Magneto-resonance methods of the relaxation rate measuring for the proton-containing flowing fluids composition studying

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Abstract. In the present work, the existing pulsed nuclear magnetic resonance methods for determining the longitudinal relaxation time in a condensed medium are analyzed. There is considered an alternative method of the nuclear magnetic momentums relaxation times determining in the current proton-containing liquid by the functional dependence of the detected signal intensity from the amplitude of the magnetic field modulation in the magnet-analyzer.

1. Introduction
Determination of the relaxation constants of proton-containing media is one of the key problems of applied nuclear magnetic resonance spectroscopy, the solution of which allows obtaining information on the internal structure of the investigated working substance used in various branches of science and technology. A typical example of such use is magneto-resonance tomography, where the contrast of the object elements image under investigation essentially depends on the accuracy of measurements of the longitudinal and transverse relaxation times. In the practice of magnetic resonance in a condensed medium, to measure these characteristics, the pulse methods for detecting of the free precession and the spin echo signals are used [1]. Three radio pulses $\pi, \pi/2, \pi$ (or series $\pi, \pi/2, \pi, \pi/2, \pi, ...$) are used to measure the longitudinal relaxation time $T_1$. The first $\pi$-pulse inverts the magnetization vector, and it is set to a new value according to the law

$$M(t) = M_0 \left[ 1 - 2 \exp \left( - \frac{t}{T_1} \right) \right].$$

The second radio pulse $\pi/2$ induces a free precession signal after a time of $\tau$, the amplitude of which is proportional to the value of $M(t)$. In this case, the spin-lattice relaxation time is determined from expression (1) by fixing the free precession signal for different time intervals $\tau$.

The method of measuring the longitudinal relaxation time measuring also applies to the pulse methods of measuring [2], according to which the ratio of the signals corresponding to two fast consecutives (in comparison with the longitudinal relaxation rate) passing, divided by a time interval $\tau$, is measured. The signal observed during the first passing is proportional to the transverse macroscopic magnetization, which at the optimum transmission speed and the corresponding intensity of the radio-frequency field is $M_0 = \chi H_0$, where $\chi$ is the static nuclear susceptibility, $H_0$ is a constant magnetic field. The signal of the second rapid passing through the resonance in the opposite direction is proportional to the longitudinal component of the macroscopic magnetization $-M_x = -M_0 \left[ 1 - 2 \exp \left( - \frac{\tau}{T_1} \right) \right]$. For a symmetric passing of a constant magnetic field,
the nuclear magnetic resonance signal corresponds to the stationary value of the nuclear magnetization $M$, defined by expression

$$M = M_0 \frac{1 - \exp\left(-\frac{\tau}{T_1}\right)}{1 - \exp\left(-\frac{\tau}{T_1}\right)}$$  (2)

Making two measurements of the nuclear magnetic resonance signal amplitude with different values of $\tau$, we can thus determine the longitudinal relaxation time $T_1$.

The methods of determining the longitudinal relaxation time considered above are fundamentally ineffective in the nuclear magnetic resonance with the flowing proton-containing sample, because of the discrepancy between the experimental parameters and the required measurement accuracy.

The latter is due to the fact that the formulas (1) and (2) are valid for a flowing sample only if the time $\tau$ is much shorter, than the time of finding of the flowing fluid in the analyzer sensor $\theta$, which is directly determined by the sensor size and the fluid flow rate (otherwise, at $\theta << \tau$, a sample change occurs in the analyzer's sensor, which leads to a loss of information on the dynamics of macroscopic nuclear magnetization during the first passage through the resonance). As an example, let us take the case of an analyzer sensor volume of 1 cm$^3$ at a flow rate for a flowing sample of 50 cm$^3$/s, (corresponding to the maximum signal to noise ratio of nuclear magnetic resonance in a flowing medium). In this case, the time $\theta = 0.02$ s, that is, the time $\tau$, must be at least several times less than this value, for example, 0.005 s. It is easy to calculate from formula (2) that the change in time $\tau$, twice from 0.005 s to 0.01 s, corresponds to a relative change in the amplitude of the signals in only 0.2%, which is substantially lower than the error limits for measuring the amplitude of the nuclear magnetic resonance signal in the flowing sample. Therefore, to measure its longitudinal relaxation time, the method of preliminary polarization of the flowing liquid in a magnetizer is used and the magnetic resonance signal is processed, the value of which is determined by both the relaxation constants and the parameters of the experimental scheme.

In figure 1 is shown variant of such scheme, where the digits indicate: 1 – pipeline with the flowing liquid, 2 – magnet-polarizer, 3 - storage volume, 4 – magnet-analyzer, 5 – receiving coil, 6 – modulation coil, 7 – autodyne detector, 8 – sound generator. When the working fluid flows through the pipeline 1 in the storage volume 3, the flowing sample proton polarization takes place, which is detected by the magnetic resonance signal with the autodyne detector 7 and the standard magnetic field scanning technique in the magnet-analyzer 4.

![Figure 1. Experimental setup.](image)

In this case, the longitudinal relaxation time $T_1$ is determined by the following empirical formula [3]

$$T_1 = \frac{V_p}{q \ln \left(\frac{V_p + V_T}{V_T}\right)}$$  (3)
where \( V_p \) – is the storage volume, \( V_T \) – is the volume of the connecting pipeline between the storage volume and the receiving coil location area, \( q \) – is the flow rate near its values, corresponding to the maximum intensity of the NMR-signal in the autodyne detector.

Expression (3) makes it possible to estimate only the order of the \( T_1 \)-magnitude, since the functional dependence of the detected signal intensity on the flow rate near its optimal value is very shallow. For example, for the parameters of the experimental setup, \( V_p = 95 \text{ cm}^3 \), \( V_T = 4 \text{ cm}^3 \), and variations in the optimal value of \( q \) within the range of 20 to 30 \text{ cm}^3/s, the longitudinal relaxation time \( T_1 \) of water protons in accordance with expression (3) varies from 1 to 1.5 seconds.

2. Investigated method of \( T_1 \) measuring

In this paper, we proposed and tested the method of the relaxation times determining by comparing the NMR-signals from the standard flowing medium with the known value of \( T_1 \) and the flowing test sample according to the functional dependence of the detected signal amplitude by expression (1). To uniquely determine the test sample longitudinal relaxation time deviation from the standard sample, it is necessary to take into account the dynamics of the behavior of the nuclear magnetic resonance signal when the amplitude of the radio-frequency field produced by the receiving coil of the autodyne detector is varied. Such dynamics was manifested in the experiment when the amplitude of the magnetic field modulation in the magnet-analyzer changed. In this case, under conditions of a slow passing of the magnetic field near the resonant value the saturation factor \( \alpha = (\gamma H_1)^2 T_1 T_2 \) should be affected on the intensity of the detected signal, where \( \gamma \) – is the gyromagnetic ratio of the working substance atoms, \( H_1 \) – is the amplitude of the radio-frequency field in the receiver coil of the autodyne detector, \( T_1 \) and \( T_2 \) – are the longitudinal and transverse relaxation [4].

Obviously, the parameter \( \alpha \) should be inversely proportional to the modulation amplitude \( \beta = 1/\alpha \). For this case, under the assumption of the Lorentz form of the absorption line, it is easy to approximate the observed signal intensity dependence \( I \) in the function of the parameter \( \beta \) by the following formula

\[
I = \frac{6.7\beta^2}{(1+\beta^2)^3},
\]

where the coefficient 6.7 in the numerator is chosen from the normalization condition for the maximum signal intensity per unit. In accordance with this expression, the change in the test sample is equivalent to the change in the parameter \( \alpha \), the value of which can be varied by changing the amplitude of the modulation of the magnetic field \( H_1 \). Comparing the dependence (4) for two samples - the reference (with the known relaxation times \( T_1 \) and \( T_2 \)) and the investigated sample at a constant value of \( H_1 \), it is not difficult to determine the required relaxation constants. The reliability of this method can be demonstrated by the example for one flowing sample with fixed constants \( T_1 \) and \( T_2 \), but with different values of \( H_1 \).

The figure 2 (a) shows a typical oscillogram of the observed signal on water protons from the main line, where the constant \( T_2 \) is determined from the time of the observed relaxation beats decrease.
Figure 2 (a, b). (a) Oscillogram of the observed signal. (b) Experimental (points) and calculated (continuous line) dependences of the observed signal.

The extremely low modulation frequencies (~7 Hz) of the working magnetic field for two values of the radio-frequency field amplitude are used in the experiment – $H_1$ and $2H_1$. The amplitude of the observed signal was fixed (pick-to-pick) and the square of this amplitude was plotted as a function of the parameter $\beta$.

The corresponding experimental and calculated dependences of the observed signal are presented in figure 2 (b), which demonstrate their close correspondence near the $\beta$ values to the left of the values $\beta = 0.35$ and $\beta = 0.7$. The observed spread of experimental and calculated dependences to the right of the values $\beta = 0.35$ and $\beta = 0.7$ is definitely explained by noncompliance with the conditions of slow passage of the magnetic field through the resonance.

The transverse relaxation time $T_2$ was measured from the decay of the beat amplitude and was of the order of 1 ms for all test samples, which was caused by the influence of the magnetic field gradient in the magnet-analyzer. The longitudinal relaxation time of the standard sample was taken $T_1 = 0.65$ s, determined from expression (4) and with respect to which the values of $T_1$ of the test samples were measured. As the tested samples, alcohol and degassed water were chosen for which the measured relaxation times were found equal to 1.7 s and 3.8 s, respectively, which is in good agreement with the literature data.

3. Conclusion

The proposed modulation technique of the longitudinal relaxation time measuring can be required for the development of the proton-containing liquids small-sized relaxometers without attracting of the expensive high-resolution NMR equipment.
References

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