

## High-resolution NMR study of light and heavy crude oils: “structure-property” analysis

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**Abstract.** Measurements of three light and one heavy crude oil samples were carried out by high-resolution nuclear magnetic resonance (NMR) spectroscopy methods. Quantitative fractions of aromatic molecules and functional groups constituting oil hydrocarbons were determined, and comparative analysis of the oil samples of different viscosity and origin was done.

### 1. Introduction

<sup>1</sup>H and <sup>13</sup>C NMR spectroscopy is well-known recognized technique for establishing structural formulas, spatial and electronic structure of either first synthesized or isolated from natural raw materials individual organic compounds. In recent years, there has been a growing interest in using NMR spectroscopy for studying various objects in petrochemistry [1]. The NMR method opens wide opportunities in studying the structure of oil disperse systems and determining their physical and chemical characteristics. The NMR method can help to determine aromatic and aliphatic hydrogens and carbons in oil samples. Areas under resonance peaks in NMR spectra characterize the amount of <sup>1</sup>H or <sup>13</sup>C atoms of corresponding chemical types. Integration of the peaks and subsequent manipulations and calculations yield quantitative proton and carbon type analyses [2]. <sup>1</sup>H and <sup>13</sup>C NMR can be applied to obtain information on content of general functional groups (tertiary and primary carbon atoms, aromatic cores) and possible presence of olefins or water impurity [3]. However, it has not been yet widely used for analysis of high-molecular weight oil samples because of their complex structural organization. Number of works on the NMR analysis of oils and petroleum products, including oil residues, is limited. This circumstance is largely due to the natural shift of interests towards the study of the properties of heavy oil, for which the possibilities of NMR are limited. In particular, the correlation between viscosity of oil and relaxation times in these objects is no longer observed clearly as for light oils, and the use of pulsed NMR method is becoming increasingly problematic.

High resolution NMR spectroscopy has provided detailed chemical information on the proton and carbon chemistry of petroleum materials for over 60 years [4]. Today high resolution NMR instrumentation used to derive detailed multinuclear hydrocarbon information is based on superconducting magnet technologies.



In the case of oil and petroleum products containing typically hundreds of compounds, mainly hydrocarbons, an important feature of NMR spectroscopy is a strict correlation of integral intensities of separate groups of signals in certain chemical shifts ranges in  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra with the content of the corresponding molecular fragments. Note that widely used in petrochemical methods of analysis approaches such as elemental (X-ray fluorescence, absorption and emission optical spectroscopy), fragment and component (IR spectroscopy, mass spectrometry, chromatography) analyses are indirect (unlike NMR) because they require using reference materials for quantitative investigations.

It should also be noted that the quantitative  $^{13}\text{C}$  NMR spectrum is the only direct method for measuring aromaticity ( $C_{\text{ar}}$ ) – relative percentage of aromatic carbon atoms in hydrocarbons.

The aim of this study was to determine the qualitative and quantitative composition of four different crude oil samples by means of the modern methods of high-resolution NMR spectroscopy.  $^1\text{H}$ ,  $^{13}\text{C}$  NMR experiments were applied to provide detailed information on the hydrocarbon chemistry of the chosen petroleum objects.

## 2. Materials and Methods

Studied samples are presented in Table 1: there are low viscosity oils from Middle-Nazym oilfield (Bazhenov formation) (**1**, **2**) (less than 8 cP), Vishanskoe oilfield (Republic of Belarus) (**3**), and the last one is high viscosity oil from Ashal'cha oilfield (Republic of Tatarstan) (**4**).

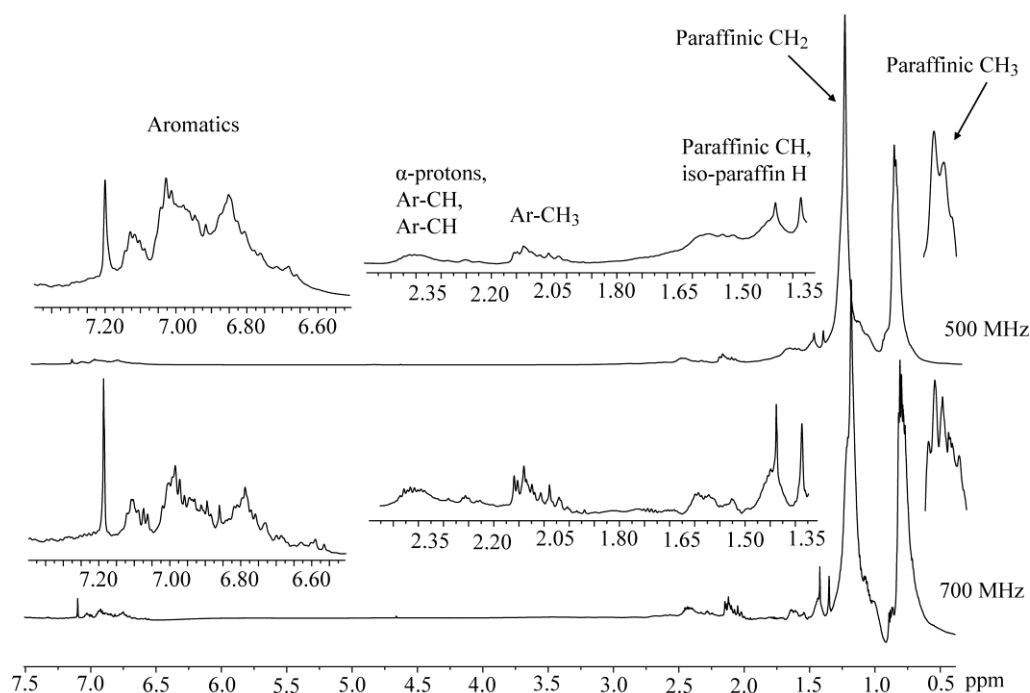
**Table 1.** Studied oil samples.

Sample number	Viscosity, mPa·s	Oilfield
<b>1</b>	7.5	Middle-Nazym (JSC «Ritek», Russia)
<b>2</b>	5.95	Middle-Nazym (JSC «Ritek», Russia)
<b>3</b>	37.2	Vishanskoe (Republic of Belarus)
<b>4</b>	2420	Ashal'cha (Republic of Tatarstan, Russia)

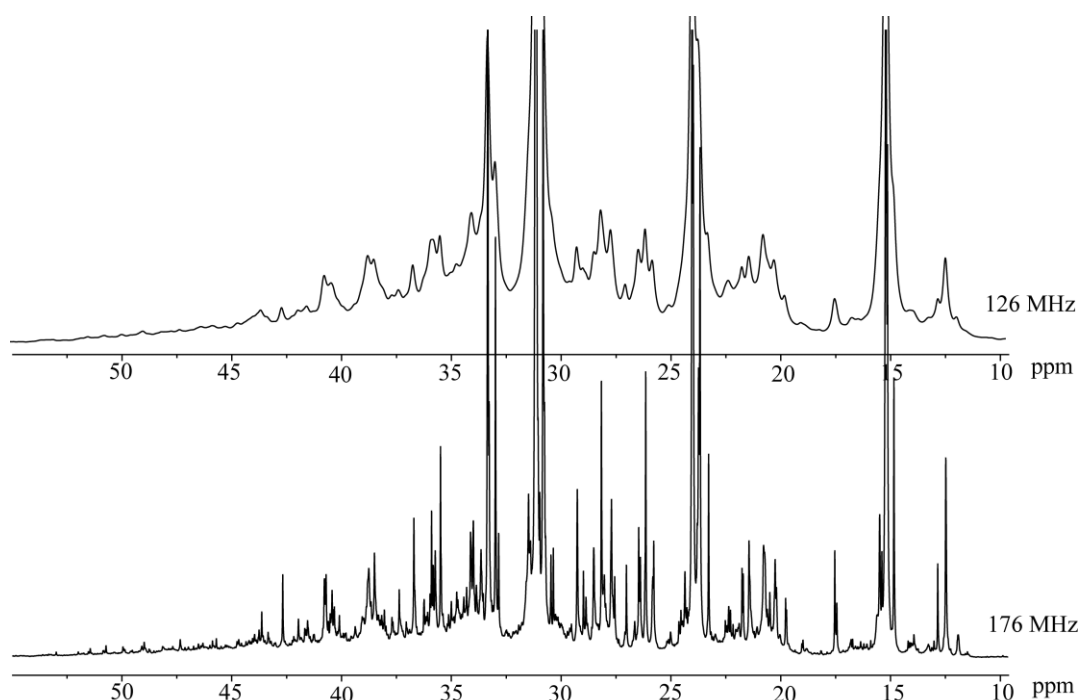
NMR experiments on studied oil samples (**1-4**) were performed on a Bruker Avance II 500 and Bruker Avance III HD 700 (equipped with a CryoProbe) NMR spectrometers. Field lock and shimming were achieved using the deuterium signal from  $\text{D}_2\text{O}$  in a glass capillary placed into the 5 mm NMR tube together with the investigated oil sample. All samples were studied without dilution.  $^1\text{H}$  NMR spectra were recorded using  $30^\circ$  pulses (zg30 pulse program); acquisition time was 4.7 s; pre-scan delay was 6.5  $\mu\text{s}$ , and the relaxation delay between scans was 2 s; spectrum width was 12.0 ppm (6000 Hz); 400 scans were accumulated.  $^{13}\text{C}$  NMR spectra were recorded using  $90^\circ$  pulses with broadband proton decoupling (zgig pulse program); relaxation delay between pulses was 9 s (and acquisition time was 3.5 s); spectrum width was set to 220.0 ppm; number of scans was 3200. Exponential digital filter with the lb parameter of 10 Hz was applied prior to Fourier transformation. Measurements were made at the temperature of  $30^\circ\text{C}$ . All the NMR spectra were integrated after baseline correction, and a mean of minimum three integration values has been taken for each calculation. The relative standard deviation of the results of manual integration did not exceed 3%. Estimation of molar fractions of primary, secondary, tertiary, an aromatic and quaternary carbons was carried out in a way similar to our previous work [3].

### 3. Results and Discussion

As a comparison of the higher resolution of  $^1\text{H}$  and  $^{13}\text{C}$  NMR experiments performed on high-resolution NMR systems, spectra of the sample 1 obtained on two spectrometers are presented in Figures 1 and 2. More peaks are resolved at 700 MHz but the general spectral view can be seen to be the same. The content of several well-resolved signals indicates the presence of branched aliphatic structures. Typical assignment intervals of  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of samples are given in our previous work [3].



**Figure 1.**  $^1\text{H}$  NMR spectra of sample 1 at resonance frequencies 500 MHz and 700 MHz. Observed proton types are indicated on the spectrum.



**Figure 2.**  $^{13}\text{C}$  NMR spectra (aliphatic region) of sample **1** at resonance frequencies 126 MHz and 176 MHz.

There are characteristic ranges of aliphatic and aromatic proton signals in the high- and low-fields regions of the spectra. For samples **1** and **2**, similar spectra with well-resolved signals in aliphatic and aromatic regions are observed (Figures 3, 4). For sample **3**, a slight broadening of the signals is observed, while for sample **4** the broadening is more prominent. Such a line broadening, indicating a strong viscosity, leads to the fact that some low-intensity signals merge with the baseline. For example, the signal at 17.5 ppm in  $^{13}\text{C}$  NMR spectrum (Figure 4) is clearly visible for samples **1** and **2**, is weakly noticeable for sample **3**, and is not visible for sample **4**.

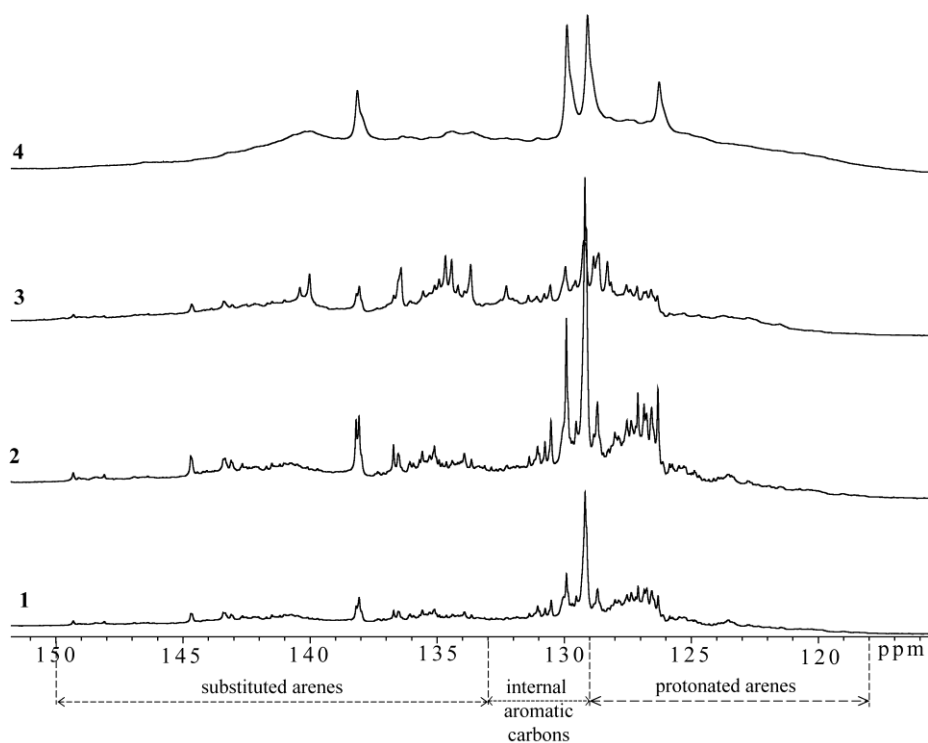
$^{13}\text{C}$  NMR spectroscopy proved to be much more efficient than  $^1\text{H}$  NMR in the study of oil samples, since the broadening of the signals here has a lesser effect on the information content of the spectra due to a much wider chemical shifts range of  $^{13}\text{C}$  [1]. In addition,  $^{13}\text{C}$  NMR spectra allow determining the content of quaternary carbon atoms and functional groups not containing hydrogen atoms.

Information obtained by quantitative integration of signals in individual spectral ranges is represented by the fraction of the corresponding carbon atoms relative to their total number:

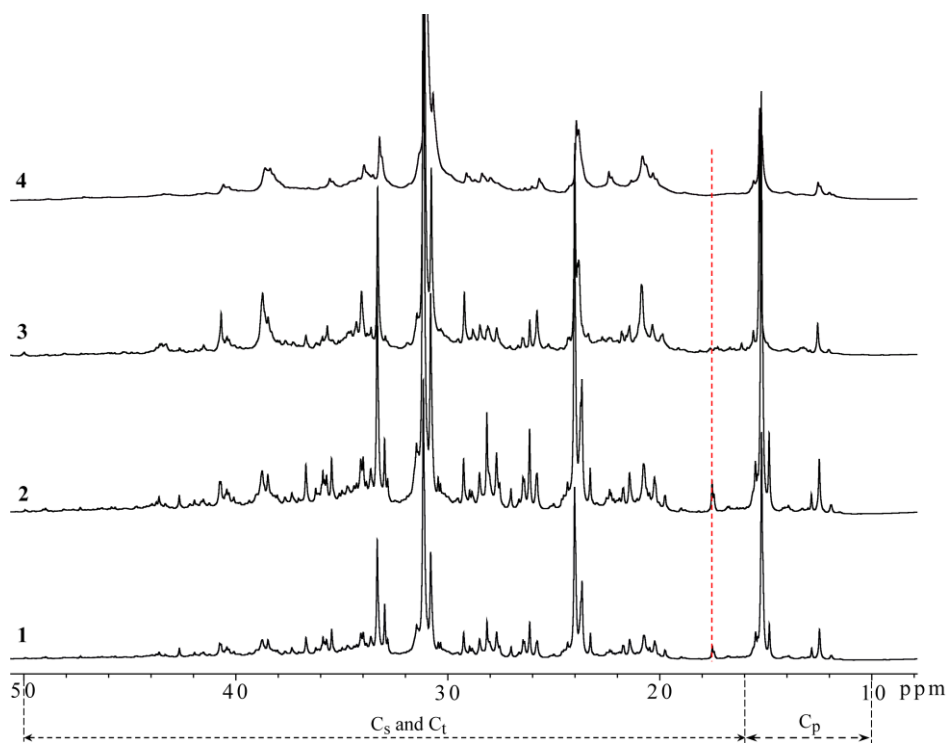
$$C_i = \frac{I_i}{\sum_j I_j}.$$

It is impossible to obtain clear information on the content of hydrocarbons (alkanes, cyclanes) from  $^{13}\text{C}$  NMR spectra, although this information is contained in the fragmentary composition, which can be determined with high accuracy [2].

Table 2 shows the results of estimating the molar content of various carbon groups made by integration of the corresponding regions of  $^{13}\text{C}$  NMR spectra.



**Figure 3.** The aromatic region of  $^{13}\text{C}$  NMR spectra (176 MHz) of samples **1-4**.



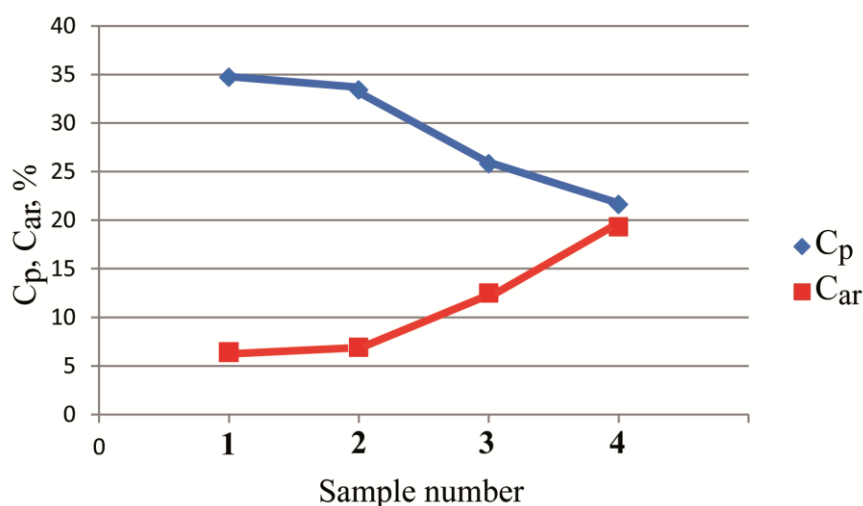
**Figure 4.** The aliphatic region of  $^{13}\text{C}$  NMR spectra (176 MHz) of samples **1-4**.  $C_p$ ,  $C_s$ ,  $C_t$  stand for primary, secondary, and tertiary carbons.

**Table 2.** Molar fractions (%) of primary ( $C_p$ ), secondary + quaternary ( $C_{sq}$ ), tertiary ( $C_t$ ), aromatic ( $C_{ar}$ ) groups and mean chain length of aliphatic hydrocarbons based on  $^{13}\text{C}$  NMR spectra of samples **1-4**.

Group type	Sample number			
	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>
$C_p$	34.7	33.4	25.8	21.6
$C_{sq}$	48.4	53.8	53.0	48.9
$C_t$	12.1	4.8	10.0	12.8
$C_{ar}$	6.4	6.9	12.5	19.3
$C_{arom} / C_{aliph}$	0.067	0.075	0.141	0.232
mean chain length	4.9	5.1	6.0	6.5

Based on obtained data (Table 2), we can see that the highest percentage of primary and secondary carbons is in sample **2**, which is however almost twice as low in the content of tertiary carbons. Also, twofold and threefold excess of the relative content of aromatic carbon atoms in samples **3** and **4**, respectively, compared with samples of light oils **1** and **2** is observed. So, in the total comparison of aromatic/aliphatic content, the smallest value belongs to sample **1** – 0.067. Mean chain length values turned out to be rather low, which indicates the approximate nature of our model, but there is an obvious tendency to increase the chain length as the viscosity of sample increases.

Evidently, molar fraction of aromatic groups ( $C_{ar}$ ) (aromaticity) changed the most while the molar fraction of aliphatic groups ( $C_p$ ,  $C_{sq}$ ,  $C_t$ ) changed not so prominently in passing from light oils (**1-3**) to heavy one (**4**). Also there is a mutually inverse dependency for primary and aromatic carbons as the viscosity of the samples increases (Figure 5).



**Figure 5.** Dependence of the molar fractions  $C_p$ ,  $C_{ar}$  (%) in the transition from light (**1-3**) to heavy (**4**) oil samples (from the data in Table 1).

#### 4. Conclusions

The samples of some light paraffinic and heavy aromatic oils were studied by high resolution NMR spectroscopy. Aromatic and aliphatic oil components can be distinguished by  $^1\text{H}$ ,  $^{13}\text{C}$  NMR analysis. High resolution NMR instrumentation with field strengths of 11.7 Tesla ( $^1\text{H}$  resonances frequencies of 500 MHz) is adequate for most liquid-state petroleum applications as the higher resolving power at very high fields does not provide any significant extra discernment of detailed chemistry. Using NMR, one cannot absolutely settle the problem of the identification and evaluation of hydrocarbon composition in the crude fluid, and it should be considered in combination with existing traditional methods for studying the oil composition. However, this technique can enrich oil researches and improve its application efficiency.

#### References

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**The work has been performed according to the Russian Government Program of Competitive Growth of Kazan Federal University**