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Isolation of Porphyrins from Heavy Oil Objects

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Additional information is available at the end of the chapter

Abstract

The chapter describes the opportunities of extracting porphyrins by polar solvents (acetone, N,N-dimethylformamide (DMF), isopropanol, and acetonitrile) and sulfuric acid from various highly molecular petroleum fractions and residues. It has been found that the predissolution of petroleum objects such as asphaltenes and resins in aromatic solvents allows improving the extraction of porphyrins by means of reducing their association with polycondensed heteroatomic structures. Based on the absorption spectra and mass spectra, primary types of porphyrins in obtained extracts were revealed. The distinctions between porphyrin extractions in resins and asphaltenes were revealed. Sulfuric acid extraction allows producing highly concentrated primary extracts of demetallated porphyrins. The share of porphyrin fractions in obtained extractions was 13.0–24.2 wt%, which depends on the concentration of metal porphyrins in initial asphaltenes and resins.

Keywords: vanadyl porphyrins, asphaltenes, resins, extraction, heavy petroleum residues, vanadium

1. Introduction

Metal porphyrins in oils are primarily represented by vanadyl and nickel porphyrins [1]. The remaining metal-containing compounds of vanadium and nickel are present in the form of chelates with pseudo-porphyrin structures or with porphyrins having atypical substitutes [2]. Due to low concentration of porphyrins having atypical structure, efficient separation and mass-spectrometry with ultrahigh definition are required to determine their structure [3], and the

structure of pseudo-porphyrin complexes is still not defined. The paper also reports of oil being present in insignificant amounts in iron and copper porphyrins [4].

The analysis of oil porphyrins in oils and their components by various instrumental methods is impossible due to their low concentration, so usually, fractions enriched with metal porphyrins are used for analysis. All concentration methods for oil porphyrins can be conditionally divided into three groups:

- Complex formation, chemical adsorption, and ion-exchanging chromatography when sufficiently labile chemical bonding is formed between various compounds and oil porphyrins.

- Chemical interaction between various compounds and oil components accompanied by new chemically stable compounds being formed.

- Extraction, separation, and sedimentation by solvents based on various solvability of individual compounds in various solvents.

For light oils having a relatively low concentration of asphaltene-resin substances, the first group of methods is mostly suitable for extraction of oil porphyrins: complex formation with Lewis acids usually represented by waterless metal halides [1]. This method consists in the formation of molecular complexes of metal porphyrins with titanium and iron halides that are insoluble in hydrocarbon systems, with further extraction of these complexes, destruction, and regeneration of metal porphyrins. This method is advantageous because of complete extraction of metal porphyrins when they are contained in trace concentrations.

The second group of methods currently used to extract porphyrins from oil is based on treating oils and oil components with strong acids. When using acids in order to extract oil porphyrins, metal porphyrins are demetaled and transformed into acid phase.

As demetaling agents, acids are used, such as sulfuric [5] and sulfonic acids [6]. A disadvantage of extracting oil porphyrins by using acids is partial destruction of porphyrins (40–80%) and inability to separately measure the concentration and study metal porphyrin complexes of vanadyl and nickel. Acid extraction is also inefficient for oils having low concentration of porphyrins. The advantages of porphyrin extraction with acids include low labor input and an opportunity to directly produce relatively clean concentrates of porphyrin compounds.

The third group includes extraction methods by using solvents that cannot be mixed with oil, with further extract treatment. Extraction methods employing selective solvents are advantageous for soft process conditions, which completely present any chemical transformations. Methanol [7] and N,N-dimethylformamide (DMF) [8] are used as solvents for extraction of metal porphyrins.

The concentration of porphyrins in extracts obtained by any of the above methods allows using them for further analysis, but in some cases, additional treatment of concentrates is needed by means of column chromatography. To identify and measure the concentrations of oil porphyrins, visible and UV-band spectroscopy is used due to three characteristics of absorption bands [9]. The most intensive absorption band also referred to as the Soret band is located at the boundary between the visible and the UV area at 400 nm. Other two bands

referred to as α and β bands are located in the area of 570 and 535 nm for vanadyl porphyrins and 575 and 540 nm for nickel porphyrins.

As compared with metal porphyrins, electronic absorption spectra of metal-free porphyrin carry much information on the structure. There are four main spectral types of oil porphyrins differing in the absorption peak intensity at 500, 535, 565, and 620 nm (bands IV, III, II, and I, respectively) [10]. This property is associated with the effects of substitutes at the porphyrin ring periphery. Each of the types is represented with a mixture of various porphyrins differing in the nature and position of substitution (**Figure 1**).

Another informative method to determine the structure of metal porphyrins is mass-spectrometry [11]. Metal porphyrins are present in oil in the form of a continuous series. Most common of them are porphyrins with alkyl substitutes called etioporphyrins (ETIO) with the molecular weight of $375 + 12n$ (M), and metal porphyrins containing an isocyclic ring, also called deoxophylloerythroetio porphyrins (DPEP) with the molecular weight of $373 + 12n$ (M-2) [12]. Their ratio in oil is the most important geochemical parameter showing the maturity of oil [13]. Other series (M-2, M-4 …) are present in oil in significantly lower concentrations and are called minor.

To study the concentrates of oil metal porphyrins other methods can be used, such as EPR spectroscopy [14, 15], LDI mass-spectrometry [16], Fourier transform ion cyclotron resonance mass spectrometry [17], and high definition inductively coupled plasma mass spectrometry [18].

Metal porphyrins in oils have a negative effect on catalysts of oil refining processes [19, 20], so currently, oil demetallization methods are used and developed [21–23]. Effective development of methods to remove vanadium and nickel from oil is impossible without having information on the structure and properties of metal porphyrins. Since the complete extraction of oil metal porphyrins from oil objects is complicated due to strong associations with asphaltene molecules, this may cause insufficiently full study of metal porphyrins. This chapter gives a new approach to the extraction of metal porphyrins from asphaltenes and heavy petroleum residues (HPR), which allows increasing the degree of extraction, and it also presents the results obtained in determining the composition and properties of concentrates obtained.

ETIO   Rhodo   Phyllo   DPEP
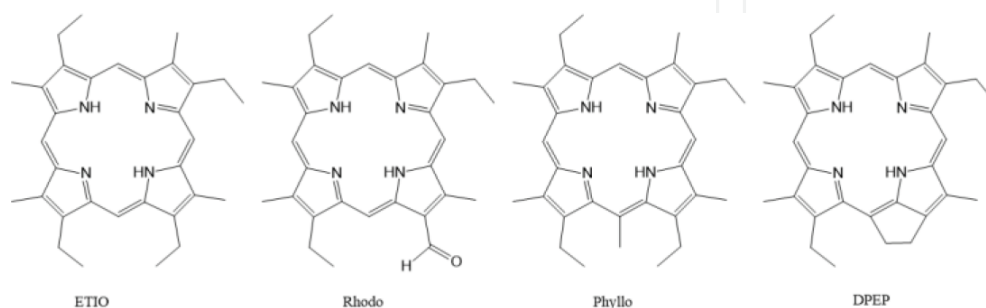
Figure 1. Spectral types of porphyrins.

2. Materials and methods

The study objects were the oil and natural bitumens of various-age deposits of Tatarstan fields and heavy residues of oil refining: vacuum residue (VR) from TAIF-NK OJSC oil refinery; asphalt (A-1) after tar propane deasphalting at the ANK Bashneft OJSC refinery; asphalt (A-2) after tar propane deasphalting at the NK Rosneft refinery; atmospheric residues of heavy oils from the Ashalchinskoe (AR-1) and Zyuzeyevskoe (AR-2) fields.

All oils and natural bitumens were separated from emulsion water and mechanical impurities by centrifugal process. Organic solvents of hch and chda classes were additionally treated and desiccated by employing widely known methods.

Asphaltenes were extracted by using a common methodology by means of diluting with 40× hexane excess with further flushing to remove sedimented resins and oils in a Soxhlet apparatus. Oils and resins were separated by means of column chromatography, using an activated granulated large-pore silica gel as an immobile phase, with the grain size of 0.2–0.5 mm, as well as the hexane/benzene mixture at 85:15 as an eluent.

Vanadium and nickel concentrations in oils and asphaltenes were measured by means of direct flame atomic absorption spectrometry using AAS-1N spectrophotometer, with approved standard samples of metal concentration in oil products used as blank solutions.

To extract asphaltenes by a boiling solvent, a 1 g sample of asphaltenes was placed into a round-bottom flask with back flow condenser, 200 mL of extractant was added, and the mixture was boiled for 1 h. After cool-down, the mixture was filtered. The resulted extract was dried in vacuum. To extract asphaltenes by sedimentation extraction, a 1 g sample of asphaltenes was diluted in 10 mL of benzene. A total volume of 100 mL of extractant was added to the result-ing solution, which was then boiled with a back flow condenser for 10 min. After the solution cooldown, asphaltenes were filtered. The resulting extract was dried in vacuum.

The concentration of vanadyl porphyrins in extracts from asphaltenes was calculated for the absorption band of 575 nm according to the following formula:

$$C_{vp} = 0.187h \cdot V / m \cdot l \qquad (1)$$

where 0.187 is the conversion factor describing the medium absorption; h is the height of absorption α-band maximum for 575 ± 5 nm; m is the extract sample, g; V is the porphyrin extract volume to be reached, mL; l is the flask thickness, cm.

Matrix-assisted laser desorption/ionization (MALDI) mass spectra of extracts from asphaltenes were obtained by UltraFlex III TOF/TOF mass-spectrometer in linear mode. The data were processed by using FlexAnalysis 3.0 software. The sample was ionized by nitrogen laser radia-tion (wave length of 337 nm) with the energy of 19 eV. Positively charged ions were recorded. A metallic target was used. Sinapinic acid was used as a matrix. Molecular ions of VPs of vari-ous homotypes are presented as peaks with the weight of 373 + 14n amu and 375 + 14n amu (where n is the number of methylene groups in pendent groups). The share of each homotype was calculated by means of internal normalization by using the peak intensity of molecular ions.

Primary porphyrinic extracts were obtained from heavy petroleum residues solutions in benzene with the concentration of 10 wt% by treating with 10× excess of concentrated sulfuric acid. The extract was separated by filtering in a Shott funnel and after being neutralized with sodium hydrate water solution, it was retreated with three portions of tetrachloromethane. The lower layer was separated and dried above anhydrous sodium sulfate. After dried solution filtering and solvent stripping, the primary porphyrinic extract was obtained.

Adsorption-chromatographic separation of primary porphyrinic extracts was carried out in a glass column 1:100 cm by using an activated granulated large-port silica gel as an immobile phase and the 0.5% isopropil alcohol solution in benzene as an eluent. The volume of the eluent sampled was 10 mL. The obtained fractions were combined according to eluent colors. Fraction spectra were obtained in Specord UV-VIS spectrophotometer with the range from 400 to 650 nm.

3. Results and discussion

3.1. Vanadyl porphyrin extraction with polar solvents

The schemes applied to extract metal porphyrin complexes from oil objects have some disadvantages that do not allow using them on a large scale. When using liquid extraction, multiple extraction is needed to achieve high degree of extraction. If asphaltenes are used as extraction objects, the number of extraction steps is multiply increased, therefore, frequently the process is performed in Soxhlet apparatuses. Such extraction conditions are explained by the fact that in oil systems, asphaltenes are associated with oils and resins due to multiple intermolecular interactions, such as electrostatic, dipole, and dispersive ones. The molecular weight of resulted aggregates can be 10,000 amu and more. Metal porphyrins tend to establish strong associations with aggregates of such weight. Metal porphyrins can also be captured into the grid of asphaltenes by the type of molecular sieves. In this connection, it becomes difficult to extract metal porphyrin complexes. It is only possible to obtain concentrates enriched with these compounds. Previously, asphaltene extraction by various solvents was used to obtain metal porphyrin concentrates [24]. It occurred that no more than 60% of the total amount of vanadyl porphyrins is extracted during asphaltene extraction. The extraction process takes place at the solvent boiling temperature in order to increase the extractant solvability. This allows increasing the extraction degree of metal porphyrins, but it also contaminates the extract with highly molecular heteroatomic components.

To increase the extraction degree of metal porphyrins, we proposed using sedimentation extraction. Unlike the direct extraction from asphaltene, this approach suggests preliminary dissolution of asphaltene in a small amount of good solvent. Asphaltene dissolution allows the partial destroying of the intermolecular links inside aggregates that results in some metal porphyrins being liberated. This is followed by metal porphyrin extraction by the solvent excess having low solvability toward asphaltenes, but good solvability toward metal porphyrins. As a result, asphaltenes are sedimented, and metal porphyrins remain in the solution. Polar nonaromatic solvents have low solvability toward asphaltene-tarry components of oil and high solvability metal porphyrins.

To assess the efficiency of metal porphyrin extraction from an asphaltene solution by using sedimentation extraction, the obtained results were compared with the results of standard extraction of metal porphyrins from dry asphaltenes. Benzene was used as an asphaltene solvent; four solvents belonging to different classes of organic compounds were used as polar solvents: acetone, DMF, isopropanol, and acetonitrile.

As an extraction object, asphaltenes of the Ashalchnskoe field oil were used. The extracts obtained in the form of toluene solutions were spectrophotometered within the range of 400–630 nm. Absorption spectra show clear absorption bands at 530 (α-band) and 575 nm (β-band) typical of vanadyl porphyrins (**Figure 2**). A 550 nm band belonging to nickel porphyrins is not recorded in spectra.

When asphaltenes are treated with a boiling solvent, the maximum extract yield is obtained when using isopropanol (**Figure 3**). When using acetone and DMF, extract yields are lower, and in case of acetonitrile, no extract is formed. When using sedimentary extraction from asphaltene solutions, the maximum extract yield occurs with DMF. The sedimentary extraction used for all solvents under study allows reaching higher extract yields and concentrations of vanadyl porphyrins in them as compared to boiling solvent extraction (**Figure 4**).

The most common types of metal porphyrins in oil are etio- and desoxophylloerytroetioporphyrins (DPEP). To assess their ratio in the DMF extract from oil asphaltenes, matrix-assisted laser desorption/ionization (MALDI) is used. (Etio-type porphyrins have the molecular weight of 375 + 14n, and DPEP-type porphyrins – 375 + 14n.) Based on the intensity of peaks, the ratio of Σetio/ΣDPEP equaled 0.73.

MALDI can be used to assess the substitution nature in the porphyrinic ring (**Figure 5**). In both series of porphyrins, alkyl substitutes on the ring periphery contain 6–19 atoms of carbon. Porphyrins of etio-series contain C26–C39 homotypes with the maximum concentration at m/z = 529, which corresponds to C31 homotype that contains alkyl substitutes with
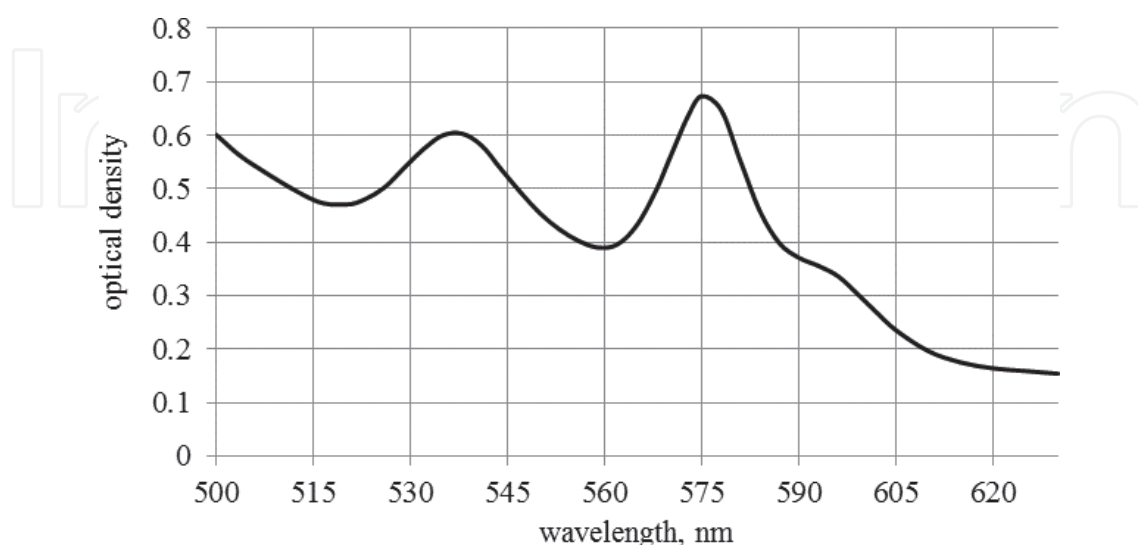
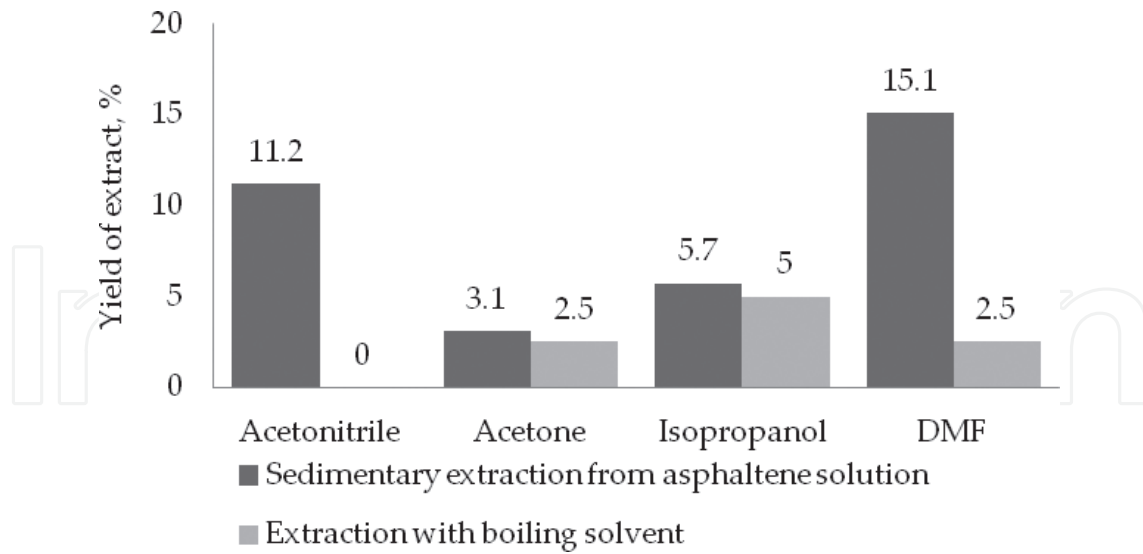**Figure 2.** Visible absorption spectrum of asphaltene extract.

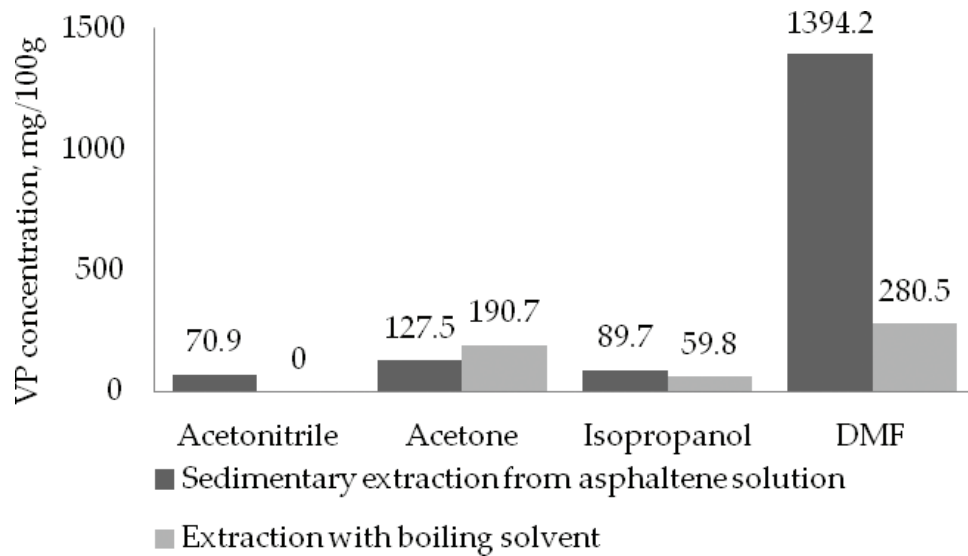**Figure 3.** Yield of vanadyl porphyrin extracts from asphaltenes.

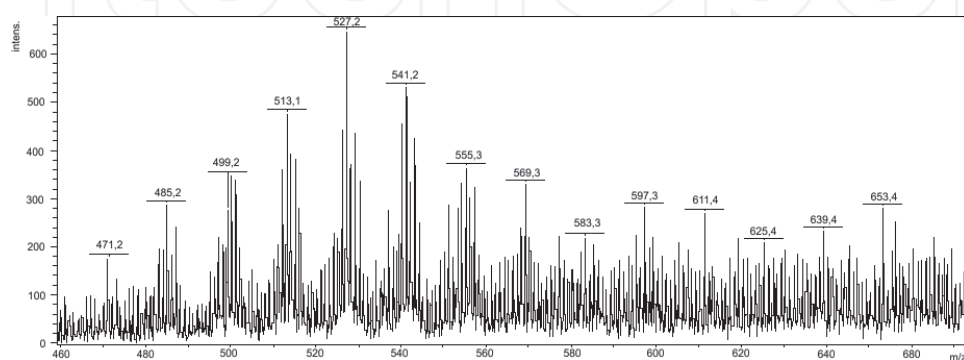**Figure 4.** Concentration of vanadyl porphyrin in asphaltenes extracts.

Figure 5. MALDI mass spectrum of vanadyl porphyrin extract from asphaltenes.

high number of carbon 11 atoms. Porphyrins of DPEP-series contain C28–C41 homotypes with the maximum concentration at m/z = 529, which corresponds to C31 homotype that contains alkyl substitutes with high number of carbon 9 atoms.

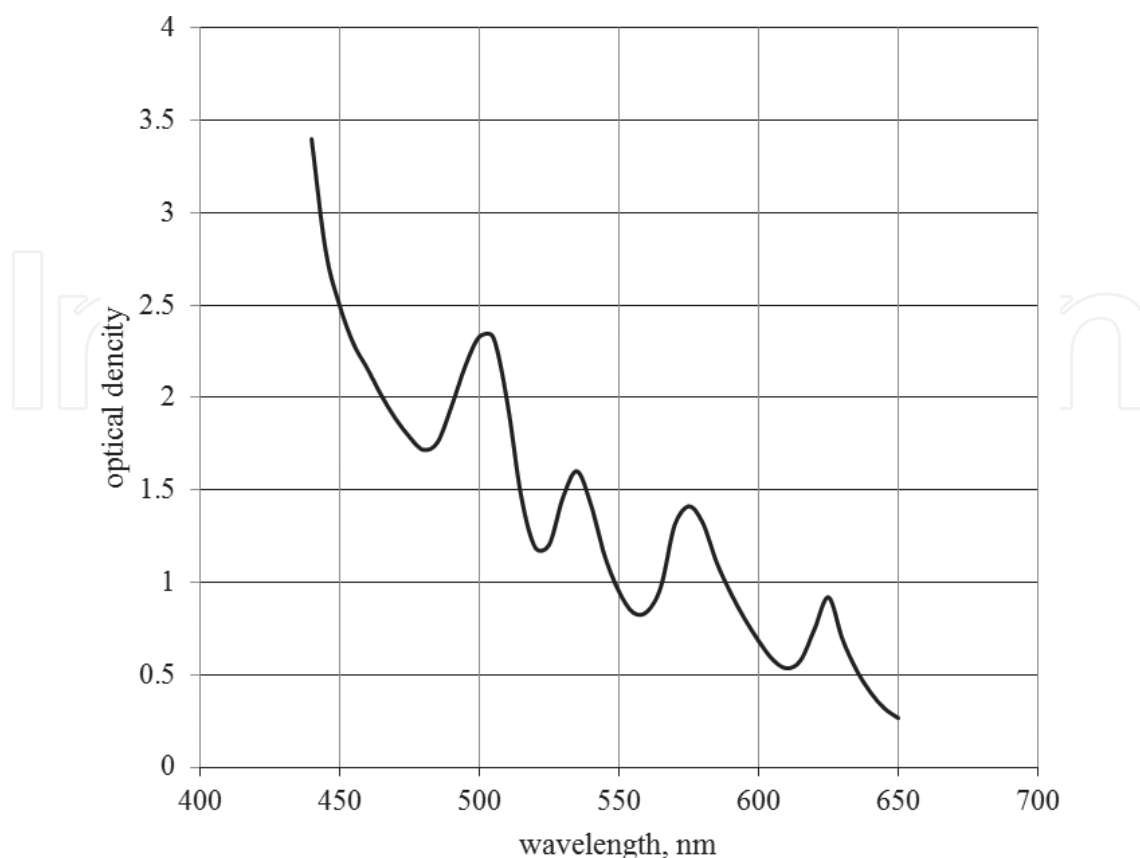### 3.2. Porphyrin extraction with sulfuric acids from asphaltenes and resins

Another methodological approach to the extraction of porphyrin complexes from oils and their components is acid extraction. Extraction methods described in the literature are adaptable and cannot be used for large-scale extraction. The extraction process also takes much time. Furthermore, all the above methodologies were developed for light oils with a low concentration of asphaltene-tarry substances. Meal porphyrin acid extraction from asphaltene-tarry substances is almost not described.

At the first stage, it seems necessary to reveal the most efficient acid extractant with the maximum yield of porphyrin extract. Extraction conditions may have a heavy effect on the results; first of all, this refers to temperature and duration. For a preliminary assessment of acid extraction capabilities, heavy oil asphaltenes from the Zyuzeyevskoe field were used. Concentrated hydrochloric, phosphorous, and sulfuric acids were used as extractants. As in case of polar solvent extraction, a 10% solution in benzene was used to reduce the association of metal porphyrins with asphaltenes, and the process itself was maintained at the room temperature. For phosphorous and hydrochloric acids, asphaltenes do not develop into the acid phase. When treating asphaltene solutions with sulfuric acids, an extractant and a benzene-insoluble residue is formed. A difference from the method currently applied to produce metal-free porphyrin from asphaltenes consists in the fact that demetaling of metal porphyrins occurs simultaneously with their extraction from asphaltenes. The need for preliminary extraction of metal porphyrins is avoided. Due to slurry formation, a centrifugal process and further filtering in a Schott's funnel were used to segregate the extract and the residue. The obtained extract was neutralized with a 20% cooled-down solution of sodium hydrate until reaching a neutral reaction. Tetrachloromethane was extracted from the resulting water solution. The yield of the primary extract after solvent stripping was 9%.

There are no metal porphyrin bands of 530 and 575 nm in the absorption spectrum in the visible area for the primary extract, and there are bands typical of free porphyrin bases (**Figure 6**). This testifies that when sulfuric acid acts on metal porphyrins, they are demetaled and metal-free porphyrins are formed. In this manner, concentrated sulfuric acid is the most optimal extractant to extract and demetaleted porphyrin from oil asphaltenes and resins.

To define the composition of porphyrin extracts in case of sulfuric acid extraction, asphaltenes and resins of heavy oils from Ashalchinskoe (TN-1 asphaltenes and resins) and Zyuzeyevskoe fields (TN-2 asphaltenes and resins) were used. Extraction was carried out according to the scheme described above. In case of sulfuric acid extraction, as for asphaltene extraction, an extract of porphyrins and an insoluble residue are formed. The results obtained for the yield of extracts are summarized in **Table 1**.

The amount of porphyrin extracted from resins or asphaltenes of heavy oils with increased vanadium concentration varies within 7.9–13.0 wt%. If oils are compared individually, the

Figure 6. Visible absorption spectrum of sulfuric acid extract of asphaltenes from Zyuzeyevskoe oil field.

porphyrin extract yield from resins as compared to that from asphaltenes is 3–4 wt% higher in both cases. When the vanadium concentration both in resins and asphaltenes increases, the yield of extracts is also increased. If the vanadium concentration in asphaltenes differs by two times, the relative extract yield increase will be about 14% just as in resins where the vanadium concentration difference is even higher (3.33 times), and the extract yield is increased by relative 15% only. In this manner, for asphaltenes and resins where the vanadium concentration will exceed the values as compared to the objects under study, it is unlikely that the porphyrin extract yield will be significantly increased.

To obtain data for the composition and types of porphyrins in extracts, silica gel adsorption chromatographic separation was used. A mixture of 0.5% isopropyl alcohol and 99.5% of

	Yield of extract, %	V content in object of extraction, %
Asphaltenes TN-1	7.9	0.186
Asphaltenes TN-2	9.0	0.384
Resins TN-1	11.3	0.042
Resins TN-2	13.0	0.140

Table 1. Yield of sulfuric acid extracts.

benzene was applied as eluent [25]. A total volume of 10 mL of liquid was sampled during elution. To decrease the number of fractions analyzed against the absorption spectra in the visible band, the obtained solutions were combined visually according to the color change (**Table 2**). A further study of absorption spectra in the visible band confirmed that this approach can be applied, since the differences in spectra allow identifying the types of porphyrins. To all colored fractions, except for the first and the last one, there are four absorption bands registered, having various intensity at 620, 565, 535, and 500 nm (bands I–IV), according to which a specific spectral type can be assigned to porphyrins.

The first (oil-like) and the last (resin-like) colored fractions obtained after separation of asphaltene extracts do not show absorption bands of metal-free porphyrin. In resin extract separation, the resin-like fraction is the first to eluted, followed by the oil-like fraction. These fractions being present in the sulfuric acid extracts are related to occluded oils and resins in asphaltenes.

The data for the yield of fractions after chromatographic separation of the sulfuric acid extract of asphaltenes are given in **Table 3**. The total concentration of oil-like and resin-like fractions in the extract reaches 53.2 wt%. Some part of the extract is not eluted and remains on the silica gel. The concentration of porphyrin fractions in extracts of resins is higher than in those from asphaltenes.

Phyllo-type porphyrins are predominant in asphaltene extracts. Apart from etio- and phyllo-porphyrins, there are also rhodo- and DPEP found in asphaltene extracts. Reduced concentration of DPEP in asphaltene extracts as compared to solvent extraction allows suggesting the isocyclic ring destruction in the porphyrins of this type during acid extraction.

Unlike asphaltenes, the porphyrins of resin extracts contain only these etio- and phyllo-types, which is the primary difference in the composition of porphyrin extracts of resins and asphaltenes. Etio-type of porphyrins is predominant in resin extracts. No rhodo-type porphyrins contained in resins is probably related to co-sedimentation of porphyrins with asphaltenes during their extraction due to polar groups presented in them and, consequently, lower solubility in hexane. As for asphaltenes, the most probable reason for no DPEP in extracts from resins can be the isocyclic ring destruction during sulfuric acid extraction.

Fraction number	Solution color	The order of decreasing intensity of the absorption bands	Spectral type of porphyrins
1	Cherry	III→IV→II→I	Rhodo
2	Dark orange	IV→I→II→III	DPEP
3	Dark red	IV→II→II→I	ETIO
4	Red	IV→II→III→I	Phyllo

Table 2. Spectral types of petroleum demetalleted porphyrins.

	Yield of fraction, %			
	Asphaltenes TN-1	Asphaltenes TN-2	Resins TN-1	Resins TN-2
Rhodo + DPEP	2.3	4.2	0	0
ETIO	2.7	7.1	6.8	11
ETIO + Phyllo	1.9	2.9	5.7	7.2
Phyllo	6.1	10.0	3.5	4.4
Oil-like	41.0	46.4	57.5	54.0
Resin-like	12.2	7.0	17.9	15.5
Residue on a column	33.8	22.4	8.6	7.9

Table 3. Yield of fractions after column chromatography of asphaltenes and resins porphyrinic extracts.

3.3. Porphyrin extraction with sulfuric acids from the solution of heavy petroleum residues

Since the extraction of individual resins and asphaltenes is a hard task, their industrial concentrates are used for porphyrin extraction—residual products of oil refining. First of all, these are the vacuum residue (tar) and asphalts from tar deasphaltizing with the total concentration of asphaltenes and resins being 50–70 wt% depending on the initial oil composition. For the vanadium concentration of 200–500 ppm in some heavy oils of Tatarstan, Samara, and Ulyanovsk region fields, the total concentration of vanadium and nickel in residual products of oil refining will be 1000 ppm and more.

As the objects of study, heavy petroleum residues of existing productions and atmospheric residues obtained in laboratory conditions (>350°C) from heavy oils with increased vanadium concentration were used. Density, component composition, and vanadium and nickel concentration were measured for all heavy petroleum residues (HPR) (**Table 4**).

Determining the concentration of these metals allows the preliminary assessing of the concentration of metal porphyrins in initial objects. The vanadium concentration in A1 and AR-2 is 9.2–9.3 times higher than that of nickel. V/Ni is also 9.8 times higher for A-2, but for

HPR	ρ, g/cm³	Content, %			Metals, ppm	
		Hydrocarbones	Resins	Asphaltenes	V	Ni
VR	1.0035	41.7	46.8	11.5	280	58
A-1	1.0762	45.6	40.7	13.7	310	63
A-2	1.1113	24.9	49.1	26.0	470	48
AR-1	1.0075	44.4	47.0	8.4	330	36
AR-2	1.0085	40.3	48.2	11.5	970	104

Table 4. Density and composition of HPR.

VR and A-1, the vanadium concentration is about five times higher than the nickel concentration. In this way, a potential share of nickel porphyrins for the selected HPRs can be about 10–20% of the vanadium porphyrin concentration.

During extraction, the most part of HPRs is transformed into an insoluble finely divided black product. As a result of sulfuric acid exposure, the composition is greatly altered primarily because of newly formed sulfonic and sulfoxide groups, which is represented by the absorption growth in the area of 1030 cm^{-1} and 1200–1400 cm^{-1} in IR bands as compared to initial objects.

The yield of primary porphyrin extracts for the selected HPRs varies within 6.9–12.9% equivalent to the weight of the initial oil stock (**Table 5**). The maximum extract yield is found for AR-2 where the vanadium and nickel concentration are also maximal. For AR-1, rather high yield of the primary extract is also found; however, the vanadium and nickel concentrations are relatively low. Thus, the total concentration of vanadium and nickel in HPRs is no determinant for forecasting the yield of porphyrin extracts in case of sulfuric acid extraction.

Based on absorption spectra analysis in the visible band, there are metal-free porphyrins found in all obtained extracts with simultaneous dissipation of characteristic absorption bands of vanadyl and nickel porphyrins, which testify demetallization of metal porphyrins during extraction. To characterize porphyrins in obtained extracts, adsorption chromatographic separation was used with further analysis of electronic spectra.

The results of adsorption chromatographic separation of primary porphyrin extracts (**Table 5**) show that about 70–75% include various oil-like and resin-like fractions containing no porphyrins, with some part of them not eluted by the recommended solvent mixture and remaining adsorbed on the silica gel.

A comparative analysis of IR spectra allowed identifying that oil-like and resin-like fractions have the same structural and group composition as resins and oils obtained when analyzing the composition of initial HPRs. The results of chromatographic separation of primary extracts show that the share of porphyrin fractions is 13.0–24.2%. The absorption spectrum analysis

	Yield, %				
	VR	A-1	A-2	AR-1	AR-2
Primary extract	7.6	6.8	8.5	11.7	13.1
Rhodo + DPEP	3.7	2.7	3.1	2.3	4.2
ETIO	5.9	6.9	5.6	2.7	7.1
ETIO + Phyllo	3.2	7.1	6.5	1.9	2.9
Phyllo	2.3	2.1	1.7	6.1	10.0
Oil-like	50.0	43.6	54.1	49.0	46.4
Resin-like	25.2	27.3	19.3	27.2	18.0
Residue on a column	9.7	10.3	11.2	11.8	11.4

Table 5. Yield of fractions after column chromatography of primary porphyrinic extracts.

in the visible band for all porphyrin fraction shows that there are all four types of porphyrins (**Figure 3**). Phyllo- and etio-porphyrins are predominant. In AR-1 and AR-2 extracts, the share of phyllo-porphyrins is significantly higher. One of the reasons for reduced concentration of DPEP in sulfuric acid extracts can be the isocyclic ring destruction when exposed to sulfuric acid. The total yield of porphyrin fractions for both the primary extract composition and in-equivalent to the initial HPRs prove no unambiguous correlation with the total vanadium and nickel concentration in the initial feed.

Metal-free porphyrins have four absorption bands in electronic spectra whose intensity depends on the type of porphyrins, so it is complicated to precisely measure the concentration of metal-free porphyrin in the obtained fractions. As an indirect method to assess the concentration of porphyrins in the extract, a comparative analysis of vanadium and nickel concentration reduction in HPRs can be used by analyzing the vanadium and nickel concentration in the extract by means of atomic absorption spectroscopy. As a result, it has been found that the sulfuric acid extract composition is extracted from 62.4 to 81.1% of vanadium contained in initial HPRs, with full extraction of nickel. Probably, the vanadium extraction from asphaltenes is incomplete, since the share of vanadium in the extract is inversely proportional to the concentration of asphaltenes in HPRs. Correspondingly, some vanadyl porphyrins remain in the insoluble residue. Since the molecular weight of vanadyl and nickel porphyrins is 10 times higher as compared to the atomic mass of vanadium and nickel, the potential concentration of metal porphyrins in HRP can be assessed, which is approximately evaluated as the total concentration increased by ten times.

A similar level of porphyrin concentration in concentrates cannot be achieved when extracted by such polar solvents as DMF or acetone with further single chromatography. It is especially important that the maximum concentration of porphyrins in obtained concentrates is reached when using heavy petroleum atmospheric residue (AR-2) as a feed, with increased vanadium and nickel concentration and simultaneously minimal ratio of asphaltenes and resins. In perspective, it is possible that such oils can be regarded as a stock to produce cheap natural porphyrins for using primarily as dyes and catalysts.

4. Conclusion

It has been found that extraction of metal porphyrins by polar solvents from a solution of asphaltenes or heavy oil residues in aromatic solvents allows increasing the level of extraction of metal porphyrins into the extract due to the destruction of aggregates of metal porphyrins and asphaltenes as compared to the direct extraction of asphaltenes or residues. In asphaltene extraction by polar solvents, the DMF appeared to be the best extractant. In the DMF extract from asphaltenes of heavy petroleum with increased vanadium concentration, vanadyl asphaltenes of etio- and DPEP-types were primarily found. The maximum distribution of the molecular weight for both types is found in vanadyl porphyrin homotype C31 containing nine carbon atoms in alkyl substitutes.

Using sulfuric acid for porphyrin extraction allows producing highly concentrated extracts of demetalated porphyrins without the need for preliminary concentration. The analysis of porphyrin fractions obtained after chromatographic separation of the primary extract of

asphaltenes shows predominantly etio- and phyllo-types of porphyrins and smaller concentrations of rhodo- and DPEP-types. Only etio- and phyllo-types of porphyrins were found in resin extracts. In asphaltene extraction, it was found that less than 75% of vanadium is extracted to the extract. In this way, some part of vanadyl porphyrins rigidly bound by a σ-linkage with polycondensed structures of asphaltenes is not extracted by using extraction methods which may be a restriction for petroleum demetallization processes. The concentration of porphyrins when switching from clean asphaltenes and resins to heavy residues is almost indiscernible, which allows proving the selectivity of the sulfuric acid extraction method. This is why the sedimentary extraction method can be used in analyzing oil objects in order to obtain additional information for the composition of metal porphyrins.

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