



Increasing the Reliability of Determining Remaining Oil Saturation in Cores Based on Gas Chromatography Results

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Abstract

The paper reports on the results of a comparative analysis of different methods for assessing residual oil saturation of the developed reservoir based on the remaining oil saturation of a sealed (sealed in the reservoir conditions) core. In addition to the traditional method (with the Dean-Stark apparatus), the chloroform extraction via the Soxhlet extractor with subsequent chromatographic analysis of the extract was applied. The study has found that the commonly utilized weight-based method of determining oil saturation has its own drawbacks. It gives distorted data on oil saturation for rocks with low filtration capacity. Furthermore, determination of the chemical composition of the extract on a gas chromatograph reveals several distorting factors, such as reduction of the low-boiling oil fraction and anthropogenic contamination.

Keywords: Residual oil saturation, sealed core, core studies, technogenic pollution of cores, extraction

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1. Introduction

Information about the residual oil saturation (S_{or}) of reservoirs is critical to develop an adequate strategy for the development of hydrocarbon resources at various stages and phases of the geological exploration process – from assessing potential hydrocarbon resources to the final stage of development. S.G. Neruchev's quantitative model of hydrocarbon generation and accumulation, focused on predicting the resources of underexplored sites relying on bituminological data, uses S_{or} in estimating oil loss on secondary migration pathways [1]. The problem of residual oil and water saturation acquires particular importance with respect to sites in the final stages of development, which are growing in number in the Western Siberia oil and gas-bearing province (WS OGP) [2]. As the pool of large deposits shrinks, smaller sites with low and/or variable reservoir filtration capacity (FC) characteristics are subjected to development [2, 3], whose effective exploitation is also connected with the problem of determining residual oil (bound oil, capillary trapped oil) [4, 5].

Residual oil saturation is investigated using various modeling methods, core studies, and geophysical methods in the bottomhole zone of the reservoir [6, 7]. All these methods identify residual oil content in a unit volume of the reservoir under specific conditions of its waterflooding with water of drilling fluid filtrate. The values of S_{or} obtained using different methods are often inconsistent and depend significantly on reservoir parameters and displacement

conditions. Several factors affecting residual oil content, such as overbalanced drilling [8], chemical additives in the drilling fluid filtrate, water washout of the reservoir void space [9], etc., are not quantifiable. The method recognized as the most reliable is determining the displacement coefficient on the core with preservation of reservoir conditions, however, it has not been implemented widely due to the difficulty of the technology [5].

The most reliable estimations of S_{or} are obtained by direct testing of the fluid component of the retrieved core – remaining oil-water saturation [10]. However, even in this case, several distorting factors need to be considered, connected in most cases with the influence of drilling fluid on both the mineral and fluid parts of the core. This influence can be ruled out by specific core sampling methods, which involve, among other things, isolating the core from the drilling fluid [11]. These technologies considerably raise the informativeness of core studies, yet they also do not exclude distorting factors when determining remaining oil saturation. The sealing agent, which is typically a hydrophobic liquid of non-petroleum origin, is also able to penetrate into the pore space of the core when the latter is sampled under reservoir thermobaric conditions. The issue of the accuracy of quantitative estimation of remaining oil saturation in a sealed core is urgent. In addition to possible anthropogenic contamination of the pore space of the core with a sealing agent, the loss of low-boiling oil fractions during direct, by weight, measurement of oil and water content should be

considered, for example, using the Dean-Stark apparatus [12].

The purpose of the study is to improve the methodology for determining the coefficient of remaining oil saturation (ROS).

2. Methods and materials

In the course of the study, comparative and methodological research on determining the ROS of the extracted core was carried out. The study employed four methods, including gas chromatography as a common method of studying the chemical composition of oils and bitumen in core studies [13]:

- the traditional method based on extraction with the Dean-Stark apparatus with determination of the volume of water extracted (samples A and B);

- photolorimetric analysis of the hydrocarbon extract recovered from samples C;

- the extraction-weighting method using the Soxhlet apparatus (samples D);

- using gas chromatographic determination of oil in extracts obtained from samples D.

The research was carried out at the laboratory base of the Tyumengeofizika Research and Production Center and the Industrial University of Tyumen.

Extraction of the soluble organic matter of rocks was carried out using chloroform extraction on a Soxhlet apparatus. Rock samples, pre-crushed to a fraction of <0.5 mm and weighed, were placed in the apparatus in a paper container and subjected to extraction for 12-24 hours. The end of extraction was determined using the luminescent method – by cessation of the glow of the solvent in the working chamber of the Soxhlet apparatus in UV light. The extract obtained was analyzed on a chromatograph using ASTM 2887-Simulated Distillation on a ten-meter capillary with polymethylsiloxane as the stationary phase. This method provides an estimation of the content of normal alkanes and the main isoprenoids – pristane and phytane. For further quantitative calculation, the volume of the extract at the time of sampling for analysis was measured in a measuring cylinder. If the concentration of the extract was suspected to be too low based on visual assessment (coloration), the extract was evaporated before taking a sample for analysis. After analysis, the extract was concentrated by temperature distillation – chloroform was distilled off at 62°C to 90-95% of the extract volume, the concentrate was evaporated at room temperature to stop the loss of weight, and the obtained oil (bitumoid) was weighed in graduated weighing bottles. For quantitative determination of oil in the extracts, the chromatograph was calibrated using solutions of West Salym oil in hexane with concentrations of 0.025, 0.01034, 0.005, and 0.00338 g/mL as calibration mixtures. An example of a calibration chromatogram is shown in Fig. 1. The tested samples of chloroform core extract were analyzed under the same conditions as the reference solutions.

3. Results and discussion

From a visual comparative analysis of the chromatograms of chloroform extract and reference oil solutions, the following conclusions can be drawn:

- all samples contain some amount of petroleum components;

- most samples contain the entire range of normal alkanes characteristic of petroleum – from C₈ to C₃₀;

- the light (gasoline) fraction in oil and bitumoid samples is significantly reduced: reference oil shows a pattern – the concentration of each normal alkane decreases with the increasing length of its hydrocarbon chain, while in the experimental samples, this pattern holds true, as a rule, only for hydrocarbons with a chain length over C₁₅ (Figs. 2-4).

Based on visual analysis of the chromatograms, the oil isolated from the core was distinguished into types:

- type 1 – pure reservoir oil (Fig. 2);

- type 2 – pure reservoir oil with signs of minor anthropogenic impurities (Fig. 3);

- type 3 – reservoir oil with clear signs of contamination in significant amounts (Fig. 4);

- type 4 – dispersed (micro-) oil (bitumoid) with no clear signs of contamination (Fig. 5);

- type 5 – bitumoid with clear signs of contamination (Fig. 6).

As criteria of "oil – bitumoid" classification, we took the ratios of n-alkanes among themselves (bitumoid is in a sorbed state, so the light fraction is not as reduced as in free reservoir oil) and the ratio of C₁₇/pristane and C₁₈/phytane, pristane/phytane: for the reference oil, these ratios are equal to 1.8, 1.3, and 0.83, respectively.

In view of the variability of petroleum composition, samples with an n-alkane/isoprenoid ratio of less than 1 are assigned to the "bitumoid" type.

Quantitative calculations of oil content relative to the reference value account for the composition of the obtained extracts: the components chosen for the construction of calibration curves were from the range not subjected to reduction on the one hand, and not affected by anthropogenic pollution on the other hand. Thus, the most informative were hydrocarbons in the range of C₁₅-C₁₉. The resulting calibration curves are provided in Fig. 7.

In most cases, oil concentrations were calculated based on n-heptadecane (C₁₇H₃₆), since this component is the most linear in the operating range of concentrations. In cases where the chromatogram showed signs of distortion of the n-heptadecane peak due to impurities or was absent at all, the calculation was carried out according to other components: C₁₈H₃₈, phytane, C₂₀H₄₂, and C₂₁H₄₆. Several key quantitative characteristics were identified during the analytical work, including total weight loss of rock during extraction, weight of the extracted organic matter, and oil concentration in the extract calculated from gas chromatography data. This initial data allowed us to calculate target core fluid characteristics: the content of oil, water, and anthropogenic impurities (sealing agent) per kilogram of rock. Water content was calculated as the difference between the total weight loss of the sample during extraction and the weight of the extracted organic matter. The content of anthropogenic impurities was calculated as the difference between the weight of the extract and the oil content determined by gas chromatography. Comparative analysis of data on core oil saturation according to the direct weighting method and the chromatographic method demonstrates that the content of oil according to chromatography can be both lower and higher than the mass of the extracted organic matter determined directly by weighing. The variation in the results of the two techniques ranges from 96 to 98% of the total weight of the extracted organic matter. Cases where the chromatographically

determined oil content exceeds the amount of organic matter determined by weighing are attributed to the fact that the light fraction of oil is reduced due to the evaporation of low-boiling components [14]. In cases where the chromatographic method indicates a lower oil content, there are obvious anthropogenic contaminations of the core.

The determination of ROS using conventional methodology is based on the identification of oil volume:

$$ROS = V_{ro}/V_p = (\Delta m - V_{rw} \cdot \delta_w) / (\delta_o \cdot V_p) \quad (1)$$

where V_p – the volume of pores, V_{ro} – the volume of the remaining oil in the sample, Δm – sample weight loss during extraction in the Dean-Stark apparatus, V_{rw} – the volume of water in the sample extracted with the Dean-Stark apparatus, and δ_w and δ_o – the density of water and oil under laboratory conditions. The displacement of a part of oil from samples B identified in the studies leads to an underestimation of their oil saturation. Fig. 8 shows a comparison of ROS values determined according to the traditional methodology (according to the Dean-Stark method) and chromatography data.

The variations of ROS values in the reservoirs, with respect to the regression line, mainly fit within 11-12%. To some extent, these variations could be explained by variations in FC in samples B and C. However, eight samples (classified as potentially uniform) show no correlation of ROS.f values defined by different methods. Overall, the ROS of samples B according to the traditional methodology is at least 5-7% lower than according to chromatography results (see angular coefficient of the approximation equation in Figure 8). The above observation owes to the capillary displacement of oil from samples B [15]. The data for non-reservoirs are fundamentally different: the Dean-Stark method gives clearly unrealistic ROS.f values. All this casts doubt on the reliability of the characterization of the remaining oil saturation of the core according to the conventional method. Fig. 9 shows a comparison of ROS values based on chromatography (samples D) and photocolormetry (samples C). In non-reservoirs, oil saturation is practically nonexistent. Variations of ROS.f relative to the approximation line in the main sample also do not exceed 10-13%. With the increasing heterogeneity of samples, the difference in ROS readings by the considered methods increases. The angular coefficient of the approximation equation is practically equal to 1 ($m=0.978$), i.e., there is no significant systematic difference in the data. However, by its physical basis in the photocolormetry method, any deterioration in the optical transparency of the extract is evaluated as the presence of petroleum hydrocarbons. Thus, we observe a small, mostly under 5%, oil saturation of non-reservoir rocks. Therefore, in further estimates of oil saturation, we apply the results derived from chromatography data.

ROS can also be calculated from the material balance equation: $ROS=100-R_w-S_g$. Here, the gas saturation factor ($S_g.c$) is given after deducting the change (increase) in pore volume due to deconsolidation deformation. The value of the corresponding correction can be calculated as:

$$\Delta S_g = (1-\beta) / (1-\beta \cdot K_{por}) \quad (2)$$

where β – core volumetric deformation coefficient ($\beta=C_p.pl/C_{pat}$), K_{por} is given in fractions of a unit. The volumetric deformation coefficient of the object of research is $\beta=0.96$. With this correction, it can be recorded as: $S_g.c = S_g - \Delta S_g$; where S_g – gas saturation coefficient determined from rock density values. The values of ROS calculated in this way, on the one hand, retain the limitations on informativeness inherent in the original parameters (R_w and S_g), but on the other hand, provide an independent estimate of ROS. This gives additional opportunities to substantiate the informativeness of the oil saturation determination methods used in these studies. Figs. 10 and 11 show comparisons of ROS coefficients according to the material balance results (based on R_w and $S_g.c$) and chromatography and photocolormetry methods.

Despite the differing physical basis of ROS calculations by these methods and their highlighted drawbacks, and in spite of variations in the properties of samples A and B and their duplicates C and D, there is a mutual correlation of ROS values obtained by different methods. Of note are more or less satisfactory estimates for non-reservoirs (ROS<5-10%, i.e., at the level of methodological error). Despite a rather significant dispersion of points, most of them fall within $\pm 10-12\%$ of the regression lines given. The larger variation corresponds either to misses in determinations or is explained by the varying FCs of the compared samples. Comparisons of ROS coefficients as per traditional methodology (using the Dean-Stark method) and by chromatography accounting for porosity and permeability and water-holding capacity (WHC) of the rocks are shown in Fig. 12. They confirm the above-mentioned features of the reliability of the considered techniques, as well as prove the existence of general regularities of oil saturation changes with the improvement of FC. These comparisons highlight a region of reservoirs with elevated values of FC: $K_{perm} (>100-140 \text{ md})$ and $K_{por} (>21-22\%)$, characterized by a relatively low oil saturation coefficient (from 18 to 32%). These mainly belong to the lower water-encroached part of the reservoir (2,631.3-2,633.4 m).

Comparison of ROS values of samples A and B calculated on the basis of the material balance equation also constitutes one of the possibilities to characterize the reliability of ROS measurements. From the comparison shown in Fig. 13, the correlation of the data obtained is predictable. As expected, the oil saturation of samples A is slightly higher than that of samples B, i.e., $ROS^a < ROS^b$. The presented analysis of the data of oil saturation studies of the selected cores confirms the above conclusions about the influence of sample preparation and treatment technology on their fluid saturation. The outlined shortcomings in determining water and oil saturation of rocks based on the data of extraction and distillation in Dean-Stark apparatuses testify to the need to adjust the methodology of determinations and to ensure control over the completeness and quality of water distillation.

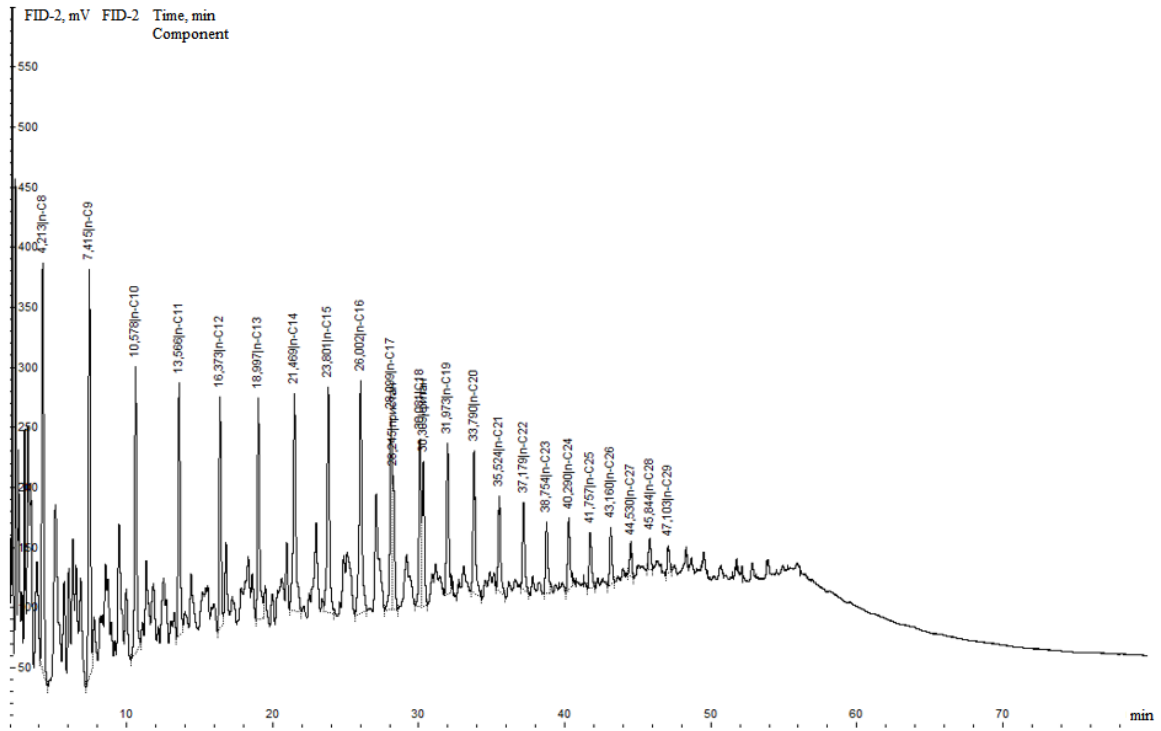


Figure 1. Chromatogram of the reference (0.005 g/mL) solution of oil in hexane

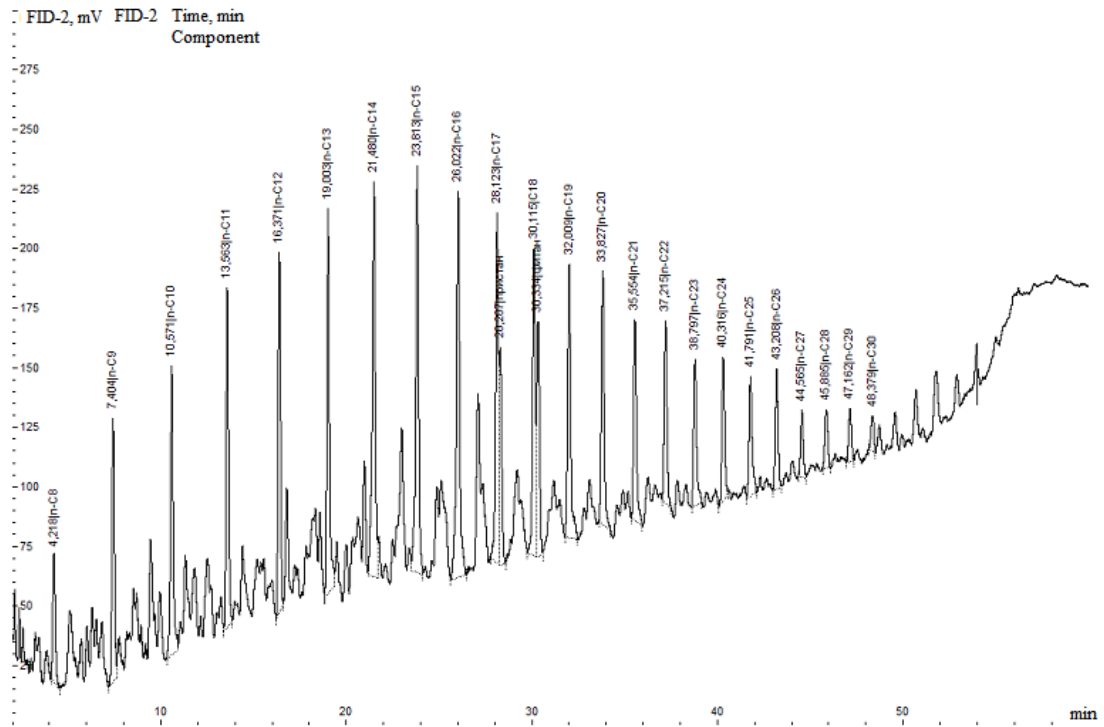


Figure 2. Example chromatogram of type 1 extract – pure reservoir oil

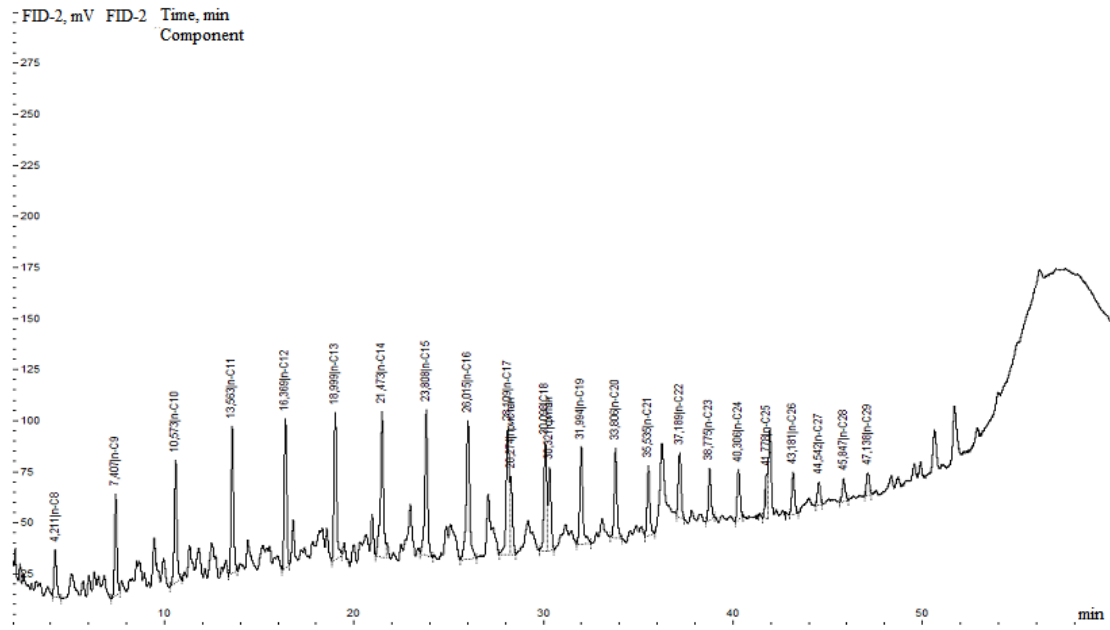


Figure 3. Example chromatogram of type 2 extract – pure reservoir oil with signs of minor anthropogenic impurities

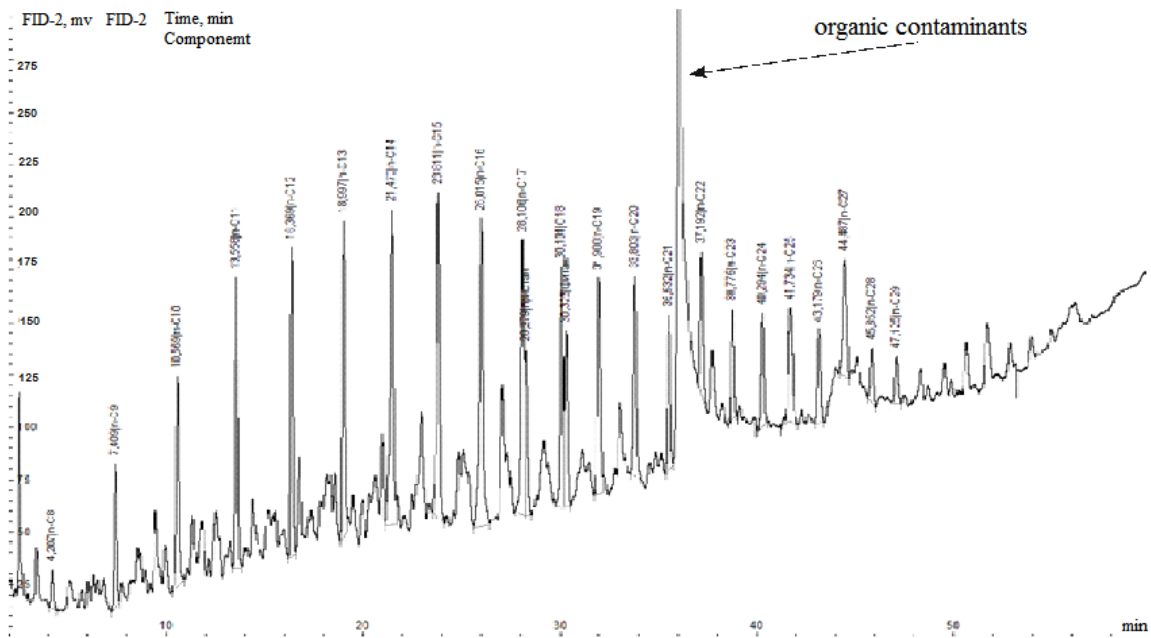


Figure 4. Example chromatogram of type 3 extract – reservoir oil with clear signs of contamination

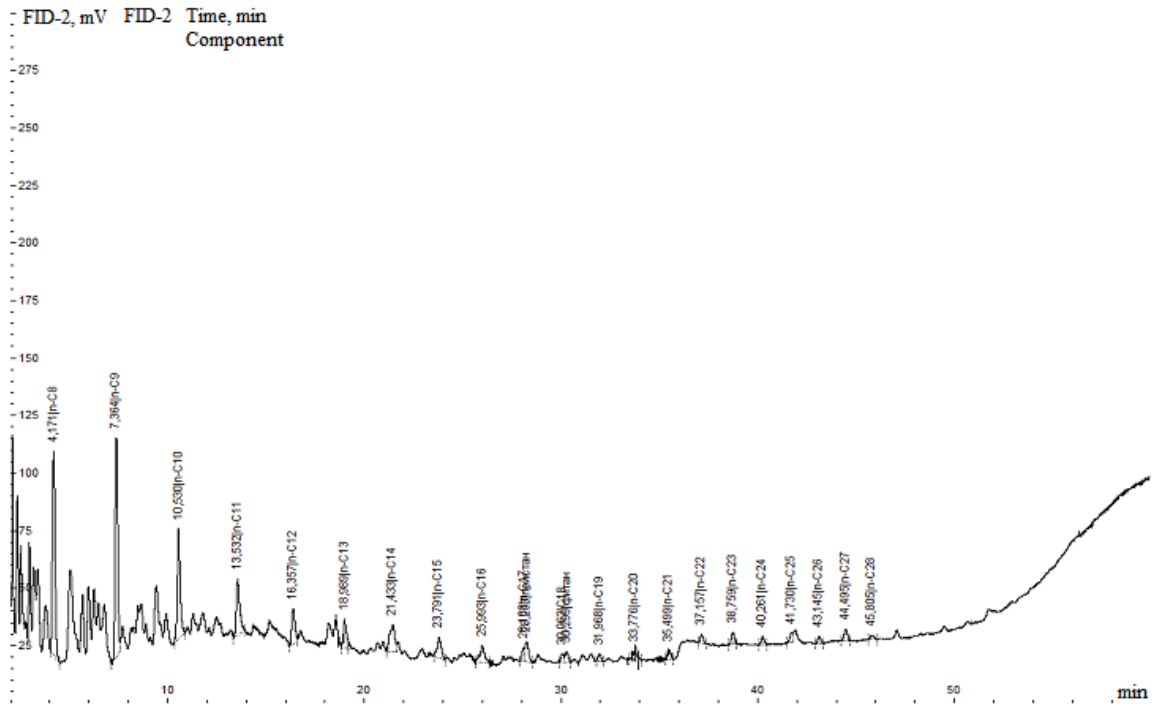


Figure 5. Example chromatogram of type 4 core extract – bitumoid with no signs of foreign impurities

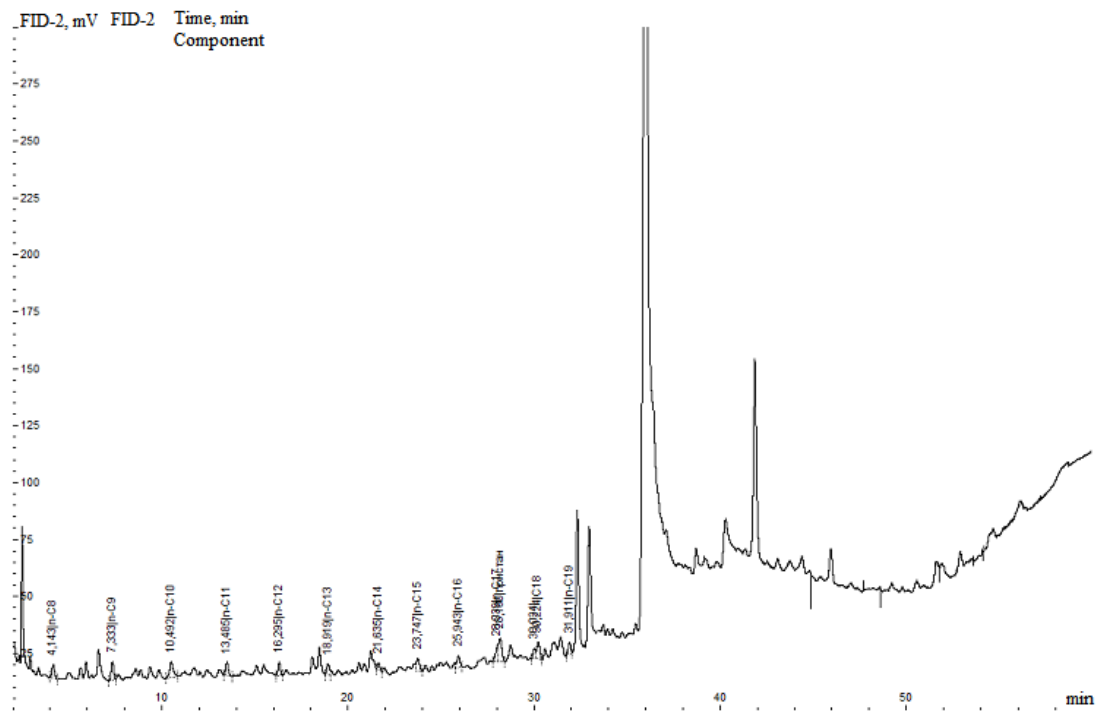


Figure 6. Example chromatogram of type 5 extract – bitumoid with signs of contamination

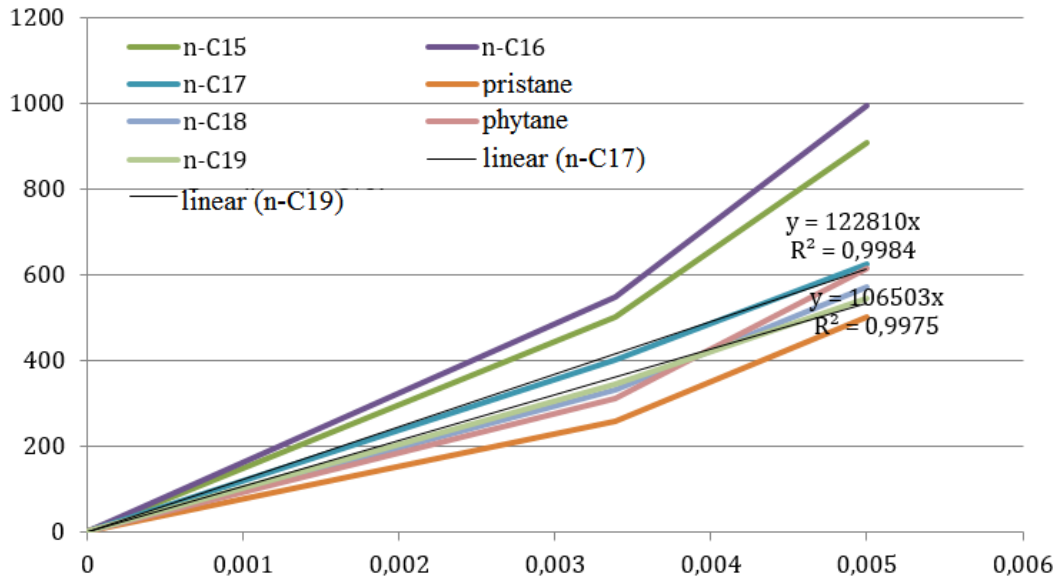


Figure 7. Dependence of peak heights of some n-alkanes on oil concentration in the solution

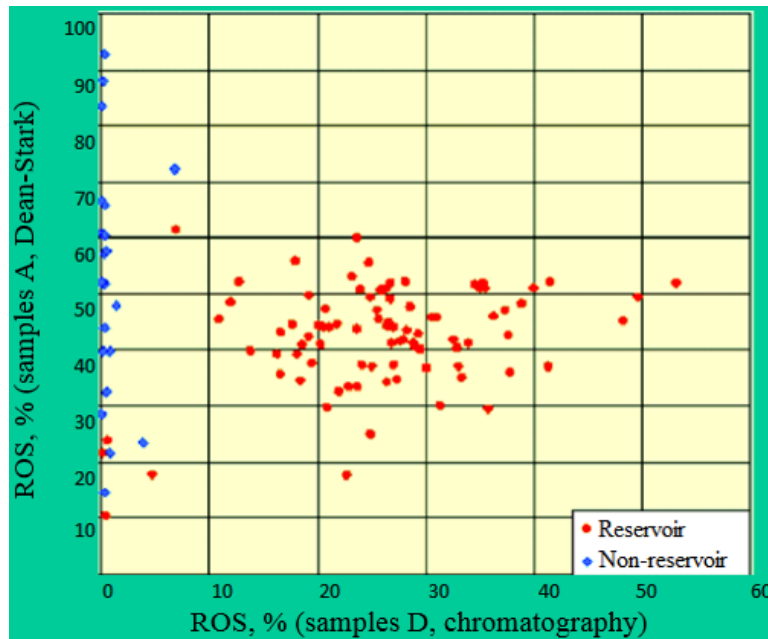


Figure 8. Comparison of ROS values as determined by the Dean-Stark apparatus and the chromatographic method

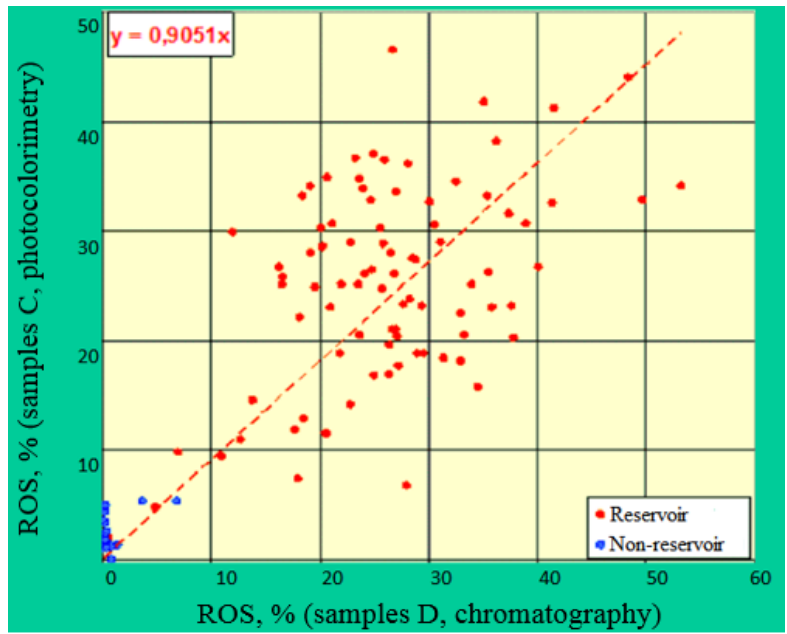


Figure 9. Comparison of ROS values as determined by photocolorimetry and gas chromatography

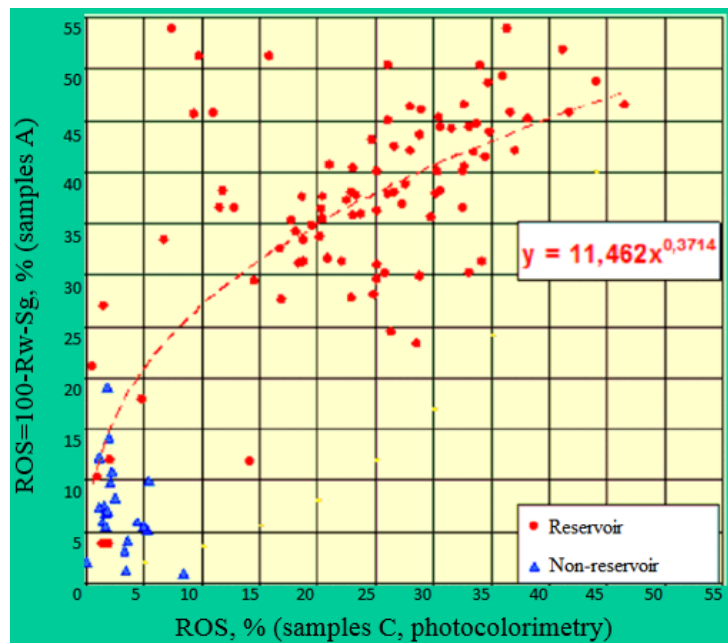


Figure 10. Comparison of ROS coefficients obtained using photocolorimetry and the material balance method

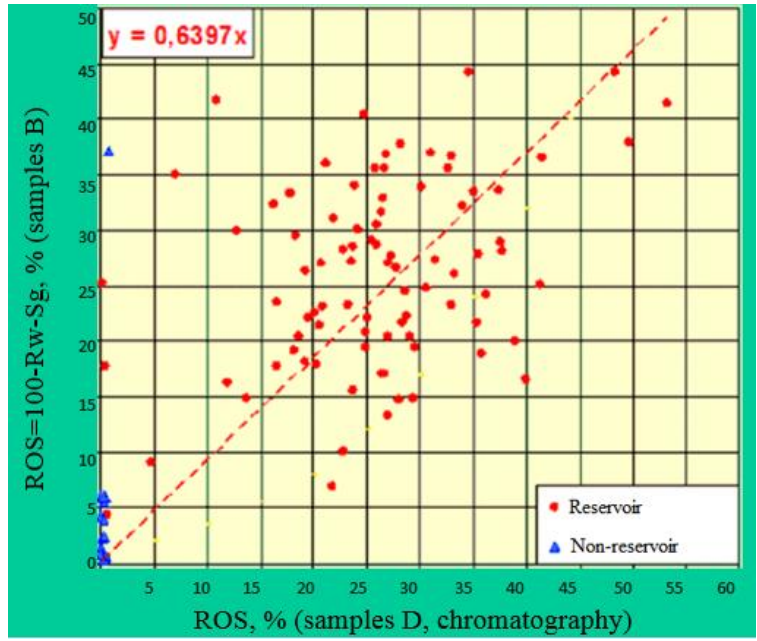


Figure 11. Comparison of ROS coefficients obtained by gas chromatography and the material balance method

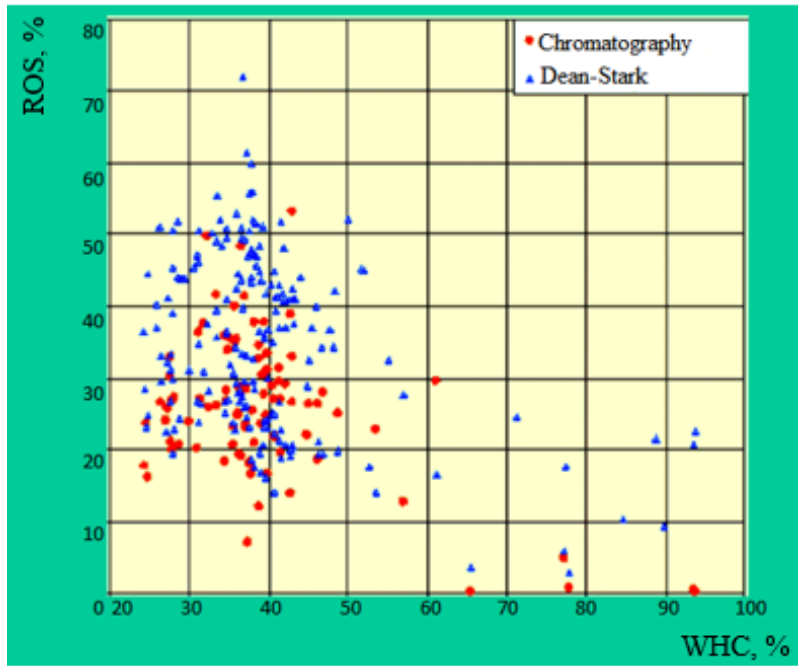


Figure 12. Comparison of ROS coefficients obtained by chromatography and the Dean-Stark method with the water-holding capacity (WHC) of rocks

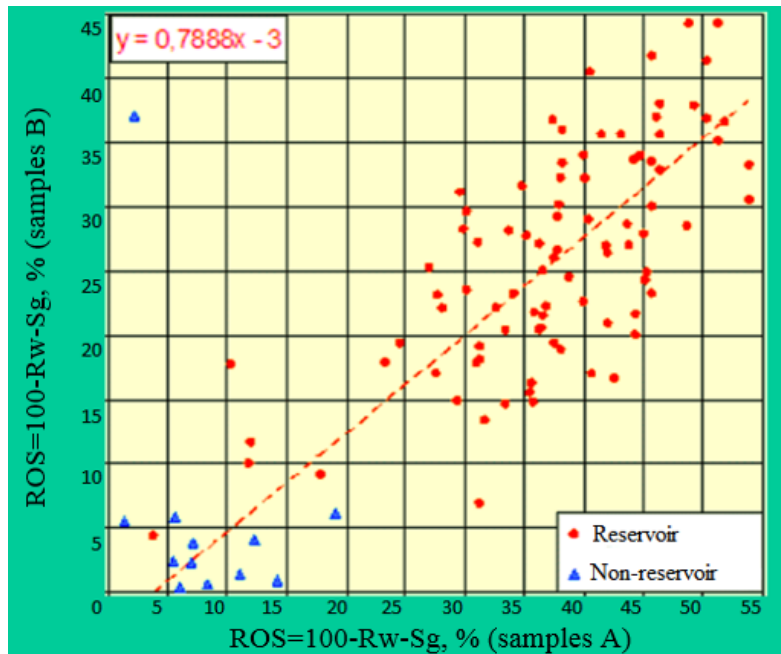


Figure 13. Comparison of remaining oil saturation in samples A and B as calculated by the material balance method

4. Conclusions

The conducted studies have provided substantiation for methods of identifying oils through gas chromatography, as well as established that gas chromatography data of core extracts increase the reliability of the results of reservoir oil saturation studies. In turn, the reliability of data obtained by the traditional (weighting) method is questionable in a number of cases, especially for samples with low FC.

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