

## IR spectroscopy in the analysis of hydrocarbons isolated from oil-contaminated soils

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**Abstract.** The study is devoted to the investigation of the chemical composition of hydrocarbons isolated from oil-contaminated soils using infrared (IR) spectroscopy in the mid-infrared region. Based on the obtained spectra, the types of bonds present in molecules and atoms were characterized, functional groups were identified, and the structural composition of the sample was determined. A comparison was carried out with data from gas chromatography–mass spectrometry (GC–MS) and nuclear magnetic resonance (NMR) spectroscopy.

**Keywords:** extraction, oil analysis, FT-IR spectroscopy, chemical composition of hydrocarbons.

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**1. Introduction.** Alteration of soil ecosystems by oil and gas production wastes, as well as oil leaks during transportation, represents one of the most complex and multifaceted environmental protection problems. It is known that oil-impregnated soils, while remaining under the influence of natural factors, undergo various structural changes [1,2].

The study of the characteristics of changes in petroleum hydrocarbons that have remained in soil for long periods is necessary to address the problem of remediation of such soils. Determination of the structural parameters of hydrocarbons isolated from oil-contaminated soils is a complex scientific task, the solution of which involves the use of various spectroscopic techniques [3–5].

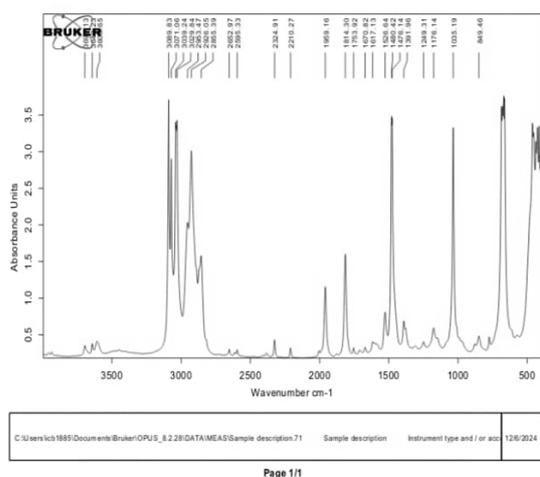
Among the many existing methods for studying the structure of chemical compounds, infrared (IR) spectroscopy is one of the most important and versatile techniques. It is well known that the features of the molecular structure of the substance under study are reflected in the IR spectrum by the presence of various characteristic absorption bands. The data obtained by this method make it possible to determine functional groups more accurately than by chemical analysis.

The complex chemical composition and intermolecular structure of such hydrocarbons can be described by analyzing IR spectra recorded in the mid-infrared region, as well as by determining the content of structural fragments of hydrocarbon and non-hydrocarbon compounds [6,7]. Using Fourier-transform IR (FT-IR) spectroscopy, we investigated the structural and group composition of petroleum hydrocarbons in the range of 4000–500 cm<sup>-1</sup>, isolated from soil samples of the studied oil field. Previously, these samples were similarly studied using gas chromatography–mass spectrometry (GC–MS) and nuclear magnetic resonance (NMR) spectroscopy [1,8]. The chromatographic method proved to be informative in describing polar components containing aromatic fragments; however, information on the naphthenic and highly oxidized fractions of the isolated hydrocarbons was lacking.

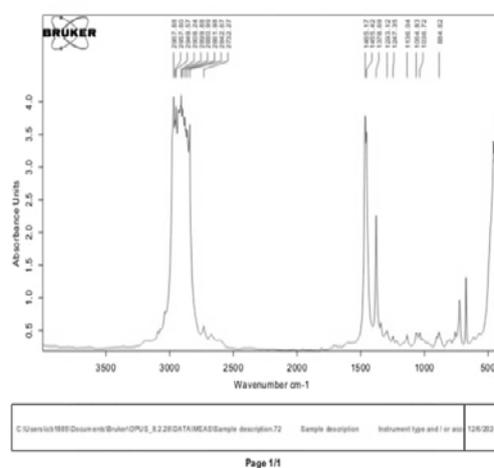
The aim of this work was to analyze the features of changes in the chemical composition of petroleum hydrocarbons isolated from oil-contaminated soils of the Balakhany oil field that had

undergone biodegradation using the above-mentioned method, and to compare the obtained results with those of chromatographic analysis and NMR spectroscopy.

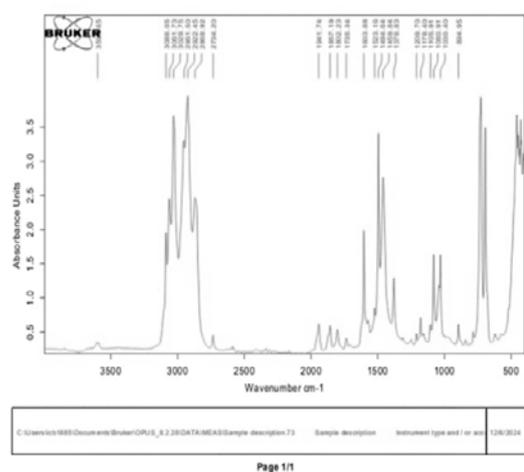
**Experimental section.** The object of our study was a sample taken from the territory of Oil Production Unit No. 4 of the Balakhany oil field. Isolation of the oil fraction from the collected sample was carried out by extraction using the following solvents: benzene, hexane, toluene, and xylene. Initially, it was observed that the degree of dissolution of petroleum products varied somewhat depending on the solvent used. Subsequently, the solvent was evaporated from the extract, and the isolated hydrocarbon residue was analyzed by IR spectroscopy; the results are presented in Fig. 1 (a, b, c, d). The oil contaminants isolated from the production area differ from produced crude oils and do not contain light fractions [8–10].



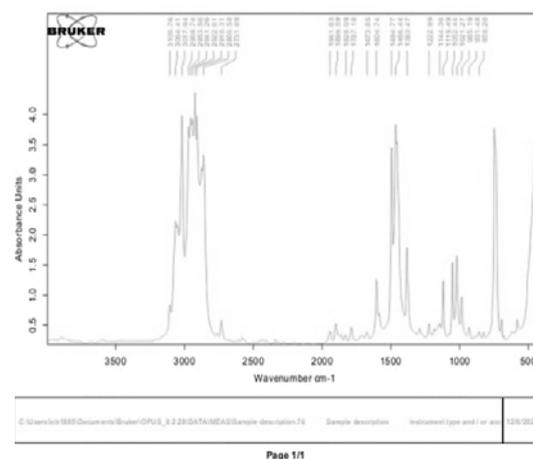
a)



b)



c)



d)

Figure 1. FT-IR spectra of hydrocarbon extracts isolated from oil-contaminated soil. Solvents: (a) benzene, (b) hexane, (c) toluene, (d) xylene.

**2. Analysis of results.** The composition of the isolated petroleum extracts differs markedly from that of the original crude oil due to an increased proportion of resinous substances, naphthenic-paraffinic, and polycyclic hydrocarbons; as a result, the density increases from 0.8486 to 0.8921. The

spectra show that the intensity of absorption bands in the regions of approximately 3029–3100  $\text{cm}^{-1}$  and the adjacent 2950–3000  $\text{cm}^{-1}$  corresponds to stretching vibrations of hydrogen atoms in methyl and methylene group fragments, which are characteristic of alkanes, especially cyclic, heterocyclic, and cycloalkane hydrocarbon rings.

Stretching vibrations in the 1450–1940  $\text{cm}^{-1}$  region of the spectra of the benzene, xylene, and toluene extracts indicate the presence of cycloolefinic compounds, esters, and ketones. In addition, interpretation of the absorption bands around  $\sim 1500 \text{ cm}^{-1}$  confirms the presence of hydrogen atoms involved in double bonds and in aromatic rings.

The 1000–1400  $\text{cm}^{-1}$  region observed in the IR spectra is considered highly informative, as the bands appearing in this range are also associated with various atomic groups. Within the same interval, bands near 1300  $\text{cm}^{-1}$  may be attributed to vibrations of C–N and C–O bonds that are part of sulfur-containing and polycyclic compounds. In the IR spectra of the toluene and benzene extracts, a stretching vibration band at 3600–3690  $\text{cm}^{-1}$  is observed, which indicates the presence of hydrogen in amino groups ( $-\text{NH}_2$ ,  $-\text{NH}-$ ). In the long-wavelength region of the spectrum ( $\sim 2600\text{--}2800 \text{ cm}^{-1}$ ), stretching vibrations of various hydrogen-containing groups characteristic of amides and mercaptans are manifested.

Thus, the analysis of the IR spectra confirms the presence of aliphatic hydrocarbons, various oxidation products of petroleum, as well as secondary decomposition products of oil. The above data are consistent with the results obtained using gas chromatography–mass spectrometry (GC–MS) and nuclear magnetic resonance (NMR) spectroscopy.

All the presented physicochemical methods for analyzing hydrocarbons isolated from contaminated soils indicate degradative and oxidative transformations of petroleum. In the isolated product, the aliphatic fraction predominates over the aromatic fraction and also contains complexes with highly stable structures that are resistant to fragmentation.

**Conclusions.** FT-IR spectroscopy was used to record the spectra of petroleum hydrocarbon extracts isolated from contaminated soils. Based on these spectra, the group-level chemical composition was characterized, which is consistent with the data obtained from gas chromatography–mass spectrometry (GC–MS) and nuclear magnetic resonance (NMR) spectroscopy.

#### **Conflict of interest.**

The authors declare that they have no conflict of interest in relation to this research.

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