tatively reduced under these conditions, probably due to the fact that aromatic poly nitro compounds are saponified after brief warming with alkalies giving variable amounts of alkali nitrite (*16*):

$$Ar\text{-}NO_2 + NaOH \rightarrow Ar\text{-}O\ Na + NaNO_2 + H_2O$$

Sodium nitrite is not quantitatively reduced under the present experimental conditions, since alkaline reduction of nitrates and nitrites with iron(II) are quantitative only in 28% sodium hydroxide (*17*) and lower alkali concentration requires silver or copper catalyst (*18*).

Interferences. The use of iron(II) in acidic and alkaline media for reduction of nitro and nitroso groups has the advantage over titanium(III), since very little interference is observed with other nitrogen functions. For example, whereas 8 equivalents of titanium(III) are required per mole of *p*-nitrophenyl hydrazine (*19*) (due to reduction of the hydrazine group along with the nitro group), only 6 equivalents of iron(II) are needed in acidic medium. The activation influence of one nitro group upon the hydrazine function is not sufficient to permit reduction with iron(II). Some reducible nonnitrogeneous groups that are occasionally present in organic compounds as ketonic, aldehydic, carboxylic, sulfonic (*e.g.*, toluene sulfonic acid), arsonic, phosphonic (*e.g.*, benzene phosphonic acid) as well as ethylenic and acetylenic (*e.g.*, diphenyl acetylene) bonds are not reduced with iron(II) in either acidic or alkaline media.

RECEIVED for review June 7, 1971. Accepted November 24, 1971.

(16) F. Feigl, "Spot Tests in Organic Analysis," Elsevier, Amsterdam, 1966, p 299.
(17) S. Carsley, *J. Phys. Chem.*, **34**, 186 (1930).
(18) Z. Szabó and L. Bartha, *Nature*, **166**, 309 (1950); *Anal. Chim. Acta*, **5**, 33 (1951).
(19) J. V. Earley, and T. S. Ma, *Microchim. Acta*, **1960**, 685.

Separation of High-Boiling Petroleum Distillates Using Gradient Elution Through Dual-Packed (Silica Gel-Alumina Gel) Adsorption Columns

D. E. Hirsch, R. L. Hopkins, H. J. Coleman, F. O. Cotton, and C. J. Thompson
Bartlesville Energy Research Center, Bureau of Mines, U.S. Department of the Interior, Bartlesville, Okla. 74003

The Bureau of Mines has developed a chromatographic separation procedure using a single dual-packed adsorption column containing silica gel and alumina that will separate high-boiling petroleum distillates into four concentrates: saturates, monoaromatics, diaromatics, and polyaromatics-polar. Spectral, adsorption, and radiotracer data indicate that the concentrates produced are predominantly as labeled. Subdividing the aromatics into major aromatic types greatly simplifies subsequent separation and characterization studies.

EARLY LIQUID–SOLID chromatographic separation methods were generally applicable only to simple binary mixtures or blends (*1*). Subsequent progress was made on methods for the complete separation of aromatics from mixtures containing paraffins, naphthenes, and aromatics (*2*, *3*).

Silica gel and, to some lesser extent, Alcoa alumina grades F-1, F-20, and H-41 were the first and most commonly used adsorbents for separating a wide variety of samples (*4–9*). The techniques of applying these adsorbents to petroleum samples usually consisted of separating the oil into an aromatic and a nonaromatic portion by adsorption on silica gel followed by rechromatographing the aromatic portion through alumina (*6*, *10*). Both steps utilized elution chromatography with solvents of differing polarity. Tenney and Sturgis (*11*), working with pure hydrocarbons and various adsorbents, established numerous guidelines for compound separability by elution chromatography. L. R. Snyder (*12–14*) later suggested the use of partially deactivated gel to achieve some degree of adsorption isotherm linearity, and several useful separation schemes resulted from his comprehensive work along these lines. However, the use of deactivated gel not only reduces sample adsorptive capacity of the gel by 10 to 100 times (*15*), but it also crowds retention volumes together close enough to reduce separability of certain compounds or compound types.

In this research a liquid–solid chromatographic procedure was developed to separate high-boiling petroleum fractions into four relatively distinct compound types—namely, saturates, monoaromatics, diaromatics, and polyaromatics-polar. A monoaromatic is defined here as any compound which has only one aromatic ring regardless of the number of saturated rings. A diaromatic is a compound having two

(1) B. J. Mair and J. D. White, *J. Res. Nat. Bur. Stand.*, **15**, 51 (1935).
(2) B. J. Mair and A. F. Forziati, *ibid.*, **32**, 165 (1944).
(3) M. R. Lipkin, W. A. Hoffecker, C. C. Martin, and R. E. Ledley, ANAL. CHEM., **20**, 130 (1948).
(4) A. E. Hirschler and S. Amon, *Ind. Eng. Chem.*, **39**, 1585 (1947).
(5) C. Karr, Jr., W. D. Weatherford, and R. G. Capell, ANAL. CHEM., **26**, 252 (1954).
(6) H. E. Lumpkin and B. H. Johnson, *ibid.*, p 1719.
(7) C. M. McKinney and R. L. Hopkins, *ibid.*, p 1460.
(8) C. J. Thompson, H. J. Coleman, H. T. Rall, and H. M. Smith, *ibid.*, **27**, 175 (1955).
(9) H. J. Coleman, C. J. Thompson, R. L. Hopkins, and H. T. Rall, *J. Chromatogr.*, **20**, 240 (1965).
(10) E. M. Charlet, K. P. Lanneau, and F. B. Johnson, ANAL. Chem., **26**, 861 (1954).
(11) H. M. Tenney and F. E. Sturgis, *ibid.*, p 946.
(12) L. R. Snyder, *J. Chromatogr.*, **5**, 430 (1961).
(13) *Ibid.*, **6**, 21 (1961).
(14) L. R. Snyder, ANAL. CHEM., **33**, 1527 (1961).
(15) *Ibid.*, **39**, 698 (1967).

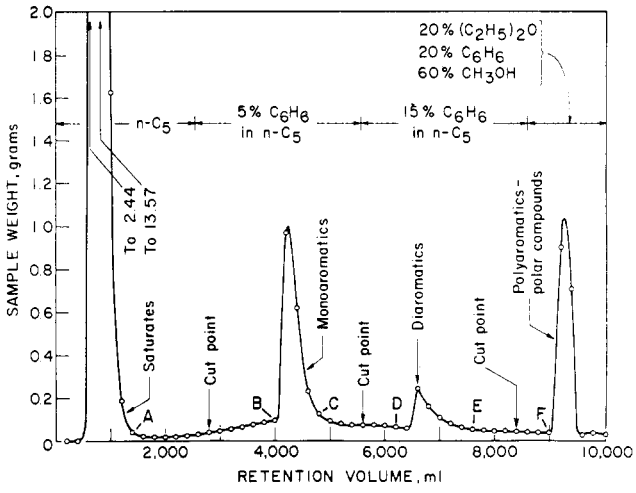

Figure 1. Liquid–solid chromatographic separation (elution through silica and alumina gel) of Recluse 335–530 °C distillate less acids and bases

aromatic rings which may be condensed, joined by a single bond, or wholly separated by a paraffin chain or naphthene rings. A polyaromatic, by the same definition, has three or more aromatic rings, and in most separations the polyaromatic concentrates will also contain some polar material which usually can be defined as compounds containing such hetero atoms as sulfur, oxygen, or nitrogen. The principal adsorption development includes the use of a single dual-packed adsorption column containing fully activated silica gel (Davison grades 12 or 62, dependent on molecular weight) in the top half and fully activated alumina (Alcoa F-20) in the bottom half. Radio-tagged compounds were used, during procedure development, to prove elution characteristics and limitations, and ultraviolet and mass spectral measurements were used for final assessment of the separation achieved by the method.

EXPERIMENTAL

Apparatus and Materials. A dual-packed (silica gel–alumina gel) column was used to separate high-boiling petroleum distillates into saturates, monoaromatics, diaromatics, and polyaromatic–polar compounds. The column is 2.54-cm o.d. by 244-cm long (1 in. by 8 ft) glass tubing of 960-ml capacity, fitted with a 600-ml eluant reservoir at the top. A stopcock [Teflon (Du Pont) bore] at the bottom of the column regulates the flow rate. The bottom half of the column is packed with fully activated (16 hr at 400 °C) 80–200 mesh Alcoa F-20 alumina gel (440 grams), and the top half is packed with fully activated (16 hr at 265 °C) 28–200 mesh Davison grade 12 silica gel (310 grams). Column size may be scaled to meet individual needs if the eluant volumes are changed by the same factor.

Procedure. Prior to the adsorption step, the distillate is treated (*16*) with an anion resin (Rohm & Haas, Amberlyst A-29) to remove acids, a cation resin (Rohm & Haas, Amberlyst A-15) to remove bases, and ferric chloride to remove neutral nitrogen compounds. Admittedly these three preliminary treatments remove only small quantities of material, but that which is removed significantly simplifies the remaining fractionation and characterization studies.

The method, applicable to distillates with boiling ranges of about 330–540 °C (650–1000 °F), employs a sample-to-gel ratio of no more than 1 gram of aromatics and polar compounds per 100 grams of gel. The volume of charge thus determined is diluted to about 10 to 1 with *n*-pentane for introduction to the column which is prewet with *n*-pentane. After the dissolved charge is poured into the column reservoir, the container is rinsed several times with *n*-pentane.

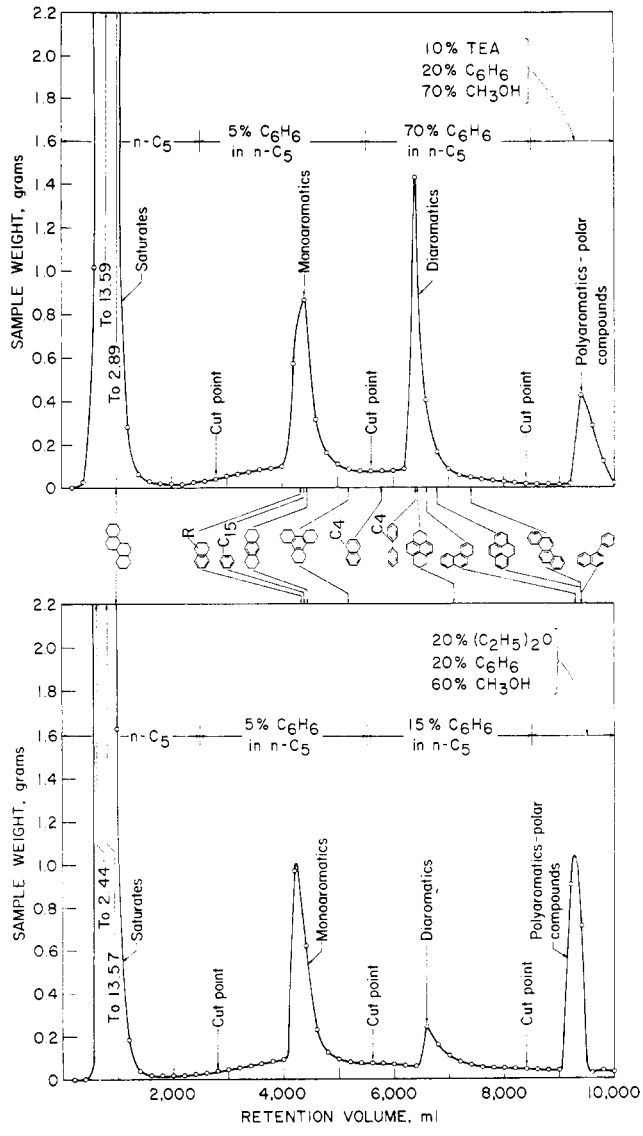

Figure 2. Adsorption studies on Recluse 335–530 °C distillate with tritium labeled compounds showing retention volume changes that occur in eluting diaromatics with different benzene concentrations (15% and 70%) in *n*-pentane

The four compound-type concentrates can be collected through a continuous solvent stripper (*17*) attached to the bottom of the column by consecutive elution, at an approximate flow rate of 200 ml/hr, with 2500 ml of *n*-pentane for saturates, 3000 ml of 5% benzene–95% *n*-pentane for monoaromatics, 3000 ml of 15% benzene–85% *n*-pentane for diaromatics, and 500 ml of 60% methanol–20% diethyl ether–20% benzene followed by 1000 ml of methanol for desorption of the polyaromatic–polar compounds. Alternatively, the material eluted can be collected in small fractions directly from the bottom of the column and individually analyzed after solvent removal. The cut points (Figure 1) at 2800, 5600, and 8400 ml coincide with those observed visually in the stripper by elution with each eluant until minimum concentration of sample in the eluant occurs. Experience has shown that 1

(16) W. E. Haines, C. C. Ward, and J. M. Sugihara, Proc. API, Refining Div., 36 Midyear Meeting, May 12–14, 1971, vol 51, pp 375–390.

(17) R. L. Hopkins, *Ind. Eng. Chem.*, **43**, 1456 (1951).

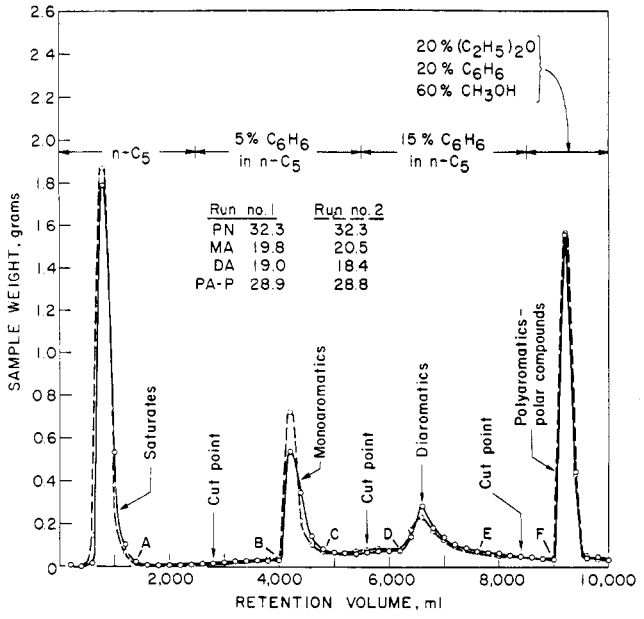

Figure 3. Liquid–solid chromatographic separations (elution through silica and alumina gel) of Gato Ridge 370–535 °C distillate less acids, bases, and neutrals showing degree of reproducibility obtainable

hour is required to complete the elution of the saturates after adding the monoaromatic eluant. At this point in the operation, the effluent is stopped temporarily, and the saturates remaining in the stripper are washed through. The monoaromatic fraction should be removed from the stripper in the same manner when the diaromatic elution is started. Likewise, the diaromatics are removed upon adding the eluant for the polyaromatic–polar concentrate. Across the top of Figure 1 are listed the eluants with arrows to indicate the volumes required.

RESULTS AND DISCUSSION

Points or regions of appearance and disappearance of many compounds and several classes of compounds on the adsorptogram were established, and some of these data are shown in Table I. These separations can be made in the absence of spectral support or monitoring of intermediate fractions through the use of appropriate cut points based solely on the amount of a given eluant through the column.

The advantages of subdividing the aromatics and polar compounds rather than collecting them as a single fraction are as follows: The three individual aromatic fractions are easier to analyze by low resolution mass spectrometry; further separations by gel permeation chromatography (GPC) and other techniques are much less complicated; heteroatom analysis for distribution and type characterization in the distillate is improved; and the polyaromatic–polar concentrate is isolated for chemical separations and spectral study.

EVALUATION OF METHOD

In the development and evaluation of this procedure, many special separations were made in which the sampling involved collecting 200-ml eluate fractions at the bottom of the column throughout the entire chromatographic run rather than the usual passing of the column eluate into the solvent stripping unit. Solvent evaporation from each of the 50 fractions followed by spectral study permitted an accurate evaluation of the separations achieved, and these data were valuable in establishing the recommended cut points.

Table I. Location and Quantities of Selected Compound Types in Recluse Crude Oil Fraction

Region	Retention volume, ml	% of charge	% of charge
Saturates	0–2800	75.9	
A–B[a]	1200–4000		1.7
Monoaromatics	2800–5600	11.3	
C–D[a]	4800–6200		2.8
Diaromatics	5600–8400	4.9	
E–F[a]	7600–9000		1.6
Polyaromatics–polar	8400–10000	7.9	
		100.0	6.1

[a] Valleys between major compound types.

Table II. Location and Quantities of Selected Compound Types in Gato Ridge Crude Oil Fractions

Region	Retention volume, ml	% of charge	% of charge
Saturates	0–2800	32.3	
A–B[a]	1200–4000		4.9
Monoaromatics	2800–5600	19.8	
C–D[a]	4800–6200		7.6
Diaromatics	5600–8400	19.0	
E–F[a]	7600–9000		5.6
Polyaromatics–polar	8400–10000	28.9	
		100.0	18.1

[a] Valleys between major compound types.

Evaluation Using Radiotracer Techniques. Radioactive tracer techniques were used to determine the point of elution of selected compounds and to confirm validity of the previously chosen cut points. Direct analysis of high-boiling fractions for a specific compound by techniques less sensitive than radiotracers is seldom feasible.

The use of selected tritium and ^{14}C-labeled reference compounds provided exact values for retention-volume shifts that occurred with eluting solvents of varying concentrations of benzene in pentane. The top chromatogram of Figure 2 shows that an eluant of 70% benzene in *n*-pentane failed to separate tri- and tetraaromatics from the diaromatics. The bottom chromatogram of Figure 2 shows the diaromatics and polyaromatics to be effectively separated by the use of 15% benzene in *n*-pentane, the eluant polarity now recommended, in place of the more polar 70% benzene eluant used in the preliminary studies.

With but two exceptions (dihydroanthracene and fluorene) among the many compounds tested, the procedure yields a separation consistent with that desired. Although the parent compound, dihydroanthracene, was not separated as a diaromatic, alkyl derivatives of this compound might well elute at the proper time for a diaromatic.

Repeatability. Figure 3, showing chromatograms from two individual adsorption runs on the same high-boiling distillate sample from Gato Ridge, reflects the repeatability obtainable in separations by this procedure. The versatility of the method was further shown by its successful application to two widely diverse distillates. These distillates—a Recluse, Wyo., crude oil high in paraffins and low in aromatics and polar compounds, and a Gato Ridge, Calif., crude oil high in aromatics and polar compounds and low in paraffins—were both satisfactorily separated (Figures 1 and 3).

Studies on the Gato Ridge distillate were useful in determining the points of elution of sulfur compounds and their influence on separations. Table II shows the points of ap-

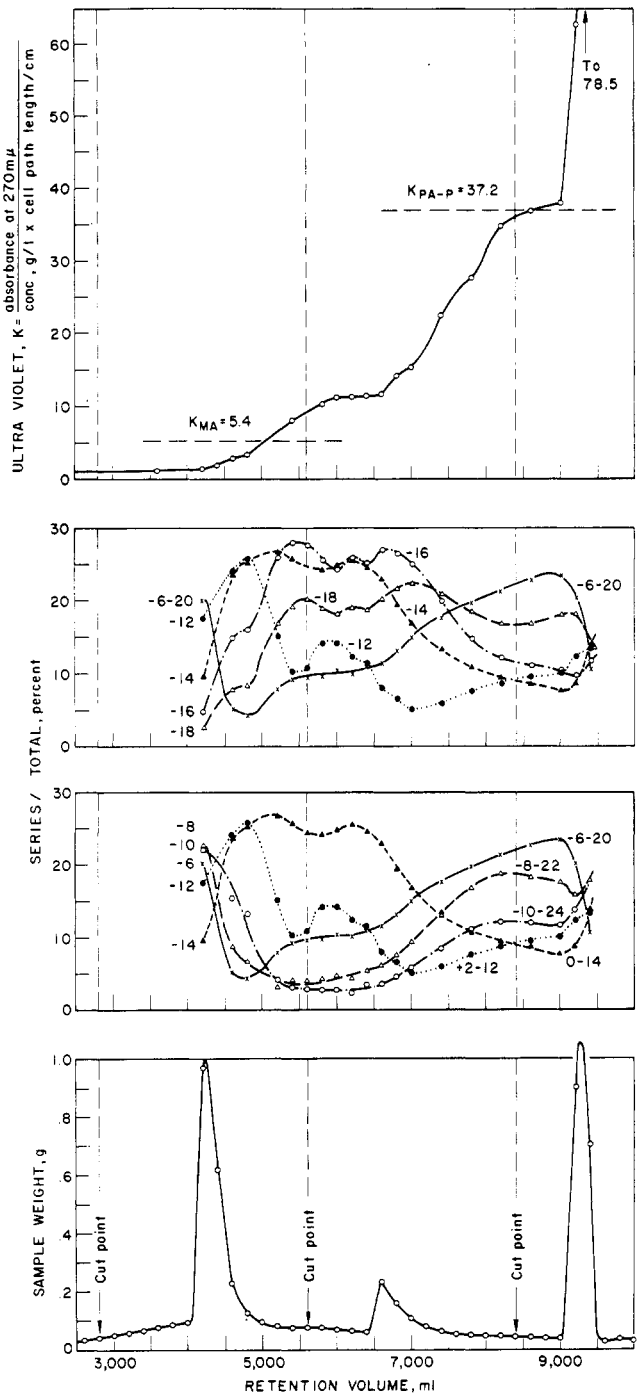

Figure 4. Spectral study of subfractions from chromatographic separation of Recluse 335–530 °C distillate to evaluate cut points

pearance and disappearance of selected types of compounds. Sample quantities in the valleys C–D and E–F are slightly larger for the Gato Ridge sample than were those observed with the Recluse sample. This is caused by the high concentration of sulfur compounds in the Gato Ridge crude oil.

Evaluation Using Mass and UV Spectral Techniques. Mass and ultraviolet data were used to determine the degree of separation achieved and the validity of the cut points selected among the four concentrates obtained in the silica–alumina adsorption procedure, Figure 4. The ultraviolet K values were obtained by averaging the absorption intensity of the 270 mμ band on about 60 aromatics. The criteria used to differentiate, by UV, between mono-, di-, and polyaromatics are summarized in Table III.

Table III. UV Absorption Characteristics for Selected Aromatic Types

Type	K values
Saturates	$K = 0$
Monoaromatics	$K < 5.4$[a]
Diaromatics	$K = 5.4$ to 37.2[b]
Polyaromatics	$K > 37.2$[c]

$$K = \frac{\text{absorbance at 270 m}\mu}{\text{concn (g/l)} \times \text{cell path length (cm)}}$$

[a] For all nine monoaromatics studied.
[b] For 25 of 33 diaromatics studied; $K < 5.4$ for five and >37.2 for three.
[c] For 18 of 19 polyaromatics studied.

Table IV. Summary of Mass and Ultraviolet Data

Type	Appearance, ml	Disappearance, ml
Saturates	600	<3800
Monoaromatics (including thiophenes)	1200	5600–6200
Chain sulfides		5600–6200
Diaromatics (including benzothiophenes)	4800–5600	9000
Mono-, di-, tri-, etc., cyclic sulfides	5400	9800
Thiaindans–thiatetralins		9800
Triaromatics	7600	10,000
Other polyaromatics–polar compounds	9200	10,000

Mass and ultraviolet data indicate that monoaromatics first appear at about 1200-ml elution volume. The low concentration plus the small amount of sample in the valley between saturate and monoaromatic peaks results in only about 1.0% monoaromatics in the saturate concentrate. The lower mass data panel shows the elution order of the monoaromatics to be alkylbenzenes (−6), mono- (−8), di- (−10), tri- (−12), and tetra- (−14), etc., naphthenologs thereof. Naphthenologs are defined here as a series of compounds formed by adding a naphthene ring or rings to a mono- or diaromatic nucleus. This definition is independent of whether the naphthene rings are 5- or 6-membered or the number of carbons involved in the addition. Ultraviolet K values <5.4, shown in the top panel, are consistent with these findings, as are elution data for a number of tagged compounds.

Both mass and ultraviolet data indicate an overlap of monoaromatic and diaromatic types in the 4800–6400 ml region. The adsorptogram shows that only 2.8% of the charge is involved in this valley, and the mass panels show that even in this region material is being separated largely as designated. The amount of material in the region before the cut point where $K > 5.4$ is only about 1.2% of the charge. The elution order for diaromatics (upper mass panel) is naphthalenes (−12), mono- (−14), di- (−16), and tri- (−18), etc., naphthenologs thereof. Benzothiophenes and their naphthenologs which elute in the same order are also detected. Ultraviolet K values of 5.4–37.2 are consistent with these findings. Cyclic sulfides also elute in this region.

Mass and ultraviolet data suggest a diaromatic–polyaromatic overlap region from 7600–9000 ml about the cut point (8400 ml). The adsorptogram shows this region to be only 1.6% of the charge, and even this material is being separated, to some extent, as designated. Neither mass nor ultraviolet could detect any tetra- or higher polynuclear aromatics in the diaromatic region. However, ultraviolet K values alone cannot preclude the presence of trinuclear aromatics of the anthracene, phenylnaphthalene, and acenaphthylene types in the diaromatics.

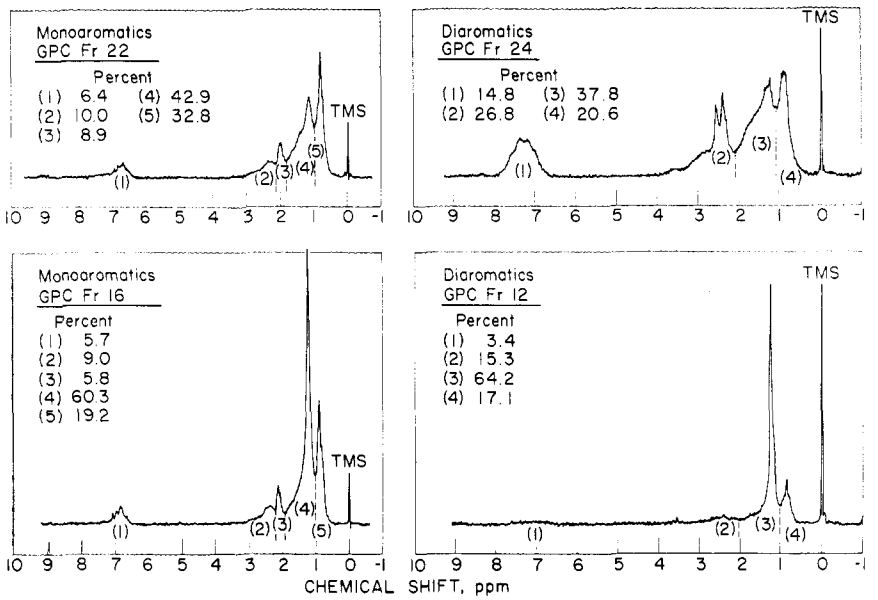

Figure 5. 60-MHz NMR spectra of selected GPC fractions of monoaromatics and diaromatics from Recluse 335–530 °C distillate, less acids and bases

The sharp rise of the ultraviolet curve and the −8, −10, −12, −14 series (lower mass panel) in the polyaromatic region (9000–9200 ml) indicate the appearance of tri-, tetra-, and higher nuclear aromatic types in the proper place.

Table IV summarizes the mass and ultraviolet data, which are in good agreement, and are compatible with the adsorption and radiotracer data, and confirm the soundness of the selected cut points. Although there is some mixing at and near the cut points, the quantity of sample involved is minimal, and each concentrate appears to be predominantly material of the type designated.

Evaluation Using GPC–MS–NMR. Gel permeation chromatography (GPC) in conjunction with mass spectrometry (MS) and/or nuclear magnetic resonance (NMR) spectrometry is a powerful tool for inspecting aromatic concentrates for contaminants. Analysis of monoaromatic concentrates prepared by the dual silica–alumina adsorption procedure shows the monoaromatics to be free of diaromatic contamination. These findings are based on the fact that if diaromatics were present in the total monoaromatic concentrate, they would be concentrated by GPC into specific fractions. Spectral study of these fractions failed to show peaks attributable to diaromatics.

Examination of the GPC subfractions of the diaromatic concentrate revealed some contamination by monoaromatics. However, mass data indicate their concentration is quite low, even after concentration, and that they only occur under the front half of the diaromatic GPC peak.

Mass spectral evidence for triaromatics (naphthenophenanthrenes and/or naphthenoanthracenes) in the diaromatic fractions was found, although in low concentration (*m/e* 231 and 245). Their retention volume was consistent with triaromatics common to this boiling range, and their low concentration was corroborated by the fact that they were observed only at 7600–8400 ml in the adsorptogram, Figure 1. Rearrangement peaks of the −18 Z series caused by phenanthrenes and/or anthracenes were not found. No GPC or spectral evidence for higher polyaromatics was found.

NMR data were obtained on selected subfractions from the GPC fractionation of monoaromatic and diaromatic adsorption fractions, and spectra of four of these appear in Figure 5. The aromatic hydrogen peak (peak No. 1, left panel, Figure 5) occurred at less than 7 ppm in GPC fraction 22 of the monoaromatic concentrate. This peak was shifted to more than 7 ppm in the diaromatic fraction caused by hydrogen atoms on condensed aromatic compounds. In addition, the early eluting subfractions of both the mono- and diaromatics (lower panels) are obviously high in methylene hydrogen compared with methyl hydrogens which are at least gamma to the ring. For the diaromatics, peak No. 1 shows a strong increase from fraction 12 to 24, indicative primarily of less substitution on the diaromatic rings. Also, for the diaromatics, the changing ratios of peaks 2, 3, and 4 at 2.4, 1.3, and 0.9 ppm, respectively, show decreasing chain length and increasing ring condensation in going from GPC subfraction 12 to 24. The increasing size of the small peak at 3.6 ppm, particularly in the diaromatic fractions, also is important proof of additional ring condensation in that this peak can be attributed to the hydrogen on a naphthene bridge of naphthenoaromatics. These NMR data confirm the previous findings by mass, UV, and radiotracers relative to the nature of these well-defined adsorption fractions.

SUMMARY

The method described is a simple, reproducible procedure that will separate 25- to 50-gram samples of high-boiling petroleum distillates into four important compound type concentrates: saturates, monoaromatics, diaromatics, polyaromatics–polar. This is accomplished by gradient elution through a dual-packed silica–alumina gel adsorption column under established conditions that make it unnecessary to monitor intermediate fractions by UV or other methods.

The concentrates prepared by this adsorption procedure have but small amounts of cross contamination. Spectral, adsorption, and radiotracer data indicate the separated compound type concentrate fractions to be predominantly as labeled. Such separations, by subdividing according to major aromatic types, greatly simplify subsequent separation and characterization studies.

ACKNOWLEDGMENT

The authors are indebted to R. F. Kendall, J. E. Dooley, and D. A. Doughty, of the Bartlesville Energy Research Center, for the ultraviolet, mass, and nuclear magnetic resonance data so necessary in the evaluation of this method.

Received for review June 23, 1971. Accepted October 27, 1971. Reference to trade names is made to facilitate understanding and does not imply endorsement by the Bureau of Mines.