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A NEW NONDESTRUCTIVE METHOD FOR DETERMINING THE COMPOSITION OF COMPONENTS IN BIOLOGICAL OBJECTS IN EXPRESS MODE

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Abstract. A new method for determining the components composition and their concentration in express mode in biological objects and liquid suspensions is proposed. It allows us to measure not only the relaxation constants T_1 and T_2, using which it is possible to determine the deviation degree of the medium from the standard state, but also the concentrations of the components included in the medium composition, at the site of sampling by a compact NMR spectrometer.

Introduction

Currently one of the urgent problems before conducting experiments with various biological solutions and liquid media is defining their suitability in the express mode [1–6], characterized by the longitudinal and transversal relaxation times [6–10]. In addition, such control is, of course, should not cause any irreversible changes in the environment [1, 2, 4–7, 10–13]. This is especially important for the space station, where samples for various tests are delivered by cargo vessels passing through the various layers of the atmosphere, at high overloads, as well as different emergency situations arising while loading or unloading the vehicle may occur in the conditions of outer space. The samples for the study can be corrupted while you move them around the station or accidental violation of the storage conditions. Since in the space environment, long-term experiments are mostly carried out and hence using samples with deviations from the standard state, can lead to losses of time, and the failure of the planned scientific program of flight (stay time of the crew on the space station is limited and some experiments must be serial).

One of the possible solutions to this problem is the small-sized nuclear magnetic spectrometer (relaxometer) considered in [1, 5, 6]. We can determine the degree of deviation from the standard state in the express mode using measured values of the relaxation constants T_1 and T_2. Recently before conducting various studies, especially when working with biological solutions and suspensions, as well as acids and salts, it has increasingly become necessary to determine in express mode not only the medium state but also the components concentration of which it is made (e.g., HCl, NaF, NaOH or $FeCl_3$), acidity (pH), etc. Experiments have shown that this is especially important if the medium is used after prolonged storage, transportation, container changes, etc.

In previously developed NMR spectrometer (relaxometer), registration of the NMR signal was possible only at the resonant frequency f_P of protons contained in the researched medium. It did not allow solving new tasks of express control.

Compact NMR spectrometer and measurement methods

To solve the considered new problems, we developed a new small-size design of the magnetic system of the spectrometer and a scheme for registering the NMR signal (fig. 1)
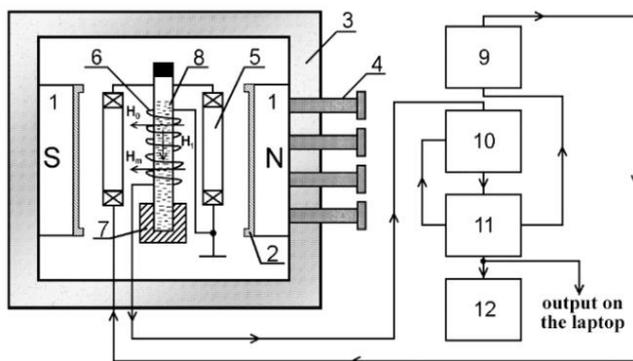

Fig. 1 Structural scheme of compact NMR spectrometer: 1 — permanent magnet; 2 — inserts; 3 — neutral for the placement and alignment of the magnets; 4 — adjusting screws; 5 — modulation coil; 6 — NMR signal registration coil; 7 — locking device for the container with the researched medium; 8 — container with the researched medium; 9 — RF generator; 10 — registration scheme; 11 — processing and control unit; 12 — oscilloscope.

In the new design of compact NMR spectrometer, S/N of the detected NMR signal is increased by 13 times by reducing the degree of inhomogeneity of the magnetic field more than tenfold and increasing the induction B_0 by several times in the registration coil placement area 6. This made it possible to register the NMR signal at the resonance frequencies of the other elements nuclei, for example, sodium or chlorine. For mediums consisting only of elements containing nuclei with magnetic moments (for example, HCl, NaF, or $ZnCl_2$) we have created a method that allows determining concentration of elements in a medium using amplitudes of the registered NMR signals from different nuclei.

However, the most significant result obtained on newly developed design is NMR signal registration with amount of "wiggles" (oscillating peaks) not less than six. This allows us to carry out many measurements with higher precision and to develop a new

method for determining components concentrations of a mixture, which is formed by substances that not enter into a chemical reaction (e.g., fats, multicomponent medical suspensions, oils, gasoline, etc.). NMR signal from such mixtures technique is the total signal from each of the components due to specific of its registration with use of modulation.

Our experiments showed that the shape of the line $G(t)$ 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:

$$G(t) = \sqrt{Av^2(t) + BU^2(t)}, \tag{1}$$

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

The obtained solution (1), 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 expression can represent the shape of the registered NMR signal $G_m(t)$ from the mixture:

$$\begin{aligned} G_m(t) &= \sqrt{A_m v_m^2(t) + B_m U_m^2(t)} \\ &= \sum_{i=1}^{k} V_i \cdot N_i \sqrt{A_i v_i^2(t) + B_i U_i^2(t)} \\ &\sum_{i=1}^{k} V_i = V_r \end{aligned} \tag{2}$$

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

In our case the only thing that influences on $v(t)$ and $U(t)$ is the relaxation constants. For the mixture itself, T_1 and T_2 can be determined using 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

(2) is satisfied, the temperature of the researched mixture is known. When eq.

(2) is fulfilled, we can determine mixture components through relaxation constants, as well as their relative concentrations through their volumes.

Results and discussion

Fig. 2 shows the sodium NMR signals from sodium hydroxide NaOH registered by the NMR spectrometer of new design.
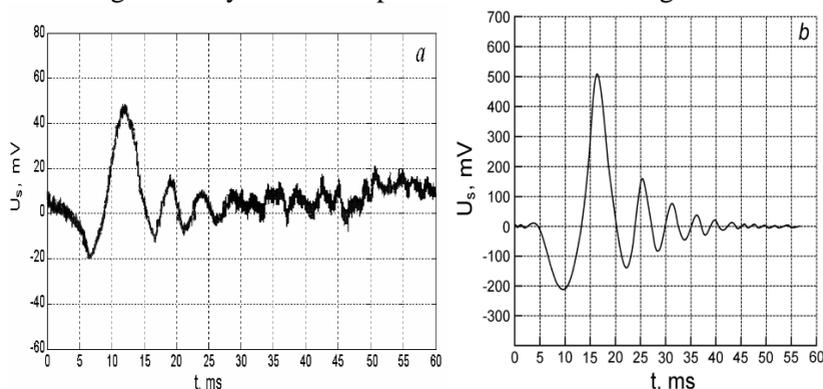

Fig. 2 The registered NMR signal from sodium hydroxide at T = 291.3 K: a) without accumulation; b) output of accumulation scheme.

The analysis of NMR signals presented in fig. 2 shows that when they are registered at the resonance frequency of sodium nuclei ω_{Na}, signal-to-noise ratio is more than 1.3. This makes it possible to perform the AFC on the resonance of sodium nuclei. However, it is impossible to carry out measurements of T_1 and T_2 with an error no more than 1.0% (which is necessary for unambiguously determining the medium state [1–4, 6, 8]) without usage of an accumulation scheme since the SNR is less than 3.0 (fig. 2, a). In addition, there are

120

noises at peaks of the NMR signal. The subsequent accumulation of the NMR signal makes it possible to obtain SNR > 10.0 (fig. 2, b), which ensures measurement of T_1 and T_2 with the required accuracy. Moreover, the relative concentrations of protons and sodium in sodium hydroxide can be determined using ratio of their amplitudes U_s in registered NMR signal.

Fig. 3 gives an example of the possibility of determining the components and their concentrations in a mixture of two gasolines AI-95 and A-76 using our method.
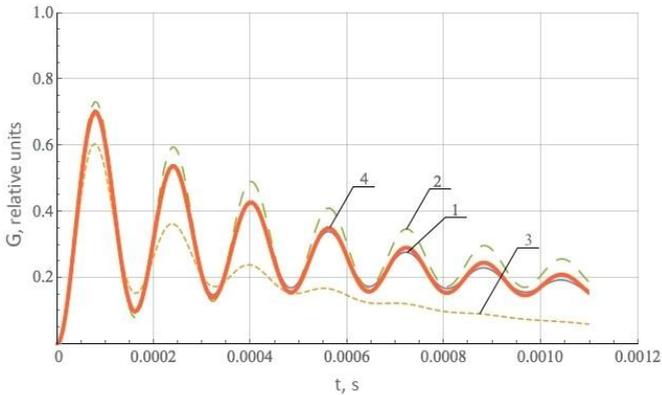

Fig. 3 NMR signal line forms. Graph 1 corresponds to the experimental signal from a mixture of gasoline AI-95 and A-76 (75 to 25 %). The NMR signal simulation: from pure gasoline AI-95 (2) and A-76 (3), mixture of gasoline AI-95 and A-76 75:25% (4).

Comparison of the results of NMR signals simulation from gasoline AI-95 and A-76, as well as their mixture, with experimental data shows the reliability of proposed method. The calculated concentrations of gasolines AI-95 and A-76 in the studied medium are in agreement with the concentrations which we have used to prepare this mixture within the measurement error.

Conclusions

The obtained results show that the usage of proposed method while carrying out studies with a new design of a small-size NMR spectrometer allows obtaining information on the composition of the medium at the site of sampling, and making conclusions about its

further use without additional measurements in a stationary laboratory. Earlier in [1, 5, 6], the measurements of T_1 and T_2 provided information only on the presence of deviation from the medium standard state that required its additional study in a stationary laboratory to make a reliable decision on the further use of this medium.

In addition, in the new design of the spectrometer, the NMR signal registration from various magnetic nuclei expands its functional capabilities greatly both in the number of possible studied mediums and in the information obtained about the state of the medium.

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