Class Separation of Higher Hydrocarbons by Thin-Layer Chromatography with Flame Ionization Detection

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3-Aminopropyl or 3-cyanopropyl-bonded silica-gel thin-layer rods (Chromarod NH_2–SII or CN–SII) were prepared and a hydrocarbon class separation of higher hydrocarbons has been investigated by flame ionization detection–thin-layer chromatography (FID–TLC) with those rods as the stationary phase. The resolutions (*Rs*) of the class separation with Chromarod NH_2–SII and CN–SII were compared with those with conventional rods on the market, which were silica-gel-sintered (Chromarod S and SII) and alumina-gel-sintered (Chromarod A) thin-layer rods. An adequate class separation of higher hydrocarbons into Saturates (Sa), Monoaromatics (M-Ar), Diaromatics (D-Ar) and Triaromatics (T-Ar) could be performed by FID–TLC with Chromarod NH_2–SII or CN–SII.

Since heavy oil comprises many kinds of compounds with complicated structures, the isolation of these compounds is impossible. A compositional analysis to determine the content of fractions with similar chemical properties in heavy oil provides an important characterization.

Adsorption column chromatography with silica gel¹⁾ or alumina gel²⁾ has been generally used for analyzing the composition of heavy oil. Since these methods have, however, such shortcomings as long times for determination and a large quantities of required solvents, high performance liquid chromatography (HPLC) has been recently tried regarding many applications.³⁻¹⁰⁾ Since Wise *et al.*⁵⁾ discovered that alkylamine-bonded silica gels had an advantage for the separation of aromatic ring compounds, these have been widely used for various hydrocarbon class analyses.⁸⁻¹⁰⁾ However, this method has not been put to practical use yet due to poor quantitativeness although HPLC has advantages such as a high separating power, and a simple and rapid procedure.

Thin-layer chromatography has a drawback regarding quantitation, although it has such advantages as high separating power, a simple and rapid procedure, and a small quantity of required sample. Recently, this drawback has been corrected due to the development of thin-layer chromatography with flame ionization detection (FID–TLC). This has been widely used for compositional analysis of heavy oil.¹¹⁻¹⁷⁾ However, a detailed hydrocarbon class separation can not be carried out by FID–TLC, since a stationary phase is limited to silica gel or alumina gel.

In this study, 3-aminopropyl or 3-cyanopropyl bonded silica gel thin layer rods were prepared and the hydrocarbon class separation of higher hydrocarbons has been investigated by FID–TLC with those rods as the stationary phase.

Experimental

Materials. For standard samples, pentacosane, dodecylbenzene, octadecylbenzene, 2,6-dimethylnaphthalene, 1-ethylnaphthalene, acenaphthene, anthracene, phenanthrene, 9,10-dimethylanthracene and chrysene (guaranteed or extra pure reagents obtained from Tokyo Kasei Kogyo) were used. Hexane (chromatographic grade from Wako Pure Chemical Industries) was used as a developing solvent for FID–TLC.

FID–TLC. Iatroscan TH-10 (Iatron Labolatories Inc.) was used for an FID–TLC analysis. Chromarod S and SII (silica-gel-sintered thin-layer rod) and Chromarod A (alumina-gel-sintered thin layer rod) were used as the stationary phase. A chromatopak C-RlA data processor (Shimadzu) was used for FID data collection and treatment. Analytical conditions, such as the weight of a sample loaded in TLC and the combustion in FID were set according to the optimun conditions described in a previous paper.¹⁴⁾ The FID–TLC procedure is described below.

(1) A 1 µl spot of the toluene solution sample (adjusted

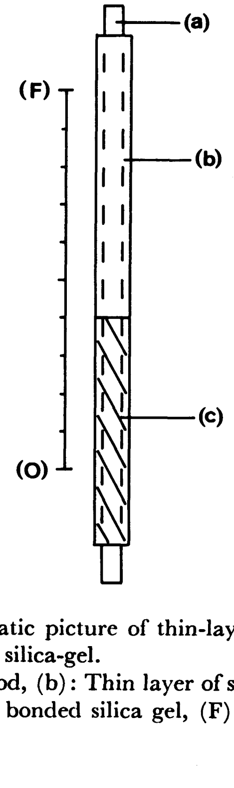

Fig. 1. Schematic picture of thin-layer rod of partially alkyl bonded silica-gel.
(a): Quartz rod, (b): Thin layer of silica gel, (c): Thin layer of alkyl bonded silica gel, (F): Front, (O): Origin.

to a concentration of 5—10 wt%) is placed on the TLC rod with a 1 μl glass capillary.

(2) The rod is developed to 10 cm after it is suspended in a developing tank containing hexane for 5 min.

(3) The rod is dried at room temperature.

(4) The components are determined as the peak area in FID chromatogram.

Preparation of Thin-Layer Rods of Alkyl Bonded Silica-gel. The constructions of the 3-aminopropyl and 3-cyanopropyl bonded silica gel thin-layer rods (Chromarod NH_2-SII and Chromarod CN-SII, respectively) are shown in Fig. 1. These were prepared by the following procedure.[18] Chromarod SII was treated with (3-aminopropyl)triethoxysilane or (3-cyanapropyl)trichlorosilane according to a procedure that is the most popular and convenient for the preparation of bonded phases. It is described in literature.[19,20] The upper portion of the rod was then passed through a hydrogen flame to reform the silica gel layer for detection by FID, as shown in Fig. 1.

Results and Discussion

The characteristics for the hydrocarbon class separation of higher hydrocarbons by FID–TLC with various Chromarods (Chromarod S, SII, A, NH_2-SII, and CN–SII) were examined.

Table 1 shows the R_f values of various standard samples developed with hexane on each Chromarod, and an FID–TLC chromatogram for a standard mixture prepared from pentacosane, octadecylbenzene, 2,6-dimethylnaphthalene and 9,10-dimethylanthracene, which are selected as representatives of Saturates (Sa), Monoaromatics (M-Ar), Diaromatics (D-Ar), Triaromatics (T-Ar), respectively, are shown in Figs. 2 and 3.

From the R_f values of the various standard samples, it is suggested that Sa, M-Ar, D-Ar, and T-Ar can be classified by FID–TLC with every Chromarod. However, Fig. 2 reveals that the separation of Sa, M-Ar, and D-Ar can hardly be carried out with Chromarod A, and that the adequate separation of D-Ar and T-Ar from each other can not be performed even with Chromarod S and SII. On the other hand, an improved separation of these can be carried out by FID–TLC with both Chromarod NH_2-SII and CN–SII, as shown in Fig. 3.

The resolution (*Rs*) between adjacent peaks in TLC can be calculated using the following equation,

$$Rs = \frac{|(Zx)_2-(Zx)_1|}{(b_2+b_1)}$$

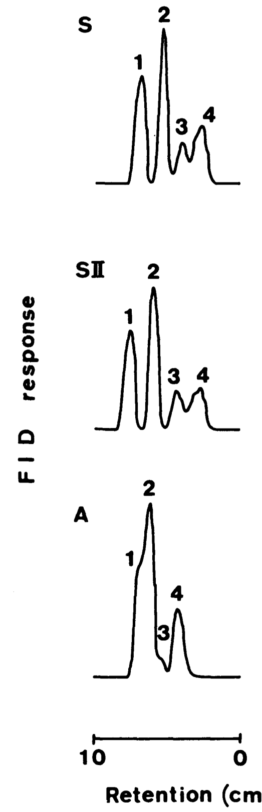

Fig. 2. FID–TLC chromatogram of standard mixture by using Chromarod S, SII, and A.
1: Pentacosane, 2: Octadecylbenzene, 3: 2,6-Dimethylnaphthalene, 4: 9,10-Dimethylanthracene.

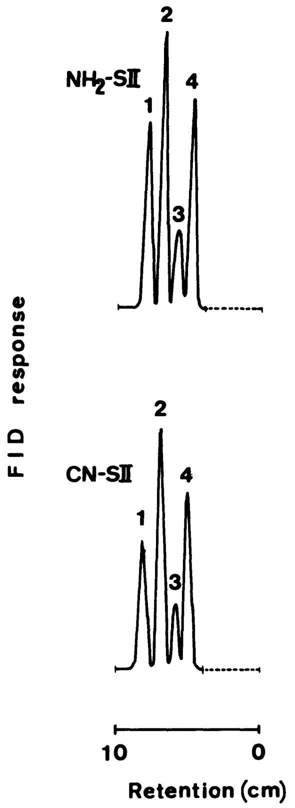

Fig. 3. FID–TLC chromatogram of standard mixture by using Chromarod NH_2–SII and CN–SII.
1,2,3,4: Described in Fig. 2.

TABLE 1. R_f VALUES OF STANDARD SAMPLES ON CHROMARODS

Sample	Hydrocarbon class	S	SII	A	NH_2-SII	CN-SII
Pentacosane	Sa	0.74	0.80	0.76	0.84	0.85
Dodecylbenzene	M-Ar	0.57	0.62	0.66	0.70	0.75
Octadecylbenzene	M-Ar	0.57	0.64	0.68	0.71	0.75
1-Ethylnaphthalene	D-Ar	0.45	0.46	0.57	0.62	0.61
2,6-Dimethylnaphthalene	D-Ar	0.40	0.43	0.59	0.58	0.59
Acenaphthene	D-Ar	0.45	0.41	0.57	0.56	0.62
Anthracene	T-Ar	0.29	0.32	0.42	0.47	0.52
Phenanthrene	T-Ar	0.30	0.36	0.48	0.51	0.52
9,10-Dimethylanthracene	T-Ar	0.26	0.28	0.43	0.44	0.53
Chrysene	P-Ar	0.05	0.06	0.05	<0.4	<0.4

TABLE 2. COMPARISON OF VARIOUS CHROMARODS FOR RESOLUTIONS(R_si) OF HYDROCARBONS

R_si*	S	SII	NH_2-SII	CN-SII
R_s1	1.07	1.09	1.07	1.06
R_s2	0.80	0.98	1.00	1.01
R_s3	0.56	0.78	1.04	0.89

* The resolution between Sa and M-Ar(R_s1) M-Ar and D-Ar(R_s2), and D-Ar and T-Ar(R_s3).

where $(Zx)_1$ and $(Zx)_2$ are the moved distances of peaks for component-1 and 2, and b_1, b_2 are the half widths of those peaks, respectively.

Following this, the characteristics of the various Chromarods used in this study for the hydrocarbon class separation of higher hydrocarbons by FID–TLC were studied using Rs values as indices. Table 2 gives the results. Rs1, Rs2, Rs3 are the resolutions between Sa and M-Ar, M-Ar and D-Ar, D-Ar and T-Ar, respectively. Since the separation of Sa, M-Ar, and D-Ar could not be carried out with Chromarod A, Chromarod A could not be compared.

Though R_s1 values for both Chromarod S and SII are large (1.07 and 1.09, respectively), both the R_s2 and R_s3 values are small. Especially, the R_s3 values for these Chromarods are very small (0.56 and 0.78, respectively). Thus, the R_s values had a tendency to decrease when the number of hydrocarbon aromatic rings increase. That is, it was found that the greater the number of aromatic rings, the more difficult it was to separate the hydrocarbons. On the other hand, the values of R_s1, R_s2, and R_s3 for Chromarod NH_2–SII (1.07, 1.00, and 1.04, respectively) are larger than those for both Chromarod S and SII. This suggests that a more clear separation of each class with Chromarod NH_2–SII can be carried out than with both Chromarod S and SII. The R_s values for Chromarod CN–SII are also larger than those for Chromarod S and SII, though the R_s3 value (0.89) is somewhat small compared to that for Chromarod NH_2–SII. Thus, it was found that a clear class separation of hydrocarbon with Chromarod CN–SII could be carried out as well as with Chromarod NH_2–SII.

Consequently, it was proved that an adequate class separation of the higher hydrocarbons into Sa, M-Ar, D-Ar, and T-Ar could be performed by FID–TLC with Chromarod NH_2–SII or CN–SII, which possesed 3-aminopropyl or 3-cyanopropyl-bonded phase.

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