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Geochemistry features of mercury in oils from the deposits of the dnipro-donetsk depth

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Abstract:

The purpose of the article is to establish the geochemical characteristics of mercury in the oils of the active deposits of the Dnipro-Donetsk depth and to create their classification according to the content of this metal. Based on the research of typomorphic features of the oils of the considered deposits, it was established that it is the low-molecular sulfur-containing heteroatomic components of the oil system that are the main carriers and concentrators of mercury. Based on the results of the cluster analysis, a dendrogram of the results of clustering by the weighted centroid method of the studied deposits by the mercury content in the oils was constructed. Taking into account the statistically significant character of mercury connections, it is proposed to divide all geochemical and geological-technological parameters into a group genetically and/or paragenetically related to the accumulation of mercury in oil and a group negatively related to an increase in mercury content in oil. This is what made it possible to develop the classification of oil fields of the Dnipro-Donetsk depth according to mercury content.

Keywords: mercury, oil, metals, clustering dendrogram, regression equation, classification

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"The geochemistry of mercury is still full of mysteries"
O. Ye. Fersman, Geochemistry, V. III, 1937. p. 454

1. Introduction

In the process of geochemical research of various directions of mercury, special attention is paid. This is due to both the positive participation of this element in a number of technological processes, where it acts as a necessary, key component, and its exclusively negative impact on the processes occurring in living organisms. Mercury is present in one or another amount in the most important types of minerals: oil, natural gas, coal, metal ores, non-metallic minerals and is often used in the practice of geological exploration as a kind of universal indicator when searching for deposits. [1].

At the same time, mercury compounds are extremely toxic, stable in the conditions of the Earth's surface, mobile at the local and regional levels, accumulate with the subsequent negative impact in the food chains of various-scale continental and aquatic ecological systems and generally create environmental problems at the local, regional and global levels. In this regard, mercury and its compounds are a global "polluter" of the environment [2].

The relevance of research aimed at establishing the features of mercury accumulation and distribution in geological environments is recognized both at the international and state levels. In 2013, under the auspices of UNEP (the United Nations Environment Program), the Mercury Convention (Minamata Convention) was agreed. A number of normative documents have been adopted in Ukraine (Laws of Ukraine "On Subsoil", "On Environmental Protection", "On Protection of Atmospheric Air", "On Environmental Expertise", "On Waste", by Resolution of the Cabinet of Ministers of Ukraine No. 22 dated 30.09.1995 and No. 688 dated 28.06.1997, decision of the National Security and Defense Council of Ukraine dated 16.07.2021 "On stimulating the search for, obtaining and beneficiation of minerals that are of strategic importance for the sustainable development of the economy and defense capability of the state", by Presidential Decree of Ukraine No. 306/2021 dated 23.07.2021, as well as regulatory documents of the State Commission on Mineral Reserves), which directly establish the need to study geological objects containing mercury.

At certain hydrocarbon deposits, the concentration of mercury in the extracted raw materials exceeds the background content in the outer geospheres of the planet by orders of magnitude. So, for example, at the Groningen (Netherlands), the largest gas deposit in Europe, the concentration of mercury in the hydrocarbon raw material exceeded the saturation limit ($1 \cdot 10^{-3}$ g/m^3), which led to the precipitation of free metallic mercury in the pipes [3].

The highest concentrations of Hg are typical for deposits located in the most permeable areas of the earth's crust – intersection nodes of deep faults. For example, a chain of deposits characterized by elevated mercury concentrations stretched along a deep fault called the Karpinsky Lineament. Most of the oil and gas deposits of the Netherlands, Germany, Poland, Ukraine, Kazakhstan, Uzbekistan and others belong to this structure. Pure mercury deposits are localized in the same fault zone.

The mercury content in oil is mainly in the range of $4x10^{-6}$-$4x10^{-5}$%, in some samples it increases, for example, in Precarpathia, to 10^{-4}%, and in the oil of the Cymric field (California) it reaches $2x10^{-3}$% [3-4]. There it is an object of incidental mining. This deposit is located on the same deep fault of San Andreas, with which the mercury deposits of California (New Almaden, New Idria, etc.) are connected. Mercury reserves in oil and gas deposits can reach very large sizes. According to the authors' calculations [3-4], based on the reserves of hydrocarbons and the average concentration of mercury in them, the reserves of mercury in the Groningen gas field (Netherlands) are about 400 tons, in the Cymric oil field about 1000 tons.

The high content of metals, in particular mercury, is also a serious technological problem in the processing of petroleum raw materials, as it leads to irreversible deactivation of catalysts as a result of the deposition of compounds of this metal on the active surface, blocking of the pore space and destruction of the catalyst structure. In addition, inorganic metal compounds formed during oil processing contribute to high-temperature corrosion of equipment surfaces, reduction of the service life of turbojet, diesel and boiler units, gas corrosion of active elements of gas turbine engines, and the growth of environmentally harmful emissions into the environment. At the same time, metals, including mercury, are valuable accompanying components, the concentration of which in oils and residues of their processing may even exceed their content in ore sources [5].

Unfortunately, in Ukraine, the industrial production of metals (in particular, mercury) from petroleum raw materials has not yet been mastered, although there are technologies in the global practice of oil refining that allow the simultaneous production of concentrates with a high content of various metals. In addition, the presence, content and ratio of metals in oils from different fields allows establishing patterns of their origin, migration and concentration in hydrocarbon systems. Among them, in particular, it is necessary to specify the ones that are of particular priority in terms of industrial and ecological importance – mercury, vanadium, cobalt, nickel, iron, manganese, aluminum, titanium, chromium and zinc.

Thus, attention to the problems of the accumulation and migration of microelements, in particular mercury in oil, is connected with the actual scientific and technical issues of the genesis of hydrocarbons, with the possibility of their industrial extraction in the process of oil refining for the purpose of further sale as an accompanying raw material. It is also related to the possibility of determining the environmental risks of using these oils as raw materials for the production of petroleum products and, primarily, gasoline and diesel fuel.

This work is devoted to the results of research on the geochemistry of mercury in the oils of the main deposits of the Eastern oil and gas region of Ukraine, which is the largest in terms of explored reserves, forecast resources and production. In tectonic terms, this region is located within the Dnipro-Donets depression, which is a complex intra-platform rift structure, and the latter, in turn, on a different scale level, is a link of the heterogeneous transcontinental Sarmatian-Turanian lineament, spatially traced from the western borders of Belarus to the spurs Tien Shan.

2. Materials and Methods

One of the first systematization of oils according to their general characteristics of metal content was carried out by Barwise A. J. G. in 1990. He considered the chemical composition, physical properties and metal content of oil samples [6]. Later in 2007, Shnyukov Ye.F. published a very interesting review article on the content of vanadium and nickel in natural oils of the world [7]. It considered in detail the concentrations of the presence of heavy metals in oils in relation to their genesis. A year later, in 2008, A.A. Sukhanov reviewed the current state of stock assessment of associated components of oil (including heavy metals) as sources of high-quality liquid metal raw materials [8]. In 2010, S.P. Yakunini published the results of a study of the relationship between the deep zoning of hydrocarbons and the enrichment of oils with heavy elements-impurities [9]. The paper indicates the existence of a correlation dependence of the content of heavy metals in oils with the depth of oil deposits. Already in 2014, Akpoveta O.V. conducted an analysis of the content of heavy metals in oil products from deposits in Nigeria (Agbor) The authors note that the high level of heavy metals in oil can pose a serious environmental threat [10].

It should be noted that not all impurities of heavy metals in oils have a natural genesis. In Ukraine, such studies were conducted in 2013 regarding high-sulfur oil of the Carpathian depression [11]. In this work, not only the fractional composition and physicochemical properties of the light fractions extracted from the oil of the Orkhivtske oil field were investigated, but also the potential content of the fractions, for which the density, refractive index, molecular weight, and sulfur content were determined. A little later Wilberforce J.O. conducted research on the content of heavy metals in crude oil used in medicine [12]. In the work, the levels of Cd, Ni, V and Pb were investigated using atomic absorption spectrophotometry. As a result of the study, the average concentration of metals was determined, indicating their impact on the human body. Previously, some geochemical features of metals in oils from deposits of the Dnipro-Donetsk depth were considered and the creation of a natural classification of these oil deposits by metal content using clustering methods was substantiated [13-16]. At the same time, there are no studies aimed at studying the geochemical features of mercury in the oil deposits of the Dnipro-Donetsk depth.

Thus, the study of metals, in particular mercury in oils from various deposits of Ukraine, which provides the opportunity to determine their genetic characteristics and environmental consequences of use, is an urgent problem, the solution of which will contribute to the development of a set of predictive criteria for hydrocarbon accumulations and a scientifically based geological, economic and environmental assessment their use.

The factual basis of the work was the results of analyzes of the content of mercury and other metals in oils from 36 deposits: Bakhmachske, Prylukske, Krasnozayarske, Kachalivske, Kremenivske, Karaykozivske, Korobochkynske, Kulychykhinske, Lipovodolynske, Monastyryshchenske, Matlakhivske, Malosorochynske, Novo-Mykolayivske, Perekopivske, Prokopenkivske, Radchenkovske, Raspashnovske, Sofiivske, Sukhodolivske, Solontsivske, Solokhivske, Talalaivske, Trostyanetske, Turutynske, Zakhidno-Kharkivtsivske, Shchurynske, Yuryivske, Yaroshivske, Khukhryanske, Sagaidatske №1, Sagaidatske №13, Kybytsivske №5, Kybytsivske №51, Kybytsivske №52, Kybytsivske №56, Kybytsivske №1.

Samples from the Sagaidatske, Kybytsivske deposits and the Bakhmachske, Prylukske, Krasnozayarske, Kachalivske, Kremenivske, Karaykozivske, Korobochkynske, Kulychykhinske, Lipovodolynske, Monastyryshchenske, Matlakhivske, Malosorochynske, Novo-Mykolayivske, Perekopivske, Prokopenkivske deposits were provided by the branch of the Ukrainian Research Institute of Natural Gases (UkrNDIgaz) of the joint stock company "UkrGazVydobuvannya".

The rest of the samples were provided from the sample and material archives of the respective companies that provided the processes of initial drilling and overhaul of the wells, with the consent of the companies that own the production facilities. These samples were obtained thanks to sampling from the well with the use of "bailer".

The technological process of selecting an oil sample using a bailer (also known as a "bailer selection equipment") from a well includes the following steps:

1. Preparation of the bailer: The bailer is a special piece of equipment consisting of a metal tube with an open bottom that has a valve or latch at the top. Before use, the bailer is cleaned, ensuring its sterility to avoid contamination of the oil sample.
2. Lowering the bailer into the well: The bailer is lowered into the well using a special rope or cable. It descends to the appropriate depth, where the oil sample is taken.
3. Oil Sampling: When the bailer reaches the desired depth, a valve or gate valve is opened, allowing the oil to flow to the bailer. The filling of the bailer is due to the natural oil pressure in the well. The filling time may take several hours or more, depending on the condition of the oil tank.
4. Lifting the core from the bailer: After the oil sample is taken, the bailer is slowly lifted from the well. It is important to ensure the safe lifting of the bailer to avoid sample destruction or loss of oil.
5. Storage and transportation of the sample: After lifting the bailer from the well, the oil sample is poured into a special container or test tube. The oil sample is provided with marking

Research of oil samples from these fields for mercury content was carried out with the help of X-ray fluorescence analysis on the energy-dispersive spectrometer "SPRUT" SEF 01. The spectrum accumulation time is 600 s.

Energy-dispersive spectrometer SPRUT SEF-01 is a high-precision device designed for measuring the energy spectrum of X-ray radiation. It is able to determine the energy of photons and determine their number based on the dispersion effect. SPRUT SEF-01 has a compact design that is easily installed on the appropriate optical system. The main components of the spectrometer are the X-ray detector and signal processing electronics.

The detector of a spectrometer usually consists of a semiconductor crystal that is capable of

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generating an electrical signal upon absorption of X-ray photons. This signal is sent to the electronics for further processing.

The spectrometer's electronics are responsible for signal amplification, noise amplification and filtering, analog signal conversion to digital format, and data processing. Usually, a specialized software tool is used to analyze and interpret the obtained spectra.

This equipment allows to determine the percentage content of components, so the weight of the initial weight is not taken into account.

The preparation and analysis were carried out according to the standard ASTM D 4927 - Determination of the elemental composition of the components of lubricants by the methods of X-ray fluorescence spectroscopy with wavelength dispersion.

The method of X-ray fluorescence spectroscopy with wavelength dispersion (XRF) is an integral part of the analysis of the elemental composition of lubricant components. This method is based on the use of the properties of X-ray radiation, which occurs when the sample interacts with high-energy X-rays.

The wavelength-dispersed XRF measurement process is as follows:

A sample of lubricant is irradiated with X-rays, which causes the atoms in the sample to fluoresce.

Fluorescent radiation resulting from the interaction of X-ray radiation with sample atoms contains characteristic lines that are unique to each chemical element.

The intensity distribution of fluorescent radiation depending on its energy (wavelength) is measured using a detector.

The obtained data on the intensity of the fluorescence spectrum are analyzed using calibration standards containing known concentrations of elements.

With the help of mathematical methods, such as the method of linear regressions or other statistical approaches, the relationship between the intensity of spectral lines and the concentrations of elements in a sample of lubricant is established.

Depending on the accuracy and sensitivity of the equipment, it is possible to determine the elemental composition of the components of lubricants, including the concentrations of various chemical elements.

It is important to note that the XRF method can be used to analyze the elemental composition of solid, liquid or powder samples, which makes it quite universal for determining the composition of lubricants.

The following samples served as standard samples of metal impurities: RM 23 (DSZU 022.122-00) MSO 0243:2001 with certified values of Cd, Mn, Pb, Hg, Zn; RM 24 (DSZU 022.123-00) MSO 0244:2001 with certified values of Fe, Co, Cu, Ni; RM 26 (DSZU 022.125-00) MSO 0246:2001 with certified values of V, Mo, Ti, Cr. Thus, from each of the 36 deposits, at least 30 oil samples taken from the wells during the five years of their operation were analyzed. Then the values of mercury content and all other geological and technological indicators were normalized according to the formula:

$$X_{i\ norm.} = (X_i - X_{i\ min})/(X_{i\ max} - X_{i\ min}) \quad (1)$$

where:

$X_{i\ norm}$ – normalized unit value of oil sample from a specific deposit,
X_i – unit value of oil sample from a specific deposit,
$X_{i\ min}$ – minimum value of oil sample from a specific deposit,
$X_{i\ max}$ maximum value of oil sample from a specific deposit.

In this way, the calculated normalized values of oil samples from each field were processed using the STATISTICA 11.6 program, in which the calculation of descriptive statistics, correlation, regression, cluster analyzes and graphical visualization of the results of the performed studies were performed.

The method of weighted centroid cluster analysis, as the most optimal for developing the classification of oil deposits of the Dnipro-Donetsk depth according to the content of metals, was substantiated in detail in studies [17]. The application of this method allows you to build a dendrogram that reflects the mutual natural hierarchy of the analyzed deposits by mercury concentration.

3. Results and discussion

On the basis of the conducted research, it was established that the average mercury content in the oil of the considered fields is 0.437±0.133 ppm with a confidence interval of 0.95, the sample variance is 0.639, the standard deviation is 0.799, the median value corresponds to 0.97 ppm, the kurtosis is 6.964, and the asymmetry is 2.616.

According to the results of the Kolmogorov-Smirnov and Shapiro-Wilk tests, the distribution of the values of the average mercury content in the oil sample of all considered fields corresponds to the lognormal distribution law.

At the same time, the authors of the work established that a more complex picture is observed for samples from oil samples from individual fields. It turned out that for the majority of deposits (96% of the cases of the considered samples), the density of the distribution of mercury content corresponds to the lognormal law, and for others – to the normal law.

Establishing the law of distribution is of great genetic importance, since the conditions for the occurrence of normal and lognormal distribution laws are determined by the implementation of various mechanisms of formation. If this value is formed as a result of the influence of several factors comparable in intensity, then the result of such a process (according to the central limit theorem) will be a normal distribution. The lognormal distribution is formed due to the influence of several factors that differ significantly in their influence on the final result. This follows from the central limit theorem of probability theory.

In relation to the discussed geochemical processes, a lognormal distribution can be expected if the concentration of this element is the result of several mechanisms or stages of enrichment and/or depletion of the mercury content, which differ significantly in their effect, with the predominant influence of one of them in the process of oil ontogenesis. A normal distribution is characteristic of geochemical processes that occur under the influence of several factors that are similar in their contribution to the final result.

The minimum average content of Hg is 0.0007ppm for oil from the Talalaivske field, and the maximum average value of this indicator of 3.4 ppm characterizes the oil from the Kybytsivske No. 51 field.

According to the results of the correlation and regression analysis and taking into account the Chedok scale in the oil samples from the considered deposits, it was established that there is a very weak inverse correlation between the content of mercury and nickel (correlation coefficient -0.05), iron (correlation coefficient -0.1), average capacity of the productive horizon (correlation coefficient -0.11), asphaltenes (correlation coefficient -0.14); a very weak direct relationship between mercury content and paraffins (correlation coefficient 0.12), oil viscosity values (correlation coefficient 0.18); a weak direct correlation between the content of mercury and resin (correlation coefficient 0.3), the total content of metals Ni, V, Zn, Cr, Mn, Co, Fe, Hg, Al (correlation coefficient 0.42); of the average inverse correlation between the mercury content and the current temperature of the productive horizon (correlation coefficient -0.52), the mineralization of formation water from productive horizons (correlation coefficient -0.62), the current depth of the productive horizon (correlation coefficient -0.63) , values of modern pressure in productive horizons (correlation coefficient -0.64); average direct correlation between mercury and zinc content (correlation coefficient 0.51), oil density values (correlation coefficient 0.53), initial boiling point temperature (correlation coefficient 0.54), manganese (correlation coefficient 0.64); high inverse correlation between mercury content and formation water density from productive horizons (correlation coefficient -0.78); high direct correlation of the content of mercury and sulfur (correlation coefficient 0.72), chromium (correlation coefficient 0.74), cobalt (correlation coefficient 0.81), aluminum (correlation coefficient 0.82), vanadium (correlation coefficient 0 ,85).

The calculated linear regression equations (Table 1) are respectively indicated below, and their graphs in the same order are shown in Figures 1-22.

Table 1. Linear regression equations between mercury content and geochemical and geological and technological parameters of oil

Regression equation; Correlation coefficient	**Regression parameters, correlation coefficient**
Hg = 0.1352 - 0.0402 x Ni; r=-0.05	between mercury and nickel content in oils,
Hg = 0.1381 - 0.1309 x Fe; r=-0.1	between the content of mercury and iron in oils
Hg = 0.1423 - 0.1484 x m; r=-0.11	between the mercury content and the thickness of the deposits
Hg = 0.1544 - 0.1324 x A; r=-0.14	between the content of mercury and asphaltenes in oils
Hg = 0.0872 + 0.1452 x C; r=0.12	between the content of mercury and paraffins in oils
Hg = 0.0726 + 0.1814 x η_{oil}; r=0.18	between mercury content and oil viscosity values
Hg = 0.0566 + 0.3525 x Re_{oil}; r=0.3	between the content of mercury and resin in oils
Hg = 0.0227 + 0.512 x Me_{total}; r=0.42	between mercury content and total metal content in oils
Hg = 0.3432 - 0.3988 x T; r=-0.52	between the mercury content and the current temperature in the horizon
Hg = 0.3869 - 0.5561 x $M_{layered\ water}$; r=-0.62	between mercury content and mineralization of reservoir water
Hg = 0.3724 - 0.4882 x h; r=-0.63	between mercury content and depth of development
Hg = 0.3955 - 0.5244 x P; r=-0.64	between mercury content and pressure indicators
Hg = -0.0017 + 0.4528 x Zn; r=0.51	between mercury and zinc content in oils
Hg = -0.1026 + 0.5337 x ρ_{oil}; r=0.53	between mercury content and oil density values
Hg = -0.0563 + 0.6404 x $T_{init.\ boil.\ point}$; r=0.54	between mercury content and oil boiling point
Hg = -0.0486 + 0.8026 x Mn; r=0.64	between mercury and manganese content in oils
Hg = 0.5431 - 0.6513 x $\rho_{layered\ water}$; r=-0.78	between mercury content and formation water density
Hg = -0.0274 + 0.6165 x S; r=0.72	between the content of mercury and sulfur in oils
Hg = 0.0319 + 0.6221 x Cr; r=0.74	between the content of mercury and chromium in oils
Hg = 0.0332 + 0.6965 x Co; r=0.81	between the content of mercury and cobalt in oils
Hg = 0.0102 + 0.7178 x Al; r=0.82	between mercury and aluminum content in oils
Hg = 0.0006 + 0.7025 x V; r=0.85	between mercury and vanadium content in oils

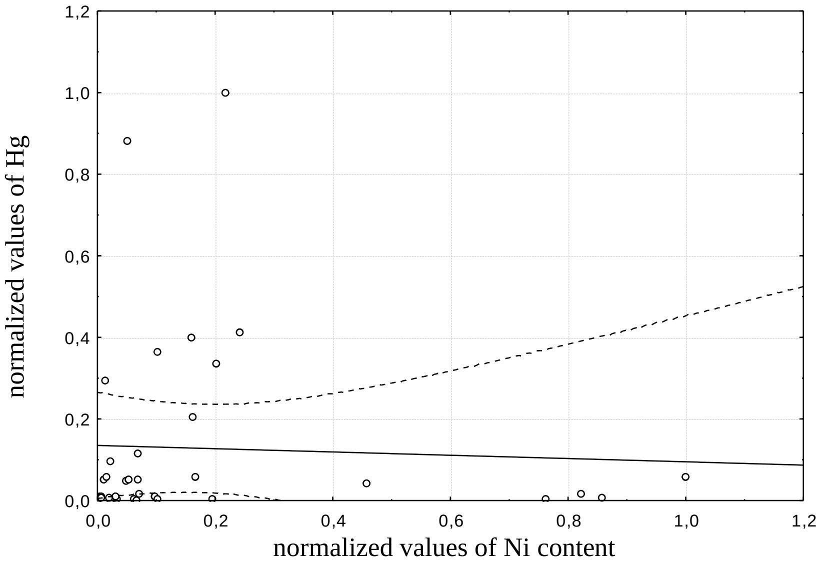

Fig. 1. Graph of the regression equation between mercury and nickel content in oils

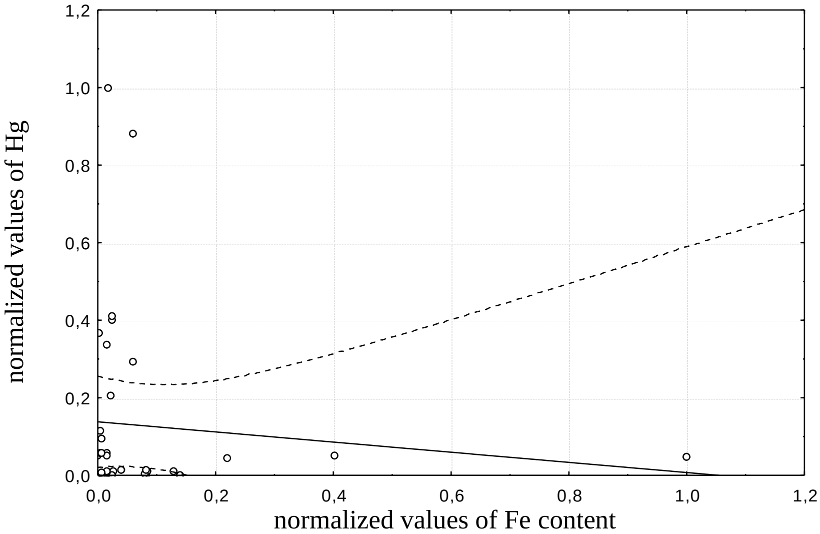

Fig. 2. Graph of the regression equation between mercury and iron content in oils

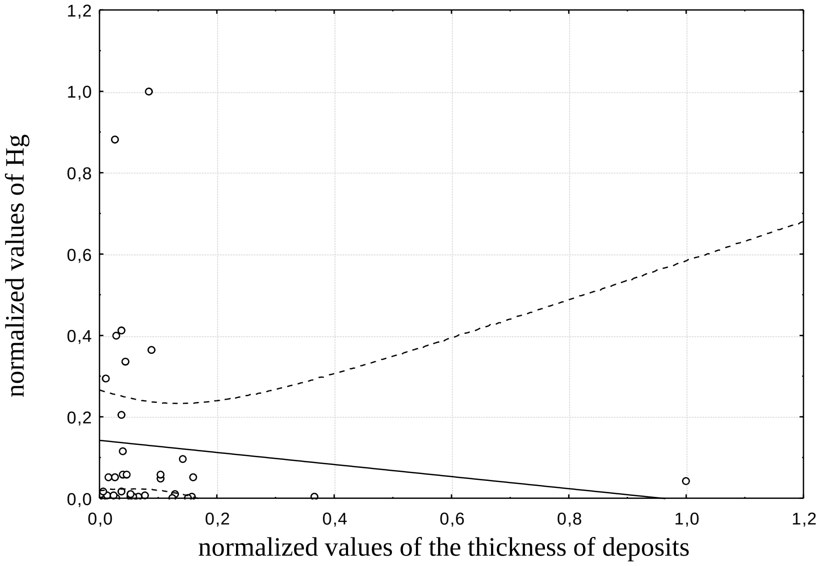

Fig. 3. Graph of the regression equation between mercury content and thickness of deposits

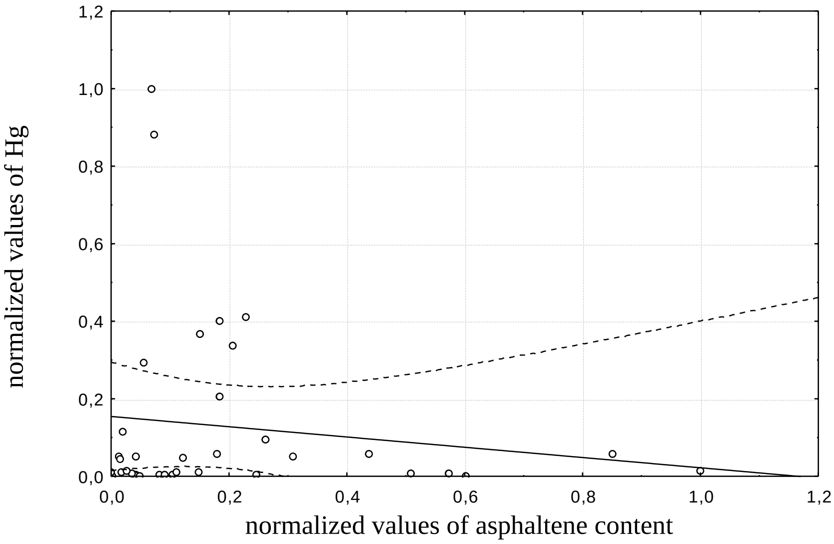

Fig. 4. Graph of the regression equation between the mercury content and asphaltenes in oils

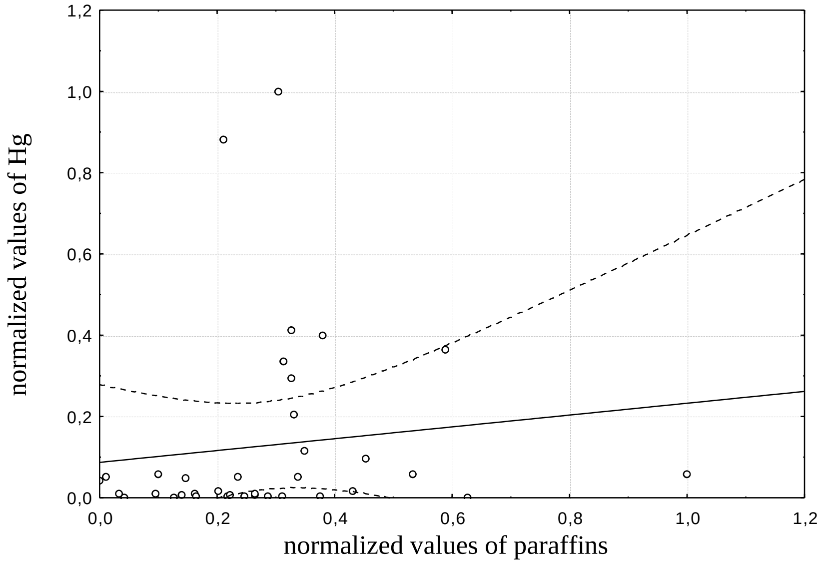

Fig. 5. Graph of the regression equation between mercury content and paraffins in oils

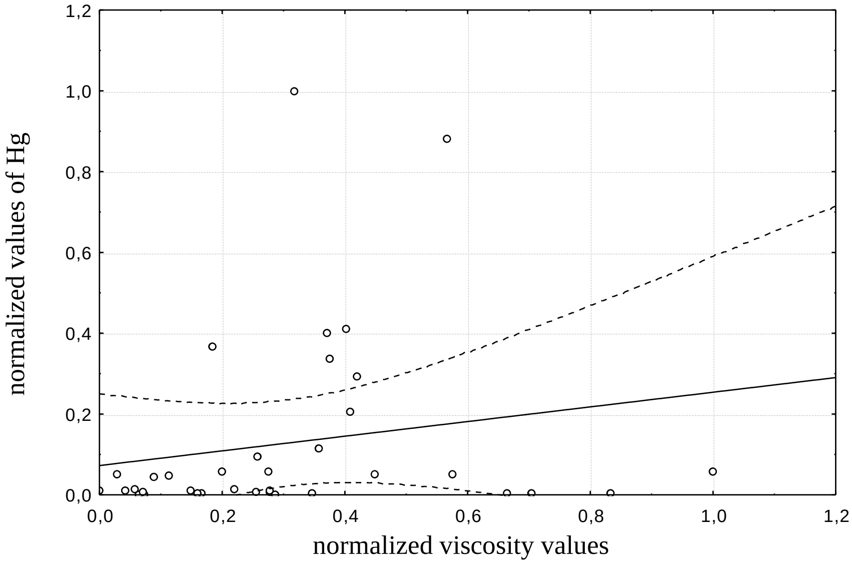

Fig. 6. Graph of the regression equation between mercury content and oil viscosity values

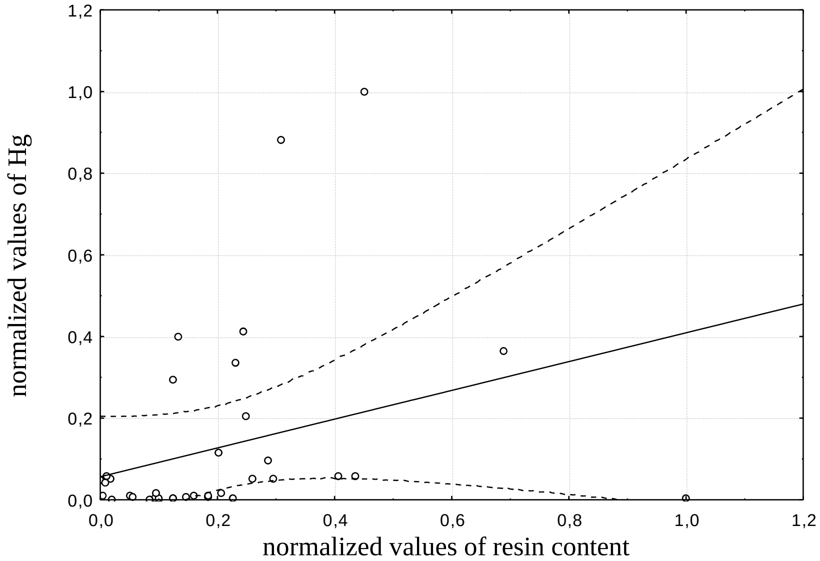

Fig. 7. Graph of the regression equation between mercury content and resins in oils

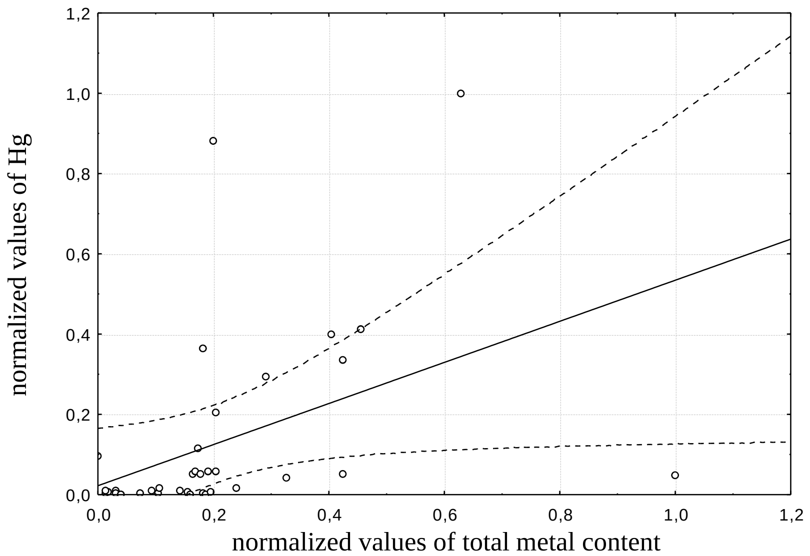

Fig. 8. Graph of the regression equation between mercury content and the total content of metals in oils

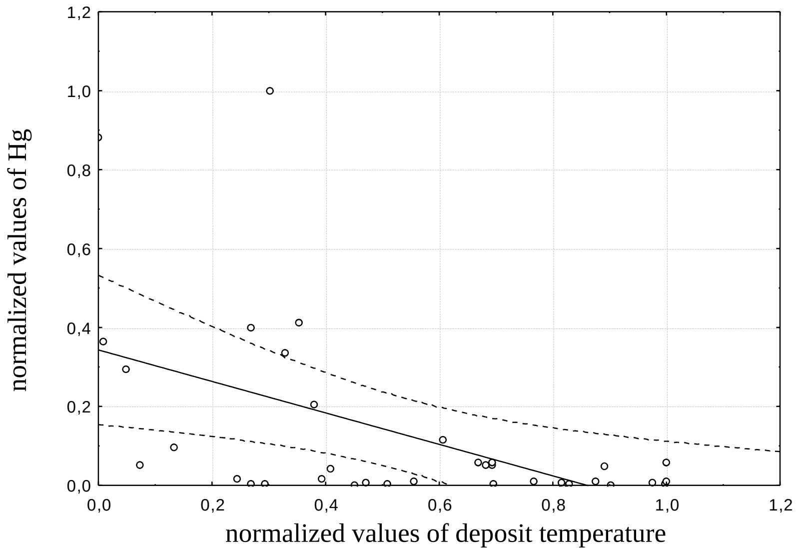

Fig. 9. Graph of the regression equation between mercury content and the current temperature in the horizon

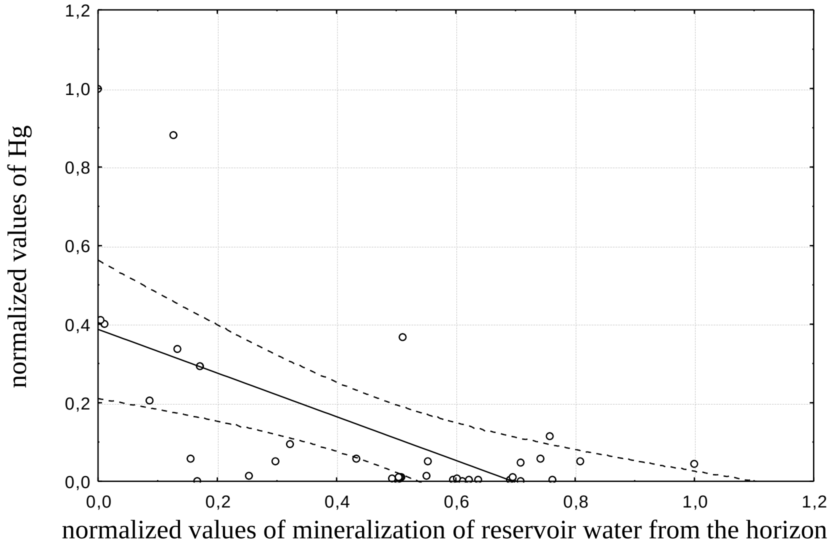

Fig. 10. Graph of the regression equation between mercury content and mineralization of reservoir water

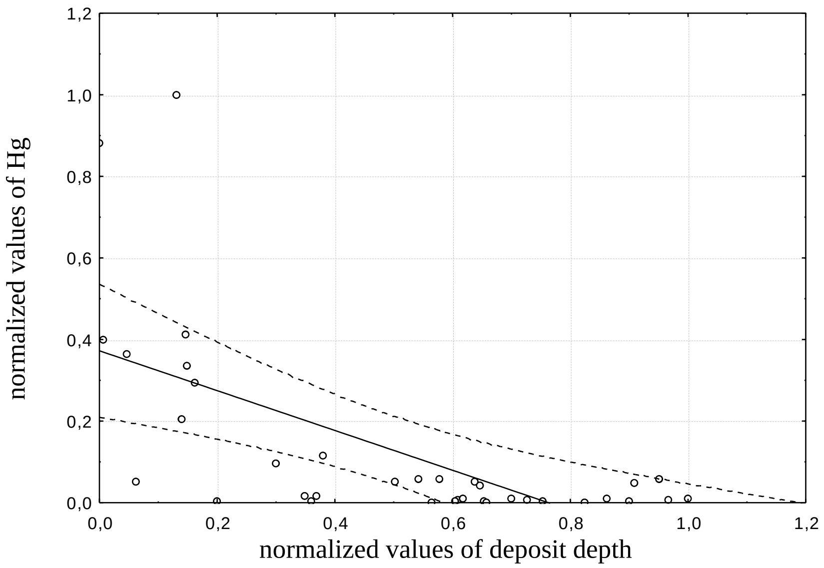

Fig. 11. Graph of the regression equation between mercury content and depth of development

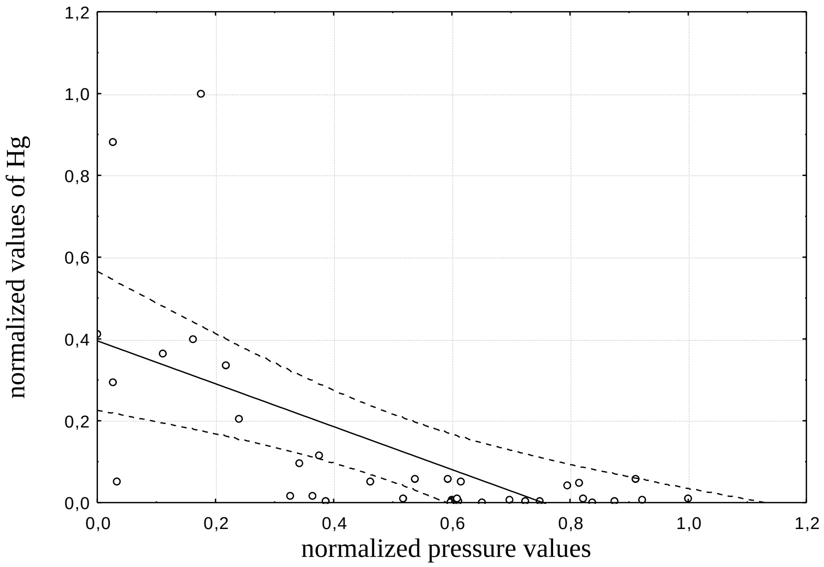

Fig. 12. Graph of the regression equation between mercury content and pressure indicators

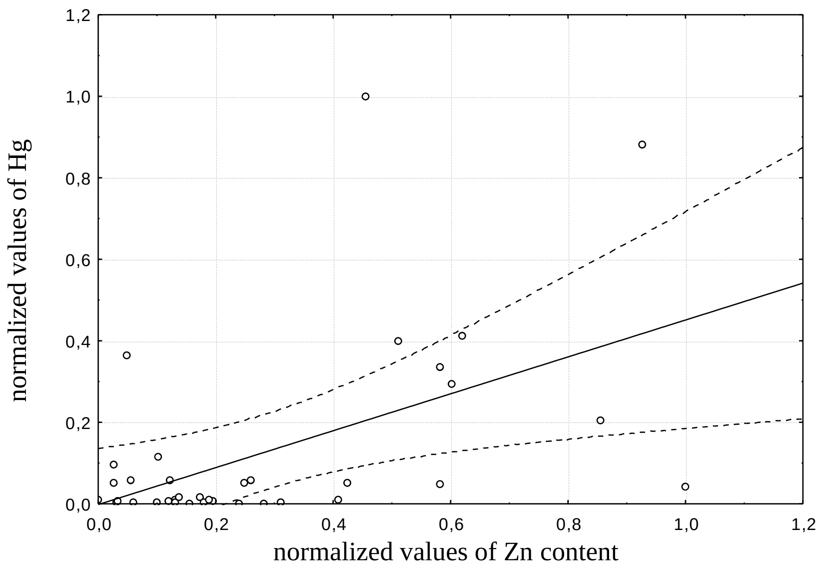

Fig. 13. Graph of the regression equation between mercury content and zinc in oils

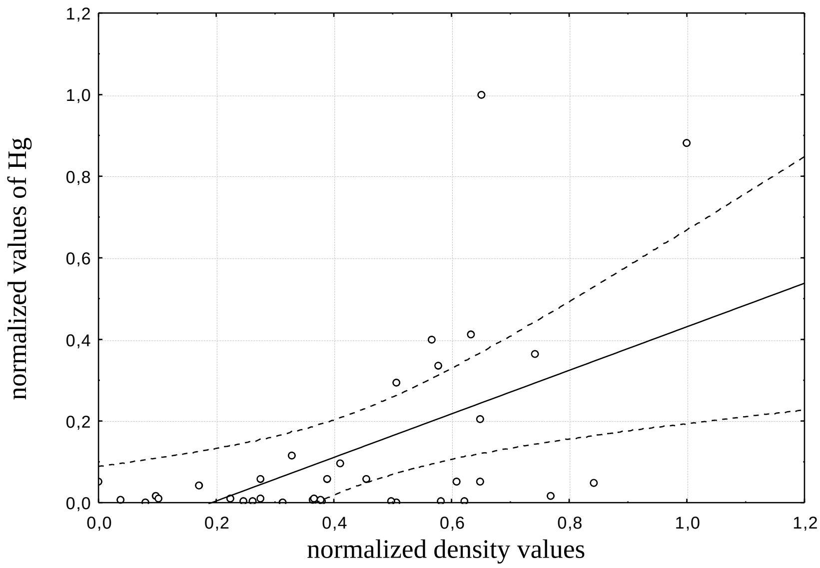

Fig. 14. Graph of the regression equation between mercury content and oil density values

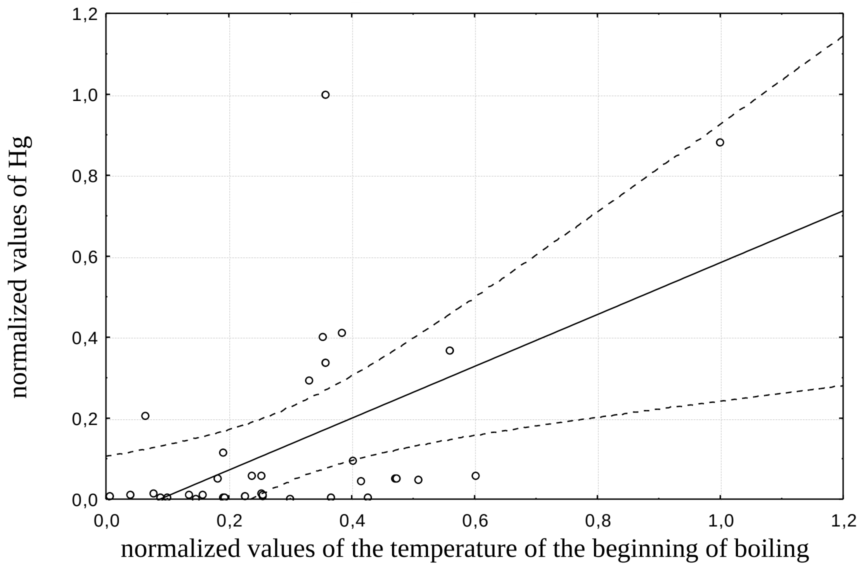

Fig. 15. Graph of the regression equation between mercury content and oil boiling point temperatures

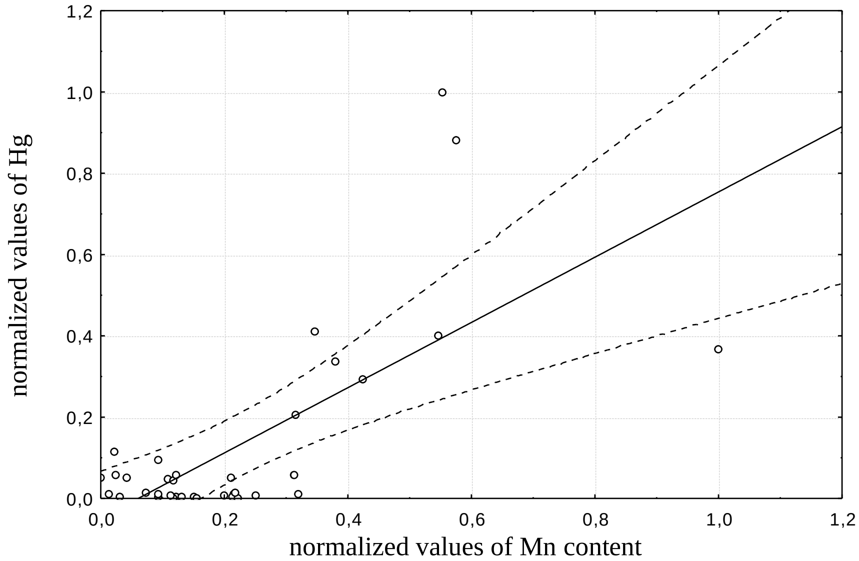

Fig. 16. Graph of the regression equation between mercury content and manganese in oils

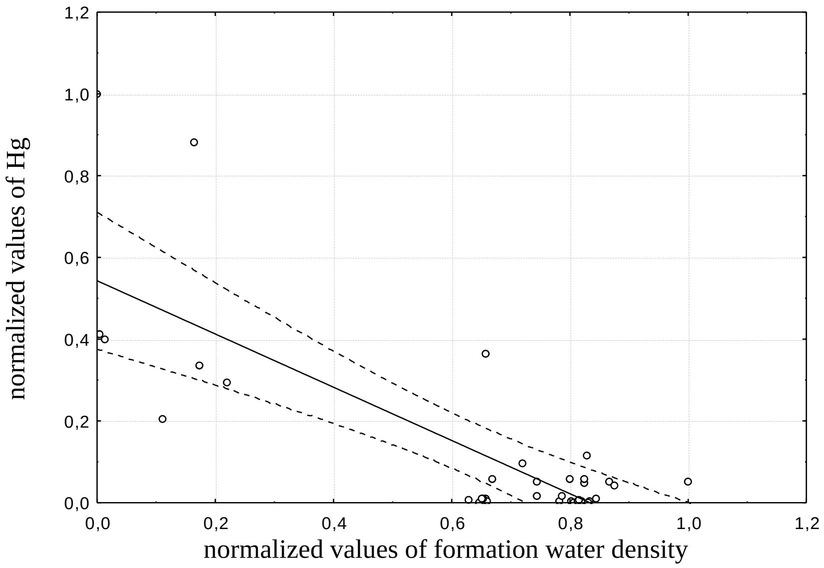

Fig. 17. Graph of the regression equation between mercury content and formation water density

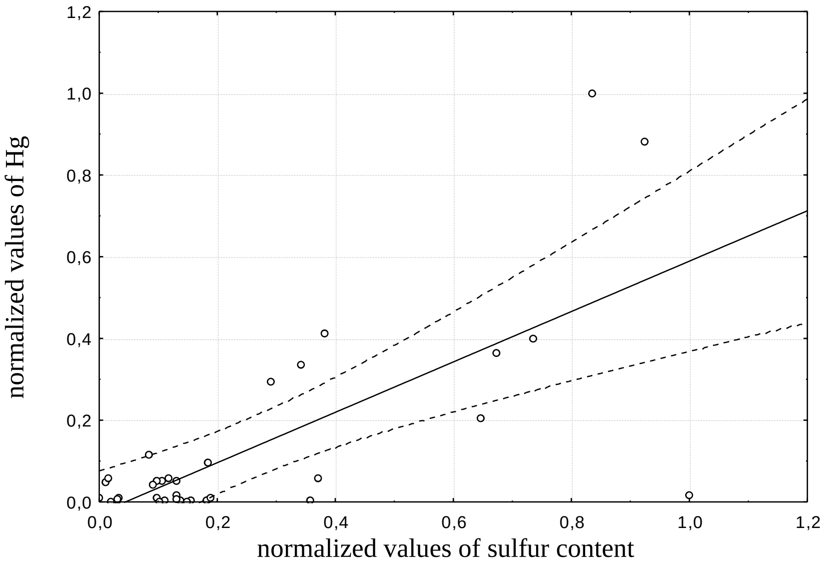

Fig. 18. Graph of the regression equation between mercury content and sulfur in oils

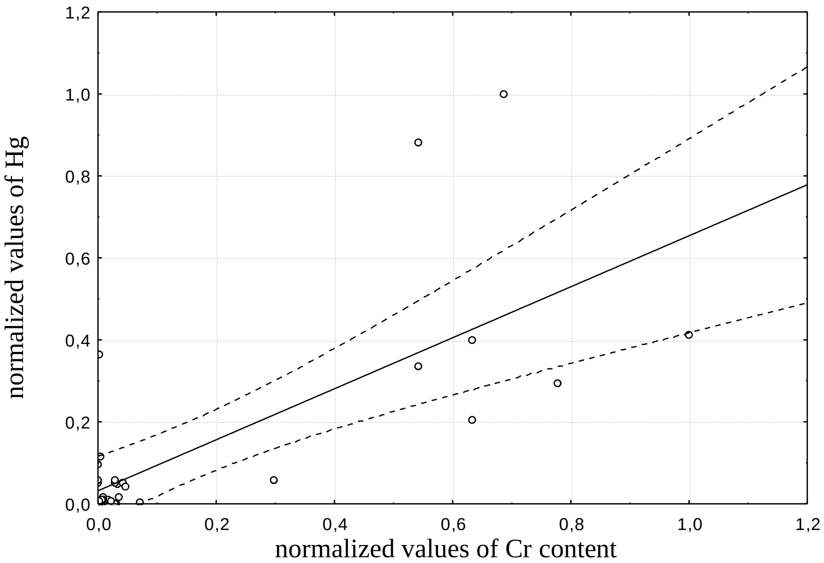

Fig. 19. Graph of the regression equation between mercury content and chromium in oils

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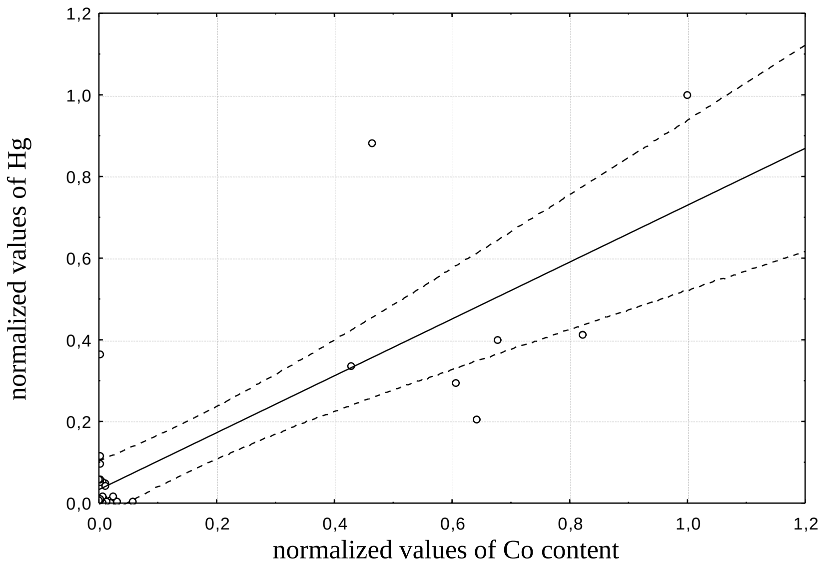


Fig. 20. Graph of the regression equation between mercury content and cobalt in oils

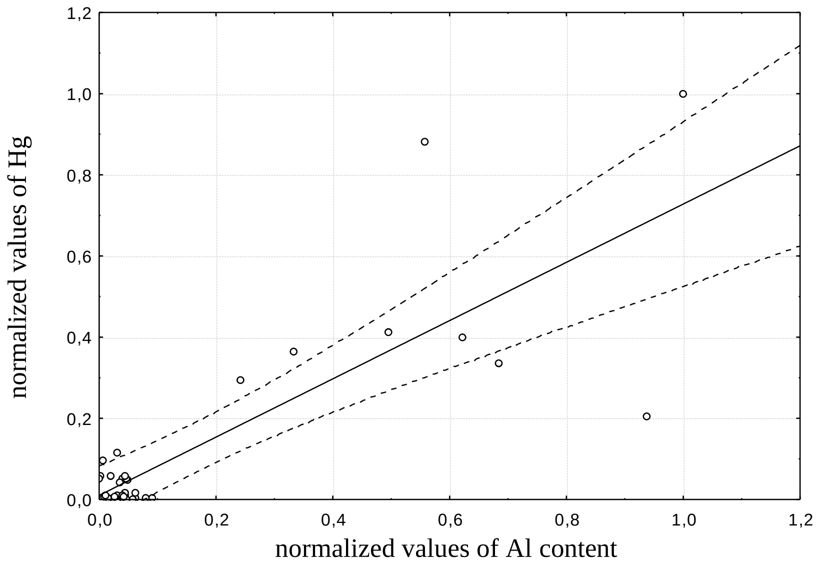


Fig. 21. Graph of the regression equation between mercury content and aluminum in oils

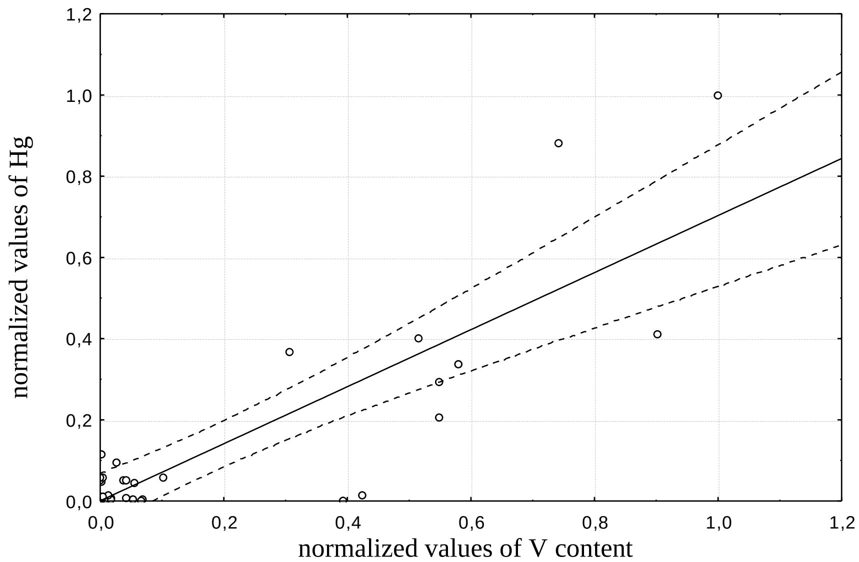
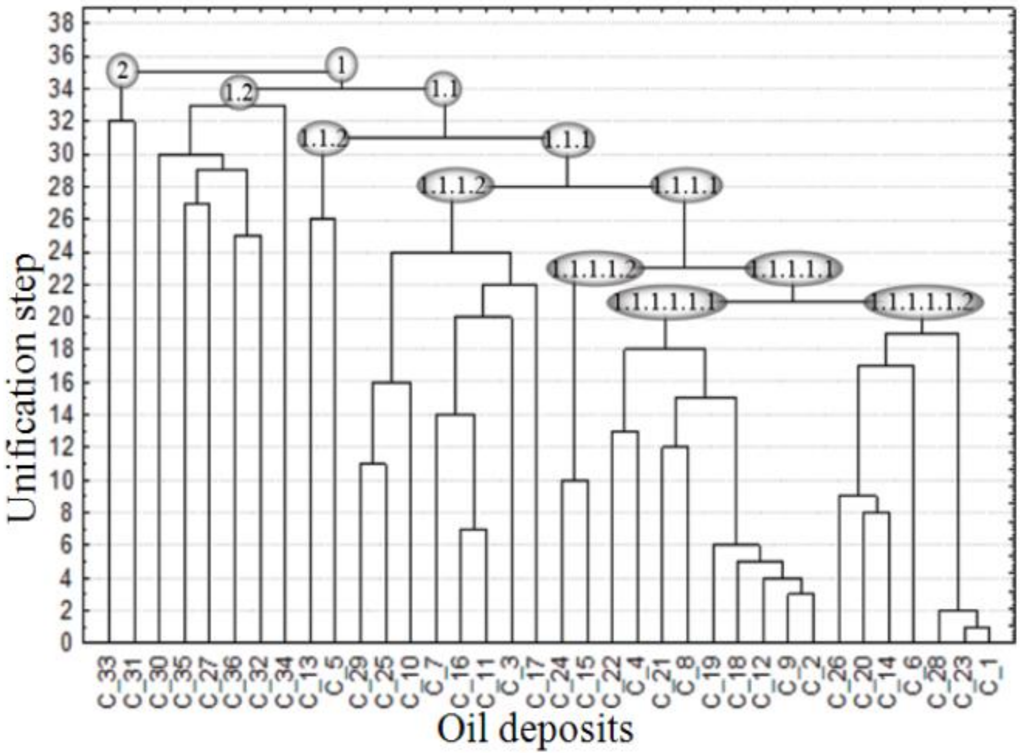


Fig. 22. Graph of the regression equation between mercury content and vanadium in oils

Based on the applying of the method of weighted centroid cluster analysis, as the most optimal for the development of the classification of oil deposits of the Dnipro-Donetsk depth according to the content of metals, the authors of the work constructed a dendrogram (Fig. 23), which reflects the mutual natural hierarchy of the analyzed deposits by mercury concentration.



Legend:
1, 2, 1.1, 1.2, 2.1, 2.2, 2.3 – clusters; a list of deposits: C_1 – Bakhmachske, C_2 – Prylukske, C_3 – Krasnozayarske, C_4 – Kachalivske, C_5 – Kremenivske, C_6 – Karaykozivske, C_7 – Korobochkynske, C_8 – Kulychykhinske, C_9 – Lipovodolynske, C_10 – Monastyryshchenske, C_11 – Matlakhivske, C_12 – Malosorochynske, C_13 – Novo-Mykolayivske, C_14 – Perekopivske, C_15 – Prokopenkivske, C_16 – Radchenkovske, C_17 – Raspashnivske, C_18 – Sofiivske, C_19 – Sukhodolivske, C_20 – Solontsivske, C_21 – Solokhivske, C_22 – Talalaivske, C_23 – Trostyanetske, C_24 – Turutynske, C_25 – Zakhidno-Kharkivtsivske, C_26 – Shchurynske, C_27 - Yuryivske, C_28 – Yaroshivske, C_29 – Khukhryanske, C_30 – Sagaidatske №1, C_31 - Sagaidatske №13, C_32 - Kybytsivske №5, C_33 – Kybytsivske №51, C_34 – Kybytsivske №52, C_35 – Kybytsivske №56, C_36 – Kybytsivske №1

Fig. 23. Dendrogram of the results of clustering by the weighted centroid method of deposits by mercury content in oils

The analysis of the dendrogram of the clustering of deposits by mercury content allows to visually distinguish seven groups of clusters: 1.1.1.1.1.1, 1.1.1.1.1.2, 1.1.1.1.2, 1.1.1.2, 1.1.2, 1.2 and 2.

Cluster 1.1.1.1.1.1 is formed by the Talalaivske, Kachalivske, Solokhivske, Kulychykhinske, Prylukske, Lipovodolynske, Malosorochynske, Sofiivske and Sukhodolivske deposits with abnormally low values of mercury content in oils from 0.0007 ppm (Talalaivske deposit) to 0.01 ppm (Sukhodolivske, Sofiivske, Malosorochynske, Lipovodolynske and Prylukske deposits), with an average content of 0.007 per cluster.

Low values of content from 0.02 ppm (Bakhmachske deposit) to 0.035 ppm (Shchurynske deposit) in oils are associated with the Bakhmachske, Trostyanetske, Yaroshivske, Perekopivske, Solontsivske, Shchurynske and Karaykozivske deposits of cluster 1.1.1.1.1.2, with an average content of this element per cluster 0.026 ppm.

Cluster 1.1.1.1.2 consists of Prokopenkivske and Turutynske deposits with mercury content below the average - 0.05 ppm.

Cluster 1.1.1.2 is represented by the Raspashnivske, Krasnozayarske, Matlakhivske, Radchenkovske, Korobochkynske, Monastyryshchenske, Zakhidno-Kharkivtsivske, and Khukhryanske deposits with mercury contents in oils from 0.14 ppm (Raspashnivske deposit) to 0.2 (Zakhidno-Kharkivtsivske and Khukhryanske deposits). with the average value of the content for the cluster – 0.18 ppm.

Cluster 1.1.2 is represented by the Kremenivske and Novo-Mykolayivske deposits with the corresponding mercury contents in the oils of 0.323 ppm - 0.39 ppm, with average concentrations for the cluster above the average for the general sample of deposits - 0.36 ppm.

Cluster 1.2 is formed by the Kybytsivske №52, Sagaidatske №1, Kybytsivske №56, Yuryivske, Kybytsivske №5 and Kybytsivske №1 fields, in which the mercury content in the oils ranges from 0.7 ppm (Kybytsivske field №52) to 1.4 ppm (Kybytsivske deposit №1) and the overall high average content for the cluster – 1.14 ppm.

Two fields Sagaidatske №13 and Kybytsivske №51 with abnormally high mercury content in oils, from 3.0 ppm to 3.4 ppm, respectively, form cluster 2 with an average value of 3.2 ppm.

According to the results of the cluster analysis, the sample mean values of mercury concentrations that differ significantly between individual deposits or groups of deposits in established ranges can be interpreted in the terminology of qualitative assessment as: abnormally low; low; below average; average; above average; tall; abnormally high. The implementation of this approach, in turn, makes it possible to propose a natural classification of the deposits of the Dnipro-Donetsk depth according to the content of vanadium, which is shown in Table 2. Noteworthy is the absence of geological differences between the fields that could explain the variability of mercury content in oils.

Table 2. Natural classification of oil deposits of the Dnipro-Donetsk depth by mercury content

No.	Mercury content (qualitative assessment of content; content from/to in ppm; average content in ppm)	Name of the deposit
1	abnormally low values; 0.0007/0.01; 0.0074	Talalaivske, Kachalivske, Solokhivske, Kulychykhinske, Prylukske, Lipovodolynske, Malosorochynske, Sofiivske, Sukhodolivske
2	low values; 0.02/0.035; 0.026	Bakhmachske, Trostyanetske, Yaroshivske, Perekopivske, Solontsivske, Shchurynske, Karaykozivske
3	values below average; 0.05/0.05; 0.05	Prokopenkivske, Turutynske
4	average value; 0.144/0.2; 0.177	Raspashnovske, Krasnozayarske, Matlakhivske, Radchenkovske, Korobochkynske, Monastyryshchenske, Zakhidno-Kharkivtsivske, Khukhryanske
5	the value is higher than average; 0.323/0.39; 0.356	Kremenivske, Novo-Mykolayivske
6	high value; 0.7/1.4; 0.141	Kybytsivske №52, Sagaidatske №1, Kybytsivske №56, Yuryivske, Kybytsivske №5
7	abnormally high values; 3.0/3.40; 3.20	Sagaidatske №13, Kybytsivske №51

The given classification will make it possible to establish the priority for the development of oil fields with the aim of further realization of Hg as an accompanying raw material, as well as the opportunity to determine the environmental risks of using these oils as raw materials for the production of petroleum products and, first of all, gasoline and diesel fuel.

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4. Conclusions

The mercury content in oil samples from 36 deposits of the most significant oil and gas province of Ukraine - the Dnipro-Donetsk depth, has significant variations (the difference in significant average concentrations in samples from the analyzed deposits is more than three orders of magnitude) with an average value of 0.437±0.133 ppm. Considering the importance of mercury concentration for fundamental scientific developments in the field of oil origin, the obtained results may indirectly indicate the implementation of several genetic models of its formation in this region.

Despite the significant variability of the close correlation of mercury content with other geochemical and geological-technological parameters, their statistically significant nature must be taken into account. This, in turn, allows us to single out from all the parameters considered in the work a group genetically and/or paragenetically related to the accumulation of mercury in oil (concentrations of vanadium, aluminum, cobalt, chromium, sulfur, manganese, zinc; the total content of metals V, Zn, Cr, Mn, Co, Fe, Hg, Al; density and viscosity of oil; initial boiling point of oil; content of resin and paraffins. By paragenetic connection between individual geochemical and geological-technological parameters of oil, the authors understand the connection that arises as a result of their simultaneous or sequential formation as a result of a single process of oil formation. By genetic connection we mean a relationship that is cause-and-effect in nature.

The established very weak correlation between the content of mercury and resins and paraffins, on the one hand, and a close relationship with the content of sulfur in the oils of the considered deposits, on the other hand, indicates the leading role as the main mercury concentrators of lower molecular weight sulfur-containing components of the petroleum system (for example, thiophyll sulfides, thioethers and dithioethers) in deposits of the region. And the presence of fairly significant concentrations of mercury in the oils of the Dnipro-Donetsk depth deposits indicates the realization of its entry into the complex oil system from abiogenic sources.

According to the results of the cluster analysis, the sample mean values of mercury concentrations that differ significantly between individual deposits or groups of deposits in established ranges can be interpreted in the terminology of qualitative assessment as: abnormally low; low; below average; average; above average; tall; abnormally high. The implementation of such an approach, in turn, makes it possible to propose a natural classification of deposits of the Dnipro-Donetsk basin by mercury content.

On the basis of the conducted research, the first natural classification of deposits of the Eastern oil and gas region of Ukraine was developed according to the content of Hg from the content of chemical elements and substances, the total content of metals and the mining and geological conditions of the occurrence of oil deposits and the physical properties of oil, which allows to establish the priority for the development of an oil deposit for the purpose of further implementation of Hg as a related raw material, as well as the possibility to determine the environmental risks of using these oils as raw materials for the production of petroleum products and, first of all, gasoline and diesel fuel.

Scientific novelty. In the results of the conducted studies and their analysis, it is indicated that Hg enters the complex oil system from abiogenic sources. This allows us to assert the possible hybrid origin of the oils in the deposits of the Dnieper-Donets depth. The dependences of changes in the concentration of Hg in oil depending on other chemical elements (Ni, Fe, Zn, Mn, S, Cr, Co, Al, V), substances (asphaltenes, paraffins, resin) and the total content of metals were established. The regularities reflecting the change in Hg content from the mining and geological conditions of oil deposits and the physical properties of oil have been established.

Practical meaning. Based on the results of clustering using the weighted centroid method, the first natural classification of deposits of the Eastern oil and gas region of Ukraine was developed according to the content of Hg from the content of chemical elements and substances, the total content of metals and mining and geological conditions of the occurrence of oil deposits and physical properties of oil. This makes it possible to establish priority for the development of an oil field for the purpose of further realization of Hg, as an accompanying raw material, as well as the opportunity to determine the environmental risks of using these oils as raw materials for the production of petroleum products and, first of all, gasoline and diesel fuel.

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