BULLETIN DE L'ACADÉMIE
POLONAISE DES SCIENCES
Série des sciences chimiques
Volume XI, No. 4, 1963

ORGANIC CHEMISTRY

Infrared Absorption Spectra of Organic Matter Extracted from Brown Coal Pretreated with Acids

by

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Presented by T. URBAŃSKI on February 8, 1963

As shown by Kuczyński and Andrzejak [1], the organic matter extracted from acid-treated coals differs remarkably in its composition from normal bitumen and resembles the original coal and the residue after its extraction. The proportion of hydrogen in the substance extracted from acid-treated coals (H — *c.* 6%) is lower than that in normal bitumen (H — *c.* 9%). The H/C atomic ratio in the matter extracted from the coals treated with acids is close to that of the crude coal and the residue after its extraction (Table).

In this work the differences in composition of bitumens and extracts from acid-treated coals were investigated by infrared spectroscopy.

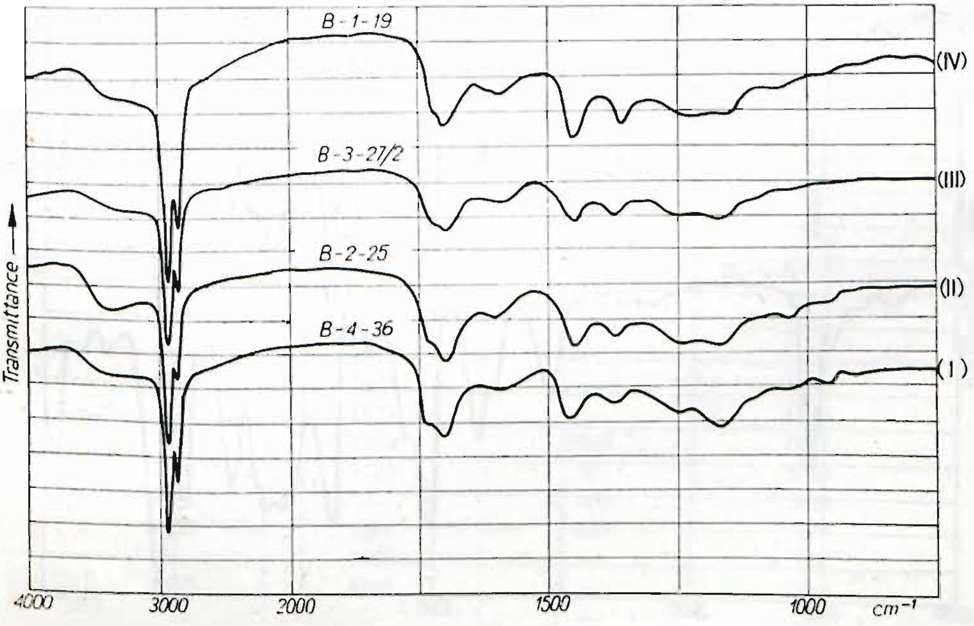

Fig. 1. Organic matter extracted from brown coals before demineralization

TABLE

H/C atomic ratios of the extracted matter and coals

Sample	H/C atomic ratio			
	matter extracted from coal		non-treated coal	residue after demineralization
	before demineralization	after demineralization		
B 1—19	1.47	1.12	1.01	0.96
B 2—25	1.52	1.03	0.91	0.90
B 3—27/2	1.52	1.10	0.96	1.00
B 4—36	1.35	1.02	1.08	0.98

Experimental

The following substances were examined:

Series 1 Bitumens from crude coals:	Spectrum	Series 2 Bitumens from coals demineralized with acids	Spectrum
B 1—19 (Konin)	IV	B 1—19 (Konin)	VIII
B 2—25 (Smogóry)	III	B 2—25 (Smogóry)	V
B 3—27/2 (Lubań)	II	B 3—27/2 (Lubań)	VI
B 4—36 (Turów)	I	B 4—36 (Turów)	VII

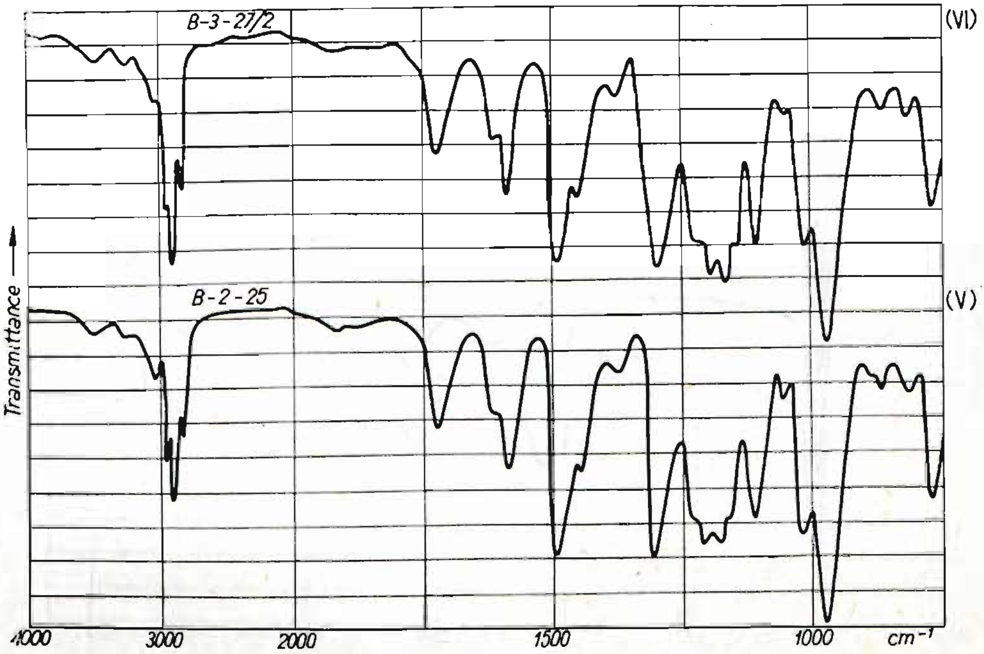

Fig. 2. Organic matter extracted from brown coals after demineralization

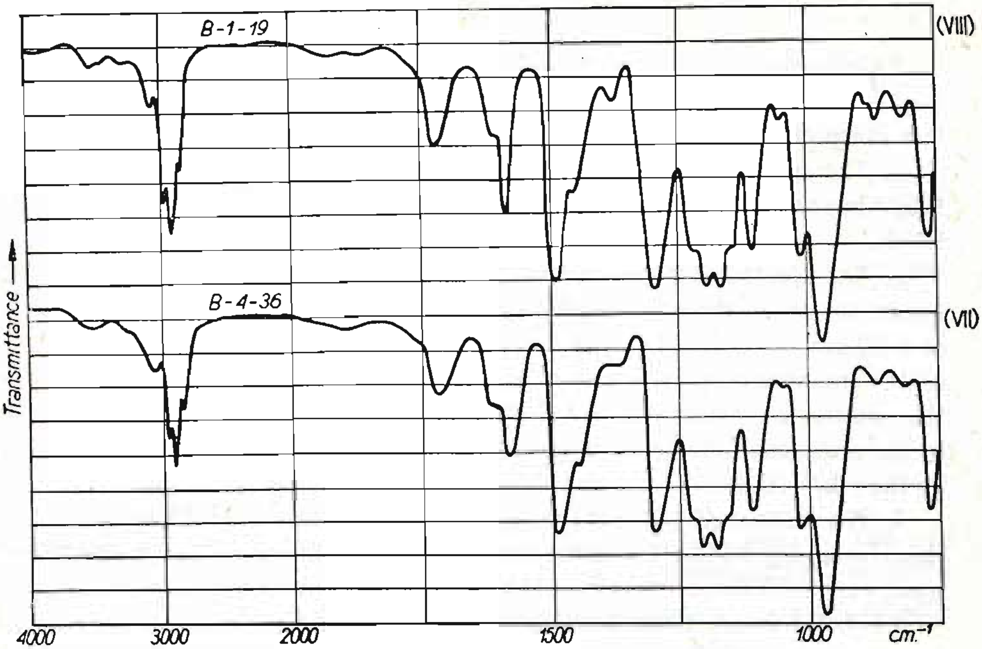

Fig. 3. Organic matter extracted from brown coals after demineralization

The bitumens were extracted from coals with a 70:30 benzene—ethanol mixture.

The infra-red spectra were measured with a Hilger double-beam recording spectrometer with rocksalt prism in the range of 4000—750 cm.$^{-1}$ as solid films deposited on rocksalt plates by evaporation of the solvent.

The spectra are nearly the same within each series apart from small differences in their intensities.

The band frequencies (in cm.$^{-1}$) are given below:

Series 1. (before demineralization)	Series 2. (after demineralization)	Series 1. (before demineralization)	Series 2. (after demineralization)
c. 3400	c. 3500	1380	1380
—	c. 3300	—	1295
—	3060	1250	1225
—	2960	—	1195
2925	2925	1165	1165
2855	2855	—	1150
—	1925	—	1110
—	1870	1040	1065
1720	1720	—	1010
1700	—	960	960
1600	1590	905	905
—	1490	—	865
1455	1455	—	815
		—	765

The spectra are presented in Figs. 1—3.

Discussion

Examination of the spectra leads to the following conclusions:

1. The spectra of bitumens are nearly the same within each series, but there is a sharp difference between the two series.

2. The spectra of series 2 (after demineralization) contain most of the bands found in spectra of series 1 (before demineralization) in addition to much stronger bands.

3. The spectra of bitumens from non-treated coals (Series 1) closely resemble typical spectra of the original coals [2] with the exception of the rather strong band at 1700 cm.$^{-1}$ (assigned to the C=0 group) which is very weak in the spectra of coals. The spectra suggest a prevailing aliphatic character of the bitumens from the non-treated coals, with a rather low proportion of aromatic rings, indicated by the presence of the bands at 1600 cm.$^{-1}$ and 960—905 cm.$^{-1}$. It is also indicated by the relatively high H/C ratio (*c.* 1.5).

4. The spectra of the bitumens from the demineralized coals (Series 2) are much richer in strong bands. The most important differences with respect to the former spectra are as follows:

4.1 There is one more band in the range of the OH and NH stretching frequencies (3500—3200 cm.$^{-1}$).

4.2 Besides the bands assigned to aliphatic CH_3 groups (2925 and 2855 cm.$^{-1}$), there is a band at 2960 cm.$^{-1}$ assigned to a methyl stretching mode.

4.3 Strong absorption bands due to skeletal aromatic vibrations (1590 and 1490 cm.$^{-1}$) relpace the weak band at about 1600 cm.$^{-1}$ The aromatic stretching C—H vibrations are clearly revealed by the presence of rather strong bands at 3060 cm.$^{-1}$. There is also a very strong band at 960 cm.$^{-1}$, characteristic of aromatic deformation C—H modes. All these changes suggest a rather high proportion of low-condensed aromatic rings in the bitumens from demineralized coals.

4.4 The stretching C=0 band (1720 cm.$^{-1}$) in the spectra of bitumens from demineralized coals is but little stronger than that for bitumens from non-treated coals (as related to comparable intensities of aliphatic C—H stretching bands at about 2900 cm.$^{-1}$).

4.5 A few strong bands appear in the range of 1300—759 cm.$^{-1}$: 1295, 1195, 1010, 960, 765 cm^{-1}. The bands at 960 and 765 cm.$^{-1}$ may be assigned to aromatic C—H deformation modes, the rest to various vibrations like the C—0 stretching mode, and skeletal ring vibrations.

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