Features of spectral analysis of nuclear magnetic resonance signal for express-control of hydrocarbon media

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Abstract. The article substantiates the need to study the structure of the nuclear magnetic resonance signal recorded using the modulation technique. The features of registration of the nuclear magnetic resonance (NMR) signal using the modulation technique, which are both in the current and in the stationary state, have been established. The influence of the properties of the medium on the features of recording the NMR signal has been determined. A new method is proposed for determining the contributions of absorption and dispersion signals to the recorded NMR signal. The features of the use of spectral analysis in the study of the NMR signal from hydrocarbon media have been determined. The results of experimental studies are presented.

1. Introduction

The development of science and technology has led to the emergence of a large number of problems in applied physics related to the control of the state of condensed media [1-10]. There are a number of difficulties in the development of fast and reliable methods of express control [2, 7, 11-15]. Measurements that are used for express control should not change the physical structure and chemical composition of the investigated medium [2, 7, 11, 16-24]. The fulfillment of this condition is possible when devices are used for express control, the principle of operation of which is based on the phenomenon of nuclear magnetic resonance (NMR) [24-32]. Other types of devices for express control of condensed media (optical, ultrasonic, X-ray, etc.) fulfill this condition when they work with a certain class of media [18, 32-35].

On the other hand, there are a number of limitations when using devices based on the phenomenon of nuclear magnetic resonance. One of them is associated with the registration of an NMR signal in a weak magnetic field. This does not allow obtaining the NMR spectrum from the studied medium [2, 7, 31-33, 36, 37]. All information about the composition and structure of the studied medium is contained in the registered NMR signal in the form of "wiggles". Therefore, the purpose of this work is to develop a method using spectral analysis to obtain the necessary information about the state of the medium from the recorded NMR signal from it using a modulation technique. And the purpose is to determine the features of its application for various conditions of physical experiments and compositions of the medium. Particular attention is paid to hydrocarbon media and their mixtures.
2. Features of the use of spectral analysis to decipher information about the state of the medium in the NMR signal recorded in a weak magnetic field

In [31, 32, 36-41], the Bloch equations obtained after substitution of coefficients that take into account the registration of the NMR signal using the modulation technique are considered in detail. They also substantiate the mathematical relation for constructing the NMR signal waveform recorded using an autodyne detector:

\[ G(t) = F(t)(\frac{A}{A+B}u^2(t) + \frac{B}{A+B}u(t))^{1/2} \]  \hspace{1cm} (1)

where \( u(t) \) and \( u(t) \) are the absorption and dispersion signals, \( A \) and \( B \) are the coefficients that determine the contribution to the recorded NMR signal from the absorption and dispersion signals, and \( F(t) \) is the coefficient taking into account phase changes.

As a result of the studies carried out, NMR signals from water were recorded, and their shapes were constructed using (1) and (2). This made it possible to establish that the value of the coefficient \( F(t) \) depends on many factors (temperature, composition of the medium, etc.). Therefore, for each case of studying a medium or a mixture of media in the express mode, it is necessary to select \( F(t) \). This can lead to large time delays or errors in research and interpretation of results. In addition, in the above description of the NMR waveforms with increasing \( t \), every \( T_m/2 \) changes in the signal phase by 180° and a successive decrease in the amplitude of the peaks occurs. In the experiment, the same NMR signal is recorded every half-period \( T_m/2 \) of the modulation field \( H_0 \). This discrepancy between theory and experiment, the previously noted difficulties with the choice of the coefficient \( F(t) \) does not allow the results of the experiment to be fully displayed.

Therefore, to solve this problem, we proposed to use spectral analysis, especially for hydrocarbon media, in which there are a number of features. The most important for express control is associated with the fact that when mixed, these media do not enter into a chemical reaction with each other. They form a conglomerate (for example, a mixture of gasoline, kerosene and gasoline, etc.). Each of the components of the mixture exists independently and can be isolated from the general mixture.

Another feature of spectral analysis is that the recorded NMR signal is a non-periodic oscillation in the form of damped peaks. Therefore, we use the discrete Fourier transform to describe it, as well as the calculated absorption and dispersion signals:

\[ y_k = \sum_{n=0}^{N-1} x_n e^{-j2\pi kn/N} \] \hspace{1cm} (2)

where \( n = 0, 1, 2, ..., N-1 \), \( x_n \) is the input data sequence, \( N \) is the number of elements of the input data sequence \( x_n \).

The harmonics of the spectrum are located on the frequency axis with a discrete \( \Delta f = f_s/N \), where \( f_s \) is the sampling frequency of the original sequence \( x \). The sampling rate is determined as follows. Let \( \tau \) be the duration of the NMR signal. Then \( f_s \) can be calculated using the following relation:

\[ f_s = N/\tau \] \hspace{1cm} (3)

In the case where \( N \) is a power of two, DFT is calculated by the FFT algorithm (Fast Fourier Transform), which is significantly faster discrete Fourier transform and requires fewer computational resources.

The discrete Fourier transform is symmetric with respect to the Nyquist frequency equal to \( f_s/2 \), which allows to combine the harmonic numbers \((N/2-k)\) and \((N/2+k)\). As a result of combining the harmonics, a one-sided complex spectrum is obtained with frequencies from 0 to \( f_s/2 \), which corresponds to the indices \( k = 0 \ldots (N/2-1) \). The scaled-sided complex spectrum of the discrete input sequence \( x_n \) is given by:
\[
\begin{align*}
  y_k &= \begin{cases} 
    y_0 & k = 0 \\
    \sqrt{2} \frac{y_k}{N} & k = 1, 2, \ldots, \left\lfloor \frac{N}{2} - 1 \right\rfloor 
  \end{cases} 
\end{align*}
\]

(4)

In relation (4), the operation in brackets \([N/2-1]\) means rounding to the nearest smallest integer. Accordingly, the amplitude spectrum \(S\) is the modulus of the one-sided complex spectrum, the phase spectrum \(P(f) = \arg y_k\) is its argument, where \(f = k \Delta f\).

3. Study of the spectra of the NMR signal taking into account the determination of the contributions of the absorption and dispersion signals

In case is recording an NMR signal in a weak magnetic field, the parameters of the autodyne detector and the modulating magnetic field are adjusted to the maximum \(S/N\). In this case, the signals \(u(t)\) and \(\upsilon(t)\) take part in the formation of the NMR signal. In figure 1 shows NMR signals from oil and kerosene as an example.

![Figure 1](image1.png)

Figure 1. The NMR waveforms from: a) oil, b) kerosene.

Analysis of the received signals shows the absence of a period by the location of the decaying peaks. In figure 2 shows the amplitude spectra of NMR signals recorded from a sample of oil and kerosene, obtained using relations (2) - (4). In figure 2 and 3 shows the phase spectra of the NMR signal from a sample of oil and kerosene.

![Figure 2](image2.png)

Figure 2. The amplitude spectra from the experimental NMR signal recorded from: a) oil, b) kerosene.
Figure 3. The phase spectra of the NMR signal from: a) oil, b) kerosene.

To obtain information on the contributions of absorption and dispersion signals to the recorded NMR signals, it is necessary to calculate the values of $\nu(t)$ and $u(t)$ using the Bloch equations. In figure 4 shows the calculated dependences $\nu(t)$ and $u(t)$ for oil as an example.

Figure 4. The calculation forms of NMR signals from oil: a) absorption, b) dispersion.

For absorption and dispersion signals, the amplitude and phase spectrum is calculated (figure 5 and 6).

Figure 5. The amplitude spectra of the NMR signal from oil: a) absorption, b) dispersion.
Comparison of the obtained results showed that the spectral components of the amplitude and phase spectrum can be expressed in terms of the spectral components of the amplitude and phase spectra from the signals $u(t)$ and $u(t)$. The coefficients that will determine this relationship will be the contribution of these signals to the recorded NMR signal.

4. Conclusion
As a result of experiments, it was found that the spectral method developed by the research has no restrictions on use. For its application must register the NMR signal from the medium containing nuclei with magnetic moments, for example, at the resonant frequency of protons (in the more than 99% of liquid media include protons) and to measure $T_1$ and $T_2$ relaxation constants to calculate the dispersion and absorption signals.

It should be noted that the registration of the NMR signal in a weak field is carried out at a maximum signal/noise ratio signal. In this case, the absorption signal is always greater than the dispersion of the signal, the coefficients are determined uniquely. In the study of such mixtures number of coefficients increases, moreover appear coefficients corresponding media concentrations in the mixture. Their determination allows one to identify the composition and concentration of the components in the mixture.

Since in mixtures from hydrocarbon media the contributions to the recorded NMR signal from protons are determined in proportion to the concentrations of the media in the mixture, it is possible to unambiguously determine the coefficients in the spectra and identify the composition and concentration of the components in the mixture.

Acknowledgments
The reported study was funded by RFBR according to the research project № 20-32-90012.

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Makeev S S, Grevtzeva A S, Glinushkin A P and Matorin D N 2020 Journal of Physics: Conference Series 1695(1) 012112