

CHROM. 12,553

Note

Preparative separation of C_9 and C_{10} monoaromatic hydrocarbon mixtures by high-performance liquid chromatography on silica gel

M. KURÁŠ, J. KRÍŽ, J. TRÍSKA and L. VODIČKA

Laboratory of Synthetic Fuels, Institute of Chemical Technology, Suchbátarova 5, 166 28 Prague 6 (Czechoslovakia)

The retention times of alkylbenzenes in adsorption elution chromatography depend on the number, position and structure of the alkyl substituents. However, the relevant differences are not very large on silica gel or on alumina¹⁻³. Thus it might be anticipated that chromatographic analysis of complex mixtures of alkylbenzenes from crude oil fractions will not result in a significant separation of different structural types of alkylbenzenes and that a complex zone will be obtained.

In this note, we present the results of separation of both synthetic and natural mixtures (petroleum cut) of aromatic hydrocarbons containing C_9 and C_{10} alkylbenzenes and indanes, using preparative high-performance liquid chromatography (HPLC) on silica gel.

EXPERIMENTAL

Separation of aromatic mixtures

The separation of aromatic mixtures into individual fractions was performed on a Chromatospac Prep 100 preparative chromatograph (Jobin Yvon, Longjumeau, France). A 200 g amount of silica gel of irregular shape (particle size 10–20 μm) was packed into a column of 40 mm I.D.; the height of the bed was 270 mm. The adsorbent was obtained from L 40 silica gel (Lachema, Brno, Czechoslovakia) by screening on a Zig-Zag classifier (Alpine AG, Augsburg, G.F.R.) and dried at 200° for 5 h before use. Dry *n*-pentane (Reachim, U.S.S.R.) was used as the mobile phase, and was degassed before use by connecting its reservoir in the preparative chromatograph to a vacuum for 10 min. The flow-rate of mobile phase was 26 ml/min at a pressure of 150 kPa. The following samples were injected directly into the column by means of a syringe: 1 ml distillation cut; 0.3 ml synthetic mixture. Individual fractions were collected according to the shape of the chromatographic curve.

Detection was carried out at 254 nm on a Variscan spectrophotometer (Varian, Palo Alto, Calif., U.S.A.) with a preparative flow-through cell (optical length 3 mm, volume 70 μl) designed in our laboratory.

Two mixtures of aromatic hydrocarbons were used for the separation: a synthetic mixture containing nine C_9 and C_{10} hydrocarbons (eight alkylbenzenes + indane), the composition of which is given in Table I; and an aromatic distillation cut (160–180°) obtained from an aromatic concentrate of a kerosene fraction of Romash-

kino petroleum by means of distillation on an analytical column of the Nester Faust NF 100 type at 7 kPa pressure. The synthetic mixture of aromatic hydrocarbons was separated into six fractions by preparative HPLC, the aromatic cut into four fractions.

TABLE I

RESULTS OF PREPARATIVE HPLC SEPARATION OF THE SYNTHETIC MIXTURE OF MONOAROMATIC HYDROCARBONS

Hydrocarbons	Concentration (% w/w)						
	Original mixture	Fraction 1	Fraction 2	Fraction 3	Fraction 4	Fraction 5	Fraction 6
Isopropylbenzene	8.9	5.0	39.8	17.5	1.1	0.4	0
<i>n</i> -Propylbenzene	10.2	40.9	26.0	1.9	0.3	0.4	0
<i>p</i> -Ethyltoluene	8.6	0.4	11.4	27.9	3.3	0.6	0.1
<i>o</i> -Ethyltoluene	13.7	0.2	0.4	5.2	29.5	18.0	5.1
1,3,5-Trimethylbenzene	14.1	0.8	0	17.4	35.7	19.2	4.4
1,2,4-Trimethylbenzene	14.7	1.2	0	0.3	6.7	50.5	87.4
<i>p</i> -Cymene	11.6	1.4	11.4	20.9	2.3	0.3	1.4
<i>n</i> -Butylbenzene	8.0	49.5	11.0	0.6	0.0	0.2	0
Indane	10.2	0.6	0	8.3	21.1	10.4	1.6
Monoalkylbenzenes	27.1	95.4	76.8	20.0	1.4	1.0	0
Dialkylbenzenes	33.9	2.0	23.2	54.0	35.1	18.9	6.5
Trialkylbenzenes	28.8	2.0	0	17.7	42.4	69.7	91.8
C ₉ alkylbenzenes	70.2	48.5	77.6	70.2	76.6	89.1	97.0
C ₁₀ alkylbenzenes	19.6	50.9	22.4	21.5	2.3	0.5	1.4

Analysis of fractions obtained by preparative separation

The identification of individual hydrocarbons in the fractions obtained by preparative separation of the synthetic mixture and of the aromatic crude oil cut was performed by gas chromatography (GC); the crude oil cut was also analyzed by analytical HPLC.

GC data were measured on a Varian Model 3700 capillary gas chromatograph with a flame ionization detector (FID) (frit type glass insert, splitting ratio 100:1) using a CDS-111 chromatography data system. Nitrogen was used as both the carrier (*ca.* 0.5 ml/min) and make-up gas (30 ml/min) for the FID. The analyses were performed on stainless-steel capillary columns (50 or 100 m × 0.25 mm I.D.) coated with squalane and programmed from 50 to 110° at 2°/min.

HPLC analysis was carried out on a Varian 8500 instrument with a UV detector (254 nm), a column (250 × 8 mm I.D.) packed with 7.5 μm silicagel (Lachema) and dry pentane as the mobile phase (flow-rate 100 ml/h).

RESULTS AND DISCUSSION

The separation of the aromatic cut (160–180°, Romashkino crude oil) on the analytical column is shown in Fig. 1. Monoaromatic hydrocarbons are separated into four peaks. This distillation cut was later subjected to preparative separation.

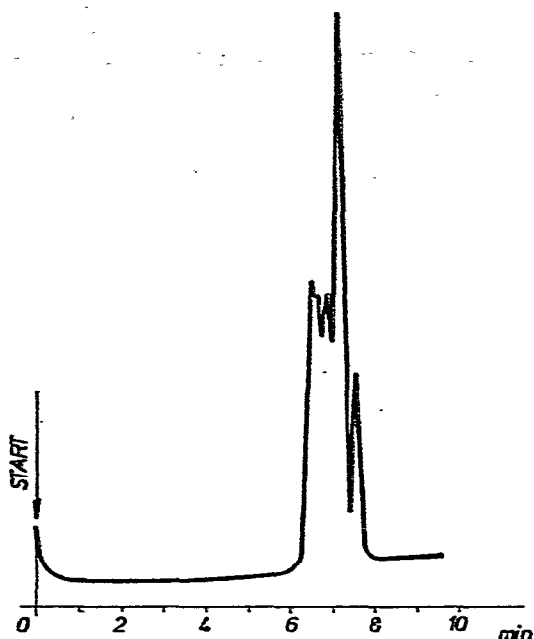


Fig. 1. Analytical HPLC chromatogram of the aromatic petroleum cut (160–180°).

The chromatogram of the preparative separation (Fig. 2) of the aromatic cut (160–180°) shows that the separation efficiency obtained is lower than that on the analytical column. However, it is evident from the results of GC analyses of individual fractions prepared from the synthetic mixture (Table I) that there is a marked shift in the concentrations of individual compounds.

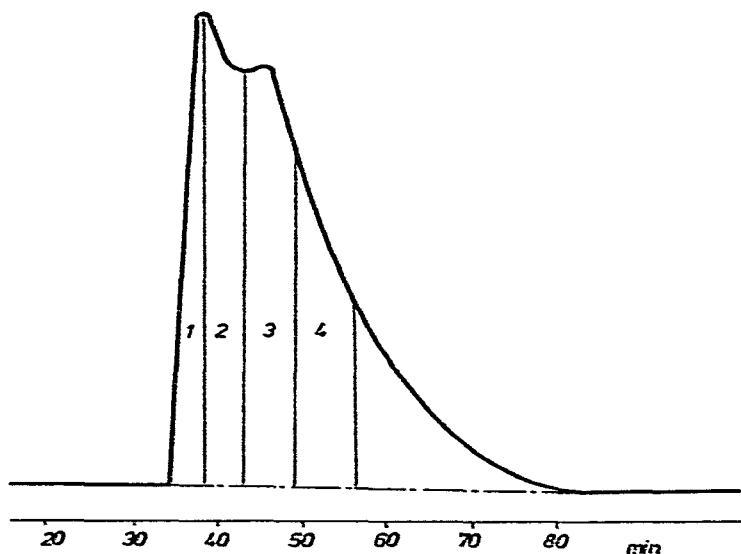


Fig. 2. Preparative HPLC chromatogram of the aromatic petroleum cut (160–180°).

The separation takes place according to:

(1) the number of substituents on the benzene ring: monoalkylbenzenes are concentrated in lower fractions and trialkylbenzenes in higher fractions

(2) molecular mass: hydrocarbons with higher values (C_{10} alkylbenzenes) are concentrated in lower fractions

(3) the type of hydrocarbon (benzenes vs. indanes); the indanes are concentrated in higher fractions

(4) the position of substituents in isomers (the *ortho* effect); *ortho*-substituted isomers are concentrated in higher fractions.

TABLE II

RESULTS OF PREPARATIVE HPLC SEPARATION OF THE MONOAROMATIC (160–180°) PETROLEUM DISTILLATION CUT

<i>Hydrocarbon type</i>	<i>Concentration (% w/w)</i>				
	<i>160–180° cut</i>	<i>Fraction 1</i>	<i>Fraction 2</i>	<i>Fraction 3</i>	<i>Fraction 4</i>
Monoalkylbenzenes	8.0	34.0	5.6	1.4	0
Dialkylbenzenes	43.9	63.3	63.0	24.7	15.6
Trialkylbenzenes	42.4	2.0	29.2	58.1	69.2
Alkylbenzenes total	94.3	99.3	97.8	84.2	84.8
Indanes	5.7	0.7	2.2	15.8	15.2
C_9 alkylbenzenes	53.7	8.6	28.0	53.9	69.2
C_{10} alkylbenzenes	40.6	90.7	69.8	30.3	15.6

As can be seen in Table I, the fractions have different and specific compositions.

All criteria found for the HPLC separation of synthetic mixtures were found to be valid also for the monoaromatic (160–180°) distillation cut from Romashkino petroleum. Even here a significant shift in the concentrations of various hydrocarbon structures in individual fractions was attained (see Table II).

REFERENCES

1. L. R. Snyder, *J. Chromatogr.*, 6 (1961) 22.
2. M. Popl, J. Mostecký, V. Dolanský and M. Kuraš, *Anal. Chem.*, 43 (1971) 518.
3. M. Popl, V. Dolanský and J. Mostecký, *J. Chromatogr.*, 117 (1976) 117.