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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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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 contents in bitumens, heavy oils and their synthetic fuel products is presented. The malthenes are separated from the asphaltenes (defined as the portion that is insoluble in n-pentane and soluble in benzene) by spotting $1 \mu L$ of a 25 mg/mL sample solution on a silica gel chromarod using n-pentane-isopropanol mixture (95:5) as developing solvent. Benzene insolubles were 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 weighing the samples and dissolving in benzene prior to spotting. The method was applied to sixteen samples of bitumen, heavy oils and synthetic fuels. Repeatability of the results was compared with that obtained by the standard procedure.

INTRODUCTION

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

A few methods have been reported in literature for the determination of asphaltene content in bitumens, heavy oils and synthetic fuels (1-4). These methods were discussed in one of our previous publications (5). The conventional I.P. procedure (2) was compared 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 and the asphaltenes removed from the plate, extracted with toluene and the concentration of asphaltenes determined colorimetrically. When we first used 415 nm on the spectrophotometer, the determined asphaltene concentrations were affected by the porphyrin content in the asphaltenes. Taking readings at 425 nm could alleviate this problem.

In this work we describe a rapid pyrolysis thin layer chromatographic method (TLC-II) for determining the malthene as asphaltene contents in bitumens, heavy oils and synthetic fuels. The malthenes are separated from the asphaltenes on a silica gel chromarod using n-pentane-isopropanol mixture (95:5) as developing solvent. The malthene and asphaltene contents were determined quantitatively using a 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 in benzene. Sixteen samples of bitumens, heavy oils and synthetic fuels were analyzed by this method. Repeatability of the results was compared with those obtained by the I.P. procedure.

EXPERIMENTAL

Instrument and Operating Conditions

The Iatroscan TH-10 TLC Analyzer, Mark III used, 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, benzene and isopropanol used as developing solvents were reagent grade. The n-pentane and benzene meeting I.P. specifications were used in the I.P. procedure.

Samples

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

Standards

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

Procedure

A. Preparation of the Standard Asphaltene Solutions

1 Weigh accurately about 15 mg of Athabasca asphaltenes in a 2 mL volumetric flask. Dissolve and complete to volume with benzene.
2 Apply 1.0 μL 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. Filtrate 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 complete with benzene.
3 Apply 1.0 μL 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.

<div align="center">CALCULATION</div>

The malthene and asphaltene contents were calculated by using the
following equations:

(1) Asphaltenes (wt %) = $\dfrac{W_A \times A_{AS}}{W_S \times A_A}$ x 100

(2) Malthenes (wt %) = 100-(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

<div align="center">RESULTS AND DISCUSSION</div>

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 developing solvent mixture n-pentane-isopropanol
(95:5) that was used in the previous work (5) was also used in the
procedure. The separation was tested on malthene (Fig. 1b) and asphaltene
samples (Fig. 1c) isolated by n-pentane precipitation from the bitumens and
heavy oils listed in Table 1. Quantitative results were obtained by
integrating the peak areas corresponding to the asphaltenes. The malthene
content was calculted by difference. When the solvent front has 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.

A typical separation is shown in Fig. 1a. In this TLC-II procedure quantification is independant of the abundance of porphyrins or colour of the asphaltenes solutions as in the TLC-I method (5). This means that one asphaltene sample from any source could be used as standard in this procedure.

Comparison with I.P. and TLC-II Methods

Comparison of the TLC-II results with those obtained by the standard I.P. procedure (Table 2 and 3) shows a very good agreement for both methods. Slightly higher asphaltene contents 1 to 2% (absolute values) were obtained by the TLC-II procedure. This could be explained by the minimum losses in the TLC-II procedure because it 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 could account for the lower values.

Comparison of the asphaltene content results (Table 4) with the previous TLC-I procedure (5) shows also 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). As shown by the standard deviation (Table 5) good repeatability of the results is obtained by this method. Repeatability of the I.P. standard procedure on samples 1 and 6 was also determined (Table 6). Comparable standard deviations were obtained which indicates that both procedures have similar precision. The TLC-II procedure is never the less much time consuming.

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Table 1 - Properties of Canadian bitumens and heavy oil

		Athabasca	Cold Lake	Lloydminster	Carbonated Triangle	Boscan	Laguna
Specific gravity	60/60°F	1.009	1.026	1.033	1.032	1.016	1.024
Sulphur	wt %	4.63	5.16	5.02	5.21	5.73	3.43
Ash	wt %	0.68	0.06	0.04	0.56	0.24	0.12
Viscosity, 210°F	cST	152	1489	3691	514	575	-
Conradson carbon residue	wt %	12.8	18.2	19.6	15.1	16.7	18.4
Asphaltenes (pentane insolubles)	wt %	15.3	21.0	22.1	19.7	22.3	19.6
Benzene insolubles	wt %	0.9	0.03	0.07	0.24	0.09	trace
Nickel	PPM	70	-	-	74	114	70
Vanadium	PPM	190	255	124	203	1174	558

Table 2 - Determination of the malthene and asphaltene contents by two different methods on feed samples

	Samples	Malthenes (wt %)		Asphaltenes (wt %)	
		I.P	TLC	I.P.	TLC
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 3 - Determination of the malthene and asphaltene contents by two
different methods on hydrocracking products (synthetic fuels)

Samples	Pitch	Malthenes (wt %)		Asphaltenes (wt %)	
Residue >350°C	Conversion %	I.P.	TLC	I.P.	TLC
8. Cold Lake 80-CG-38	100.0	89.?	88.0	10.1	12.0
9. Cold Lake 77-T-77	47.7	68.7	66.0	31.3	34.0
10. Cold Lake 74-CG-83	86.0	85.5	85.0	14.5	15.0
11. Athabasca 93-3-1	36.8	83.5	84.9	16.5	15.1
12. Athabasca 92-1-1	26.1	82.8	81.0	17.2	19.0
13. Boscan 79-CG-222	69.2	82.9	84.0	17.1	16.0
14. Boscan 79-CG-224	79.2	84.7	84.3	15.3	15.7
15. Lloydminster 77-TG-27	38.7	69.0	72.8	31.0	27.2
16. Lloydminster 77-TG-29	58.3	61.2	61.1	38.8	38.9

Table 4 – Comparison of the asphaltene content determined by
the standard I.P. and two different TLC methods

| Samples | n-Pentane Asphaltene Content (wt %) | | |
	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

Table 5 - Determination of analytical precision of the TLC method

	wt % Asphaltenes			
Analysis	Athabasca bitumen (Sample 1)	Boscan heavy oil (Sample 6)	Hydrocrackd Cold Lake bitumen (Sample 9)	Hydrocracked Boscan heavy oil (Sample 14)
1	18.8	24.4	23.1	17.4
2	19.4	24.4	24.6	18.0
3	20.7	23.6	23.1	17.4
4	19.4	23.6	23.8	18.0
5	20.1	24.4	23.8	18.0
6	20.1	25.9	23.1	18.6
7	19.4	24.4	23.1	18.6
8	20.7	25.2	23.8	18.0
9	20.1	24.4	24.6	17.4
10	19.4	23.6	23.8	19.2
Mean	19.8	24.4	23.7	18.0
Standard Deviation	0.62	0.73	0.58	0.59

Table 6 - Determination of analytical precision of the
standard I.P. procedure

	wt % Asphaltenes	
	Athabasca bitumen	Boscan heavy oil
Analysis	(Sample 1)	(Sample 6)
1	16.4	22.3
2	16.8	21.3
3	16.0	21.5
4	15.3	21.3
5	15.4	22.2
6	15.6	22.5
7	17.0	22.0
8	16.2	23.2
Mean	16.1	22.0
Standard deviation, σ	0.63	0.66