Determination of Microelement and Hydrocarbon Composition of Rocks and Their Change in Depth When the Search for Oil and Gas Deposits.

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Abstract: The mineral composition of rocks was investigated using the mass spectrometer with inductively coupled plasma. According to these data, the composition of rocks is calculated by the proportion of these minerals in the rock and on the basis of them are constructed lithological-petrographic profile sections with the selection of zones of change of rocks. The data obtained in the aggregate allowed us to outline the zone of migration of fluids from oil and gas deposits, which provides additional information when assessing the prospect for prospecting areas.

The integrated use of these methods made it possible to confidently predict oil and gas fields.

Key words: hydrocarbon, organic matter, oil and gas fields, mass spectrometry with inductively coupled plasma, wells, rocks.

I. Introduction

Methods have been created for prospecting and exploration of oil and gas fields, based on chemical and physicochemical studies of dispersed and concentrated oil and bituminous substances, hydrocarbon and acid gases of rocks and waters back in the 50th of the last century [1].

At the first stages of the formation of geochemical methods, the object of the study was the upper 60 meters of the sedimentary cover, within which the gas and microbiological survey of gas logging was attempted to reveal the presence of oil and gas hydrocarbons in the sedimentary [2].

At the stage of geochemical studies, the search began for anomalous features of hydrocarbon accumulations associated with migration, and the main accumulation of hydrocarbons in reservoirs of the entire section of the sedimentary cover.

The development of this stage (“direct” geochemical methods) led to the formation of laboratory research up to the molecular and atomic levels and the development of methods for assessing the scale of oil and gas generation. For a long time, “direct” geochemical methods of prospecting and exploration of oil and gas fields are used to determine the deposits of oil and gas deposits and to increase the reliability of oil and gas forecasts within the search facility. Methods of local forecast are divided into three main groups: geological, geochemical and geophysical. All of them were widely distributed and brought encouraging results. Therefore, their use is relevant in modern economic conditions.

Geochemical search indicators are based on the interaction of hydrocarbon components (methane, ethane, propane, etc.) with the environment during their vertical migration from oil and gas deposits. It should be assumed that, theoretically, the penetration of noticeable amounts of migration gases into the overburden deposits should lead to a violation of the primary regular relationships in the system [2].

Experiments show that during migration, part of the hydrocarbons dissolves in the water part of the rocks, which are collected by its mineral part, penetrates into micro cracks. Another part of migration hydrocarbons in the higher horizons is subject to destruction and alteration, which leads to an abnormal accumulation of the products of their formation and the development of specific microflora.

The listed geochemical indicators could be widely and successfully used in the search and exploration of oil and gas fields. The lack of highly sensitive methods and measurement tools, as well as methods for processing primary information for a long time led to the fact that out of 10 exploratory wells drilled, 3 wells turned out to be productive, at best.

This article is devoted to the method of obtaining and processing geochemical information in order to increase the efficiency of exploration to increase the reliability of forecasting and, consequently, improve their technical and economic indicators [3].
At the stage of substantiation of methods for exploring oil and gas fields by geochemical methods, the initial distribution of synthetic rubber gas or organic matter during their vertical migration of hydrocarbons during their interaction with the environment varies completely. The study of the nature of these changes gave rise to the assessment of the diagnostic criterion in the principle of new issues and their resolution. It was precisely because of the necessity of choosing complex indicators of geochemical searches.

Recent achievements in organic chemistry have also been based on the successful separation and detection of complex components of compound organic compounds, with the help of new analytical and physicochemical methods. In this regard, the tandem consisting of gas-chromatographic and mass spectrometric methods can be considered as the main driving force of these achievements.

The main advantage of this tandem, known as the Chromatograph-Mass spectrometer (Ch-MS), is that of high accuracy of gas chromatography (5000) and mass spectrometry \((10^{-8} \text{ percent mass})\) with great sensitivity. In other words, chromatograph is an analyzer of gaseous substances and a mass spectrometer fulfills the function of the ion detector.

At the figure 1 is given the schematic structure of the Ch-MS. The investigated gas carrier is transmitted from the sprayer to the column of the chromatograph (4) with the help of He gas.

![Figure 1. Schematic structure of Ch-MS.](image-url)

The liquid adsorbent applied to the inner wall of the column absorbs the gas passing through it and after a while the gums that are absorbed are separately desorbed (each gas has a precise desorption duration). Gases gradually leave the adsorbent and come to the end of the tube (colon). Column diameter \(D = 0.1-1 \text{ mm}\), length 15-20 meters. The chromatographic separation factor is determined by the dimensions of the column (the column is long distinctly distinct).

II. Experimental part

Experimental technique. The experiments were carried out by mass spectrometry with inductively coupled plasma (ICP-MS), which is based on argon plasma at atmospheric pressure and a quadruple mass analyzer [4; 5]. The choice of this method is due to the fact that in recent years, the ICP-MS method has made a huge leap in its development and has become the main method for solving the problems of elemental and isotopic analysis of rare and trace elements. ICP-MS analyzes more than 80 elements, both naturally occurring and man-made. The main advantages of this method are: high sensitivity, availability of most elements of the periodic table, wide linear dynamic range (9 orders of magnitude) determined concentrations, ease of sample entry into the ion source.

Sample preparation method (direct decomposition). In most cases, the objects of analysis in ICP-MS are aqueous solutions. Solid samples (rocks) are dissolved using acids and then analyzed. The most suitable medium...
for analysis is diluted 2-5% nitric acid. The total content of solid solutes in the sample should not exceed 0.2-3% (2-3 mg/l).

The sample preparation sequence is shown in Figure 2 [6].

The desorbed compound molecular ions are recorded in the quadruple or other mass analyzer according to the m/z as mass spectrum in the output.

**Fig. 2.** The procedure of sample preparation of soil on the heating plate

**Figure 3** shows the chromatograms taken from samples taken from two different (a, b) depths. In this case, the chromatogram is a spectrum of kernel (sludge) carbohydrates extracted from the depth of the drilled well several times (10 years). The figure shows that the composition of these gases is C1-C19.
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Figure 3 Chromatogram of carbohydrates of kernels (samples) taken from 2000 to 2070 m (a), 900-970 m (b)

Figure 4 shows the results of a mass spectrometric analysis of rocks taken from various depths. The depth range covers 900-2145 m. Nevertheless, the depth of 2145 meters accurately reflects the change in the concentration of both hydrocarbon gases and trace elements that “linger” in core materials during the vertical migration of gases and waters.

III. Results and discussion

It is difficult to prevent the direct chemical interaction of saturated hydrocarbons with rocks at low temperatures. However, an indirect effect on rocks migrating hydrocarbons with the participation of bacteria or under the influence of radioactive processes is quite real. In this regard, in the present work, only preliminary schematic data are presented on the lithochemical method, which in the near future will probably take a certain place in the complex of geochemical methods for searching for oil and gas deposits.
Indeed, in the zone of obstructed gas exchange under the influence of penetrating waters and dissolved gases, the following changes in rocks can be expected:

1. Due to the exchange reaction between the Ca and Mg ions, the Mg ion penetrates into the calcium carbonate lattice (cement rock), i.e. partial dolomitization occurs. At the same time, reservoir properties of rocks are improved, which contributes to an increase in the concentration of migratory hydrocarbon gases (HCG).

2. As a result of tectonic processes that continue after the formation of deposits, during the so-called geological time, migration paths are created for fluids, along which the migration flow of deep highly mineralized waters rushes into the upper horizons together with dissolved and free hydrocarbons. Waters are usually relatively rich in Mg, J, Cu, Zn, Br, Pb, Th, V and others and contain dissolved CO₂ [7].

The interaction of hydrocarbons with rocks in this hydrodynamic zone leads to the formation of CO₂ of a number of organic-mineral complexes, which partially migrate to the upper geochemical zone. As a result, the concentration of such important rock-forming elements as Ca, Si, Mg, Na, K, Fe etc. changes to a different degree [8].

In contrast to other types of geological exploration, the geochemical method of searching for oil and gas deposits is based on the study of spatial patterns and mainly gas fields. The specificity of these fields as an object of study leaves a definite imprint on the results of geochemical searches, giving the latter (for example, microelements) some originality [6]. For example, the concentration of oil and gas in the oil and gas fields increases with depth and their qualitative composition approaches the composition of the deposits as they deepen, the more geochemical explorations are targeted to the deeper horizons, the more representative their obtained data. Some words about changing the composition of rocks. It is known that (for example, [7, 8]) as a result of tectonic processes continuing after the formation of deposits, migration routes are created during geological time, along which the migration flow of deep mineralized waters together with dissolved free hydrocarbons are eliminated to the upper horizons. Waters are usually enriched with magnesium, bicarbonates, iodine, bromine, etc., contain in dissolved form CO₂, and in some cases H₂S [9].

One of the indicators for evaluating oil and gas wells is the nature of the distribution of elements and changes in their ratios. Therefore, it is first necessary to identify the average elemental composition of the rocks of the section (statistically) in comparison by the clarks of the elements of the corresponding rocks. Against the background of the established values of these elements, increased and decreased contents of individual elements in the area under study are detected. The ratios of the elements are calculated and the characters of changes of these quantities are constructed over the section and area of the studied area.

Therefore, it is advisable to study the mineral composition of rocks using a mass spectrometer and X-ray analysis. Having these data on the composition of the rocks, the proportion of these minerals in the rock is calculated and on the basis of their lithologic-petrographic profile sections which made with the selection of zones of change of rocks.

IV. Conclusion

It should be noted that in the geochemical exploration of oil more attention is paid to natural bitumen and organic extracts of boron. This is particularly important for the study of molecular biomarkers and xerophosphates. The composition and molecular structure of these compounds are investigated intensively in the search for oil geology, as more organic and geochemical in the last 20 years. The data obtained together allow us to outline the zone of migration of fluids from oil and gas deposits, which provides additional information when assessing the prospect for prospecting areas.

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