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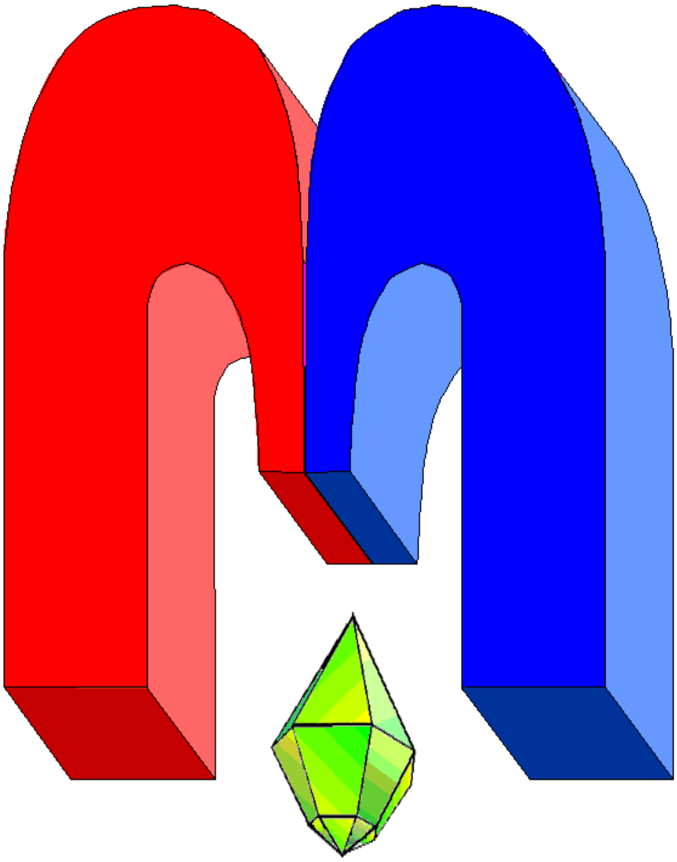

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Rapid evaluation of asphaltene-paraffin content in crude oil by solid-state NMR

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The paper presents results demonstrating, using a series of crude oil samples, the negative impact of resin glass transition effects on the accurate determination of the solid-state component of the NMR signal attributed to crystalline paraffins. To address this issue, a modified NMR-based method for quantifying paraffins and asphaltenes is proposed. The approach involves separating the crystallization temperature of paraffins from the glass transition temperature of resins by plasticizing the resins through the preliminary addition of a specific amount of solvent or precipitant to the crude oil.

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Keywords: nuclear magnetic resonance, solid echo, heavy oils, crude oils, asphaltenes, paraffins, resins.

1. Introduction

Magnetic resonance (MR) techniques have wide possibilities for studying substances in various states of aggregation, such as gas, liquid, and solid [1–4]. However, there is a large class of objects that are characterized by a situation where a substance exists in an intermediate state. This can include various composite materials, partially crystalline polymers, complex molecular mixtures, porous structures, and catalysts, among others. For such types of samples, conventional solid-state high-resolution NMR (HR-NMR) methodologies are generally inapplicable. Instead, the most effective technique is NMR relaxometry, also known as "time domain NMR". This powerful NMR method often uses low magnetic fields and does not require a high degree of magnetic field homogeneity. In terms of application, this method is quite versatile and can be used to study systems with relaxation times ranging from a few seconds for low-viscosity liquids to tens of microseconds for solids. Due to its low requirements for sources of the constant magnetic field, these NMR installations are relatively affordable and can be used to solve various scientific and practical problems. For example, they can be used in the field of catalysis research, including in tightly packed layers and porous materials. These installations cover scales from tens of nanometers to tens of micrometers, as shown in the article by Murilo [5]. In the papers [6, 7] have proposed a low-field NMR relaxation technique as a fast and simple method for in-situ determination of the SARA (Saturates, Aromatics, Resins, and Asphaltenes) composition of crude oils. This method can be used to determine the quantitative content of asphaltenes and resins in oil without extracting them from the oil sample. The work [3, 4, 8] is also relevant to this area of research.

The relevance of such studies is determined, in particular, by the fact that existing laboratory methods ASTM D6560, IP 143, ASTM D-3279, ASTM D-4124, ASTM D-4055, ASTM D7171, GOST 11851-2018 for determining the component content (asphaltenes, paraffins, and resins) of crude oil have a number of drawbacks. These include the time it takes to complete both the analysis of asphaltenes and paraffins, as well as the use of a significant number of toxic chemicals. For instance, to determine asphaltene content using the GOST 11858-66 methodology, crude oil must be dissolved in heptane at a ratio of 1:40.

In this paper, we will show that application of NMR relaxometry methods to determine the presence of paraffins and asphaltenes in crude oil is not always an unambiguous task, even when using solid-state NMR techniques such as Solid-Echo [4, 9]. This is despite the fact that, according to the works [7, 8, 10] and others, this task seems relatively easy.

2. Materials and research methods

To study multicomponent "solid-liquid" systems such as crude oil, we used registration of the free induction decay waveform (FID) [11] and the solid echo signal [9] as the main NMR techniques. The determination of the relative content of solid and liquid phase components in crude oil, which is presumably attributed to different oil fractions, is based on the proportionality of the NMR signal to the number of resonating nuclei and the difference in shape and time characteristics between NMR signals for solid and liquid components.

The FID signal $S_{\mathrm{FID}}(t)$ shown in Figure 1. In a relatively homogeneous magnetic field, $S_{\mathrm{FID}}(t)$ can be represented as a combination of two components: a solid-state component p_{s} with a Gaussian function $f_{\mathrm{s}}(t)$, and a liquid-phase component p_{l} with an exponential or multiexponential waveform $f_{\mathrm{l}}(t)$

$$S_{\mathrm{FID}}(t) = p_{\mathrm{s}} f_{\mathrm{s}}(t) + p_{\mathrm{l}} f_{\mathrm{l}}(t). \tag{1}$$

The NMR signal from the solid component usually decays within a time comparable to the "dead time" (the time immediately after the radio frequency pulse when the receiver is unable to detect the signal), making it difficult to accurately determine the shape and amplitude of this contribution to the free induction decay after a single $\pi/2$ radiofrequency (RF) pulse. However, this challenge is addressed effectively by employing the Solid-Echo pulse sequence shown in Figure 1. This echo does not form for the liquid-phase component.

Solid echo theory [9] originally developed for crystalline solids. However, in [8, 12] the applicability of this technique to a wider range of objects has been proven, provided that the time interval between RF pulses is small. In particular, this requirement is related to the fact that the solid echo signal also contributes to the liquid-phase component, for which no solid echo is formed. Thus, in a homogeneous external magnetic field, the solid echo signal is described as follows

$$S_{\mathrm{SE}}(2\tau + t) = p_{\mathrm{s}} f_{\mathrm{s}}(t) + p_{\mathrm{l}} f_{\mathrm{l}}(2\tau + t). \tag{2}$$

One possible method for quantifying paraffins and asphaltenes in oil is based on the fact that asphaltenes remain in a solid state even at temperatures above 373 K, according to the work [13]. At the same time, paraffins, which have a crystalline state at low temperatures, melt at temperatures between 333 K and 353 K, depending on their molecular weight, according to [14].

Therefore, at temperatures below the melting point of paraffins, the p_{s} is expected to be determined by the combined contribution of crystalline paraffins and asphaltenes. At temperatures above the paraffin melting point, p_{s} is associated only with asphaltene presence. Thus, the content of paraffins and asphaltenes can be defined from the analysis of the experimentally measured temperature dependence $p_{\mathrm{s}}(T)$ in the solid echo signal.

Dehydrated oil samples were chosen for the study. The values of the relative content of asphaltenes, paraffins, and resins were determined using standard deposition methods (see table 1)

According to the data presented in the table 1, the selected crude oils show a wide range of

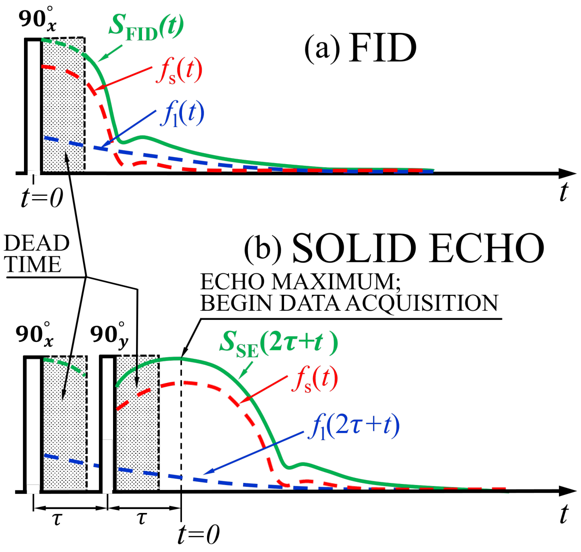

Figure 1. The pulse sequences of the FID (above) and Solid-Echo (below). The dotted lines represent the contributions to the NMR signal from the solid and liquid components. The figure also indicates the receiver "dead time".

Table 1. Chemical composition of crude oil samples.

Sample No	Asphaltenes, wt%	Paraffins, wt%	Resins, wt%
1	3.3 ± 0.8	5.8 ± 1.3	6.2 ± 0.8
2	3.1 ± 0.7	4.5 ± 0.9	19.4 ± 4.3
3	0.3 ± 0.1	3.2 ± 0.4	14.5 ± 2.3
4	0.7 ± 0.2	2.0 ± 0.5	11.1 ± 2.1

variability in their chemical composition. In order to prevent the loss of volatile components, all samples were stored in sealed glass bottles.

Temperature studies of the solid-echo waveform for all samples were conducted over a temperature range of 223 K to 373 K in 5 K increments. During the experiment, the temperature was gradually increased, and the sample was held at each temperature for at least 15 minutes, including the time spent measuring the solid-echo in accumulation mode.

To determine the solid and liquid component contents, we used a nonlinear approximation of the waveform by the sum of two components: a Gaussian function for the solid component $f_{\mathrm{s}}(t)$, and an exponential function for the liquid component $f_{\mathrm{l}}(t)$.

$$S_{\mathrm{SE}}(2\tau + t) = p_{\mathrm{s}} f_{\mathrm{s}}(t, T_{2\mathrm{s}}) + p_{\mathrm{l}} e^{-\frac{2\tau+t}{T_{2\mathrm{l}}}}, \tag{3}$$

where p_{s} is solid component fraction characterized by spin-spin relaxation time $T_{2\mathrm{s}}$; p_{l} is liquid component fraction characterized by spin-spin relaxation time $T_{2\mathrm{l}}$.

All signals with a relaxation time of less than 10-20 μs were attributed to the solid component p_{s} in the NMR signal. Thus, the proportion p_{s} of the solid component in the ^{1}H NMR signal was determined at different temperatures using expression 3. Finally, a set of experimental data representing the temperature dependences of $p_{\mathrm{s}}(T)$ for each oil sample was obtained for further analysis. All experimental studies were conducted using a Proton 20M NMR relaxometer from

"Chromatech" Inc. with a resonant frequency of ^{1}H 22.5 MHz and the ability to accurately adjust the temperature. The "dead-time" of the sensor was 11 μs and the interval between radio frequency pulses was 12 μs. All the relaxation decays data obtained were processed using OriginLab software.

3. Experimental Results and Discussion

Figure 2 illustrates a typical decay of solid echo signals for various temperatures using sample No. 1 as an example.

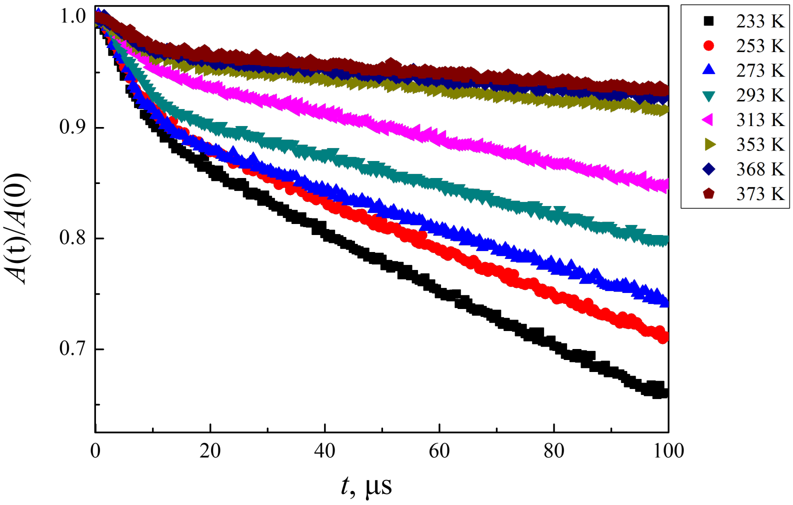

Figure 2. Relaxation decay for sample No. 1. The decays obtained using the Solid-Echo pulse sequence and normalized to the amplitude at the initial time moment ($t = 0$). Pulse sequence parameters: the duration of the $\pi/2$ pulse is 2.5 μs; the sequence repetition time (TR) is 1000 ms; the number of acquisitions is 3000. Measurements were carried out at temperatures ranging from 253 K to 373 K.

Relaxation decays shown in Figure 2 were approximated by the expression 3, where $f_{\mathrm{s}}(t, T_{2\mathrm{s}}) = e^{-\frac{t^2}{T_{2\mathrm{s}}^2}}$. Temperature dependences $p_{\mathrm{s}}(T)$ for crude oil samples No. 1-4 are presented in Figure 3.

For all crude oil samples, there is a decrease in the fraction of the solid component as the temperature increases. This is evident both from Figure 2 and directly from the $p_{\mathrm{s}}(T)$ dependences presented in Figurev 2. However, only for oil sample No. 1, as expected in accordance with [11], are there two temperature ranges in which the proportion of the solid component is independent of temperature. Moreover, in the high-temperature region ($T \geq 330$ K), the registered proportion of p_{s}, presented as a percentage of the relative total NMR signal, is 3.0% and correlates with the signal from asphaltenes, and in the temperature range ($T \leq 280$ K) below the melting points of paraffins, the registered proportion of p_{s} is 8.5%, which, according to [11], corresponds to the total signal from asphaltenes and paraffins. Taking into account the insignificant differences in the proton densities for asphaltenes and paraffins, the obtained values, as a first approximation, can be presented as mass percentages reflecting the content of asphaltenes and paraffins in oil. Then, in this particular case, the proportion of paraffins is easily determined as 5.5 wt.%. For oil sample No. 1, this result is in good agreement with the corresponding data presented in Table 1.

At high temperatures (above 320 K), the p_{s} content, as expected, is also independent of

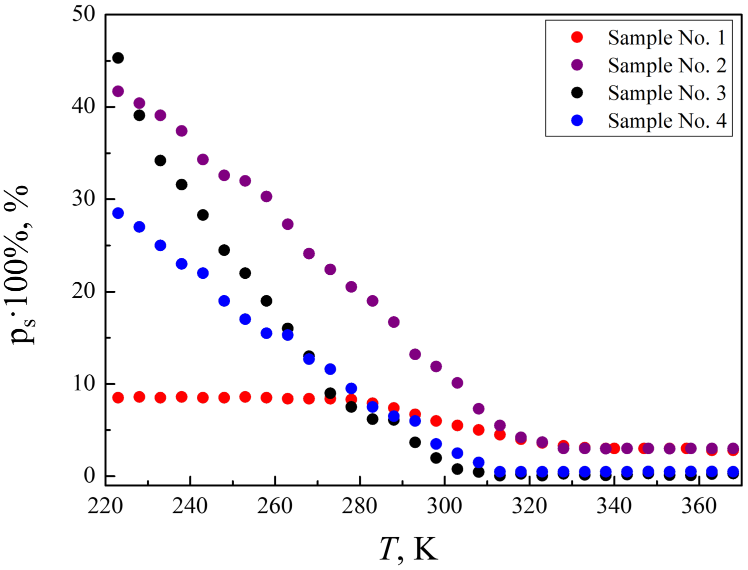

Figure 3. Temperature dependences of the solid component fraction $p_s(T)$, registered during heating of samples No. 1-4

temperature for the remaining three oil samples. Moreover, the recorded p_s values for samples No. 3 and No. 4 are close to zero, amounting to 0.2% and 0.45%, respectively, while for sample 2, the p_s content is 3%. Overall, if these data are interpreted as mass percentages of asphaltene content, they correlate well with the corresponding chemical analysis results presented in Table 1.

A different situation occurs when attempting to use the temperature dependence $p_s(T)$ to determine the relative content of paraffins. As shown in Figure 3, the expected independence of the solid component fraction from temperature in the region below paraffin melting temperatures is not observed. However, table 1 indicates that paraffins are present in all four oil samples. It should be noted that the only difference between oil sample No. 1, which allows us to observe a $p_s(T)$ plateau at low temperatures, is its reduced resin content. It can be assumed that a glass-liquid phase transition occurs in the temperature range below 330 K for resin molecules, which are characterized by a wide range of molecular and group compositions. In the glassy state, resin molecules have relaxation times typical of the solid state. This obstacle will lead to the fact that, in the low-temperature region, the solid component of the NMR signal will reflect not only asphaltenes and crystalline paraffins, but also resins in a glass-like state.

Thus, the presence of resins, which can form glass in the temperature range where paraffins are crystalline, does not allow the evaluation of the relative paraffin content in crude sample using NMR relaxometry. Attempts to expand the temperature range and increase the accuracy of experimental data to identify paraffin signs in $p_s(T)$ curves have not yielded positive results.

The only effective way was found, to shift the temperature region, where paraffins exist in the crystalline state, and the region of resin glass transition, turned out to lower the resin glass transition temperature. This can be achieved by adding a solvent or plasticizer to the crude oil that can dissolve resins but not asphaltenes or paraffins in their crystalline state. N-heptane is one such solvent/plasticizer that could be used for this purpose. Note that n-heptane is recommended as an oil solvent for methods used to determine the asphaltene content. When using this method, the so-called “heptane-insoluble” asphaltenes are separated from the oil.

In Figure 4 we can see the study of the temperature dependence $p_\mathrm{s}(T)$ with the addition of n-heptane to crude oil sample No. 3.

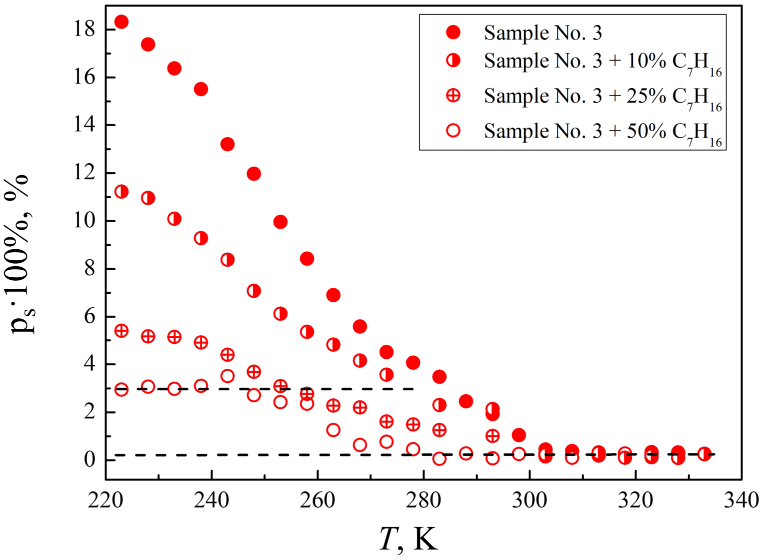

Figure 4. Temperature dependence of the solid component fraction for sample No. 3 diluted with with different (10%, 25%, and 50%) portion (w/w) of n-heptane. The dashed lines represents the constant solid component fraction in sample containing 50% heptane.

As can be seen in the figure, when 10% of n-heptane is added, a noticeable decrease in the solid component fraction in the low temperature range is observed. Note that the fractions p_s shown in Figure 4 are normalized for the oil content in the oil/n-heptane system. This makes it possible to compare these values with those for the initial oil samples. An increase in the portion of n-heptane up to 25% results in a further decrease in the solid component fraction. However, there is still no clear plateau in the $p_\mathrm{s}(T)$ dependence. Nevertheless, a confident plateau is observed in the low temperature region at an n-heptane concentration of 50%. Thus, the 50% portion (w/w or in a ratio of 1:1) of heptane in the sample is the minimum required to ensure that the temperature ranges of crystalline paraffins and glassed resins existence do not overlap. Figure 5 shows the temperature dependence of $p_\mathrm{s}(T)$ for all four samples under mixing conditions in a mass ratio of 1:1.

As can be seen in Figure 5, for all oil samples with n-heptane addition (ratio 1:1), there are two temperature ranges where the solid component does not depend on temperature. In the temperature range of 220-270 K, the solid component fraction was 8.5%, 7.5%, 3.0% and 2.0%, respectively for samples 1-4. The level of the solid-state NMR signal was also constant above the melting temperature of paraffin (above 330 K), with values of 3.0%, 3.0%, 0.2% and 0.45%, respectively for samples 1-4.

So, the asphaltene content can be determined from the p_s value in the high-temperature region. At the same time, the paraffin content is easy to find, since in the low-temperature region, the solid component fraction p_s is defined by joint contribution of asphaltenes and paraffins in oil composition. The results of comparing NMR data with data obtained by chemical extraction for asphaltenes and paraffins are presented in Table 2.

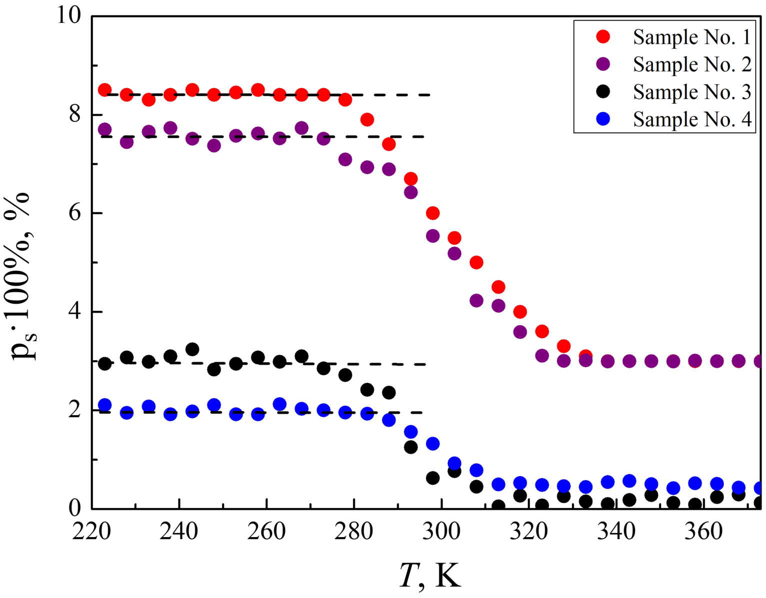

Figure 5. Temperature dependences of the solid component fraction p_s for samples No. 1-4 with 50% heptane addition. The dashed lines indicate constant levels of p_s in the temperature range 220-270 K.

Table 2. Relative content of paraffins and asphaltenes based on chemical analysis and NMR relaxometry.

Sample No	**Asphaltenes, wt%**		**Paraffins, wt%**	
	Chem. analysis	TD NMR	Chem. analysis	TD NMR
1	3.3 ± 0.8	3.0 ± 0.3	5.8 ± 1.3	5.5 ± 0.4
2	3.1 ± 0.7	3.0 ± 0.3	4.5 ± 0.9	4.5 ± 0.4
3	0.3 ± 0.1	0.2 ± 0.2	3.2 ± 0.4	2.8 ± 0.2
4	0.7 ± 0.2	0.5 ± 0.2	2.0 ± 0.5	1.5 ± 0.2

So, the data on the content of paraffins and asphaltenes in crude oil, obtained by NMR relaxometry, generally corresponds to the data from chemical analysis. It should be noted that, in principle, for rapid (express) analysis of the relative content of paraffins and asphaltenes in crude oil, it is sufficient to perform measurements at two temperatures. The first temperature should be chosen to ensure that the paraffins in the sample would be in a crystalline state. Based on the results obtained, this range corresponds to temperatures between 220 and 270 K. The second measurement should be made at a temperature higher than the melting point of paraffins, which is above 330 K. The only condition for conducting these measurements is to exclude in the low-temperature region an additional contribution to the solid component of the NMR signal from the presence of resin molecules in the glassy state. To achieve this, as shown in this study, it is necessary to reduce the glass transition temperature of the resins by adding to sample a specified amount of solvent, such as n-heptane.

4. Conclusion

Based on the study of temperature dependencies of the solid-state component of the NMR signal, a rapid and efficient method has been proposed for determining the content of paraffins and asphaltenes in crude oil. In contrast to conventional approaches, the method employs the effect of lowering the glass transition temperature of resins by adding a low-molecular-weight plasticizer – n-heptane – to the oil, thereby separating the temperature ranges of paraffin crystallization and resin glass transition. A comparison of paraffin and asphaltene contents obtained by standard techniques and by the NMR method demonstrates good agreement, indicating that the proposed NMR experimental methodology is promising for further development and practical implementation.

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