Analysis of Heavy Oils by Thin-Layer Chromatography with Flame Ionization Detection[†]

Yojiro YAMAMOTO

Research Center, Maruzen Petrochemical, Co., Ltd,
Minamikaigan 3, Goi, Ichihara-shi, Chiba 290

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Several rapid methods for compositional analysis of heavy oils by thin layer chromatography with flame ionization detection (FID-TLC) were investigated. Separating into four fractions, Saturates, Aromatics, Resins, and Asphalten, SARA analysis of heavy oils could be accurately performed by three stage development using *n*-hexane, toluene, and tetrahydrofuran. Detailed hydrocarbon type analysis of Maltene (Ma) in heavy oils could be performed adequately by using chemically bonded silica gel thin layer rods, which possess an aminopropyl or a cyanopropyl functional group, as the stationary phase. Saturates (Sa), Monoaromatics (M-Ar), Diaromatics (D-Ar), Triaromatics (T-Ar), Polyaromatics (P-Ar), and Polar compounds (Po) could be accurately determined. The standard deviation and the coefficient of variation in repeated measurements by FID-TLC method were as low as 1.5 wt% or less and 10% or less, respectively. A silica gel thin layer rod coated partially with silver nitrate was prepared; and Sa, Olefins (Ol), and Aromatics (Ar) in heavy distillates could be accurately determined by using the rod as the stationary phase. The coefficient of variation in repeated measurements by this method was as low as 8% or less.

1. Introduction

The development of technology to produce light fractions from heavy oils has become an important subject of research. Characterization of heavy oils and their products is necessary for understanding the reactions involved in the treatment of heavy oils.

Since heavy oils comprise a variety of structurally complex compounds, it is almost impossible to isolate them. Compositional analysis to determine the contents of various fractions with similar chemical properties in heavy oils provides an important characteristic means. Adsorption column chromatography with silica gel¹⁾ or alumina gel²⁾ has been generally used for analyzing chemical compositions of heavy oils, but the method has certain drawbacks; it is time-consuming and it requires large quantities of solvents. Thus, much interest in and study on high performance liquid chromatography (HPLC) are being made to replace the method for many applications.^{3)–5)} However, any method using HPLC will have shortcomings in quantitation. Unsatisfactory quantitative analysis of HPLC stems mainly from the difference in the sensitivity response of each component to the RI or to the UV

detector.

Although thin layer chromatography also has shortcomings in quantitation, it has, at the same time, such advantages as high separability, simple and rapid procedures, and smaller sample requirement. Moreover, some of the shortcomings have been removed by the development of thin layer chromatography with flame ionization detection (FID-TLC) which is now used in many applications.^{6)–9)}

In this study, several rapid methods for compositional analysis of heavy oils by FID-TLC have been investigated.

2. Experimental

2.1 Materials

The following 6 samples of heavy oils were used: three atmospheric residues (AR), Arabian Light (AL), Arabian Heavy (AH), and Iranian Heavy (IH); and those hydrocracked products (HCRP), AL-HCRP, AH-HCRP, IH-HCRP. The following 2 samples of heavy distillates (HD) were also used: HD from thermal cracked products (TCRP) of AH-vacuum residue (VR) and Athabasca oil sand (AB)-VR.

As standard samples, *n*-dodecane, *n*-eicosane, 1-dodecene, 1-eicosene, *n*-pentacosane, *n*-dodecylbenzene, *n*-octadecylbenzene, acenaphthene, 2,6-dimethylnaphthalene, 1-ethylnaphthalene, anthra-

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cene, 9,10-dimethylantracene, phenanthrene, and chrysene (guaranteed or extra pure reagents obtained from Tokyo Kasei Kogyo) were used. As developing solvents for column chromatography or FID-TLC, *n*-hexane, cyclohexane, benzene, toluene, methanol, and tetrahydrofuran (guaranteed or for liquid chromatography use of Wako Pure Chemical Industries) were used.

For adsorption column chromatography, silica gel (Silica Gel 60 of Merck) activated at 250 °C for 20 hours and alumina gel (of chromatography use of Wako) activated at 400 °C for 20 hours were used.

2.2 Apparatus and Method

2.2.1 FID-TLC

Iatroscan TH-10 (Iatron Laboratories Inc.) was used for FID-TLC analysis. Chromarod S and SII (thin layer rod sintered with silica gel) and Chromarod A (thin layer rod sintered with alumina gel) were used as stationary phases. C-R1A type Datalyzer (Simadzu) was used for treatment of FID data.

2.2.2 Column Chromatography

Separating into four fractions, namely, Saturates, Aromatics, Resins, and Asphaltene (SARA), SARA analysis of heavy oils by column chromatography was carried out according to the ASTM proposed method¹⁰ and Iijima's method²⁰. 2 g of sample was dissolved in 60 ml of heptane. Insoluble asphaltene (As) was separated from the soluble maltene (Ma) which was introduced into a column packed with silica gel or alumina gel. The ratio of Ma to gel was 40. Saturates (Sa), Aromatics (Ar), and Resins (Re) were eluted successively by column chromatography with 300 ml each of *n*-heptane, benzene, and 50% methanol-50% benzene mixture.

Hydrocarbon type separation of Ma by column chromatography was carried out using a modified method of USBM-API.¹⁰ 1 g of Ma dissolved in 10 ml of cyclohexane was introduced into a column packed with silica gel and alumina gel. The ratio of Ma to gel was 50 for each gel. Sa, Monoaromatics (M-Ar), Diaromatics (D-Ar), Triaromatics (T-Ar), and Polyaromatics plus Polar compounds (P-Ar+Po) were eluted successively by column chromatography with 700 ml each of cyclohexane, 5% benzene-95% cyclohexane mixture, 15% benzene-85% cyclohexane mixture, 70% benzene-30% cyclohexane mixture, and 50% methanol-50% benzene mixture.

2.2.3 Preparative HPLC

HPLC system 500 (Waters) was used for preparative HPLC analysis, and silica gel (Silica gel 60 of Merck) coated with AgNO₃ was used as the stationary phase as reported in our paper.¹¹

3. Results and Discussion

3.1 SARA Analysis by FID-TLC

At first, a rapid method for SARA analysis of heavy oils by FID-TLC was investigated.¹²⁾

3.1.1 Analytical Conditions

Since accuracy of analysis by FID-TLC largely depends on analytical conditions such as developing solvent and method, weight of sample loaded in TLC and combustion conditions in FID, these conditions must be thoroughly investigated for each sample.

In this study, combustion conditions were adjusted to the optimum conditions described elsewhere,¹³⁾ the developing method was examined, and weight of sample loaded was assessed.

The three stage development was applied to clearly and reproducibly separate the four fractions, Sa, Ar, Re, and As, from each other. The optimum solvent in each stage development was investigated. Development distances of the first, second, and third stage developments were 10 cm, 5 cm, and 2.5 cm, respectively. Because of the lack of marked differences among the solvents of from C₅ to C₇ saturated hydrocarbons to develop Sa, *n*-hexane was selected for the first stage development. Carbon disulfide, carbon tetrachloride, and toluene were selected to develop Ar in the second stage; and ethyl ether, ethyl acetate, and tetrahydrofuran were selected to develop Re in the third stage. Separating characteristics and repeatability were examined using various combinations of these nine solvents.

When carbon disulfide and carbon tetrachloride were used in the second development, the peaks of Ar and Re overlapped each other due to insufficient development of Ar, stemming probably from insufficient polarity of the developing solvents. FID-TLC chromatograms developed

1st solv.	<i>n</i> -Hexane	<i>n</i> -Hexane	<i>n</i> -Hexane
2nd solv.	Toluene	Toluene	Toluene
3rd solv.	Ethyl ether	Ethyl acetate	THF

Fig. 1 FID-TLC Chromatograms of AH-AR Developed with Three-stage Solvents

Table 1 Comparison of Solvents Used for Development in Composition Analysis by FID-TLC

No.	Developing Solvent			Composition (wt%)				CV (%)
	1st	2nd	3rd	Sa	Ar	Rs	As	
1	<i>n</i> -Hexane	Toluene	Ethyl ether	27.1	55.9	5.3	11.7	1—7
2	<i>n</i> -Hexane	Toluene	Ethyl acetate	26.7	57.7	6.2	9.4	2—5
3	<i>n</i> -Hexane	Toluene	THF	25.7	55.4	14.3	4.5	1—3

with toluene in the second development, and ethyl ether, ethyl acetate, and tetrahydrofuran in the third development are shown in Fig. 1. Mean values of compositions and coefficients of variance of the measurements repeated 5 times are listed in Table 1.

Re were not clearly separated when ethyl ether and ethyl acetate were used. Repeatability by tetrahydrofuran was the best, though hardly any difference existed among them. It became clear from the separating characteristics and repeatability that combination of *n*-hexane for the first stage, toluene for the second stage, and tetrahydrofuran for the third stage was most suitable for development.

Spotting 1 μ l of the sample solution containing 1~15wt% of three AR, two VR, and the HCRP, the relation between weight of sample loaded,

ranging from 10 to 150 μ g, and contents of components were examined. Mean values for 5-repeated measurements are shown in Figs. 2~4.

Fig. 2 Composition Analysis of AR for Various Weights of Sample Loaded

Fig. 3 Composition Analysis of VR for Various Weights of Sample Loaded

Fig. 4 Composition Analysis of HCRP for Various Weights of Sample Loaded

Table 2 Comparison of FID-TLC and SARA Analysis (wt %)

Sample	FID-TLC				SARA-1*1)				SARA-2*2)			
	Sa	Ar	Rs	As	Sa	Ar	Rs	As	Sa	Ar	Rs	As
AL-AR	34.7	55.8	7.7	1.8	43.7	45.9	6.6	3.7	55.9	32.2	8.2	3.7
AL-HCRP	45.2	49.4	3.6	1.7	60.9	33.8	3.2	2.1	76.2	18.3	3.4	2.1

*1) Using the silica gel column chromatography.
*2) Using the alumina gel column chromatography.

Although these figures showed that the content of each component varied with the weight of sample loaded up 40 µg, the content hardly varied with the weight varying in the range from 100 to 150 µg.

3.1.2 Rapid Method for SARA Analysis

Procedures for rapid analytical method to determine the contents of Sa, Ar, Re, and As by FID-TLC are described. It takes about 2 hours to analyze 10 samples.

- (1) Hang a rod for 10 minutes in the humidity tank containing NaNO₂ aq. solution.
- (2) Spot 1 µl of the sample toluene solution adjusted to a concentration of 10 wt% on the rod with a 1 µl glass capillary for TLC.
- (3) Hang the rod for 10 minutes in the humidity tank again.
- (4) Develop it up to 10 cm on the rod after having it hung in the developing tank containing *n*-hexane for 10 minutes.
- (5) Dry the rod at 80 °C and then hang it in the humidity tank for 10 minutes.
- (6) Develop it up to 5 cm on the rod after having it hung in the developing tank containing toluene for 10 minutes.
- (7) Repeat step (5).
- (8) Develop it up to 2.5 cm on the rod after having it hung in the developing tank containing THF for 10 minutes.
- (9) Dry the rod at 80 °C.
- (10) Measure peak areas of the individual components in FID chromatogram; then calculate the contents of components from these peak areas.

3.1.3 Comparison with the Conventional Method

Table 2 shows a comparison of analytical results of AL-AR and AL-HCRP obtained by FID-TLC with those obtained by the conventional SARA methods.

Table 2 reveals that analytical results of the components obtained by the conventional SARA methods are not the same as those obtained by FID-TLC. These discrepancies are caused by different separation mechanisms stemming from using different elution solvents or gels in the adsorption column. It cannot be definitely stated

which method is to be preferred, but the components are generally not so clearly separated from each other by adsorption column chromatography due to the overlapping of Sa and Ar. Analytical values of Sa by FID-TLC are smaller than those by the conventional methods as shown in Table 2. This proves that Sa and Ar are more clearly separated from each other by FID-TLC. It, therefore, suggests that FID-TLC could be more appropriate than the conventional methods for SARA analysis of heavy oils.

3.2 Hydrocarbon Type Analysis by FID-TLC

Preparation of thin layer rods with partially chemically bonded silica gel was developed;¹⁴⁾ and using the rods as the stationary phases a rapid method for detailed hydrocarbon type analysis of Ma in heavy oils by FID-TLC was investigated.¹⁵⁾

3.2.1 Preparation of Thin Layer Rods with Chemically Bonded Silica

Thin layer rods with aminopropyl or with cyanopropyl bonded silica gel (Chromarod NH₂-SII or Chromarod CN-SII) were prepared by the following procedures.

Chromarod SII was treated with (3-aminopropyl)triethoxysilane or (3-cyanopropyl)trichlorosilane according to the common and convenient method for preparation of bonded phases described in literature.^{16), 17)} The upper part of the rod was then passed through a hydrogen flame to reform the silica gel layer for detection by FID, as shown in Fig. 5.

Effects of the lengths of chemically bonded layers in Chromarod on resolution were investigated, since separability is considered to be strongly affected by layer lengths. In TLC, resolution (*Rs*) between adjacent peaks can be calculated from the following relation:

$$Rs = I(Zx)_2 - (Zx)_1 / (b2 + b1)$$

where (*Zx*)₁ and (*Zx*)₂ are the moved peak distances of component-1 and 2; and *b*₁, *b*₂ are the half widths of those peaks, respectively.

Relationships between lengths of aminopropyl bonded layers in Chromarod NH₂-SII ranging from 0 to 4 cm and resolutions (*Rs*₁, *Rs*₂, *Rs*₃) were examined, using a standard mixture prepared from *n*-pentacosane, *n*-octadecylbenzene,

- a: Thin quartz rod
- b: Thin layer of silica gel
- c: Thin layer of chemically bonded silica gel
- F: Front point
- O: Original point

Fig. 5 Schematic Picture of Thin Layer Rod of Partially Chemically Bonded Silica Gel

- : R_{s1} (Resolution between Sa and M-Ar)
- △: R_{s2} (Resolution between M-Ar and D-Ar)
- : R_{s3} (Resolution between D-Ar and T-Ar)

Fig. 6 Effect of Length of Chemically Bonded Layer in Chromarod on Resolution

2,6-dimethylnaphthalene, and 9,10-dimethylantracene which were selected as representatives of Sa, M-Ar, D-Ar, and T-Ar, respectively. The results are shown in Fig. 6 in which R_{s1} and R_{s2}

- 1: *n*-Pentacosane, 2: *n*-Octadecylbenzene,
- 3: 2,6-Dimethylnaphthalene,
- 4: 9,10-Dimethylantracene

Fig. 7 FID-TLC Chromatograms of Standard Mixture by using Chromarods NH₂-SII and CN-SII

hardly varied with the length of aminopropyl bonded layer, whereas R_{s3} increased with its length.

From these results, it may be concluded that Chromarod composed of 40% chemically bonded layer and 60% silica gel layer will exhibit good separability in FID-TLC for hydrocarbon type analysis of heavy oils. Fig. 7 shows FID-TLC chromatograms of the standard mixture obtained using Chromarods NH₂-SII and CN-SII. Both chromatograms give sharp separation of typical components. Fig. 8 shows FID-TLC chromatograms of the standard mixture by using conventional Chromarods for comparing the chromatograms in Fig. 7. Table 3 shows a comparison of resolution indicated as R_{si} ($i=1\sim3$) values for Chromarod NH₂-SII and Chromarod CN-SII with those for conventional Chromarods. Since separation of Sa, M-Ar, and D-Ar could not be carried out with Chromarod A because of its lack of adequate separability, R_{si} for Chromarod A was not shown. Table 3 reveals that both R_{s2} and

1,2,3,4: Described in Fig. 3

Fig. 8 FID-TLC Chromatograms of Standard Mixture by using Chromarods S, SII, and A

Table 3 Comparison of Various Chromarods for Resolutions (R_{si}) of Hydrocarbons

R_{si}	S	S II	NH ₂ -S II	CN-S II
R_s 1	1.07	1.09	1.07	1.06
R_s 2	0.80	0.98	1.00	1.01
R_s 3	0.56	0.78	1.04	0.89

$i=1$: Resolution between Sa and M-Ar
 $i=2$: Resolution between M-Ar and D-Ar
 $i=3$: Resolution between D-Ar and T-Ar

Table 4 R_f Values of Various Standard Samples for Chemically Bonded Chromarods

Sample	Hydrocarbon Type	NH ₂ -S II	CN-II
<i>n</i> -Pentacosane	Sa	0.84	0.85
<i>n</i> -Dodecylbenzene	M-Ar	0.70	0.75
<i>n</i> -Octadecylbenzene	M-Ar	0.71	0.75
1-Ethynaphthalene	D-Ar	0.62	0.61
2,6-Dimethylnaphthalene	D-Ar	0.58	0.59
Acenaphthene	D-Ar	0.56	0.62
Anthracene	T-Ar	0.47	0.52
Phenanthrene	T-Ar	0.51	0.52
9,10-Dimethylanthracene	T-Ar	0.44	0.53
Chrysene	P-Ar	<0.4	<0.4

R_{s3} for Chromarod NH₂-SII and CN-SII, respectively, are larger than those for conventional Chromarods. This indicates good separation of Sa, M-Ar, D-Ar, and T-Ar by FID-TLC with Chromarods NH₂-SII and CN-SII, suggesting that these Chromarods have better separability in FID-TLC than the conventional Chromarods for hydrocarbon type analysis of heavy oils.

3.2.2 Analytical Conditions

Table 4 gives R_f values of 10 standard samples developed with *n*-hexane.

It is suggested that Sa, M-Ar, D-Ar, and T-Ar could be separated by FID-TLC with Chromarod NH₂-SII or with Chromarod CN-SII. Chrysene as P-Ar could not be detected, because it was not developed up to the part of detection whose R_f value was smaller than 0.4. It could, however, be detected by developing it with toluene for which the R_f value was 0.8.

It is suggested, therefore, that a rapid and detailed hydrocarbon type separation of Ma in heavy oils could be carried out according to the three-stage development as follows. At first, by developing the sample up to 10 cm on the rod with *n*-hexane, Sa, M-Ar, D-Ar, and T-Ar are detected by FID. Then, by developing the sample up to 6 cm on the rod with THF after it was developed with toluene up to 8 cm, P-Ar and Po are detected by FID.

Figs. 9 and 10 show FID-TLC chromatograms of AL-AR-Ma by Chromarod NH₂-SII and Chromarod CN-SII, respectively. Both figures show that Sa, M-Ar, D-Ar, T-Ar, P-Ar, and Po

1: Saturates (Sa) 4: Triaromatics (T-Ar)
 2: Monoaromatics (M-Ar) 5: Polyaromatics (P-Ar)
 3: Diaromatics (D-Ar) 6: Polar compounds (Po)

Fig. 9 FID-TLC Chromatograms of AL-AR-Ma by Chromarod NH₂-SII

1,2,3,4,5,6: Described in Fig. 1

Fig. 10 FID-TLC Chromatograms of AL-AR-Ma by Chromarod CN-SII

Fig. 11 Hydrocarbon Type Analysis of AL-AR-Ma for Various Weights of Sample Loaded by Chromarod NH₂-SII

were separated sharply from each other.

Since separation conditions and accuracy of analysis vary with the weight of sample loaded in FID-TLC as described above, effects of weight on the sensitivity of components and repeatability of measurements were also investigated.

Spotting 0.5 μ l of a sample solution containing 5~20 wt% of AL-AR-Ma, relations between weights of sample loaded ranging from 25 to 100 μ g and contents of the components were examined. Mean values for 5-repeated measurements by Chromarod NH₂-SII are shown in Fig. 11.

Although this figure showed that the content of each component varied with weight of sample loaded up to 40 μ g, the content hardly varied with the weight varying between 50 and 100 μ g. The standard deviations of the contents of components for those repeated measurements decreased with increasing weight of sample loaded, but they were as low as 1.5 wt% or less between 50 and 100 μ g as shown in Fig. 12. The coefficient of variation becomes smaller than 10% between 50 and 100 μ g of sample loaded, although it scatters widely in the lower region of weight of sample loaded, as shown in Fig. 13. Table 5 gives the results of the measurements repeated 10 times at 50 μ g of sample loaded. It is also observed that Chromarod CN-SII has the same tendency as has Chromarod NH₂-SII.

3.2.3 Rapid Method for Hydrocarbon Type Analysis

Procedures for rapid analytical method to

Fig. 12 Standard Deviation of Hydrocarbon Type Analysis for Various Weights of Sample Loaded

determine the contents of Sa, M-Ar, D-Ar, T-Ar, P-Ar, and Po by FID-TLC are described below. It takes about 90 minutes to analyze 10 samples.

(1) Spot 0.5 μ l of the sample toluene solution adjusted to a concentration of 10 wt% on the rod with a 0.5 μ l glass capillary for TLC.

(2) Develop it up to 10 cm on the rod after having it hung in the developing tank containing

n-hexane for 5 minutes.

(3) Dry the rod at room temperature and then measure the peak areas of Sa, M-Ar, D-Ar and T-Ar in the FID chromatogram for silica gel thin layer.

○,●,□,■,△,▲: Described in Fig. 3
Fig. 13 Coefficient of Variation of Hydrocarbon Type Analysis for Various Weights of Sample Loaded

Table 5 Repeatability of Hydrocarbon Type Analysis for Optimum Weight of Sample Loaded by Chromarod NH₂-S II (wt%)

No.	Composition					
	Sa	M-Ar	D-Ar	T-Ar	P-Ar	Po
1	34.0	15.9	18.8	13.0	8.7	9.6
2	33.5	16.2	18.3	12.4	8.4	11.2
3	34.5	16.9	18.6	11.5	8.5	10.0
4	37.0	16.6	16.3	13.2	7.9	9.0
5	33.1	20.0	17.7	10.4	7.9	10.9
6	34.9	17.4	18.5	12.6	7.7	8.9
7	35.0	15.5	20.8	13.5	6.4	8.8
8	34.2	17.2	18.4	12.1	8.2	9.9
9	37.0	18.8	15.2	11.1	7.9	10.0
10	32.9	19.0	18.4	12.7	7.1	9.9
$\bar{X}$	34.6	17.4	18.1	12.3	7.9	9.8
SD	1.4	1.5	1.5	1.0	0.7	0.8
CV (%)	4.2	8.5	8.3	8.0	8.7	8.1

(4) Develop it up to 8 cm on the rod after having it hung in the developing tank containing toluene for 5 minutes.

(5) Dry the rod at room temperature.

(6) Develop it up to 6 cm on the rod after having it hung in the developing tank containing THF for 5 minutes.

(7) Dry the rod at room temperature and then measure the peak areas of P-Ar and Po in the FID chromatogram for silica gel thin layer.

(8) Calculate the contents of components from the peak areas of those measured in (3) and (7).

3.2.4 Comparison with the Conventional Method

Table 6 shows a comparison of analytical results of three AR and respective HCRP by FID-TLC with those by silica-alumina dual column chromatography.

Table 6 reveals that analytical results by FID-TLC are not the same as those by dual column chromatography. These discrepancies are caused by different separation mechanisms in which different elution solvents or gels are used. It cannot be stated unequivocally which method is to be preferred, but the components are generally not so clearly separated from each other by adsorption column chromatography due to the overlapping effect of Sa and Ar with each other. Analytical values of Sa by FID-TLC are smaller than those by the conventional method as shown in Table 6. This also indicates that Sa and Ar are more clearly separated from each other by FID-TLC, suggesting that FID-TLC is more satisfactory than the conventional method for hydrocarbon type analysis of Ma in heavy oils.

3.3 Determination of Olefin Contents by FID-TLC

In thermal cracking reactions, the olefin content is a particularly important characteristic factor.

Olefins are generally determined by use of the FIA (Fluorescent Indicator Adsorption) methods (JIS K2536 and UOP 501-71). These methods are, however, restricted to the determination of olefin contents in the 315°C- and 150~400°C fractions, respectively.

Table 6 Comparison of FID-TLC and Column Chromatography (wt %)

Sample	FID-TLC						Column Chromatography				
	Sa	M-Ar	D-Ar	T-Ar	P-Ar	Po	Sa	M-Ar	D-Ar	T-Ar	P-Ar+Po
AL-AR-Ma	34.6	17.4	18.1	12.3	7.9	9.8	37.0	16.5	11.3	12.2	23.0
AH-AR-Ma	21.5	12.6	15.7	17.4	14.3	18.5	30.4	16.5	11.3	13.1	28.7
IH-AR-Ma	32.5	10.7	15.1	11.7	11.6	18.3	38.0	14.8	9.3	10.2	27.7
AL-HCRP-Ma	57.4	17.7	15.8	2.6	3.5	3.1	57.8	18.3	10.8	5.3	7.8
AH-HCRP-Ma	47.3	18.4	18.1	3.2	6.7	6.4	56.4	16.3	8.2	7.3	11.8
IH-HCRP-Ma	55.7	16.8	13.8	2.8	4.4	6.5	58.7	15.0	10.5	4.4	11.4

- a: Thin quartz rod
- b: Thin layer of silica gel
- c: Thin layer of silica gel coated with AgNO₃
- F: Front point
- O: Original point

Fig. 14 Schematic Drawing of Chromarod AgNO₃-SII

In this study, a rapid method for the determination of olefins contained in heavy distillates of thermal cracked products by FID-TLC has been investigated.¹⁸⁾

3.3.1 Analytical Conditions

Determination of olefins (Ol) cannot be carried out by FID-TLC, since the stationary phase is limited to silica gel or alumina gel.

In this study, the separation of heavy distillates into Sa, Ol, and Ar using silica gel coated with AgNO₃ as the stationary phase was investigated.

As shown in Fig. 14, a silica gel thin layer rod coated partially with AgNO₃ (Chromarod AgNO₃-SII) can be prepared by spotting 1 μl of a 10% AgNO₃ acetonitrile solution at 6 cm from the original point on Chromarod SII.

Separation patterns of a standard mixture developed with *n*-hexane by FID-TLC with Chromarod SII and Chromarod AgNO₃-SII are shown in Fig. 15. Sa, Ol, and Ar are clearly separated by Chromarod AgNO₃-SII but not by Chromarod SII. Fig. 16 shows FID-TLC chromatograms of AH-TCRP-HD obtained in the same manner as described above with Chromarod SII and Chromarod AgNO₃-SII. From the R_f values of standard samples shown in Fig. 15, peak 1, 2, 3 in Fig. 3 are Sa, Ol, Ar, respectively; thus, they are clearly separated by Chromarod AgNO₃-

- 1: *n*-Eicosane 3: *n*-Octadecylbenzene
- 2: 1-Eicosene 4: 2,6-Dimethylnaphthalene

Fig. 15 FID-TLC Chromatograms of Standard Mixture by using Chromarod SII and AgNO₃-SII

SII which should be most suitable for the determination of olefin contents on heavy distillates.

Since the conditions for separation and accuracy of analysis seemed to vary with the weight of sample loaded in FID-TLC, as described above, the effects of weight on the sensitivity of components and repeatability of measurements were investigated.

Spotting 1.0 μl of a sample solution of 1~10 wt% concentration of AH-TCRP-HD, the relationship between weight of sample loaded ranging from 10 to 100 μg and content of components was examined. In Fig. 17, mean values of measurements repeated 10 times are shown.

Although Fig. 17 indicated that the content of each component varied with the weight of sample loaded up to 20 μg, the content hardly varied with the weight varying from 25 to 100 μg. The standard deviation of the content of each

1: Saturates (Sa), 2: Olefin (Ol), 3: Aromatics (Ar)
Fig. 16 FID-TLC Chromatograms of AH-TCRP-HD
by using Chromarod SII and AgNO₃-SII

○: Saturates (Sa), ●: Olefin (Ol), ◐: Aromatics (Ar)
Fig. 17 Composition Analysis of AH-TCRP-HD for
Various Weights of Sample Loaded

component in the repeated measurements increased with increasing weight of sample loaded. The coefficient of variation showed the same tendency as that of the standard deviation. Table 7 gives the results of the measurements repeated

Table 7 Repeatability of Composition Analysis for
Optimum Weight of Sample Loaded (wt %)

No.	Composition		
	Saturates	Olefins	Aromatics
1	31.4	8.1	60.5
2	30.5	8.8	60.7
3	30.5	8.4	61.1
4	29.5	8.8	61.7
5	33.0	6.9	60.1
6	33.5	7.9	58.6
7	29.9	8.6	61.5
8	30.6	8.9	60.5
9	30.7	8.3	61.0
10	30.8	8.1	61.1
$\bar{X}$	31.0	8.3	60.7
SD	1.3	0.6	0.9
CV (%)	4.1	7.2	1.4

Table 8 Comparison of FID-TLC and Preparative
HPLC (wt %)

Sample	FID-TLC			Prep-HPLC		
	Sa	Ol	Ar	Sa	Ol	Ar
AH-TCRP-HD	31.0	8.3	60.7	35.7	6.6	57.7
AB-TCRP-HD	25.3	6.0	68.7	31.0	3.8	65.2

10 times for 25 μ g of sample loaded.

3.3.2 Rapid Method for Determination of Olefin Contents

Procedures for rapid analytical method to determine the content of Ol by FID-TLC are described below. It takes about 60 minutes to analyze 10 samples.

(1) Spot 1 μ l of the sample toluene solution adjusted to a concentration of 3~5 wt% on Chromarod AgNO₃-SI with a 1 μ l glass capillary for TLC.

(2) Develop it to 10 cm on the rod after having it hung in the developing tank containing *n*-hexane for 10 minutes.

(3) Dry the rod at room temperature for 2 minutes.

(4) Measure the peak areas of Sa, Ol, and Ar in the FID chromatogram and then calculate the contents of the components from these peak areas.

3.3.3 Comparison with the Conventional Method

Table 8 shows a comparison of analytical results of two TCRP-HD by FID-TLC with those by preparative HPLC, and the Table also shows that the results obtained by the two methods are somewhat different.

These differences are caused by different separation mechanisms stemming from the use of different gels. It is difficult to state which method is more relevant, but it is generally observed that

the components are not so clearly separated from each other by adsorption chromatography due to the overlapping of Sa and Ar as described above. Analytical values of Sa by FID-TLC are smaller than those by preparative HPLC as shown in **Table 8**, indicating that Sa and Ar are more clearly separated from each other by FID-TLC; thus, suggesting FID-TLC to be more satisfactory than the conventional method for the determining olefin contents in heavy distillates.

4. Conclusions

Several rapid methods for compositional analysis of heavy oils by FID-TLC were investigated.

SARA analysis of heavy oils into Sa, Ar, Re, and As could be performed by three stage development using *n*-hexane, toluene, and tetrahydrofuran. The standard deviation and coefficient of variation in repeated measurements by this method were as low as 1 wt% or less and 10% or less, respectively. Time required for determination of 10 samples could be as short as 2 hours.

Detailed hydrocarbon type analysis of Ma in heavy oils into Sa, M-Ar, D-Ar, T-Ar, P-Ar, and Po could be performed adequately by using Chromarod NH₂-SII (a thin layer rod with aminopropyl bonded silica gel) serving as the stationary phase. The results of standard deviation and coefficient of variation in repeated measurements by this method were as low as 1.5 wt% or less and 10% or less, respectively. Time required for determination of 10 samples could be as short as 90 minutes.

Type analysis of heavy distillates into Sa, Ol,

and Ar could be performed by using Chromarod AgNO₃-SII (the silica gel thin layer rod coated partially with AgNO₃). The coefficient of variation in repeated measurements by this method was as low as 8% or less. Time required for determination of 10 samples could be as short as 60 minutes.

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要 旨

水素炎イオン化検出-薄層クロマトグラフィーによる重質油の迅速組成分析

山本洋次郎

丸善石油化学(株)研究所, 290 市原市五井南海岸 3

水素炎イオン化検出器 (FID) を備えた薄層クロマトグラフィーの FID-TLC を用いて, TLC の特徴である分離性の良さ, 迅速性, 簡易な操作性等を十分に発揮させた正確で迅速な重質油の組成分析を検討した。

まず最初に, 重質油を飽和分 (Sa), 芳香族 (Ar), レジン (Re), およびアスファルテン (As) の 4 成分に分離する SARA 分析法を検討した結果, **Fig. 1** に示したようにヘキサン, トルエン, およびテトラヒドロフランの 3 回展開によれば, Sa, Ar, Re, および As を良好に分離できることがわかった。繰り返し測定精度も変動係数が 1~3% と良好であり, 分析所要時間も 10 試料の分析で約 2 時間と短い。

さらに, より詳細な炭化水素タイプ分析の開発を目指し, 新たに従来のシリカゲル薄層棒の一端 (試料添加側) にアミノプロピル基あるいはシアノプロピル基を導入する化学結合型シリカゲル薄層棒 (クロマロッド NH₂-S II, 同 CN-S II) を考案した。**Fig. 5** に模式的に示したように, 3-アミノプロピルトリエトキシシランあるいは 3-シアノプロピルトリクロロシランを用いてトルエン溶液で, 従来のシリカゲル薄層棒 (クロマロッド S II) を数時間還流することによって, アミノプロピル基あるいはシアノプロピル基を導入し, 続いて FID で検出するための部分として, 薄層棒の先端から一部を水素炎中で焼成することによって, 化学結合部を取り除き再生した。本薄層棒では **Fig. 6** に示したように, 化学結合相の長さが 4 cm のものが最も高い炭化水素タイプ分離能を有することがわかった。従来品と比較しても明らかに優れていることがわかった (**Table 3**)。クロマロッド NH₂-S II を用いて, 以下の 3 回展

開によれば重質油のマルテン分 (Ma) を Sa, 単環芳香族 (M-Ar), 2 環芳香族 (D-Ar), 3 環芳香族 (T-Ar), 多環芳香族 (P-Ar), および極性物質 (Po) の 6 成分に精度よく分離定量できることがわかった。すなわち, まず *n*-ヘキサンで 1 回目展開を 10 cm まで行い, 展開された Sa, M-Ar, D-Ar, および T-Ar を FID で検出する。その後, トルエンで 2 回目展開を 8 cm まで行い, P-Ar を展開した後, 引き続いて, 3 回目展開を THF で 6 cm まで行い残分の Po を展開し, FID で P-Ar と Po を検出する。**Figs. 9, 10** にクロマロッド NH₂-S II および同 CN-S II を用いて AL-Ar-Ma を分離した結果を示した。いずれにおいても Sa, M-Ar, D-Ar, T-Ar, P-Ar, および Po の 6 成分は明りょうに分離されていることがわかる。繰り返し測定精度についても, 標準偏差 1.5 wt% 以下と小さく, 変動係数も 10% 以下と良好であった。分析所要時間も 10 試料の分析で約 90 分と短い。

熱分解生成油中の重質留分に含まれるオレフィン分 (Ol) を迅速に定量する事を目的とし, 一部に硝酸銀修飾を施したシリカゲル薄層棒を用いて重質留分を Sa, Ol, および Ar の 3 成分に分離定量することを検討した。**Fig. 14** に示したように, 原点から 6 cm の位置に 10% 硝酸銀-アセトニトリル溶液を 1 μ l スポティングすることによって, 部分的に硝酸銀修飾を施したシリカゲル薄層棒 (クロマロッド AgNO₃-S II) を調製できることがわかった。**Figs. 15, 16** に示したように本薄層棒を用いれば, Sa, Ol, および Ar を精度良く分離定量できることがわかった。繰り返し測定精度も変動係数が 8% 以下と優れ, 分析所要時間も 10 試料の分析で約 60 分と短い。

Keywords

Chemically bonded silica, Composition analysis, Heavy oil, TLC-FID, Type analysis