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SOME REGULARITIES OF THE DISTRIBUTION OF THE CONTENT OF FREE RADICALS AND VANADIUM (IV) IN OIL BY GEOLOGICAL SECTIONS OF THE EMBA REGION DEPOSITS

Abstract. In laboratory practice, is proposed a method for determining vanadium (IV) and free radicals (FR) in crude oils by electron paramagnetic resonance (EPR) at liquid nitrogen temperature. An important scientific and practical result of the proposed method for the determination of vanadium in crude oils, in contrast to the method of American authors is low nitrogen consumption, and an additional advantage of the method lies in the low cost of the process, since it eliminates the use of expensive temperature attachments for mass laboratory determinations of vanadium. In scientific work, this method was applied to determine vanadium and FR from the section of the Emba region's oil fields.

It has been established that with increasing depth and age of oil-bearing rocks, the density of oil decreases, as well as the content of tetravalent vanadium and FR in it. In some fields of the Emba oil-bearing region (North Kotyrtas, Kara-Arna), is noted an inverse pattern - an increase in the density of oil, the concentration of vanadium and FR is observed during the transition from an elevated part of the formation to a lower part.

Key words: electron paramagnetic resonance, vanadium (IV), free radical, depth of oil.

In recent years, students of higher education on the subjects: oil chemistry and oil geology have lectures on EPR-spectroscopy [1,2]. In laboratory practice, a method for determining vanadium (IV) and free radicals (FR) in crude oils at liquid nitrogen temperature is proposed. An important scientific and practical result of the proposed method for determining vanadium in crude oils, in contrast to the method of American authors [3], is the reduction of nitrogen consumption, as well as an additional advantage of the method is to reduce the cost of the process, since the use of an expensive temperature set-top box is excluded in the mass laboratory definitions of vanadium [1]. In this paper, we used this method to determine vanadium and FR from the oil fields of the Emba region.

Table 1 – The relationship between density and oil content of vanadium (IV) and FR section of field Kyrykmyltyk

Well number	Age	Depth of occurrence, m	Density, g/sm^3	Oil content	
				V(IV),g/t	FR·10^{-17}, spin/g
16	K_1a	398…407	0,9273	26,30	9,36
7	K_1a	389…395	0,9275	23,20	9,20
7	K_1в	431…436	0,9163	14,93	8,38
7	K_1в	436…440	0,9127	11,38	8,38
7	K_1в	465…467	0,9269	13,39	8,67
11	J_2	883…891	0,8878	8,43	3,56
11	J_2	937…943	0,8867	5,96	2,86
15	J_2	918…925	0,8897	6,29	2,64
15	J_2	930…932,5	0,8883	5,13	2,46
1	J_1	911.917	0,8880	4,94	2,44
Note. K_1a –apt, K_{1b}-barrem, K_1q-goter, J_2 – middle jur, J_1 – lower jur.					

Some regularities of the distribution of the content of FR and vanadium (IV) by the section of oil fields with different physical and chemical characteristics by the stratigraphic section were revealed for the Kyrykmyltyk field (table 1 and 2) and South Tagan (table 2). As can be seen from the results of data analysis, with increasing depth and age of oil content of FR and vanadium (IV) naturally decreases.

Paramagnetic characteristics of the oil field Kyrykmyltyk were studied by EPR-spectroscopy with the aim of establishing a relationship between density and oil content of vanadium (IV) and FR. The level of paramagnetism of the oil field Kyrykmyltyk is due to the different compounds of vanadium V(IV) and FR. Table 1 shows that the relationship between oil density and vanadium (IV) and FR content is quite clear. From the results of the analysis of the data given in table 1, it is also seen that with the increase in the depth and age of oil, the vanadium (IV) and FR content naturally decreases. The highest content of vanadium (28 g/t) and FR falls on the oil horizon K_1a (apt). The content of vanadium is much higher in oils in lower Cretaceous sediments than in the oils of the Jurassic sediments (that was previously installed for the oil between the rivers Ural and Volga) [4]. A similar change is typical for FR. In oils of lower Cretaceous deposits the concentration of FR is higher than in oils of Jurassic deposits.

For the oil fields Kyrykmyltyk and South Tagan also established the relationship between content FR, vanadium (IV) and physico-chemical characteristics. As can be seen from table 2, the content of sulfur, resins, asphaltenes, as well as the density and viscosity of oils increases with the content of FR and vanadium (IV). There is an inversely proportional relationship between the content of FR and vanadium (IV) in oils and the yield of gasoline fractions.

Within one field with increasing geological age and depth of oil vanadium content decreases (table. 1 and table. 2). In the oil fields of the Emba region, the concentration of FR also decreases with the depth of the oil, similar to that observed in the Maikov deposits of the Hadyzhensk and oil and gas fields lying at shallow depths [5].

Table 2 - Interdependence between vanadium (IV), FR content
and physico-chemical characteristics of low vanadium oils of the South-Emba region

Well number	Deep, m	Age	Vanadium Content, g/t	$FR \cdot 10^{-17}$, spin/g	Density, g/sm^3	Viscosity at 20^0C	Content, %			Fraction output up to 300^0C, %
							sulfur	resins	Asphaltenes	
Kyrykmyltyk										
11	389...396	Cret.	23,2	9,2	0,927	1449	0,35	20,0	2,56	24,1
15	930...931	J_2	5,1	2,5	0,888	99	0,25	8,46	0,76	28,8
11	883...891	J_2	8,4	3,6	0,887	105	0,39	9,01	0,29	32,3
16	469...477	Cret.	17,9	5,9	0,914	519	0,38	14,1	1,19	15,2
South Tagan										
1	274...288	J_2	29,2	42,4	0,972	1785*	0,49	29,5	6,89	8,0
1	597...601	Trias	10,7	12,4	0,905	560	0,23	13,8	0,67	14,8
*Note – Viscosity is calculated at 50^0C										

In some fields of the Emba oil-bearing region (North Kotyrtas, Kara-Arna) the reverse pattern is observed – the increase in the content of vanadium and free radicals with depth, which is explained by vertical migration or gravitational differentiation of oil [6]. This process seems to be due to the complex geological structure of the salt dome structures, which are often subject to tectonic processing.

Oil components containing paramagnetic centers are the most chemically active part of oils. Their free radical form determines the increased activity in the processes of both oil genesis and migration. Paramagnetic centers of oil, which are caused by the presence of compounds of tetravalent vanadium and free radicals, are part of the resinous-asphaltene components of oil [7]. In the transition from the increased part of the fields to the reduced one, there is an increase in oil density, vanadium and FR concentration. For illustration, in fig. 1 it is shown about the central parts of the EPR spectra of oils from the well sections of the 23 North Kotyrtas Deposit, taken at – 900C, containing one of the components of the hyperfine structure V4+ and the singlet from the FR. As can be seen, the amplitude of the signal of EPR of V4+ and FR with increasing depth of oil occurrence is growing. The increase in paramagnetism of oils with increasing depth of their occurrence is clearly observed in the section of the Kara-Arna field located in the southern coastal part of the Emba district. The field is tectonically Diptera is a salt dome structure of closed type with deep (up to 1800m) salt core.

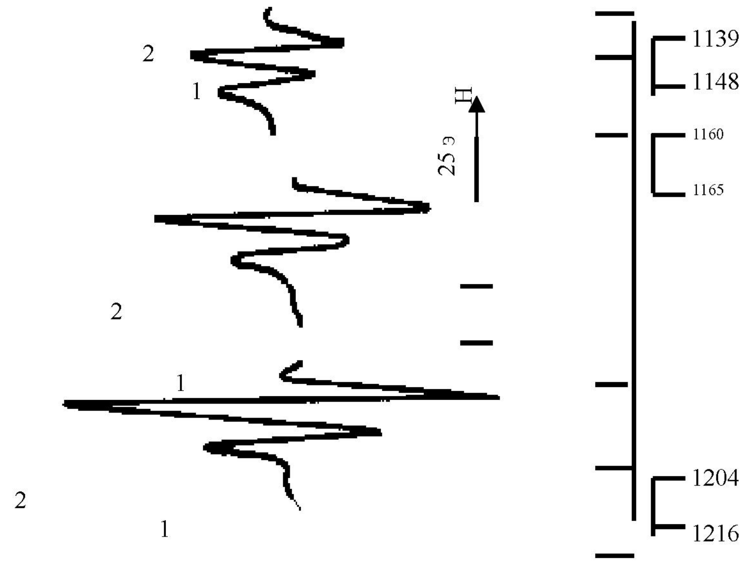

Figure 1- Change of EPR signal of oils in the section of the Kotyrtas North field, well 23.
Deep: a - 1139-1148 m, b-1160-1165 m, c –1204-1216,5 m; EPR signals:1–from V^{4+},2–from FR

Table 3 - Characteristics of oils in the North Kotyrtas field

Well number	Age, horizon	Oil extraction interval,m	Oil density, g/sm^3	V^{4+}, g/t	FR$\cdot 10^{-17}$, spin/g
23	T; III	1139-1145	0,8588	11,50	4,60
	T; III	1160-1165	0,8954	19,97	8,31
	T; IV	1204-1216,5	0,9051	22,51	10,65
22	T; II	1119,5-1128,5	0,8254	2,26	0,69
	T; III	1138,2-1155	0,8315	3,05	1,06
	T; III	1176-1185,7	0,8509	5,05	2,37
38	T; I	1079,5-1085	0,8715	7,80	4,93
	T; II	1133-1139	0,8810	12,10	6,20
5	T; I	1059-1073,5	0,8000	0,37	0,14
	T; II	1100-1104	0,8461	4,59	1,92

Analysis of the results (table.4) shows that there is a fairly clear difference in the distribution of the average vanadium content between the studied productive horizons. It should be noted that the Cenomanian horizon is characterized by the conditioned content of vanadium, and with the increase in the age and depth of oil, the content of vanadium and FR increases, so the industrial importance of the Kara-Arna field as a raw source of vanadium is of practical interest.

Table 4 – Change of paramagnetic properties of Kara-Arna oil field

The number of the studied wells	Oil extraction interval, m	Age	The average content of vanadium, g/t	FR$\cdot 10^{-17}$, spin/g
3	510-555	Senoman	60,08	8,36
4	967-983	Early alb	93,83	10,95
11	1047-1074	Apt	102,44	11,99

Experimental part

EPR spectra were recorded on the E-12 spectrometer of "Varian". We have found EPR signals from both vanadium and FR ions in the oils of the studied fields. The most intensive hyperfine structure line (HSL) from the complexes of tetravalent vanadium and the single line from FR were used to determine the concentration [8]. The standard concentrations were the oil from Urichtausk field (from well. 8) with known vanadium content (27.6 g/t) and FR ($7,8 \cdot 10^{17}$ spin/sm^3). Oil samples before the analysis were purified from associated water and mechanical impurities by centrifugation (centrifuge T-22) at a speed of 4000 rpm. The oil samples prepared in this way were sealed in order to avoid evaporation of gasoline fractions into glass ampoules 0.2 cm in diameter and 10-15 cm in length.

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ЕМБІ АЙМАҒЫНДАҒЫ МҰНАЙ КЕНІШТЕРІНІҢ ГЕОЛОГИЯЛЫҚ ҚИМАЛАРЫ БОЙЫНША ЕРКІН РАДИКАЛДАР МЕН ВАНАДИЙДІҢ (IV) ТАРАЛУ ЗАҢДЫЛЫҚТАРЫ

Аннотация. Шикі мұнайдағы ванадий мен еркін радикалдарды (ЕР) электрондық парамагниттік резонанс (ЭПР) көмегімен сұйық азот температурасында анықтау әдісі ұсынылды.Зертхана жағдайында ванадийді жаппай анықтаудың бұл ұсынылған әдісінің американдық ғалымдардың әдісінен өзгешелігі азот шығынының өте аз болуы және қымбат тұратын температура қондырғысының керексіздігі, прибор резонаторындағы орналасқан ампула көлемінің барлық жағдайда бірдейлігі.

Бұл әдісті Ембі аймағындағы мұнайларға ЕР мен ванадийді анықтау үшін қолдандық. Зерттеу нәтижесі, мұнай үлгілерін алу тереңдігіне және орналасатын жыныстардың геологиялық жасына байланысты, мұнай тығыздығының кемитіні және ондағы төрт валентті ванадий мен ЕР концентрациясының азаятындығын көрсетті. Ал Ембі аймағының кейбір мұнай кеніштері (Солтүстік Қотыртас, Қара-арна) үшін жоғарғы қабаттардан төменгі қабаттарға өту кезінде мұнайдың тығыздығының өсетіндігі және ванадий мен ЕР концентрациясының артатындығы , яғни кері заңдылық тағайындалды.

Түйін сөздер: электрондық парамагниттік резонанс, ванадий (IV), еркін радикал, мұнай орналасу тереңдігі.

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НЕКОТОРЫЕ ЗАКОНОМЕРНОСТИ РАСПРЕДЕЛЕНИЯ СОДЕРЖАНИЯ СР И ВАНАДИЯ (IV) В НЕФТИ ПО РАЗРЕЗАМ МЕСТОРОЖДЕНИЙ ЭМБИНСКОГО РЕГИОНА

Аннотация. В лабораторной практике предлагается способ определения ванадия (IV) и свободных радикалов (СР) в сырых нефтях методом электронного парамагнитного резонанса (ЭПР) при температуре жидкого азота. Важным научно-практическим результатом предлагаемого способа определения ванадия в сырых нефтях, в отличии метода американских авторов является снижение расхода азота, а дополнительное преимущество способа заключается в удешевлении процесса, так как исключается применение дорогостоящей температурной приставки при массовых лабораторных определениях ванадия. В данной работе этот метод применен для определения ванадия и СР по разрезу месторождений нефти Эмбинского региона.

Было установлено, что с увеличением глубины и возраста нефтевмещающих пород происходит уменьшение плотности нефти, содержания в ней четырехвалентного ванадия и СР. На некоторых

месторождениях Эмбинского нефтеносного района (Котыртас Северный, Кара-Арна) отмечается обратная закономерность – при переходе от повышенной части пласта к пониженной отмечаются увеличение плотности нефти, концентрации ванадия и СР.

Ключевые слова: Электронный парамагнитный резонанс, ванадий (IV), свободный радикал, глубина залегания нефти.

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