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Column Liquid Chromatography

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1. Introduction

In the processing of coal and petroleum, there are many products produced such as gas and lighter liquid which is easy to use. At the same time, there is heavy material produced which is difficult to use. Such as, in crude oil refine processing, oil thermal cracking and catalytic cracking of petroleum, many residua oils, asphalts, and heaviest "waste" residual will be produced. The quantity of heavy oils is often large. So, it is important to study the property of heavy oils.

The column liquid chromatography (CLC) is an important and indispensable analysis method to study heavy oils. It is not only a separation means, but is also analysis means, especially for analysis of hydrocarbon group type.

Hydrocarbon group type analysis means the determination of the following classes of compounds:

1. Saturated compounds, including paraffinic and naphthenic hydrocarbons.
2. Aromatic compounds, (containing at least one benzene ring). Their molecules containing one benzene ring are classified as mono-aromatics, those with two aromatic rings as di-aromatics, etc.
3. Resins, including polar substances containing elements other than C and H in the molecule (nitrogen, sulphur and oxygen in particular)
4. Asphaltenes, including polar substances and asphaltenes only soluble in one or two polar solvents such as quinoline , which have large molecular weight and high aromatic ring number.

Now analysis methods existed have some deficiencies. Such as GC method can not be used to analyze compounds having high boiling point. The application of high performance liquid chromatography (HPLC) to hydrocarbon group-type analysis is characteristic with its high efficiency, high speed, and high sensitivity. But HPLC is only suitable for analysis of substances soluble in *n*-pentane [1].

TLC-FID [2-3] method can be also used to analysis the THF-soluble party in asphalt-samples and show great advantages. But, the components were combusted during TLC-FID analysis

process and this lack made it not suitable for other analysis with preparation fraction. It should be pointed that the conventional method such as ASTM method use amount of solvent is large and some solvents has high toxicity [4, 5]. Moreover, there are too troublesome for some operation in traditional method. Hence, the separation of products containing heavy components remains a difficult task up to now.

Refereeing the literatures [4-10], the authors of this paper establish an optimum CLC method to analyze group-type of heavy oils through a series of studies. This paper detail introduces this method and its many applications which include preparation of high-level road asphalt, the characterization of molecular weight distributions (MWDs) and analysis of heterocyclic aromatic components of heavy oils.

2. The establish of CLC method

2.1 Column, support and heating apparatus

The dimension of glass chromatographic column is 90 mm length and 6 mm I. D. Silica gel with particle size range from 100 to 200 meshes was provided by marine chemical plant of Qingdao China. Silica gel was active under temperature of 180oC for 4 hours before use. Oxide of alumna 0.047-0.147 mm used was purchased from chemical and medical reagent company in Shanghai China. Muffle furnace (50℃-1000℃) and oven was used for sample preparation and heating.

2.2 Reagents

N-heptane, dichloromethane, trichloromethane as eluent solvents all were analytical grade reagents produced by Tianjin Chemical Reagent Factory (China). Pure reagents as model compounds were supplied by Aldrich Chemical Company (USA), including tetracosane (99.5% pure), dibenz[ah]anthracen (98%, pure), and acetanilide (99% pure), etc.

2.3 Analytical instruments

Fourier transforms FT-IR spectra were measured by a Bio-Rad Excalibur Series FTS 3000 spectrometer in the range of 4000-400 cm^{-1} using KBr pellets. ^{1}H NMR measurements were made with a Bruker Avance 500 spectrometer operating at 500.1 MHz.

3. The establish of group-type analysis method by CLC

3.1 Optimum chromatographic condition

As a base line, some pure reagents were chosen as model components prepared for CLC. These model compounds were tetracosane for saturates, dibenz[ah]anthracen for aromatics and acetanilide for resins. There is no appropriate pure reagent used for asphaltene fraction, so the insoluble fraction of tetrahydrofuran in one asphalt sample was used for asphaltene fraction.

Through a series of investigations,the optimum chromatographic operation was performed. The final optimum conditions were obtained as follows: Chromatographic column was glass column being 90 mm length, 6 mm i.d. The amount of silica gel used was from 1 to 1.5 gram.

The amount of alumina was from 1.5 to 1.8 gram. Total sample used was about 0.1 gram. The solvent of heptanes, mixture of heptanes/ dichloromethane (1/2.5, V/V) and mixture of dichloromethane/ trichloromethane (1/3, V/V) were as elutes corresponding to saturated hydrocarbon, aromatic hydrocarbon and resin respectively. The amount of heptanes, heptanes/ dichloromethane, and dichloromethane/ trichloromethane was 20ml, 35ml and 30ml respectively. Each fraction collected was dried in vacuum under 60°C until the weight keep constant.

Through above group analysis, the experimental deviation and recovery of CLC method are summarized in Table 1. From Table, it can be seen that the average of deviation and recover are -1.546% and 100.681% respectively; the results are good.

Pure Reagents	Weight of preparation	Content W%	Determination W%	Deviation W%	Recover %	No.
Tetracosane	0.0547(g)	100	98.095	-1.905	98.095	1017
Tetracosane	0.0508	100	97.964	-2.036	97.964	1020
Tetracosane	0.0311	27.154	26.658	-0.496	98.173	1201
Tetracosane	0.0285	26.571	25.638	-0.933	96.489	1202
Average				-1.343	97.680	
Dibenz(ah)anthracen	0.042	100	98.095	-1.805	98.095	1030
Dibenz(ah)anthracen	0.0442	100	97.964	-2.036	97.964	1103
Dibenz(ah)anthracen	0.0259	22.629	20.909	-1.720	92.399	1201
Dibenz(ah)anthracen	0.0294	27.402	26.843	-0.559	97.960	1202
Average				-1.530	96.605	
Acetanilide	0.0875	100	97.600	-2.400	97.600	1024
Acetanilide	0.0247	23.024	22.642	-0.382	98.341	1202
Acetanilide	0.0365	100	96.438	-3.562	96.438	1222
Acetanilide		27.402	26.843	-0.559	97.853	1201
Average				-1.726	97.558	
Asphltene	0.0261	22.815	24.790	1.975	108.657	1201
Asphltene	0.0395	100	94.937	-5.063	94.937	1211
Asphltene	0.0387	100	98.450	-1.550	98.450	1301
Average				-1.546	100.681	

Table 1. Experimental deviation and recovery of model compound.

3.2 Check of chromatographic resolution rate by FT-IR

The result of CLC method was checked by Fourier transform infrared (FT-IR) method .The spectra IR were acquired in the transmission mode as 64 scan in the IR range from 4000 to 500cm^{-1} at a resolution of 4cm^{-1}. KBr standard pellets were used, and the samples were dried and then mixed with KBr, ground, and palletized.

IR spectrums of pure reagents including tetracosane, dibenz(ah)anthracen and acetanilide were obtained and used for standards. The IR spectrums of different fractions collected from flow out separated of the mixture reagents, and spectrums were compared with above standard spectrums. The results were shown in Figure 1.
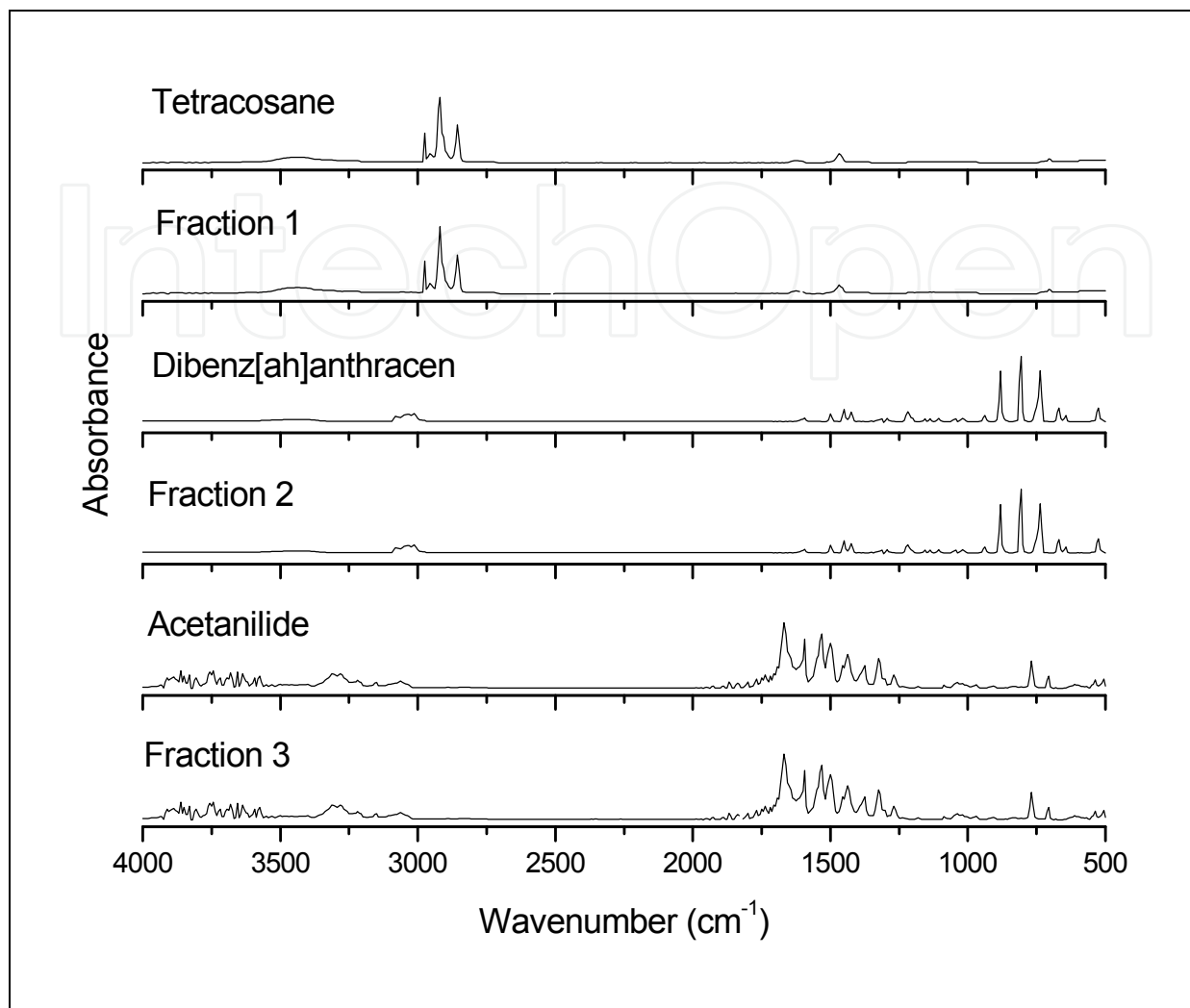
Fig. 1. Infrared spectrum for pure reagents and different fraction.

It is important to indicate that the IR spectra of fraction 1 collected (from 1202# sample) show similarity with pure tetracosane reagent. IR spectra for fraction 2 and fraction 3 show accordant results with dibenz(ah)anthracen and acetanilide respectively.

3.3 Check of chromatographic resolution rate by ^{1}H NMR

The CLC method was checked also by ^{1}H NMR. It measured different fractions collected from flow out separated of the mixture reagents and spectrums were compared with above standard spectrums. The high resolution ^{1}H NMR spectra of pure model compounds and fraction 1-3 are shown in Figure 2.

It is difficult to separate complex and heavy sample, however the IR and ^{1}H NMR analysis of the prepared fractions from CLC were all good agreement with pure reagents. This observation indicate the optimum CLC parameter in this work guarantee a good qualitative results.
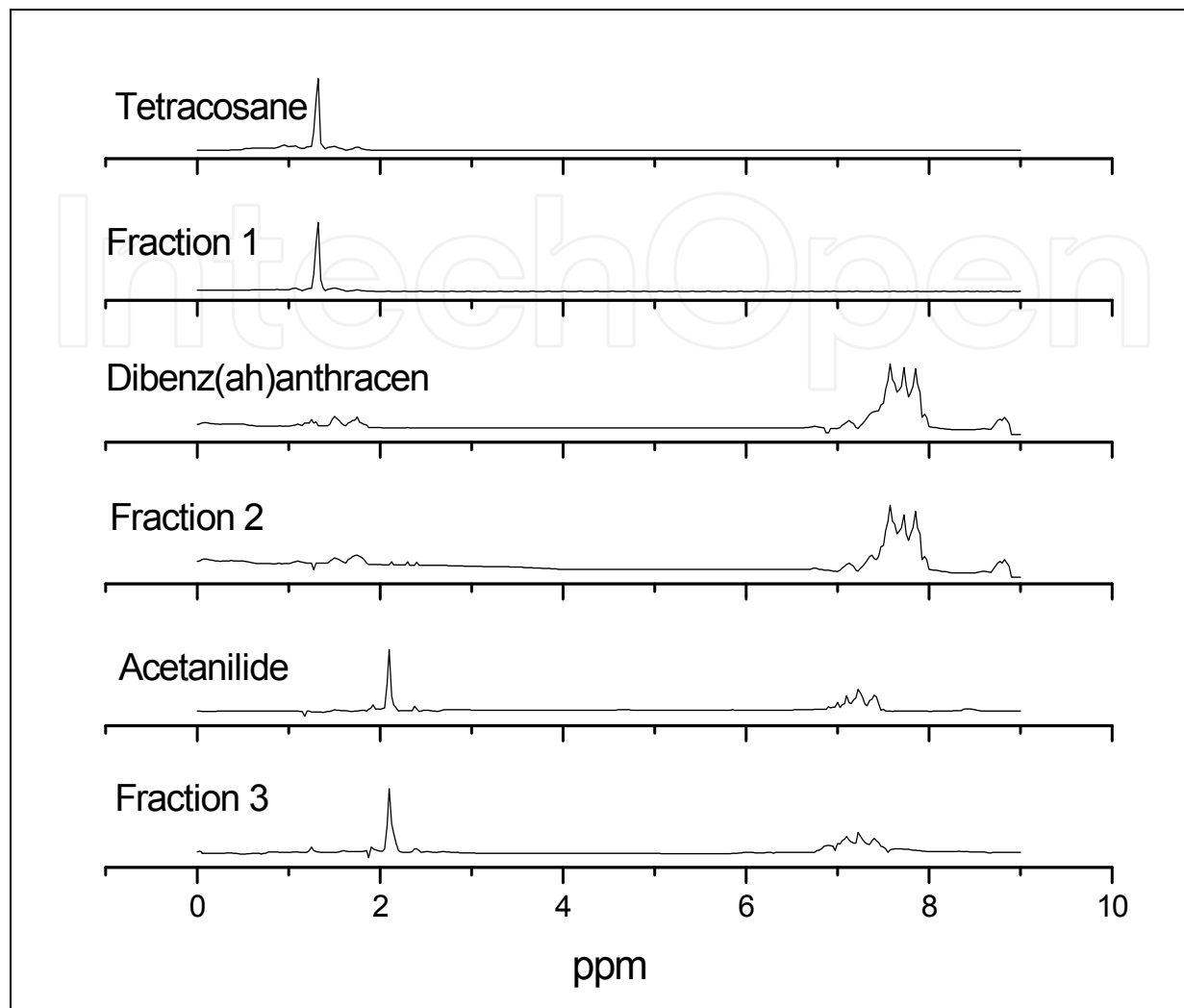
Fig. 2. ^{1}H NMR results of pure reagents and different fraction.

3.4 Evaluation of analysis of group composition by CLC

The recover rate and experiment deviations for model compounds were summarized in Table 1. It can be seen that the experiment result are fine.

Compared with routine ASTM method, these optimum chromatographic conditions show many advantages. First, the reagent and sample consumed was fewer than total solvent of 300 ml of classic ASTM method. Second, the dichloromethane and trichloromethane used in present study, compared with toluene and benzotrichloride used, has lower toxicity.

4. Applications of group type analysis by CLC

4.1 The application in making high grade road asphalt

Coal is used as the main source of energy in China. The crude oil produced in China is paraffinic; therefore, it is not suitable for road asphalt. China is trying to produce high grade road asphalt from the mixture of coal and petroleum [11, 12].

Three asphalt samples from petroleum and coal processing for high grade paving asphalt were characterized by established method. Sample NE-6, NE-9, NE-11 were the heavy products by co-processing of Shijiazhuang oil (a petroleum factory in China) and Yanzhou coal (a typical coal in China). The coal and oil ratio was 1:1. Among asphalt samples, the preparation of NE-6 sample was under the role of Fe catalyst during co-processing. NE-9 sample was related to Mo catalyst. The sample TLA is from Trindid Lake Asphalt. The results of group type analysis for four asphalt samples were shown in Table 2.

Name	Test	Saturates	Aromatics	Resins	Asphaltenes
NE-6	(1)	5.496	60.154	17.327	17.023
	(2)	4.986	58.230	20.128	15.855
	Average	5.241	59.191	18.727	16.439
	Deviation	0.255	0.961	1.401	0.584
NE-9	(1)	9.950	21.379	52.906	15.765
	(2)	8.001	22.087	52.348	17.554
	Average	8.975	21.733	52.627	16.659
	Deviation	0.974	0.354	0.279	0.895
NE-11	(1)	7.375	66.379	23.659	2.586
	(2)	8.497	67.984	20.850	2.668
	Average	7.936	67.182	22.254	2.627
	Deviation	0.561	0.802	1.404	0.041
TLA	(1)	5.496	60.154	17.327	17.023
	(2)	4.986	58.230	20.928	15.855
	Average	5.241	59.191	19.128	16.439
	Deviation	0.255	0.961	1.800	0.584

Table 2. Results of groups composition of asphalts (W%).

From Table 2 it can be seen that the application of established method to real asphalt samples show good results. Different samples have different group composition characterize. The experiment deviations of contents(W%) are in the ranges from 0.255% to 1.800%.

FTIR experiments were performed to check the qualitative ability of established method. IR spectra of saturated fraction, aromatic fraction and resin fraction for sample NE-9 were shown in Figure from 3 to 5. It is important to note intense absorption peaks for saturated fraction (Fig.3). Based the standard IR handbook, the absorption peaks around 719.45cm^{-1}, 1377.17 cm^{-1}, 2850.78 cm^{-1}, 2918.29 cm^{-1} and 2959.79 cm^{-1} was attributed to characteristics peak for δ (CH$_2$)$_N$ N>6, δ (CH$_3$), υ $_s$CH$_3$, υ $_{as}$ (CH$_2$) and υ_{as} CH$_3$ respectively. These data show that the prepared saturated fraction has a high purity.

As Figure 4 show, the absorption peaks around 748.38 cm^{-1}, 812.03 cm^{-1}, 877.61 cm^{-1} and 3049.45 cm^{-1} belong to character peak of aromatic C-H absorption. The peaks at 1602.84 cm^{-1},1580 cm^{-1} and 1410 cm^{-1} were characteristics absorption peak of aromatic carbon. Obviously, the obtained aromatic hydrocarbon fraction has a good purity.
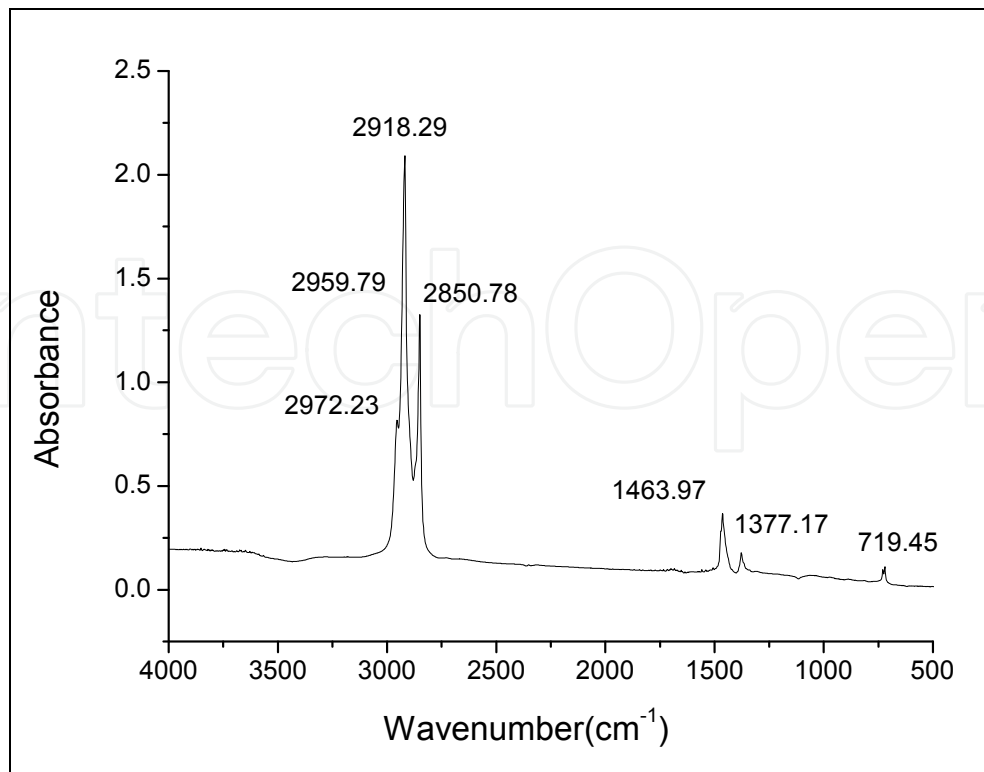
Fig. 3. Infrared spectrum of the saturated hydrocarbon fraction of sample NE-9.
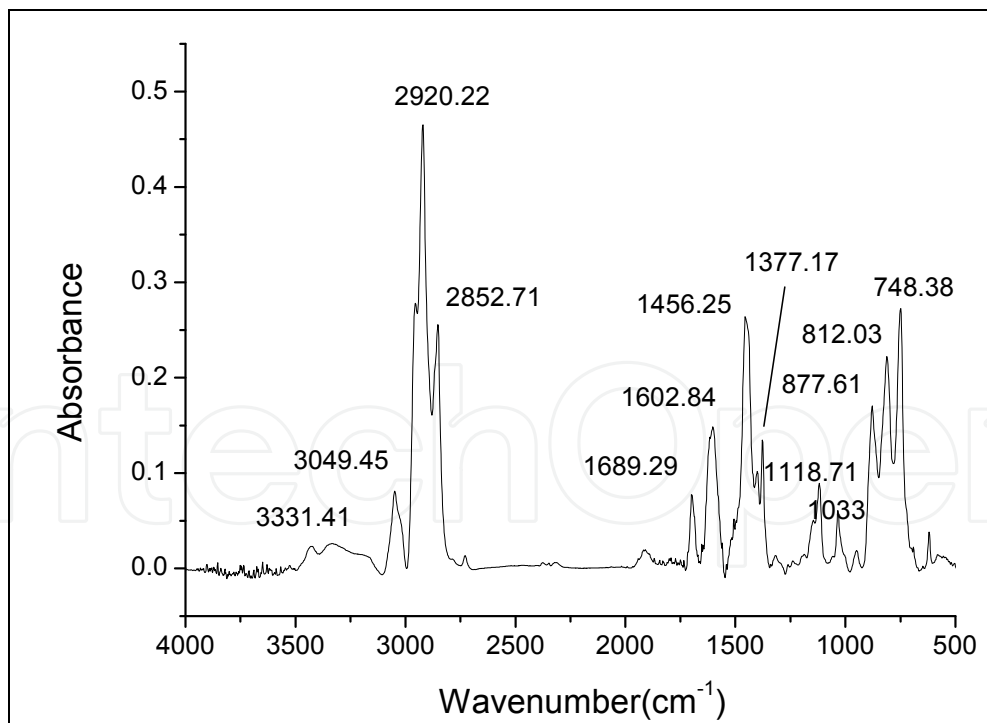

Fig. 4. Infrared spectrum of the aromatic fraction of sample NE-9.

The results from Figure 5 show that the resin fractions concentrate some oxygen-containing compounds. This conclusion can be approved by the appearing peak around 1215.15 cm-1, which is characteristics absorption peak for phenol compounds, and peak around 3649.31

cm-1, which is characteristics absorption peak for dissociate OH. The peaks at 1033.84 cm-1 and 1608.63 cm-1 attribute to the absorption from OH and C-O-C group. This is comprehensible because OH group in the structure the phenol connects to the aryl group, which may induce some aromatic absorption peaks.

The FTIR results show high resolution of CLC method established. It is difficult to separate complex and heavy sample, however the IR analysis of the prepared fractions from the CLC chow all good results This observation indicate that chromatographic parameter guarantee a good qualitative results.
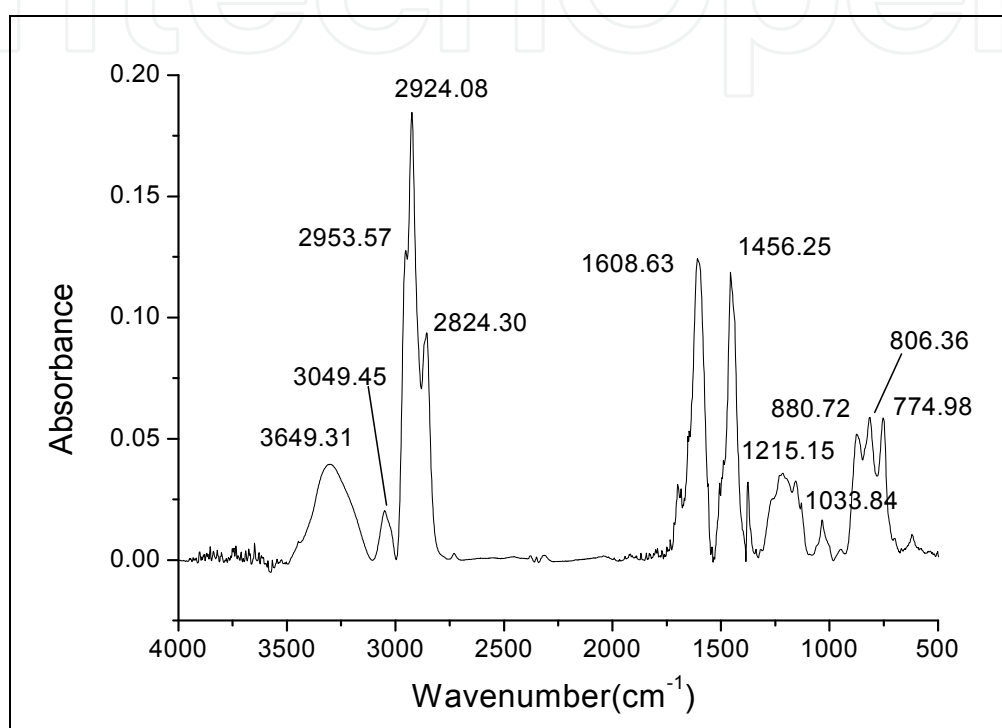
Fig. 5. Infrared spectrum of the resin fraction of sample NE-9.

4.2 The determination of MWDs by CLC coupled with SEC

Among characteristics of heavy oil, the size exchange chromatography (SEC) can be used to determine molecular weight distributions (MWDs), weight average molecular weight (Mw) and number average molecular weight (Mn), etc. With heavy oil of a group as example, the conditions of SEC are summarized as follows.

The analysis conditions are: a Shimadzu LC-10A high performance liquid chromatograph with an SPD-10AUP UV detector, the chromatographic column of SHIMPACK -801 (30 cm length, 0.8 cm i.d., polystyrene 6 μm), mobile phase of THF; flow rat with 1.2 ml/min; column temperature at 25oC.

The SEC chromatograms are shown in Figure 6, MWDs results are listed in Table 3.

In Figure 6, the sources of coal asphalt , KP petroleum asphalt, ethylene residue oil and vacuum residue oil are from Shanxi coking plant in China, Korea refining, Xinjiang oil refinery in China and Saudi Arabia's oil refining, respectively.
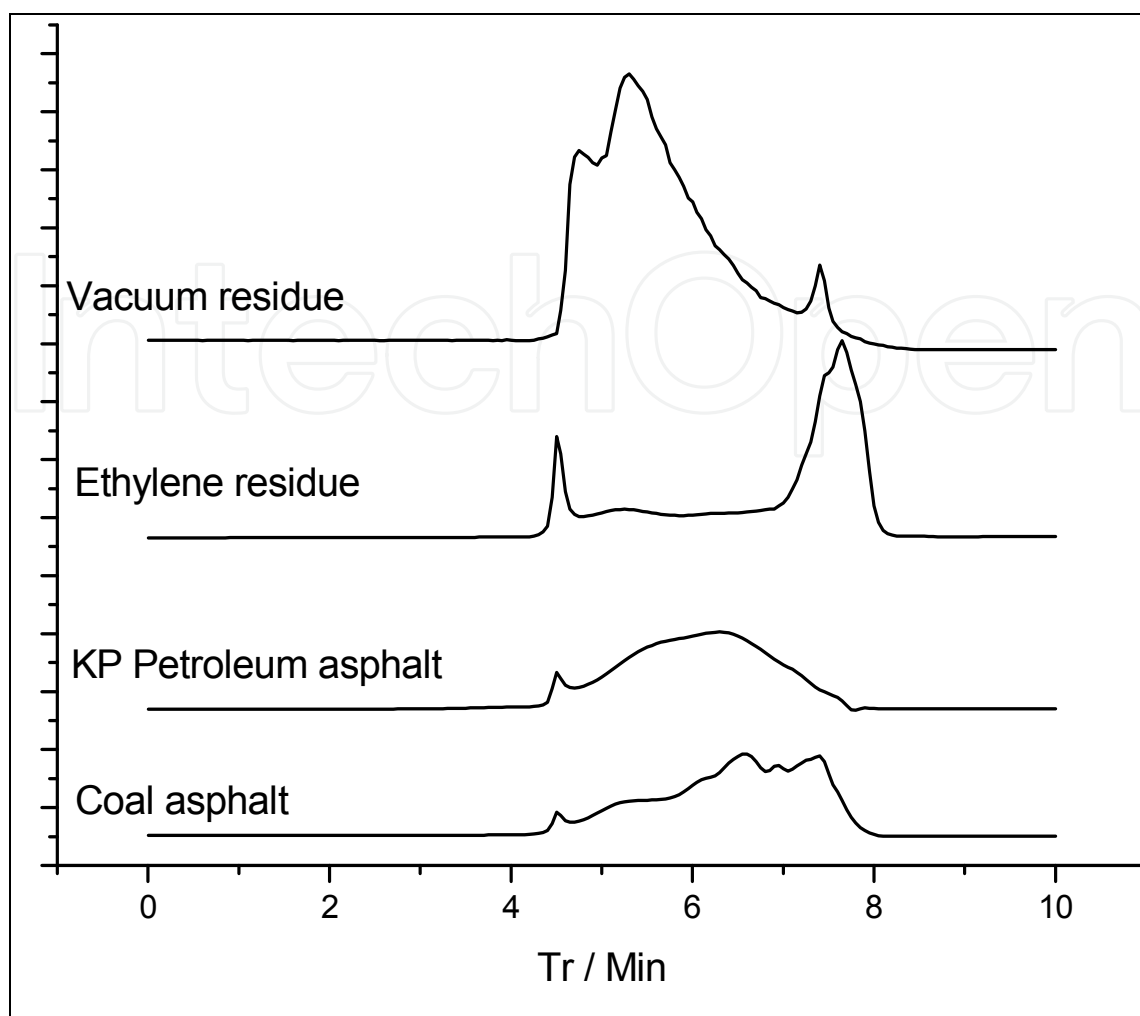
Fig. 6. The SEC chromatograms of typical heavy oils.

Samples	Mw	W%					
		M>5000	M5000 -3000	M3000 -1000	M1000 -500	M500 -300	M<300
Coal asphalt	1032.200	1.658	2.802	21.199	29.730	22.745	21.863
KP Petroleum asphalt	1905.674	0.804	17.169	59.899	12.274	3.979	5.873
"Ethylene" residue oil	764.788	0.191	7.481	15.201	9.648	9.666	57.810
Vacuum residue oil	1886.698	3.683	1.490	61.166	20.566	6.399	6.693

Table 3. The MWDs of typical heavy oils

How much is the "representative" characteristics of this SEC method? This is an important problem to need know to treating these spectra and data of SEC. The so-called "representative" refers that extent which could be determined out of sample. Because most present SEC method is only suitable to compounds having UV adsorbent and soluble of THF, so, it is needed to know representative of whole sample. This problem will be completed only by CLC. Because the four groups: saturates, aromatics, resins and

asphaltenes quantitatively could be obtained by CLC determination, then the "representative "(R index) will be calculated as the following.

$$R = 100\% - W_{asp}\% - W_{alk}\% \tag{1}$$

Which R represents the representation index; $W_{asph}\%$ and $W_{alk}\%$ represent the weight percent of asphaltene in sample and the weight percent of saturated hydrocarbons in sample, respectively.

With samples of Figure 6 as example, their R indexes from this CLC analysis are listed in Table 4.

Name of samples	(1)	(2)	(3)	Average	Max of deviation %
Coal asphalt	73.64	72.89	73.86	73.46	-0.78
KP petroleum asphalt,	99.33	99.28	98.76	99.12	-0.36
Ethylene residue oil	90.36	89.87	90.56	90.26	-0.43
Vacuum residue oil	96.17	96.21	95.76	96.05	0.33

Table 4. The R indicators.

These results show that the CLC coupled with SEC is an effective mean to analyze MWDs.

4.3 Analysis of resin component by CLC coupled with HPLC

As components of resin of heavy oil are very complicated, so to analyze them is very difficult by only one method. However, CLC coupled with high performance liquid chromatography (HPLC) can separate successfully, quality and quantity these compositions. Because the resin fraction got concentrate oxygen-containing compounds and other hetero-atom-containing compounds by CLC separation, then the analysis of these hetero-atom-containing compounds became easy to by HPLC. With slurry oil (Tianjing Refinery of China) as an example, the analysis of components in resin was summarized as follows.

The preparation of resin fraction was same as that of above description of CLC; the HPLC was performed on a Shimadzu LC-3A chromatogram with a SPD-1 UV detector, operated at 254 nm. Two ODS (4.6x20 cm) columns in series were operated at 40 °C with methanol /water=78:22(V/V) as the mobile phase, flowing at a rate of 0.8 ml/min. Typical separation chromatogram is shown in Figure 7.

From Figure 7 it can be seen the high resolution separation rate of complex compositions, these confirmed that the CLC preparation is successful and HPLC analysis is better.

The three qualitative methods of HPLC were selected to determine compositions of resin fraction. The three methods [13] are follows.

1. The qualitative method of relative retention time (RRT).
2. The qualitative method of stop- flow UV scanning.
3. The qualitative method of UV characteristic index V'.

The quantitative determination of compositions was by the method of external standard (E-X) and the calculation formula uses the following.

$$W_x\% = (R_{ex}/C_x) * (S_x/S_{ex}) * (V_{ex}/V_x) * R_{es}\% \tag{2}$$

where W_x % is the weight content percent of x composition in heavy oil sample, R_x % and C_{ex} % are the concentration of preparation solution of resin fraction and external standard solution, respectively, S_x and S_{ex} are the peak areas of component x and external standard, respectively, V_{ex} and V_x are the injection volumes of external standard solution and resin solution, respectively, R_{es}% is the weight percent of resin fraction in heavy oil sample. The qualitative and quantitative results are in Table 5.
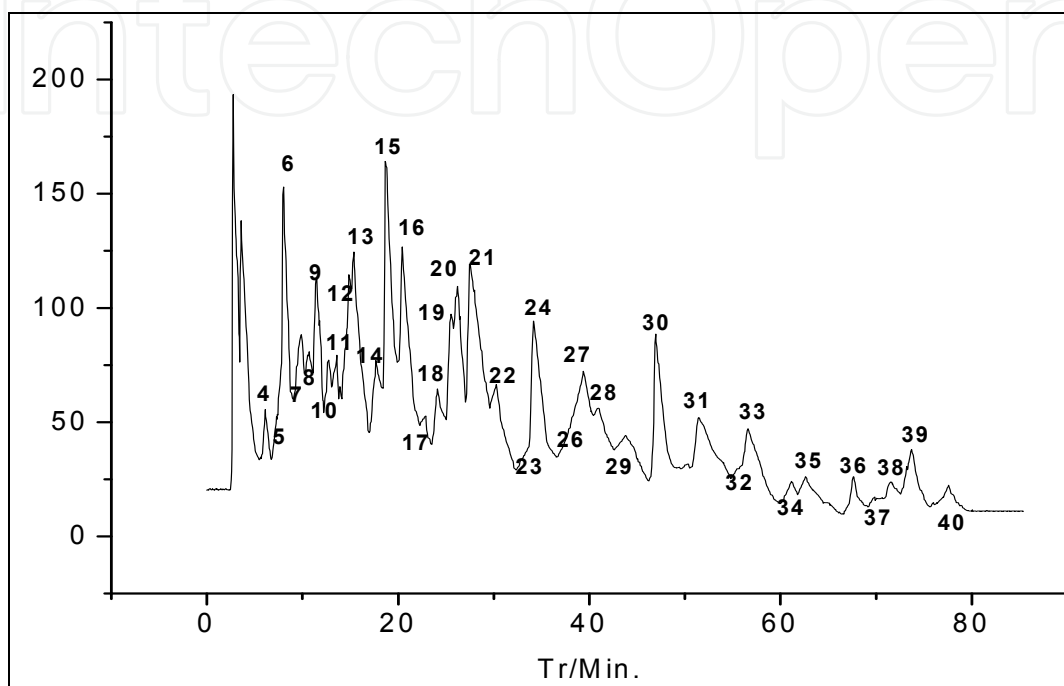
Fig. 7. HPLC chromatogram of resin fraction.

Number of peak	Component	Quantitative results	Number of peak	Component	Quantitative results (ppm)
9	3-Methyl indole	610	15	N-phenyl pyrrole	800
10	Quinoline	240	16	7,8-Benzoquinoline	1000
11	Phenanthrene-quinone	240	18	p-phenyl phenol	500
12	Carbazole	500	20	N-phenyl indole	600
13	4-Methylquinoline	640	24	Dibenzofuran	630
14	2-Amino-phenol	570	33	N-Ethyl carbozole	370
Note		ppm	35	2,2′-Biquinoline	290

Table 5. Results of components of resin (ppm).

5. Conclusion

A modified method for group type analysis of asphalt using CLC was established. The small-type CLC technique shows many advantages, such as high resolution rate, rapid operation, and requires minimal quantities of sample and solvent. The both of IR and ^{1}H NMR results check the high resolution of this method.

The CLC method compared with routine ASTM method, the reagents used in this method are small amount and lower toxicity. These are beneficial to environmental protection and human health. This is very important for modern analysis.

The CLC method of this paper is an important and indispensable analysis method to study heavy oils. It is not only a separation means, but is also analysis means.This method was successfully applied to many analysis aspects, such as making high grade road asphalt, characterizing MWDs and analysis heterocyclic of aromatic compositions of heavy oils.

The analysis of heavy oil is a long and difficult task. We systematically summarized these studies and hope that these will help our colleagues.

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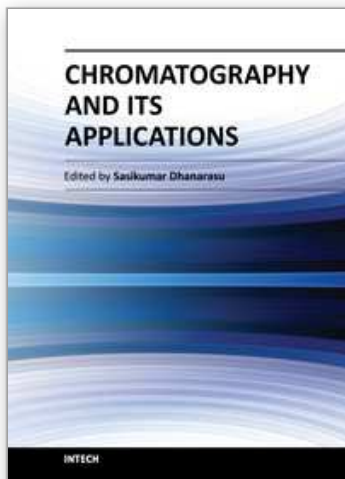
Chromatography and Its Applications

Edited by Dr. Sasikumar Dhanarasu

Chromatography is a powerful separation tool that is used in all branches of science, and is often the only means of separating components from complex mixtures. The Russian botanist Mikhail Tswett coined the term chromatography in 1906. The first analytical use of chromatography was described by James and Martin in 1952, for the use of gas chromatography for the analysis of fatty acid mixtures. A wide range of chromatographic procedures makes use of differences in size, binding affinities, charge, and other properties. Many types of chromatography have been developed. These include Column chromatography, High performance liquid chromatography (HPLC), Gas chromatography, Size exclusion chromatography, Ion exchange chromatography etc. In this book contains more details about the applications of chromatography by various research findings. Each and every topics of this book have included lists of references at the end to provide students and researchers with starting points for independent chromatography explorations. I welcome comments, criticisms, and suggestions from students, faculty and researchers.

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