Express – control of biological solutions by portable nuclear – magnetic spectrometer

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Abstract. The portable nuclear–magnetic spectrometer for express control of biological solutions and ecological monitoring is presented. The designed construction of nuclear–magnetic spectrometer allows measuring longitudinal relaxation time $T_1$ and transverse time $T_2$ of condensed media in low magnetic field $B_0 = 62$ mTl. The presented nuclear magnetic resonance signal accumulation scheme can measure the relaxation times of small amounts of liquid media (1 ml).

1. Introduction
Express-control of biological solutions is actual task for ecological monitoring of liquid media. The longitudinal relaxation time ($T_1$) and transverse time ($T_2$) of condensed media give information about impurities presence, changes of chemical composition and other changes of medium state. Multifunctional X-ray, optical and magnetic resonance spectrometers provide precise analysis of liquid media but they are expensive, power consuming and not portable.

It is known that state of liquid medium can be evaluated by analysis of shifts in temperature, $T_1$ and $T_2$ relaxation times in comparison with initial values [1-4]. The valid method of analysis should include simultaneous measurement of $T_1$ and $T_2$ [2-6]. But commercially-available portable nuclear – magnetic spectrometers usually measure only $T_2$ time, and the weight of the spectrometers for simultaneous measurement of $T_1$ and $T_2$ is usually higher than 40 kg.

Development of small portable spectrometer for preliminary express analysis of biological media or water in field conditions is actual task for timely ecological monitoring. We report about a new construction of portable nuclear – magnetic spectrometer for analysis of longitudinal relaxation time and transverse time of small amount of condensed liquid media (1 ml) in low magnetic field ($B_0 = 62$ mTl).

2. The construction of portable nuclear – magnetic spectrometer
Based on our previous work a new construction of compact spectrometer on the nuclear-magnetic resonance (NMR-spectrometer) was developed.

The structural scheme of the designed NMR-spectrometer is presented in figure 1.
Figure 1. Block scheme of NMR spectrometer: 1 – permanent magnet, 2 – container with test media, 3 – coil for NMR signal registration, 4 – fixing gripper for container, 5 – modulation coil, 6 – radiofrequency generator, 7 – weak fluctuations generator (autodyne receiver), 8 – processing and control equipment, 9 – conversion diagram.

It is known that magnet systems make the main contribution to weight of the devices based on NMR effect [1,5-6]. So, the miniaturization of the spectrometer is related to reduction of magnets size. In this situation the modern high-energy magnetic materials with high level of magnetic field induction and homogeneity should be used.

In the presented construction of the device the distance between the magnetic poles is 12 mm, the magnetic field induction is $B_0 = 62$ mTl, inhomogeneity level is $0.5 \times 10^{-3}$ cm$^{-1}$ and frequency of NMR signal registration is $f_{\text{NMR}} = 2614$ kHz.

The NMR signal in weak field $B_0$ was registered by coil for NMR signal registration (3) and the developed weak fluctuations generator (7). The special models of the coil and autodyne receiver allowed us to measure signal from minute volumes of liquid media (1 – 1.5 ml). The circuit of weak fluctuations generator (autodyne) was based on the differential stage with planar field-effect transistor with drain detection and amplification of NMR signal. The autodyne receiver based on suggested scheme is characterized by steady operation in broad band and has high level of common noise suppression.

3. Results and discussion
In figure 2 the NMR signal on generator output is presented. The signal was registered in wide bandwidth (10 kHz) with modulation frequency $f_{\text{mod}} = 50$ Hz.
The shape of NMR signal line is approximated by function [7,8]:

\[ U_c(t) = U_0 e^{-t/T_2^*} \cdot \cos \left( \frac{at^2}{2} \right), \]

where \( U_0 \) is the maximal value of signal amplitude, \( T_2^* \) is the effective transverse relaxation time, \( a \) is the rate of magnetic field detuning change. The rate of magnetic field detuning change is defined by:

\[ a = \gamma \frac{\partial H_z}{\partial t} = \partial \left( \frac{\Delta \omega}{\partial t} \right), \]

where \( \gamma \) is the nuclear gyromagnetic ratio, \( \Delta \omega \) is the resonance frequency detuning.

The effective transverse relaxation time \( T_2^* \) is calculated from the envelope curve decay (dashed line in figure 2). The transverse relaxation time \( T_2 \) is defined by:

\[ \frac{1}{T_2^*} = \frac{1}{T_2} + \frac{\gamma \Delta H}{\pi}, \]

where \( \Delta H \) is the magnetic field nonuniformity in the area of NMR signal registration coil.
The Julotto method for registration of NMR signal in weak magnetic field was implemented for the first time. The method was used for registration of $T_1$.

Let us consider the periodic modulation which is symmetric with respect to:

$$B_0 = f_{NMR}/\gamma.$$  

The maximal amplitude of the signal is registered if time between two resonance crossings is much more than $T_1$. Otherwise the registered NMR signals decrease according to:

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

where $M$ is the value of magnetization (which is directly proportional to amplitude of the signal), $\tau$ is modulation period, $M_0$ is the magnetization of liquid medium in the absence of magnetic field modulation:

$$M_0 = \chi_0 B_0,$$

where $\chi_0$ is the static nuclear magnetic susceptibility.

From equation (1) it follows that for computation of $T_1$ it is necessary to measure NMR signal amplitude at two different modulation frequencies (which correspond to different modulation period $\tau$). $T_1$ is usually defined graphically.

Size reduction of registration coil allowed us to decrease $\Delta H$, improve accuracy of $T_2$ measurements and decrease the sample volume to $1 \text{–} 1.5 \text{ml}$. But it caused the signal to noise ratio degradation. To solve this problem a new process and control unit (based on microcontroller STM32) was developed. The process and control unit use the effective signal-summing scheme and can regulate the parameters for optimal registration of the signal. The microcontroller stores the signal to suppress the noise, and at necessary level of signal to noise ratio the process and control unit calculates the relaxation times. The advantage of suggested approach is the flexible system of signal-summing, which provides the optimal choice of accumulation cycles number and save measuring time.

The experimental results showed that the spectrometer can measure the longitudinal relaxation time $T_1$ from 1 ms to 20 s, the transverse time – from 0.5 ms to 4 s. The relative error of measured parameters was less than 1 %. The operating range of temperatures of the spectrometer is $4\text{–}45^\circ C$.

The obtained experimental results confirmed effectiveness of developed spectrometer for measurement of $T_1$ and $T_2$ relaxation times for biological liquids and showed possibilities of detection impurities in low concentration.

4. Conclusion

The portable nuclear–magnetic spectrometer for express control of biological solutions and ecological monitoring is presented. We developed the scheme of autodyne receiver based on differential amplification stage for signal detection, which increase signal to noise ratio and save measuring time.

The main advantages of the device are the possibility to analyze small amounts of liquid media (volume is about 1 ml), short time of measurements, transportability and capability of field analysis.

References

[1] Davydov V V and Karseev A U 2013 Proc. of XIV Int. Environmental Forum Baltic Sea Day “BSD’13” 13 34
[2] Davydov V V 1997 J. Phys. B: Atomic, Molecular and Optical Physics 30 3993
[3] Chen B, Ivanov I, Klein M L and Parrinello M 2003 Phys. Rev. Lett 91(21) 2155
[4] Davydov V V, Dudkin V I and Karseev A U 2013 Opt. Mem. & Neural Networks (Information Optics) 22 112
[5] Lopez E, Ortiz W and Quintana I M 1998 Chemical Physics Letters 287 429
[6] Davydov V V 1998 Int. J. of Modern Phys. 7 798
[7] Abragam A 1963 Nuclear magnetism 646
[8] Leshe A 1963 Nuclear induction 684