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QUANTITATIVE ANALYSIS OF COAL-DERIVED LIQUIDS RESIDUES BY TLC  
WITH FLAME IONIZATION DETECTION

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## ABSTRACT

A reliable method for the determination of maltenes, asphaltenes, pre-asphaltenes (MAP) and tetrahydrofuran (THF) insolubles in coal liquefaction distillation residues is needed to establish the degree of coal conversion during the development of coal liquefaction processes.

In this work a new method is described for the determination of MAP, which involves thin layer chromatography (TLC) and quantitative flame ionization detection (FID). The THF insolubles content is calculated by difference. This method is applicable to bitumen, heavy oils and coal-derived liquid distillation residues.

The maltenes are separated from the asphaltenes and pre-asphaltenes on a TLC silica gel "chromarod" using n-pentane/isopropanol (95:5) developing solvent. The asphaltenes are then separated from the pre-asphaltenes with benzene/isopropanol (80:20) developing solvent. Results are compared with the sequential solvent extraction procedure.



ANALYSE QUANTITATIVE DE RÉSIDUS LIQUIDES DÉRIVÉS DU CHARBON,  
PAR CCM (TLC) AVEC DÉTECTION PAR IONISATION DE FLAMME

par

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RÉSUMÉ

Le besoin se fait sentir de trouver une méthode fiable pour la détermination des maltènes, des asphaltènes et des pré-asphaltènes (MAP) ainsi que des insolubles dans le tétrahydrofuranne (THF) dans les résidus de distillation de liquéfaction du charbon. Cette méthode servirait à l'établissement du degré de conversion du charbon lors du développement des procédés de liquéfaction du charbon.

Ces travaux décrivent une nouvelle méthode de détermination des MAP, au moyen de la chromatographie sur couche mince (CCM) avec détection quantitative par ionisation de flamme. Le pourcentage des insolubles dans le THF est calculé par différence. Cette méthode s'applique aux résidus liquides dérivés du bitume, des huiles lourdes et du charbon.

On sépare les maltènes des asphaltènes et des pré-asphaltènes par TLC sur une tige de gel de silice "Chromarod" en utilisant une solution de n-pentane/iso-propanol (95:5) comme solvant de développement. On sépare ensuite les asphaltènes des pré-asphaltènes en utilisant un solvant composé de benzène/iso-propanol (80:30). On compare les résultats avec ceux obtenus par une méthode de fractionnement utilisant différents solvants. La répétabilité de la méthode a montré une variation de  $\pm 2\%$ .



## INTRODUCTION

At present there is no standard method to separate and quantify maltenes, asphaltenes and pre-asphaltenes (MAP) in coal-derived liquids. Solvent fractionation methods have been used frequently to separate coal-derived liquids into (MAP) (1-3). The components separate according to their solubilities in different solvents. No consistency was observed between values obtained by the different fractionation methods currently used (4-5). A liquid chromatographic method was also reported in which a sample injected onto a chromatographic column packed with glass beads is separated by sequential solvent elution (6).

In this work, we developed a procedure for the determination of MAP contents in coal-derived liquids by thin layer chromatography (TLC) with flame ionization detection (FID). Our laboratory reported a similar procedure for determining maltene and asphaltene contents in bitumen and heavy oils (7). The TLC-FID technique was also used by Selucky for the separation of saturates, aromatics, resins and asphaltenes (SARA) in coal-derived liquids (8). Our TLC separation is based on the solubility of the component-types to be analysed. The component-types are defined as follows:

maltenes: pentane solubles

asphaltenes: pentane insolubles - benzene solubles

pre-asphaltenes: benzene insolubles - tetrahydrofuran (THF) solubles.

This procedure does not require time-consuming solvent fractionation.

The separation possibilities were investigated using pure maltenes, asphaltenes and pre-asphaltenes obtained by extraction-precipitation of a coal-derived sample with the appropriate solvent. These component-types were then used as standards in the procedure. The maltenes are separated from the asphaltenes and pre-asphaltenes on a TLC silica gel "chromarod" using a n-pentane/isopropanol (95:5) developing solvent. The asphaltenes are then separated from the pre-asphaltenes with benzene/isopropanol (80:20) developing solvent. The MAP contents are determined quantitatively using an Iatroscan TH-10 FID Analyzer. The THF insolubles are then calculated by difference.

The overall time required for the analysis of 7 samples is about 1 h excluding the time necessary to weigh and dissolve the samples. Seven samples obtained from co-processing bitumen with sub-bituminous coal were analysed by this method. The repeatability of this method has been demonstrated.





## EXPERIMENTAL

INSTRUMENT AND OPERATING CONDITIONS

The Iatroscan TH-10 Analyzer, Mark III, was equipped with a flame ionization detector and a HP 3390A 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 1  $\mu$ l HAMILTON syringe was used in this work.

SOLVENTS

The n-pentane, benzene, THF and isopropanol used in this work were reagent grade.

THIN LAYER CHROMATOGRAPHY WITH FLAME IONIZATION DETECTIONSamples

Seven distillation residues boiling above 524°C (samples 1-7, Table 1) obtained from co-processing Cold Lake bitumen with Forestburg coal under different conditions were used in this study.

Standards

Maltenes, asphaltenes and pre-asphaltenes used as standards in this procedure were isolated from sample 4 by solvent fractionation using n-pentane, benzene and THF.

ProcedureA. Preparation of the standard solutions

1. Weigh accurately about 20 mg of maltenes in a 2 mL volumetric flask. Dissolve and complete to volume with benzene.
2. Weigh accurately about 15 mg of asphaltenes in a 2 mL volumetric flask. Dissolve and fill to volume with benzene.
3. Weigh accurately about 8 mg of pre-asphaltenes in a 2 mL volumetric flask. Dissolve and fill to volume with THF.



4. Apply 1.0  $\mu\text{L}$  of the standard solutions to individual silica gel-II "chromarods".

#### B. Preparation of the sample solutions

1. Weigh accurately about 50 mg of the sample (distillation residue boiling above 524°C) in a 2 mL volumetric flask. Add about 1.5 mL of THF and agitate in an ultrasonic bath for 8 min. Fill to volume with the solvent.
2. Apply 1.0  $\mu\text{L}$  of the solution to a silica gel "chromarod".

#### 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 the first developing solvent.
2. Remove the "chromarods" from the tank when the solvent front has travelled 8 cm. Allow the rods to dry at ambient temperature for a few minutes.
3. Develop the "chromarods" in a second TLC tank with benzene/isopropanol (80:20) as the developing solvent.
4. Remove the rods from the tank when the solvent front has travelled 3 cm. Allow the rods to dry for a few minutes in an oven at 120°C.
5. Place the rods in the Iatroscan TLC pyrolyser and pyrolyse the separated components in the FID.

#### CALCULATION

The maltene, asphaltene, pre-asphaltene and THF insolubles contents were calculated using the following equations:

$$(1) \text{ Maltenes (wt \%)} = \frac{W_m \times A_{ms}}{W_s \times A_m} \times 100$$

$$(2) \text{ Asphaltenes (wt \%)} = \frac{W_a \times A_{as}}{W_s \times A_a} \times 100$$



$$(3) \text{ Pre-asphaltenes (wt \%)} = \frac{W_p \times A_{ps}}{W_s \times A_p} \times 100$$

THF insolubles (wt %) = 100 - (wt % maltenes + wt % asphaltenes + wt % pre-asphaltenes).

where  $W_m, W_a, W_p$  = weight of maltenes, asphaltenes and pre-asphaltenes as standards

$W_s$  = weight of the sample to be analyzed

$A_{ms}, A_{as}, A_{ps}$  = area of the maltene, asphaltene and pre-asphaltene peaks of the sample

$A_m, A_a, A_p$  = area of the maltene, asphaltene and pre-asphaltene peaks of the standard

#### RESULTS AND DISCUSSIONS

To understand the chromatographic behaviour of the maltenes, asphaltenes and pre-asphaltenes, different chromatographic systems were investigated (7). The method used in previous work with petroleum related samples, to separate the maltenes from asphaltenes on a silica gel "chromarod" with pentane/isopropanol (95:5) mixture was also applied to coal-derived liquid samples. Selective separation of the asphaltenes from the pre-asphaltenes can be accomplished using benzene/isopropanol (80:20) mixture as developing solvent. Maltenes, asphaltenes and pre-asphaltenes previously isolated from a co-processing sample by precipitation with the appropriate solvent were used to develop the separation procedure (Fig. 1). After complete resolution of these component-types (about 45 min) the  $R_F$  of the MAP were 0.65, 0.23 and 0 respectively. The separation obtained for a co-processing sample is shown in Fig. 2.

The pre-asphaltenes are strongly retained on silica and remain at the origin. Quantitation is not affected by the presence of porphyrins in the asphaltenes or pre-asphaltenes (9). This independence of the abundance of porphyrins in the sample implies that MAP from different sources can be used as standards in this procedure.



The results obtained from the analysis of the co-processing samples by our (TLC) procedure and by sequential solvent extraction (SE) are shown in Table 2. The data obtained from these two different methods are not in agreement. Higher maltene content and lower pre-asphaltene content was obtained by the SE procedure. We believe that these differences can be explained by the passing of fine particles through the extraction thimble in the SE procedure. The presence of fine particules was observed in the maltene fractions obtained from fractionation procedure. This observation was also reported by Schultz et al. in their work on the comparison of different solvent extraction procedures (4).

The effect of the presence of the THF insolubles in the sample solution was investigated. Results on the analysis of the co-processing samples with and without the presence of the THF insolubles in the solution are shown in Table 3. The small variation observed could be explained by the change of the species which are in equilibrium in solution and the calculation procedure which is slightly different. However, allowing the THF insolubles to settle prior to spotting and using a 1  $\mu$ L syringe which does not allow fine particles to pass through the needle tip, overcame the effect of these insolubles had on the results.

The precision of the procedure was determined using three co-processing samples (Table 4). The average standard deviation coefficients for 10 replicate analyses for maltenes, asphaltenes, pre-asphaltenes and THF insolubles were, 1.54, 1.45, 0.91 and 1.64 respectively. Comparison with the SE procedure was not possible because of the small amounts of co-processing sample available. The standard deviation coefficients show (Table 4) this method is reliable. Because of the short time required for analysis, precision of the determination can be improved by replication.

Linearity of the response with the concentration is important in quantitation. Four sample solutions of concentration range from 10 to 45 mg/mL were prepared. In this case, dilution of a stock solution was not possible because of the presence of the THF insolubles in the solution. The response was linear over the concentration range from about 20 to 45 mg/mL and which falls within the sample concentration range used in this procedure (Fig. 3).

We have found that quantitative TLC with FID is a very promising technique for the analysis of bitumens, heavy oils and synthetic fuels (7,10). It avoids the problems encountered in high performance liquid chromatography





(HPLC) such as lack of a suitable detection mode, and time-consuming procedure for calibration. Moreover, quantitative recovery of the material from the column is difficult. In this work we have demonstrated that time-consuming fractionation with solvents can be avoided.

#### CONCLUSION

This TLC method has great potential as a standard method for the quantification of MAP in coal-derived liquids. It is rapid, accurate, needs a small amount of sample and does not involve complicated instrumentation.



## CAPTIONS

- Fig. 1 - a) Chromatogram of standard maltenes on "chromarod" using pentane/isopropanol (95:5) mixture.
- b) Chromatogram of standard asphaltenes on "chromarod" using benzene/isopropanol (80:20) mixture.
- c) Chromatogram of standard pre-asphaltenes on "chromarod" using benzene/isopropanol (80:20) mixture.

Fig. 2 - Typical chromatogram showing the component-type separation of a co-processing sample using pentane/isopropanol (95:5) and benzene/isopropanol (80:20) mixtures successively.

Fig. 3 - Linearity of the response of maltenes (M), asphaltenes (A) and pre-asphaltenes (P).



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Table 1 - Gross composition of the co-processing samples

Samples	Res. <524°C	Res. >524°C
	afr, wt %	afr, wt %
1	79.8	20.2
2	70.5	29.5
3	84.9	15.1
4	81.4	18.6
5	82.9	17.1
6	80.6	19.4
7	80.4	19.6

afr = ash free residue





Table 2 - Analysis of the co-processing residues >524°C by TLC-FID and sequential extraction procedure (SE)

Samples	wt %							
	Maltenes		Asphaltenes		Pre-asphaltenes		THF insolubles	
	TLC	SE	TLC	SE	TLC	SE	TLC	SE
1	50.3	54.5	25.7	39.7	12.8	0.1	11.2	5.7
2	41.1	48.4	33.9	34.6	11.4	3.5	13.6	13.4
3	43.4	44.5	26.1	26.0	19.4	4.0	20.1	25.5
4	29.4	35.1	31.1	36.6	14.4	1.1	25.1	27.2
5	37.1	47.9	27.3	25.8	17.3	4.8	18.3	21.5
6	26.1	33.4	22.4	25.3	26.8	4.6	24.7	36.7
7	46.0	-	26.6	-	19.5	-	7.9	-

Table 3 - Analysis of the THF solubles co-processing residues >524°C by TLC-FID

Samples	wt %					
	Maltenes		Asphaltenes		Pre-asphaltenes	
1	51.0	(56.6)*	35.3	(29.0)	13.7	(14.4)
2	47.7	(47.6)	42.2	(39.2)	10.1	(13.2)
3	39.6	(43.0)	36.3	(32.7)	24.1	(24.3)
4	37.6	(39.2)	44.5	(41.5)	17.9	(19.3)
5	41.3	(45.4)	35.6	(33.4)	23.1	(21.2)
6	35.3	(34.7)	29.0	(29.7)	35.7	(35.6)
7	52.8	(49.9)	31.8	(28.9)	15.4	(21.2)

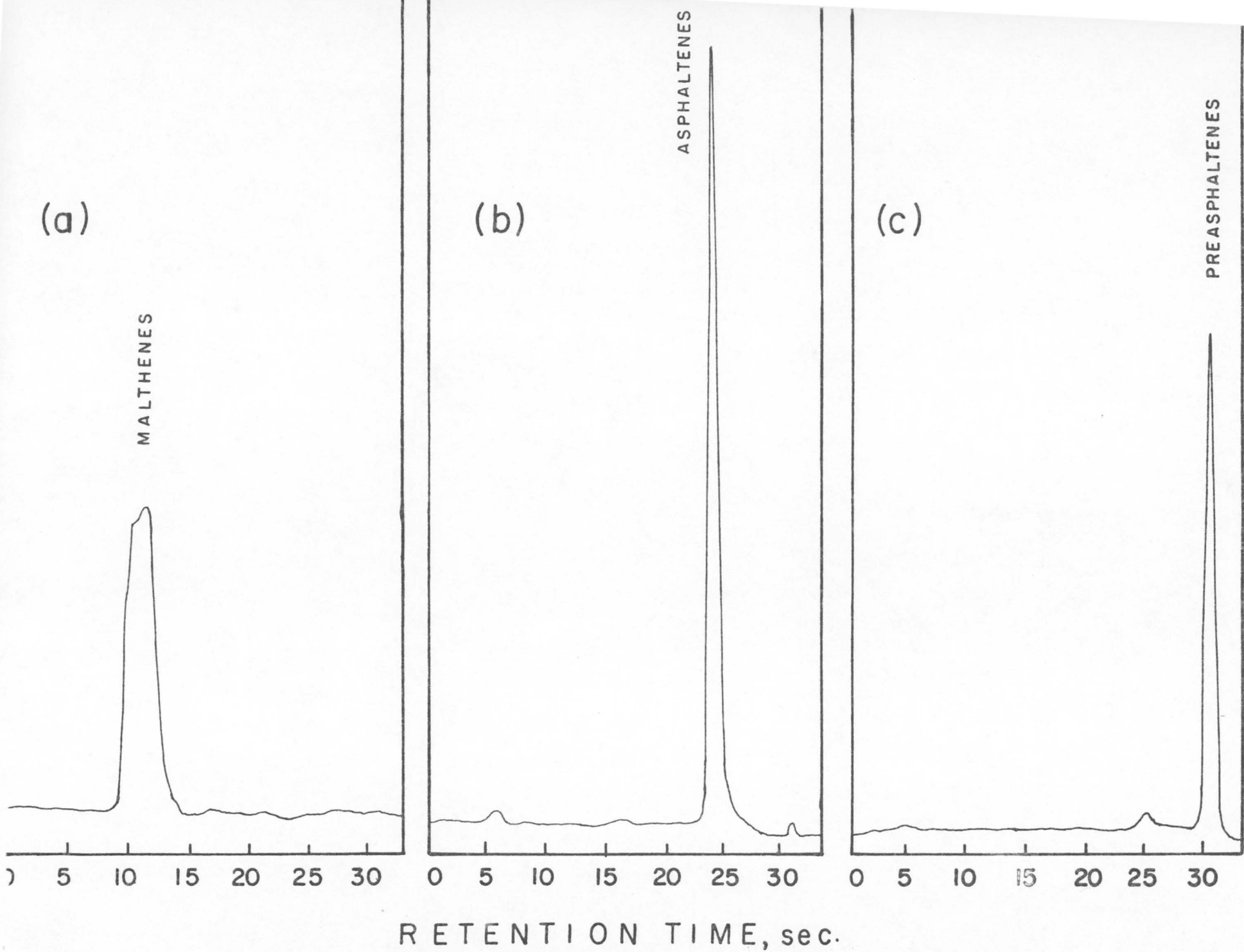
\* Numbers in brackets represent results obtained from analysis of total co-processing residue >524°C



Table 4 - Determination of the analytical precision of the TLC method  
(Average of 10 replicate analyses of the sample)

Samples	wt %			
	Maltenes	Asphaltenes	Pre-asphaltenes	THF insolubles
1	51.1	27.4	11.4	10.1
4	30.4	28.7	16.1	24.6
5	36.8	24.9	18.6	19.7
Average	—	—	—	—
std. dev.	1.54	1.45	0.91	1.64
$\sigma$				





(a)

MALTHENES

(b)

ASPHALTENES

(c)

PREASPHALTENES

RETENTION TIME, sec.



