

METHOD OF DETERMINATION OF GENETIC TYPE OF NATIVE UNSATURATED HYDROCARBONS IN OILS AND OIL FRACTIONS OF DISPERSED ORGANIC MATTER WITH ^1H NMR SPECTROSCOPIC DATA

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Abstract

The method of determining the genetic type of native unsaturated hydrocarbons in crude oils and oil fractions of dispersed organic matter according to ^1H NMR spectroscopy data is proposed. Analysis of 300 specially selected samples of 160 fields of major petroleum basins of Russia proved the possibility of using directly the spectra of crude oils as a base version of the method.

Key Words: ^1H NMR spectroscopy; crude oils; dispersed organic matter; unsaturated hydrocarbons; radiogenic and thermogenic types.

1. Introduction

In analytical support of petroleum geochemistry methods oriented to mass analysis of the samples are of main importance [1–3]. The reason of this is the fact that solution of almost every task in this field is based on comparative study of composition of hundreds of petroleum samples and of dispersed organic matter (DOM).

Nowadays unsaturated hydrocarbons are being the less studied class of petroleum hydrocarbons and DOM. There are only two methods useful for mass analysis for these substances allowing getting data on concentration of the only one group of unsaturated hydrocarbons (olefins) [4, 5]. However any hydrocarbons having in their structure at least one isolated C=C bond should be considered to be unsaturated hydrocarbons (UHC). Molecules of UHC which do not contain aromatic rings should be treated as olefins. To some extent it has historical reasons as it was considered for a long time that oils with the exception of a very few samples do not contain UHC due to low stability of the latter [1, 2, 6]. However in [4, 5, 7–10] it was shown that UHC are typical petroleum components. One can often be seen in the petroleum fields containing 2 to 10% of these compounds. Investigation of UHC composition from such fields showed that those were monoens (these were olefins – the structural analogues of saturated petroleum hydrocarbons with near statistical distribution of double bound – and aromatic compounds with isolated C=C bond). These substances were the products of the radiolytic nonselective dehydrogenation of petroleum hydrocarbons under natural radioactive radiation [4, 5, 8–10]. Let's call them radiogenic UHC. Besides, according to [11–13] oils can contain other types of UHC which are products of thermocatalytic reactions ("thermogenic" UHC), unsaturated polycyclic biomarkers. Concentrations of the latter are always low. The other genetic types of UHC in oils are also possible.

Still open is the question on the popularity of oils with different genesis of UHC because of the absence of analytical methods. There are no data at all on UHC in DOM. Methods used in [4, 5, 8–10] are not useful for mass analysis. At the same time study of UHC of various origin turns the investigation towards some tasks which are almost unavailable for study by now such as extent of natural radiation and thermal influence on oils and DOM. So the aim of this study is development of productive and cheap method for differentiation of UHC of different genesis in oils and oil fractions from DOM using ^1H NMR data with embedded procedure for applicability test for every sample analysis.

2. Experimental

The ^1H NMR spectra of solutions of oil fractions and crude oils in CDCl_3 (400 MHz) with 300 – 450 mg/ml concentration were obtained at 313 K using DRX-400 spectrometer ("Bruker",

Germany) with 5-mm detection probe without sample spinning. Registration modes: data acquisition time AQ = 4.09 s, relaxation delay d1 = 20 s, flip angle p1 = 70° (regime 1, no signal saturation), d1 = 2.91 s, p1 = 60° (regime 2, rapid recording). Correction factors for all analytical groups of signals with allowance for their saturation in regime 2 were measured by comparison of the integral intensities of the spectra obtained with and without saturation (11 samples, three spectra for each recorded in both regimes). Chemical shift values (CS) were determined starting from the most intense signal of resonance of CH₂-groups in the middle of alkyl chains considering that $\delta = 1.280$ ppm. For baseline correction mode with spline function based on manually set points as automatic correction programs can't be used in this case.

¹³C NMR (100.6 MHz) spectra of the same solutions were registered in the same spectrometer in the mode of $\{^1\text{H}\}$ -¹³C decoupling and with total Nuclear Overhauser Effect (NOE), AQ = 4 s, d1 = 1 s, p1 = 55°, NS = 320. Correction factors were used in calculation of methyl group contents. Correction factors were measured via comparison of spectra of some samples which were received in the mode with NOE elimination (inversion gated decoupling method, delay with switched off decoupler was 30 s, AQ = 4 s, NS = 1200).

Oil fractions from oils and bitumen after precipitation of asphaltenes with n-hexane (40:1) were prepared with the column chromatography (sorbent – silicagel Silperl 40/100, sorbent/oil ratio was 10:1, eluent – n-hexane). The blank analysis was performed to take into account the possible pollution of samples during sample preparation: whole chain of analytical procedures was performed with standard solvents, sorbent and glass but without oil sample.

3. Results and discussion

The obvious demand to the method for mass analysis is inexpensive and fast sample preparation. For bitumen of DOM ¹H NMR samples are the standard objects during geochemical investigations of oil fractions. As for oils then it is necessary to investigate an opportunity to use spectra of the crude oil. For this purpose ¹H and ¹³C NMR methods were used to study the representative set of petroleum samples from the main Russian petroliferous basins (PB): the Timan-Pechora, Volga-Ural, North Caucasus, Western Siberia and Lena-Tungus, as well as promising Anadyr PB. Some samples (30) were studied as crude oils and as oil fractions as well. Also presence of gas condensates was ensured in the oil samples with the following conditions:

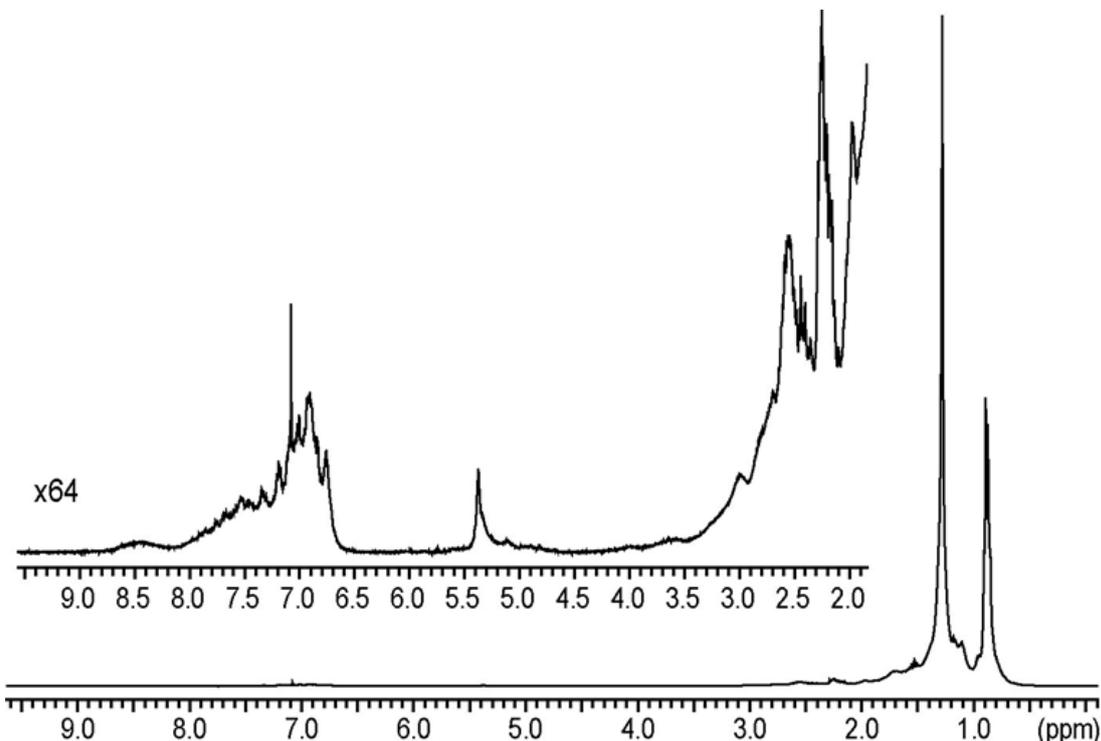
- with the known nature of unsaturated hydrocarbons in the sample [4, 5, 8 – 10, 12];
- from the area with possible recent hydrothermal activity [14];
- from different tectonic areas in limits of each of the main PB;
- including the main ranges of age of overlain deposits, reservoir temperature, depth of occurrence and reservoir lithology (from those existing on the territory of Russia);
- of different composition (molecular weight distribution, concentration of *n*-alkanes, saturated cyclic and aromatic components) including whole range of UHC concentrations in crude oils.

The general description of the set is shown in Table 1. Reservoirs were represented by sandstones and carbonates. UHC content varied from the maximum value known for crude oils (~500 mkmol/g or 20 % (w/w)) to values which are lower than detection limit (~2 mkmol/g or 0.1 % (w/w)). Hereinafter let's refer as high UHC concentrations > 80 mkmol/g; medium concentrations will be 15 to 80 mkmol/g and concentrations < 15 mkmol/g will be referred as low. Concentration of *n*-alkanes varies from the lower than detection limit up to ~ 30%; aromatics – from ~ 5% up to 70%. Besides petroleum, two oil samples of DOM bitumen were studied, one of them with radiogenic UHC, another one – with thermogenic UHC.

The typical ¹H NMR spectrum of crude oils and oil fractions is shown in Fig. 1. The region of proton signals of aliphatic moieties (0.3 – 4.2 ppm, H_{al}) could be divided into three subdivisions [15]. The first one corresponds to resonances of CH₃-groups, which are away from aromatic rings no less than three C-C-bonds (H_γ, $\delta < 1.02 - 1.04$ ppm; selected according to minimum of spectral density). The second one corresponds to -CH₂- and -CH< groups, which are two and more C-C bonds away from aromatic rings (H_β, $1.02 - 1.04 < \delta < 2.02 - 2.05$ ppm, the upper limit is simple average of chemical shift of minimum of spectral density in the range 2.0 – 2.15 ppm and 2.00 ppm which is often referred as a boundary of this subdivision). The third one corresponds to signals of H atoms in α -position to aromatic rings ($2.02 - 2.05 < \delta < \sim 4.2$ ppm). The resonance area for H atoms of the isolated C=C bonds (H_{db}) is ~4.6 – 5.9 ppm.

Table 1. General characteristics of the studied set of crude oils samples.

Basins	Age	Diapasons		Number of	
		Depth (m)	T_{res} (°C)	Fields	Samples
Lena-Tungus	R – E ₁	800 – 3600	5 – 50	27	75
Western Siberian	Pz, J ₂ – K ₂	900 – 3900	30 – 140	36	49
Volga-Ural	D ₂ – P ₁	400 – 3900	12 – 74	41	85
Timan-Pechora	D ₁ – T ₁	25 – 4300	6 – 100	23	41
North Caucasus	T – N ₁	300 – 5800	24 – 185	31	44
Anadyr	Pg ₂ – N ₁	1200 – 2800	42 – 114	3	9
Total	R – E ₁ , D ₁ – N ₁	25 – 5800	6 – 185	161	303

Figure 1. Typical ¹H NMR (400 MHz) spectrum of crude oil or oil fraction solution in deuteriochloroform.

It is found that there are two reasons for difficulties of utilizing spectra of crude oils which are signal broadening due to high concentrations of paramagnetic components and existence of the signal of “exchange protons” (broadened signal of hydrogen in –OH, –SH, –NH groups) in the H_{db} resonance area. The detailed analysis including analysis of pairs of crude oil – its oil fraction showed that only 4% of samples were difficult for quantitative analysis of crude oil spectra. (Oil fractions were getting from the samples of crude oils with complicated quantitative analysis; all met combinations were included). So it is proved that it is possible to use the crude oil samples as is in the basic variant of the method.

Fig. 2 shows spectra (H_{db} resonance area) for typical products of model radiolysis of crude oils (2a) and of three extreme variants of native petroleum UHC composition which were proved to have the radiogenic nature: with the maximal percentage of α-olefins (2b), with minimal and maximal means of average substitution degree of C=C bond (2c and 2d). These three samples correspond to the whole range of compositions of radiogenic UHC [4, 5, 9, 10]. Similar character of spectral density distribution was fixed for all the studied crude oils with high content of UHC.

Investigation of crude oils with medium and low contents of UHC samples with differing spectra in the region of H_{db} resonance were found (see Fig. 3). There were two different types of these obviously non-radiogenic UHC. In the first group (Fig. 3a, 3b) the typical products of thermal destruction were predominant which α-olefins were (see later). The thermogenic nature of these UHC is obvious [12]. Spectra of the second type are lackluster (Fig. 3c) with low signals of H_{db}. Comparing to radiogenic UHC this group has definitely higher part of H_{db} resonances in the 4.6 – 5.0 ppm region but the absence of signals for α-olefins. The additional study is needed to know their origin. Let’s call them “third type of UHC”.

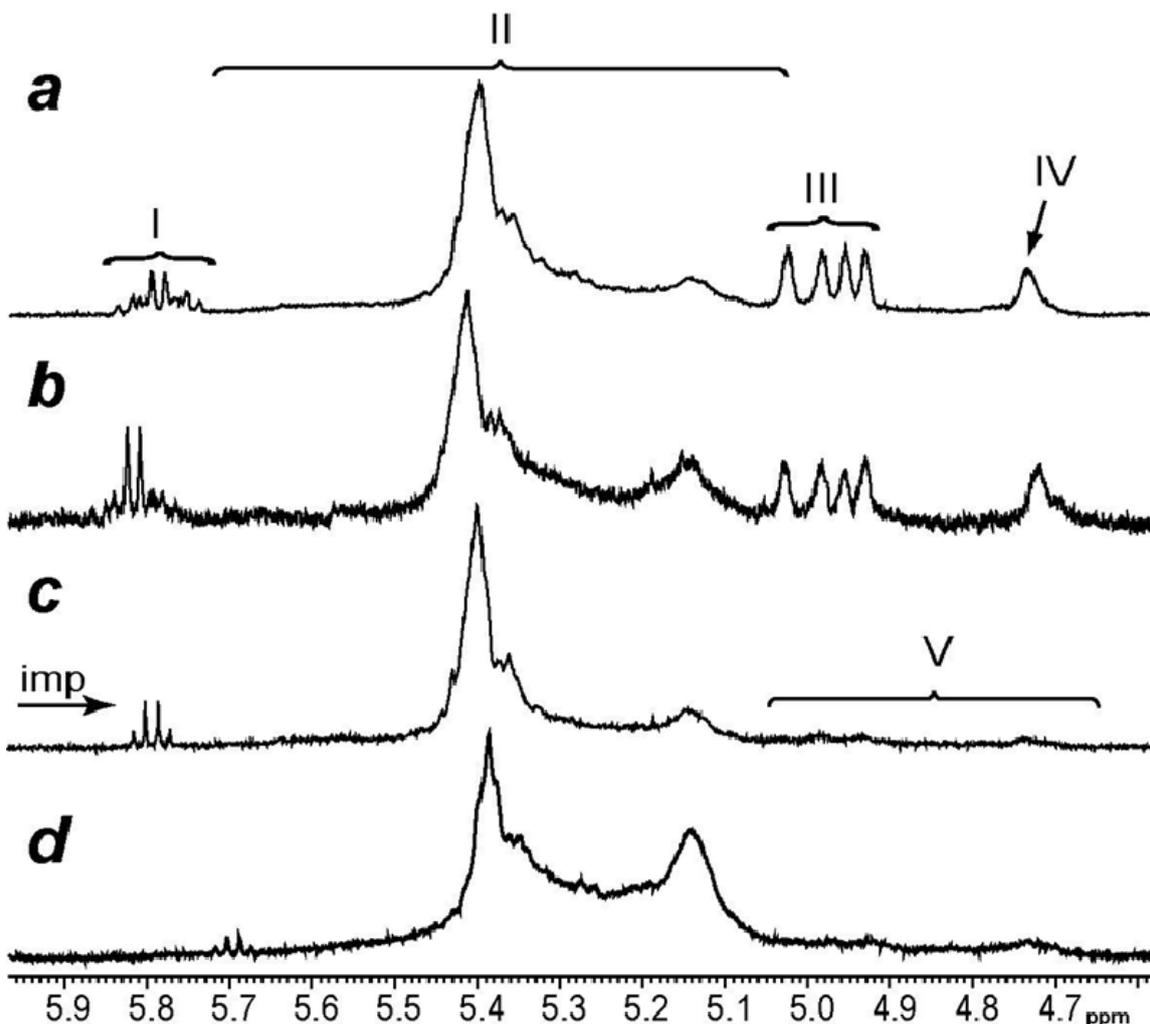


Figure 2. The area of the isolated double bond hydrogen signals in the ^1H NMR spectrum (400 MHz) of a solution of crude oil or oil fractions in deuteriochloroform with radiogenic unsaturated hydrocarbons. I - multiplet of the CH-group of $\text{CH}_2=\text{CH}-\text{CH}_2\text{R}$ α -olefins, II - subzone of $-\text{CH}=\text{}$ resonance ($\sim 5.05 - 5.9$ ppm), III - $\text{CH}_2=\text{}$ groups of $\text{CH}_2=\text{CH}-\text{CH}_2\text{R}$ α -olefins, IV - hydrogen of vinylidene CH_2 -groups ($\text{CH}_2 = \text{CRR}'$), which basically can be considered as substitutes for alkyl chains, V - subzone of $\text{CH}_2=\text{}$ resonance ($4.6 - \sim 5.05$ ppm) (see text).

One can see from the shown data that there are no problems in qualitative differentiation of crude oils with UHC of different origin. However it is impossible to develop method only on qualitative analysis. We can't exclude a priori the possibility of simultaneous existence of components of different genesis in crude oils. We need quantitative parameters to use as differentiation criteria. The same parameters are necessary for embedded procedure of the method applicability test for each sample. It is obvious that we need at least two parameters. It is also important that numerical parameters significantly simplify the procedure of automatic objects differentiation.

The bases for searching of quantitative parameters have been general laws of UHC formation. The main process at saturated hydrocarbons irradiation for the studied class of hydrocarbons is almost nonselective dehydrogenation resulting in formation of $\text{C}=\text{C}$ bonds [17, 18]. The double bonds are formed more frequently at $-\text{CH}<$ groups than at CH_3 -groups resulting in lower concentration of α -olefins. The small break of $\text{C}-\text{C}$ bonds relatively compensates this decrease. Thermal processes in turn result in distribution of double bonds far from equal probable. First of all yield of α -olefins is significantly higher. With the course of time processes of natural degradation of less stable components occur. Then the target parameters should be the dimensionless values characterizing deviation of double bounds distribution from the statistical one.

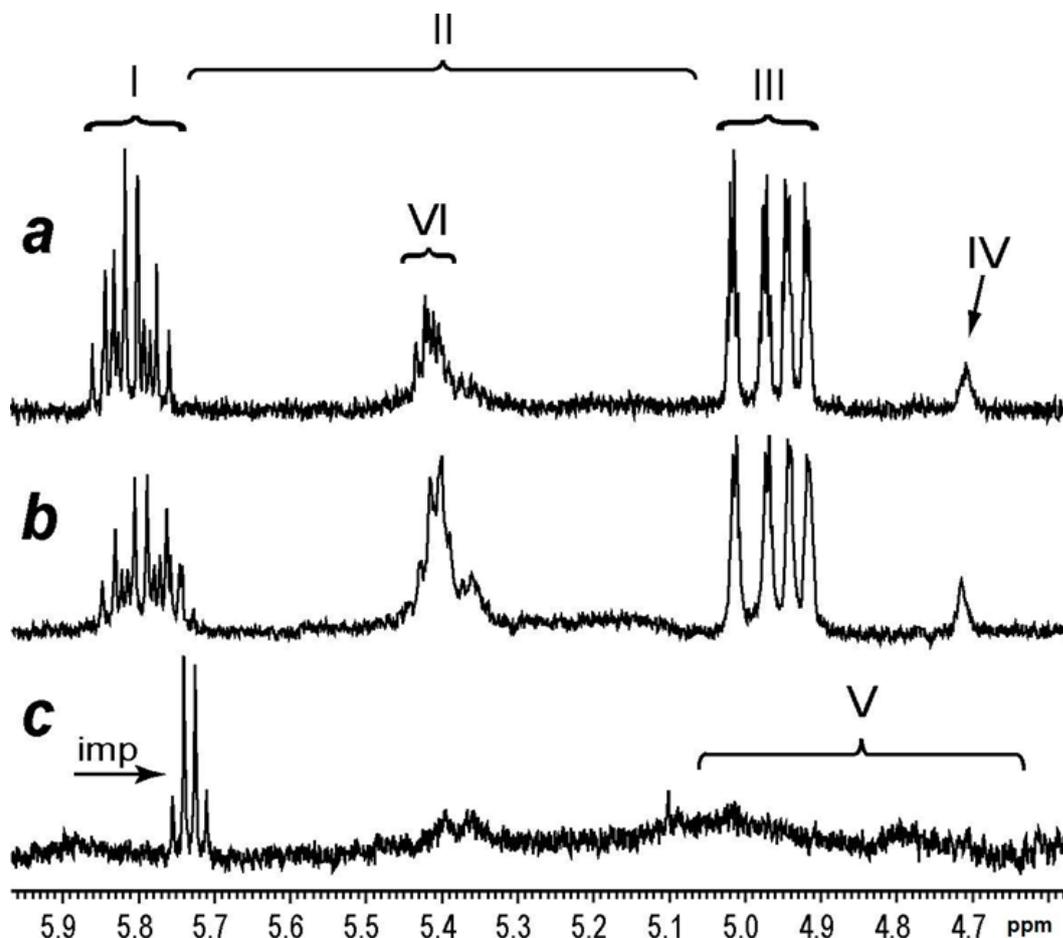


Figure 3. The area of the isolated double bond hydrogen signals in the ^1H NMR spectrum (400 MHz) of a solution of crude oil or oil fractions in deuteriochloroform with nonradiogenic unsaturated hydrocarbons. I - V - see Fig. 2, VI - multiplets of H-atoms of disubstituted C=C bonds of alkenyl chains $\text{RCH}_2\text{-CH=CH-CH}_2\text{R}'$.

The absolute method for introducing such parameters is based on ^{13}C NMR data for fractions of olefins and saturated hydrocarbons [12]. For example, for olefins of type C=CCCCR these parameter should be value of $P_{\text{C,ter}} = (\text{C}_{\text{db}}^{\text{ter}}/\text{C}_{\text{db}}):(\text{C}_{\text{al}}^{\text{ter}}/\text{C}_{\text{al}})$. The first brackets represent the part of C-atoms of $\text{CH}_2=$ terminal double bounds ($\text{C}_{\text{db}}^{\text{ter}}$) of n-alkyl fragment of molecules from all carbon in the double bonds (C_{db}), the second - the part of the C- atoms of the terminal CH_3 -groups in CCCCR ($\text{C}_{\text{al}}^{\text{ter}}$) of the total carbon of the sample (C_{al}). The first value is calculated from the ^{13}C NMR spectrum of the olefin fraction, the second - from the ^{13}C NMR spectrum of the saturated hydrocarbon fractions of the same crude oil. Also similar parameters P_{C} are defined for other groups which are identified by ^{13}C NMR spectra. However, being necessary for the development of methods, they do not apply in the case of mass analysis, as require the preparation of olefin fractions.

For development of parameters based on ^1H NMR detalization of information on distribution of H_{db} according to the structure types is necessary. Area of 4.6 – 5.9 ppm may be divided into subzones of resonance of $\text{CH}_2=$ ($\text{H}_{\text{db},2}$, 4.6 – ~5.05 ppm) and $-\text{CH}=\text{}$ ($\text{H}_{\text{db},1}$, ~5.05 – 5.9 ppm), although this boundary is somewhat conditional (see later) [16]. One can mark out (Fig. 2 – 4) the multiplets of terminal CH_2 - group $\text{CH}_2=\text{CH-CH}_2\text{R}$ of α -olefins ($\text{H}_{\text{db},\alpha}$; AP-part of spin system APXY_2 , $\delta_{\text{A}} = 4.92$ ppm, $\delta_{\text{P}} = 4.98$ ppm; signals are frequently broadened). Multiplet of its CH-group ($\delta_{\text{X}} = 5.80$ ppm) is overlapped by impurity quartet at $\delta = 5.815$ ppm. Almost symmetrical group of signals centered near 4.70 ppm corresponds to hydrogen of vinyliden CH_2 -groups ($\text{CH}_2=\text{CRR}'$; $\text{H}_{\text{db},\nu}$); the main contribution to this signal is from $\text{CH}_2=$ groups which can be considered substituents for alkyl chains. The other H atoms of vinyliden structures constitute the unresolved group in the region of 4.6 – 4.9 ppm. Multiplets of H atoms of di-substituted C=C bonds of alkenyl chains ($\text{RCH}_2\text{-CH=CH-CH}_2\text{R}'$) form the compact group centered near 5.40 ppm ($\text{H}_{\text{db},\text{ch}}$) [5, 12, 15, 16]. Protons of other di- and tri-substituted C=C- bonds ($\text{H}_{\text{db},\text{oth}}$) may be determined as difference between

$H_{db,1}$ and sum of $H_{db,ch} + 0.5 \cdot H_{db,\alpha}$. So one can measure the following values: $H_{db,\alpha}$, $H_{db,v}$, $H_{db,ch}$ and $H_{db,oth}$, as well $H_{db,1}$ and $H_{db,2}$.

As the first parameter one can use the previously introduced value P_H . This value is equal to ratio of number of $CH_2=$ groups to number of $CH=$ groups divided into ratio of number of CH_3-CH_i- ($i = 0 - 2$) groups to number of $-CH_2-$ groups which are two and more bonds away from aromatic rings [12]. It is obvious that at nonselective dehydration $P_H = 1$. Its value is calculated from 1H NMR data by the following relationships:

$$P_H = 1,5 \cdot \{ H_{db,2} / H_{db,1} \} \cdot (gH_\beta / H_\gamma) \quad (1)$$

Here g is the proportion of methylen H atoms to H_β . For crude oils with high parafin content $g = 0.9 \pm 0.05$, for substantially biodegraded ones – ~ 0.7 ($\pm 10\%$ rel.) and 0.8 ± 0.08 for the others. An alternative variant is to assign $g = 0.8$ for all samples. The additional measurement error in this case is $P_H = 20\%$ rel. [12] which is possible (see later).

The main uncertainty in the calculation of P_H is associated with the ambiguity of the assignment of H_{db} signals in the 5.05 - 4.9 ppm region, in which the resonances of the $CH=$ and $CH_2=$ groups overlapped [16] (Fig. 4). Therefore, for all samples we calculated two values: P_H^{max} and P_H^{min} , and for the evaluation of the parameter P_H their simple average was taken. In the calculation of P_H^{max} all the signals in the 5.02 - 4.60 ppm region were attributed to $CH_2=$ resonance, P_H^{min} - signals in the 4.60 - 4.85 ppm (of course corresponding to the H atoms of $CH_2=$ groups), and stand out against the backdrop of a broad unresolved peak α -olefins signals in the 4.88 - 5.02 ppm (for a spectrometer with a working frequency of 400 MHz, Fig. 4). The border in the 5.02 ppm is chosen to minimize the spectral density. The first value is certainly larger than the true, the second is too low, because in its calculation of the vinylidene structures are lost, and probably some part of α -olefins. For this case in order to estimate an error in P_H (ε_1) for each sample it is possible to use difference $P_H^{max} - P_H^{min}$. This value is assumed 80% from $0,5 \cdot (P_H^{max} - P_H^{min})$, that is $\pm 0,4 \cdot (P_H^{max} - P_H^{min})$. For the thermogenic UHC this ambiguity can be neglected (Fig. 4c). It was shown that for radiogenic UHC the maximum of ε_1 consists $\sim 25\%$ rel., more often $\sim 15\%$ rel. For radiogenic UHC the most part of ε_1 is about equal and in this respect the error is systematic, so it influences only on limits of experimental diapasons of parameter P_H .

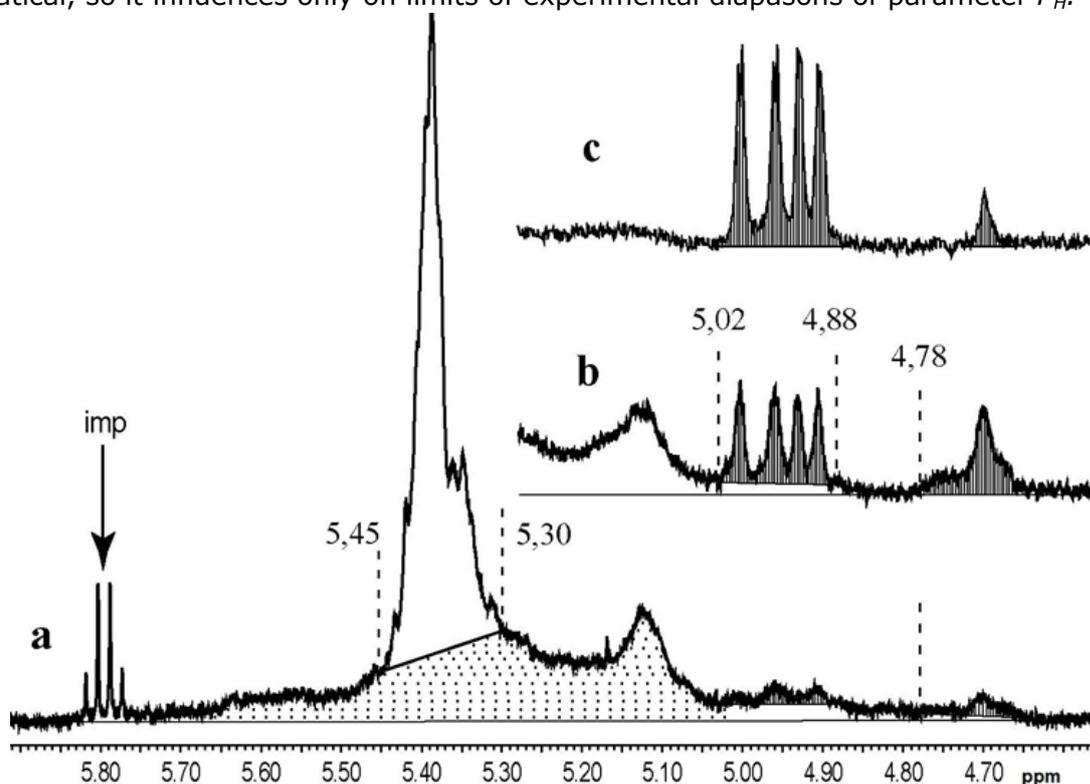


Figure 4. Isolation of specific groups of signals in the resonance region H_{db} . The vertical shading are signals $H_{db,\alpha}$ (4.88 – 5.02 ppm) and $H_{db,v}$ (b, c) or $H_{db,v}^M$ (a) (~ 4.60 – 4.78 ppm); dots – $H_{db,oth}$ (legend – see text).

First of all P_H values were calculated for crude oils and oil fractions isolated from these crude oils with UHC of known origin: radiogenic (crude oils after the model radiolysis and the samples studied in [4, 5, 8 - 11]), and thermogenic [12]. Results are shown in Table 2. Since the theoretical boundary between radiogenic and thermogenic UHC is the value of $P_H \approx 1,0$, the resulting difference can be considered great and it clearly exceeds the uncertainties inherent in the methodology of P_H calculation. Thus, the calculation of total statistical error for estimate of values of this parameter according to [20] have showed that for the radiogenic UNC it was $\leq 30\%$ rel. by satisfactory signal/noise ratio and $\leq 55\%$ rel. by poor ratio of signal/noise. For thermogenic UNC the statistical error is smaller in about 1,5 times. The cause of multiple deviations to the lower side of the P_H values of native radiogenic UHC of crude oils from those observed for the products of model radiolysis are the natural degradation processes ("aging") of less stable components. This follows from the regularity in the series P_C values for different structures in crude oils with proven radiogenic nature of the UHC. The same table summarizes results for the other samples that have type of UHC determined on the basis of qualitative analysis of the spectra.

As a second parameter for the differentiation of radiogenic and thermogenic UHC based on joint consideration of ^{13}C and ^1H NMR data one can use the ratio of $\text{CH}_2=\text{CHCH}_2-$ and $\text{CH}_2 =$ substitutes of alkyl chains. Strictly speaking, this ratio should be considered with the following value

$$P_{H,C}^{\alpha,v} = (H_{db,\alpha}/H_{db,v}) : (C_{al}^t/C_{al}^s) \quad (2)$$

Here the second bracket is the ratio of content in the sample of carbon of CH_3 groups at the end of the chain CCCR (C_{al}^t) to the content of carbon of methyl substituent of the chains (C_{al}^s), measured by ^{13}C NMR [19]. However, measurements for all the samples in Table 1 showed that in most cases, $C_{al}^t/C_{al}^s = 3 \pm 1$ and is beyond the specified limits only for crude oils with high paraffin contents and for biodegraded oil. However, as can be seen from Table 2, the difference ratios $H_{db,\alpha}/H_{db,v}$ in the vast majority of crude oils with radiogenic and thermogenic UHC greatly exceeds the range of changes of C_{al}^t/C_{al}^s . Accordingly, as a rule, we can use only the ^1H NMR data. Given that all analyzed crude oils with the thermogenic UHC are highly paraffinic, then values of $H_{db,\alpha}/H_{db,v} < 2.0$ should be considered as a sign of radiogenic (more reliable - < 1.5), > 3.0 - as a sign of unsaturated thermogenic. The range of 2.0 - 3.0 (or 1.5 - 3.0) is the zone of ambiguous conclusion. For these samples, if the issue is not solved jointly considering the three parameters, one have to use ^{13}C NMR method with the calculation of $P_{H,C\alpha}^v$.

Selection signals $H_{db,\alpha}$ and $H_{db,v}$ is shown in Figure 4b, c. If it is impossible then one have to consider all selected by the baseline method signals in the range $\sim 4.60 - 4.78$ ppm and $4.88 - 5.02$ ppm (Fig. 4a) and calculate the value of parameter $H_{db,\alpha}/H_{db,v}^M$, which is equal to the ratio of integral intensities of these groups of signals (Fig. 4a). For the thermogenic UHC $H_{db,\alpha}/H_{db,v}^M = H_{db,\alpha}/H_{db,v}$; for radiogenic UHC (if there is possibility for comparison) value of $H_{db,\alpha}/H_{db,v}^M$ is a little less (the lower boundary on the second line of Table 2 - instead of $0.5 \sim 0.4$).

At low concentrations of UHC calculation of the ratio of $H_{db,\alpha}/H_{db,v}^M$ is not possible (signals are at the limit of detection). Therefore, the third parameter is introduced, reflecting the approximate ratio between the part of H atoms in the disubstituted $\text{C}=\text{C}$ bonds of alkenyl chains $H_{db,ch}$, and in other $-\text{CH}=\text{}$ groups. As a measure of the $H_{db,ch}$ integral intensity one can use the area evolved over the "hump" in the 5.30 - 5.45 ppm region as measured by the base line method (Fig. 4). Accordingly, $H_{db,oth}$ include all other signals of $\text{CH}=\text{}$. Analysis of the ^{13}C and ^1H NMR spectra of olefin fractions [4, 8] showed that such a non-strict partition correctly reflects the change of $H_{db,ch}/H_{db,oth}$ for the number of radiogenic UHC of different composition. It was found that this ratio is measurable for any fixed concentration of UHC. The summarized results are shown in Table 2. Despite the ambiguity of the selection signals $H_{db,ch}$ the border ranges vary so much that this kind of uncertainty does not affect the final result of the UHC belonging to a particular type. The statistical error in changing of $H_{db,ch}/H_{db,oth}$ does not exceed 25% rel. (standard deviation is no more than 10% rel.) except for cases, when it is limited by detection.

Analysis of the spectra of artificial mixtures together with the data of Table 2 shows that the same parameters can be used to find the presence of a sample mixture of UHC's of different genesis in the important for the petroleum chemistry cases. The criterion for the presence of thermogenic UHC (20 - 25%) in the radiogenic UHC is the higher value of

$H_{db,a}/H_{db,v}$ with a typical for the radiogenic UHC values of $H_{db,ch}/H_{db,oth}$ and P_H . Indicator of the reverse situation is lowering against the typical for the thermogenic UHC values of $H_{db,ch}/H_{db,oth}$ and P_H at a typical value of $H_{db,a}/H_{db,v}$. The admixture of the third type of UHC in the radiogenic UHC is fixed as a result of increase of the P_H value at $H_{db,ch}/H_{db,oth} = 0.2 - 0.3$, in the thermogenic - as a result of decrease of $H_{db,ch}/H_{db,oth}$ at typical for the thermogenic UHC values of $H_{db,a}/H_{db,v}$. The reverse situation is of no interest because of low concentrations of UHC of the third type.

Table 2. General results of calculation of parameters P_H , $H_{db,\alpha}/H_{db,v}$ (or $H_{db,\alpha}/H_{db,v}^M$) and $H_{db,ch}/H_{db,oth}$ for crude oils with different types of UHC (in brackets - the extreme values, interval - the typical).

UHC type*	Samples	P_H	$H_{db,\alpha}/H_{db,v}$ (or $H_{db,\alpha}/H_{db,v}^M$)	$H_{db,ch}/H_{db,oth}$
Radiogenic	Model radiolysis of crude oils (for conditions see [5])	0.6 – 1.0	1.0 – 1.6	0.5 – 1.0 (0.4; 1.3)
	Strictly fixed genesis**	0.2 – 0.3 (0.7)	0.5 – 1.2 (0.2; 1.6)	0.3 – 0.7 (0.2; 1.3)
	Others	0.1 - 0.4 (0.8)	0.4 – 1.1 (0.3; 1.8) or n.i.****	0.4 – 0.7 (0.2; 1.1)
Thermogenic		4 – 7	5 – 15	2 – 4
"Third type"		1 – 2*** or n.i.****	n.i.****	<0.2

* Minimal quantity of samples of one type is 7 (thermogenic UHC).

** Samples with complex proof of their nature [4, 5, 8 11].

*** In fact P_H^{max} ; P_H^{min} – no data.

**** N.i. – parameter can't be calculated as it is impossible to measure necessary values.

4. Conclusion

From 260 samples with confirmed presence of UHC, their type according to the criteria in Table 2 it was not possible to identify only 4% of cases. Most of them contain UHC close to the detection limit, so one can get a good upper bound concentrations of radiogenic and thermogenic UHC - <4 mkmol/g and <3 mkmol/g, which is only twice the limit of detection. Thus, the proposed method provides unambiguous results for the vast majority of the samples.

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