

## GERMANIUM INTERRELATIONSHIP WITH ASH AND "TOXIC" ELEMENTS IN COAL ON THE EXAMPLE OF SEAM C<sub>4</sub> OF THE "SAMARSKA" MINE FIELD OF WESTERN DONBAS

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**Abstract.** The character and level of statistical relationship between the content of germanium and "toxic elements" in coal seam c<sub>4</sub> of the "Samarska" mine and the main features of their distribution were established for the assessment of possible environmental risks during the selective processing of coal enriched with this element. It is proven that the correlation between germanium and all "toxic" elements is inverse and very weak. The existence of genetically different forms of germanium and arsenic, fluorine, mercury and beryllium was revealed.

The research materials included analysis of 129 coal samples for the content of germanium, beryllium, fluorine, mercury and arsenic, performed in accredited state laboratories after 1981. The content of germanium, beryllium and fluorine was determined by quantitative emission spectral analysis, mercury and arsenic - by atomic absorption analysis. Samples were taken during the work of production enterprises and research organizations with the participation of the authors, using the furrow method of sampling in mine workings and from the core of wells from 1981 to 2018. For primary processing of geochemical data, STATISTICA 13.3 and IBM SPSS Statistics 22 programs were used to calculate basic statistical characteristics, including mean, standard error of the mean, median, kurtosis, mode, standard deviation, variance, minimum and maximum values, coefficient of variation, and sample skewness. To achieve the objectives of the study, correlation and regression analyzes were carried out using the functions available in Micromine - the leading professional mining and geological information system for 3D modeling, statistical data processing and mining planning.

The presence of genetically different forms of germanium and arsenic, fluorine, mercury and beryllium in coal seam c<sub>4</sub> of the Samarska mine was revealed. The polymodality of the distributions was established for all the considered components, while the displacement of the density of their distribution to the left was proved, except for germanium and beryllium. It was proven that the correlation between germanium and content of ash and all "toxic" elements (except beryllium) is inverse and very weak.

**Keywords:** germanium, coal seam, mine field, toxic elements, regression analysis, frequency histograms, correlation analysis.

### 1. Introduction

The importance of studying germanium (Ge) in coal seams is due to its potential for industrial use and importance as a strategic raw material. In particular, coal is the main source of germanium in many countries, including Ukraine, China, Uzbekistan, Canada, and the USA [1]. This is also emphasized by the strategic importance of germanium-containing ores for the sustainable development and defense capabilities of countries, as it is indicated in the decisions of the National Security and Defense Council of Ukraine dated July 16, 2021 and the Decree of the President of Ukraine No. 306/2021 "On stimulation of exploration, mining and beneficiation of minerals that are of strategic importance for the sustainable development and defense capability of the state".

According to forecasts by the US Geological Survey, global demand for germanium is expected to grow to 320-400 tons annually by 2030, with a possible increase in production almost one and a half times. The price of germanium single crystals can reach 10–15 thousand dollars per kilogram. At the same time, about 100

tons of germanium are lost annually during coal mining in Donbas, which is approximately 60% of the total global annual production of this metal.

**Analysis of previous studies.** Previous studies of the microelement composition of coal in Donbas focused on the analysis of the distribution of trace elements, thought to be "toxic" and "potentially toxic", in the coal seams of the region [2]. A methodology was developed for the classification of coal deposits [3] and oil fields of the Dnipro-Donetsk basin according to the content of various trace elements [4–5]. Other studies were focused on the analysis of the distribution of germanium in individual coal seams of the Pavlohrad-Petropavlivka area [6–8]. According to the regulatory documents of the State Commission of Mineral Resources of Ukraine, the "potentially toxic elements" in coal include Co, Mn, Ni, Pb, Cr, V, and the "toxic elements" - As, Be, Hg, F.

This study focuses on identifying the statistical relationship between the concentrations of germanium and toxic elements in the coal seam c<sub>4</sub> of the Samarska mine, as well as on the analysis of the key features of their distribution. This is the first comprehensive study of this coal seam using geochemical, statistical, informational and analytical methods.

**The purpose of the research.** The main purpose of the publication is to determine the character of the distribution and the level of statistical relationship between the contents of germanium and toxic elements and ash content in coal seam c<sub>4</sub> of the Samarska mine, as well as to assess possible environmental risks during the selective processing of coal enriched with this element.

## 2. Methods

The research materials and methods included analysis of 129 coal samples of germanium, beryllium, fluorine, mercury and arsenic carried out in accredited state laboratories after 1981. The samples were taken during the work of production enterprises and research organizations with the participation of the authors, using the furrow method of sampling in mine workings and from the core of wells from 1981 to 2018. Prior to mining, power measurements and other visual examinations of coal seams and rock layers were conducted to select the most representative areas. Quality control of analyzes included checking 7% of all samples. The quantitative determination of germanium was carried out using the method of spectral emission analysis, and the accuracy and reproducibility of the results were evaluated according to the Student and Fisher criteria, the accepted level of systematic and random error was recognized as insignificant, which proved the satisfactory quality of the corresponding analyses.

For primary processing of geochemical data, STATISTICA 13.3 and IBM SPSS Statistics 22 programs were used to calculate basic statistical characteristics, including mean, standard error of the mean, median, kurtosis, mode, standard deviation, variance, minimum and maximum values, coefficient of variation, and sample skewness. Frequency histograms were created for visual assessment of the studied parameters, as well as the characteristics of their distribution were determined. At the same time, the number of groups (intervals) was determined

according to the well-known Sturges formula. To achieve the objectives of the study, correlation and regression analyzes were performed using the functions available in Micromine - a leading professional mining and geological information system for 3D modeling, statistical data processing and mining planning (license MM5123).

### 3. Results and discussion

Research results and their discussion. First of all, the conducted studies indicate significant variability of concentrations of germanium and other toxic elements in coal seam c<sub>4</sub> of the Samarska mine.

Thus, the germanium concentration varies from 1.3 g/t to 23.5 g/t, with an average value of  $7.09 \pm 0.33$  g/t, the median value is 6.2 g/t, the modal value is 6.7 g/t, the standard deviation is 3.7, the variance of the sample is 13.69, its asymmetry and kurtosis are equal to 1.73 and 4.08, respectively.

At the sampling sites, the content of Fe varies from 0.23 g/t to 4.2 g/t, the average value is  $2.24 \pm 0.08$  g/t, the median is 2.18 g/t, the mode is 1.62 g/t, standard deviation 0.94, variance 0.88, kurtosis -0.82, asymmetry 0.18.

The concentration of F ranges from 59.27 g/t to 253.66 g/t, with an average value of  $100.39 \pm 2.01$  g/t, median and mode values coincide and are equal to 100.4 g/t, standard deviation is 22.84, variance 521.68, kurtosis 15.06, asymmetry 2.55.

The content of Hg in the coal of layer c<sub>4</sub> varies from 0 g/t to 1.48 g/t, the average value is  $0.24 \pm 0.02$  g/t, the median is 0.22 g/t, the mode is 0.01 g/t, standard deviation 0.21, variance 0.044, kurtosis 9.74, skewness 2.3.

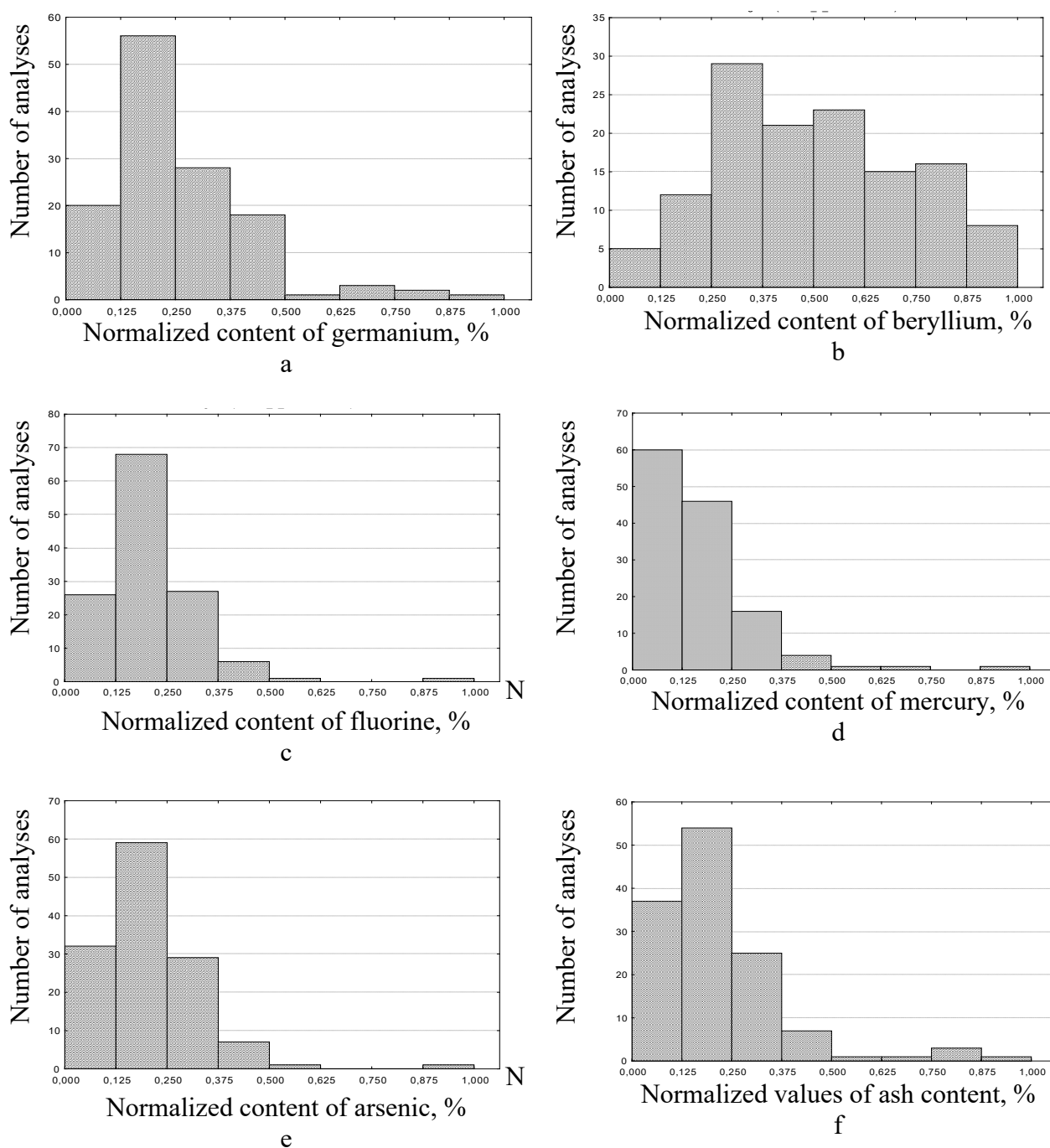
The concentration of As within the mine plastic varies from 18.5 g/t to 78.34 g/t, the average value is  $30.70 \pm 0.64$  g/t, the median is 29.79 g/t, the mode is 26.25 g/t, standard deviation 18.83, variance 354.44, kurtosis 0.1, skewness 0.86.

The ash content of the coal seam varies from 1.06% (on the site with a simple structure) to 31.5% (it was recorded on the site with a two-patch structure), the average value corresponds to  $7.53 \pm 0.43\%$ , the median is 6.7%, standard deviation 4.94, variance 24.4, kurtosis 7.21, skewness 2.3, mode 5%.

The obtained results testify to the diversity of levels of concentrations of the investigated elements in mine seam, which is important for the assessment of environmental risks and the planning of appropriate measures for the processing and processing of coal.

An important aspect of the research is visualization of the distribution of concentrations of germanium and toxic elements, for which frequency histograms were constructed (Fig. 1).

Analysis of constructed histograms revealed that all samples do not correspond to lognormal or Gaussian distribution laws. All samples are characterized by polymodal distribution, and on most histograms the core of the distribution density is shifted to the left, except for beryllium. The drawer diagram with whiskers in (Fig. 2) clearly illustrates these shifts. Analytical calculations, which were performed using the Lilliefors, Kolmogorov-Smirnov, Pearson (chi-square) and Shapiro-Wilk tests, confirmed these findings.



a – Ge, b – Be, c – F, d – Hg, e – As, f – total sulfur

Figure 1 – Cumulative histograms of normalized content values

The obtained results indicate that for a more accurate assessment of the central tendency in the distribution of concentrations of germanium and toxic elements, it is better to use median values, rather than arithmetic means, as was previously believed. According to the authors, the polymodality of the distributions of the studied parameters indicates the presence of several different mechanisms of accumulation and possibly different forms of finding these elements. It is most likely that the forms of their occurrence, which are responsible for the minimum contents, were jointly accumulated at the syngenetic stage of formation of the seam.

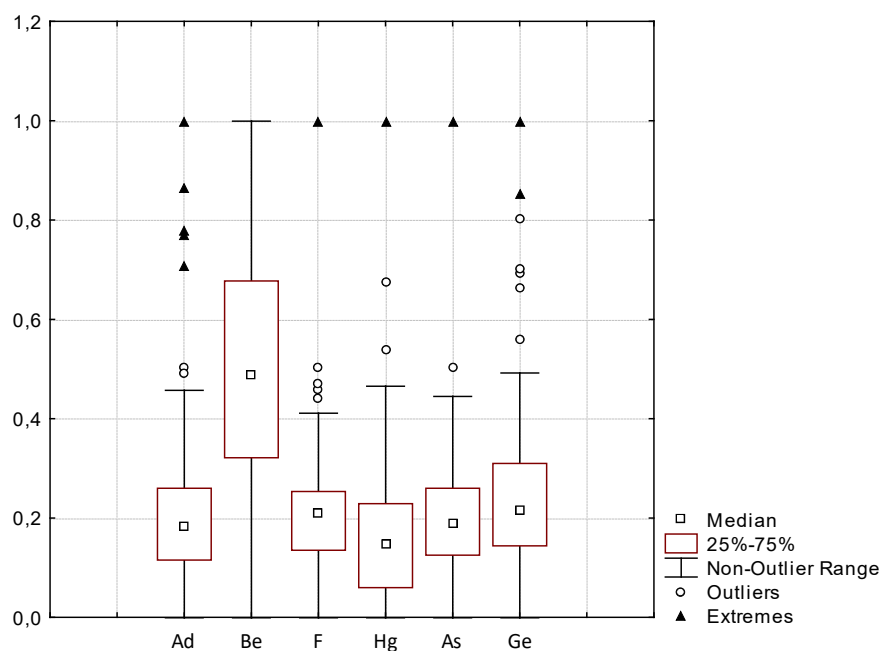


Figure 2 – Box diagram with whiskers of the density distribution of ash, mercury, arsenic, beryllium, fluorine, and germanium

According to the Chedok scale, the relationship between Ge concentrations and Be content in the considered coal seam, according to the results of correlation (Pearson's linear correlation coefficient 0.06) and regression analyzes is direct and very weak. According to Fisher's exact test calculations, this correlation coefficient is not significant. Despite this, taking into account the peculiarities of the analyzed samples, the authors believe it possible to consider such connections as a manifestation of a general trend in the multidimensional, polygenic and multi-scale system of geochemical evolution of the object under study. Fig. 3a shows the graph of the result of the regression analysis of modeling the linear relationship between Ge content values and Be concentrations. The regression equation of this model is:  $Ge = 0,2332 + 0,0469 \cdot Be$ .

In the considered coal seam, taking into account the data of correlation (Pearson's linear correlation coefficient 0.21) and regression analyses, the relationship between Ge and Hg concentrations according to the Chedok scale is direct and very weak. Fig. 3b shows the graph of the result of the regression analysis of modeling the linear relationship between Ge concentration and Hg content. The regression equation for this model is:  $Ge = 0,2166 + 0,251 \cdot Hg$ .

The relationship between Ge concentration and F content on the Chedok scale in view of the results of correlation (linear correlation coefficient 0.19) and regression analyzes is also direct and very weak. Fig. 3c shows the graph of the result of the regression analysis of the modeling of the linear relationship between the content of Ge and the concentration of F. For this model, the regression equation is:  $Ge = 0,1982 + 0,2775 \cdot F$ .

The established relationship between Ge content and As concentrations in the c<sub>4</sub> coal seam of the Samarska mine, according to the results of analyzes on the Chedok scale, taking into account the data of correlation (Pearson's correlation coefficient 0.25) and regression analyses, is direct and very weak. Fig. 3d shows the graph of regression analysis of the linear relationship between Ge concentration and As content. The regression equation of this model is:  $Ge = 0,1842 + 0,3567 \cdot As$ .

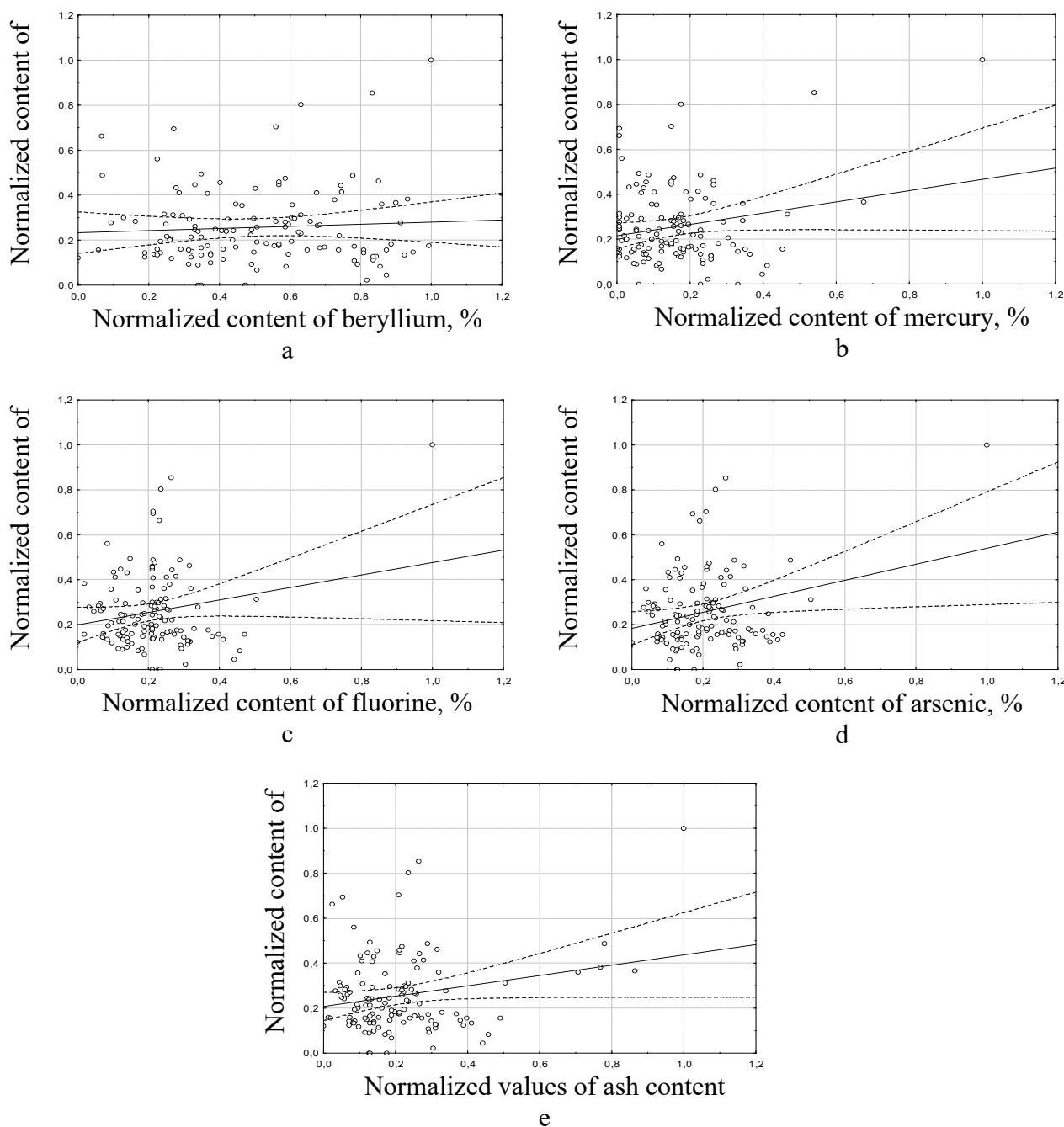


Figure 3 – The result of the regression analysis of modeling the linear relationship between germanium concentrations and contents of  
a – beryllium, b – mercury, c – fluorine, d – arsenic, and e – ash

According to the Chedok scale, the relationship between Ge concentrations and ash content in the c<sub>4</sub> coal seam, according to the results of correlation (Pearson's linear correlation coefficient 0.22) and regression analyzes is also direct and very weak. Fig. 3d shows the graph of the result of the regression analysis of modeling the linear relationship between the values of the Ge content and this indicator. The regression equation for this model is:  $Ge = 0,2082 + 0,2293 \cdot Ad$ .

A detailed analysis of the forms of both germanium and toxic elements in coal from various deposits of the world, carried out using the methods of coal chemistry and coal petrography [9-30], showed that germanium can be contained in coal in the following forms: isomorphic impurities in the mineral composition of coal (for example, in sulfides and silicates), in the form of organogermanium compounds (including those associated with humic and fulvic acids in the form of simple humates and fulvates and in the form of complex humates or chelates), as well as in a physically sorbed form on mineral and organic components of coal.

A similar analysis was carried out for "toxic" elements in coal [29–31]. Ge, As, F, Hg and Be were found to have some forms of occurrence of elements, such as mineral phases in which these elements are found as isomorphous impurities or as major components, and in physically sorbed form on mineral and/or organic parts. These common and different forms of accumulation form integral relationships which determine the characteristics of the distribution of these elements in the c<sub>4</sub> coal seam in the Samarska mine field, and are also reflected in the results of correlation analyses.

#### 4. Conclusions

The conducted studies allow us to formulate the following main conclusions:

1. The various probable forms of the considered impurity elements occurrence in coal, which were realized in the specific geological conditions of layer c<sub>4</sub> of the Samarska mine, allow us to consider the regularities revealed with the help of regression and correlation analysis as a kind of trend of dependencies between them.
2. A general feature of the distribution of ash content, germanium, arsenic, fluorine, mercury, and beryllium in the c<sub>4</sub> coal seam of the Samarska mine field is their non-compliance with normal and lognormal laws and the polymodality of the distributions with a shift of the density nuclei to the left, except for beryllium.
3. Each of the investigated elements in layer c<sub>4</sub> of the Samarska mine was accumulated in several forms, which differed significantly in their genesis. At the same time, the forms, which are responsible for the minimum contents, were jointly accumulated at the initial, syngenetic stage.
4. The existence of a direct and very weak correlation between germanium concentrations and content of ash, arsenic, fluorine, beryllium and mercury in the c<sub>4</sub> coal seam of the Samarska mine was established.

**The main scientific novelty** is that: 1) the existence of genetically different forms of germanium and arsenic, fluorine, mercury and beryllium was discovered in the coal seam c<sub>4</sub> of the Samarska mine; 2) the polymodality of the distributions was established for all the considered components, while the shift of the density of their

distribution to the left was proved, except for beryllium; 3) it was proven that the correlation between germanium and ash content and all "toxic" elements is direct and very weak.

**The main practical value** of the performed research is the substantiation of the method of the most accurate assessment of the central tendency in the distribution of a sample population of concentrations of germanium and arsenic, fluorine, mercury and beryllium in the  $c_4$  coal seam of the Samarska mine. The presence of a very weak correlation between the content of germanium and "toxic" elements makes it possible to predict the minimal nature of possible environmental risks during the selective processing of germanium-enriched coal.

*Notes:  $c_4$  – The fourth coal seam of the lower coal pack (Lower Carboniferous).*

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#### ЗВ'ЯЗОК ГЕРМАНІЮ ІЗ ЗОЛЬНІСТЮ ТА «ТОКСИЧНИМИ» ЕЛЕМЕНТАМИ У ВУГІЛЛІ НА ПРИКЛАДІ ПЛАСТА С4 ПОЛЯ ШАХТИ «САМАРСЬКА» ЗАХІДНОГО ДОНБАСУ

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**Анотація.** Встановлено характер та рівень статистичного зв'язку між вмістом германію і «токсичних елементів» у вугільному пласті с<sub>4</sub> шахти «Самарська» та основними особливостями їх розподілу для оцінки можливих екологічних ризиків при селективній переробці вугілля збагаченого цим елементом. Доведено, що кореляційний зв'язок германію з усіма «токсичними» елементами є зворотним та дуже слабким. Виявлено існування генетично різних форм знаходження германію та арсену, фтору, меркурію і берилію.

Матеріали дослідження включали аналіз 129 проб вугілля на вміст германію, берилію, фтору, ртуті та арсену, виконаних в акредитованих державних лабораторіях після 1981 року. Вміст германію, берилію і фтору визначався кількісним емісійним спектральним аналізом, меркурію і арсену – атомно-абсорбційним аналізом. Проби відбиралися в процесі роботи виробничих підприємств та науково-дослідних організацій за участю авторів, з використанням борознового методу відбору проб у шахтних виробках та з керну свердловин з 1981 по 2018 рік.

Для первинної обробки геохімічних даних використовувалися програми STATISTICA 13.3 та IBM SPSS Statistics 22 для розрахунку основних статистичних характеристик, у тому числі середнього, стандартної помилки середнього, медіани, ексцесу, моди, стандартного відхилення, дисперсії, мінімальних та максимальних значень, коефіцієнту варіації та асиметрії вибірки. Для досягнення цілей дослідження були проведені кореляційний та регресійний аналізи за допомогою функцій, доступних у Micromine - провідної професійної гірничо-геологічної інформаційної системи для 3D-моделювання, статистичної обробки даних та планування гірничих робіт.

Виявлено існування у вугільному пласті  $c_4$  шахти «Самарська» генетично різних форм знаходження германію та арсену, фтору, ртуті і берилію. Встановлено для всіх розглянутих компонентів полімодальність розподілів, при цьому доведено зміщення щільності їх розподілу вліво, крім германію та берилію. Доведено, що кореляційний зв'язок германію з зольністю та усіма «токсичними» елементами (крім берилію) є зворотним та дуже слабким.

**Ключові слова:** германій, вугільний пласт, поле шахти, токсичні елементи, регресійний аналіз, кореляційний аналіз, частотні гістограми.