Synthesis of compact patterns for NMR relaxation decay in intelligent "electronic tongue" for analyzing heavy oil composition

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Abstract. The article is devoted to the problem of pattern creation of the NMR sensor signal for subsequent recognition by the artificial neural network in the intelligent device "the electronic tongue". The specific problem of removing redundant data from the spin-spin relaxation signal pattern that is used as a source of information in analyzing the composition of oil and petroleum products is considered. The method is proposed that makes it possible to remove redundant data of the relaxation decay pattern but without introducing additional distortion. This method is based on combining some relaxation decay curve intervals that increment below the noise level such that the increment of the combined intervals is above the noise level. In this case, the relaxation decay curve samples that are located inside the combined intervals are removed from the pattern. This method was tested on the heavy-oil NMR signal patterns that were created by using the Carr-Purcell-Meibum-Gill (CPMG) sequence for recording the relaxation process. Parameters of CPMG sequence are: 100 µs - time interval between 180° pulses, 0.4s - duration of measurement. As a result, it was revealed that the proposed method allowed one to reduce the number of samples 15 times (from 4000 to 270), and the maximum detected root mean square error (RMS error) equals 0.00239 (equivalent to signal-to-noise ratio 418).

1. Introduction
The electronic tongue (e-tongue) is a device that is designed for the analysis and comparison of chemical compositions of liquid and solid objects. The application area of this device type is very wide, it includes: the composition analysis of a drinking water [1], the foods analysis (wine, tea) [2, 3], analysis of the human body tissues [4], control of the composition of raw materials in the oil industry [5], detection of traces of pesticides and toxic agents in water and soil [6].

In the classical version of the e-tongue, the acquisition information devices are voltammetric sensors, chemoresistors, sensors based on ion-selective field effect transistors [7]. Usually, each electrochemical sensor responds to one kind of molecules or ions, and a required condition for its operation is the contact between the sensing element and the analyzed object. The analysis by these sensors is extremely difficult for solid object. An alternative type of sensors without these drawbacks are sensors based on the nuclear magnetic resonance (NMR). They have more possibilities for nondestructive analysis of the objects composition. However, in scientific works, devoted to the design of e-tongue device, the NMR-based sensors are often found as unsuitable because of high cost,
long processability, and low in situ measurability [8]. But the current level of development of low-field NMR sensors allows one to refute these statements [9] and to substantiate its use in the modern e-tongue.

Usually, the following methods are used to analyze signals from sensors and recognition object composition: principal component analysis (PCA), cluster and hierarchical cluster analysis (CA, HCA), a support vector machine (SVM), various regression methods and artificial neural networks [10]. The method based on the use of artificial neural networks is very promising for intelligent devices such as the e-tongue, since it allows them to be "trained in the operation process ".

The present article is devoted to an important problem such as removing redundant data from a signal pattern. Their presence causes the need for additional computing resources in the operation of e-tongue device, which will be discussed follow of the article. This is especially important in the process of objects (for example, oil and petroleum products) composition analysis by measuring the spin-spin relaxation time of NMR, since the relaxation decay curve obtained by recording the spin echo upon excitation by standard RF-pulses can contain several thousand samples.

2. Features of the e-tongue device based on NMR
The structure of the e-tongue device based on NMR and the signal recognition by an artificial neural network (Figure 1) can be represented by three main elements. First, it is a measuring system consisting of the transmitter of stimulating RF pulses, an NMR sensor with the analysis object that is placed in its magnetic field, and the NMR signal receiver.

The transmitter generates sequences of RF pulses that create an alternating magnetic field in the NMR sensor coil with Larmor precession frequency \( \omega_L \), which depends on the intensity of the permanent magnetic field. These pulses stimulate the rotation of the macroscopic magnetization vector, the signal from which is received by the receiver using of the same coil. The receiver digitizes and transmits it to creating a signal pattern. The low-field NMR sensor makes it possible to create two types of signal pattern: the pattern of the free induction decay (FID) and the pattern of the spin-spin NMR relaxation. Discussion of the FID pattern will be left for the future scientific works. The present article is devoted the spin-spin relaxation decay pattern synthesis.

![Figure 1. The structure of the e-tongue device based on NMR and an artificial neural network](image)

The pattern of the spin-spin relaxation of liquid components with long relaxation times is recorded as a relaxation decay curve from the results of spin-echo stimulation using a specialized pulse sequence containing one 90° pulse and a sequence of 180° pulses. An example of the classical CPMG sequence [11] is shown in Figure 2.
The created patterns of the relaxation decay can be entered to the input of an artificial neural network without pre-processing. However, they are often pre-processed, in particular, to remove redundant data.

3. Formulation of the problem
To record the NMR relaxation decay curve, in analyzing the physical-chemical composition of oil and other objects, the sequence of CPMG pulses is used with intervals of $2\tau$ equal to 100 $\mu$s or 200 $\mu$s between 180° pulses [12]. The pattern of the acquired decay curve can consist of 2000 or 4000 samples provided that the time of recording relaxation process in heavy oil equals 0.4 s.

Due to the NP-complexity of the recognition problem, its solution is executed traditionally using high power computers. The problem is that the existing algorithms for processing a large amount of information, including the use of artificial neural networks, are laborious for performing on-site generation of sensory data. In measuring devices that are used at the place of measurement, low-power processors and microcontrollers are usually used. Thus, real-time information processing on the site of its acquisition system is impossible, on the one hand, and, on the other hand, access to remote computing powers leads to both high energy consumption and loss of data, which ultimately results in a loss of accuracy recognition. Also, if classical artificial neural network is used for recognition then the number of inputs of the neural network increases, which increases the need for computing resources during its operation and training. These facts require reducing the volume of data of recognizable signal patterns without loss of information.

The methods based on the non-regular sampling of the signal can be used for these purposes. They are published in modern scientific papers that devote to signals pre-processing in two-dimensional NMR techniques [13]. These methods are usually based on removing a part of the samples randomly, but usually, the smaller the amplitude of the signal, the more samples are removed [14,15]. These approaches are inconvenient in the synthesis of the signal pattern for its recognition by an artificial neural network, because the procedure for recovering partially distorted information takes place either on the neural network itself or on preprocessing procedures.

Thus, there is a problem of creating the method that allows removing samples in the spin-spin relaxation signal pattern without introducing additional distortion, in fact, removing redundant data.

4. Mathematical base of proposed method
The spin-spin NMR relaxation decay of liquid objects is described by the equation (1):

$$A(t) = \sum_{i=1}^{n} A_{0i} \times e^{-\frac{t}{T_{2i}}},$$

where $A_{0i}$ is FID signal amplitude of the $i$-th component at time $t = 0$ (after the first 90° pulse); $n$ is number of components in the object; $t$ is time; $T_{2i}$ is spin-spin relaxation time of the $i$-th component.
The relaxation process is described for each \( i \)-th component by an inverse exponential decay curve. Therefore, the signal increment between two neighboring points’ \( t_1 \) and \( t_2 \), digitized with the intervals of \( 2\tau \), will be less than the average noise value \( N_s \) of the measuring system (equation (2)). That is, it does not make sense to include the samples in relaxation decay pattern acquired with interval \( 2\tau = t_2 - t_1 \), thus it is required to increase the value of \( \Delta t \):

\[
N_s > \Delta A(t_1, t_2) = A_0 \times (e^{-\frac{t_2}{T_2^i}} - e^{-\frac{t_1}{T_2^i}})
\]  

(2)

Let us solve equation (3) for \( \Delta t \) to estimate the minimum value of \( \Delta t \) at any time \( t_j \):

\[
-A_0 \times (e^{-\frac{t_j + \Delta t}{T_2^i}} - e^{-\frac{t_j}{T_2^i}}) = N_s
\]  

(3)

The minus sign indicates a negative value of the increment in the relaxation decay curve. As a result, let us obtain equation (4) for estimating minimum \( \Delta t_{i,\text{min}} \):

\[
\Delta t_{i,\text{min}}(t_j) = -T_2^i \times (\ln(1 + e^{-\frac{t_j}{T_2^i}}) + \frac{t_j}{T_2^i}),
\]  

(4)

where \( N_f = \frac{N_s}{A_0} \). The results of the calculations are significant only if \( e^{-\frac{t_j}{T_2^i}} > N_f \).

At result, the following method is suggested:

1. Creation of the mathematical model the relaxation decay for objects consisting of \( n \) most expected \( i \)-th components with spin-spin relaxation times \( T_2^i \).

2. Calculation in accordance with equation (4) of the minimum durations of intervals \( \Delta t_{i,\text{min},j} \) for each \( i \)-th sample at time moments \( t_j \), starting with \( t_0 = 0 \) and with increment \( t_j = t_{j-1} + 2\tau \).

3. Synthesis the graph of minimum interval values \( \Delta t_{i,\text{min},j} \) for the total decay curve at each time moment \( t_j \) with the condition that \( \Delta t_{i,\text{min},j} \) is the nearest larger for \( \Delta t_{i,\text{min},j} = \min_{v=0}^{n-1}(\Delta t_{i,\text{min},v}) \) and multiple of \( 2\tau \).

4. Synthesis the grid of intervals \( \Delta t_k \) in conformity with the obtained graph by following \( t_j \) from \( t_0 \). As a result, a part of intervals \( \Delta t_k \) will have duration of more than \( 2\tau \) (Figure 3).

The created grid will be used to remove from the signal pattern the samples obtained with an interval of \( 2\tau \) but located inside the \( \Delta t_k \) intervals (the empty circles in Figure 3). It is important to note that the training of the artificial neural network is required after calculating the grid of intervals \( \Delta t_k \) and signal patterns should be created conformity with this grid. If for some cause the grid is changed, then the artificial neural network will need to be retrained.
5. Results and Discussion

The proposed method was tested by computer-based mathematical modeling using the SciLab software [16]. The authors used as input data both artificial mathematical models of the relaxation decay and the heavy oil relaxation decay curve. The root-mean-square error (RMSE) between the relaxation decay and its patterns synthesized during digitization with a base interval of \(2\tau\) (RMSE1), and after removing samples by the considered method (RMSE2) is taken as a measure of error.

During the testing, grid \(\Delta t\) was synthesized for the most expected relaxation decay curve of heavy oil components [17]. The duration for the detecting process of the relaxation decay was chosen equal to 0.4 s, basic step \(2\tau\) equal to 100 \(\mu s\), the signal-to-noise ratio of the measuring system was accepted no more than 200, although often it is not more than 100 [18].

As a result of the formation of the grid, the number of significant samples including the pattern is equal to 270, which is much less than 4000 samples that contain the pattern digitized with selected base interval \(2\tau\). The relative values of the RMSE1 and RMSE2 for the relaxation decay patterns synthesized by digitizing using a base step of \(2\tau\) and step \(\Delta t\) for objects with the different components population \(P(i) = \frac{A_i}{A_0}\), where \(A_0\) is the initial amplitude of the \(i\)-th component) and relaxation time \(T2(i)\) are shown in Table 1. The first four items of the table show the parameter extreme values of the four main liquid groups of heavy oil components. In items 5 and 6, additional components with relaxation times are modeled, which were not taken into during the synthesis of the grid, but these components are also possible in the analyzed objects.

As a result, it was noted that the relative RMSE for the pattern constructed with the grid of \(\Delta t\) did not exceed 0.00239, which is equivalent to the signal-to-noise ratio 418. At the same time, the number of samples in the relaxation decay pattern decreased by approximately 15 times (from 4000 to 270).

To test the method on a real sample, the relaxation decay curve acquiesced during the analysis of heavy oil from the Ashalchinsky field of the Russian Federation Tatarstan Republic by the Proton-20M NMR-relaxometer was used.

Table 1. Results of testing on the relaxation decay mathematical models for different oil compositions.

| Parameters of the object components: | \(T2(i)\) – the relaxation time of the \(i\)-th component (ms); \(P(i)\) – the population of the \(i\)-th component. |
|--------------------------------------|--------------------------------------------------------------------------------------------------------|
|                                       | \(\frac{RMSE1}{RMSE2}\)                                                                                   |
| Original pattern with grid of \(2\tau\) |                                                                                                         |
| Pattern with grid of \(\Delta t\)     |                                                                                                         |
| 1                                    | \(1)T2(1) = 1.275, P(1) = 0.35; 2)T2(2) = 6.75, P(2) = 0.3; 3)T2(3) = 30, P(3) = 0.25; 4)T2(4) = 97.5, P(4) = 0.1; | 0.00088 0.00120 |
| 2                                    | 1)T2(1) = 0.425, P(1) = 0.35; 2)T2(2) = 2.25, P(2) = 0.3; 3)T2(3) = 10, P(3) = 0.25; 4)T2(4) = 32.5, P(4) = 0.1; | 0.00154 0.00157 |
| 3                                    | 1)T2(1) = 0.425, P(1) = 0.1; 2)T2(2) = 2.25, P(2) = 0.25; 3)T2(3) = 10, P(3) = 0.3; 4)T2(4) = 32.5, P(4) = 0.35; | 0.00082 0.00103 |
| 4                                    | 1)T2(1) = 1.275, P(1) = 0.3; 2)T2(2) = 1.275, P(2) = 0.3; 3)T2(3) = 30, P(3) = 0.3; 4)T2(4) = 2.25, P(4) = 0.3; | 0.00044 0.00100 |
| 5                                    | 1)T2(1) = 0.425, P(1) = 0.1; 2)T2(2) = 2.25, P(2) = 0.1; 3)T2(3) = 10, P(3) = 0.12; 4)T2(4) = 32.5, P(4) = 0.1; | 0.00136 0.00138 |

As a result of testing, the RMSE2 was calculated 0.000535. The registration period of the relaxation decay was 0.1 s, which allowed disregarding insignificant samples in the range of 0.1 - 0.4 s and reducing the signal pattern size to 228 samples.

Figure 4 shows the plot of the relaxation decay pattern after removing redundant samples, superimposed on the graph of the raw decay from the real heavy oil sample.
6. Conclusion
At result, the method is proposed that allows removing redundant data from the NMR relaxation decay pattern. The proposed method can be used to pre-process the signal pattern before it is recognized by an artificial neural network in the e-tongue of intelligent devices. The resulting pattern does not contain any distorted information and does not require restoration. However, as it was shown during testing, it makes it possible to reduce the number of samples almost 15 times with the introduced distortions below the noise value of the measuring system.

![Figure 4. The created the relaxation decay pattern for the heavy oil sample](image)

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