



Energy, Mines and  
Resources Canada

Énergie, Mines et  
Ressources Canada

## CANMET

Canada Centre  
for Mineral  
and Energy  
Technology

Centre canadien  
de la technologie  
des minéraux  
et de l'énergie

### HYDROCARBON-TYPE SEPARATION OF MIDDLE DISTILLATES AND ASPHALT CEMENT FRACTIONS

S. Coulombe and M.A. Poirier

FEBRUARY 1985

ENERGY RESEARCH PROGRAM  
ENERGY RESEARCH LABORATORIES  
DIVISION REPORT ERP/ERL 85-14 (OPJ)

ERP/ERL. 85-14 (OPJ)

ABSTRACT

This paper describes a hydrocarbon-type separation method which allows the separation of heavy oil and synthetic fuel fractions boiling above 200° C of deasphalted samples into saturates, mono-diaromatics, polynuclear aromatics and resins. These fractions could be used for further separation and characterization using other analytical and spectroscopic techniques. The method has been tested on middle distillate fractions and on asphalt cement samples. The separation of a 1.5g sample can be performed in about 3.5 h. Repeatability and yield recovery results are also presented.

## RÉSUMÉ

Dans cette étude, nous présentons une méthode de séparation des hydrocarbures par famille. Cette méthode permet la séparation d'huiles lourdes et de carburants synthétiques déasphaltés, de point d'ébullition supérieur à 200°C, en hydrocarbures saturés, mono-diaromatiques, polyaromatiques et résines. Ces fractions peuvent être utilisées pour des études ultérieures en utilisant des techniques spectroscopiques. Nous avons appliqué cette méthode à des échantillons de distillats moyens et de bitumes routiers. La séparation sur une prise d'échantillon de 1,5 g peut être obtenue en 3,5 heures. La répétabilité ainsi que le rendement de la récupération de la méthode sont présentés.

## INTRODUCTION

Hydrocarbon-group type analysis is recognized as a very useful technique for the chemical characterization of feedstocks and petroleum products (1-5). From the literature it appears that each laboratory uses its own method to analyze distillate fractions. This paper reviews some of the existing methods and describes one developed in our laboratory.

The API-60 method developed by the US Bureau of Mines is probably the most well-known separation method (1). Ion-exchange resins are used to remove the acids and bases which are later recovered with convenient solvents. The neutral nitrogenous compounds are then removed using  $\text{FeCl}_3$ -Attapalpus clay. The neutral eluate is then percolated on a dual alumina-silica column which allows the separation of the saturated, mono-, di- and polynuclear aromatic hydrocarbons using solvents of increasing displacement capacity. This method has some merit but it is very time consuming since it uses an open column with gravity elution. Another drawback is the large amount of adsorbents and sample required to perform the analysis.

The SARA (saturates, aromatics, resins and asphaltenes) method (2) developed by Gulf scientists is a modification of the API-60 method. Here the sample is introduced in a thimble at the top of a column containing ion-exchange resins and  $\text{FeCl}_3$  with Attapalpus clay. Continuous extraction with a paraffinic solvent leaves the asphaltenes behind while

the maltenes are eluted through the resins and clay. The non-retained material is then percolated through a silica-alumina column to give the saturates and aromatics. The method is less time-consuming than the API 60 method but in some cases the complete recovery of the resins from the ion-exchange column is not possible which could falsify the quantitation results.

The SAPA (saturates, aromatics, polar aromatics and asphaltenes) method is a modification of the SARA method developed at the Laramie Energy Technology Center (LETC) in which the Attapalgus clay is replaced by alumina (3,4). Researchers at LETC and Alberta Research Council reported that the reproducibility problems observed with the clay were associated with the lack of quality control during its production. They also observed that the clay as received contained non negligible amounts of water and organic material.

Another modification to the API-60 method was reported from our laboratory (5). In this case the sample is first deasphalted with a paraffinic solvent and the maltenes (the soluble portion) are separated under pressure on a dual packed silica-alumina column into saturates, monoaromatics, diaromatics, polynuclear aromatics, polar and basic compounds with solvents of increasing polarities.

More recently, Vercier and co-workers at TOTAL-Compagnie Française de Raffinage developed a procedure similar to ours where the sample is first deasphalted using an ELF extractor unit (6,7).

It has been recognized that first the sample has to be deasphalted, then the maltenes are separated into saturates, mono-, di- and polynuclear aromatics and resins in a sequence similar to the Sawatzky method but using different eluting solvents (5). Vercier emphasized the importance of a separation method leading to the conventional classes (asphaltenes, resins, saturates and aromatics). However, one must be aware that the asphaltenes are defined by the solvent which is used to precipitate them. On the other hand, Vercier pointed out that whatever solvent is used, the sum of asphaltenes and resins will remain constant and therefore the saturates and aromatics would not be affected.

Numerous papers have been published about the use of high performance liquid chromatography (HPLC) for rapid compound-type separation (8-16). None of these methods could fractionate the sample in many classes like the previous liquid chromatographic methods. Moreover, these methods are not well adapted for the separation of large amounts of sample in view of further characterization. However, HPLC seems to be well adapted for the analysis of light distillate fractions such as naphthas.

The major drawback of HPLC methods is the quantitation because the usual detectors do not respond the same way to the different classes of compounds. Colin and Vion have demonstrated how the response factor could vary with the type of compound when using a refractive index detector (17). Moreover, the response factors also vary within the same class of compounds. In this regard Miller et al. pointed out that the use of HPLC for quantitation is questionable even for routine analysis (18).

In order to avoid problems associated with HPLC methods, a thin-layer chromatography (TLC) method using flame ionization detection was developed in our laboratory (19). This method allows a rapid quantitation of saturates, mono- and diaromatics, polynuclear aromatics and resins using successive developing solvent mixtures on chromatographic rods which are then placed into a TLC pyrolyzer for quantitation with a flame ionization detector. It is rapid and repeatable but destructive.

In order to recover the fractions, this simplified method was adapted to a scale similar to the Sawatzky method (5). The deasphalted sample is separated into four classes (saturates, mono-diaromatics, polynuclear aromatics and resins) on a dual-packed silica-alumina column using n-pentane, 10% toluene in pentane, 5% ethyl acetate in toluene and finally methanol followed by benzene then pentane. The purity of individual fractions was also checked by infrared and the results are presented. This method has been particularly adapted for the hydrocarbon-type separation of asphalt cements.

## EXPERIMENTAL

### Sample

The method was tested on two sets of a samples having different boiling ranges. The first set consisted of two middle distillates (190-350°C) prepared from Suncor and Syncrude synthetic crudes. The second set of samples consisted of three asphalt cements of 85-100 penetration.

### Deasphalting

Deasphalting of asphalt cement samples was performed prior to hydrocarbon-type separation. The asphaltenes were precipitated at room temperature by adding 20 vol. of n-heptane to 1 vol. of sample. The slurry was stirred for 15 minutes in an ultrasonic bath and asphaltenes (n-heptane insolubles) were separated by filtration on a Whatman filter paper No. 1. The asphaltenes were then washed with 10 vol. of n-heptane and dried at 50°C under reduced pressure. The maltenes (n-heptane solubles) and washing were combined and the solvent was removed using a Buchi Rotavapor. The asphaltenes obtained by this method also contained the toluene insolubles.

### Compound-type separation

About 1.4 g of sample (deasphalted asphalt cement or middle distillate) was separated into saturates, mono-diaromatics, polynuclear aromatics and resins on a dual packed silica gel-alumina column. The separation schematic is shown in Fig. 1. The column consists of a vertical stainless steel tube (137 x 1.25 cm o.d.) packed in its lower half length with 37 g of activated Davison grade 12 silica gel and in its top half length with 47 g of activated F-20 alumina.



The following solvent sequence was used to elute the corresponding compound-type concentrates: n-pentane (330 mL), 10% toluene in n-pentane (500 mL), 5% ethyl acetate in toluene (130 mL) and finally methanol (200 mL) followed by toluene (100 mL) and n-pentane (100 mL). Solvents were eluted at a flowrate of about 5 mL/min using a Lapp pump LS-30. Effluents were collected according to these fractions and solvents were evaporated using a Buchi Rotavapor. Heat was applied only in the case of the asphalt cement samples because of the low boiling range of the middle distillates.

## RESULTS AND DISCUSSION

### Separation of middle distillate and asphalt cement samples

Table I shows the hydrocarbon-type separation obtained by this simplified method on various samples. Two sets of samples were selected to test the method with samples having different boiling ranges. The first two samples are middle distillates. It can be seen that the polynuclear aromatics content is very small and reported as traces. This was expected since their final boiling point is low (lower than 350°C). The three asphalt cement samples are significantly different in their compound-type distribution. Because of their higher boiling range an increase in polyaromatic and resin content is expected.

The recovery yield of the method is different for the two sets of samples. Losses were expected with the middle distillates. The solvent evaporation of the middle distillates is very critical because of their low boiling range. This is especially true of the saturate fraction. Gas chromatograms of the sample taken at different stages of the evaporation step showed that the hydrocarbons of low boiling point are gradually lost upon longer solvent stripping. Comparison with FIA analyses of these two samples showed a loss of  $\approx 5\%$  for MD-1 and  $\approx 4\%$  for MD-2. As determined by the GC analyses the aromatics do not seem to be affected to the same extent by the evaporation step. For the asphalt cement samples there is obviously no difficulty in solvent evaporation. The losses are attributed to a small portion of the polar materials that remain on the column. However, the recovery yield is high and determination of the resin content could be obtained by difference with the sum of all the hydrocarbon type contents.

### Efficiency of separation

The hydrocarbon-type fractions were analyzed by infrared spectroscopy to check for possible overlap between the various classes. Comparison of the spectra is shown in Fig. 2. The saturates spectrum shows bands at 2860 and 2930  $\text{cm}^{-1}$  (C-H absorption) and at 1380 and 1460  $\text{cm}^{-1}$  (C-C absorption) characteristic of the aliphatic compounds. The aromatics spectra show the same bands as the saturates characteristic of the aliphatic substitution on the aromatic rings. However, the spectrum show one additional band at 1600  $\text{cm}^{-1}$  characteristic of the C=C absorption of aromatic compounds. The spectra show no overlap between these two fractions. The sequence of solvents used in the method was previously demonstrated to be very selective for the separation of the saturates from the aromatics (5). Although collection of the fractions is obtained volumetrically, a neat separation of the mono-diaromatic fraction from the polyaromatic fraction is monitored visually. Separation of the polyaromatic fraction from the resin fraction is always a compromise. The use of 5% ethyl acetate in toluene allows the complete elution of the polyaromatics which in other cases would remain with the resins. However, the infrared shows about 2-3 wt % based on the carbonyl band at 1700  $\text{cm}^{-1}$  in the polyaromatic fraction. Previous results have shown that toluene by itself does not elute the polyaromatics completely (5). Repeatability of the method

Tables II and III show the repeatability results on middle distillate and asphalt cement samples respectively. The relative standard deviation for the aromatic fraction is relatively low for the middle distillate sample. The slightly higher standard deviation for the saturate fraction could be explained by the solvent evaporation

problems. However, it is still at an acceptable level while it is not for the resin fraction where the low content (about 20 mg for the total fraction) is difficult to quantify. However, the relative standard deviation on the recovery is still good probably because the low resin content affects the total amount only slightly. Inspection of the results in Table II also shows that the recovery yield depends on the saturate content. These results also supported the assumption that losses in middle distillate samples are mainly due to low boiling point material evaporating along with the solvent. Therefore precautions must be taken when evaporating the solvent from such a sample.

Repeatability on the asphalt cement samples is shown in Table III. These results show that the relative standard deviation is lower than 5% for most of the fractions. The total recovery yield varies with the amount of resins recovered. This is supported by the fact that the losses in such heavy material are due to strong retention of polar and basic material on the column.

### CONCLUSION

In this study we have developed a chromatographic method which allows hydrocarbon-type separation of middle distillates and asphalt cements. Although the analysis of a sample takes about 3.5 hours, several hydrocarbon-type fractions could be obtained and could be used for further analysis. The method is particularly well adapted for the analysis of asphalt cements and is currently used in our laboratory for this purpose. Analysis of middle distillates could be performed if precautions are taken in the evaporation step. The method would be more appropriate for the analysis of middle distillates having an initial boiling point of 200°C.

## REFERENCES

1. D.E. Hirsch, R.L. Hopkins, H.J. Coleman, F.O. Cotton and C.J. Thompson. Separation of high-boiling petroleum distillates using gradient elution through dual-packed (silica gel-alumina gel) adsorption columns. Anal. Chem. 44: 915-9 (1972).
2. D.M. Jewell, E.W. Albaugh, B.E. Davis and R.G. Ruberto. Combination of techniques for the characterization of residuals. Preprints ACS Div. Petrol. Chem. 17: F81-91 (1972).
3. D. Wallace, K.P. Thomas, J. Starr and S.M. Dorrence. Characterization of Oil Sand Resources. Report on the Activities concerning Annex I of the U.S. Canada Cooperative Agreement on Tar Sand and Heavy Oil, 77 pp. (1984).
4. R.V. Barbour, S.M. Dorrence, T.L. Vollmer and J.D. Harris. Pyrolysis of Utah tar sands. Preprints ACS Div. Fuel Chem. 21: 278-89 (1976).
5. H. Sawatzky, A.E. George, G.T. Smiley and D.S. Montgomery. Hydrocarbon-type separation of heavy petroleum fractions. Fuel 55: 16-20 (1976).
6. P. Vercier. Structure des fractions lourdes. Rev. Inst. Français Petrol. 36: 45-63 (1981).
7. P. Vercier, B. Thiault, M. Morton, J.M. Colin, P. Doligez and A. Allain. A routine method for characterizing heavy ends of petroleum. Preprints ACS Div. Petrol. Chem. 26: 882-97 (1981).
8. J.C. Suatoni and R.E. Swab. Rapid hydrocarbon group-type analysis by high performance liquid chromatography. J. Chromatogr. Sci. 13: 361-6 (1975).
9. J.C. Suatoni and H.R. Garber. Hydrocarbon group-type analysis of petroleum fractions (b.p. 190<sup>o</sup> -360<sup>o</sup>C) by high performance liquid chromatography. J. Chromatogr. Sci. 14: 546-8 (1976).
10. J.C. Suatoni and R.E. Swab. Preparative hydrocarbon compound type analysis by high performance liquid chromatography. J. Chromatogr. Sci. 14: 535-7 (1976).
11. J.C. Suatoni and R.E. Swab. HPLC preparative group-type separation of olefins from synfuels. J. Chromatogr. Sci. 18: 375-8 (1980).
12. C. Bollet, J.C. Escalier, C. Souteyrand, M. Gaude and R. Rosset. Rapid separation of heavy petroleum products by high-performance liquid chromatography. J. Chromatogr. 206: 289-300 (1981).
13. P. Pei, J. Britton and S. Hsu. Hydrocarbon type separation of lubricating base oil in multigram quantity by preparative HPLC. J. Liq. Chromatogr. 6: 627-45 (1983).

14. S. Matsushita, Y. Tada and T. Ikushige. Rapid hydrocarbon group analysis of gasoline by high-performance liquid chromatography. J. Chromatogr. 208: 429-32 (1981).
15. K. Jinno, H. Nomura and Y. Hirata. Group-type analysis of gasoline range materials by high performance liquid chromatography. J. High Res. Chromatogr. and Chromatogr. Comm. 3: 503-6 (1980).
16. T.V. Alfredson. High-performance liquid chromatographic column switching techniques for rapid hydrocarbon group-type separations. J. Chromatogr. 218: 715-28 (1981).
17. J.M. Colin and G. Vion. Routine hydrocarbon group-type analysis in refinery laboratories by high-performance liquid chromatography. J. Chromatogr. 280: 152-8 (1983).
18. R.L. Miller, L.S. Ettore and N.G. Johansen. Quantitative analysis of hydrocarbons by structural group-type in gasolines and distillates. J. Chromatogr. 259: 393-412 (1983).
19. M.A. Poirier and A.E. George. A rapid method for hydrocarbon-type analysis of heavy oil and synthetic fuels by pyrolysis thin layer chromatography. Energy Sources 7: 151-64 (1983).

## FIGURE CAPTIONS

- Fig. 1 - Hydrocarbon-type separation schematics
- Fig. 2 - Infrared analysis of hydrocarbon-type fractions (MDS=middle distillate saturates, AS=asphalt saturates, MDM=middle distillate mono and diaromatics, AM=asphalt mono and diaromatics, AP=asphalt polyaromatics, MDR=middle distillate resins, AR=asphalt resins)



Table I - Hydrocarbon-type separation of asphalt cement samples (A) and middle distillates (MD) (wt %)

Sample	Saturates	Mono-diaromatics	Polyaromatics	Resins	Recovery
MD-1	68.74	21.34	traces	2.84	92.92
MD-2	57.37	33.59	traces	3.28	94.24
A-1	25.4	23.1	28.5	19.2	96.2
A-2	21.4	19.6	27.4	30.1	98.5
A-3	22.6	19.1	26.7	29.1	97.5
A-4	17.4	17.1	16.8	46.3	97.6
A-5	17.7	26.3	20.2	35.3	99.5

Table II - Repeatability of the hydrocarbon-type separation of a middle distillate sample (MD-1) \*

No.	Saturates	Mono-diaromatics	Resins	Recovery
1	68.83	21.05	2.51	92.39
2	67.45	21.75	2.25	91.45
3	68.00	22.03	3.08	93.11
4	71.23	22.17	2.59	95.99
5	69.26	21.14	2.42	92.82
6	69.60	20.31	4.60	94.51
7	69.90	21.57	2.48	93.95
8	64.00	21.42	3.63	89.05
9	70.56	20.47	2.30	93.33
10	68.61	21.52	2.50	92.63
Average	68.74	21.34	2.84	92.92
Std.Dev.	2.02	.61	.75	1.85
Rel.S.D.(%)	2.94	2.86	26.4	1.99

\* Only traces of polynuclear aromatics were observed.

Table III - Repeatability of the hydrocarbon-type separation of asphalt cements (wt %)

Sample No.		Saturates	Mono-diaromatics	Polyaromatics	Resins	Recovery
A-6	1	17.7	26.3	20.2	32.8	97.0
	2	16.5	25.5	21.5	34.7	98.2
	3	17.0	26.0	21.8	32.7	97.5
	Ave.	17.1	25.9	21.2	33.4	97.6
	S.D.	0.6	0.4	0.9	1.1	0.6
	Rel.S.D.	3.5	1.6	4.0	3.4	0.6
A-7	1	20.6	19.2	25.7	32.7	98.2
	2	20.2	20.0	26.5	30.1	96.8
	3	19.7	20.5	25.2	31.6	97.0
	Ave.	20.2	19.9	25.8	31.5	97.3
	S.D.	0.5	0.7	0.7	1.3	0.8
	Rel.S.D.	2.2	3.3	2.5	4.1	0.6
A-8	1	22.3	20.3	28.5	26.4	97.5
	2	21.5	19.8	27.8	30.1	99.2
	3	21.2	20.7	29.0	25.6	96.5
	Ave.	21.7	20.3	28.4	27.4	97.7
	S.D.	0.6	0.5	0.6	2.4	1.4
	Rel.S.D.	2.6	2.2	2.1	8.8	1.4



