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OF HEAVY OILS AND SYNTHETIC FUELS BY PYROLYSIS
THIN LAYER CHROMATOGRAPHY

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A RAPID METHOD FOR HYDROCARBON-TYPE ANALYSIS OF HEAVY
OILS AND SYNTHETIC FUELS BY PYROLYSIS THIN LAYER CHROMATOGRAPHY

by

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ABSTRACT

Hydrocarbon-type fractions (saturates, aromatics, polynuclear aromatics and polar compounds) from heavy crude oils and synthetic fuels were separated by thin layer chromatography (TLC) on chromarods using a Iatroscan TH-10 analyzer. The best results were obtained on a silica gel chromarod when n-hexane, 10% benzene in n-hexane and 5% ethyl acetate in benzene were used as developing solvent. A complete analysis of six samples takes 60 min and requires only 60 mg of sample. Separation was applied to pure hydrocarbon mixtures as well as hydrocarbon-type concentrates isolated from Athabasca bitumen by liquid chromatography. The method is applicable to middle distillates, b.p. 200-350°C, as well as to deasphalted fractions (malthenes) boiling higher than 350°C. Seven samples of malthenes (pentane-solubles) were analyzed by this method. Repeatability of the results was compared with that of the USBM-API procedure.

INTRODUCTION

Hydrocarbon group-type analysis has become a widely used technique in analytical laboratories for chemical characterization of feedstocks and products from petroleum industries (1-8). Processing and analysis of non-conventional fuels e.g., synthetic fuels from bitumens and coal derived liquids has created an even greater need for reliable analytical techniques.

Many of the class separations reported in the literature apply high performance liquid chromatography (HPLC) (1-7). This technique has been successfully used for the naphtha range (9-11). The major drawback to the HPLC methods is the strong retention of the polar material, particularly from the high boiling range distillate residues on the column.

A reliable chromatographic method for hydrocarbon-type analysis, based on gravimetric measurements, has been developed by the USBM-API Project 60 (8) and was modified in our laboratory (9). This method is time consuming (one day per analysis) and uses large volumes of solvents and adsorbing gels.

This work describes a rapid method for hydrocarbon-type analysis applying thin layer chromatography (TLC) to the pentane-soluble fraction (malthenes) of the petroleum and synthetic fuels boiling above 200°C.

The principal component types encountered in this paper are saturates (SA), aromatics (AR), (mono and di together) polynuclear aromatics (PNA) and polar material (PO). The method uses a Iatroscan TLC pyrolyzer which combines the resolution capabilities of TLC with the possibility of quantification by using a flame-ionization detector (FID). Comparison of the results with those obtained by the API-60 procedure is presented.

EXPERIMENTAL

INSTRUMENT AND OPERATING CONDITIONS

The Iatroscan TH-10 TLC Analyzer, Mark III (Iatron Labs., Tokyo, Japan; distributed by Technical Marketing Associates, Canada) used is equipped with a FID and an electronic stepping integrator. The FID was operated with a hydrogen flow-rate of 160 mL/min and an air flow-rate of 2L/min. The scanning speed was 0.36 cm/sec. A two-pen Molytek recorder Model 3300 was used at 50 mV full-scale deflection and chart speed of 0.21 cm/sec.

SOLVENTS

HPLC-grade n-hexane, benzene and ethyl acetate were used as developing solvents. The n-pentane, benzene, ethyl acetate and methanol used in the liquid chromatographic separations were "reagent" grade.

SAMPLES

1. Malthenes:

Ten samples (Nos. 1 to 10, Table 1 and 2) of bitumens, crude oils and synthetic fuels were distilled up to 200°C and deasphalted by precipitation with twenty volumes of pentane. The deasphalted oils (malthenes) were used in the hydrocarbon-type analysis.

2. Standard Hydrocarbons:

(a) The analytical procedure was tested on pure model hydrocarbon mixtures listed in Table 3. The mixtures were prepared by dissolving 15 mg of each individual hydrocarbon in 25 mL benzene.

(b) Hydrocarbon-type fractions used as standards were separated from Athabasca malthenes using a silica-alumina dual packed glass column and a series of solvents: n-pentane (saturates), 10% benzene in pentane (aromatics), 5% ethyl acetate in benzene (polynuclear aromatics) and methanol (polar compounds).

PROCEDURE

Preparation of Standard Solutions

1. Weigh accurately about 15 mg of each hydrocarbon-type fraction (saturates, aromatics, PNA and polars) into individual 2 mL volumetric flasks. Dissolve the two first fractions in n-hexane and the others in benzene.
2. Apply 1.0 μ L of each of the standard solutions on separate silica II chromarods.

Preparation of Sample Solutions

1. Weigh accurately about 60 mg of each of the malthene samples in a 2 mL volumetric flask. Dissolve the malthenes in benzene.
2. Apply 1.0 μ L of each sample solution on a separate chromarod.

Sample Analysis

1. Develop the rods in a TLC tank, equipped with a filter paper as a wick, using n-hexane as developing solvent.
2. Remove the rods from the tank when the solvent front has travelled 10 cm. Allow to dry for 5 minutes in an oven at 120°C.
3. Place the rods in the TLC pyrolyzer and set the screw/scan stop position at 6 cm so this length of the rods remain unburned. Pyrolyse the rods in the FID.
4. Remove the rods from the instrument and develop again in 10% benzene in n-hexane as developing solvent.
5. Remove the rods from the tank when solvent front has travelled 40 cm. Allow to dry 2 minutes at room temperature.
6. Develop the rods in a third solvent mixture of 5% ethyl acetate in benzene. Remove the rods from the tank when solvent front has travelled 2.5 cm. Allow to dry for 8 minutes in an oven at 120°C.
7. Place the rods in the pyrolyzer and set the screw/scan stop position so it permits scanning the whole rods (10 cm). Pyrolyse the rods in the FID.

Calculation

The hydrocarbon-type content is calculated by using the following equations:

$$\frac{W_{SA} \times A_{MSA}}{W_M \times A_{SA}} \times 100 = \text{saturates (wt \%)}$$

$$\frac{W_{AR} \times A_{MAR}}{W_M \times A_{AR}} \times 100 = \text{aromatics (wt \%)}$$

$$\frac{W_{PO} \times A_{MPO}}{W_M \times A_{PO}} \times 100 = \text{polars (wt \%)}$$

$$100 - (SA(\text{wt \%}) + AR(\text{wt \%}) + PO(\text{wt \%})) = \text{PNA}(\text{wt \%})$$

where,

W_{SA} , W_{AR} , W_{PO} = weight of the corresponding hydrocarbon fraction used as standard

- W_M = weight of the malthenes sample
- $A_{MSA}, A_{MAR}, A_{MPO}$ = area of the corresponding hydrocarbon peak in the malthenes samples
- A_{SA}, A_{AR}, A_{PO} = area of the corresponding hydrocarbon peak used as standard.

RESULTS AND DISCUSSION

MODEL COMPOUNDS AND STANDARD HYDROCARBON-TYPE FRACTIONS

The analytical procedure was tested on three mixtures representing different hydrocarbon-types. Thirty individual paraffins, mono-, di- and polynuclear aromatics were used, Table 3. The separation obtained for each hydrocarbon-types fractions is shown in Figure 1. The R_F values of the saturated, aromatic and PNA hydrocarbon mixtures were 0.63, 0.36-0.64 and 0.10 respectively.

Also hydrocarbon-type fractions were isolated from Athabasca malthenes and used as standards. The latter is more representative of the hydrocarbon-type mixtures present in the sample. The separation obtained for the various fractions is shown in Figure 2. The R_F value for polar compound fractions was zero.

SEPARATION OF HYDROCARBON-TYPE FROM MALTHENES

Separation of the malthenes into saturates, aromatics, PNA and polar compounds was accomplished by using different ratios of solvent mixtures. A system using three mobile phases described previously under "sample analysis" gave the best results. Separation on chromarods is limited to two types of sorbent-coated rods; silica gel and alumina. In order to obtain a baseline separation of the aromatics from the PNA, it was necessary to remove the saturates from the rods. This was accomplished by eluting the saturates with n-hexane. Scanning 4 cm of the rod was sufficient to pyrolyse all the saturates. The second elution system (10% benzene in n-hexane) permits the separation of aromatics from the PNA. The third elution system (5% ethyl acetate in benzene) separates PNA from the polar compounds.

Quantitative results were obtained by integrating the peak areas representing the hydrocarbon-types. The PNA content was obtained by difference. Direct quantification of this hydrocarbon-type was less reliable because of the susceptibility of their standard fraction to oxidation.

COMPARISON WITH THE API-USBM PROCEDURE

The weight per cent of saturated, aromatic, PNA hydrocarbons and polar material obtained for various bituminous, heavy oils and synthetic fuels by the TLC procedure is shown in Tables 1 and 2. A typical chromatogram for Lloydminster malthenes is shown in Figure 3. Comparison of the TLC results with those obtained by the API procedure, Tables 1 and 2, shows that the former give higher PNA and lower polar material contents. This difference could be explained by the incomplete recovery of PNA with benzene in the API procedure. When polar fractions, obtained from the API procedure, were submitted to TLC separations, they were found to contain PNA hydrocarbons. The use of 5% ethyl acetate in benzene allows for total elution of the PNA hydrocarbons, Figure 2. The weight per cent of the saturated and aromatic hydrocarbons are comparable for both methods.

REPEATABILITY AND PRECISION OF THE PROCEDURE

The repeatability of the method was determined using Athabasca malthenes (> 200°C), Table 4. Comparison of the standard deviation of the TLC method with that of the USBM-API procedure, Table 5, indicates the superiority of the TLC method. The relative precision (R) of the alternate method is given by the ratio of the standard deviation of the TLC procedure to that of the API-USBM procedure. The R values were 0.43, 0.59 and 1.25 for the saturated, aromatic and polyaromatic hydrocarbons respectively. The relative smaller precision of the PNA content is attributed to the indirect calculation by difference.

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Table 1 - Comparison of Hydrocarbon-Type Determination* In
Deasphalted Fractions (> 200°C) by TLC and
API-USEM Methods

Sample	Method	Hydrocarbon contents (wt %)			
		Saturates	Aromatics	PNA	Polar Material
1. <u>Athabasca</u>					
	TLC	25.0	23.3	37.3	14.4
	API	24.8	22.2	23.8	29.2
2. <u>Cold Lake</u>					
	TLC	26.8	27.8	33.6	11.8
	API	26.3	28.7	18.2	26.8
3. <u>Lloydminster</u>					
	TLC	26.8	27.4	33.5	12.3
	API	27.5	30.0	14.5	28.0
4. <u>Medicine River</u>					
	TLC	59.6	19.7	18.4	2.3
	API	57.5	23.7	8.6	10.1
5. <u>Boscan</u>					
	TLC	20.2	30.0	32.0	17.8
	API	21.9	30.2	23.2	24.7

* Each results is the average of three determinations.

Table 2 - Comparison of Hydrocarbon-Type Determination in
Deasphalted Fractions (> 200°C) of Processed Samples
by TLC and API-USBM Methods

Sample	Pitch		Hydrocarbon Content (wt %)			
	Method	Conversion %	Saturates	Aromatics	PNA	Polar Material
6. <u>Lloydminster</u>		38.7				
	TLC		29.0	27.5	26.6	16.9
	API		27.5	26.8	11.3	34.3
7. <u>Lloydminster</u>		52.9				
	TLC		35.2	30.3	24.6	9.9
	API		40.5	29.0	10.3	20.1
8. <u>Cold Lake</u>		100.0				
	TLC		45.5	37.9	12.6	4.0
	API		44.6	37.8	8.4	9.2
9. <u>Cold Lake</u>		47.7				
	TLC		28.1	28.3	30.2	13.4
	API		27.2	27.8	17.8	27.2
10. <u>Boscan</u>		42.6				
	TLC		30.4	27.5	24.9	17.2
	API		29.0	26.0	10.6	34.4

Table 3 - Model Hydrocarbon Used in this Study

Hydrocarbon	B.P. (°C)	M.P. (°C)
<u>Paraffins</u>		
1. n-tridecane	235	-
2. adamantane	-	267
3. eicosane	342	-
4. heneicosane	355	-
5. n-docosane	367	-
6. n-tricosane	378	-
7. tetracosane	389	-
8. dotriacontane	463	-
9. hexatriacontane	493	-
10. 4,5-dimethylperhydroanthracene	-	-
<u>Aromatics</u>		
11. tetrahydronaphthalene	208	-
12. β -methylnaphthalene	241	-
13. biphenyl	256	-
14. ethylnaphthalene	258	-
15. 2,6-dimethylnaphthalene	261	-
16. 3,3'-dimethylbiphenyl	-	-
17. 2,3-dimethylnaphthalene	266	-
18. 1,4-dimethylnaphthalene	268	-
19. 15-phenylnonacosane	-	-
20. 17-phenyltriacontane	-	-

Table 3 (Cont'd)

Hydrocarbon	B.P. (°C)	M.P. (°C)
<u>PNA</u>		
21. phenanthrene	-	100
22. 3 - methylphenanthrene	-	-
23. fluoranthene	-	108
24. fluorene	-	113
25. 1,2-benzanthracene	-	-
26. 7,12-dimethylbenz(a)anthracene	-	122
27. pyrene	-	156
28. p-quaterphenyl	-	318
29. naphthacene	-	> 300
30. naphthanthracene	-	-

Table 4 - Repeatability of the TLC Procedure With
Athabasca Malthenes (Sample 1)

Analysis	Hydrocarbon contents (wt %)			
	Saturates	Aromatics	PNA	Polar Material
1	24.7	23.1	38.5	13.7
2	25.0	22.9	37.1	15.0
3	25.3	24.0	36.2	14.5
4	24.8	22.6	37.8	14.8
5	25.6	24.6	35.0	14.8
6	25.6	24.3	35.3	14.8
7	25.2	24.8	35.3	14.7
8	24.9	23.0	36.9	15.2
9	23.5	22.4	39.8	14.3
10	<u>25.0</u>	<u>23.5</u>	<u>36.8</u>	<u>14.6</u>
Standard deviation, σ	0.60	0.85	1.53	0.41
<u>mean</u>	25.0	23.5	36.9	14.6

Table 5 - Repeatability of the USBM-API Procedure
With Athabasca Malthenes

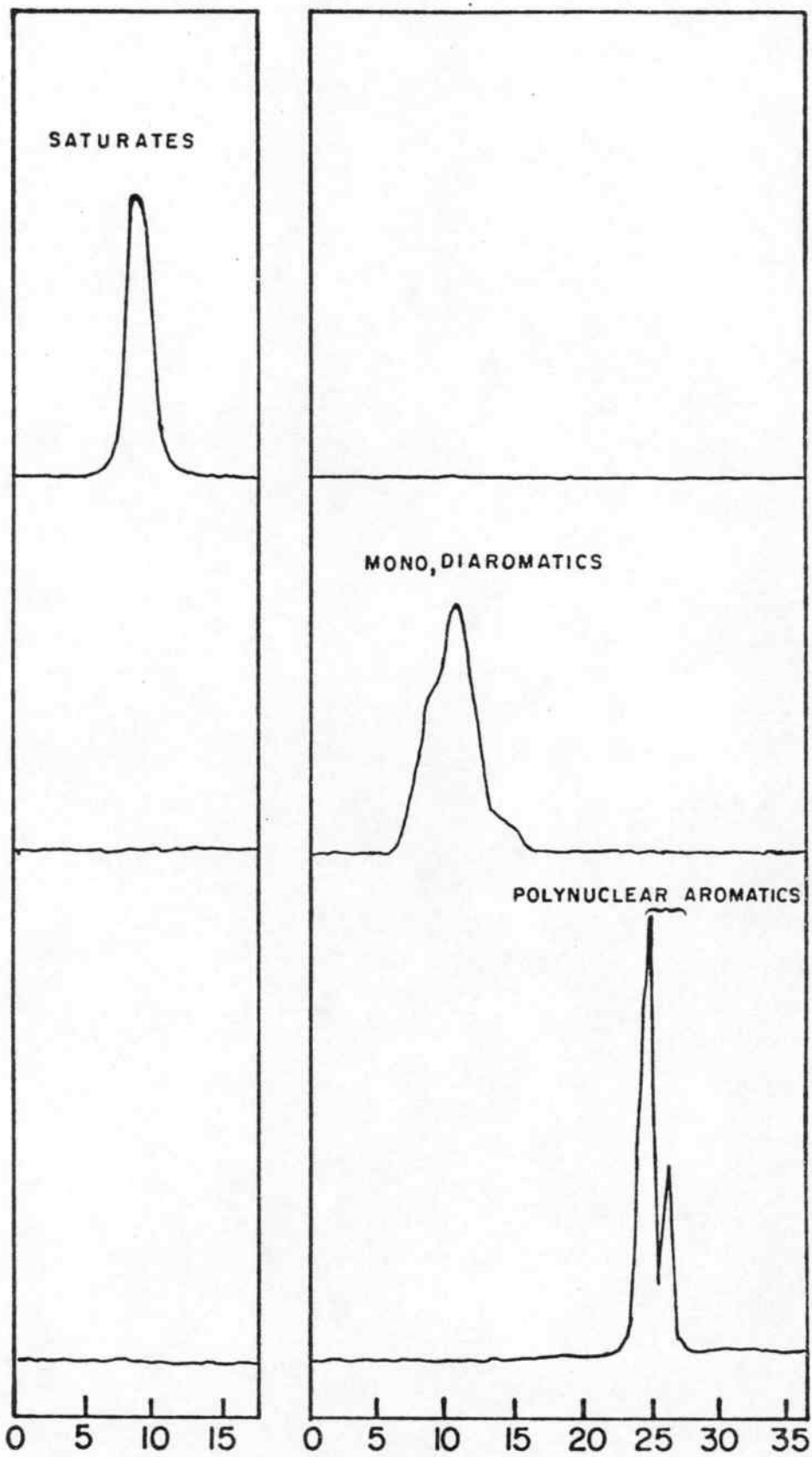
Analysis	Hydrocarbon contents (wt %)			
	Saturates	Aromatics	PNA	Polar Material
1	24.8	22.2	23.8	29.2
2	26.1	21.9	24.8	27.2
3	26.4	22.2	23.1	28.3
4	22.8	24.6	26.0	26.6
5	23.7	21.7	26.5	28.1
6	25.6	20.5	23.3	30.6
7	22.9	24.2	24.7	28.2
8	<u>24.4</u>	<u>24.0</u>	<u>24.4</u>	<u>27.2</u>
Standard deviation, σ	1.39	1.44	1.21	1.27
mean	24.6	22.7	24.6	28.2

CAPTION

Figure 1. Separation of Model Hydrocarbons on Chromarods

Figure 2. Separation of Standard Hydrocarbon-Type Fractions on Chromarods

Figure 3. Hydrocarbon-Type Separation of Lloydminster Malthenes ($> 200^{\circ}\text{C}$)
on Chromarods



RETENTION TIME, sec.

Fig 2

