

FRACTIONATION OF LOW TEMPERATURE COAL TAR
BY GEL PERMEATION CHROMATOGRAPHY

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Abstract

The use of gel permeation chromatography as a separation tool makes it possible to fractionate coal tar or similar products into three groups of compounds. These are aliphatics, aromatics, and tar acids. The aliphatic hydrocarbons are fractionated as a function of molecular length or carbon number. The aromatic ring compounds are fractionated as a function of molecular size and shape. The effect of adsorption between the polar tar acids and the column support material delays their elution until the other two groups have passed through the column. The elution curves of selected coal tars show the distribution conditions and permit the calculation of percentage composition.

Gel permeation chromatographic data from coal tar distillates (150° to 350°C) were compared to the results of chemical extraction (USBM NaOH-H₂SO₄ procedure) and the results of FIA (ASTM D-1319 fluorescence indicator adsorption) on the same distillation fraction. A gas chromatograph was used for the qualitative identification of these products. The portion boiling above 350°C also can be analyzed with GPC where chemical extraction, FIA, GC, and mass spectrometric methods are not generally applicable. Because GPC is performed at room temperature, the problems of thermal cracking and polymerization that occur with distillation techniques are avoided.

Introduction

Gel permeation chromatography (GPC) was first mentioned in the literature by Moore in 1964 (1). A comprehensive historical review was published by Cazes (6) in 1966. This technique has since become an accepted method for the determination of molecular weight distribution of polymers and for the fractionation of medium and high molecular weight materials (6). This analytical tool is still somewhat limited to use in the area of polymer sciences and biochemistry. Very few articles have appeared which apply this technique to coal, coal tar, and petroleum products. Hendrickson and Moore (2) first described the elution behavior of aliphatic and aromatic hydrocarbons. Altgelt (3) has studied the molecular weight distribution of asphaltenes by GPC and infrared spectroscopy. Edstrom and Petro (4) reported that aromatic hydrocarbons were fractionated by GPC and also gave elution curves of coal tar pitch and thermal aromatic residues. These authors concluded that separations occur not as a function of a single parameter, but as a complex function of molecular size, shape, and polarity. Their elution curves were correlated with the softening point of the pitch samples with reference to standard aromatic materials. In our laboratory we have applied GPC to the elution

behavior of various kinds of coal tar, crude petroleum, and related materials based on molecular size, shape, and polarity. We have also measured separation characteristics of neutral oils, tar acids, and thermal distillation fractions from coal tar. These were compared to standard aliphatic and aromatic hydrocarbons by means of conventional gas chromatography.

Experimental Procedure

The general operation technique for gel permeation chromatography is to dissolve the sample containing materials of different molecular weight in a small volume of solvent. The sample and solvent are introduced at the top of the column. High molecular weight materials pass more rapidly through, while low molecular weight materials pass more slowly due to their diffusion into pores in the beads of the column support materials (5, 6, 7). Chemical affinity of polar materials may act to retard passage of a specific species more than would be expected on the basis of molecular size alone. ^{1/} Edstrom and Petro (4) first pointed out this effect and it has been verified in our work. The overall effect of the procedure is a separation based on molecular size and shape, but some chemical affinity effects must also be considered.

Tetrahydrofuran (THF) was chosen as the solvent for elution through a Sephadex organic solvent resistant column packed with Sephadex LH-20 beads. The column and support material were supplied by Pharmacia Fine Chemicals, Inc. ^{2/} The advantages of using THF were pointed out by Hendrickson and Moore (2). A reagent grade tetrahydrofuran from J. T. Baker Chemical Company was used. Its purity was checked by gas chromatography. A small amount of Butylated Hydroxytoluene as stabilizer was added by the manufacturer.

The separation range of Sephadex LH-20 is reported to be from molecular weight 100 to 2000 by the manufacturer (5). A column of approximately 86.5 cm length was operated at room temperature and the solvent was degassed at 55°C before introduction to the column. Samples were introduced by injection with a syringe through a Y-shaped junction with a rubber septum mounted at the head of the column.

The eluted fractions were collected automatically with a Gilson ^{3/} volumetric fractionator at approximately 10-minute intervals and a flow rate near 0.34 ml per minute. This resulted in 3.40 ml collected for each fraction. Qualitative identification of standard materials passing through the column was

^{1/} Moore and Hendrickson (7) considered the adsorption and partition effects "are not significant in GPC, since the gel is quite free from associative forces with the sample and is eluted with a solvent having a similar polarity, so that negligible partition of the solute occurs between the gel and solvent phases."

^{2/} Pharmacia Fine Chemicals, Inc., 800 Centennial Avenue, Piscataway, N. J. 08854.

^{3/} Gilson Medical Electronics, Middleton, Wisconsin.

attained by injection of fractions into an F&M Model 720 gas chromatograph. Apiezon L (4 ft.), silicone grease (2 ft.), and carbowax 20M (8 ft.) columns were used. This unit was programmed from 100° to 300°C at 10 degrees per minute. He carrier gas was used at a flow rate of 100 ml/min.

Quantitative measurement of the amount of sample material collected in each fraction by GPC was done by evaporating the tetrahydrofuran at about 70°C and weighing the residue. Duplicate weighings were reproducible within 0.10 mg on the same fraction residues

Samples of Spring Canyon, Big Horn, and River King coals were selected for study. These coals were carbonized at 550°C. The coal tars from this process were distilled to 150°C. The portions distilling below 150°C were discarded and the portions distilling about 150°C were used as samples. Spring Canyon coal tar was again distilled to give two fractions: 150° to 350°C (distillate) and above 350°C (pitch). The neutral oil and tar acids were chemically separated from the Spring Canyon coal tar distillates by the Bureau of Mines extraction method (8). One other pyrolysis coal tar was studied. This was furnished by Food Machinery Corporation and was examined without further treatment. A petroleum crude oil, a shale oil distillate, and a tar sand benzene extract were fractionated by GPC without prior treatment

Results and Discussion

Since chemical affinity or absorption between specific materials in the sample and column support beads may affect the physical separation of components, it is important that standard reference materials be measured on the column. Figure 1 is a plot of molecular weight of known reference materials, paraffinic, olefinic, and aromatic hydrocarbons, versus the fraction number where the greatest concentration of each material can be expected to occur. Although each reference material will occur in 4 or 5 adjacent fractions, its greatest concentration, as found by gas chromatography (GC), will occur in the fraction indicated in Figure 1. As shown by this comparison, there is a considerable overlap between aliphatic and aromatic-type compounds. A plot of the data from Hendrickson and Moore (2) where paraffinic and olefinic hydrocarbons and their isomers are all in one group and all aromatic hydrocarbons in another group is in agreement with Figure 1.

The fractions of the Spring Canyon coal tar distillate elution curve, shown in Figure 2, are clearly divided into three groups. The first two groups contain the aliphatic and aromatic hydrocarbons. The third group contains the polar tar acids. Evidence for these statements is found in Figure 3 where elution curves for neutral oil without tar acids and for tar acids alone are shown. The presence of material in the total coal tar distillate, Figure 2, in fractions numbered greater than 85 is attributed to acids and bases that could have an affinity for the Sephadex LH-20. These materials are not found in the sample of neutral oil, Figure 3.

Gas chromatography was used in an effort to more fully understand the GPC separation of coal tar. The fractions collected from GPC were combined into three groups by redissolving the fraction residues in THF. Group I was taken

from fraction number 50 to 66. Group II was taken from fraction number 67 to 85, and group III was taken from fraction number 86 to 125 as indicated in Figure 2. These three portions of the original sample were then analyzed with gas chromatography. A comparison of results from these three composited groups of fractions with standard paraffinic hydrocarbons, aromatic compounds, and tar acids are shown in Figures 4-6. Also, the aromatic compounds were extracted from the same coal tar distillate with pyridine by the method of Qader, et al. (9), for comparison with the composited groups.

The pyridine extraction removes both aromatic and tar acid compounds from the distillate. This is shown by a comparison of Figure 5a (Group II) and Figure 5b (pyridine extract). Removal of the tar acid peaks from Figure 5b shows good agreement between the two. The pattern of Group I shown in Figure 4a compares very well with that from selected standard straight chain paraffinic compounds shown in Figure 4b. The pattern of Group III, Figure 6a, agrees almost exactly with the pattern of tar acids chemically separated from the same distillate, Figure 6b.

In Figures 4-6 peak (1) was identified as the inhibitor from the THF solvent. Although in low concentration in the solvent, its concentration is increased by evaporation of the solvent.

The GC chart of the original coal tar distillate is shown in Figure 7. The total pattern of Figure 7 is the summation of the three separate patterns of Figures 4a, 5a, and 6a. These three group samples were analyzed with an Apiezon L column and also with Silicone Grease and Carbowax 20M columns. Different known standard paraffins, aromatics, and phenols were added to these three samples separately. Some peaks were matched and identified as paraffins, aromatics, and phenols in the three composited fraction portions of the original sample, respectively.

Using GPC, it is possible to separate coal tar products into aliphatic and aromatic fractions by molecular shape. Tar acids are separated into a third fraction by chemical affinity with the GPC column support material. This separation is as precise and accurate as the standard chemical methods which are used for coal tar analysis (8, 10, 11).

The fundamental separation of GPC is determined by molecular size. Figure 8 shows a comparison of two distillation fractions from a low temperature coal tar sample. The solid line represents the chromatogram obtained from the 150° to 350°C fraction, distillates, and the dotted line that from the 350° to 550°C fraction, pitch. These curves show that in the pitch or high boiling material, the paraffinic group and the aromatic group are both distributed toward the lower fraction numbers. In the low boiling distillates the two groups are distributed toward the higher fraction numbers. This indicates that the pitch portion contains compounds of greater molecular size than does the distillates portion, as would be expected. The summation of these two curves gives the total coal tar distribution curve almost identical to that of the original material shown in Figure 9c.

The pattern of the distillate portion, Figure 2, begins with fraction number 50. From this we infer (Figure 1) that the highest molecular weight paraffinic

compound in the distillate is C₃₁. This is in agreement with the GC data. Although we can find C₃₂ and C₃₃ peaks on the GC pattern, they are very small compared to the C₃₀ and C₃₁ peaks. At the low temperature boundary of the distillate range (150°C), the smallest paraffinic number possible is C₉ (boiling point 150.8°C). This is also in agreement with the GC pattern, Figure 7, where C₉ is the first peak indicated. Termination of Group I at fraction number 66 would suggest, from Figure 1, that C₁₁ paraffins could be included. However, the paraffins C₉ to C₁₁ are easily vaporized and may be lost in the solvent evaporation step. As a result, C₁₂ is the lowest boiling compound found in Group I by GC, Figure 4a.

It is important that the coal tar components that boil below 150°C be removed prior to GPC. The aliphatic materials that boil in this range, primarily components of the conventional "gasoline cut," may overlap into the aromatic portion of the GPC curve. The lower boiling aromatic components, such as benzene, xylene, and toluene which are also removed by this process, do not overlap into the tar acid portion of the GPC curve. The GC patterns of Groups II and III show no evidence of overlapping materials (Figures 5a and 6a).

GC peaks of Group I, Figure 4a, are produced by paraffinic hydrocarbons. Although olefinic compounds may be present, they are low in concentration (2-3%) as shown by FIA tests and are not registered in Figure 4a. The absence of aromatics in group I is evidence that aromatic compounds of high ring number (over 4) are not present in coal tar. If present, these high-boiling materials would elute with the C₉-C₁₂ aliphatic hydrocarbons. The lack of high ring number aromatics is to be expected since low temperature carbonization (550°C) should produce only those coal tar components with boiling point below this temperature. The most significant aromatic materials (Figure 5) are those boiling in the naphthalene to anthracene range (218° to 354°C).

Again, reference to Figure 1 shows a different slope or separation factor for homologous aromatic compounds of different size or configuration. The slope of the curve propyl benzene, ethyl benzene, and toluene was plotted from the data of Hendrickson and Moore (2). The slopes of the two curves (a) 2 methyl anthracene, 2 methyl naphthalene, and toluene, and (b) biphenyl, terphenyl, quaterphenyl, etc., are plotted from the data of Edstrom and Petro (4). All the data were transposed to our reference scales based on the slope of the benzene, naphthalene, anthracene, and naphthacene curve. From these four curves we infer that a simple curvilinear function does not describe the GPC separation characteristic for aromatic compounds. Therefore, in Group II, we do not find an orderly distribution of components by number of rings or any other single parameter.

The distribution curves of coal tars from some representative coal types are shown in Figure 9. The chemical characteristics of these coals are listed in Table 1. All these coals were carbonized at 550°C and the fraction boiling below 150°C removed prior to separation by GPC. Figure 10 shows the GPC curves for a crude petroleum, a shale oil, and a tar sand extract.

Table 2 contains the percentages of aliphatics, aromatics, and tar acids found in the samples of Figures 9 and 10. Coal tars from the low temperature

carbonization of three coals (Big Horn, River King, and Spring Canyon), a petroleum crude (Red Wash), a shale oil distillate from Rifle, Colorado, a tar sand extract from the Utah Geological Survey, and a pyrolysis low temperature tar (FMC) were included. Also included in Table 2 are GPC data for products from Spring Canyon coal tar. Pitch (B.P. 350° to 550°C), duplicate measurements on distillates (B.P. 150° to 350°C), and neutral oil from the distillate fraction are shown. A chemical measurement of the tar acids in the distillate sample and an FIA (10) measurement of the aliphatics and aromatics in the neutral oil sample are also shown. The weights of residues in fractions 1-66 (aliphatics), 67-85 (aromatics), and 86 to 125 (tar acids) were used in the calculation of percentage composition. The figures in parentheses represent the calculated percentages of aliphatics and aromatics in the neutral oil; that is, the product following removal of tar acids and bases from each sample.

Spring Canyon coal, which is a high volatile bituminous coal, was used for most of our determinations. The percentages of aliphatics and aromatics in the total coal tar from this coal are about the same. The tar acids percentage in the total coal tar is less than that reported from the distillates. This means that the tar acids are distributed toward the lower boiling point (or low molecular weight) compounds. In pitch, the opposite is true. The tar acids percentage is lower than in the total coal tar and aliphatic compounds are predominant. Another high volatile bituminous coal used in this study was River King, which contains 3.30 percent sulfur. The GPC elution curve indicates that this coal tar contains a high percentage of aromatic and tar acid compounds and a relatively low percentage of aliphatic hydrocarbons. Coal tar from a subbituminous coal, Big Horn, is little different from coal tar from Spring Canyon coal. However, this low rank coal (17.2% O₂), when carbonized, did produce more water and somewhat more acids than did the Spring Canyon coal.

The three low temperature coal tars studied show very little weight percent in fractions numbered less than 50. This is an indication that aliphatic hydrocarbons of length C₄₀ and higher are not produced in the low temperature carbonization process at 550°C. However, the GPC curve from a pyrolysis coal tar (FMC), also shown in Figure 9, does show a significant weight percent in fractions numbered less than 50. This curve indicates a predominantly aliphatic content rather than aromatic or tar acid composition. This is due to the fact that this material was pyrolyzed at a temperature of 870°C.

Shale oil distillates, petroleum crude oil, and benzene extractants from a tar sand sample, Figure 10, show high percentages of aliphatic hydrocarbons. The increased proportion of high carbon number paraffins can be seen in the higher weight percent in fractions numbered less than 50

Conclusions

The results of this investigation show that GPC is a useful tool for the study of distribution of coal-derived liquids. These liquids may come from carbonization coal tars, hydrogenation or hydrocracking products, or solvent extracted products, etc. Similar composition materials such as petroleum

crude and its products, shale oil, gilsonite, and tar sand extractants, etc., can also be fractionated. GPC readily fractionates these samples into three groups, aliphatics, aromatics, and tar acids, based on the factors of molecular size, shape, and polarity. This procedure is specifically interesting because it is capable of making separations of these high boiling, high molecular weight materials at room temperature. The problems of thermal cracking and polymerization when distillation is used for fractionation are minimized. High boiling pitches and tars that cannot be analyzed with gas chromatography, mass spectrometry, the ASTM FIA or the USBM chemical extraction method can be fractionated with this procedure.

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Table I. Proximate and ultimate analysis of selected coals

	Spring Canyon H.V. bituminous		Big Horn subbituminous		River King H.V. bituminous	
V.M.	47.60	(53.10)	38.80	(46.49)	38.64	(48.26)
Moisture	1.90	Free	14.30	Free	8.26	Free
Ash	8.46	Free	2.22	Free	11.68	Free
F.C.	42.04	(46.90)	44.68	(53.51)	41.42	(51.74)
S	0.46		0.60		3.30	
O	9.67		17.21		9.61	
C	71.10		62.40		62.40	
N	1.40		0.70		1.40	
H	5.10		4.10		4.20	

Table II. Percentage results from GPC fractionation method.

Sample	I	II	III
	aliphatics 0-66	aromatics 67-85	tar acids 86-125
Red Wash (Crude oil)	82.21% (87.89%)*	11.33% (12.11%)*	6.46%
Tar sand (Benzene extractants)	69.10% (79.30%)	18.04% (20.70%)	12.86%
Shale oil (Distillate from Rifle, Colorado)	68.24% (83.21%)	17.77% (16.79%)	13.99%
F.M.C. (Pyrolysis coal tar)	57.71% (67.89%)	27.30% (32.11%)	14.99%
Spring Canyon (High volatile bituminous coal)	37.22% (47.98%)	40.36% (52.02%)	22.42%
Big Horn (Subbituminous coal, 17.2% O ₂)	31.21% (44.80%)	38.45% (55.20%)	30.34%
River King (High volatile bituminous coal, 3.30% S)	18.37% (29.71%)	43.47% (70.29%)	38.16%
Pitch (From Spring Canyon coal tar)	47.07% (58.87%)	32.88% (41.13%)	20.05%
Neutral oil (From Spring Canyon coal tar distillate)	42.60% (41.77%)	57.40% (58.23%)	
Tar acids from Spring Canyon coal tar by chemical method			34-36%
Neutral oil from Spring Canyon coal tar by FIA method	(38-42%)	(58-62%)	
Distillates (1) from Spring Canyon coal tar (150°-350°C)	24.09% (38.28%)	38.03% (60.43%)	37.88%
Distillates (2) from Spring Canyon coal tar (150°-350°C)	22.62% (36.72%)	38.98% (63.27%)	38.40%

* The percentages of aliphatics and aromatics in the neutral oil where tar acids and tar bases have been removed are indicated by the use of parentheses.

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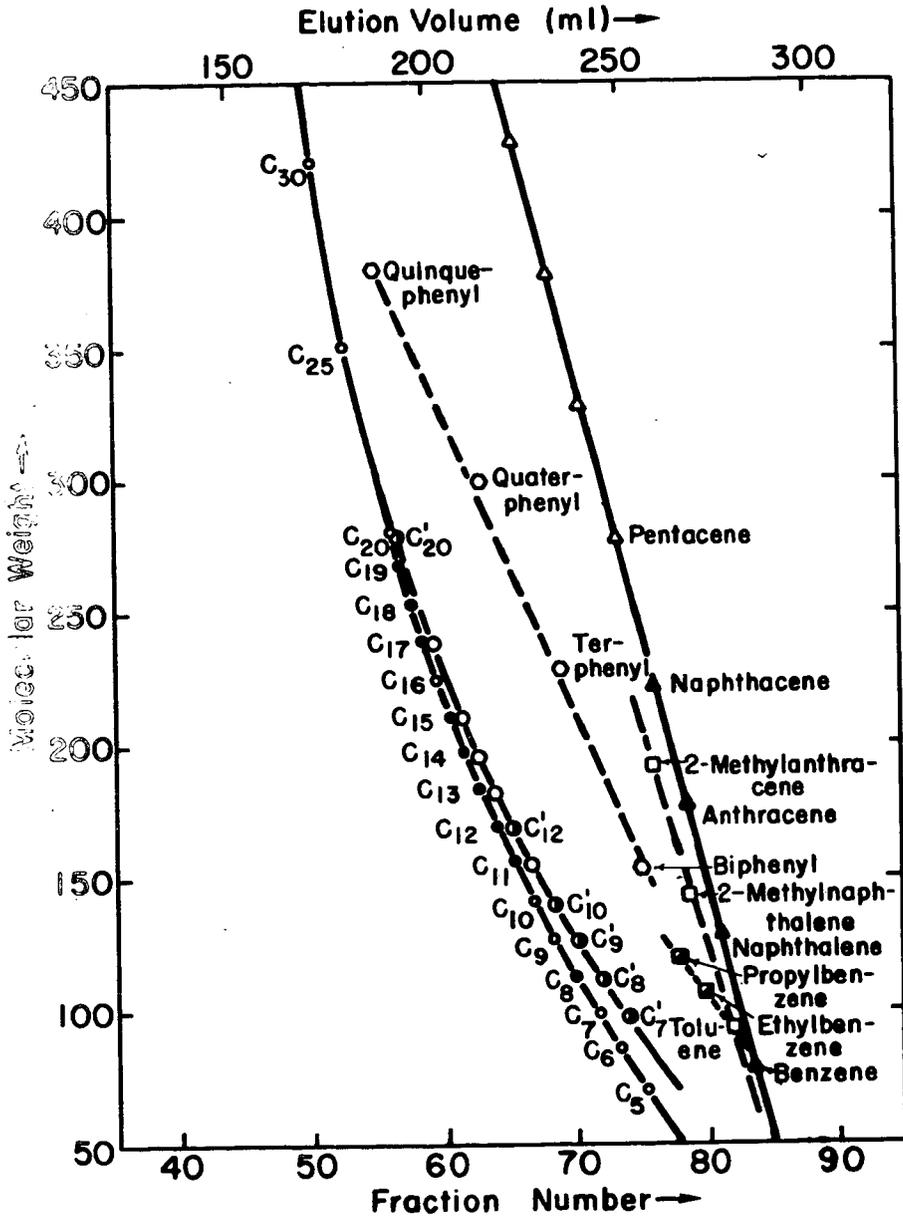


Figure I. GP Chromatography of known hydrocarbons: paraffins, olefins, and aromatics.

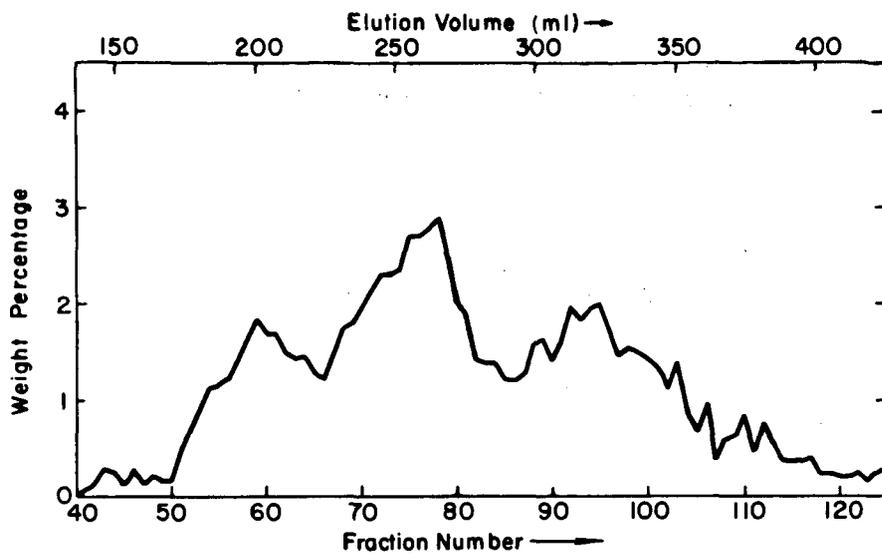


Figure 2. Elution curves (GPC) of low temperature coal tar distillates (150°–350°C) from Spring Canyon coal.

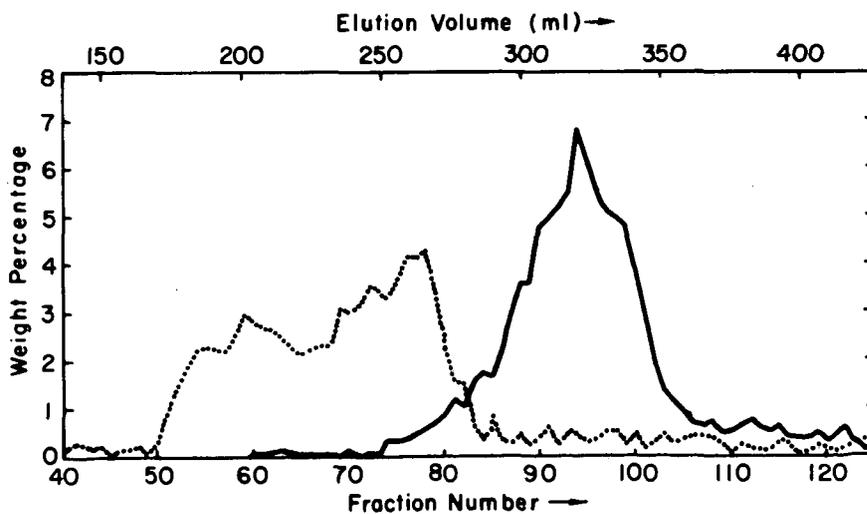


Figure 3. Elution curves (GPC) of neutral oil and tar acids from Spring Canyon coal tar distillates (150°–350°C).

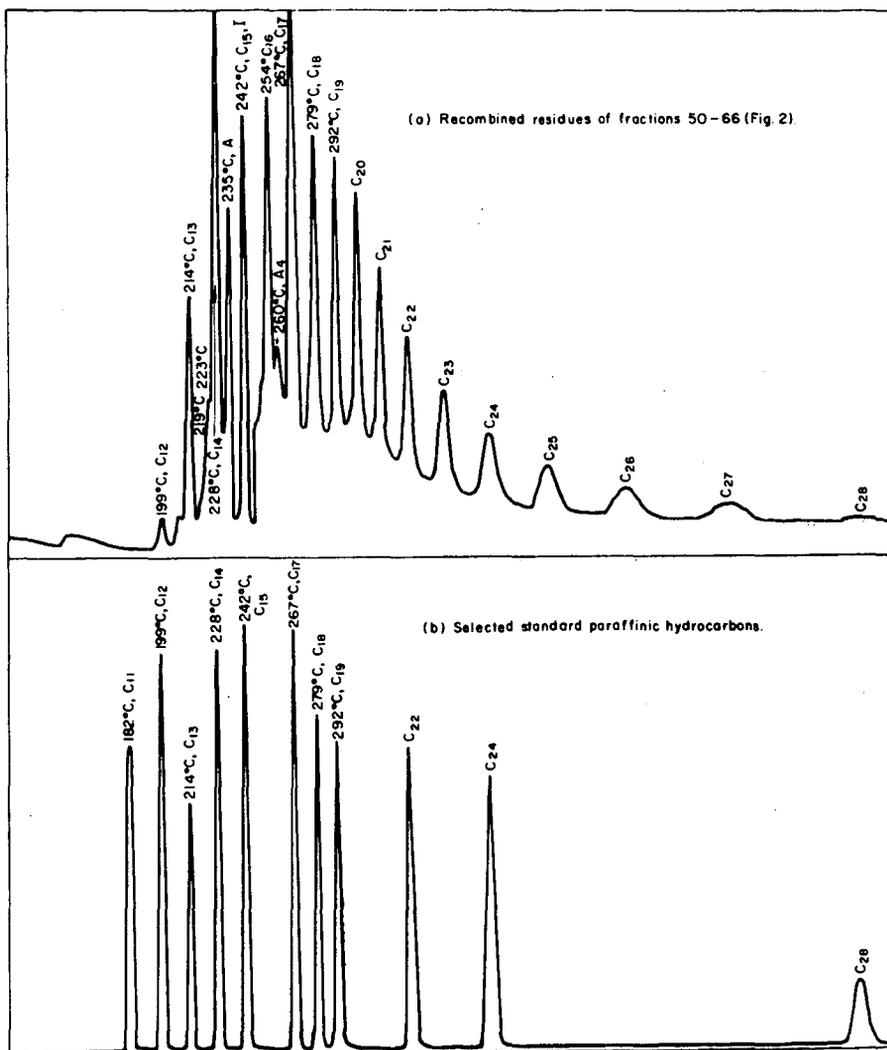


Figure 4. GC Chromatograms.

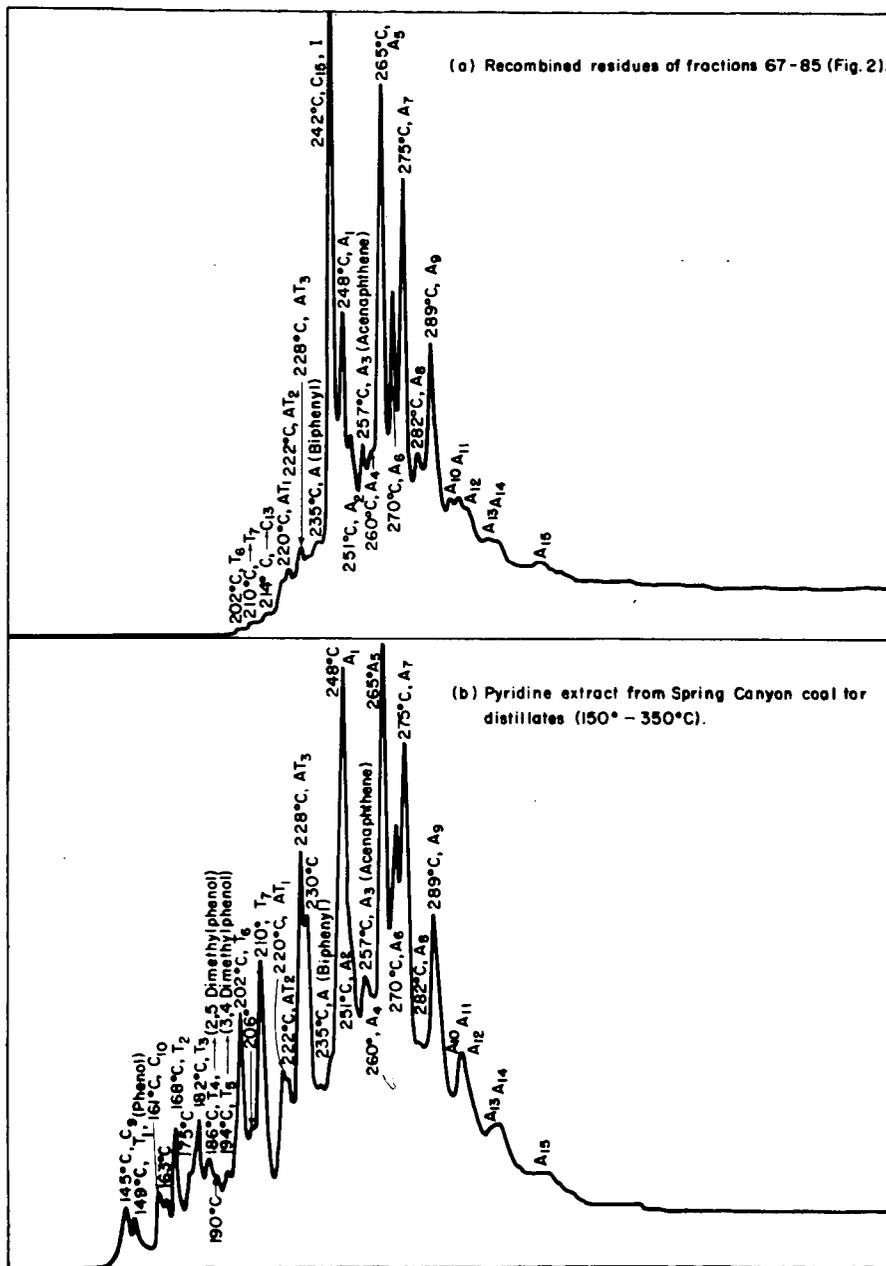
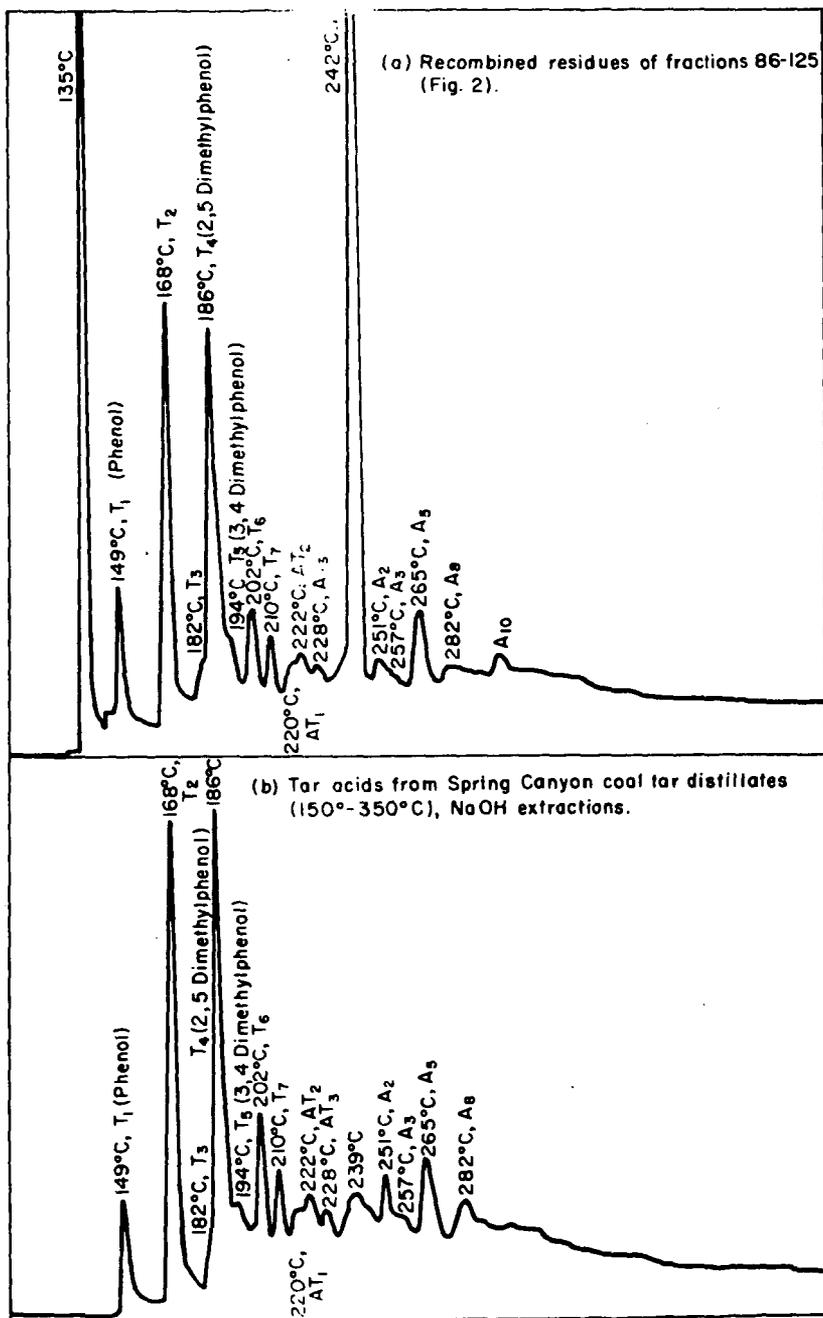


Figure 5. GC Chromatograms



DSC thermograms.

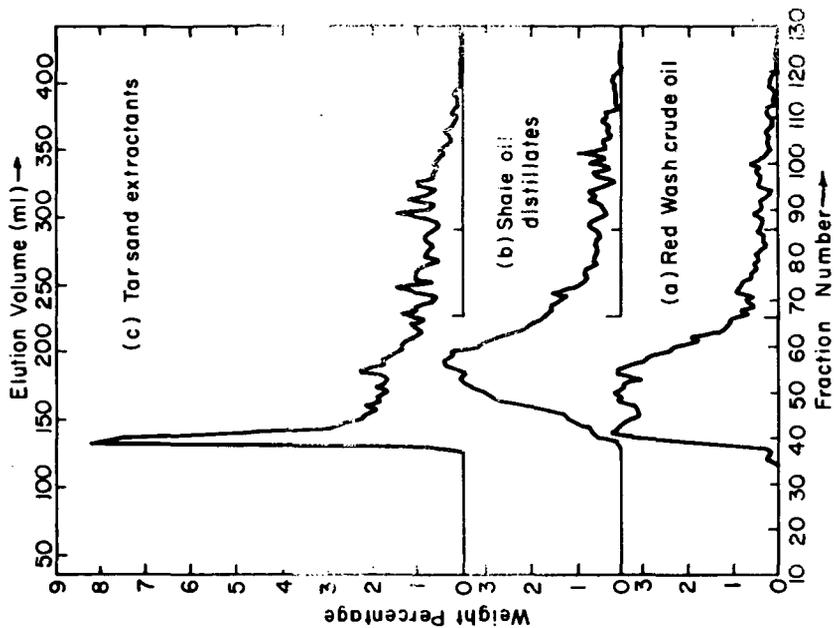


Figure 10. GPC elution curves.

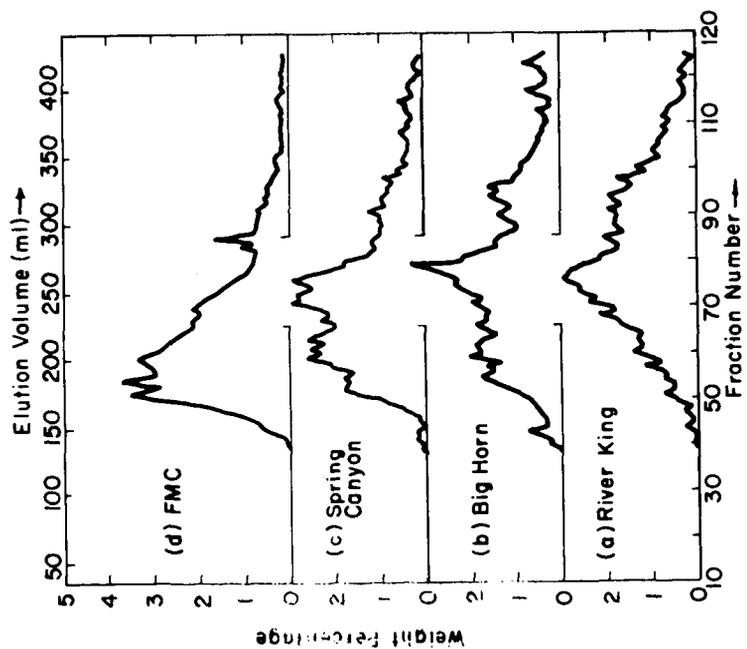


Figure 9. GPC elution curves.

(a) River King coal tar (150°-550°C)

(b) Big Horn coal tar (150°-550°C).

(c) Spring Canyon coal tar (150°-550°C.)

(d) Food Machinery Corporation pyrolysis coal tar.