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A RAPID METHOD FOR THE DETERMINATION OF ASPHALTENE CONTENT IN CRUDE OILS AND BITUMENS USING THIN LAYER CHROMATOGRAPHY

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A RAPID METHOD FOR THE DETERMINATION OF ASPHALTENT CONTENT IN CRUDE OILS AND BITUMENS USING THIN LAYER CHROMATOGRAPHY

by

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ABSTRACT

A rapid method for the determination of asphaltene content in bitumens and processed bitumens using thin layer chromatography (TLC) and colorimetry is presented.

The method separates asphaltenes from the maltenes (oils and resins) on a TLC plate. The asphaltene band is removed from the plate, extracted in toluene and the concentration determined by colorimetry.

The method determines the weight percent of asphaltenes defined as the portion that is insoluble in n-pentane and soluble in toluene. It is applicable to all light and heavy oils, and to petroleum distillate residua.

The procedure has been applied to Athabasca and Cold Lake bitumens, Lloydminster heavy oil and their processing products containing different amounts of asphaltenes.

Asphaltene content from 0% to 100% could be determined by this method. Comparison of the results with the standard IP procedure is presented.

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INTRODUCTION

The chemical structure of petroleum asphaltenes has been the subject of numerous studies, but remains a matter of considerable conjecture (1-6). Asphaltenes are constituted mainly of sulphur and oxygen-bridged polymers containing a large number of polynuclear aromatic rings.

Asphaltenes must be defined by the solvent used to precipitate it. The amount of precipitation and mulecular size of the asphaltenes differ according to the boiling point of the hydrocarbon solvent used. We compared n-pentane, n-heptane and n-nonane as precipitation solvents.

The purpose of this work was to develop a fast analytical method for the determination of asphaltene content in different crude oils. There are very few existing methods for the determination of asphaltene content in bitumen (7-10).

The I.P. method (7) consists of dissolving the material to be analyzed in n-heptane and the insoluble precipitate, composed of asphaltenes, waxy substances and inorganic material is separated by filtration through a fine filter paper. The precipitate is dissolved in toluene and the asphaltene content is calculated as the difference between the n-heptane insolubles and the toluene insolubles for sake of comparison with the TLC method. The method is lengthy and uses a large amount of solvent. The results are highly affected when the asphaltenes are present in small amounts.

Another method for bitumen analysis by pyrolysis gas chromatography has been reported by Ramljak et al. (8). It involves the determination of a characteristic ratio of light unsaturated and saturated hydrocarbons in bitumen pyrolyzate which is used for calculating the asphaltene and maltene contents in bitumen samples. The procedure is not applicable for samples having an asphaltene content higher than 30%, and employs sophisticated instrumentation.

A method published by Burke et al. (10) involves the separation of a sample injected onto a liquid chromatographic column packed with glass beads by sequential solvent elution. Although the method has shown good reproducibility, comparison with the conventional method shows deviation in asphaltene content of ± 21%.

This paper describes an analytical method based on Beer's Law. The oil and resins 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. By using a calibration curve obtained from known concentrations of asphaltenes, it is possible to determine the asphaltene content for a sample. The overall time required for analyzing ten samples is about 3 h. The method was first investigated using asphaltenes from different sources. The results were affected by the source of asphaltenes used as a standard for establishing the calibration curve. Asphaltenes precipitated by different hydrocarbon solvents (n-pentane, n-heptane and n-nonane) produced calibration curves of different slopes. Also asphaltenes of processed samples were different from those of unprocessed samples. By using the TLC method, determination of asphaltene content in bitumens was accomplished with a precision of ± 10%.

EXPERIMENTAL

Apparatus

1. Ultrasonic bath Bransonic 20.
2. Silica gel precoated TLC plates, 0.25 mm thickness, 10 x 20 cm available from Brinkman, Rexdale, Ontario.
3. 100 μl syringe available from Hamilton Company.
4. Bausch and Lomb Spectronic 20 colorimeter.
5. Glass TLC tank 20 x 20 cm available from Brinkman.
6. 10 mL, 25 mL volumetric flasks
7. 5 mL, 2 mL pipettes
8. 1 mL graduated to 0.1 mL pipette.

Solvents

n-pentane, n-heptane, n-nonane and toluene conforming to the IP specification, iso-propanol.

Samples

1. Asphaltenes (n-pentane insolubles) extracted from Athabasca bitumen.
2. Asphaltenes (n-pentane insolubles) extracted from Lloydminster heavy oil.
3. Asphaltenes (n-pentane insolubles) extracted from Cold Lake bitumen.
4. Asphaltenes (n-pentane insolubles) extracted from Cold Lake residue > 350°C.
5. Asphaltenes (n-heptane insolubles) extracted from Cold Lake residue > 350°C.
6. Asphaltenes (n-nonane insolubles) extracted from Cold Lake residue > 350°C.
7. Asphaltenes (n-pentane insolubles) from mildly processed Lloydminster heavy oil.
8. Asphaltenes (n-pentane insolubles) from severely processed Lloydminster heavy oil.
9. Asphaltenes (n-pentane insolubles) from mildly processed Cold Lake bitumen.
10. Asphaltenes (n-pentane insolubles) from severely processed Cold Lake bitumen.
11. Athabasca bitumen.
12. Cold Lake bitumen.
13. Maltenes (n-pentane solubles) from Lloydminster heavy oil.
14. Residue > 350°C from mildly processed Athabasca bitumen.
15. Maltenes (n-pentane solubles) from severely processed Lloydminster heavy oil.
16. Residue > 350°C from severely processed Lloydminster heavy oil.
17. Residue > 350°C from mildly processed Cold Lake bitumen.
18. Residue > 350°C of Cold Lake bitumen.
19. Lloydminster heavy oil.

Preparation of Petroleum Asphaltenes

Asphaltene content was determined on 10 g of sample according to the IP procedure using different hydrocarbon solvents (8).

Preparation of the Standards

1. Into a 25 mL volumetric flask weigh accurately about 500 mg asphaltenes. Add about 15 mL toluene and agitate in the ultrasonic bath for 20 min and complete to volume with toluene (concentration of 20 mg/mL).
2. Transfer 7.5 mL and 5.0 mL of the solution into a 10 mL volumetric flask and complete to volume with toluene. These two dilutions correspond to concentrations of 15 and 10 mg/mL respectively ( ).
3. Transfer 5.0 mL of the latter into a 10 mL volumetric flask and complete to volume (concentration of 5 mg/mL). Repeat the dilution using 5.0 mL of the latter solution in a 10 mL volumetric flask (concentration of 2.5 mg/mL).
4. Apply on the larger side of the TLC plate, with a microsyringe 40 μl of each solution (5 solutions) as a narrow band (7 x 35 mm). Four solutions can be spotted on the same plate.

Preparation of the Samples

1. Into a 25 mL volumetric flask weigh accurately about 500 mg of the sample. Proceed as in Step 1 under "Preparation of the Standards".
2. Apply on the side of the TLC plate with a microsyringe 40 μl of the sample as a narrow band.
3. Repeat Steps 1 and 2 for each additional sample.
4. Develop the plates in a TLC tank using n-pentane-isopropanol (95:5) as the developing solvent.
5. Remove the plate from the tank, when the solvent front has travelled 7 cm. Allow to dry for a few minutes and scrape the bands at $R_f=0$ into individual 10 mL volumetric flasks.
6. Add about 5 mL of toluene to each flask and agitate in the ultrasonic bath for 20 min. Complete to volume with toluene.
7. Set the colorimeter to zero with a blank composed of equivalent amount of pure silica gel extracted from a plate and 10 mL toluene.
8. Shake the flask before each measurement and rapidly transfer a few milliliters of the solution into the spectroscopic cuvette and take the reading at 415 nm.

CALCULATION

The asphaltenes content is calculated as a percentage by weight of the original sample by using the following formula:

$$\frac{A_s - b}{C_s \times m} \times 100 = \text{wt \% asphaltenes}$$

where m = slope of the calibration curve, determined by the least square method

A_s = absorbance of the sample at 415 nm

b = intercept of the calibration curve

C_s = concentration of the sample in mg/mL

RESULTS AND DISCUSSION

Separation of the maltenes from asphaltenes in bitumens and residues above 350°C was investigated by TLC using different solvent mixtures at various concentrations. The developing solvent which has given the best results was pentane-isopropanol (95:5). Asphaltenes are strongly adsorbed on silica and remain at the bottom of the plate (11). The asphaltenes adsorbed on the silica gel are removed from the plate and extracted with toluene. The extraction was relatively difficult because the asphaltenes remained partially adsorbed on the fine silica particles forming a suspension in the solvent. The solution had to be agitated before each measurement on the colorimeter. The wavelength chosen (415 nm) for the analysis corresponds to the maximum absorbance of an asphaltenes sample in the visible range of the spectra. Linearity of the calibration curve, absorbance versus asphaltenes concentration, was investigated using different types of asphaltenes described in the Experimental Section. The results show negligible deviation of slope (24 ± 2) for asphaltenes obtained from different unprocessed bitumens and a heavy oil. Asphaltenes of processed samples and those obtained from unprocessed bitumens by n-heptane or n-nonane extractions give a slightly different slope (20 ± 1) but remain consistent within the same type of asphaltenes. The severity of processing (expressed by various pitch conversions) had little effect on the slope of the calibration curve. Results of the analyses, obtained by TLC for different asphaltenes of known content, is shown in Table 1.

The difference in the slope could be explained by differences in the chemical structure and molecular weights of the asphaltenes. Hydrocracking bitumens could contribute to the increased aromaticity of the asphaltenes due to the loss of paraffinic side chains resulting in a higher absorbance for processed asphaltenes compared to unprocessed asphaltenes of the same concentration. The analytical procedure was tested on a wide variety of samples including bitumens, processed bitumens and residua boiling higher than 350°C. The results show very little deviation from the asphaltene content determined by the standard I.P. method (7) shown in Table 2. Two maltene samples (asphaltene-free) from different sources were analyzed by TLC. The results obtained were close to zero (Table 2). The values obtained lie within the detectability limit of the method. Analysis was repeated three times for two different samples, the results (Table 3) show small deviation from the mean value.

Fractionation of petroleum products involves, in most cases, separation to maltenes and asphaltenes. For a sample containing preasphaltenes (toluene insoluble, THF soluble), such as a coal-derived liquid, the analysis could be performed by first dissolving the sample in toluene. Preasphaltenes are determined gravimetrically and the toluene solubles, maltenes and asphaltenes can be analyzed by TLC. We are currently conducting research in this area.

CONCLUSIONS

A quantitative TLC method has been developed for the determination of asphaltene content in bitumens, heavy oils and distillation residua. The method is rapid, accurate and offers an adequate alternative to the conventional standard procedure using precipitation in aromatic free hydrocarbon solvents. Asphaltene content from 0 to 100% could be determined by this method.

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Table 1 - Analysis of Known Concentration of n-pentane Asphaltenes by the TLC Method

Sample*	wt % asphaltenes (prepared)				
	12.5	25.0	50.0	75.0	100.0
	wt % asphaltenes (determined)				
2	14.5	29.2	56.1	79.4	100.3
3	9.6	23.1	46.4	70.0	95.6
4	14.5	29.2	50.0	78.2	105.1
5	12.6	28.2	56.1	74.8	92.4
6	12.6	27.1	43.7	70.0	102.8
7	10.6	28.2	51.0	73.8	102.7
8	13.7	29.2	58.2	74.8	102.7
10	13.7	27.1	46.8	71.7	97.6
mean	12.7	27.6	51.0	74.1	99.9

* Samples 1 and 9 (see samples under the Experimental Section) have been used to determine the calibration curves for the two sets of results:

Sample 1 m = 0.0407 b = 0.0421

Sample 9 m = 0.0477 b = 0.0622

Table 2 - Comparison of the n-pentane Asphaltene Content (wt %) in Petroleum Samples Obtained by Two Different Methods

Sample	I.P.	TLC
11	16.4	17.4
12	21.0	23.8
13	nil	0.3
14	20.1	21.5
15	nil	1.2
16	38.0	42.4
17	26.1	27.8
18	21.7	22.6

Table 3 - Determination of Analytical Precision of the TLC Method

Analysis	wt % Asphaltenes			
	Sample 16	Sample 17	Sample 18	Sample 19
1	42.2	27.8	22.6	22.8
2	41.0	27.5	22.0	22.1
3	41.5	28.0	22.6	21.7
4	42.0	27.0	22.9	22.3
Standard Deviation	0.61	0.43	0.38	0.46

PROPERTIES OF CANADIAN BITUMENS AND HEAVY OIL

		ATHABASCA	COLD LAKE	LLOYDMINSTER	CARBONATE TRIANGLE
SPECIFIC GRAVITY	60/60°F	1.009	1.026	1.033	1.032
SULPHUR	WT %	4.63	5.16	5.02	5.21
ASH	WT %	0.68	0.06	0.04	0.56
VISCOSITY, @ 210°F	cST	152	1489	3691	514
CONRADSON CARBON RESIDUE	WT %	12.8	18.2	19.6	15.1
ASPHALTENES (PENTANE INSOLUBLES)	WT %	15.3	21.0	22.1	19.7
BENZENE INSOLUBLES	WT %	0.9	0.03	0.07	0.24
NICKEL	PPM	70	-	-	74
VANADIUM	PPM	190	255	124	203

EXISTING METHODS FOR DETERMINING THE ASPHALTENE CONTENT

ASTM OR IP	PYROLYSIS GAS CHROMATOGRAPHY	LIQUID CHROMATOGRAPHIC SEPARATION
LENGTHY PROCEDURE	INVOLVES SOPHISTICATED INSTRUMENTATION	EMPLOYS LIQUID CHROMATOGRAPHIC EQUIPMENT
USES LARGE AMOUNT OF SOLVENT	NOT APPLICABLE TO SAMPLE OF ASPHALTENE CONTENT HIGHER THAN 30 WT %	AVERAGE DEVIATION OF 21% COMPARED TO THE CONVENTIONAL METHOD
HIGH ERRORS		

SAMPLES USED IN THIS WORK

1. asphaltenes extracted from Athabasca bitumen.
2. asphaltenes extracted from Lloydminster heavy oil.
3. asphaltenes extracted from Cold Lake bitumen.
4. asphaltenes extracted from Cold Lake bitumen, residue >350°C.
5. asphaltenes from mildly processed Lloydminster heavy oil.
6. asphaltenes from severely processed Lloydminster heavy oil.
7. asphaltenes from severely processed Cold Lake bitumen.
8. asphaltenes from mildly processed Cold Lake bitumen.
9. Athabasca bitumen.
10. Lloydminster heavy oil.
11. Cold Lake bitumen.
12. maltenes (n-pentane solubles) from Lloydminster heavy oil.
13. residue > 350°C from mildly processed Athabasca bitumen.
14. residue > 350°C from severely processed Lloydminster heavy oil.
15. residue > 350°C of Cold Lake bitumen.

ANALYTICAL TLC METHOD

1. WEIGHING STANDARD ASPHALTENES.
2. PREPARE 5 DIFFERENT KNOWN CONCENTRATIONS OF ASPHALTENES IN TOLUENE.
3. RUN THE 5 SOLUTIONS ON A SILICA GEL TLC PLATE.
4. SCRAPING OF THE ASPHALTENES ADSORBED ON SILICA GEL AT $R_F=0$.
5. DETERMINING THE ABSORBANCE COLORIMETRICALLY AT 415 NM.
6. ESTABLISHING A CALIBRATION CURVE OF THE ABSORBANCE VS. CONCENTRATION.
7. CORRELATE A SAMPLE OF UNKNOWN ASPHALTENE CONCENTRATION WITH THE CALIBRATION CURVE.

CALCULATION OF THE ASPHALTENE CONTENT

$$\frac{A_s - b}{C_s \times m} \times 100 = \text{wt\% ASPHALTENES}$$

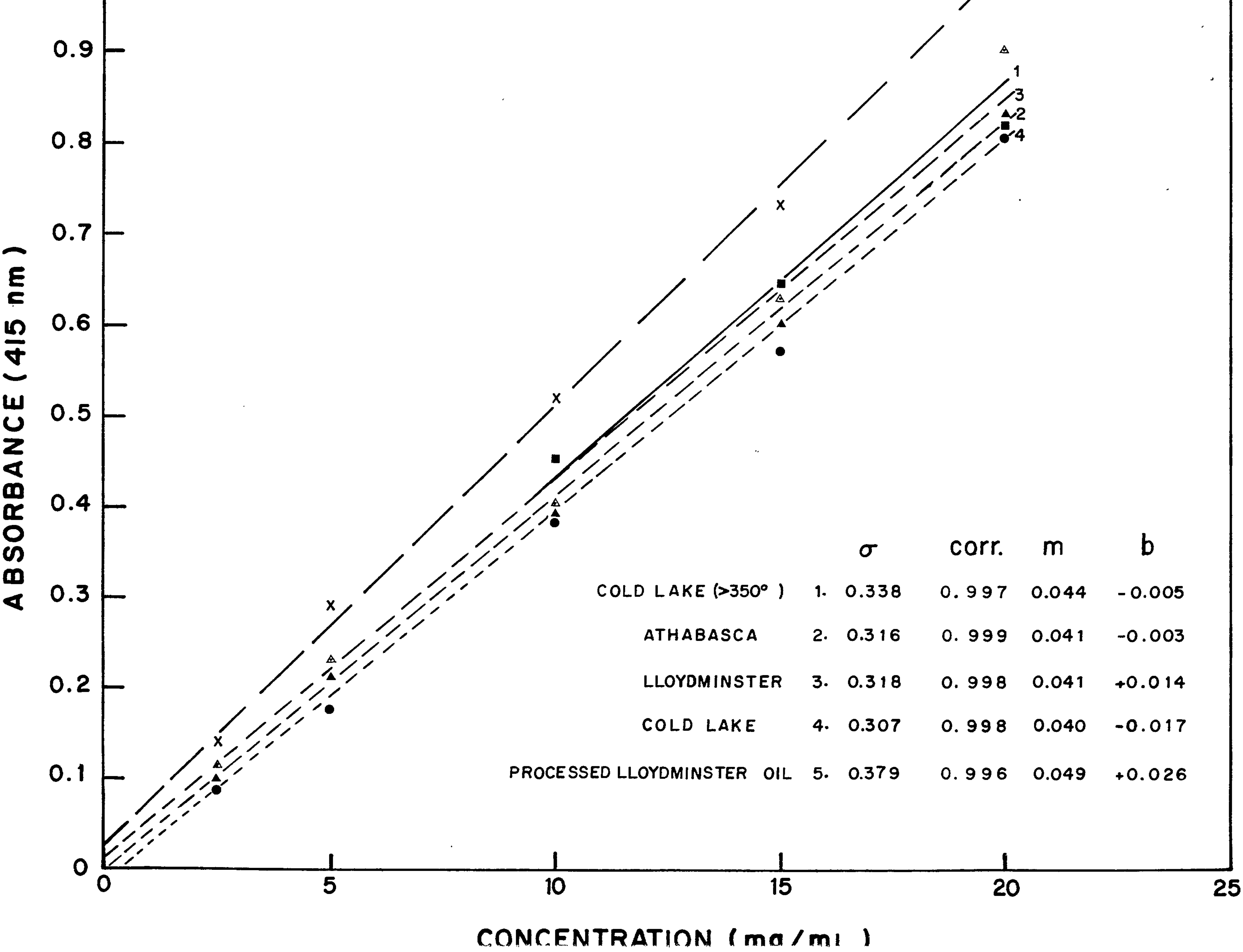
Where: A_s = absorbance of the sample

C_s = concentration of the sample in mg/mL

$b^\star$ = intercept of the curve

$m^\star$ = slope of the curve

*determined by the least square method.



		σ	corr.	m	b
COLD LAKE (>350°)	1.	0.338	0.997	0.044	-0.005
ATHABASCA	2.	0.316	0.999	0.041	-0.003
LLOYDMINSTER	3.	0.318	0.998	0.041	+0.014
COLD LAKE	4.	0.307	0.998	0.040	-0.017
PROCESSED LLOYDMINSTER OIL	5.	0.379	0.996	0.049	+0.026

ANALYSIS OF KNOWN CONCENTRATION OF ASPHALTENES BY THE TLC METHOD

SAMPLE*	WT % ASPHALTENES (PREPARED)				
	12.5	25.0	50.0	75.0	100.0
	WT % ASPHALTENES (DETERMINED)				
2	14.5	29.2	56.1	79.4	95.6
3	9.6	23.1	46.4	70.0	95.6
4	14.5	29.2	50.0	78.2	105.1
5	10.6	28.2	51.0	73.8	102.7
6	13.7	29.2	58.2	74.8	102.7
7	13.7	27.1	46.8	71.7	97.6
STANDARD DEVIATION	2.12	2.38	4.83	3.64	3.55

* SAMPLES 1 AND 8 HAVE BEEN USED AS STANDARDS TO DETERMINE THE CALIBRATION CURVES.

SAMPLE 1 $m = 0.0407$ $b = 0.0421$
SAMPLE 8 $m = 0.0477$ $b = 0.0622$

DETERMINATION OF THE ASPHALTENE CONTENT (WT %) IN PETROLEUM SAMPLES BY TWO DIFFERENT METHODS

SAMPLE	I.P.	TLC
11	16.4	17.4
12	21.0	23.8
13	-	0.3
14	20.1	21.5
15	-	1.2
16	38.0	42.4
17	26.0	27.8
18	21.7	22.6

DETERMINATION OF THE ANALYTICAL PRECISION

ANALYSIS	ASPHALTENES (WT %)			
	SAMPLE 16	SAMPLE 17	SAMPLE 18	SAMPLE 19
1	42.2	27.8	22.6	22.8
2	41.0	27.5	22.0	22.1
3	41.5	28.0	22.6	21.7
4	42.0	27.0	22.9	22.3
STANDARD DEVIATION	0.61	0.43	0.38	0.46