Studies of the characteristics of compounded pitch by chromatography-mass spectrometry and NMR of carcinogenic activity

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Abstract. The spectral characteristics of coal and oil pitch are compared among themselves. An insignificant contribution of aliphatic functional groups to the total spectrum intensity for coal pitch is noted. Analysis of the obtained $^{13}$C NMR spectra showed qualitative structural features of the pitch components, such as the absence of signals in the range of 150-200 ppm, which indicates the absence of carbonyl- and carboxyl-containing fragments in the components of the pitch components. The content of radiocarbon in the samples of oil pitch and carbon nanoparticles was measured.

1. Introduction
Oil and coal sands are one of the important sources of raw materials for the production of carbon materials: carbon, heat and chemical resistant structural products, metal-carbon, carbon-carbon composite materials, graphite electrodes, self-baking anode masses, carbon fibers, blast furnace and foundry coke, molded solid fuel, etc. The quality of the pitch is determined by the elemental and group composition, its structure and physico-chemical properties. The greatest interest in assessing the prediction of pitch behavior during processing and the properties of products obtained from them is the study of the molecular structure and group composition of organic pitch components and the identification of the effect of the composition on the practical properties of the products. A large number of publications [1-5] are devoted to such issues, in which the authors widely use EPR and IR spectroscopy, GLC, and thermogravimetric analysis methods. NMR spectroscopy for these purposes is used relatively rarely, although this method has significant advantages when using quantitative techniques for recording spectra on $^1$H and $^{13}$C nuclei. The present work is devoted to the study of the group composition of two oil, coal, and compound [6] pitches by high resolution NMR spectroscopy.

2. Materials and research methods
A fragment analysis of the molecular structure of the pitch is associated with the need to choose a solvent and ensure high reproducibility of the results.

The only acceptable solvent with a sufficiently high solubility and the absence of signals in the analytical regions of the spectrum is carbon disulfide. The problem of the presence of residual solvent signals in the proton spectra (7.25 ppm) was solved by taking into account the contribution from the solvent to the total integrated spectrum intensity. In $^{13}$C NMR spectra, the solvent signal does not overlap significant spectral regions, additionally allowing its calibration (77.1 ppm).
$^{13}$C NMR spectra were obtained for 10 K passes. In all cases, the processing of the spectra included Fourier transform using the weighting function, phase adjustment, baseline correction, and automatic digital signal integration.

Samples 1 – petroleum pitch, 2 – pitch from heavy pyrolysis resin, 3 – coal tar pitch (Zaporozhye), 4 – coal tar pitch (Russia) [10, 11, 12].

Comparison of the obtained $^1$H NMR spectra for oil pitch (1, 2) and coal tar (3, 4) allows us to detect a significant difference in the contributions to the integrated intensity of the spectra from aromatic hydrogen atoms $\Sigma H_{ar}$ (range 6–9.5 ppm) and aliphatic hydrogen atoms $\Sigma H_{al}$ (for which the integration of signals was carried out in the range of 0-5 ppm). The total integrated intensity of the spectrum in all cases was normalized to 100 units; Table 1 presents the corresponding contributions. The ratio $H_{ar}/H_{al}$ allows you to quantify the proportion of the corresponding aromatic and aliphatic fragments in their mixture.

Table 1. Contributions of the spectral intensity of signals of various ranges (in %) according to $^1$H NMR spectra.

| Sample | Spectral range, ppm | $\Sigma H_{al}$ | Spectral range, ppm | $\Sigma H_{ar}$ | $H_{ar}/H_{al}$ |
|--------|---------------------|----------------|---------------------|----------------|----------------|
| 1      | 0-1.0 | 1.0-2.0 | 2.0-3.0 | 3.0-5.0 | 6.0-8.5 | 8.5–9.5 | 19.8 | 3.3 | 23.1 | 0.30 |
| 2      | 1.7   | 9.4    | 20.5   | 11.9   | 43.5   | 51.9   | 4.6   | 56.5 | 1.30 |
| 3      | 0.1   | 1.1    | 8.8    | 4.8    | 14.8   | 75.5   | 9.7   | 85.2 | 5.76 |
| 4      | 0.1   | 2.1    | 7.3    | 5.1    | 14.6   | 74.3   | 11.1  | 85.4 | 5.85 |

3. Results and Discussion

Analyzing the data of the table, it can be noted that for the investigated coal tar pitch of various origin (3, 4), the spectral parameters are close in magnitude. Well-resolved $^1$H NMR spectra indicate a low molecular weight composition of pitch components with a predominance of aromatic and polyaromatic structures with a low content of aliphatic functional groups.

For samples of oil pitch, the data of $^1$H NMR spectra are different. The spectra are characterized by broadened lines characteristic of polymer structures. In sample 1, the main components contributing to the integral of the aliphatic part are the resonances of methylene groups of saturated fragments (1.0–2.0 ppm) corresponding to long chains of ($\text{–CH}_2\text{–}$)$_n$ ($n > 3$). In sample 2 (pyrolysis resin), a significant contribution to the intensity of the aliphatic part of the spectrum is made by the signals of hydrogen atoms in the $\alpha$-position to aromatic cycles. For pitch samples 1 and 2, the relative contribution of the aliphatic part of the spectrum to the total integrated intensity is significantly different, which is reflected in the value of the $\Sigma H_{al}$ integral and the $H_{ar}/H_{al}$ ratio. Undoubtedly, these differences in the $^1$H NMR spectra indicate a different component composition of the pitch, which is reflected in their physical properties. For sample 1, the softening temperature and viscosity are lower than for sample 2. (Figure 1).

Analysis of the obtained $^{13}$C NMR spectra allows us to note the qualitative structural features of the components of pitch 1-4. First of all, this is the absence of signals in the range of 150-200 ppm. This fact allows us to establish with confidence the absence of carbonyl- and carboxyl-containing fragments in the components of the pitch components. It is also possible to assert the absence of O-alkyl and O-aryl functional groups, which are characterized by signals in the spectral range of 50-60 ppm and 145-160 ppm respectively (Figure 2).
For oil pitch 1, narrow intense signals in the range of 10-30 ppm typical of saturated linear aliphatic chains are observed in the $^{13}$C NMR spectrum. According to the relative integrated intensity of these signals, the length of such fragments can be estimated at 7-8 carbon atoms.

For oil pitch 1 and 2, a greater contribution of $^{13}$C signals is observed in the region of 130-150 ppm in comparison with the data for coal pitch. This region of the spectrum corresponds to the resonances of the Quaternary atoms of aromatic structures directly associated with aliphatic fragments ($\text{C}_{\text{ar}}$-$\text{alkyl groups}$).

To determine the difference in such a property as carcinogenic activity, a comparative analysis of two samples of the pitch was carried out: 1 - coal tar pitch (Zaporozhye); 2 - a laboratory sample of compounded oil pitch with the addition of fullerene-like carbon similar [7, 8, 9]. The results of chromatography-mass spectrometric analyzes are presented in Figs. 3 and 4.
Figure 3. Chromatography-mass spectrum of coal tar pitch (Zaporozhye). The molecular peak of 252 is 3,4-benzpyrene.

Figure 4. Chromatography-mass spectrum of oil pitch. The molecular peak 252 - 3,4-benzpyrene - is absent.

A mass number of 252 corresponds to a molecule of 3,4-benzpyrene. From Figs. 3 and 4, with an intensity of 252 peaks, it can be concluded that the presence of 3,4-benzpyrene in the sample of compounded oil pitch is lower than in the sample of coal tar pitch, and therefore it can be argued that oil pitch is characterized by lower carcinogenic activity, in comparison with coal tar pitch.

Also, measurements were made of the content of radiocarbon in samples of oil pitch and carbon nano-additives at the Unique Scientific Installation “Accelerator Mass Spectrometer of the INP SB RAS” (UNU UMC Institute of Nuclear Physics SB RAS, Novosibirsk, Russian Federation).

In Figure 5, the results of the UMC analysis of 23 samples in a drum in which the oil pitch sample was placed at position 5.6 and the “fullerene-like additives” sample at position 7.8. At position 3.14 were samples obtained from OX1 calibration material with a relative concentration of C-14 1.04, at 4.15 were samples of OX2 with a concentration of C-14 1.34 relative to the 1954 background standard. These samples were used to calibrate UMC data. The concentration of C-14 in the presented samples turned out to be very small and comparable with the background of UMC. Figure 6 shows data in the range of relative concentration C-14 0-0.04.

The signals from the samples fluctuate around the background of the UMC. At position 20, there is a sample obtained from the collagen of the ancient mammoth bone (> 200 thousand years), in which the entire C-14 disintegrated.
Table 2 shows the UMC data for part of the drum samples: 0 - sample number, 1 - C-14 content, 2 - content error, 3 - total C-14 number, 4 - radiocarbon age (r.a.), 5 years - error of measurement of r.a. Values in columns 4,5 are significant only for ancient samples.

Figure 5. The relative content of radiocarbon in 23 samples of the drum, measured using UMC.

Figure 6. The relative content of radiocarbon in samples with a low content of C-14.

Table 2. UMC analysis of some drum samples.

| D0= | 0 | 1 | 2 | 3 | 4 | 5 |
|-----|---|---|---|---|---|---|
| 0   | 0 | 0 | 0 | 0 | 0 | 5·10^4 | 0 |
| 1   | 1 | 0 | 0 | 0 | 0 | 5·10^4 | 0 |
| 2   | 2 | 0 | 0 | 0 | 0 | 5·10^4 | 0 |
| 3   | 3 | 1.02 | 0.011 | 9.145·10^3 | -8.723 | 8.019 |
| 4   | 4 | 1.371 | 0.011 | 1.435·10^4 | 35.357 | 0.456 |
| 5   | 5 | 0.016 | 1.29·10^3 | 160 | 5.911·10^4 | 635.059 |
| 6   | 6 | 0.017 | 1.785·10^3 | 96 | 5.066·10^4 | 819.857 |
| 7   | 7 | 0.012 | 1.135·10^3 | 115 | 5·10^4 | 749.074 |
| 8   | 8 | 0.016 | 1.454·10^3 | 117 | 8.23·10^4 | 742.644 |
| 9   | 9 | 0.883 | 8.066·10^3 | 1.198·10^4 | 1.02·10^3 | 73.404 |
| 10  | 10 | 0.863 | 7.823·10^3 | 1.216·10^4 | 1.206·10^3 | 72.834 |
| 11  | 11 | 0.875 | 7.595·10^3 | 1.327·10^4 | 1.094·10^3 | 69.744 |
| 12  | 12 | 0 | 0 | 0 | 5·10^4 | ... |
4. Conclusion
The 13C NMR spectra show qualitative structural features of the pitch components:

1. The absence of signals in the range of 150-200 ppm, which confirms the absence in the structures of the components of the pitch carbonyl and carboxyl containing fragments.
2. We can state the absence of O-alkyl and O-aryl functional groups, which are characterized by signals in the spectral region of 50-60 ppm. and 145-160 ppm. respectively (Figure 2).
3. The presence of 3,4-benzpyrene in the sample of compounded oil pitch is lower than in the sample of coal tar pitch, therefore, oil pitch is characterized by lower carcinogenic activity, in comparison with coal tar pitch.

The relative content of C-14 radiogenic carbon in the presented samples is 0.017, which is below the detection limit by UMC and two orders of magnitude lower than the current concentration of C-14 in the atmosphere.

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