Analysis of the composition and properties of heavy oils in situ by Low Field NMR relaxation method

V.Ya. Volkov[1,2], B.V. Sakharov[1,3], N.M. Khasanova[1], D.K. Nurgaliev[1]*

[1]*Kazan Federal University, Kazan, Russian Federation*
[2]*MIREA – Russian Technological University, Moscow, Russian Federation*
[3]*State Research Center for Applied Microbiology and Biotechnology, Obolensk, Russian Federation*

Abstract. For the analysis of heavy oils, the method of simultaneous measurement of the free induction decay (FID) together with the decay of the echo signal in the Carr-Purcell-Meiboom-Gill (CPMG) pulse program was used. The measurements were carried out on a «Chromatek-Proton 20M» NMR analyzer operating at a frequency of 20 MHz. A special control program was created on the NMR analyzer that automatically tunes and measures the full FID curve, then switches to measuring the decay of the echo amplitude by the CPMG pulse sequence, and then the investigation ends with a joint processing of all the experimental data. This method makes it possible to measure the amplitudes of NMR signals and the relaxation times T2 of protons of heavy oil components in situ, including asphaltenes, without any perturbations in the analyzed system. Under the influence of paramagnetic centers located in asphaltenes, the amplitude-relaxation characteristics of oil protons are divided into 7 groups associated with solid asphaltenes in crystalline and amorphous states, resins with high and low density, aromatic and saturated compounds. The NMR amplitudes of these fractions correlate well with the group composition of heavy oils as determined by gravitational-chromatographic SARA method. The combined FID + CPMG method can be recommended for determining the SARA composition and other properties of oil in situ. The behavior of fractions of heavy oil in the temperature range (-15°C ÷ +60°C) was investigated by SARA-NMR method. For the first time in situ, it has been shown that resins participate in the formation of asphaltenes in a closed volume when the oil is cooled from a stable state at room temperature, and vice versa, asphaltenes are disaggregated by heating with the release of resins.

The SARA-NMR method is promising for the on-line monitoring of the production, transportation and processing of heavy oil in real conditions of temperature, pressure and dissolved gases. However, the design of the NMR sensor must be adapted to industrial applications. The possibilities of designing NMR probes on process pipelines of larger diameter than in laboratory instruments can be extended taking into account the procedure proposed for correcting the inhomogeneity of the magnetic field in the probed volume based on the FID signal of the liquid oil fraction.

Keywords: LF-NMR, vanadyl, SARA, asphaltenes, resins, saturated, aromatic compounds

Introduction

As the reserves of conventional oil in the world continue to decline, more attention is being paid to improving the technology of extraction, transportation and processing of heavy oils and bitumen, the projected reserves of which can ensure the future of the oil industry for many decades. However, high viscosity and high density of heavy oils and natural bitumen create serious obstacles along this path (Akbarzade et al., 2007; Yang et al., 2008; Yashchenko et al., 2012).

Traditional methods of analyzing crude oil are laborious, usually associated with the extraction of the analyzed components, which destroys the informational integrity (nativity) of the research object and, to a large extent, devalues the results obtained. In addition, they take a long time and require the use of toxic organic solvents. Analytical technologies based on nuclear magnetic resonance (NMR) have attracted special attention from oil industry workers because they are fast and non-destructive methods that can be used to analyze dense and opaque samples, such as crude oil, with little or no additional training (Yang et al., 2008; Maqbool et al., 2011; Silva et al., 2011). Particularly keen interest in the possibilities of the NMR method for the study of samples in the initial state (in situ) increased after

Corresponding author: Vladimir Ya. Volkov
E-mail: volkovobolensk@mail.ru

NMR logging tools became commercially available at the beginning of the 1990s. NMR measurements of fluid properties that were performed previously only in the laboratories now have been used in well conditions (Coates et al., 2001; Dunn et al., 2002; Akkurt et al., 2008-2009). At the same time, the needs for ground-based laboratory NMR research have only increased to use results for correctly interpretation a log data.

The so-called NMR methods in low magnetic fields (Low Field NMR, LF NMR) have contributed the most to this information. Low fields are conventionally considered fields from hundredths of the Tesla to ≈1Tl (Mitchell et al., 2014). Resonance frequencies for protons in such fields lie in the range from hundreds of kHz to ≈42.5 MHz. Most small-sized laboratory NMR relaxometers operate at these frequencies, relatively cheap and reliable enough for field use (Maran-II 2.0MHz, Maran Ultra 23MHz, NMR Analyzer mq10 10MHz, Minispec mq20 20MHz, Proton 20M 15÷20÷25MHz, etc.).

When NMR is registered, the amplitudes of the proton signal of hydrogen-containing molecules of oil, water and dissolved gases and rates of signal decay after the radio pulses are measured. The relaxation times of the components in the analyzed samples are determined from the rate of the amplitude damping at different sections of the relaxation curve. The initial amplitude of the NMR signal is directly proportional to the number of protons, and it can be correlated with the volume or mass of substances in the measurement domain. The relaxation time depends on the mobility of molecules in the sample. When the viscosity increases, or the movement of molecules containing hydrogen is limited in space, for example, by pore sizes, then relaxation takes place faster.

On this basis, methods have been developed for the simultaneous determination of the physicochemical properties of oil of interest to the petroleum industry, such as viscosity, density in API degrees and the relative hydrogen index (RHI). Comparison of the NMR data and the results of standard measurements showed good results, confirmed by high correlation coefficients ($R^2 > 0.96$). Moreover, by times of transverse relaxation, it was possible to predict the kinematic viscosity of anonymous crude oil samples in the range 21÷1892 mm^2s^{-1}, and also the API density between 17° and 29.4°, without any preliminary preparation of the samples. In addition, the oil was identified in connection with their origin. This observation makes it possible to justify a new methodology for obtaining a "chemical signature" of crude oil from various deposits (Barbosa et al., 2013; Muhammad et al., 2014). Some features of the relationship between viscosity and NMR relaxation times were found in oil dispersed systems (Kashaev, 2017).

In the study of heavy oils and bitumen, the situation becomes more complicated. With an increase in the viscosity and molecular weight of hydrocarbons, their spin-spin NMR relaxation time T_2 is greatly reduced to such an extent that the apparatus used does not allow lossless recording of signals from large and slow-moving asphaltene aggregates and other solid-phase components, for example paraffin. When the viscosity of bitumen exceeds 100000 cP, the relaxation decay of big hydrocarbons is partially or completely not detected either by logging tools or by laboratory NMR methods at comparable resonance frequencies. As a result, the quantity of long-chain and / or aggregated hydrocarbons is reduce, which underestimates the reserves of heavy oil and bitumen.

To obtain the missing information Yang et al. (Yang et al., 2008) heated the samples analyzed and studied their NMR characteristics at elevated temperatures when the viscosity decreased significantly. This approach was used to correct the initial amplitude of the FID by measuring the relaxation time T_2 of bitumen at different temperatures in the range (8÷90°C) using the Carr-Purcell-Meiboom-Gill pulse sequence (CPMG). Then, the true hydrocarbon content and water saturation were determined.

Back in 2001, to increase the mobility of heavy oil molecules and, thus, to shift their relaxation times to the measured range, Mirotchnik with co-authors (Mirotchnik et al., 2001a) added an equal amount of solvent to the crude oil. Hexane, tetrahydrofuran, trichlorethylene, toluene, kerosene and n-pentadecane were used as the solvent. It was shown that the spectrum of transverse relaxation times (T_2) of oil components can be divided into ranges (or frames) in the interval from 5·10^{-2} to 3 seconds. For conventional oils, frames can be represented as follows. The slowest relaxation frame corresponds to C4-C15 saturated compounds, then aromatic hydrocarbons, olefins, waxes, resins, asphaltenes, in descending order of relaxation time. For heavy oils and bitumen samples, the frames can be arranged in the following order. The fastest relaxation frame represents asphaltenes, the second shortest relaxation frame represents resins, and the subsequent slower frame is responsible for saturated compounds. The slowest frame characterizes aromatic compounds.

Comparison of the obtained data with the results of an independent analysis of the same samples by the traditional SARA method had a good agreement between them. The NMR method turned out to be suitable for analyzing the group composition in oil-saturated, uncemented sandstones even in the presence of relict water (Mirotchnik et al., 2001b). Besides, the duration of NMR analysis turned out to be about an order of magnitude less than of the chromatographic method of SARA (tens of minutes versus several hours).

Unfortunately, the addition of a solvent destroys the informational "virginity" of the samples. The main advantage of the NMR method, non-invasiveness, is practically lost. Despite the fact that extraction of components from the sample does not take place in this method and all the components of the oil remain in the mixture, however, the relationships between them undoubtedly change significantly under the influence of the introduced solvent. As a result, the method is not suitable for the analysis of crude and, especially, "live" oil in the unperturbed state "as is" (in situ). It is possible that a good coincidence of NMR data with the results of chromatographic SARA analysis in this case is explained by the fact that both methods work with "dead" samples partially or completely destroyed by the introduction of the same type of solvents. Thus, the task of creating a non-invasive analysis of the composition and properties of heavy oils in situ continues to remain relevant to the present.

In a number of cases, the necessary information can be obtained indirectly by analyzing the effect of asphaltenes on the NMR-characteristics of lighter oil fractions. Mutina et al. (Mutina et al., 2008) showed that asphaltenes act as relaxing contrast agents on surrounding substances without affecting their diffusion coefficient D. This is explained by the presence of free radicals and paramagnetic centers of vanadyl in asphaltenes. Prunelet et al. in time of flocculation study by NMR find out that the relaxation rate of the solvent molecules increases linearly with the concentration of asphaltenes (Prunelet et al., 2004).

Zielinski et al. (Zielinski et al., 2010; Zielinski et al., 2011) investigated the aggregation of asphaltenes in model solutions and crude oil by the LFNMR method at two frequencies of 2 and 5 MHz, when no own signal of solid asphaltenes was detected. However, under the influence of the paramagnetism of asphaltenes, spin-spin relaxation of protons in solutions was observed to be directly proportional to the intrinsic proton relaxation rate in hydrocarbon molecules. In other words, the longer the hydrocarbon chain, the faster it relaxes under the influence of dissolved asphaltenes. In addition, the efficiency of asphaltene clusters as relaxation agents increased with their size. These results were interpreted from the point of view of the theoretical model, which explains the enhancement of relaxation in the aggregation of asphaltenes due to entanglement of the hydrocarbon motion of the solvent in asphaltene clusters and subsequent limitation of rotational mobility and diffusion within clusters. Comparing the longitudinal and transverse relaxation rates, the authors were able to estimate in crude oil. This model is confirmed by other physical methods, including solid-state techniques and multidimensional NMR experiments in high fields, and continues to

improve, exerting a great influence on the research and deciphering of new experimental data (Korb et al., 2013; Stapf et al., 2014; Vorapalawut et al., 2015).

A little over 10 years ago, Shkalikov et al. for the first time (Shkalikov et al., 2006; Shkalikov et al., 2008), when studying oil by the solid-echo method at 19.8 MHz, recorded components with short spin-spin relaxation times (9.8÷31.2 μs) and the form of the signal of free induction (FID), characteristic for solids. It was found that these signals are due to the presence in the oil of asphaltenes and/or resins in the glassy state, or paraffins in the crystalline phase, depending on the temperature of the sample. On this basis, a method has been developed for determining the content of paraffins and asphaltenes in petroleum, which involves processing two of the three parallel samples with solvents and removing asphaltenes from one of them. By the ratio of the amplitudes of the FID of protons of the solid and liquid phases in these samples, the authors judged the unknown quantities (Nikolin et al., 2008). Unfortunately, the non-invasiveness of the method is lost in this case.

Later, the authors developed a technique for determining the content of liquid-phase and solid-state components in a mixture of hydrocarbons only from the temperature dependence of the fraction of the solid-phase component in the total NMR signal without affecting the composition of the sample (Nikolin et al., 2010). It was shown that each oil fraction has its own temperature range for the existence of a solid component in the NMR signal, which makes it possible to obtain quantitative information on the content of asphaltenes, resins and paraffins in oil. However, the state of the mixture under analysis changes very substantially, since measurements are made over a wide temperature range from -150 to +150°C. The phase transitions observed in this temperature range were explained by the melting of solid phases of asphaltenes, resins and paraffins upon heating and their solidification upon cooling. Meanwhile, resins can participate in the formation of the asphaltene aggregates and complicate the picture. The nature of these transitions and, in general, the effect of temperature on the interaction between the components of oil systems is precisely the subject of the close interest of oil industry workers. It is uncontrolled asphaltene deposition with pressure and temperature changes that causes blockage of pores in the oil reservoir, obliteration of pipelines and other problems that arise during the production, transportation and subsequent processing of heavy oils. Unfortunately, these processes in situ have not been investigated to date.

At the same time, Trezza et al. (Trezza et al., 2006) demonstrated the potential of low-field NMR at 20 MHz to obtain detailed information on the phase state and composition of multicomponent lipid systems used in food technology. Combining the CPMG series with

the measurement of FID after a single 90°th pulse, the authors were able in one experiment to obtain data sufficient to describe a system with contributions from the liquid, semisolid and solid phases, including lipid crystals in various polymorphic states.

In our works (Sakharov et al., 2015, Volkov et al., 2016, 2017; Khasanova et al., 2017) presents the results of the application of such a pulsed FID-CPMG program with some modifications for the investigation of crude heavy oils. The envelopes of the signals of the spin echo of oil protons, recorded in the interval from 0.1 ms to several seconds, are described by the sum of exponentials whose amplitudes (A_i) allow estimating the content of liquid-phase components, and the relaxation times (T_{2i}) – characterize the interaction of molecules of liquid oil fractions with each other and with solid phase of asphaltenes. The FIDs after the 90°th pulse have a complex shape largely determined, as is well known, by the inhomogeneity of the magnetic field in the sample volume. At the initial section in the interval from 10 to 50÷100 µs, when the influence of the field inhomogeneity does not yet significantly affect the damping of the transverse magnetization of the protons, the shape of the FID is described by the sum of the Gaussian and exponential functions, which is characteristic of solid crystalline or amorphous bodies, including asphaltenes (Shkalikov et al., 2008). The rest of the FID to 2÷3 ms is described by the product of exponents by a function describing the inhomogeneity of the magnetic field in the sensor coil. This function is individual for each instrument and requires further analysis and accounting when processing data or compensation in preparation for measurements. Contributions to this part of the FID are from viscous oil components with relaxation times from hundreds of microseconds to milliseconds (mostly resins).

These results were discussed at Russian and international conferences both on magnetic resonance (Sakharov et al., 2015, Volkov et al., 2016a), and on topical problems of the oil and gas industry (Volkov et al., 2016b, 2017; Khasanova et al. 2017) and aroused great interest of the participants. The purpose of this article is to provide an in-depth understanding of the methodological features, existing and potential capabilities of the above methodology for non-contact (for personnel) and non-invasive for oil analysis in the natural state ("as is", in situ).

Materials and methods

The sample of crude oil from different wells of the Ashalchinsky field of the Volga-Ural oil and gas bearing basin, characterized by asphaltene content (7.7%, well No.2127 and 5.8%, well No.2270) was the subject of the study. Average composition of Ashalchinsky oils: light hydrocarbons – 57.5%, resins – 35.6%, asphaltenes – 6.8%. Five samples were prepared from the selected oils: No. 1 (well 2127) and No. 2 (well 2270). To obtain samples No. 3 and No. 4 with a lower content of asphaltenes, the deasphalted (DA) residue (maltene) was added to the crude oil from well No.2270 with a petroleum/maltene ratios of 1: 1 [(oil 2270 + 1DA) = samples No. 3]; and ratios 1: 2 [(oil 2270 + 2DA) = samples No.4]. The deasphalted residue (DA2270) was sample No. 5. The content of asphaltenes was checked by hexane precipitation in accordance with the standard procedure (Akbarzade et al., 2007). Oil samples were placed in ampules with a diameter of 4 mm (EPR) and 10 mm (NMR) and sealed with rubber stoppers. The spectrometer CMS-8400 (ADANI, Belarus) X-band (with a frequency of 9.4 GHz) was used to record the EPR spectra.

NMR measurements were made on a Proton 20M NMR analyzer, manufactured by CJSC SKB Chromatec, Russia (http://www.chromatec.ru). The device is designed in the form of two blocks: a magnetic unit and a control unit. The resonance frequency for protons is 20 MHz. Dead time of the NMR receiver signals: no more than 10 microseconds. The phase of filling the high-frequency pulses is set independently on the 4 channels 0°, 90°, 180° and 270°. Signals of FID and echo in the CPMG series were obtained in phase-sensitive mode. Subsequent quadrature detection provided an increase in the signal-to-noise ratio by a factor of $\sqrt{2}$ and the independence of the result from the possible drift of the phase of the frequency base oscillator. To reduce the influence of inhomogeneities the static B_0 and high-frequency B_1 magnetic fields on the accuracy of setting 180° pulses in the detectable volume, the sensor was placed in the most homogeneous part of the magnetic gap (the FID half-life time of the Glycerin was $t_{1/2} \geq 1.6$ ms) and sample filled the ampoule no more than 80% ($\leq 1,1$ cm) from the height of the high-frequency coil. The effectiveness of these measures was evaluated by checking the differences between the amplitudes of the first odd and even echo signals in the CPMG series.

Thermostabilization of the magnet at 40°C provided the instability of a constant magnetic field no worse than 5.10^{-6} per hour. The device automatically adjusts resonant conditions based on the phase detection of the free-induction signal of a standard sample, usually glycerin, or the FID of the test substance if it has a sufficiently intense slow component. All the oil samples studied in this study met this requirement. Thus, the resonant conditions in the process of measuring and accumulating NMR signals (FID and echo) were maintained with accuracy not much different from the accuracy of the stabilization of spectrometers equipped with separate NMR magnetic field stabilizers.

The experimental results were obtained under the following measurement conditions. The duration of the 90⁰th pulse was 2.4 µs, the 180°th pulse was 4.7 µs. The

FID after the 90°th pulse was recorded in the interval 11÷2000 μs with a sampling step of 0.5 μs with the passband width of the receiver $\Delta f_1 = 1$ MHz, 100 accumulations (N_1) were used with a repetition period of 1 second. Immediately after this, the receiver band automatically decreased to $\Delta f_2 = 100$ kHz and the echo measurement program in the Carr-Purcell-Meiboom-Gill series (CPMG) was activated (Fig. 1). In this case, the signal-to-noise ratio increases by a factor of 10, which makes it possible to reduce the number of accumulations by an order of magnitude and, thus, to shorten the measurement time. The narrowing of the band did not distort the shape of the relaxation curve, since the rate of change in the amplitudes of the echo signals is an order of magnitude smaller than the rate of change of the FID.

The number of 180°th pulses in the CPMG series was n = 1000, the interval 2τ between them and, correspondingly, the echo signals was 50, 100, usually 200 μs. Taking into account the duration of the CPMG pulse series, the cycle repetition period was set to not less than 1.5 s, the number of accumulations N_2 varied from 9 to 25 or 36, depending on the need to extract the signals of the minor components. Before the measurements, the samples were kept in a water thermostat at a specified temperature for at least an hour. The results were processed using a specially designed multi-stage fitting program based on the Solver Excel software package. Previously, all wishes were fulfilled regarding the subtraction of the background signal, the maximum sample volume, and the correction of the inhomogeneity of the constant magnetic field B_o, which were proposed (Trezza et al., 2006) to improve the accuracy of the analysis, with some additional modifications.

Accounting of the inhomogeneity of the magnetic field and processing of the results

The evaluation and correction of inhomogeneity of B_0 in our work was carried out without using a separate ampule with triolein, in contrast to the way it was done in the work cited above (Trezza et al., 2006). The inhomogeneity of the magnetic field was determined directly in the volume of the sample under analysis in the form of a part of the FID at $t \geq 200$ μs,

generated by maltene with long transverse relaxation times. In an ideally homogeneous magnetic field, the envelope of the amplitudes of the echo signals in the CPMG series must coincide with the relaxation decay of the transverse magnetization of the nuclei (FID). As is known, this impulse program was specially created to eliminate the influence of inhomogeneity, which is always present in the magnets of real devices (Carr, Purcell, 1954). In most commercial NMR relaxometers, the duration of the FID of homogeneous liquids does not exceed 1÷3 milliseconds, while the actual time of their spin-spin relaxation T_2 is usually much greater. Thus, the duration and shape of the FID of such liquids is almost completely determined by the magnitude and nature of the inhomogeneity of the magnetic field in the volume of the ampule occupied by sample. The relaxation contribution to the "inhomogeneous" form of the FID can be eliminated by dividing by an exponential with the corresponding exponent T_2. In our case, when the sample is a macroscopically homogeneous mixture of asphaltenes and liquid maltenes with different relaxation times, the shape of the FID is described by the equation:

$$FID(t, T_2, T_{2g}^*) = F(t, T_{2g}^*) \times fit[CPMG(t)], \qquad (1)$$

where $F(t, T_{2g}^*)$ is the factor that describes the "inhomogeneous" form of the FID, determined by the interference of Larmor frequencies associated only with the deviations of the magnetic field in different parts of the sample from the resonance value $w_0 = \gamma B_0$, and the relaxation contribution is represented by the envelope of the amplitudes of the maltene echo signals ($fit[CPMG]$). In this decay, the signal of asphaltenes is practically absent, since the first echo is measured at $2\tau = 200$ μs, and the typical time T_2 of asphaltenes does not exceed 50 μs.

As follows from equation (1), the form of the function describing the shape of the FID in an inhomogeneous magnetic field, can be determined from the formula:

$$F(t, T_{2g}^*) = fit\left[\frac{FID(t, T_2, T_{2g}^*)}{fit[CPMG(t)]}\right]_{t1}^{t2}, \qquad (2)$$

where the index (*) at T_2 indicates that the decay of nuclear magnetization is due to the dephasing of spin
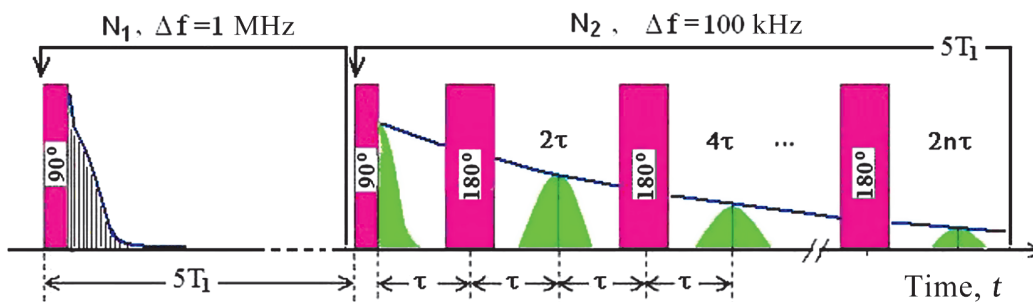
Fig. 1. Scheme of the combined impulse sequence FID + CPMG

packets in an inhomogeneous magnetic field, and borders: $t_1 = 200$ μs, $t_2 = 2000$ μs, are of the interval in which the fitting of the experimental array of points was carried out to determine the function $F(t, T^*_{2g})$. The shape of this function, describing the inhomogeneity of the magnetic field in our instrument, is described with good accuracy by the product of the ordinary and Gaussian exponentials:

$$F(t, T^*_{2g}) = (\exp(-t/T_{2gr})^2) \times \exp(-t/T_{2gl}). \qquad (3)$$

At the same time, it is natural to expect that the effect of this function extends on the interval $0\div200$ μs (Fig. 2) missed at the fitting, which allows us to clarify the parameters of the solid-phase part of the FID. This kind of inhomogeneity of the constant magnetic field in the sample is probably related to the cylindrical shape of the ampule and its location in the gap of a permanent magnet with axial symmetry of the field in the XY plane and a linear gradient along the OZ axis. Thus, the corrected form of the $FID^{cor}(t)$ is described by the equation:

$$FID^{cor}(t) = \frac{FID(t, T_2, T^*_{2g})}{\exp(-t/T_{2gr})^2 \times \exp(-t/T_{2gl})}. \qquad (4)$$

Graphically, the result is shown in Fig. 2, where the product Gauss*exp (eq. 3) is prolonged to an interval from $t = 200$ to $t = 0$ μs, which allows correction of the entire *FID*, including the section containing the signal of asphaltenes. This figure is specially presented in the form of two parts to clearly show the sequence of actions during the correction (Fig. 2A), and also to demonstrate the almost complete coincidence of the $FID^{cor}(t)$ with the envelope of the amplitudes of the echo signals in the zone of their intersection $t_1 < t < t_2$ (Fig. 2B). Note that the signal-to-noise ratio for $FID^{cor}(t)$, as you move away from the origin, deteriorates due to the division of the $FID(t)$ on the function decreasing with time (eq. 4).

Let us once again pay attention to the fact that under such an approach the influence of the inhomogeneity of the magnetic field is corrected directly in the volume occupied by a particular sample in an ampule whose diameter and filling height will be automatically reflected in the parameters of the function of the *FID* form (eq. 2,3, Fig. 2). This softens the requirements for the use of calibrated ampules and the precise positioning of the sample in the NMR analyzer magnet gap. As a consequence, the accuracy of measurements increases substantially throughout the entire length of the *FID*, and not only at its initial site, as in (Majumdar et al., 2017). A large number of *FID* digitization points in the analyzed interval from 10 to 2000 microseconds (3880 pieces) significantly supplement one thousand amplitudes of echo signals, that improve the statistical characteristics of the components decomposition from the total relaxation decay of the transverse magnetization and, thereby, increases their reliability. This is especially important for the determination of minor components with short relaxation times, the amplitude of which is a few percent on the background of strong signals of slowly relaxing fractions, whose content is an order of magnitude larger.

Experimental results and discussion

As follows from the review of the literature, the main influence on the relaxation of protons in heavy oil is determined by the dipole interaction of protons with stable radicals located on the molecules of asphaltenes. The samples of the Ashalchinsky oil prepared for the study also have signals of free radicals (R) and paramagnetic centers of the vanadyl-porphyrin complex VO^{2+} (Fig. 3).

The connection between EPR signals and asphaltenes is confirmed by their decrease if dilution of crude oil with maltene, however, this dependence is nonlinear. The explanation is the presence of a small number of the same radicals in the resin molecules. Thus, in the deasphalted sample No. 5, the EPR amplitude of the vanadyl-porphyrin signal is about 15% of the signal in the initial oil (Fig. 3c). Later it turned out that one-third
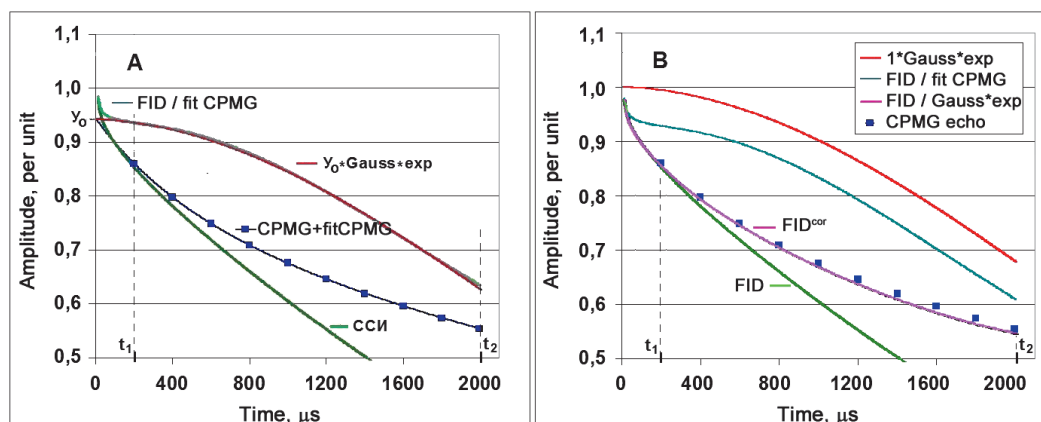

*Fig. 2. A) Experimental definition of the function describing the shape of the FID in an inhomogeneous magnetic field; B) Obtaining the corrected FID^{cor}(t) by point-wise dividing the experimental values of the FID into values of the form function at the same instants (FID/Gauss*exp)*
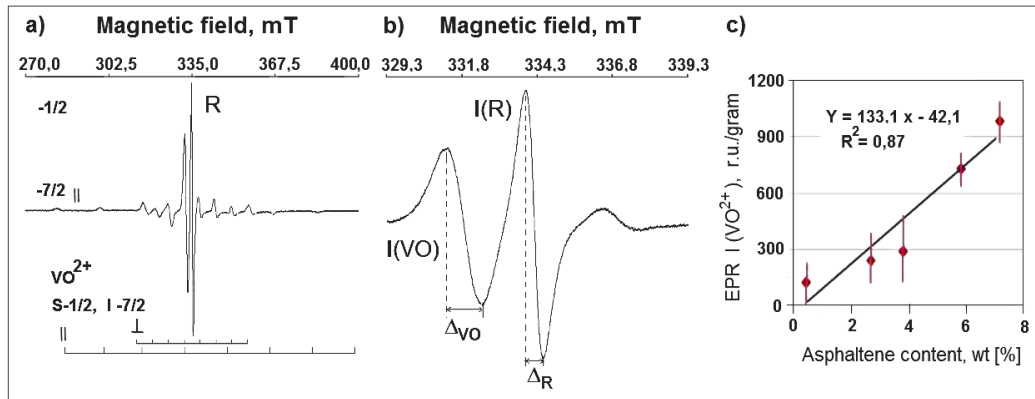
Fig. 3. The EPR spectrum (a) of vanadyl-porphyrin VO^{2+}-P {S = 1/2, I = 7/2 (^{51}V)} and (b) the free radical R (S = 1/2) in the Ashalchinsky crude oil. The structure of super-hyperfine splitting is shown schematically for the direction of the magnetic field along (||) and perpendicular to (⊥) the axis of the V-O direction; (c) Correlation of the vanadil EPR signal with the amount of asphaltenes

of this signal can refer to asphaltenes, which condensed some time after sample preparation and were detected by NMR. Since the content of resins and asphaltenes in the samples is known, it is possible to estimate the number of paramagnetic centers in these fractions per unit mass. In the resins of the investigated Ashalchinsky oils it is approximately 30÷100 times less than in asphaltenes. These facts were taken into account later in the planning and interpretation of experiments.

Figure 4A shows the experimental decays of the transverse magnetization of two crude heavy oil samples differing in the content of asphaltenes (7.7% and 5.8%, respectively), and one sample of deasphalted oil (maltene). The top line with dots is the experimental decay envelope of the nuclear spin echo amplitudes of the maltene (CPMG), which characterizes the shape of the relaxation curve (FID) of a homogeneous liquid in an ideally homogeneous magnetic field. It can be clearly seen that the real FID form of maltenes is significantly distorted by the inhomogeneity of the static magnetic field in the sample. In addition, FID is reduced due

to the influence of paramagnetism of asphaltenes, and, the faster, the more content of asphaltenes in sample (compare 2270 and 2127). This decrease can be separated from the influence of the magnet field inhomogeneity on the basis of taking into account the FID form of the maltene, as shown in the Materials and Methods section, and to determine the true values of the NMR signal amplitudes and the transverse relaxation times of petroleum protons.

Fig. 4B in the semilogarithmic coordinate system shows the result of the preliminary decomposition into components of the FID signal of crude oil (well No. 2270) with an asphaltenes content of about 5.8%. As expected, the FID shape at t > 200 microseconds is well approximated by eq. (3) with the following values of the parameters characterizing the field inhomogeneity: T_{2gr} = 2.01 ms and T_{2gl} = 5.95 ms. After subtracting this part of the FID related to the liquid maltene from the total free induction signal, two other components are separated in the remainder: (1) the exponential with the relaxation time $T_{2d'}$ = 416 microseconds, as it later turned
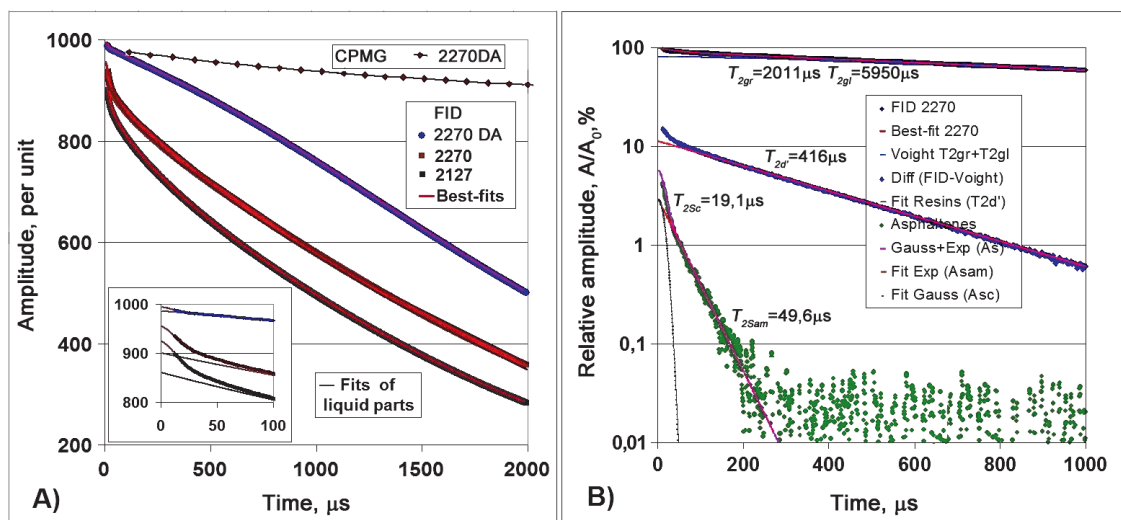

Fig. 4. A) FID's of heavy oil samples (2127, 2270), FID and CPMG of the maltene (2270DA), on the inset: the initial sections of the FID with fitting lines; B) Scheme of graphical FID decomposition of the 2270 crude oil into components on the basis of the model described by eq. (5)

out, related to the high-viscosity fraction of the resins, and (2) the solid phase related to asphaltenes, which is described by the sum of Gaussian (T_{2Sc} = 19.1 μs) and the usual exponent (T_{2Sam} = 49.6 μs).

Completely the FID form is well approximated by the set of functions entering into equation (5):

$$A(t) = A_{S0} \times [(1 - f_{Sam}) \times (\exp(-t/T_{2Sc})^2) +$$
$$+ f_{Sam} \times \exp((-t/T_{2Sam})] + A_{d''} \times (\exp(-t/T_{2d'}) +$$
$$+ A_{lm} \times (\exp(-t/T_{2gr})^2) \times \exp(-t/T_{2gl}) \qquad (5)$$

where A_{S0}, $A_{d'}$ and A_{lm} – true amplitudes (at t = 0) of the mathematically extracted components by fitting, T_{2Sc}, T_{2Sam} – transverse relaxation times characterizing crystalline (Sc) and amorphous (Sam) constituting the solid phase (S – solid) with total amplitude A_{S0}, and f_{Sam} is the fraction of the amorphous part of the solid phase. A_{lm} is the amplitude of liquid maltene (lm – liquid maltene) without the contribution of the amplitude of high-viscosity $A_{d'}$ resins. For the convenience of approximation and analysis of the results obtained, the "solid" part of formula (5) is assembled into one term in square brackets. The results of the fitting are shown in the drawings with thin red lines inside the experimental curves. The relative fraction of the components in the NMR signal of all protons in the sample is determined by dividing by A_0 the function of the fitting (5) at t = 0, which must coincide with the sum of the amplitudes $(A_{S0} + A_{d'} + A_{lm})$. (Sakharov et al., 2015; Volkov et al., 2016a, b).

Fig. 5 shows FID of asphaltenes in dry powder form, extracted from oil 2270, and a fragment of FID of this oil relating to asphaltenes in crude oil (in the natural environment), normalized to the maximum amplitude of the solid-phase fraction described as the function Gauss + exp. The fastest relaxation times are close to each other (15.5 and 19.1 μs) and belong to the hard asphaltene core, since the shape of the relaxation curve is described by the Gaussian function typical for solids. The relaxation times of the exponential parts of the FID differ by almost three times (17.2 and 49.6 μs), and the greater time relates to asphaltenes in crude oil. This is consistent with the current knowledge of the existence of asphaltene molecules in crude heavy oil, which combine into hard nanoaggregates of 8-10 molecules, and when the concentration is increased, into larger clusters consisting of stacked nanoaggregates and a fairly loose porous environment of asphaltene and resins molecules, in which the molecular mobility is substantially higher than in the nucleus (the modified model of Jena, Mullins et al., 2012).

In dry asphaltene powder mobility of molecules around the core is low (T_2 = 17,2 μs) due to lack of the liquid phase and the close to the mobility in the nucleus (T_2 = 15,5 μs). However, due to the disorder of the porous structure around core (amorphous) of the relaxation decay shape remains exponential at 40°C and higher temperatures. When the temperature is lowered to room temperature and lower, in our experiments to -15°C, it gradually assumes a Gaussian form, that is, the rigidity of the system rises up to the level close to typical solids. We note that the fraction of the exponential (amorphous) part of the FID in crude oil is one third larger (f_{Sam} = 0.49) than in the dry powder (f_{Sam} = 0.31). The explanation is that the porous structure of asphaltenes in oil is impregnated with maltene and large resin molecules lose mobility due to spatial limitations and increase in adhesion time with "pore walls". As a result, the amplitude increases by an amount proportional to the mass of the absorbed molecules, and the relaxation time of protons of asphaltenes and resins in the porous environment of the nucleus is averaged at about 45-50 μs (at +40°C). This is consistent with the well-known fact of the isolation of resins from asphaltene precipitate at additional purification of asphaltenes by solvents.
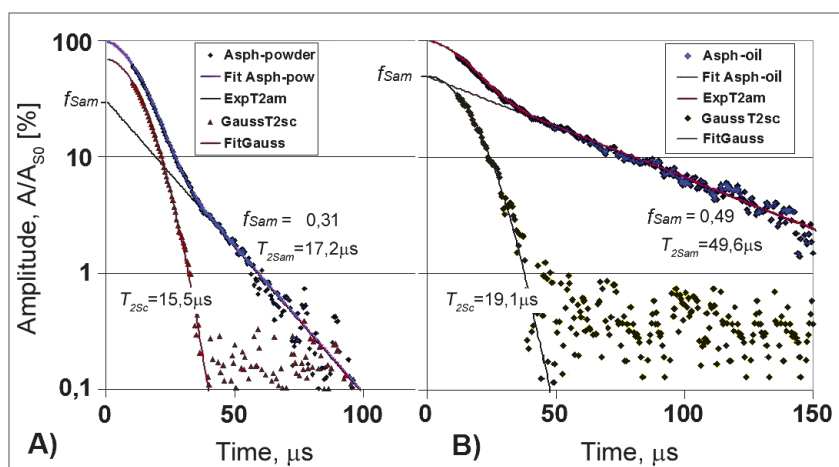

Fig. 5. A) The FID of dry powder of asphaltenes extracted from crude oil 2270, and B) a fragment of the FID from Fig. 4, relating to asphaltenes in crude oil 2270. Solid lines are the results of approximating the experimental curves by part of equation (5) in square brackets

Furthermore, recently high-field NMR techniques with magic angle spinning have experimentally confirmed that there are two domains in the asphaltene clusters: rigid central core consisting of stacked aggregates and substantially smaller proportion of peripheral movable alkyl side chains. (Majumdar et al., 2017). Apparently, it is these chains that participate in the formation of a viscoelastic network between the clusters, ensuring the stability of the colloidal crude oil system at high concentrations of asphaltenes in the natural state (Akbarzade et al., 2007).

Figure 6 shows the results of simultaneous measurement of FID and echo signals in the CPMG series of the same sample of crude oil with an asphaltenes content of 5.8%. The envelope of the echo signals of the CPMG series (the top line in Fig. 6B) is best described by the sum of 4 exponents (eq. 6) (Sakharov et al., 2015; Volkov et al., 2016):

$$A_{CPMG}(t) = A_d \times (\exp(-t/T_{2d}) + A_c \times \exp(-t/T_{2c}) +$$

$$+ A_b \times \exp(-t/T_{2b}) + A_a \times \exp(t/T_{2a}) \qquad (6)$$

These exponents are represented in the figure by tangential straight lines that have slopes determined by the transverse relaxation times of the protons T_{2i} of the corresponding fractions of the maltene. The indices $i = a, b, c, d$ are arranged in order of increasing relaxation rates $1/T_{2i}$. Tangents intersect the y-axis (abscissa) at points that characterize the fraction of protons (in percent) of these maltene in the total signal of oil protons, including asphaltene protons, since the amplitudes of the echo signals are normalized to the maximum amplitude of the FID at $t = 0$.

Figure 6A shows the result of approximating the FID of the same sample by the formula (5), the dark triangles show the amplitudes of the echo signals transferred from the right side of the figure. It can be seen that after taking into account the inhomogeneity of the magnetic field the liquid-phase part of the FID^{cor} practically coincides with the envelope of the echo signals, and their amplitudes at $t = 0$ are equal within the measurement error. In turn, the amplitudes and relaxation times of the fastest component CPMG (A_d, T_{2d}) and the intermediate component of the FID ($A_{d'}$, $T_{2d'}$), calculated from the results of the fitting of FID and CPMG, also practically do not differ from each other (Table 1). Firstly, this confirms the adequacy of the procedure for compensating for the inhomogeneity of the field. Secondly, it allows us to more accurately determine the parameters of the intermediate (d') component according to the FID data, when the number of points in the CPMG series pertaining to this component decreases to several units, which is observed with a higher content of asphaltenes in oil.

Note that with decreasing the amount of asphaltenes, when the time $T_{2d'}$ increases to 1 ms or more, the accuracy of its measurement by the FID decreases due to the deterioration of the signal-to-noise ratio. In this case, the measurement is preferably performed by the CPMG method. Thus, the combined sequence of pulses FID + CPMG provides the possibility of analyzing samples with relaxation times from 10 μs to many seconds without any losses and omissions on the time scale. This makes it possible to observe all the components of heavy oil from light fractions to resins and asphaltenes without resorting to heating (Yang et al., 2008) or the use of solvents (Mirotchnik et al., 2001a, 2001b) to increase the mobility of molecules, as in the works cited above. Thus, a tool for the analysis of heavy oils in situ appears which does not have any noticeable effect on the state of the object under study.

Below are the results of using this tool to analyze the group composition of heavy oils. Figure 7 shows the experimental FID and relaxation decays of the echo
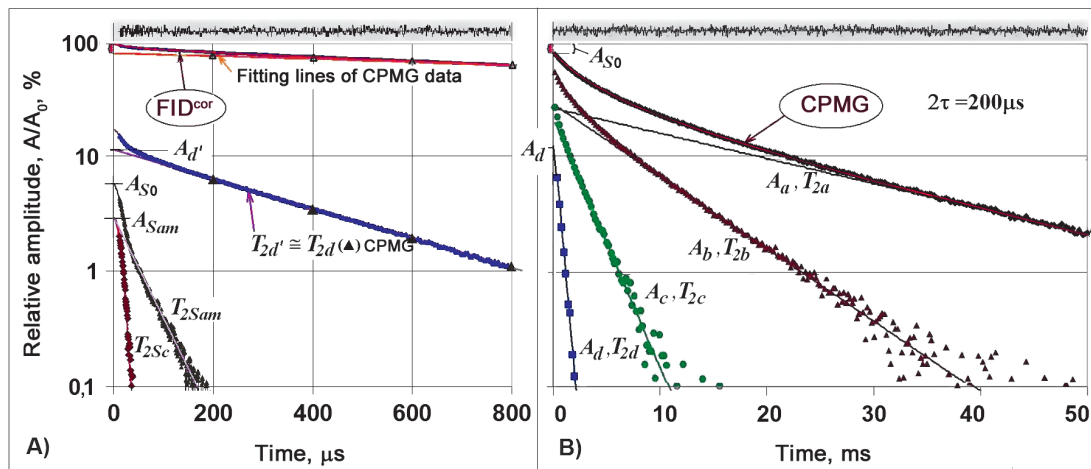

Fig. 6. The results of approximation (fitting): A) FID, after correction of magnetic field inhomogeneity, and B) envelope amplitudes of signals of nuclear spin echo of protons in CPMG series of crude oil sample of Ashalchinsky field (2270). Noisy lines at the top characterize the accuracy of the approximation – these are the differences between the experimental points and the fitting lines multiplied by factor 5. The amplitudes of the echo signals are normalized, as well as the FID points, to the value A_0 of the function of the FID fitting (eq. 5) at $t = 0$

No	C_{asph}	A_{S0}	T_{2Sc}	f_{Sam}	T_{2Sam}	$A_{d'}$	A_d	$T_{2d'}$	T_{2d}	A_c	T_{2c}	A_b	T_{2b}	A_a	T_{2a}
	%	%	µs	part	µs	%	%	ms	ms	%	ms	%	ms	%	ms
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
1	7,7	7,2	19,7	0,5	49,7	13,9	14,1	351	0,37	27,6	1,7	32	5,2	19,1	12,3
2	5,8	6	19,1	0,5	49,6	11,4	11,6	416	0,41	24,8	2,1	30,7	7,3	26,9	20,3
3	3,8	3,7	17,4	0,53	58,2	10,7	11,5	648	0,62	21,9	2,7	32,5	9,8	30,4	30,2
4	2,7	2,4	17,9	0,51	50,1	n/d	13,3	n/d	0,85	25,2	4,2	33,4	15,4	25,7	44,4
5	0,4	0,7	15,9	n/d	44,6	n/d	13,7	n/d	1,74	25,5	8	32,6	29,8	27,5	81,7
Average values		6,6[1,2]	17,6		50,6		12,5			24,4		32,3		24,1	
	Asphaltenes					Alcohol-benzen resins				Benzene resins		Saturated		Aromatic	
SARA[1,2]	<6,8 %>					<35,6 %>						<32,4%>		<25,2%>	
SARA*	7,5%					13,3%				24,2%		54,4%			
No1	Anmr - Asara		-5,9%			-6,0%				-14,0%		1,2%		24,2%	
No2	Asara		11,8%			12,8%				-2,5%		5,2%		-6,7%	

Table 1. The results of the relaxation curves analysis (Fig. 7) of heavy oils with different content of asphaltenes
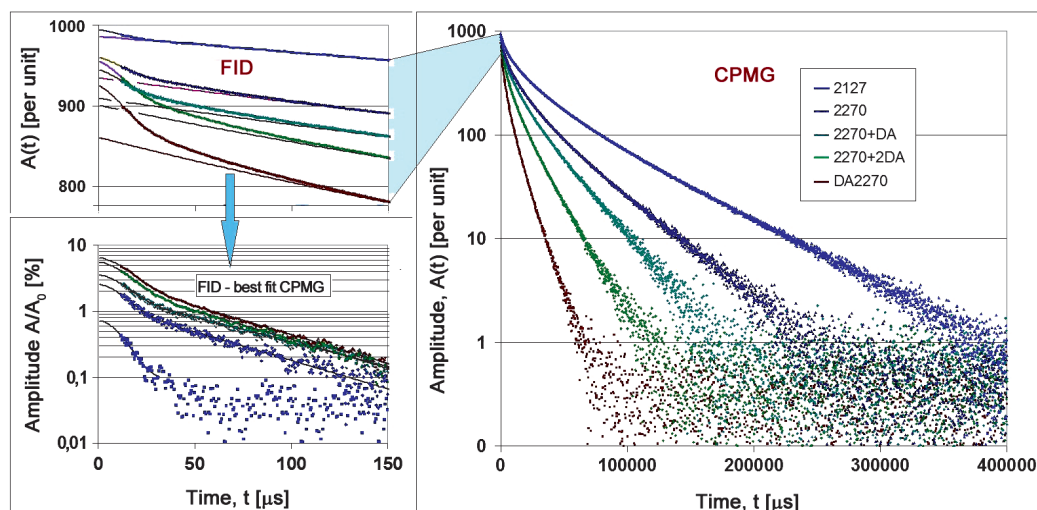

Fig. 7. Transverse magnetization decays (FID and CPMG) of the crude oils (2127, 2270), maltene (DA2270), and samples obtained by mixing oil and maltene in the ratio 1:1 (2270 + DA) and 1:2 (2270 + 2DA)

signals of samples with different asphaltene content obtained in one of the three series of experiments using a combined pulse train (Fig. 1), and in Table 1 the results of approximation of the experimental data by equations (5) and (6). As was proved above, the microsecond relaxation region from 10 to 100 microseconds unambiguously refers to protons of asphaltenes, minus the amplitude of maltenes. The results obtained by precipitation of asphaltenes with hexane and NMR data (the second and third columns of Table 1) correlate well with each other and are related to each other by a linear dependence with a slope close to unity and a coefficient $R^2 > 0.98$.

The components with the longest relaxation times (with the index "a"), according to Mirotchnik et al. (2001a), should refer to aromatic compounds, the following – with shorter T_2 (subscript "b") characterize the saturated compounds, and components with times in the intermediate zone from hundreds of microseconds to several milliseconds (indices "c" and "d") should be viscous resins.

When analyzing the group composition of oil, the standard SARA method determines the total resin content, while the NMR method clearly registers two components with fairly short relaxation times from 350 µs to 8 ms. The sum of the amplitudes of these components, expressed as a percentage of the total amplitude of the oil signal, practically coincides with the percentage of resins (%) in the SARA analysis of the samples. The explanation is that the resins are well divided into two fractions by two kinds of solvents, benzene and a mixture of ethyl alcohol and benzene. Apparently, the NMR method, sensitive to the peculiarities of intermolecular interactions, fixes this readiness of different properties of resin fractions to react differently to the introduction of solvents into the system. The isolated resins are called "benzene resins" (BR) or "low-density resins" and "alcohol-benzene" (ABR) or "high-density resins".

Let us pass to the analysis of information represented by the spin-spin relaxation times of protons of heavy oil fractions in situ. The relaxation time of T_{2Sc} protons in the asphaltene core are the shortest (18.0±1.3 µs) and practically does not change in samples with different asphaltenes content (Table 1). As noted above, this

is due to the rigid lattice of solid asphaltenes and the rapid averaging of the nuclear magnetization of the protons around the paramagnetic vanadyl-porphyrin complex due to direct spin-spin interaction. In the amorphous part of aggregates of asphaltenes, the lattice is less ordered and, in addition, the molecules of mobile fractions penetrate into it, so that T_{2Sam} is noticeably larger than the proton T_{2Sc} of the crystalline nucleus (~ 2.5 times), but also varies little with the concentration of asphaltenes (50,0±4.1 μs). It can be safely assumed that the nearest environment of asphaltenes is the same in all samples No.1 to No.5 for all asphaltene particles, despite the differences in their quantity. This is natural, since the composition of the maltene in the samples is practically the same, and the particles are distributed uniformly in the samples and do not form large aggregates (sediment).

In contrast, the relaxation times of protons of liquid fractions strongly depend on the content of asphaltenes in the samples. The relaxation rates $1/T_{2i}$, calculated from the data in Table 1, increase in proportion to the concentration of asphaltenes with high correlation coefficients close to unity (Fig. 8). Judging by their slope, the paramagnetism of asphaltenes exerts the greatest influence on closely spaced high-density resins (the "d" index) and has a much weaker effect on the more distant low density resins ("c"), as well as on saturated ("b") and aromatic ("a") compounds.

The increase in the proton relaxation rate of all fractions is due to an increase in the number of paramagnetic particles per unit volume of the sample. It would seem that protons of highly mobile light-fraction molecules must quickly exchange magnetization with paramagnetic centers of asphaltenes and should have shorter relaxation times than viscous slow-moving resins, but this is not observed.

In addition, Fig. 8 clearly shows that the spin-spin systems of protons of different fractions are sufficiently isolated from each other, so that their relaxation times are not averaged to one common time for all protons. Consequently, the molecules of the fractions are not

distributed uniformly as in an ideal solution, but form microphases bound in the volume, exchanging by particles so slowly that their relaxation times are determined separately. Analysis of the porous model of asphaltenes (Zielinski et al., 2010) suggests that the lifetime of the resins in contact with asphaltenes is large enough to make it difficult to access of light fractions to the surface of the asphaltenes. As a result, the relaxing effect of paramagnetic centers of asphaltenes is transmitted through spin-spin systems of resins to protons of saturated and aromatic compounds with velocities that depend on the size of molecules and the local viscosity.

This weakening is characterized by the coefficients of the slope of the straight lines on (Fig. 8). It is likely that the very existence of such microphases, with developed boundaries and surface tension forces, is the basis for the stability of heavy oils with both large and small amounts of asphaltenes prone to aggregation. It is not by chance that the equilibrium in such a complex structured system is very sensitive to the influence of many external and internal factors and can be investigated only by methods that do not introduce additional perturbations in time of analytic process.

Determination of the SARA composition

The NMR amplitudes of asphaltenes, resins, saturated and aromatic compounds presented in Table 1 vary simbatically with the results of the SARA analysis. Figure 9 shows a histogram that clearly indicates the degree of proximity of these data, as well as a graph illustrating the statistical evaluation of this correlation. The slope of the straight line on the chart is almost equal to 1 and the correlation coefficient $R^2 = 0.94$ indicates a high degree of reliability of the revealed relationship. However, absolute discrepancies between NMR and SARA estimates of the content of fractions in this case vary in a fairly wide range from 5 to 25%, averaging about 15% (Table 1). In this connection, the question arises whether SARA can be a reference test for NMR and other methods of analyzing oils.

The method of determining the group composition, based on the precipitation of the asphaltene fraction using with an excess of alkane solvent and the subsequent chromatographic separation of maltene into resins, saturated and aromatic compounds, was widely used and was repeatedly certified by the American Society for Testing Materials (ASTM D3279-07, ASTM D412409-2012 / GOST 32269-2013). Nevertheless, this method has been widely criticized because of the low accuracy, the length of the analysis, the large amount of oil and solvents required, the difficulty of automating the process (Kharrat et al., 2007; Bissada et al., 2016). Thus, simultaneous testing of samples of the same oil in four certified laboratories revealed significant
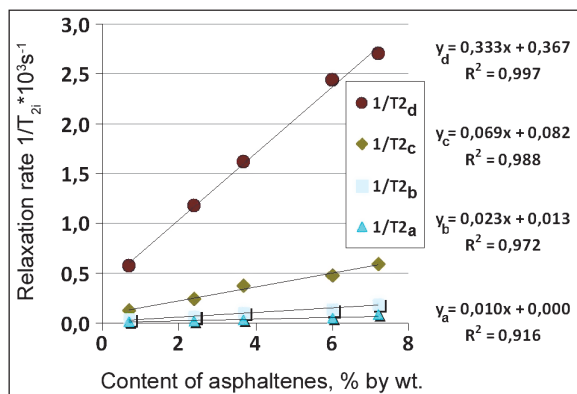

Fig. 8. Dependences of the spin-spin relaxation rates of liquid fractions on the content of asphaltenes in oil
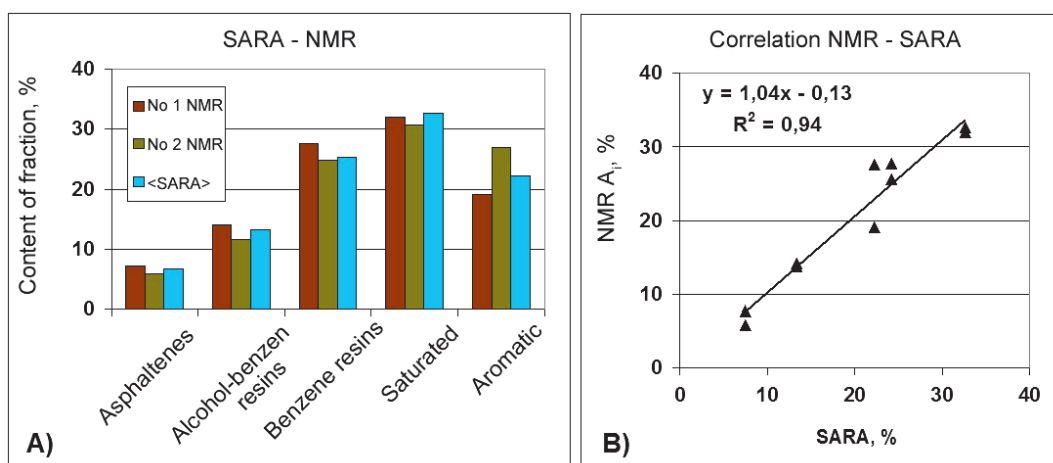
Fig. 9. A) Group composition of Ashalchinsky oil according to NMR and standard SARA analysis; B) Statistical evaluation of the correlation of these data with each other

differences in the results of the analyzes. The laboratory data differed by 2-10% for resins and asphaltenes, for 12-28% for aromatic, and reached 40-60% for saturated compounds. Moreover, repeated chromatography of the isolated components revealed significant impurities of neighboring fractions in them. For example, up to 69% of asphaltenes and aromatic compounds were contained in the resins, and almost 26% of aromatic compounds, resins and asphaltenes were found in saturated compounds (Bissada et al., 2016).

It has been repeatedly noted in the literature that the amount of precipitated asphaltenes depends on the type of alkanes and the sequence of their application (Shkalikov et al., 2010; Achugasim et al., 2015). Therefore, the result is specific for the solvent/oil system and may not coincide with the actual content of asphaltenes in the original oil. It is generally accepted that even in small quantities, asphaltenes are an essential component that contributes significantly to the harmony of the interaction of the phases of crude oil. The removal of asphaltenes disrupts the very delicate balance that exists between fractions in crude oil, and a strictly structured system turns into a mixture far from the properties of the original oil. It is no accident, to date, methods for predicting the stability of crude oil based on SARA analysis are of low efficiency and need further development (Guzmán et al., 2017).

Thus, on the formal side of the problem under discussion, the SARA chromatographic method can not serve as a standard test for metrological certification of the proposed NMR method for determining the group composition of oils. It is necessary to search for a stable natural standard and/or to develop an artificial test of the composition and methodology of certification, which is necessary for the application of this express method in industrial laboratories responsible for the economic result of enterprises. In the meantime, until the problem of the official recognition of the SARA-NMR analysis method is being solved, there

is nothing to prevent the use of certified measuring instruments, the NMR analyzer, and the founded correlation for research purposes. Moreover, in the list of tasks that are of interest to the solution, non-invasive methods are needed to solving practically all the actual problems of the oil industry.

Effect of temperature on SARA composition

It is believed that the main causes of uncontrolled asphaltene deposition are changes in pressure, temperature and composition in the extraction, storage, transportation and refining of oil. However, as noted above, it is not yet possible to create a method for confidently predicting such events (Guzmán et al., 2017). In the article (Shadman et al., 2017), the authors concluded that to determine the onset of asphaltene precipitation, it is necessary to know the mechanism of precipitate formation. Zielinski et al. (2010) noted that aggregation of asphaltenes strongly depends on the properties of the solvent and the presence of polar molecules, such as resins, and underscored the need for reliable methods that would allow observing asphaltenes in their natural surroundings-in natural oil.

In our studies, we used the NMR relaxation method presented here to analyze the interactions of oil fractions in situ without extraction of asphaltenes (Volkov et al., 2017; Khasanova et al., 2017). Figure 10 shows the experimental results of the effect of temperature on the relaxation decays of protons of heavy oil during heating and cooling in sealed ampoules. Before carrying out the measurements, the samples were kept in thermostats at a specified temperature for at least two hours.

When the ampules are heated to 30°C, 40°C, 50°C and 60°C, the total amplitude A_0, which is the sum of the signals of all the protons in the sample, decreases according to the Curie law, while the relative amplitudes (A_i/A_0) of the fractions depend only on their quantity at a given temperature. When heated from room temperature to +60°C, the relative amplitude (A_s/A_0),
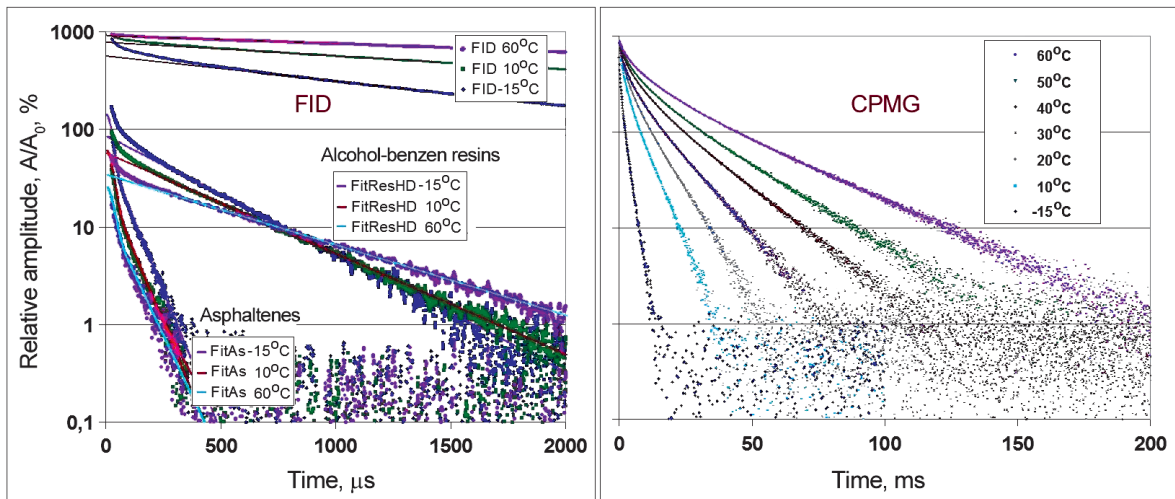
Fig. 10. Decays of the transverse magnetization (FID and CPMG) of protons of crude oil (well 2127) in situ at different temperatures

reflecting the content of all asphaltenes, decreases, the relative amplitudes of benzene resins (A_c/A_0) increase, but in alcohol-benzene resins (A_d/A_0), aromatic (A_b/A_0) and saturated (A_a/A_0) components of the amplitude practically do not change (Fig. 11). The times of spin-spin relaxation of protons of all fractions increase monotonically.

When the samples are cooled to 12°C, 10°C, 4°C, 0°C and -15°C, the amplitude of asphaltenes increases with the simultaneous decrease in the amplitudes of the BR and ABR resins, and the number of light fractions remains practically unchanged. The times of relaxation of T_{2i} decrease monotonically. In these experiments, the observed changes were completely reversible, after the samples returned to a temperature of +20° C, their state is described by the indices (A_i, T_{2i}), which are close to the initial values within the limits of measurement errors.

Thus, for the first time in situ, direct experimental confirmation has been obtained of the statement that resins are a potential source for the formation of asphaltenes in aggregation and precipitation processes, and asphaltenes in turn are a source of resins, for example, in refining heavy oils and bitumen. If there are enough thermostats, this experience can be performed within one working day. At the same time, the possibility of multiple repetition of measurements remains, since the samples are returned to storage in thermostats in an unchanged state. This allows not only to check the results, but also to improve the accuracy of measurements by improving the signal-to-noise ratio when adding digital data and their statistical processing.

Let's pay attention to the linear dependences of the relaxation times T_{2i} of the components on the reciprocal temperature (Fig. 12), which allow us to determine the activation energies of the relaxation processes in crude oil. This parameter can be useful for assessing the stability of oils in various conditions.
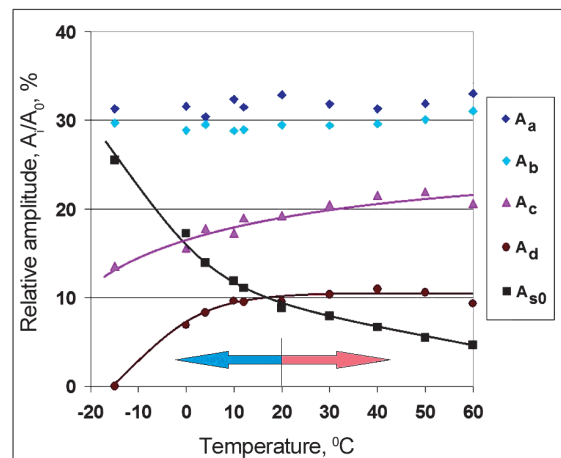

Fig. 11. Temperature dependences of the NMR amplitude of SARA protons of heavy oil fractions upon cooling from room temperature to -15°C and heating to + 60°C
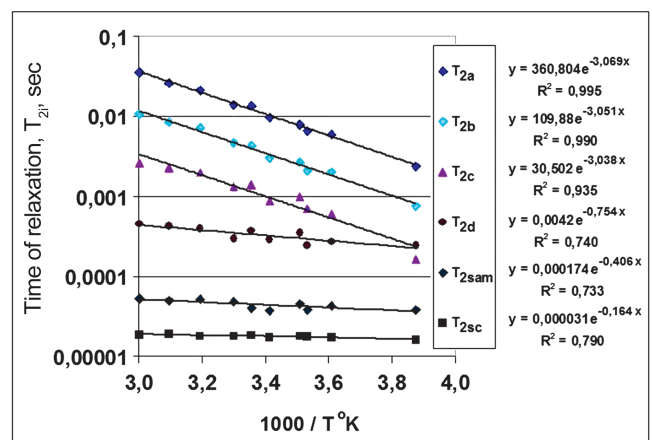

Fig. 12. Temperature dependences and activation energies of spin-spin relaxation of SARA protons of heavy oil fractions upon cooling from room temperature to -15°C and heating to + 60°C

For comparison, the study of reversibility of precipitation of asphaltenes in crude oil by the gravity-chromatographic method of SARA (Abedini et al., 2011) at 25°C, 40°C, 50°C and 60°C required more than a day for each point both at increase in and with a decrease in temperature. To obtain the result, it was necessary to create conditions for maintaining the temperature for a long time in the laboratory, where more than fifteen operations are performed. They include the preparation of a large number of samples, accurate dosing and weighing of reagents, holding at a given temperature, continuous mixing for complete extraction, centrifugation, washing for complete discoloration of the solvent, etc. As a result of the analysis, the samples are destroyed. To exclude possible accidents and increase the accuracy of the measurements, the authors processed three samples at each temperature. As a result, this experience can last up to two weeks. It is no accident that the methods of magnetic radiospectroscopy (NMR, EPR) are increasingly used for non-invasive analysis in the oil industry.

Conclusion

Despite the identified shortcomings (Bissada et al., 2016), the standard gravimetric chromatography method SARA (ASTM 2012. D412409) is widely used to analyze the group composition of oils. The density and viscosity of the oil, the relative hydrogen index RHI, the acid number and many other factors that affect the economic efficiency of the technological processes at each stage of the creation of the surplus value from the development of the fields to the production, transportation and refining of oil depend on the amount and ratio of the fractions. The results of this analysis are associated with an assessment of the compatibility and, as a consequence, the stability of mixtures of crude oils, which allows foreseeing the problems of sedimentation during their further storage and transportation, although the effectiveness of such predictions is recognized as low (Guzmán et al., 2017).

The SARA-NMR method presented above is a good alternative to the procedures recommended by ASTM for analyzing the group composition of heavy oils. On the accuracy of determining the content of individual SARA components, the NMR method is not inferior to ASTM methods, and the reproducibility is potentially higher, since it is performed automatically, without the use of chemical reagents and any other interference in the state of the samples. If necessary, the absolute accuracy of measurements can be increased in 3÷5 times due to an increase in the accumulation time of data. The resolving power in the amplitude of the proton signal is ≈3 mg H_2O under standard measurement conditions (see the section "Materials and Methods"), which is 0.5% with a sample weight of 600 mg. Thus, the absolute content of asphaltenes in crude oil of about 5% can be determined

with a relative accuracy of not worse than 10%, and with the accumulation of data may be improved to 2÷3%.

The accuracy of the measurements is provided not only by the stability of the electronic systems of the instrument, but also by the fundamental features of the NMR method: the amplitude of the signal is strictly proportional to the number of protons in the sample, regardless of the phase state of the substance in which the protons are stay: solid, liquid or gaseous. Since the content of the components is determined with respect to the content of all the protons in the sample, the accuracy in significant limits does not depend on the volume (weight) of the sample within the sensor coil and on the possible drift of the gain of the NMR receiver of the relaxometer during long signal accumulation.

The main advantage of the proposed method is its non-invasiveness. This quality provides adequate information corresponding to the real properties of the object of research. NMR data accurately reflect the true composition and nature of the interaction of components in the analyzed samples, in contrast to the results of chemical analysis, since the use of solvents violates the physical-chemical and information structure of the original oil. There is an opportunity to receive detailed information on the processes occurring inside the crude, and potentially "live" oil under such conditions by temperature, pressure, the presence of dissolved gases, etc., which exist in reality.

Unfortunately, the realization of this perspective of the method application in full is impossible on the usual NMR instruments without solving the problem of sampling with preservation and maintenance of natural conditions during the analysis. However, innovative development of low-field NMR sensors has already been developed to measure the relaxation and diffusion times in liquids, including oil, at very high pressures (up to 2500 atm) and high temperatures (up to 175°C) (Freedman et al., 2014) . A cylindrical magnet with a diameter of 9 cm and a length of 20 cm had an aperture along the axis of 6.6 cm in diameter, in the middle part of which the magnetic field provided a resonance frequency for protons of 2.18 MHz. The signal-to-noise ratio of the new sensor is more than 15 times higher than that of existing commercial systems, i.e. data can be obtained more than 200 times faster than it was possible before.

Such high technical characteristics make it possible to predict that soon NMR sensors will be created on process pipelines, or on their branches of sufficiently large diameter, for on-line monitoring of various technological processes in the oil industry. Only non-contact methods in the course of actual operation can provide true information on complex and delicate processes in "live" oil, analyzed as close as possible to the wellhead, and then through the stages of de-gasification, dehydration, mixing, transportation up to distillation and

manufacturing of many types of commodity products. The objective information will enable to optimize the technological processes of extraction and processing of hard-to-recover hydrocarbon reserves, and the installed equipment will enter the automated digital system of industry management.

Acknowledgments

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About the Authors

Vladimir Ya. Volkov – DSc (Chemistry), Professor
Kazan (Volga region) Federal University
MIREA – Russian Technological University
78, Vernadsky Ave., Moscow, 119454, Russian Federation

Boris V. Sakharov – Researcher
Kazan (Volga region) Federal University
State Research Center for Applied Microbiology and Biotechnology
Obolensk, Serpukhov district, Moscow region, 142279, Russian Federation

Nailia M. Khasanova – PhD (Phys. and math.), Associate Professor, Researcher, Institute of Geology and Petroleum Technologies,
Kazan (Volga region) Federal University
4/5, Kremlevskaya st., Kazan, 420008, Russian Federation

Danis K. Nurgaliev – Professor, DSc (Geology and Mineralogy), Vice-Rector for Research
Kazan (Volga region) Federal University
4/5, Kremlevskaya st., Kazan, 420008, Russian Federation