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Abstract

Full Text

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ON THE CHEMICAL CHARACTERIZATION OF ORGANIC GERMANIUM COMPOUNDS IN COALS

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At present, most researchers adhere to the view that a considerable portion of the rare and dispersed elements in coals—in particular germanium—is bound in them by an organic bond. However, the type of bond and the character of the organometallic compounds present in coals have still been little studied. It was shown earlier that the principal binding link for germanium in coals is humic acids (1); later, stable compounds of germanium with humic acids of peats were obtained (2).

The complex-forming properties of germanium with many organic addends are widely known, and some of them find extensive application in the analytical chemistry of germanium (3). Among the organic compounds that bind germanium into stable complex compounds, there are known, along with phenylfluorone, diphenols, dioxynaphthalenes, oxyanthracenes, and similar compounds, distinguished by a ring structure and the presence of phenolic groups. This character of the organic addends of germanium may serve as indirect evidence of the possible presence, in the macromolecule of the organic matter of coal or of humic acids, of complex compounds of germanium, since in composition and structure the addends mentioned may be regarded as structural elements of the organic mass of coal.

Table 1

Distribution of germanium in the products obtained in the extraction of humic acids

Name of humic acids	Germanium content in micrograms	Germanium content in micrograms	Germanium content in micrograms	Germanium content in micrograms
	in humic acids	in filtrate	in wash waters	total
Natural	786	32.5	none	818.5
Regenerated	30440	161.8	40.9	30642.7
Total	31226	194.3	40.9	31461.2

Name of humic acids	Germanium content in micrograms	Germanium content in micrograms	Germanium content in micrograms	Germanium content in micrograms
In percent	99.2	0.6	0.2	100.0

For the investigation, vitrain varieties of brown coal were selected, from which fractions with a specific gravity of less than 1.4 were separated. From the samples obtained, natural humic acids were quantitatively extracted with a 1% sodium hydroxide solution, after which the alkaline treatment was continued in the presence of hydrogen peroxide, as a result of which regenerated humic acids were extracted. Table 1 presents data on the distribution of germanium in the products obtained.

The data of Table 1 show that about 98% of the germanium passed into solution with the regenerated humic acids. A comparative characterization of the two types of acids obtained is given in Table 2.

As is seen from the data of Table 2, the essential differences between the types of humic acids consist in an increase in phenolic oxygen and organic sulfur compounds in the regenerated acids. Since the latter compounds are extracted by alkali and, consequently, have an acidic character, they may be assigned the structure SH, characteristic of organic sulfides or mercaptans.

To determine the molecular weight of the germanium-organic compound present in the regenerated humic acids, 0.7 g of them was dissolved in 1% alkali, and to the resulting solution of humates there was added 0.06 g of germanium in the form of dioxide, after which the humic acids were isolated by the addition of sulfuric acid, filtered off, and washed with water.

Table 2

Elemental composition and content of acidic functional groups

Name of acids	C	H	N	O	S_{org}, %	COOH + OH	COOH	OH
Natural	62.7	6.1	0.4	30.6	0.08	10.7	6.3	4.4
Regenerated	54.5	5.8	0.4	37.4	1.94	15.1	6.9	8.2

The experiment was carried out with humic acids obtained at the "moment of their formation," since it had previously been shown that finished humic acids have a small surface area and are not very active with respect to germanium in its solutions (4). The distribution of germanium in the products of the experiment proved to be as follows: the amount that entered into reaction was 57250 μg;

the amount in the filtrate and wash waters was 1550 μg. The concentration of germanium in its organic compound in the humic acids was

$$\frac{0.05725 \cdot 100}{0.7} = 8.2 \text{ wt. \%.}$$

If, subsequently, one proceeds from the analogy between the properties of the organic compounds of germanium in humic acids and in germanium phenylfluoronate, i.e., assumes that one germanium atom is bound to two molecules of the organic residue (5), then it is possible to calculate the molecular weight of the organogermanium compound characteristic of humic acids. It will be equal to

$$\frac{72 \cdot 100}{8.2} = 878,$$

of which 72 units are accounted for by germanium and approximately 800 units by the organic residue.

We give a comparison of the molecular weights and germanium content in phenylfluoronate and in its organic compound in humic acids:

Germanium compounds	Phenylfluoronate	Organic compound in humic acids
Mol. wt.	710	878
Germanium content, %	10.2	8.2

These data show a satisfactory closeness of the compounds in their principal indices.

Deciphering the organic residue, carried out from the data of the elemental composition and molecular weight, gave the following gross formula: $C_{36}H_{47}O_{20}S$, which, taking into account the content of functional groups, is transformed into $C_{30}H_{33}(COOH)_6(OH)_8S$.

Additional deciphering according to the degree of aromatization, performed on the basis of the C/H ratio, made it possible to obtain the following formula: $C_{12}H_{23}$ (paraff.) $C_{18}H_{10}$ (arom.) $(COOH)_6(OH)_8S$.

This compound corresponds to a doubled radical in the organogermanium compound; therefore, each of the radicals must contain 6 carbon atoms in compounds of paraffinic structure and 9 carbon atoms of aromatic structure. One sulfur atom is accounted for by the total organic residue, in connection with which the organogermanium compound may schematically be represented in the following form: $(R—Ge—R)_2S$.

The results obtained make it possible to approach an understanding of the composition of organic compounds of germanium in fossil coals.

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REFERENCES CITED

1. S. A. Gordon, K. Yu. Volkov, M. A. Menkovsky, *Geochemistry*, No. 4, 385 (1958).
2. S. M. Manskaya, T. V. Drozdova et al., *Geochemistry*, No. 5, 433 (1961).
3. V. A. Nazarenko, *Methods for the Determination and Analysis of Rare Elements*, Publishing House of the Academy of Sciences of the USSR, 1961, p. 400.
4. S. A. Gordon, *Collection of Scientific Works of the Moscow Mining Institute*, No. 27, 1959, p. 47.
5. F. G. Zharovsky, A. P. Pilipenko, *Zav. lab.*, No. 10, 1192 (1958).

Note: Figure translations are in progress. See original paper for figures.

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