Notes

CHROM. 5502

The characterization of bitumens using pyrolysis gas chromatography

Bitumens are complex mixtures of high molecular weight compounds, often several thousands in number, of which only a few have been isolated and identified.

Conventional methods of analysis *e.g.* straight chromatography and IR examination do not always successfully characterise different samples because of the very small differences in composition and the extreme difficulty of coping with the separation of such complex mixtures[1,2].

Such differences as there are between one bitumen and another would seem to be in the proportions of the same, or very similar, compounds, rather than in the existence of different, characteristic, and easily identifiable components.

This difficulty has been partially overcome by the "Outline/Unit Area" chromatographic method of POXON AND ELLIS[3], but the method is tedious and time-consuming.

Pyrolysis gas chromatography has proved successful with other complex materials and it was decided to try to apply this method to bitumens.

Experimental

Two samples of Gilsonite, labelled S and BV, and five samples of Mexphalte, labelled as indicated in Tables I, II and III, were examined.

Saturated solutions of the bitumens in carbon tetrachloride were applied to the

TABLE I

t-TEST AT 610° TO EXAMINE THE DIFFERENCE OF RELATIVE AREAS FROM BITUMEN TO BITUMEN

Comparison of means of	*Confidence limit (%)*[a] *of peaks*										
	1	2	3	4	5	6	7	8	9	10	11
R75/30 and 10/20	95	98	[b]	[b]	[b]	99.9					
R75/30 and 400/500	[b]	[b]	[b]	[b]	[b]	[b]					
R75/30 and 190/210	99	98	[b]	[b]	[b]	[b]					
R75/30 and R 85/25	99	98	95	[b]	[b]	99					
10/20 and 400/500	98	99	[b]	98	99	99.9					
10/20 and 190/210	[b]	[b]	[b]	[b]	[b]	99					
10/20 and R85/25	[b]	[b]	99	[b]	[b]	99					
400/500 and 190/210	99	99	[b]	[b]	[b]	[b]					
400/500 and R85/25	99	99	99	98	[b]	99					
190/210 and R85/25	[b]	[b]	99	[b]	[b]	[b]					

[a] It is normal to work to a 95% confidence limit, *i.e.* there is only one chance in twenty that the two sets of results belong to the same sample.

[b] Signifies that the results lie outside the 95% confidence limit.

TABLE II

t-TEST AT 770° TO EXAMINE THE DIFFERENCE OF RELATIVE AREAS FROM BITUMEN TO BITUMEN

Comparison of means of	*Confidence limit (%)[a] of peaks*										
	1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10*	*11*
R75/30 and 10/20	95	95	[b]	[b]	[b]	95				[b]	[b]
R75/30 and 400/500	[b]	[b]	[b]	[b]	[b]	[b]				[b]	[b]
R75/30 and 190/210	[b]	[b]	[b]	[b]	[b]	98				98	[b]
R75/30 and R85/25	[b]	[b]	95	[b]	[b]	[b]				[b]	[b]
10/20 and 400/500	95	95	[b]	[b]	[b]	[b]				[b]	95
10/20 and 190/210	98	95	[b]	[b]	[b]	[b]				[b]	95
10/20 and R85/25	99	99	[b]	95	[b]	99				[b]	95
400/500 and 190/210	[b]	[b]	[b]	[b]	[b]	[b]				[b]	[b]
400/500 and R85/25	95	95	99	[b]	[b]	98				[b]	[b]
190/210 and R85/25	99	99	99	[b]	95	98				99.9	[b]

[a] It is normal to work to a 95% confidence limit, *i.e.* there is only one chance in twenty that the two sets of results belong to the same sample.

[b] Signifies that the results lie outside the 95% confidence limit.

TABLE III

t-TEST AT 980° TO EXAMINE THE DIFFERENCE OF RELATIVE AREAS FROM BITUMEN TO BITUMEN

Comparison of means of	*Confidence limit (%)[a] of peaks*										
	1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10*	*11*
R75/30 and 10/20	[b]	[b]		[b]	[b]	[b]				[b]	[b]
R75/30 and 400/500	[b]	[b]		[b]	99	99				[b]	[b]
R75/30 and 190/210	[b]	[b]		[b]	[b]	95				[b]	99
R75/30 and R85/25	[b]	[b]		[b]	[b]	[b]				[b]	[b]
10/20 and 400/500	[b]	[b]		[b]	99	99				[b]	[b]
10/20 and 190/210	[b]	95		[b]	[b]	98				95	[b]
10/20 and R85/25	[b]	[b]		[b]	[b]	[b]				[b]	[b]
400/500 and 190/210	98	[b]		[b]	[b]	[b]				[b]	[b]
400/500 and R85/25	[b]	[b]		[b]	99	[b]				[b]	[b]
190/210 and R85/25	95	[b]		[b]	[b]	[b]				[b]	[b]

[a] It is normal to work to a 95% confidence limit, *i.e.* there is only one chance in twenty that the two sets of results belong to the same sample.

[b] Signifies that the results lie outside the 95% confidence limit.

wire of a Phillips Curie Point Pyrolyzer, the excess solvent being removed by heating the wire in an oven at 100° for 1 h.

The volatile pyrolysis products were then analysed by means of a Pye Series 104 dual column instrument using a 10% Apiezon on Chromosorb P column. Carbowax and Silicone Gum Rubber columns were also tried, but gave inferior results.

The pyrolysis time found most suitable was 5 sec at temperatures of 610, 770 and 980°.

The instrument conditions were as follows: column temperature 53°; detector, F.I.D. (H_2 and air), temperature 65°; carrier gas, nitrogen (40 ml/min).

Four runs were made for each bitumen and the average area for corresponding peaks calculated. In the case of the Gilsonites the recorder trace showed characteristic

differences, but with the Mexphaltes no obvious differences were noticeable in most cases and the relative areas of various peaks were therefore taken.

In order to test whether these relative areas differed significantly from bitumen to bitumen the *t*-test was applied to the differences of the means, a computer being used to speed up the necessary arithmetic[4,5]. The results are shown in Tables I, II and and III.

Discussion

Inspection of Tables I and III shows that by comparing the relative areas of peaks 1, 3 and 6 at 610°, and peak 6 at 980° it is possible to distinguish between the five Mexphaltes to a 99 % confidence limit. Peak 1 (at 610°) distinguishes: R75/30 and 190/210; 400/500 and 190/210. Peak 3 (at 610°) distinguishes: 190/210 and R85/25. Peak 6 (at 610°) distinguishes: R75/30 and 10/20; R75/30 and R85/25; 10/20 and 400/500; 10/20 and 190/210; 10/20 and R85/25; 400/500 and R85/25. Peak 6 (at 980°) distinguishes: R75/30 and 400/500.

It would thus appear that it is not necessary to carry out pyrolysis at 770°, although this could be used to confirm the other results. It should also be noted that the pyrolysis runs for each sample and for each temperature were made over a period of several weeks, thus testing the reproducibility of the method over a fairly long period of time.

Conclusions

The method has proved its usefulness for the characterization of closely related bitumens. It is not, however, straightforward. The differences in the recorder traces are slight and without the use of a computer the task of comparing the means would be almost impossible.

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