x .

$x \in (0; x_0]$: $f'(x) < 0 \Rightarrow f(x)$ decreases at this interval

$x \in [x_0; +\infty)$: $f'(x) > 0 \Rightarrow f(x)$ increases at this interval.

The result shows that the point x_0 is the minimum (the only extremum). The number of solutions to the equation $f(x) = 0$ depends on the value $f(0)$, which can be zero. There may be one numerical solution or two. Extremes are sought to determine the number of solutions.

In general, the equation $f(x) = C$ has at most two real solutions for all real C . If the equation has two different real solutions, then they are located on different sides of the minimum point, the existence of the second root depends on the value of $f(0)$ (since the roots must be positive, which follows from the conditions). Let us substitute the critical point x_0 in (5). The following ratio is obtained as a result:

$$f(x_0) = k \left(\frac{\tau_2}{k\tau_1}\right)^{\frac{\tau_1}{\tau_1-\tau_2}} - \left(\frac{\tau_2}{k\tau_1}\right)^{\frac{\tau_1}{\tau_1-\tau_2}} + k - 1. \quad (6)$$

There are three possible cases for equation (6):

1. $f(x_0) > 0 \Rightarrow$ equation $f(x) = 0$ has no solutions;
2. $f(x_0) = 0 \Rightarrow$ equation $f(x) = 0$ has one solution;
3. $f(x_0) < 0 \Rightarrow$ equation $f(x) = 0$ has one or two solutions. The number of solutions depends on the value $f(0)$.

Let us consider 1 case:

$$k \left(\frac{\tau_2}{k\tau_1}\right)^{\frac{\tau_1}{\tau_1-\tau_2}} - \left(\frac{\tau_2}{k\tau_1}\right)^{\frac{\tau_1}{\tau_1-\tau_2}} + k - 1 > 0,$$

$$k \left(\left(\frac{\tau_2}{k\tau_1}\right)^{\frac{\tau_1}{\tau_1-\tau_2}} + 1\right) > \left(\frac{\tau_2}{k\tau_1}\right)^{\frac{\tau_1}{\tau_1-\tau_2}} + 1.$$

Let us make the degrees of the relations in parentheses on each side the same and introduce additional notation:

$$k \left(\left(\frac{k\tau_1}{\tau_2}\right)^{\frac{\tau_1}{\tau_2-\tau_1}} + 1\right) > \left(\frac{k\tau_1}{\tau_2}\right)^{\frac{\tau_1}{\tau_2-\tau_1}} + 1,$$

$$\frac{\tau_1}{\tau_2} = l, \quad \frac{\tau_1}{\tau_2 - \tau_1} = \frac{l}{1-l}, \quad \frac{\tau_2}{\tau_2 - \tau_1} = \frac{1}{1-l}.$$

(6) will have the following form after that:

$$k \left((kl)^{\frac{l}{1-l}} + 1\right) > (kl)^{\frac{l}{1-l}} + 1. \quad (7)$$

Let us consider a number of numerical examples with different values k and l . 1. $\tau_1 = 300 \mu s, \tau_2 = 200 \mu s \Rightarrow l = \frac{\tau_1}{\tau_2} = \frac{3}{2}$.

The following inequality is obtained after substituting these values into (7):

$$k \left(\left(k\frac{3}{2}\right)^{-3} + 1\right) > \left(k\frac{3}{2}\right)^{-2} + 1.$$

Let us move all the terms to the right side and get the following function after the transformation:

$$g(k) = 27k^3 - 27k^2 - 4.$$

The inequality is now represented as

$$g(k) > 0.$$

Additionally, let us consider the derivative of $g(k)$:

$$g'(k) = 81k^2 - 54k = 27k(3k - 2).$$

Let us construct graphs $g(k)$ and $g'(k)$ to determine the presence of the root of the equation (Fig. 7). The analysis of the dependencies presented in Fig. 7 shows that $k = 0$ — the point of the local maximum, $k = \frac{2}{3}$ — the point of the local minimum, $g(0) = -4$. In this case, $g(k) = 0$ has one solution, which is in the range $\left[\frac{2}{3}; +\infty\right)$. Let us convert $g(k)$ to the following format:

$$g(k) = 27k^3 - 27k^2 - 4 = 27 \left(k^3 - k^2 - \frac{4}{27}\right).$$

The value of the root k_0 can be found using the Cardano formula for this equation:

$$k_0 = \sqrt[3]{-\frac{q}{2} + \sqrt{\frac{q^2}{4} + \frac{p^3}{27}}} + \sqrt[3]{-\frac{q}{2} - \sqrt{\frac{q^2}{4} + \frac{p^3}{27}}} - \frac{a}{3},$$

where $a = -1, p = -\frac{1}{3}, q = -\frac{4}{27} - \frac{2}{27} = -\frac{2}{9}$.

$$\begin{aligned} k_0 &= \sqrt[3]{\frac{1}{9} + \sqrt{\frac{1}{81} - \frac{1}{729}}} + \sqrt[3]{\frac{1}{9} - \sqrt{\frac{1}{81} - \frac{1}{729}}} + \frac{1}{3} \\ &= \sqrt[3]{\frac{1}{9} + \frac{1}{27}\sqrt{8}} + \sqrt[3]{\frac{1}{9} - \frac{1}{27}\sqrt{8}} + \frac{1}{3} \approx 1.118. \end{aligned}$$

It can be concluded that there are no solutions taking into account a certain interval for k .

The experiments demonstrated that a change of the modulation frequency, for example, an increase of the case of recording of an NMR signal from various types of nuclei, can lead both to an increase of the amplitude of the recorded NMR signal on some nuclei and to its decrease in case of recording of an NMR signal on other nuclei. Therefore, it is necessary to consider two different options:

- 1) $A_1 = 1.14 \text{ V}, A_2 = 0.89 \text{ V}$. In this case $k = 1.281 > k_0$, which means there are no solutions in the equation $f(x) = 0$.

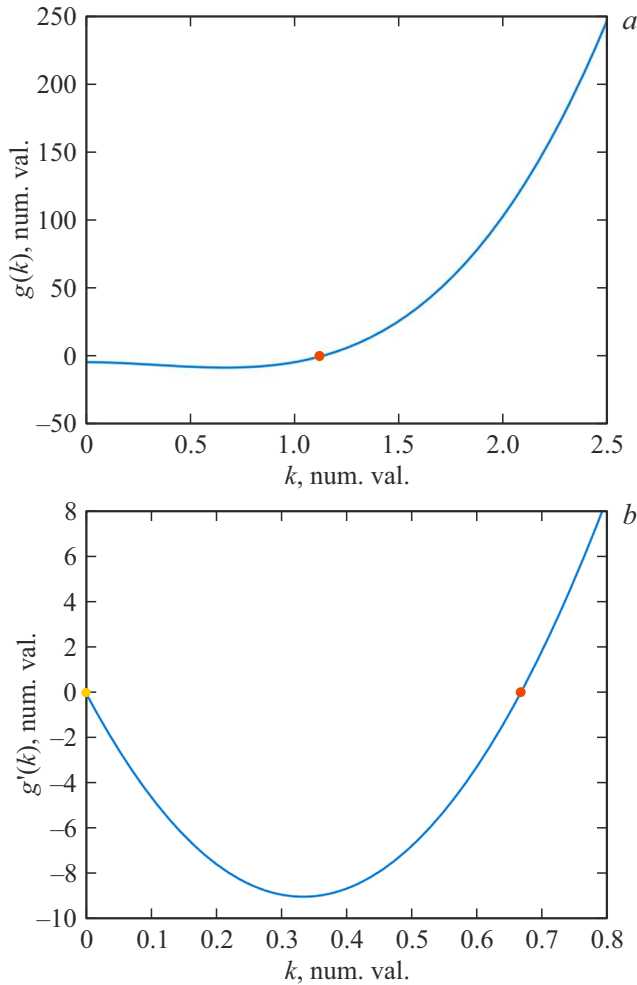


Figure 7. Dependence of the change $g(k)$ and $g'(k)$ on k on the interval of existence of a possible solution. The red and yellow dots correspond to the intersection of the graphs of functions with the axis $g = 0$ and $g' = 0$.

2) $A_1 = 0.89 \text{ V}, A_2 = 1.14 \text{ V}$. In this case $k = 0.781 < k_0$, which means that equation $f(x) = 0$ has at least one solution. The following function is considered as $f(x)$:

$$f\left(e^{\frac{1}{T_1}}\right) = ke^{\frac{1}{T_1}} - e^{\frac{2}{T_1}} + k - 1,$$

$$\tau_1 = 30 \mu\text{s}, \tau_2 = 200 \mu\text{s}, k = \frac{89}{114}.$$

The following equation is obtained after substituting all the values and entering the additional designation $e^{\frac{200}{T_1}} = t$:

$$F(t) = 89t^{\frac{3}{2}} - 114t - 25 = 0. \tag{8}$$

It is possible to transform (8) into the following equation:

$$F_1(t) = 7921t^3 - 12996t^2 - 5700t - 625 = 0. \tag{9}$$

Figure 8 shows the results of studies of two functions (8) and (9). The root of equation (9) is $-t = 2.017$.

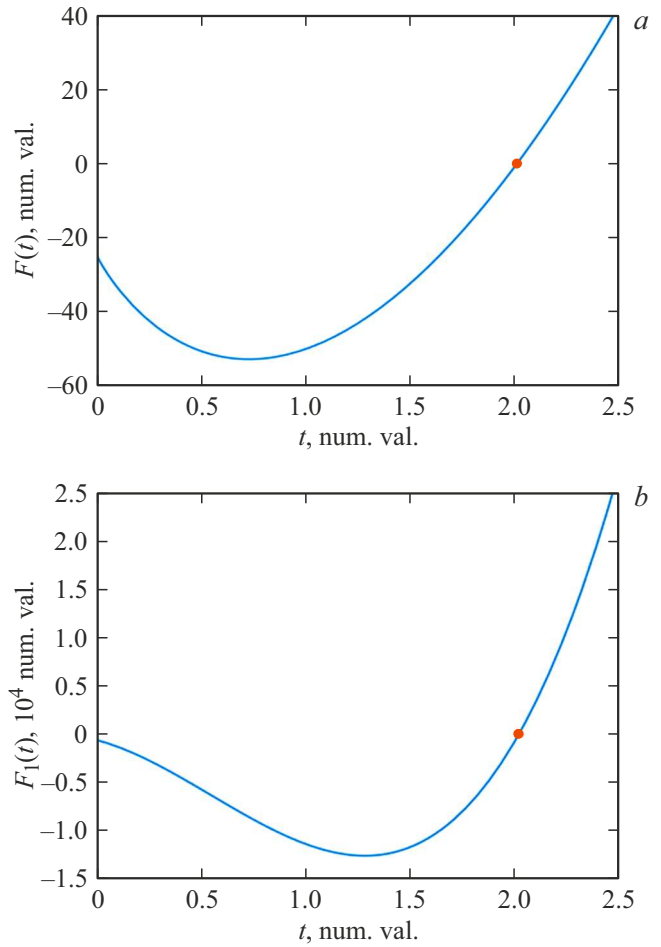


Figure 8. Dependence of the change of functions $F(t)$ and $F_1(t)$ on t . a — corresponds to the change $F(t)$, b — $F_1(t)$. The red dots correspond to the intersection of the graphs of functions with the axis $F = 0$ and $F_1 = 0$.

Let us return to the original notation $e^{\frac{200}{T_1}} = t$ for finding T_1 and obtain the value for $T_1 = 286 \mu\text{s}$. The allowed range of values is $T_1 \in [0.001; 21]$. The result shows that the solution does not fit the constraint, i.e. the original equation has no roots. Let us transform the expression (7) for considering other options:

$$k((2k)^{-2} + 1) > (2k)^{-1} + 1,$$

$$4k^2 - 4k - 1 > 0,$$

$$(2k - 1)^2 - 2 > 0, k > 0.$$

Let us consider two cases

$$\begin{cases} 2k - 1 > \sqrt{2} \\ 2k - 1 < -\sqrt{2}, k > 0 \end{cases} \Rightarrow k \in \emptyset, \quad k > \frac{1 + \sqrt{2}}{2} \approx 1.207.$$

$k = 1.195 < k_0 = 1/207$ was obtained taking into account previously determined values of amplitudes $A_1 = 1.14 \text{ V}, A_2 = 0.89 \text{ V}$, of recorded NMR signals for two modulation frequencies. This means that the equation

$f(x) = 0$ has one or two solutions. Let us consider (5) taking into account a number of transformations

$$f\left(e^{\frac{1}{T_1}}\right) = ke^{\frac{\tau_2}{T_1}} - e^{\frac{\tau_2}{T_1}} + k - 1.$$

The following relation is obtained for the case $\tau_1 = 2\tau_2$ with $k = 104/87$

$$\frac{104}{87}e^{\frac{2\tau_2}{T_1}} - e^{\frac{\tau_2}{T_1}} + \frac{104}{87} - 1 = 0.$$

The following equation is obtained as a result of the transformation $e^{\frac{\tau_2}{T_1}} = t$:

$$F_2(t) = 104t^2 - 87t + 17 = 0.$$

Figure 9 shows the graph $F_2(t)$ in the interval of possible solution finding.

The ratio for $F_2(t)$ has two roots: $t_1 = 0.525$; $t_2 = 0.311$. Two values are obtained T_1 taking into account the previously performed designations. These values are less than zero:

$$\begin{cases} T_1 = \frac{\tau_2}{\ln(0.525)} < 0. \\ T_1 = \frac{\tau_2}{\ln(0.311)} < 0. \end{cases}$$

This allows drawing a conclusion that the resulting solution does not fit the constraints. This means that the first equation has no solutions.

For example, let us consider another case when the modulation frequencies of the field H_0 are greater than 200 Hz.

$$3) \tau_1 = 0.0025 \text{ s}, \tau_2 = 0.0014 \text{ s} \Rightarrow l = \frac{\tau_1}{\tau_2} \approx 1.786,$$

$$A_1 = 1.04 \text{ V}, A_2 = 0.87 \text{ V} \Rightarrow k = \frac{A_1}{A_2} = \frac{104}{87} \approx 1.195 < k_0.$$

$f(x) = 0$ has one or two solutions in this case. Let us transform (5) into the following ratio taking into account the initial data:

$$f\left(e^{\frac{1}{T_1}}\right) = ke^{\frac{\tau_2}{T_1}} - e^{\frac{\tau_2}{T_1}} + k - 1.$$

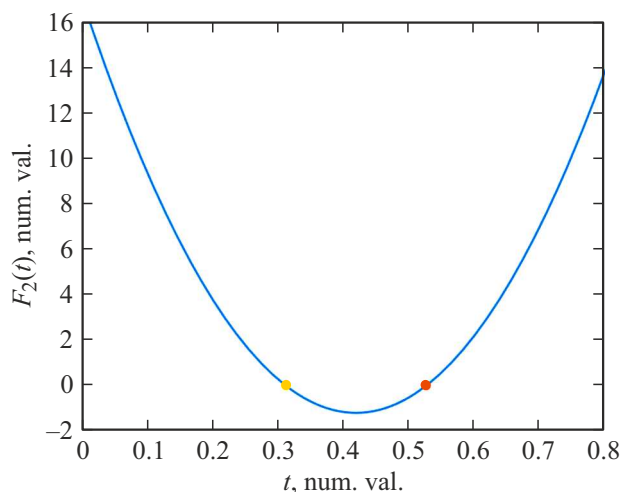


Figure 9. Dependence of change of functions $F_2(t)$. The red and yellow points correspond to the intersection of the graphs of functions with the axis $F_2 = 0$.

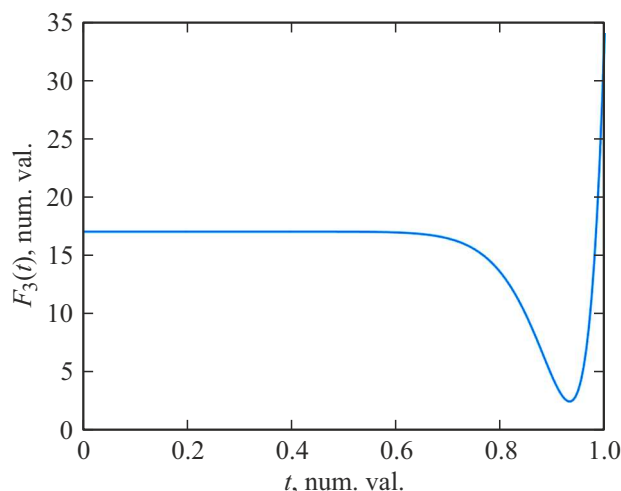


Figure 10. Dependence of the change of function $F_3(t)$ on t . The equation has no solution.

The following ratio is obtained for two values of times τ_1 and τ_2 by converting this equation:

$$F_3(t) = 104t^{25} - 87t^{14} + 17 = 0.$$

The equation $F_3(t)$ has one root, which is equal to $t = -0.875$. This solution does not fit the constraints, i.e. the first equation has no solutions. Figure 10 shows a graph of the function $F_3(t)$ to control the reasoning.

The graph presented in Fig. 10 clearly confirms this (there is no intersection with axis $F_3 = 0$). The other possible solutions of (2) also show absence of solutions at certain ratios between frequencies.

Conclusion

The analysis of the obtained results showed that there are a number of features for determining the longitudinal relaxation time T_1 when using the equation (2). It was found that these features are the same for both the current medium and the stationary condensed medium, except for two. One feature is related to the residence time of the magnetized liquid in the recording coil at the time of exposure to the modulation field during the recording of the NMR signal. This circumstance plays a key role in many studies given that the speed of the current environment can vary by an order of magnitude or more. The second feature is associated with a change of the temperature of the liquid flow. The value T of the condensed medium is adjusted in the required range in stationary studies. Changes of T can be significant and difficult to control in the flowing environment, especially in cooling systems. These features should be taken into account when deriving a new relation to determine T_1 from Bloch equations.

In addition, the results of the analysis of the ratio (2) show that it is necessary to ensure at least a five-fold change of the modulation frequency f_m to obtain the value T_1 from

the ratio (2) when measuring two amplitudes U_s of NMR signals. Additionally, it was found that the dependence of the difference between the amplitudes of the recorded NMR signals with two changes of the modulation frequency f_m depends on which nucleus resonant frequency the NMR signals from the condensed medium are recorded.

Our studies allowed us determining that the ratio (2) is not a universal formula for determining the value T_1 using NMR signals recorded using a modulation technique. The constraints for usage of (2) that we defined when studying liquid media flows in laboratory installations can be implemented with great difficulty using manual adjustment of the frequency range under human control, which will allow obtaining reliable results and solving a number of complex tasks, especially when working with biological solutions. It cannot be implemented in industrial devices since they require automatic adjustment to ensure measurements of T_1 using the ratio (2). Therefore, it is necessary to obtain a new ratio to determine T_1 from the solution of the equation (1) without approximations, which does not require the definition of constraints on its use in measurements. This will be our next scientific task.

Conflict of interest

The authors declare that they have no conflict of interest.

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