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RAPID METHOD FOR THE DETERMINATION OF MALTHENE AND ASPHALTENE CONTENT
IN BITUMEN, HEAVY OILS AND SYNTHETIC FUELS BY PYROLYSIS TLC

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ABSTRACT

A rapid pyrolysis thin layer chromatographic (TLC) method for the determination of malthene and asphaltene content in bitumens, heavy oils and their synthetic fuel products is described. The malthenes are separated from the asphaltenes (defined as the portion that is insoluble in n-paraffinic hydrocarbon and soluble in benzene) by spotting 1 μ l of a 25 mg/mL sample solution on a silica gel chromarod followed by development with an n-paraffinic hydrocarbon-isopropanol mixture (95:5). Benzene insolubles are removed prior to the determination. The separation is quantified by an Iatroscan TH-10 Analyzer that uses FID detector.

Complete analysis of 9 samples requires 30 minutes excluding time necessary for sample preparation prior to spotting. The method was applied to sixteen samples of bitumen, heavy oils and synthetic fuels. Repeatability of the results has been compared with that obtained by a standard procedure.

INTRODUCTION

Asphaltenes have been always considered as undesirable components in bitumens and heavy oils because they create serious difficulties in upgrading heavy ends. One of the areas of interest today is the conversion of petroleum residues and asphaltenes into lighter oils. Rapid methods for the determination of asphaltene content are needed to follow upgrading processes.

A few methods have been reported in the literature for the determination of asphaltene content in bitumens, heavy oils and synthetic fuels (1-4). These methods were discussed in our previous publications which compared the conventional I.P. (Institute of Petroleum) procedure (2) with a thin layer chromatographic method (TLC-I) developed in our laboratory (5). Our TLC-I method is based on Beer's law. The oil and resins (malthenes) are separated from the asphaltenes on a TLC plate; the asphaltenes are removed from the plate, extracted with toluene and the concentration of asphaltenes determined colorimetrically.

In this work we describe a rapid pyrolysis thin layer chromatographic method (TLC-II) for determining the malthene and asphaltene content in bitumens, heavy oils and synthetic fuels. The pyrolysis TLC technique was first applied to petroleum by Suzuki et al. (6) for rapid analysis of fuel oil constituents. In our procedure the malthenes are separated from the asphaltenes on a silica gel chromarod using n-paraffinic hydrocarbon isopropanol mixture (95:5) as developing solvent. The malthene and asphaltene contents are determined quantitatively using an Iatroscan TH-10 Analyzer equipped with a flame ionization detector (FID).

The overall time required for the analysis of 9 samples is about 30 minutes excluding the time necessary for weighing the samples and dissolving them in benzene. Sixteen samples of bitumens, heavy oils and synthetic fuels have been analyzed by this method. Repeatability of the results has been compared with those obtained by the I.P. procedure.

EXPERIMENTAL

Instrument and Operating Conditions

The Iatroscan TH-10 TLC Analyzer, Mark III, was equipped with a flame-ionization detector and an electronic stepping integrator. The flame-

ionization detector was operated with a hydrogen flow-rate of 160 mL/min and an air flow-rate of 2 L/min. The scanning speed was 5 in/min. A two-pen recorder was used at 50 mV full-scale deflection and chart speed of 2 in/min.

Solvents

The n-pentane, n-heptane and isopropanol used as developing solvents were reagent grade. n-Pentane, n-heptane and benzene meeting I.P. specifications were used in the I.P. procedure.

Samples

- 1 Seven bitumens and heavy oils (Table I).
- 2 Nine processed samples (Table II), distillation residues boiling above 350°C were used in the determination of malthene and asphaltene content by both methods.

Standards

Athabasca asphaltenes isolated by n-pentane and n-heptane precipitation according to the I.P. procedure were used as standards in the TLC method.

Procedure

The following procedure is described for the determination of n-pentane asphaltene content. Determination of n-heptane asphaltene content is accomplished by substituting n-heptane for n-pentane in the procedure.

A. Preparation of Standard Asphaltene Solutions

- 1 Weigh accurately about 15 mg of Athabasca asphaltenes in a 2 mL volumetric flask. Dissolve and fill to volume with benzene.
- 2 Apply 1.0 μ L of the standard solution on a Silica gel II chromarod.

B. Preparation of the Sample Solutions

- 1 Dissolve about 200 mg of bitumen, heavy oil or distillation residue sample in 25 mL benzene. Filter through a Whatman filter paper No. 40 to remove any insolubles. Evaporate the filtrate to dryness.
- 2 Weigh accurately about 50 mg of the sample (insolubles-free) in a 2 mL volumetric flask. Dissolve and fill to volume with benzene.

- 3 Apply 1.0 μ L of the solution on a Silica gel chromarod.
- 4 Repeat steps 1 to 3 for each additional sample.

C. Sample Analysis

- 1 Develop the chromarods in a TLC tank using filter paper as a wick, and n-pentane-isopropanol mixture (95:5) as developing solvent.
- 2 Remove the chromarods from the tank when the solvent front has travelled 8 cm. Allow the rods to dry for a few minutes in an oven at 120°C.
- 3 Place the rack in the Iatroscan TLC pyrolyser and pyrolyse the rods in the FID.

CALCULATION

The n-pentane and n-heptane malthene and asphaltene contents were calculated using the following equations:

$$(1) \quad \text{Asphaltenes (wt \%)} = \frac{W_A \times A_{AS}}{W_S \times A_A} \times 100$$

$$(2) \quad \text{Malthenes (wt \%)} = 100 - (\text{wt \% Asphaltenes})$$

where

W_A = weight of asphaltenes used as standard

W_S = weight of the sample to be analyzed

A_{AS} = area of the asphaltenes peak in the sample

A_A = area of the asphaltenes peak in the standard

RESULTS AND DISCUSSION

Separation of the Malthenes from Asphaltenes

Separation of the malthenes from asphaltenes in bitumens, heavy oils and synthetic fuel residues (b.p. higher than 350°C) was accomplished on a silica gel chromarod. The separation obtained for sample 1 is shown in Figure 1. The developing solvent mixture n-pentane or n-heptane-isopropanol (95:5) used in the previous work (5) was also used in this procedure. The separation was tested on malthene and asphaltene samples isolated by n-pentane and n-heptane precipitation from the bitumens and heavy oils listed in

Table I. Linearity of the response was demonstrated with different concentrations of Athabasca n-pentane asphaltenes used as standards in the procedure with concentration range of 0-15 mg/mL. Quantitative results were obtained by integrating the peak areas corresponding to the asphaltenes. The malthe content was calculated by difference. When the solvent front had travelled 8 cm, the R_F of the malthenes and asphaltenes were 0.67 and 0 respectively. The asphaltenes were strongly retained on silica and remained at the origin. In this TLC-II procedure quantification is independant of the abundance of porphyrins or colour of the asphaltene solutions as was found in the TLC-I method (5). This means that one asphaltene sample from any source could be used as a standard in this procedure.

Comparison of I.P. and TLC-II Methods

Comparison of the TLC-II results with those obtained by the standard I.P. procedure with n-pentane and n-heptane (Tables I-III) shows good agreement for both methods. Slightly higher asphaltene contents 1 to 2% (absolute values) were obtained in most cases by the TLC-II procedure. This could be explained by the minimum losses in the TLC-II procedure which involves only weighing the samples. In the I.P. standard procedure precipitation and filtration steps are also involved. Very fine asphaltene particles could pass through the pores of the filter paper which would account for the lower values.

Comparison of the asphaltene content results (Table IV) with the previous TLC-I procedure (5) also shows good agreement.

Repeatability of the TLC-II Procedure

The repeatability of the procedure was determined using Athabasca bitumen (sample 1), Boscan heavy oil (sample 6) and two synthetic fuel samples residue >350°C, hydrocracked Cold Lake bitumen and Boscan heavy oil (samples 9, 14). The standard deviation for 10 analyses of each sample were 0.62, 0.73, 0.58 and 0.59 respectively. As shown by the standard deviation the results obtained by this method were of acceptable reliability. Repeatability of the I.P. standard precipitation procedure on samples 1 and 6 was also determined. Standard deviation for 8, analyses of each sample were 0.63 and 0.66 respectively. The results show that comparable standard deviations were obtained which indicates that both procedures have similar precision. However, the TLC-II procedure is much less time consuming.

Conclusions

Our rapid TLC method for the determination of asphaltene content in bitumen, heavy oils and synthetic fuels is as precise as the IP 143 procedure. Furthermore our method offers a viable alternative to the standard IP 143 method since it is less time consuming.

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Table I - Determination of the n-pentane malthene and asphaltene contents of feed samples by two different methods

Samples	Malthenes (wt %)		Asphaltenes (wt %)	
	I.P	TLC-II	I.P.	TLC-II
1. Athabasca	83.1	80.8	16.4	19.2
2. Lloydminster 4LL79	75.0	74.3	25.0	25.7
3. Cold Lake 6CL79	78.5	76.3	21.5	23.7
4. Carbonate triangle 950-80	80.0	79.3	19.7	20.7
5. Medicine River (residue >350°C)	99.5	99.4	0.5	0.6
6. Boscan heavy oil	77.6	75.1	22.3	24.9
7. Laguna heavy oil	80.4	76.6	19.6	23.4

Table II - Determination of the n-pentane malthe ne and asphaltene contents of hydrocracking products (synthetic fuels) by two different methods

Samples Residue >350°C	Pitch Conversion %	Malthenes (wt %)		Asphaltenes (wt %)	
		I.P.	TLC-II	I.P.	TLC-II
8. Cold Lake	100.0	89.	88.0	10.1	12.0
9. Cold Lake	47.7	68.7	66.0	31.3	34.0
10. Cold Lake	86.0	85.5	85.0	14.5	15.0
11. Athabasca	36.8	83.5	84.9	16.5	15.1
12. Athabasca	26.1	82.8	81.0	17.2	19.0
13. Boscan	69.2	82.9	84.0	17.1	16.0
14. Boscan	79.2	84.7	84.3	15.3	15.7
15. Lloydminster	38.7	69.0	72.8	31.0	27.2
16. Lloydminster	58.3	61.2	61.1	38.8	38.9

Table III - Determination of the n-heptane maltheane and asphaltene contents of feed samples by two different methods

<u>Samples</u>	<u>Malthenes (wt %)</u>		<u>Asphaltenes (wt %)</u>	
	<u>I.P.</u>	<u>TLC-II</u>	<u>I.P.</u>	<u>TLC-II</u>
1. Athabasca	87.8	87.3	12.2	12.7
2. Lloydminster	84.6	83.7	15.4	16.3
3. Cold Lake	83.0	84.6	17.0	15.4
4. Carbonate triangle	85.3	84.5	14.7	15.5
5. Boscan heavy oil	84.3	84.0	15.7	16.0

Table IV - Comparison of the asphaltene content determined
by the standard I.P. and two different TLC
methods

Samples	<u>n-Pentane Asphaltene Content (wt %)</u>		
	I.P.	TLC-I	TLC-II
1. Athabasca	16.4	17.4	19.2
2. Lloydminster	25.0	25.6	25.7
3. Cold Lake	21.5	23.8	23.7
4. Carbonate Triangle	19.7	14.6	20.7

CAPTIONS

Figure 1 Typical separation of n-pentane malthene and asphaltenes on a silica chromarod.

