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THERMAL ANALYSIS OF BITUMENS FROM BLACK COAL, EXTRACTED SUCCESSIVELY WITH DIFFERENT SOLVENTS

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A successive extraction of bitumes from black coal was carried out using the following solvents: petroleum ether, petroleumether-benzene (1:1), benzene, benzene-ethyl ether (1:1), ethyl ether, ethyl ether ethanole (1:1), ethanol. These extract organic products as follows: 0.06, 0.16, 0.11, 0.21, 0.07, 0.29 and 0.70% respectively. The obtained by the above mentioned solvents chujniuds were compounds to the thermal and IR-spectral analysis.

The first experiments to apply thermal analysis for the study of bitumens extracted from solid fuels with organic solvents started in the sixties. Rustschev and Mihailov [1, 2] found that the separation of bitumens from lignite coal with ethanol-benzene results in a reduced exothermic effect at 400° in the DTA curve. Later, Rustschev and Atanassov [3] proved the disappearance of the exothermic effect at 375° after the separation of the bitumens from the peat. They also proved that the DTA curve of the extracted peat bitumens is characterized by several endothermic effects in the temperature range 380-450°. Zhukov *et al.* [4, 5] also used thermal analysis to study coal bitumens and their components (hydrocarbons, resins, etc.). Kichova, Minkova and Rustschev [6] performed the thermal analysis of peat bitumens ("A" and "C") and found typical exothermic effects at 480° and 540°, respectively. Malovska *et al.* [7] observed differences in the DTA and especially the TG curves of the oil–like and solid bitumens (accordingly soluble and insoluble in petroleum ether) from Dobrudja black coal (layer n_2, formation "*N*"). On heating to 200°, the solid bitumen loses only 7.2% of its mass, whereas the oil–like bitumen loses 29.5%. This suggests that high–molecular compounds with high melting and boiling temperatures predominate in the composition of the solid bitumen.

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The aim of this paper* was to conduct thermal analysis of the products extracted from Dobrudja carbon coal through selective extraction with solvents having different polarities. The studies were carried out with the same sample from the same layer (layer n_2, formation "N") [7], with the following parameters: ash (A^d) – 8.2%, yield of volatile compounds (V^{daf}) – 39.1%, total sulphur (S_t^d) – 0.92%, swell index 1, yield of bitumens extracted with ethanol : benzene (1:4) – 1.60%, plastic layer after Sapozhnikov – 8 mm, and code number according to the Geneva classification – 611. The experiments were carried out with the following solvents and mixtures (in a 1 : 1 ratio) of solvents:

petroleum ether → petroleum ether + benzene → benzene → benzene + ethyl ether → ethyl ether → ethyl ether + ethanol → ethanol.

Table 1 shows the yields of the extracted bitumens in these selective extractions. They reveal that the smallest amounts relate to the substances soluble in petroleum and ethyl ether (0.06 and 0.07, respectively), with the highest percentages for bitumens extracted with ethanol (0.70%) and with ethyl ether + ethanol (0.29%).

Table 1 Effects of solvents on bitumen yield

No.	Solvent	Bitumen yield, %
1	Petroleum ether	0.06
2	Petroleum ether + benzene	0.16
3	Benzene	0.11
4	Benzene + ethyl ether	0.21
5	Ethyl ether	0.07
6	Ethyl ether + ethanol	0.29
7	Ethanol	0.70
	Total	1.60

The total yield of the bitumens obtained through a single extraction only with ethanol + benzene (1 : 4) was 1.60%, whereas the successive application of the above-mentioned solvents and mixtures resulted in a total of 1.58% bitumens.

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Infrared spectral analysis of the substances extracted through successive use of the solvents given in Table 1 showed the domination of long-chain hydrocarbons and esters in the petroleum ether extract. The spectrum of the substances extracted with a mixture of petroleum ether and benzene exhibited absorbance bands characteristic of compounds containing carbonyl and carboxyl groups. The different character of the spectra of the bitumens extracted from the black coal after its successive extraction with solvents

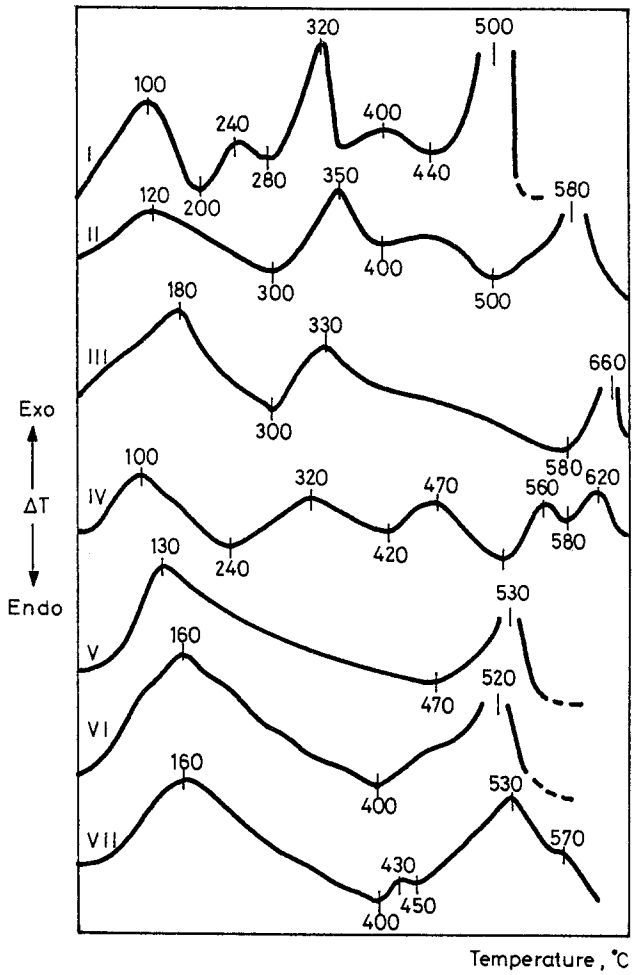

Fig. 1 DTA-curves of bitumens extracted using different solvents: petroleum ether →petroleum ether + benzene →benzene → benzene + ethyl ether → ethyl ether → ethyl ether + ethanol → ethanol

having different polarities demonstrated that they are complex, polycomponent mixtures.

The selectively soluble bitumens were subjected to DTA and TG, using the Hungarian apparatus MOM, model OD 102, under the following conditions: sample, about 100 mg; inert substance, Al_2O_3; heating rate, 5 deg/min; final temperature, 800°; in air. Figure 1 shows the DTA curves obtained in this analysis, which differ considerably, though they have some common effects, i.e. the marked endothermic effect with a maximum in the temperature range 100-160° and the enormous final exothermic effect at 500 to 660°, which is probably connected with the ignition of vapour and gaseous products released during the thermal destruction of the bitumens. The DTA curves of the products extracted with petroleum ether and benzene are similar (Fig. 1, curves I and II). The endothermic effects registered at 200, 240, 280 and 300° result from the evaporation of the low-molecular hydrocarbons, whereas the effects at 400, 440, 450, 470, 500 and 520° are connected with pyrolysis of the high-molecular compounds which are not volatile up to these temperatures.

The bitumens extracted with benzene (Fig. 1, curve III) give only two endothermic effects (at 300 and 580°), whereas those extracted with benzene + ethyl ether (Fig. 1, curve IV) exhibit four clearly manifested endothermic maxima (at 240, 420, 520 and 580°). The DTA curves of the extracts with ethyl ether, ethyl ether + ethanol and ethanol are almost identical (Fig. 1, curves V, VI and VII). They possess a characteristic endothermic effect with a maximum in the temperature interval 400-470° which is typical of the destructive pyrolytic processes.

Table 2 gives the results of the loss in mass when the bitumens studied are heated to different temperatures. The loss in mass is calculated from the TG curves of these bitumens. The experimental data obtained clearly show that the bitumens extracted from Dobrudja black coal, using solvents with different polarities, differ substantially in their fraction compositions. Thus, for example, the quantity of the substances evaporated below 200° varies from 5.8% for the bitumens extracted with petroleum ether to 32.0% for those extracted with a mixture of benzene + ethyl ether. The first three types of bitumens (Table 2, nos 1-3) yield a very small coke residue below 800° (0.5 to 1.8%), whereas for the remaining four bitumens this residue varies from 4.7 to 8.0%. These experimental thermal analysis results confirm the large differences in the chemical compositions of the bitumens studied, which was also demonstrated by their infrared spectra.

Table 2 Quantity of volatile and pyrolytic products

Final temperature °C	Loss in mass, %, and type of bitumens						
	1	2	3	4	5	6	7
100	1.0	6.2	2.0	14.5	1.4	12.4	17.3
200	5.8	24.9	10.8	32.0	12.9	20.4	25.5
300	38.6	47.3	30.4	41.2	35.8	37.2	40.4
400	70.5	64.7	49.1	58.2	46.4	45.1	55.2
500	90.7	79.6	70.7	72.7	63.6	72.6	80.7
600	98.4	87.1	98.2	93.7	84.2	92.0	92.3
700	99.4	90.4	98.2	95.3	92.1	92.0	93.9
800	99.4	99.5	98.2	95.3	92.1	92.0	93.9

Conclusions

1. Black coal samples from the Dobrudja basin were extracted successively with the following solvents and mixtures of solvents having different polarities:

petroleum ether → petroleum ether + benzene → benzene → benzene + ethyl ether → ethyl ether → ethyl ether + ethanol → ethanol.

2. The highest amounts of substances were found to be extracted by ethanol (0.70%) and the mixture of ethanol + ethyl ether (0.29%), the lowest amount of bitumens being extracted with petroleum and ethyl ether (0.06 and 0.07%, respectively). DTA, TG and IR spectral analysis were used to prove the essential differences in the chemical compositions of the bitumens extracted from the black coal samples by successive application of different solvents and mixtures of solvents having different polarities.

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Zusammenfassung – Mittels folgender Lösungsmittel wurde eine sukzessive Extraktion von Bitumen aus Steinkohle durchgeführt: Petrolether, Petrolether-Benzol (1:1), Benzol, Benzol-Ethylether (1:1), Ethylether, Ethylether-Ethanol (1:1), Ethanol. In dieser Reihenfolge konnten organi- sche Produkte zu 0.06, 0.16, 0.11, 0.21, 0.07, 0.29 bzw. 0.70 % extrahiert werden. Die durch aufgeführte Lösungsmittel erhaltenen Verbindungen wurden einer Thermo- und einer IR-Analyse unterzogen.