New method for determining concentrations of the mixture components during rapid control

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Abstract. The paper discusses the features of the signal registration of nuclear magnetic resonance in a weak magnetic field from small volume of condensed medium. Method for determining the state of condensed medium in express mode, using measured by nuclear magnetic resonance relaxation time constants T1 and T2, is proposed. We have developed the new method of determining the composition of the investigated mixture and relative concentrations of its components. That method is applicable for mixtures that formed by condensed media similar in both physical structure and chemical composition.

1. Introduction
One of the important directions of condensed media researches is the improvement of existing and development of new methods of rapid control [1–3]. For example, this is especially relevant for environmental monitoring of inaccessible areas of the water bodies and coastal zones, as well as in checking the quality of food products [3–5].

Nowadays requirements for methods of the rapid control became higher. Among them, for example, high measurement accuracy (error not exceeding 1.5%) and universality (method should be applicable for investigation of a large amount of media). However, there is one more criteria, and in most cases, it became primary. Investigation by the rapid control should not change the chemical composition and physical structure of the researched medium. This is required for obtaining confirmation about identified deviations in the sample of condensed medium (this is especially relevant in the customs control or verification of product quality) using the high-resolution spectrometers (e.g., multi-functional X-ray, optical or magneto resonance). Results of the medium researches in these devices provide comprehensive information about its composition. However, these devices are set in stationary laboratories (at significant distance from the place of rapid control conducting). In addition, they are expensive equipment that require special operating conditions and quite expensive for maintenance [1-5]. Therefore, it is desirable to load them only by samples, which shows a deviation from the standard state in order to confirm the results of the rapid control.

Such high requirements significantly restricts the possibility of use of the common rapid control techniques. For example, use of the small-sized optical devices (spectrophotometers, fluorimetric indicators, etc.) for investigation of the liquids with high turbidity require increasing in the laser power.
[4 6], which leads to the medium heating. Because of an increase in temperature, significant structural changes can occur in the environment, living in biological solutions organisms may die, etc.

The use of nuclear magnetic resonance phenomena for rapid control is one of the solutions to this problem, because researches carried out by nuclear magnetic spectroscopy do not make irreversible changes in the physical structure and chemical composition of the investigated medium.

Nevertheless, use of nuclear magnetic spectroscopy have a number of difficulties. Those difficulties related primarily to the fact that the weight of the magnetic system is the main part of the NMR spectrometer weight. In order to maintain mobility of devices for rapid control their weight should not exceed 4–5 kg. This has led to the fact that the NMR signal is registered in a weak magnetic field with induction \( B_0 \approx 100 \text{ mT} \) from small volume of liquid medium [1, 3, 5]. In such circumstances, the effective registration of the NMR signal from liquid medium should be carried out at the protons resonance frequency because protons have the highest sensitivity to the NMR method [3, 4, 7]. In the case of the NMR signal registration at the resonant frequencies of other nuclei signal/noise ratio (S/N) in most cases will be less than 1.3. This S/N value does not allow carrying out measurements with an accuracy higher than 1.5%. This fact eliminates the possibility of the spectrum registration from the investigated medium, as it is implemented in stationary NMR spectrometers [2–4]. Therefore, we developed a method of determining the state of the medium, based on measuring the time of longitudinal \( T_1 \) and transverse \( T_2 \) relaxation. The articles [3, 5] has showed that we can unmistakably determine the state of the medium only by using results of simultaneous measurements of both relaxation constants.

2. The compact nuclear magnetic spectrometer

To implement the proposed methodology of the rapid control of condensed media we have assembled compact layout of the NMR spectrometer, its structural diagram is shown in figure 1.

![Figure 1](image)

**Figure 1** Structural diagram of a small-sized NMR spectrometer: 1 — permanent magnet; 2 — neutral for the placement and alignment of the magnets; 3 — adjusting screws; 4 — locking device for the container with the investigated medium; 5 — container with the investigated medium; 6 — NMR signal registration coil; 7 — modulation coil; 8 — RF generator; 9 — autodyne detector (weak oscillation generator); 10 — processing and control unit; 11 — oscilloscope.

We have designed and manufactured compact magnetic system based on two flat (rectangular) samarium-cobalt magnets 1 (figure 1) with a platinum admixture. In addition, we have designed compact "neutral" 2 with adjusting screws 3 (figure 1) for aligning mutual arrangement of the magnetic system poles. The weight of proposed magnetic system design reduced to 2.8 kg, what corresponds to the requirements of mobility. In our NMR spectrometer design the distance between the magnet poles is 13 mm, magnetic induction \( B_0 = 52.8 \text{ mT} \), inhomogeneity \( 10^{-3} \text{ cm}^{-1} \), the frequency of the NMR signal registration from protons \( f_{\text{NMR}} = 2249 \text{ kHz} \).

Taking into account such conditions, signal registration is possible only with the use of modulation technique. The signals in this case are damped oscillations ("wiggles"). The implementation of pulse
methods that are used in stationary NMR spectrometers and relaxometers for registration of the NMR signal is extremely difficult in such small interpolar space [1, 3, 5]. Moreover, compact power sources cannot provide necessary energy for pulse methods for the NMR signal registration even for 20-30 minutes.

For NMR signals registration in a small magnetic system using the modulation technique we designed special probe (figure 2).

![Figure 2](image1.png)

**Figure 2** The measuring probe and container for medium

It includes registration coil 6, the modulation coil 7 and device for placing the container (cuvette) (figure 1, 2). The inner cuvette diameter is 3.2 mm; external diameter is 4.8 mm. In high-resolution NMR spectrometers diameters of the cuvette is about 3.0 and 4.6 mm. On figure 3 as example are shown NMR signals from synthetic motor oil ZIC XQ 5W-40 at a temperature T = 291.6 K.

![Figure 3](image2.png)

**Figure 3 (a, b)** Registered NMR signal from the engine oil: (a) — without accumulation; (b) — after accumulation

The analysis of presented in the figure 3 NMR signals shows that we have to use accumulation schemes, because without them it is impossible to be sure that the S/N ratio will be greater than 3.0 which is necessary for the measurement with an accuracy higher than 1.5%

It should also be noted that the use of a probe developed by us allows NMR signal registration from the investigated medium volume $V_R$ less than 0.3 ml. This is important because for precision measurement we have to know sample temperature. If the medium contains in a small volume, after 10–15 s its temperature becomes equal to air temperature, which we can measure using standard instruments with high precision. Use of small container with volume $V_R$ is one of the advantages of the compact NMR spectrometer in comparison with other devices.
3. Methods for determining the relaxation constants

To determine the transverse relaxation time $T_2$ we use a standard method based on the determination of the effective transverse relaxation time $T_2^*$ from the decay parameters of the line shape envelope of the registered NMR signal [1, 3, 5, 7]. Figure 4 shows an example of the construction envelope of the NMR signal from gel that contains protons.

![Figure 4](image_url)

**Figure 4** The line shape of the NMR signal registered from the gel at $T = 292.3$ K

Transverse relaxation time $T_2$ of investigated medium can be calculated using the ratio:

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

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

Almost all successfully used in high-resolution NMR spectrometers standard methods for determining $T_1$ cannot be implemented in compact NMR spectrometer, except one based on a Giulotto method [8]. But in this method it is necessary to register the shift of the resonance frequency, which in a weak magnetic field is about 0.1–0.2 Hz. Measuring this change in frequency is quite difficult even in the laboratory and almost unrealizable task in field conditions. That is why to determine the longitudinal relaxation time $T_1$ in a weak magnetic field we have develop the new technique. The amplitude of the registered NMR signal using a modulation method is proportional to the magnetization $M$ of the investigated medium nuclei. Registration of the NMR signal from the medium on a resonant frequency $f_{NMR}$ in a weak magnetic field carried out with the rapid passage through resonance, which corresponds to ratio [7, 8]:

$$H_1 \gg (|\gamma T_2^*|)^{-1}$$

In this case, the investigated medium magnetization $M$ in the registration coil will change as:

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

(1)

Then, for determination $T_1$ using (1) we have to measure NMR signal amplitude at two different $\tau = T_m/2$ ($T_m$ – modulation period of field $B_0$) and solve the system that consist of the equations (1) for various $\tau$. The resulting system of equations is easily transformed into:
where $A_{1,2}$ — the amplitude of the registered NMR signal for $\tau = \tau_{1,2}$ respectively.

The solution of system (2) for $T_1$ can obtained both numerically and graphically. To confirm the validity and reliability of used measurement techniques in compact NMR spectrometer we have determined relaxation constants for motor oil (figure 3): $T_1 = 1.021\pm0.005$ s and $T_2 = 720.36\pm3.59$ ms.

Also we have investigate same sample at the same temperature in a stationary NMR relaxometer Minispec mq20 (manufactured by BRUKER), measurement results: $T_1 = 1.0207\pm0.0021$ s and $T_2 = 718.94\pm1.44$ ms. The values of the relaxation constants matched within the measurement error.

4. The new method for medium components concentrations determining

Recently, during monitoring of the medium state using express methods, often occurs situations when it is desirable to make a decision at place of research, rather than wait for the results of additional studies from a stationary laboratory. This is especially relevant for express control of fuels and other hydrocarbon compounds. To solve this problem using the results of measurements by a small-size NMR spectrometer in the express mode, we developed a new method for processing the detected NMR signal of the medium. New method allows determining the concentration of components in the researched medium if it is formed by substances that are close in both chemical composition and physical structure (for example, a mixture of gasolines, oils or fats). In this case, there is no dissolution of one medium into another, and substances forms a conglomerate. The detected NMR signal from such mixture is the sum signal from each of the mixture components. We proposed a mathematical model that allows us to describe the detected NMR signal from the researched mixtures. The proposed model uses solutions of the Bloch equations in a rotating coordinate system [7, 8]:

$$\frac{du}{dt} + \frac{u}{T_2} + \Delta\omega \cdot v = 0$$

$$\frac{dv}{dt} + \frac{v}{T_2} - \Delta\omega \cdot u = -\gamma H_1 M_Z$$

$$\frac{dM_Z}{dt} + \frac{M_Z}{T_1} - \gamma H_1 v = \frac{M}{T_1}$$

where $\Delta\omega = \gamma H_0 - \omega$ — field frequency deviation from resonance, $M = \chi_0 H$ — magnetization of the investigated medium in the magnetic field of the spectrometer, $v(t), u(t)$ — absorption and dispersion signals.

In case of using a modulation technique to detect the NMR signal in a weak magnetic field, the value of $H$ varies as follows:

$$H = H_0 + H_m\sin(\omega_m t),$$

where $H_0$ — constant magnetic field, $H_m$ — modulation coil field, $\omega_m$ — modulation frequency (figure 1).

In this case, in the system of Bloch equations the change in the field frequency deviation from the resonance, with allowance for (4), will have the following dependence:

$$\Delta\omega = \gamma H_0 + \gamma H_m \sin(\omega_m t) - \omega$$

One of the features of registering the NMR signal in a weak magnetic field using the modulation technique is that registering should be performed only at the resonance frequency of medium. For most researched media, in the case of detuning the frequency of NMR signal registration $\omega$ from the resonance frequency $\omega_0$, the S/N ratio can become less than 1.3. With such value of S/N, the operation of the NMR
signal accumulation circuit will be ineffective (without accumulation it is impossible to measure the relaxation constants $T_1$ and $T_2$ with the required accuracy) \cite{3, 5, 6}. Therefore, to describe the detected NMR signal using the modulation technique, we can transform equation (5) to the following form:

$$\Delta \omega = \gamma H_m \sin(\omega_m t)$$  \hspace{1cm} (6)

At the resonant registering frequency $\omega = \omega_0$, taking into account (6), the system of Bloch equations (3) takes the following form:

$$u'(t) + \frac{u(t)}{T_2} + \gamma H_m \sin(\omega_m t) v(t) = 0$$

$$v'(t) + \frac{v(t)}{T_2} - \gamma H_m \sin(\omega_m t) u(t) - \gamma H_z M_z(t) = 0$$

$$M'_z(t) + \frac{M_z(t)}{T_1} - \gamma v(t) H_z - \frac{M}{T_2} = 0$$  \hspace{1cm} (7)

where $M = \chi_0 H_0 + \gamma H_m \sin(\omega_m t)$ — magnetization of the investigated medium in the magnetic field of the spectrometer, $\chi_0 = N(I + 1) \mu^2 / 3kT$ — statistical nuclear magnetic susceptibility, $N$ — concentration of paramagnetic particles; $\mu$ — particle magnetic moment; $k$ — Boltzmann’s constant; $T$ — absolute temperature.

This system of equations is solved for $v(t)$, $u(t)$ and $M_z(t)$ components, taking into account the initial conditions:

$$M_z(0) = \chi_0 H_0; \quad u(0) = v(0) = 0$$

The experimental researches carried out by us showed that the shape of the $G(t)$ line of the registered NMR signal from the substance in a weak magnetic field when tuning the autodyne detector circuit to the maximum of the S/N ratio is described by the following relation:

$$G(t) = \sqrt{A v^2(t) + B U^2(t)},$$  \hspace{1cm} (8)

where $v(t), U(t)$ — absorption and dispersion signals, $A, B$ — coefficients determining the contribution to the NMR signal of the absorption and dispersion signals.

The obtained solution (8), which is in good agreement with the experimental results, made it possible to develop a technique for simulating the detected NMR signal from the mixture, by dividing the received signal into signals from its constituent components. Following relation can represent the shape of the registered NMR signal $G_m(t)$ from the mixture:

$$G_m(t) = \sqrt{A_m u_m^2(t) + B_m U_m^2(t)} = \sum_{i=1}^{k} V_i \cdot N_i \sqrt{A_i v_i^2(t) + B_i U_i^2(t)}$$

$$\sum_{i=1}^{k} V_i = V_r$$  \hspace{1cm} (9)

where $v(t), U(t)$ — absorption and dispersion signals, $A, B$ — coefficients determining the contribution to the NMR signal of the absorption and dispersion signals ($m$ — mixture, $i$ — mixture components).

Since in the experiment all NMR signals, both from the mixture and its components, are formed in the same fields $H_0$, $H_1$ and $H_m$, the solutions obtained for their components $v(t)$ and $U(t)$ from the Bloch equations (7), differ only in the relaxation constants. For the mixture itself, $T_1$ and $T_2$ are determined by the NMR signal detected from it. In addition, we know relaxation constants for one of the mixture components, because initially this mixture should be this component in its pure form. The relaxation constants of the remaining components of the mixture, as well as the volumes in which they are contained in the researched medium, are chosen so that (9) is satisfied, the temperature of the researched mixture is known. When relation (9) is fulfilled, through relaxation constants we can determine mixture components, as well as their relative concentrations through their volumes.
Figure 5 shows, as an example, the possibility of determining the components and their concentrations in a mixture of two gasolines AI-95 and A-76.

![Figure 5](image)

**Figure 5** NMR signal line forms. Graph 1 corresponds to the experimental signal from a mixture of gasoline AI-95 and A-76 in the proportion of 75% to 25%. The NMR signal simulation: from pure gasoline AI-95 and A-76 - graphs 2 and 3, mixture of gasoline AI-95 and A-76 in a proportion of 75% to 25% - graph 4.

### 5. Conclusion
These results demonstrate that the proposed method allows determining composition and ratio between the components during rapid control of the conglomerates. This is greatly extends the functionality of the NMR methods for rapid control. Previously, measurements of $T_1$ and $T_2$ gave information only about the presence of deviation from the medium standard state and required its additional study in a stationary laboratory to make a reliable decision on the further use of this medium.

### 6. References
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