PACS 552.778.3, 665.521.80

CHANGES IN THE STRUCTURAL-GROUP COMPOSITION OF OIL DURING THE DEGRADATION ON WATER SURFACE

S.R. Hajiyeva[1], A.A. Samadova[1], N.K. Guliyeva[2], S.M. Mammadova[2]
[1]Baku State University, Azerbaijan
[2]Institute of Radiation Problems of ANAS

Abstract. Degradation of Surakhani oil of Absheron peninsula in the water surface has been studied. The content of the main components – hydrocarbons, tar and asphaltenes in the crude and extracted oil samples were quantitatively determined. The studies of content and structural-group changes have been carried out by using of IR-spectroscopy and chromatography methods. It is shown that changes occur in the structural-group composition of oil under the influence of natural factors on water surface.

Key words: oil, environment, degradation, hydrocarbon, tar, asphaltene.

1. Introduction

The most widespread pollutants of waste water are oil products – a group of hydrocarbons of oil, fuel oil, kerosene and their impurities, which, due to their high toxicity, belong to the list of ten most dangerous pollutants of the environment. Oil products can be in solutions in emulsified, dissolved form and form a floating layer on the surface, and spill of oil into the hydrosphere of the Earth remains quite actual issue. Most oil pollution is caused by the following factors: off-shore extraction, preparation, transportation of oil and also catastrophes, natural sources, industrial and municipal wastes /1/.

Every year 5 million tons of oil fall into the World Ocean from different sources as a result of human activity. Only Azerbaijan dumps annually more than 500 million m^3 of normatively-purified water to the Caspian Sea, as a result of which the sea receives more than 3,000 tons of oil products, 25 tons of phenols, 28,000 tons of suspended solids, 520,000 tons of synthetic surfactants /2/.

During the spill of oil and oil products in the environment, changes occur in the composition of oil, that depend on their physical and chemical properties, and insufficient knowledge about which can lead to the problems in the application of purification technology of oil pollution from water.

2. Methodology

The paper presents the results of the study of changes in physical and chemical properties of Surakhani oil, taken from well and from water surface under the influence of environmental factors. Samples taken from both water surface and from well have a very complex composition and the study of their physical and chemical characteristics involves methodological difficulties. Therefore, they were separated into three components according to GOST 1158-66: oil, tar and asphaltene.

The structural-group composition of these components has been determined by absorption spectroscopy (IR-spectra) method on "Varian 640-IR" spectrophotometer in the wavelength of 600-4000 cm^{-1}. The assignment of the bands of the obtained spectra has been carried out according to /3/. The liquid products were analyzed by the Chromatography «GCFID (GS-450, Varium-2010 USA)» with a flame ionization detector.

3. Results and discussions

The test oil samples were extracted from water by extraction using benzene as an extractant. For comparison, oil samples taken directly from a nearby well were used. Table 1 shows the content of these components (mass,%) in two types of oil samples.

Table 1

Fraction content of oil samples (mass, %)

Sample	Hydrocarbon	Tar	Asphaltene
Well	92,5	7,45	0,05
Water	82,8	16,8	0,4

From the table it is seen that, after prolonged stay of oil on water surface under the influence of natural factors, its material composition changes – the content of hydrocarbons decreases, but tar and asphaltenes increase. It is explained by the influence of solar radiation, microorganism, air and radiation of various origins on destructive transformations of oil components /4/.

The formation of more condensed aromatic rings in the oil structure after prolonged stay of oil on water is indicated by the results obtained by IR spectroscopy. Figure 1-2 shows IR spectra of the samples of oil fraction taken from well and water surface.

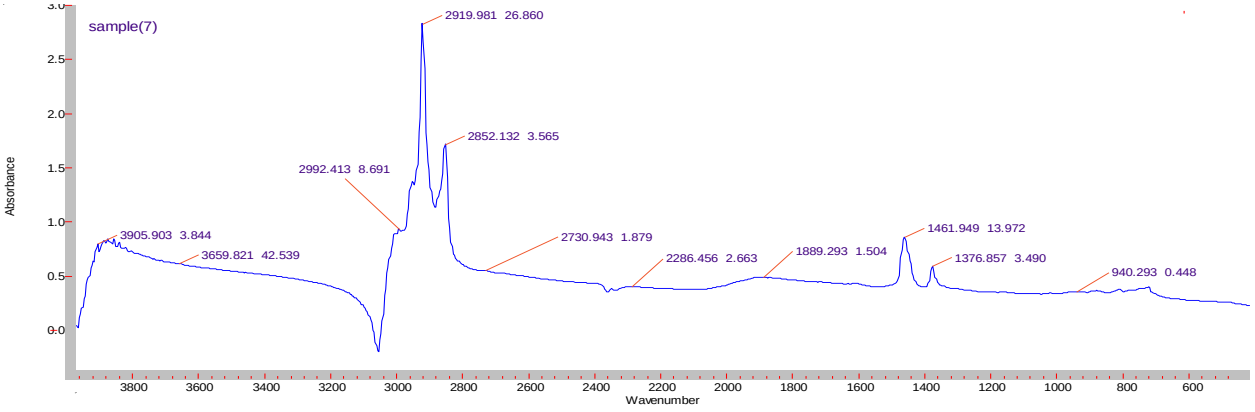

Fig.1. IR spectrum of the oil fraction taken from the well

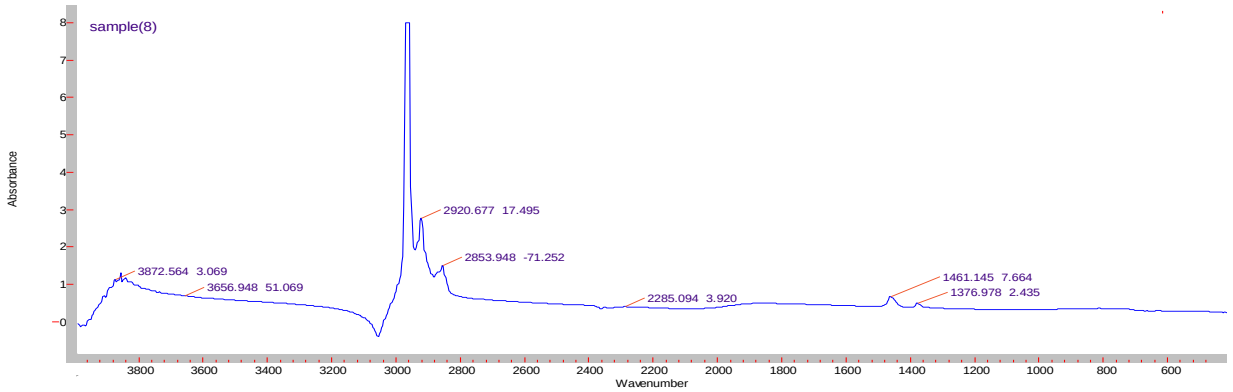

Fig.2. IR spectrum of the oil fraction taken from the water surface

The infrared spectra show that in the absorption bands of 1461 cm^{-1}, 1376 cm^{-1}, 2860 cm^{-1} and 2920 cm^{-1}, there is observed a redistribution of the intensity of -CH_2- and -CH_3 groups, changes in absorption bands corresponding to aromatic rings are not observed. The composition of oil fractions is significantly different from the composition of tar fractions. In the oil fractions there is not a significant amount of condensed aromatic rings, mainly they consist of paraffin of normal structure, and cyclo-paraffins are mainly monocyclic. Differences in the change of structure of the oil and tar fractions are indicated by the IR spectra of the initial and degraded tar fractions (Fig. 3-4).

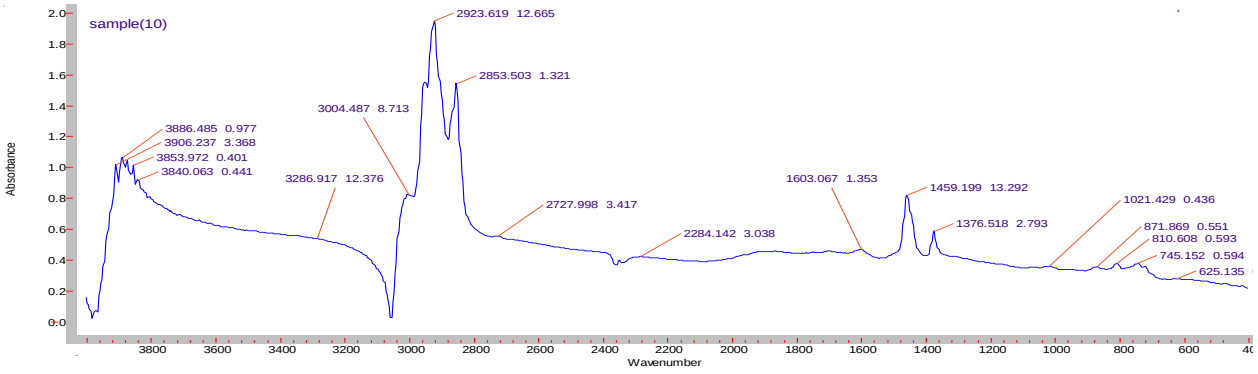

Fig.3. IR spectrum of a resinous fraction of oil taken from well

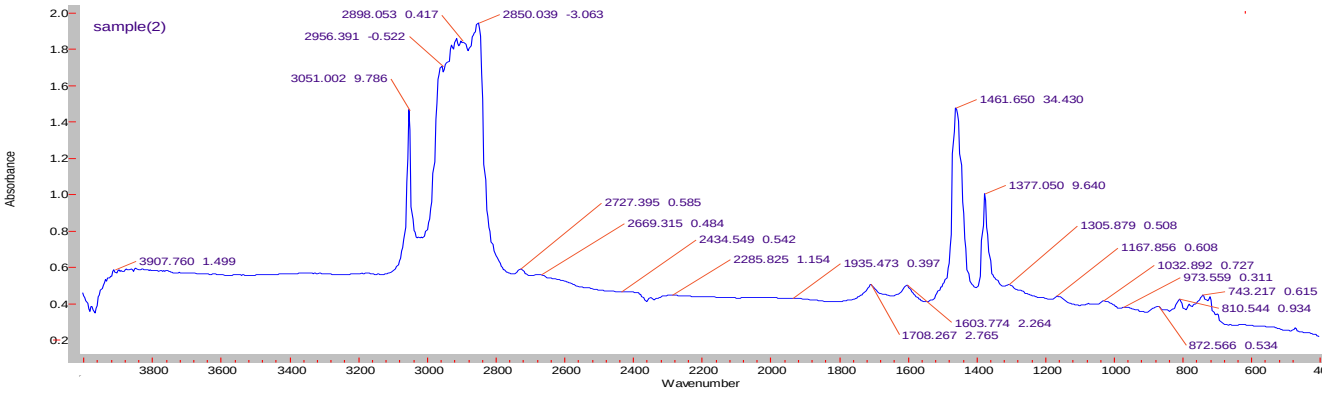

Fig.4. IR spectrum of resinous fraction of oil taken from the water surface

Analysis of IR spectra of initial and degraded samples of tar fraction of oil showed that after prolonged stay of oil on water surface, the process of tar oxidation occurs as a result of degradation, as evidenced by the appearance of band at 1708 cm^{-1}, belonging to C=O groups. This absorption band is an objective criterion for the accumulation of oxygen-containing products. It has been observed intensive absorption bands at 3051 and 1603 cm^{-1}, characteristic for stretching vibrations of C = C bonds of a cyclic or benzene (aromatic) ring, a band of 1030 cm^{-1}, corresponding to binuclear aromatic structures, appears. It has been also observed the strongest accumulation of aromatic rings - by 3-4 times in comparison with the samples from the well - the increase of condensed aromatic rings. It has been also strongly appeared the absorption bands at wavelengths of 600-1000 cm^{-1}, corresponding to the stretching and deformation vibrations of -CH_2 and -CH_3 groups, in the region of 1461 cm^{-1} and 1377 cm^{-1} - an intensive increase in these groups in branched paraffin and cycloparaffin hydrocarbons. The presence of

absorption bands in the region of wave numbers 2920 and 2860 cm^{-1} is due to stretching vibrations of the structural groups $-CH_3$, and $-CH_2-$. The composition of resinous fractions, in contrast to oil, includes hydrocarbons in the form of condensed aromatic rings with a large number of side paraffin chains /5/.

Thus, it can be seen from the IR spectra of the samples that in case of prolonged stay of oil on water surface, its structural-group composition changes. The change is mainly affected by the resinous oil fraction.

The hydrocarbon compositions of samples of oil fractions were determined by chromatographic method (Fig. 5-6).

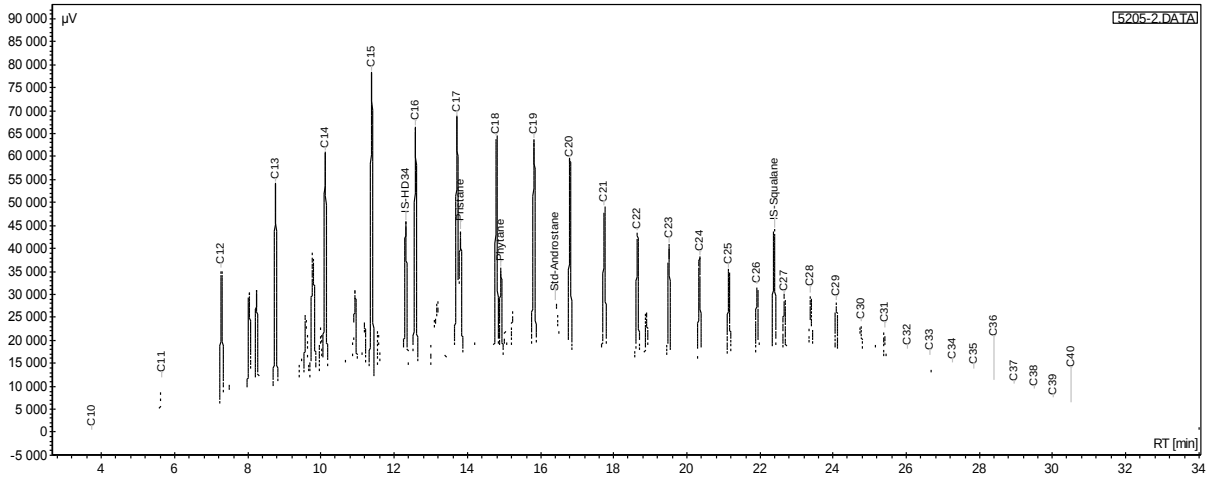

Fig.5. Chromatogram of tar fraction of oil from water surface.

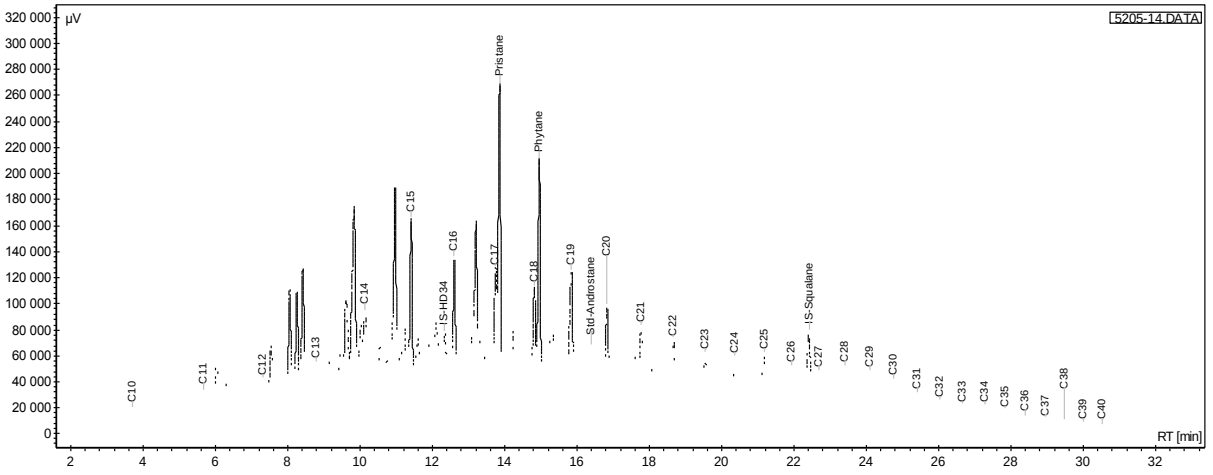

Fig.6. Chromatogram of tar fraction of oil taken from the well.

It can be seen from the chromatograms that, in comparison with the samples from the well, significant changes in the peaks of n-alkanes are observed in the samples from the surface of the reservoir, which is associated with destructive processes occurring during the degradation of oil.

The obtained data indicate the changes in the structural-group composition of oil associated with the impact of environmental factors. The ratio of processes, facilitating the removal of petroleum hydrocarbons from the aqueous medium has been poorly studied, there is no information on changes in the composition of oil as a result of its degradation. Data on the

composition of oil contamination in water bodies are necessary for considering methods of purification of water from degraded oil in the environment.

Acknowledgement
This work was carried out with the financial support of the Science Development Foundation under the President of the Republic of Azerbaijan - **Grant No. EIF-KTRL-2-2015-1 (25) - 56/23/**

References

1. Peters A. Oil spills and the environment// Ecology – 2006 - No.4 – p. 16-33**.**
2. Mir-Babaev M.F. Protection of the environment of the Caspian Sea. Azerbaijan's oil industry.- №10, 2010, p.77-79.
3. Tarasevich B.N., IR spectra of the main classes of organic compounds. Moscow, MSU, 2012, 55 pages.
4. Davydova S.L., Tagasov V.I. Oil and oil products in the environment: School-book. - Moscow: Publishing House of the PFUR, 2004. – 163 p.
5. Mustafayev I., Rzayev R., Guliyeva N. Radiation-thermal purification of wastewater from oil pollution// Wastewater reuse-risk assessment, decision-making and environmental security, Published by Springer, 2007, p, 315-322.

ИЗМЕНЕНИЕ СТРУКТУРНО-ГРУППОВОГО СОСТАВА НЕФТИ ПРИ ЕЕ ДЕГРАДАЦИИ НА ВОДНОЙ ПОВЕРХНОСТИ

С.Р. Гаджиева, А.А. Самедова, Н.Г. Гулиева, С.М. Маммадова

Резюме: Исследована деградация нефти Сураханского месторождения Абшеронского полуострова на поверхности воды. Количественно определено содержание основных компонентов нефти - углеводородов, смол и асфальтенов. Состав и молекулярная структура определены с использованием ИК –спектроскопии и хроматографии. Установлено, что под воздействием природных факторов на поверхности воды изменяется индивидуальный и структурно-групповой состав нефти.

Ключевые слова: нефть, окружающая среда, деградация, углеводороды, смолы, асфальтены.

SU SƏTHİNDƏ DEQRADASİYAYA MƏRUZ QALMIŞ NEFTİN MOLEKULYAR-STRUKTUR TƏRKİBİNİN DƏYİŞMƏSİ

S.R. Hacıyeva, A.A. Səmədova, N.Q. Quliyeva, S.M. Məmmədova

Xülasə: Abşeron yarımadasının Suraxanı neftlərinin su səthində deqradasiyasının qanunauyğunluqları tədqiq olunmuşdur. Xam və deqradasiyaya uğramış neftin əsas qrup fraksiyalarının- yağ, qətran və asfaltenin miqdarı təyin olunmuşdur. Bu fraksiyaların karbohidrogen tərkibi və molekulyar-qrup strukturu İnfraqırmızı spektroskopiya və xromatoqrafiya üsulları ilə tədqiq olunmuşdur.

Müəyyən olunmuşdur ki, su səthində deqradasiya zamanı neft fraksiyalarının karbohidrogen və molekulyar–qrup tərkibi dəyişir.

Açar sözlər: neft, ətraf mühit, deqradasiya, yağ, qətran, asfalten.