CHROM. 8823

CHARACTERIZATION OF BITUMENS BY PYROLYSIS GAS CHROMATO-GRAPHY

ZDRAVKO RAMLJAK

Civil Engineering Institute of Croatia, Zagreb (Yugoslavia)

ĐURĐA DEUR-ŠIFTAR

INA-Petroleum Industry Zagreb, Research and Development Department, Zagreb (Yugoslavia)

and

ALEKSANDAR ŠOLC

Civil Engineering Institute of Croatia, Zagreb (Yugoslavia)

(Received August 29th, 1975)

SUMMARY

A method for bitumen analysis by pyrolysis gas chromatography is described. The characteristic ratio of light unsaturated and saturated hydrocarbons in bitumen pyrolyzate was used for the determination of the maltene and asphaltene fractions in bitumens. Bitumens of various types and origins were investigated.

INTRODUCTION

Pyrolysis gas chromatography (GC) is a successful technique for the characterization of complex materials such as polymers, and has also proved to be effective in the characterization of bitumens. Publications on investigations of bitumens by pyrolysis GC imply that it can possibly be used also for the elucidation of bitumen structures and for the identification of different bitumen types[1–6], but the procedures described did not result in an analytical method for the quantitative determination of bitumen composition. The main reasons for this lack of success are the complex compositions of numerous non-volatile compounds in bitumens and the similarity of structures and amounts of the various components in different types of bitumens.

The purpose of this work was to investigate the influence of the differences in structure of the average asphaltene and maltene molecules on their degradation products and to develop a pyrolysis GC method for the determination of these constituents in bitumens. The light fraction of pyrolyzate was analyzed qualitatively and quantitatively in order to establish the characteristic behaviour in the degradation processes of asphaltenes and maltenes.

EXPERIMENTAL

Apparatus and operating conditions

The pyrolysis was carried out in a furnace-type micro-reactor[7]. A short pre-cut column was situated between the pyrolyzer and analytical column so as to prevent the heavy fragments from entering the column. The analysis of the light fraction of pyrolyzate was performed under the following conditions. Pre-cut column: glass, 5 cm × 3 mm I.D., 10% di-2-ethylhexyl sebacate on Chromosorb P, 30–60 mesh. Analytical column: glass, 2 m × 4 mm I.D., 5% Carbowax 20M on alumina pre-treated with 50% sodium hydroxide in methanol[8,9]. Carrier gas: nitrogen at a flow-rate of 40 ml/min. Temperature programme: 2-min isothermal period at 25° then programmed to 200° at 10°/min. Chromatograph: Perkin-Elmer M-800 with a flame ionization detector.

Samples

The bitumen samples investigated, classified according to their penetration data, and the origins of the related naphthas, were as follows:

IA: Iraq B-200 (9.0% asphaltenes);
IB: Iraq B-80 (11.7% asphaltenes);
IC: Iraq B-65 (14.0% asphaltenes);
IIA: Iran B-200 (7.6% asphaltenes);
IIB: Iran B-80 (9.5% asphaltenes);
IIC: Iran B-65 (11.5% asphaltenes);
IID: Iran B-45 (16.5% asphaltenes);
IIIA: Vacuum residue "Velebit" N.S. (6.3% asphaltenes);
IIIB: Vacuum residue "Velebit" Z. (1.7% asphaltenes);
IIIC: Vacuum residue "Kelebija" (4.7% asphaltenes);
IVA: Bitumen of unknown origin (23.7% asphaltenes);
IVB: Bitumen of unknown origin (27.6% asphaltenes);
VA, VB and VC: Asphaltene fractions of bitumens IA, IID and IIIC;
VIA, VIB and VIC: Maltene fractions of bitumens IA, IID and IIIC.

The samples of asphaltene and maltene fractions of bitumens were prepared by the I.P. method based on the precipitation of asphaltenes with *n*-heptane[10].

RESULTS

The GC separation of individual light hydrocarbons under the conditions used permitted a reliable interpretation of bitumen pyrograms for both qualitative and quantitative purposes (Fig. 1).

The influence of the differences in the structures of maltenes and asphaltenes on the composition of the light pyrolyzate was investigated at various pyrolysis temperatures. In addition to the increase in the total amount of the light degradation products with increasing pyrolysis temperature, the composition of the pyrolyzate changed characteristically with the samples of bitumen fractions pyrolyzed. Table I shows the relationship between the particular light saturated and unsaturated hydrocarbons found in the pyrolysis products of maltenes and asphaltenes prepared from bitumen sample IA for pyrolysis temperatures in the range 400–700°. The results given are the averages of six peak area (*P*) measurements.
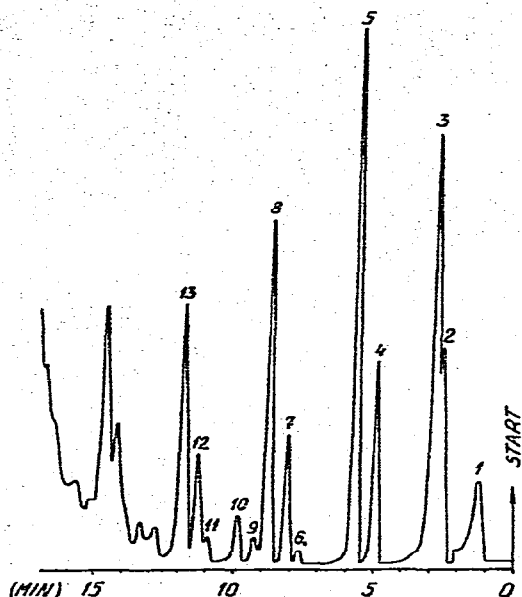
Fig. 1. Typical pyrogram of bitumen. Pyrolysis temperature 500°. Peaks: 1, methane; 2, ethane; 3, ethene; 4, propane; 5, propene; 6, isobutane; 7, n-butane; 8, butene-1, isobutene, *trans*-butene-2; 9, *cis*-butene-2; 10, butadiene; 11, neopentane; 12, isopentane; 13, n-pentane, pentene-1, pentene-2, 2-methylpentene-1, 2-methylpentene-2.

TABLE I

THE RELATIONSHIP OF THE PEAK AREA (P) OF UNSATURATED AND SATURATED HYDROCARBONS IN PYROLYZATE OF ASPHALTENES (A) AND MALTENES (M) AT DIFFERENT TEMPERATURES

Pyrolysis temperature (°C)	$P_{\overline{c3}}/P_{c3}$		$P_{\Sigma\overline{c4}}/P_{nc4}$		$P_{\Sigma\overline{c5}}/P_{ic5}$		$\dfrac{P_{\overline{c3}} + P_{\Sigma\overline{c4}} + P_{\Sigma\overline{c5}}}{P_{c3} + P_{cc4} + P_{ic5}}$	
	A	M	A	M	A	M	A	M
400	1.01	1.27	1.17	1.66	1.13	1.35	1.11	1.39
500	1.28	2.03	1.68	2.37	1.59	2.24	1.49	2.19
550	1.81	3.41	2.06	3.80	1.88	3.41	1.90	3.52
600	3.29	8.77	4.34	14.12	3.19	7.97	3.63	10.24
650	5.66	10.13	7.22	40.07	11.78	42.80	6.41	14.61
670	7.15	13.67	12.35	48.33	9.62	102.50	7.92	20.47

All of the relationships considered differ strongly in the asphaltene and maltene fractions, particularly at higher pyrolysis temperatures. The greatest differences for the bitumen fractions investigated were found in the ratio of pentenes to isopentane content in the pyrolyzate.

However, the best repeatability of the results was established where the sum of the peak areas of unsaturated C_3–C_5 hydrocarbons was related to the sum of the peak areas of saturated C_3–C_5 hydrocarbons; this ratio is denoted by $I_{u/s}$. The graph of $I_{u/s}$ against pyrolysis temperature (Fig. 2) shows the increase in the difference between the $I_{u/s}$ values for maltenes and asphaltenes with increasing temperature.
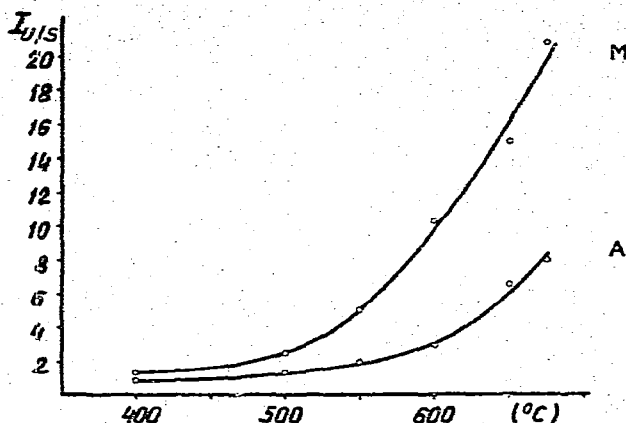
Fig. 2. $I_{u/s}$ *versus* pyrolysis temperatrue for asphaltene (A) and maltene (M) fractions of bitumen.

The experimental results for $I_{u/s}$ *versus* pyrolysis temperature can be expressed by the following equation:

$$Y = \frac{X}{K + LX}$$

where for asphaltenes $K = 942.588$ and $L = -1.282$ and for maltenes $K = 553.096$ and $L = -0.786$.

The characteristic ratio of light unsaturated and saturated hydrocarbons in bitumen pyrolyzate were used for the determination of the asphaltene and maltene contents in bitumen samples. The pyrolysis temperature was 560°, which was high enough to obtain distinctive $I_{u/s}$ values for each fraction determined in bitumen, but not too high to affect the repeatability of the results. Using a sample size of 0.5–1.0 mg, the repeatability under the above conditions was $\sigma_{rel} = \pm 0.12$. The asphaltene and maltene fractions prepared from bitumens of various sources and types were investigated in order to prove the influence of origin on the pyrolysis products (Table II). The $I_{u/s}$ values are the means of six measurements.

A plot of $I_{u/s}$ *versus* asphaltenes content, obtained by analysis of bitumens of known composition (IA, IB, IC, IIIC, IIIA, IVA and maltene fraction of bitumen IA) was used as a calibration graph (Fig. 3).

TABLE II

$I_{u,s}$ VALUES FOR ASPHALTENES AND MALTENES OF BITUMENS OF DIFFERENT ORIGINS

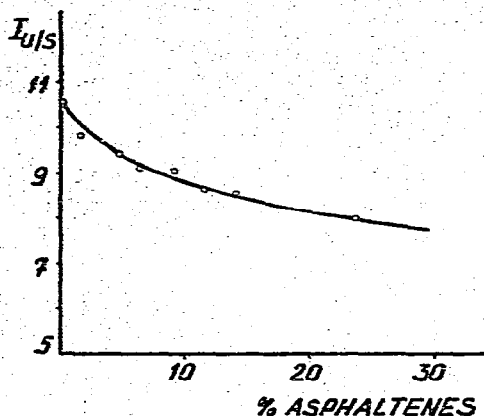| Bitumen sample	Asphaltenes* (%)	Pyrolysis GC	
		$I_{u/s}$	Asphaltenes (%)
II A	7.6	9.05	7.8
II B	9.5	8.75	10.6
I B	11.5	8.64	12.4
II D	16.5	8.29	16.8
V B	27.3	7.78	29.2

* I.P. method[10].

Fig. 3. Relationship between $I_{u/s}$ and asphaltene content in bitumens. Pyrolysis temperature 560°.

Table III gives the results of the pyrolysis GC analysis of bitumen samples of known composition. The found asphaltene contents in investigated samples are in good agreement with the results obtained by the I.P. method[10].

TABLE III

RESULTS OF BITUMEN ANALYSES

Bitumen sample	$I_{u/s}$	
	Asphaltenes	Maltenes
Iraq B-200		
(I A)	2.36	10.64
Iran B-45		
(II D)	2.37	10.33
Vacuum residue		
"Kelebija"		
(III C)	2.45	10.69

DISCUSSION

The application of pyrolysis GC for analytical purposes requires very strict control of the pyrolysis conditions and the complete resolution of the degradation products. A reliable interpretation of pyrograms was achieved by meeting these requirements in the light fraction of bitumen pyrolyzate investigated. With the exception of n-pentane + pentenes, the saturated light hydrocarbons were completely resolved from the unsaturated hydrocarbons.

The relationship between all of the unsaturated and saturated pyrolytic fragments studied shows a characteristic behaviour of structurally different bitumen fractions. Maltenes, which possess more paraffinic structures compared with the polyaromatic structures of asphaltenes, show higher values of the ratio of unsaturated to saturated light hydrocarbons in pyrolyzate. These differences increase with increasing chain length of the pyrolytic fragments and with increasing pyrolysis temperature. Consequently, at the highest applied temperature of 670°, the propene to n-propane

ratio for maltenes is twice, the butenes to n-butane ratio four times and the pentenes to isopentane ratio more than ten times that for asphaltenes (Table I).

However, with high values of these ratios, the small alkane peaks result in a lower accuracy in the peak area measurements and a much reduced repeatability of results. For this reason, the advantage of having the greatest differences in the characteristic peak area ratios between maltenes and asphaltenes was not realized, and the most convenient condition that gave the required repeatability was the sum of C_3–C_5 unsaturated hydrocarbons against the sum of C_3–C_5 saturated hydrocarbons in the pyrolyzate ($I_{u/s}$) at a pyrolysis temperature of 560°.

The relationship established between structurally different fractions of bitumen and their pyrolyzate compositions is valid for fractions prepared from bitumens of various types and origins (Table II). It is obvious that the parts of the maltene and asphaltene molecules which, under the conditions of thermal degradation applied, produce light fragments appear to have the same or very similar structures regardless of the origin of the bitumen. Taking this fact into account, it is possible to characterize bitumens with a high degree of reliability on the basis of the established $I_{u/s}$ values. The achieved repeatability of results ($\sigma_{rel} = \pm 0.12$) permits the determination of asphaltenes in bitumens with an accuracy in asphaltene content of $\pm 1\%$. These values refer to asphaltene contents up to 30%, which represents the usual levels found in bitumens.

The results obtained by pyrolysis GC for the asphaltene content of bitumens (Table III) probably give a more accurate picture of the actual asphaltene contents than the I.P. method, as the results obtained by the latter include errors due to a variation of 20% in reproducibility.

The differences in the composition of saturated and unsaturated light hydrocarbons in maltene and asphaltene pyrolyzate indicate the distinct structure of the pyrolyzed samples. The very different values of the pentanes to isopentane ratio in maltenes and asphaltenes show the presence of much larger amounts of isopentane in asphaltenes. This result agrees with the observations of Karr et al.[1], who found a large amount of highly branched paraffins in the pyrolyzate of asphaltenes. However, the unresolved normal and branched olefins do not permit any conclusions to be drawn regarding the type and amount of branching in degraded aliphatic chains, as was shown by Brown[11]. On the basis of the light pyrolytic fragments, one can derive more conclusions regarding the bitumen constituent structures than has been done so far.

REFERENCES

1 C. Karr, J. R. Comberiati and W. C. Warner, Anal. Chem., 35 (1963) 1441.
2 S. G. Perry, J. Gas Chromatogr., 2 (1964) 54.
3 M. Ariet and H. E. Schweyer, Ind. Eng. Chem., Prod. Res. Develop., 4 (1965) 215.
4 J. Knotnerus, Ind. Eng. Chem., Prod. Res. Develop., 6 (1967) 43.
5 P. Leplat, J. Gas Chromatogr., 5 (1967) 128.
6 D. W. Poxon and R. G. Wright, J. Chromatogr., 61 (1971) 142.
7 Ð. Deur-Šiftar, T. Bistrički and T. Tandi, J. Chromatogr., 24 (1966) 404.
8 A. J. Kuley, Anal. Chem., 35 (1963) 1472.
9 Ð. Deur-Šiftar, Tehnika (Belgrade), 21 (1966) 1605.
10 Standard Methods for Testing Petroleum and its Products, Institute of Petroleum, London, 17th ed., 1958, p. 38.
11 R. A. Brown, Anal. Chem., 43 (1971) 900.