Qualitative and quantitative analysis of oil samples extracted from some Bashkortostan and Tatarstan oilfields based on NMR spectroscopy data

I.Z. Rakhmatullin, S.V. Efimov, B.Ya. Margulis, V.V. Klochkov*

Kazan Federal University, 18 Kremlevskaya St., 420008 Kazan, Russian Federation

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- $^{13}$C NMR spectroscopy
- Crude oil
- Functional group
- Qualitative analysis
- Quantitative composition

ABSTRACT

Measurements of crude oil samples by nuclear magnetic resonance spectroscopy were carried out. The quantitative fractions of aromatic molecules and functional groups constituting oil hydrocarbons in several samples were determined and their slight variation from sample to sample was shown. Information on content of general functional groups (tertiary and primary carbon atoms, aromatic cores) and possible presence of olefins or water impurity can be obtained. Basic $^1$H measurements are rather fast and require several minutes. Experiments on modern high-field spectrometers provide better resolution of overlapping regions in $^{13}$C NMR spectra and thus would be more convenient to get detailed information on the amount of different alkyl substituents. Slight but obvious differences were observed between the spectra of the samples taken from different levels of the same oil well.

1. Introduction

Knowledge of the chemical composition and physicochemical properties of crude oils, along with features of the geological and geochemical conditions, is of primary importance for solving problems of the origin of crude oils and for petroleum refining, since it enables variations in the commercial and technical characteristics of crude oils to be predicted and the expediency of combining crude oils from different fields during refining to be assessed (Kvalheim et al., 1985).

Petroleum as a natural object contains hundreds of substances mainly belonging to the three homologous series of hydrocarbons (alkanes, cycloalkanes, and aromatic hydrocarbons), as well as heteroatomic compounds (particularly, asphaltene-resinous substances) containing non-metals (sulfur, oxygen, nitrogen) and trace elements (V, Ni, Fe, Zn, etc.) (Speight, 2014; Pokonova et al., 1984; Van Ness and Van Westen, 1951). Each petroleum variety has a unique mix of molecules, which define its physical and chemical properties and ultimately its behavior during refining. Structural recognition of the oil constituents is the prerequisite of different techniques used for heavy oil upgrading. In contrast to other physical-chemical methods (De Peinder et al., 2008; Satya et al., 2007; Jebljčika et al., 2003; Sjoblom et al., 1998), nuclear magnetic resonance (NMR) spectroscopy allows obtaining both qualitative (type of molecules) and quantitative (content of compounds) information on a mixture of organic compounds. The history of $^1$H and $^{13}$C NMR spectroscopy shows that application of these techniques for compositional characterization of petroleum fractions was a breakthrough and was considered a novel development in this area (McLean and Kilpatrick, 1997; Trejo et al., 2004).

There are many methods for investigation of oil composition including gas chromatography and quantitative fluorescence techniques (Xixian et al., 2000; Fuhua et al., 2001a, 2001b; Xiexian et al., 2003; Xingli et al., 2007). Although these methods can resolve some problems, they can only qualitatively describe the fluorescence characteristics based on the variable chromatography curves (Zhizhan et al., 2015).

NMR has the advantage to provide directly molecular details determining physical-chemical properties of a sample at a macroscopic level (Lintelmann, 1995). In fact, an NMR spectrum contains information in terms of the molecular functional groups and, if recorded with the proper resolution, may allow characterizing a sample at the molecular level (Allen et al., 1985; Behera et al., 2008). Modern NMR spectroscopy technique is based not only on increased sensitivity and resolution, but also applies two-dimensional methods, which provide additional information on the composition of oil samples from NMR spectra. Taking into account the importance of oil to the economy, there is a very important and urgent task for adaptation of modern 1D NMR ($^1$H, $^{13}$C) and 2D NMR (COSY, HSOQC experiments) spectroscopy to determination of oil composition.

$^1$H NMR spectroscopy is a relatively fast method, which does not require complex sample preparation. Accessible spectral range of proton resonances is not wide, and hence little information can be

* Corresponding author.
E-mail address: vladimir.klochkov@kpfu.ru (V.V. Klochkov).

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obtained from direct comparison of $^1$H spectra. $^1$H NMR spectra of crude oils contain a great number of signals reflecting their chemical complexity (Gupta et al., 1986; Kushnarev et al., 1989; Hasan et al., 1983). Therefore, to exploit the full information content of the NMR data acquired on complex systems, different multivariate data analysis methods were developed (Alam and Alam, 2004). Statistical analysis may be successfully used to predict important properties of oil (API gravity, carbon residue, wax appearance temperature, and basic organic nitrogen) based on a large set of studied samples (Duarte et al., 2016). Use of $^1$H NMR spectroscopy on neat crude oil samples combined with partial least squares (PLS) modeling has high potential to predict crude oil properties (Masilli et al., 2012). If $^{13}$C data is added, much more information on chemical composition can be extracted; however, this requires more experimental time. NMR data can be combined with other experiments (mass-spectrometry, elemental analysis, etc.); an example of such a study using Monte Carlo simulation to reconstruct molecular composition of gasoils and heavy fractions is presented in Hudebine and Verstraete (2004); Verstraete et al. (2010). Organic compounds contained in rocks can also be studied in solid phase by NMR using the magic-angle spinning method; as an example, studies of kerogen can be mentioned (Bushnev et al., 2010; Bushnev and Burdelnaya, 2012).

The aim of this study was to determine the qualitative and quantitative composition of a number of oil fields from the Republics of Bashkortostan and Tatarstan by modern methods of NMR spectroscopy. Oil samples from the following fields: Kontuzlinsk (I), Hatyrovsk (II), Akansk (III), Selengush (IV) were studied. Also a comparative analysis of oil samples from top (V) and lower (VI) parts of Bashkirian oil well (Akansk field) was done.

2. Materials and methods

$^1$H (500.1 MHz) and $^{13}$C (125.8 MHz) NMR experiments on oil samples (I – VI) were performed on a Bruker Avance II 500 NMR spectrometer. Oil samples were diluted with carbon tetrachloride or deuterated benzene to reduce viscosity and to facilitate shimming (in the case of CsD$_3$); relaxation measurements were made without dilution. The volume fraction of oil in the mixture with a diluent was 65–80%. $^1$H NMR spectra were recorded using 30° pulses; acquisition time was 4.09 s and the additional relaxation delay between scans was 1 s; spectrum width was 16.0 ppm; 100 scans were accumulated. $^{13}$C NMR spectra were recorded using 30° pulses with broadband proton decoupling; delays between pulses were 40 s (and acquisition time was 1.44 s); spectrum width was set to 180.7 or 200.8 ppm; number of scans was 250 or 1000. Exponential digital decoupling; delays between pulses were 40 s (and acquisition time was 2.00 s); spectrum width was 16.0 ppm; 100 scans were accumulated. $^{13}$C NMR spectroscopy to the analysis of oil fractions is limited by a small range of chemical shift values for all classes of organic compounds (15 ppm), so compounds with a similar structure in complex mixtures give an average, strongly broadened signal. Also, the spin–spin interaction between protons leads to further complication of spectra, thus $^1$H NMR spectroscopy is used to solve a number of particular problems of structural analysis. $^1$H NMR spectrum allows defining the degree of substance’s aromaticity in mixture. Also a comparison of proportions of aromatic atoms of hydrogen and carbon (from $^{13}$C NMR spectrum) determines the degree of substitution of the aromatic oil fraction.

$^{13}$C NMR spectroscopy is much more informative due to the wide range of chemical shifts (200 ppm) of $^{13}$C nuclei (Breitmaier and Woelter, 1986; Frieboel, 1991). Moreover, broadband decoupling between $^1$H and $^{13}$C nuclei facilitates interpretation of $^{13}$C NMR spectra. This method can be applied for analysis of mixtures containing molecules of known type; the paper (Makhiyanov and Safin, 2006) gives an example applied for polymers, and (Tomii et al., 1995) describes study of essential oils. Crude oil contains vast number of compounds; however, spectral width of $^{13}$C spectra still allows classifying them into several classes even if individual components cannot be identified. Both $^1$H and $^{13}$C NMR spectra of oil samples in solution already have been described in literature (Kalabin et al., 2000); corresponding detailed information is presented in Tables 1 and 2.

$^1$H and $^{13}$C NMR spectra of the oil sample from upper part of Bashkirian horizon (V), mixed with CCl$_4$, are shown in Figs. 1 and 2. $^1$H NMR spectra, as it was expected, provide little information because resonance lines of similar-structure organic fragments merge in broad lines. NMR spectra, as it was expected, provide little information because resonance lines of similar-structure organic fragments merge in broad lines. Also, the spin–spin interaction between protons leads to further complication of spectra, thus $^1$H NMR spectroscopy is used to solve a number of particular problems of structural analysis. $^1$H NMR spectrum allows defining the degree of substance’s aromaticity in mixture. Also a comparison of proportions of aromatic atoms of hydrogen and carbon (from $^{13}$C NMR spectrum) determines the degree of substitution of the aromatic oil fraction.

Some byproducts of oil refining are difficult to study due to their high viscosity at the room temperature and their stickiness to all kinds of containers. This makes the analysis of such objects rather cumbersome and costly procedure. Some of these analyses have to be performed for days and weeks (Speight and Öziüm, 2001). Faster and less expensive approaches to analysis in this case are spectroscopic methods. Thus optimization of NMR is of great interest to investigate refinery products at significantly lower prices and in much shorter times (Molina et al., 2010).

According to the definition given in the literature for the chemical shift parameter as a quantitative measurement used in NMR spectroscopy, the integration can be performed using the specified regions in $^1$H and $^{13}$C NMR spectra. Different integration domains for $^1$H NMR spectra are discussed in the Calemma et al. (1995). Application of $^1$H NMR spectroscopy to the analysis of oil fractions is limited by a small range of chemical shift values for all classes of organic compounds (15 ppm), so compounds with a similar structure in complex mixtures give an average, strongly broadened signal. Also, the spin–spin interaction between protons leads to further complication of spectra, thus $^1$H NMR spectroscopy is used to solve a number of particular problems of structural analysis. $^1$H NMR spectrum allows defining the degree of substance’s aromaticity in mixture. Also a comparison of proportions of aromatic atoms of hydrogen and carbon (from $^{13}$C NMR spectrum) determines the degree of substitution of the aromatic oil fraction.

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$^{13}$C NMR spectra contain numerous distinguishable signals, which can be assigned to different typical regions and thus give information

Table 1 Distribution of $^1$H NMR chemical shifts of functional groups defining the composition of oil samples (Kalabin et al., 2000).

<table>
<thead>
<tr>
<th>$^1$H NMR chemical shifts, ppm</th>
<th>Organic functional group</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5–1.0</td>
<td>γ-CH$_3$-groups and some CH- and CH$_2$- groups in naphthenic fragments</td>
</tr>
<tr>
<td>1.0–1.7</td>
<td>β-CH$_2$- and some β-CH- groups in aromatic compounds</td>
</tr>
<tr>
<td>1.7–1.9</td>
<td>β-CH-, CH$_2$- groups in hydroaromatic compounds</td>
</tr>
<tr>
<td>1.9–2.1</td>
<td>Methyl groups (CH$_3$) in α-olefins</td>
</tr>
<tr>
<td>2.1–2.4</td>
<td>Methyl groups (CH$_3$) in α-position to aromatic carbons</td>
</tr>
<tr>
<td>2.4–3.5</td>
<td>CH- and CH$_2$- groups in α-position to aromatic carbons</td>
</tr>
<tr>
<td>3.5–4.5</td>
<td>Bridging CH$_2$- group (diphenylmethane)</td>
</tr>
<tr>
<td>4.5–6.0</td>
<td>Protons of olefin groups</td>
</tr>
<tr>
<td>6.0–7.2</td>
<td>Protons of single-cycle arynes</td>
</tr>
<tr>
<td>7.2–8.3</td>
<td>Dv- three- and tetra-aromatic protons</td>
</tr>
<tr>
<td>8.3–8.9</td>
<td>Some three- and tetra-aromatic protons</td>
</tr>
<tr>
<td>8.9–9.3</td>
<td>Protons of some four-cycle arynes</td>
</tr>
</tbody>
</table>
on the fractions of aromatic, primary (CH₃), secondary (CH₂), and other types of carbon atoms. The combination of ¹H and ¹³C NMR spectra allows estimating the average length and branching of aliphatic chains.

¹H and ¹³C NMR signals of the oil samples were assigned following the literature data. To identify the mole fractions of functional groups in the samples, integral intensities of ¹H NMR signals were normalized according to the number of protons in each group. Thus, signal intensities of methyl groups were divided by 3; methylene groups, by 2. With this recalculation, integral intensities of signals in ¹H NMR spectra can be represented as proportions of functional groups. Results are shown in Tables 3 and 4.

Analysis of data from Tables 3 and 4 leads to a number of conclusions regarding the use of NMR spectroscopy in quantitative studies of oil. Quantitative content of methyl groups was readily determined since their resonances fall into the high-field region in both ¹H and ¹³C NMR spectra for vast majority of organic compounds (to 1.1 ppm and to 22 ppm, respectively) (Breitmaier and Woelter, 1986; Friebolin, 1991; Kalabin et al., 2000).

It is evident from Tables 3 and 4 that both ¹H and ¹³C NMR spectroscopy evaluate the content of methyl groups in samples identically. Due to the complexity of separation of methylene and methine signals, summary contents of these groups in different samples were compared. In the ¹H NMR scale these signals appear in the region from 1.1 to 2.4 ppm: β-CH₂, some β-CH groups in aromatic compounds, and CH₃- group in alkyl groups (Table 1). In ¹³C NMR scale they are in the region from 22 to 60 ppm: methylene (CH₂) groups in aliphatic compounds, and β-CH₂- groups in hydroaromatic and naphthenic compounds (Table 1). In ¹³C NMR scale they are in the region from 22 to 60 ppm: methylene (CH₂) groups in aliphatic compounds, and β-CH₂- groups in hydroaromatic and naphthenic compounds (Table 1).

<table>
<thead>
<tr>
<th>¹³C NMR chemical shifts range, ppm</th>
<th>Organic functional group</th>
</tr>
</thead>
<tbody>
<tr>
<td>11.0–12.5</td>
<td>γ-CH₃-groups and some CH- and CH₂- groups in aromatic fragments, CH₃- group in ethyl-substituted cyclohexane</td>
</tr>
<tr>
<td>12.5–15.0</td>
<td>γ-CH₃ (and more distant) methyl groups of aromatic cycle; CH₂- group, shielded by two neighboring aromatic rings</td>
</tr>
<tr>
<td>15.0–18.0</td>
<td>β-CH₂- substituent in ethylene group</td>
</tr>
<tr>
<td>18.0–20.5</td>
<td>α-CH₂- group, shielded by one aromatic; some α-CH₂- and CH₂- groups in hydroaromatic and naphthenic fragments</td>
</tr>
<tr>
<td>20.5–22.5</td>
<td>α-CH₂- group, shielded by aromatic; some α-CH₂- and CH₂- groups in hydroaromatic and naphthenic fragments</td>
</tr>
<tr>
<td>22.5–24.0</td>
<td>γ-CH₂- and CH₂-groups; β-CH₂- groups in unsubstituted tetralin structures</td>
</tr>
<tr>
<td>24.0–27.5</td>
<td>Methylenes (CH₂) groups in naphthenic fragments; α-CH₂- and β-CH₂- groups in propyl and indan fragments; β-CH₂- group in isopropyl</td>
</tr>
<tr>
<td>27.5–37.0</td>
<td>Methylene (CH₂) groups, do not neighboring with methine (CH) group in alkyl compounds; methylene (CH₂) group in cycle</td>
</tr>
<tr>
<td>37.0–60.0</td>
<td>Methylene (CH₂) group in alkyl fragments; CH and CH₂ alkyl groups of naphthenic fragments, adjacent to CH group</td>
</tr>
</tbody>
</table>

108.0–11.0                         | Olefin fragments |
118.0–129.5                        | Protonated amines |
129.5–133.0                        | Internal aromatic carbon atoms |
133.0–135.0                        | Methyl substituted amines |
135.0–138.0                        | Arenes, substituted by naphthenes |
138.0–160.0                        | Alkyl substituted (except for methyl substituted) amines; heteroatomic (N, O, S) amines |
165.0–175.0                        | Ester or amide carboxy carbon atom |
170.0–182.0                        | Acid carboxy carbon atom |
182.0–192.0                        | Quinone carboxy carbon atom |
195.0–205.0                        | Aldehyde carboxy carbon atom |
202.0–220.0                        | Ketone carboxy carbon atom |

Fig. 1. ¹H (500.1 MHz) NMR spectrum and integral intensities of oil sample (V) from Bashkirian horizon mixed with CCl₄ (insert shows increased signals of aromatic protons). Methyl and methylene groups appear as two distinct peaks; signals from 2 to 3 ppm belong to substituents at aromatic groups.
mined by $^1$H and $^{13}$C NMR spectroscopy methods. In each sample these mentioned groups determine alkanes and cycloalkanes content in total. Also data from Tables 3 and 4 show close fractions of olefin groups in the samples determined from $^1$H (chemical shifts range of 5.8–7.3 ppm) and $^{13}$C NMR spectra (108–118 ppm). Integral intensities of remaining signals in $^1$H and $^{13}$C NMR spectra of studied samples were assigned to aromatic molecules. The main contribution to the total intensity of aromatic molecules in $^1$H NMR comes from signals in the range from 2.4 to 4.4 ppm: CH$_3$, CH$_2$, and CH groups in the $\alpha$-position to aromatic carbons (Table 1). The same information in $^{13}$C NMR scale is contained in signals in the range from 118 to 160 ppm: protonated arenes, internal aromatic carbon atoms, methyl substituted arenes, naphthen substituted arenes, allyl substituted arenes, and heteroatomic arenes containing nitrogen, oxygen or sulfur atoms (Table 2).

Comparison of the samples (V) and (VI), taken actually from a single oil field, reveals some minor differences, which are most clearly seen for the weakest signals. Thus, a small $^1$H NMR signal at 5.43 ppm is observed in sample (V), while it is absent in the sample taken from the bottom part of the well. A number of $^{13}$C NMR signals are stronger or present only in the spectrum of (V), e.g., lines at 31.4, 41.5, 49.2 ppm, etc.

$^1$H spectra of five samples are compared in Fig. 3. All of them show more or less the same pattern with slightly differing ratios of the characteristic lines. Spectrum (IV) has a peculiar signal of $\delta=4.9$ ppm which reveals the presence of water admixture in this oil sample. Note that the presence of unsaturated hydrocarbons would also be clearly seen by their signals in the region from 4.5 to 7 ppm, which usually contains no other peaks for crude oil.

If all aliphatic hydrocarbons are assumed to be unbranched, then the mean chain length can be calculated from intensities of CH$_3$ (C1) and CH$_2$ groups (C2) as (C2/C1)·2+2. In our case this gives values from 6.2 (sample (I)) to 7.3 (III). Similar results are obtained from analysis of $^1$H spectra. Underestimation of the mean chain length can be

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**Table 3**

<table>
<thead>
<tr>
<th>Chemical shift range, ppm</th>
<th>(I)</th>
<th>(II)</th>
<th>(III)</th>
<th>(IV)</th>
<th>(V)</th>
<th>(VI)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H1 0.1–1.1</td>
<td>20.9</td>
<td>21.1</td>
<td>18.9</td>
<td>18.6</td>
<td>18.1</td>
<td>19.1</td>
</tr>
<tr>
<td>H2 1.1–2.1</td>
<td>50.7</td>
<td>54.9</td>
<td>52.3</td>
<td>53.3</td>
<td>53.9</td>
<td>54.1</td>
</tr>
<tr>
<td>H3 2.1–2.4</td>
<td>3.0</td>
<td>2.5</td>
<td>2.4</td>
<td>2.6</td>
<td>2.3</td>
<td>2.3</td>
</tr>
<tr>
<td>H4 2.4–4.4</td>
<td>13.6</td>
<td>10.7</td>
<td>13.4</td>
<td>13.3</td>
<td>14.2</td>
<td>13.5</td>
</tr>
<tr>
<td>H5 5.8–7.3</td>
<td>6.7</td>
<td>6.3</td>
<td>5.2</td>
<td>6.0</td>
<td>5.7</td>
<td>5.8</td>
</tr>
<tr>
<td>H6 7.3–8.3</td>
<td>4.8</td>
<td>4.3</td>
<td>6.4</td>
<td>5.7</td>
<td>5.2</td>
<td>4.9</td>
</tr>
<tr>
<td>H7 8.3–9.2</td>
<td>0.3</td>
<td>0.2</td>
<td>1.4</td>
<td>0.5</td>
<td>0.6</td>
<td>0.3</td>
</tr>
</tbody>
</table>

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**Table 4**

<table>
<thead>
<tr>
<th>Chemical shift range, ppm</th>
<th>(I)</th>
<th>(II)</th>
<th>(III)</th>
<th>(IV)</th>
<th>(V)</th>
<th>(VI)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1 4–22</td>
<td>23.1</td>
<td>24.5</td>
<td>20.1</td>
<td>20.2</td>
<td>18.6</td>
<td>17.7</td>
</tr>
<tr>
<td>C2 22–37</td>
<td>48.8</td>
<td>53.8</td>
<td>53.5</td>
<td>52.5</td>
<td>43.7</td>
<td>43.0</td>
</tr>
<tr>
<td>C3 37–60</td>
<td>12.5</td>
<td>10.9</td>
<td>11.4</td>
<td>14.7</td>
<td>15.9</td>
<td>16.5</td>
</tr>
<tr>
<td>C4 108–118</td>
<td>0.8</td>
<td>&lt;0.1</td>
<td>0.1</td>
<td>0.6</td>
<td>3.8</td>
<td>3.8</td>
</tr>
<tr>
<td>C5 118–129</td>
<td>8.7</td>
<td>5.6</td>
<td>7.7</td>
<td>7.5</td>
<td>7.9</td>
<td>7.9</td>
</tr>
<tr>
<td>C6 129–133</td>
<td>1.6</td>
<td>1.4</td>
<td>1.5</td>
<td>1.6</td>
<td>2.0</td>
<td>2.0</td>
</tr>
<tr>
<td>C7 133–160</td>
<td>4.5</td>
<td>3.7</td>
<td>5.7</td>
<td>3.9</td>
<td>8.1</td>
<td>9.1</td>
</tr>
</tbody>
</table>

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Fig. 2. $^{13}$C NMR (125.8 MHz) spectrum of oil sample (V) from Bashkirian horizon mixed with CCl$_4$. Inset show increased NMR signals of aromatic and aliphatic carbons.

Fig. 3. Comparison of $^1$H NMR spectra (500.1 MHz) of five studied oil samples.
assessed by comparing with data of independent methods to estimate the degree of branching. On the other hand, we can assume that most of the hydrocarbons have the formula CH₃(CH₂)ₙ(CH₃)mCH₃; in this case effective length n+m+2 can be estimated as ((C₂+C₃)/C₁)·2+2, which gives larger values from 7.3 ((I) and (II)) to 8.7 (VI). Thus, methyl substituted heptane, octane or nonane can be regarded as representative compounds in the studied hydrocarbon mixtures.

More sophisticated data interpretation should allow for partial overlapping of spectral ranges. If intensities of signals of primary groups (CH₃) is designated Iₚ; secondary and quaternary, Iₛ; ternary, Iₜ, then corresponding molar fractions of these groups are given by the following formulas introduced by Kalabin et al. (2000):

\[ C_p = \frac{(1.04I_p - 0.043I_q)(I_q + I_t)}{(1 - C_{ar})}, \]

\[ C_s = \frac{(1.02I_p - 0.066I_q)(I_q + I_t)}{(1 - C_{ar})}, \]

\[ C_t = \frac{(1.04I_q - 0.04I_p)(I_q + I_t)}{(1 - C_{ar})}, \]

where the fraction of aromatic carbons C_{ar} can be straightforwardly found from NMR spectra.

Being applied to the considered six oil samples, this approach leads to data shown in Table 5. Note that fraction of tertiary groups, which allows estimating the degree of molecular branching, varies within a wide range.

Samples (I–IV) were studied with deuterated benzene added for shimming and long-term stabilizing of the magnetic field (note that ¹³C NMR measurements lasted about 11.5 h in experiments with 1000 scans). However, even without the field lock (which was the case for samples (V) and (VI)) the field was sufficiently stable to obtain good spectra; this can be controlled by the lineshape of the CCl₄ signal at δ_C=97.3 ppm. A drawback of this approach is the necessity to optimize the field homogeneity using the FID area as the homogeneity criterion, which is a time-consuming procedure. If a series of similar samples is to be analyzed, this shortcoming becomes less significant. Another benefit from using CCl₄ as a diluent is the fact that signals in the aromatic region can be processed immediately without preliminary subtraction of the benzene signal at δ_C=127.6 ppm.

Time needed for acquiring ¹³C NMR spectra depends on the desired signal-to-noise ratio (SNR). In a typical spectrum recorded for our samples, SNR calculated for small but still clearly distinguishable signals is ~34; for the highest line at 29.7 ppm SNR exceeds 600. Duration of the experiment thus can be shortened several times with SNR remaining at an admissible level. Special INEPT-based experiments can also be used which provide uniform signal amplifications for carbons of CH₃ groups (Berger and Braun, 2004; Mikelis et al., 2010); relaxation pause in this case is defined by protons’ T₁ which is 0.5–0.6 s for the considered oil samples.

Another property of NMR spectra which is even more important in analysis of complex mixtures is resolution. Spectral resolution is generally proportional to the operating frequency, and thus recording spectra at high-field spectrometers yields more information provided that other requirements for obtaining good-quality spectra are fulfilled (low viscosity of solution, absence of paramagnetic impurities, etc.).

Fig. 4 demonstrates a ¹H NMR spectrum of sample V dissolved in CCl₄ obtained at 700 MHz. Several new details appear, for instance, we can distinguish multiple individual methyl signals (0.8–1.0 ppm). It means that the oil sample contains hydrocarbon chains of several types, each of which has its own set of terminal methyl groups. Also the aromatic region (6.0–9.0 ppm) here has a more interesting view. ¹³C APT NMR spectrum with proton decoupling is shown in Fig. 5. This experiment allows distinguishing between primary and tertiary carbons from secondary and quaternary ones. If a ¹³C atom is bound to an odd number of protons, a negative peak appears. It facilitates assignment of corresponding signals in overlapping areas of CH and CH₂ resonances; however, integration of signal intensities in spectra of this kind does not give exact information on the fraction of corresponding nuclei.

It is known that even for relatively simple molecules assignment of signals in one-dimensional ¹H and ¹³C NMR spectra can be ambiguous. Modern two-dimensional NMR spectroscopy experiments are often required to overcome this difficulty: COSY, TOCSY, HSQC (Fig. 6), HMBC, NOESY, etc. These methods have shown themselves particularly well in determining the chemical and spatial structure (Galullina et al., 2017; Usachev et al., 2016). Fig. 5 shows an HSQC NMR spectrum of oil sample V, dissolved in CCl₄ (80% w/w). Two groups of signals in spectrum are observed: aliphatic area of signals (¹H: [1–4 ppm], ¹³C [10–60 ppm]) and aromatic ones (¹H: [6–8 ppm], ¹³C [115–135 ppm]). Compared to 1D ¹³C spectroscopy, it is favorable due to its higher sensitivity; however, low digital resolution in both dimensions and fast decay of signal of fast-relaxing compounds make

![Fig. 4. ¹H (700 MHz) NMR spectrum of oil sample (V) in CCl₄ (inserts show zoomed signals of aromatic and aliphatic protons). Residual water signal in the capillary is marked by an asterisk (*).](image)

![Fig. 5. ¹³C (700 MHz) APT NMR spectrum of oil sample (V) in CCl₄.](image)

Table 5

<table>
<thead>
<tr>
<th>Group type</th>
<th>(I)</th>
<th>(II)</th>
<th>(III)</th>
<th>(IV)</th>
<th>(V)</th>
<th>(VI)</th>
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<td>Cₚ</td>
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<td>24.3</td>
<td>19.8</td>
<td>19.9</td>
<td>18.2</td>
<td>17.4</td>
</tr>
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<td>55.6</td>
<td>55.4</td>
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<td>45.3</td>
<td>44.6</td>
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<td>9.4</td>
<td>9.9</td>
<td>13.8</td>
<td>18.5</td>
<td>19.1</td>
</tr>
<tr>
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<td>10.7</td>
<td>14.8</td>
<td>12.0</td>
<td>17.9</td>
<td>19.0</td>
</tr>
</tbody>
</table>

![Table 5](image)
its use in petroleum spectroscopy less informative; for example, individual signals in the high-field region (1H: [0.5–2 ppm], 13C [20–50 ppm]) in Fig. 6 are hardly distinguishable.

4. Conclusions

Considering analysis of data from Tables 3–5, some assumptions in determining of quantitative content of oil samples by 1H NMR spectroscopy, and our own experience, we can conclude that 13C NMR spectroscopy on higher frequencies (increased sensitivity and determining of quantitative content of oil samples by 1HN M R) support the Program of Competitive Growth of Kazan Federal University.

Acknowledgments

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References


Fig. 6. 1H,13C-HSQC (700 MHz) NMR spectrum of oil sample (V) in CCl4.