

SELECTIVE GAS-LIQUID CHROMATOGRAPHIC SEPARATION OF AROMATIC COMPOUNDS WITH TETRAHALOPHTHALATE ESTERS

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(Received May 8th, 1959)

The problem of separating compounds of closely similar structure by gas-liquid chromatography is currently under attack from two distinct but complementary viewpoints. One is the development of more efficient columns and techniques to refine the separation process; the other is the use and development of selective liquid substrates. With the latter course, a liquid substrate is used which is sensitive to structural differences and brings about separation through these differences.

Because of the importance of aromatic materials in synthetic fuel products derived from coal and because of the difficulty in analyzing these complicated products the initial objective of this study was to develop selective liquid substrates for separating aromatic compounds. The separation of *m*- and *p*-xylene was of particular interest because until recently¹⁻⁷ these two materials, which are among the simplest aromatic isomers, had not been separated by gas chromatography. The tetrahalophthalate esters were selected as potential selective liquid substrates for aromatic compounds because they contain an aromatic ring with a large number of electro-negative substituents⁵. Therefore, they would be expected to be electron acceptors in "charge transfer" interactions of the " π - π " type^{8,9}. Variations in the behavior of aromatic hydrocarbons as electron donors, as well as their vapor pressures and activity coefficients¹⁰⁻¹³ should then serve to separate these materials in the gas chromatographic column.

EXPERIMENTAL

Apparatus

A flow diagram of the gas chromatography apparatus is shown in Fig. 1. The Foxboro regulator Type 67-R222 was modified by plugging the bleed hole with solder to prevent loss of gas. The Gow-Mac thermal conductivity cell and stainless steel columns were operated in an insulated circulating air bath in which temperature was controlled to $\pm 0.1^\circ$. Helium was used as the carrier gas.

Materials

Dimethyl tetrachlorophthalate was prepared (in low yield) by a modification of the method of KOLLONITSCH AND VITA¹⁴ in which methyl borate-methanol azeotrope was

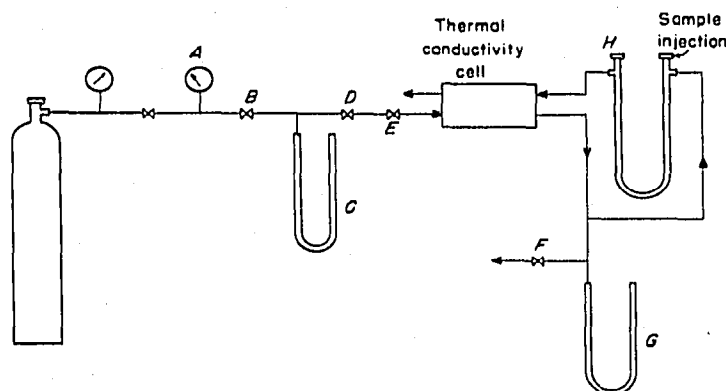


Fig. 1. Schematic diagram of apparatus for gas-liquid chromatography. *A*: reduced pressure gage. *B*: system pressure regulator valve; modified Foxboro regulator. *C*: mercury manometer. *D*: control orifice; needle valve. *E*: gas shut-off valve. *F*: pressure bleed; needle valve. *G*: mercury manometer; column pressure. *H*: chromatographic column.

initially refluxed with tetrachlorophthalic anhydride. Preparation of other tetrahalophthalates is described elsewhere¹⁵. Narrow mesh range firebrick was used as a solid support. The firebrick, predried in an oven at 140°, was treated with an acetone solution of the liquid phase with or without stirring under nitrogen. In later experiments, the flask used for treating the firebrick was shaken occasionally without stirring. Hydrocarbons used in the mixtures were mostly 98% pure or better as obtained from Phillips Petroleum Co., Eastman Organic Chemicals, or A.P.I. standard samples.

Columns

Stainless steel U-shaped columns were connected into flow lines with Ermeto fittings (Weatherhead Co., Cleveland 8, Ohio). Long columns were constructed of 6 foot U-shaped sections connected with stainless steel capillary tubing. The 35 foot di-*n*-propyl tetrachlorophthalate column, however, was of one piece construction and carefully wound on a 2 in. mandrel. All columns were packed while being shaken by an electric vibrator. These columns are described in Table I. Conditions of operation are indicated in Table II. Data for the dimethyl tetrachlorophthalate column were obtained on an auxiliary vapor-heated apparatus.

TABLE I
COLUMNS USED IN THIS STUDY

Column	Liquid substrate	Packing, g	Percent liquid substrate (w/w)	Column dimensions, cm		Firebrick, mesh size
				length	diameter	
A	90% Dimethyl tetrachlorophthalate + 10% di- <i>n</i> -propyl tetrachlorophthalate	12.1	25	120.7	0.45	35-60
B	Methyl propyl tetrachlorophthalate	65.1	20	692.0	0.45	42-48
C	Di- <i>n</i> -propyl tetrachlorophthalate	89.5	7	889.0	0.5	35-42
D	Di- <i>n</i> -butyl tetrachlorophthalate	32.7	10	304.8	0.5	42-48
E	Di- <i>n</i> -propyl tetrabromophthalate	12.3	10	181.6	0.45	42-48

TABLE II
CONDITIONS OF OPERATION OF CHROMATOGRAPHIC COLUMNS

Column	Temperature, °C	p_1 , mm Hg	p_0 , mm Hg	Flow rate, ml/min*	Pressure correction factor**
A	97.8	1167.3	741.8	35.4	0.765
B	110.0	1660.8	734.8	44.6	0.584
	95.0	1675.6	744.6	45.3	0.586
C	110.0	1725.2	743.2	88.2	0.572
	100.0	1709.0	740.0	90.0	0.574
	90.0	1674.6	737.6	84.1	0.582
D	110.0	1386.2	735.2	112.8	0.672
	100.0	1372.0	740.0	109.3	0.681
E	110.0	1020.3	743.3	48.5	0.836
	100.0	1055.7	742.2	56.8	0.817

* Flow corrected to column temperature and atmospheric pressure.

** Correction for pressure drop across column is $\frac{3}{2} \frac{(p_1/p_0)^2 - 1}{(p_1/p_0)^3 - 1}$ (ref. 17).

Sample injection

Samples were injected by means of a microsyringe of a type described earlier¹⁶. For sample injection, the gas flow was stopped and when column pressure fell to 100–200 mm, the bleed valve was slowly opened until the inlet of the column was depressurized. The valve was then closed, sample injected and gas flow resumed. When the marker air peak emerged, the column pressure had reached 99 % of operating value.

Approximately 3 μ l samples were generally used. Where a mixture contained only two or three compounds of interest the sample was diluted with more volatile materials so that the column would not be greatly overloaded for the materials of interest.

A preheater was not used for the sample injection section. For xylene separations, in which we were particularly interested, a preheater effected little or no improvement in peak resolution with our apparatus.

DISCUSSION

Relative retention volume data for hydrocarbons on dimethyl tetrachlorophthalate, methyl *n*-propyl tetrachlorophthalate, di-*n*-propyl tetrachlorophthalate, di-*n*-butyl tetrachlorophthalate and di-*n*-propyl tetrabromophthalate are presented in Tables III and IV. Toluene was used as the standard reference material. Retention volume data for *m*- and *p*-xylene are given to 4 significant figures since special attention was given to their determination. For a particular column these values were reproducible to 1–2 parts per thousand. While absolute values did vary slightly more with different columns, relative values (for the xylenes) were close to this range of reproducibility. 10 % by weight of di-*n*-propyl tetrachlorophthalate was included in the dimethyl tetrachlorophthalate, m.p. 90°, with the idea of decreasing its viscosity at the operating temperature of 97.8°. This temperature was apparently slightly high for the dimethyl

TABLE III
RELATIVE RETENTION VOLUMES ON TETRACHLOROPHTHALATE ESTERS (TOLUENE = 1)*

	<i>Methyl propyl tetrachlorophthalate</i>		<i>Di-n-propyl tetrachlorophthalate</i>			<i>Di-n-butyl tetrachlorophthalate</i>	
	110°	95°	110°	100°	90°	110°	100°
Benzene	0.459	0.43	0.455	0.439	0.421	0.451	0.435
Toluene	(1.000) ^a	(1.000) ^b	(1.000) ^c	(1.000) ^d	(1.000) ^e	(1.000) ^f	(1.000) ^g
<i>m</i> -Xylene	2.038	2.158	2.045	2.125	2.203	2.071	2.152
<i>p</i> -Xylene	2.122	2.255	2.125	2.217	2.302	2.144	2.231
<i>o</i> -Xylene	2.71	—	2.70	2.81	—	2.71	2.84
Ethylbenzene	1.70	1.76	1.74	1.79	1.82	1.77	1.81
Styrene	—	—	2.82	2.93	—	2.80	—
Phenylacetylene	—	—	2.68	2.81	2.20	2.60	2.72
Propylbenzene	—	—	3.12	3.28	—	3.19	3.34
Cumene	—	—	2.45	2.56	—	2.49	2.60
1-Methyl-2-ethylbenzene	—	—	4.31	4.63	—	4.40	4.72
1-Methyl-3-ethylbenzene	—	—	3.37	3.57	—	3.46	3.67
1-Methyl-4-ethylbenzene	—	—	3.53	—	—	3.61	3.83
Mesitylene	—	—	3.85	4.14	—	3.98	4.28
1,2,4-Trimethylbenzene	—	—	5.32	—	—	5.41	5.89
Hemimellitene	—	—	6.88	7.49	—	6.96	—
Butylbenzene	—	—	6.29	6.89	—	6.45	7.03
Heptane	0.20	—	0.25	0.24	0.22	0.26	0.24
Octane	0.42	—	—	—	0.49	0.54	0.53
Nonane	—	—	—	—	—	1.10	1.12
Decane	1.71	—	—	—	—	2.24	2.38
Heptene	—	—	0.27	0.26	—	0.28	0.27
Octene	0.47	—	0.56	0.55	0.59	0.58	0.57
Nonene	—	—	1.14	1.16	—	1.19	1.22
Decene	1.93	—	2.33	2.43	—	2.43	2.58
2-Methylhexane	—	—	0.20	0.19	—	0.21	0.19
2-Methylheptane	—	—	0.40	0.39	—	0.42	0.41
2-Methyloctane	—	—	0.83	0.83	—	0.87	0.88
2-Methylnonane	—	—	1.70	1.74	—	1.79	1.87
Cyclohexane	—	—	—	—	—	—	0.21
Methylcyclohexane	0.32	—	0.37	0.35	0.33	0.39	0.37
Dimethylcyclohexane	0.71	—	—	—	—	—	0.85
Butanol	~ 0.47	—	~ 0.31	—	—	—	—
2-Butanone	~ 0.27	—	—	—	—	—	—

* Retention volume of air taken as zero. Corrected retention volumes in ml/g of liquid phase, for columns of Table I at column temperature: a = 142, b = 215, c = 162, d = 221, e = 290, f = 163, g = 217.

ester since some difficulty was encountered with condensation of the solid ester when the capillary tubing connecting the column to the cell (heated separately) was not heated.

The data of Tables III and IV make it possible to characterize the tetrahalophthalates qualitatively as liquid phases for gas chromatography.

Selectivity

The tetrahalophthalates are selective for aromatic materials in that aliphatic compounds of the same boiling range are eluted from the column first. (They are not as selective for aromatics as the dipropionitriles from which decane emerges long before

TABLE IV
RELATIVE RETENTION VOLUMES ON TETRAHALOPHTHALATE ESTERS (TOLUENE = 1)*

	<i>Di-n-propyl tetrabromophthalate</i>		<i>Dimethyl tetrachlorophthalate-90% + di-n-propyl tetrachlorophthalate-10%</i> 97.8°
	110°	100°	
Benzene	0.470	0.451	0.45
Toluene	(1.000) ^a	(1.000) ^b	(1.000) ^c
<i>m</i> -Xylene	1.967	2.023	2.076
<i>p</i> -Xylene	2.030	2.094	2.167
<i>o</i> -Xylene	2.66	2.80	2.85
Ethylbenzene	1.72	1.76	1.72
Styrene	2.86	3.01	—
Phenylacetylene	2.82	2.94	—
Propylbenzene	3.03	3.17	—
Cumene	2.38	2.46	—
1-Methyl-2-ethylbenzene	4.21	4.50	—
1-Methyl-3-ethylbenzene	3.22	3.40	—
1-Methyl-4-ethylbenzene	3.36	3.55	—
Mesitylene	3.51	3.73	—
1,2,4-Trimethylbenzene	4.95	5.39	—
Hemimellitene	7.26	7.87	—
Butylbenzene	5.97	6.45	—
Heptane	0.21	0.20	0.16
Octane	0.42	0.43	0.33
Nonane	0.87	0.88	—
Decane	1.76	1.83	1.41
Heptene	0.24	0.23	—
Octene	0.48	0.48	—
Nonene	1.00	1.01	—
Decene	2.00	2.11	—
2-Methylhexane	0.17	0.16	—
2-Methylheptane	0.34	0.33	—
2-Methyloctane	0.68	0.69	—
2-Methylnonane	1.40	1.46	—
Methylcyclohexane	0.35	0.33	—
Butanol	—	1.30	—
1-Propanol	—	—	0.22

* Retention volume of air taken as zero. Corrected retention volume in ml/g of liquid phase at column temperature: a = 101, b = 134, c = 159.

benzene¹⁸. However, the use of dipropionitriles is limited by their volatility.) The selectivity of the tetrahalophthalates appears to be controllable to some extent since it is governed by the proportion of alkoxy group comprising the ester. Whereas octane is eluted before benzene from dimethyl tetrachlorophthalate and methyl propyl tetrachlorophthalate, it is eluted after benzene from di-*n*-butyl and di-*n*-propyl tetrachlorophthalate. Increasing the atomic weight of the halogen has an effect similar to decreasing the size of the alkoxy group and octane emerges before benzene from di-*n*-propyl tetrabromophthalate.

Naphthenes and olefins are retained longer than paraffins of comparable boiling point while alcohols and ketones emerge earlier and exhibit marked peak distortion due to tailing. The retention volumes of these oxygenates is greater when the alkoxy

groups are smaller; this may be due to increased accessibility and concentration of the polar ester groups.

For the saturated hydrocarbons and olefins on the substrates reported here, the same general observations apply as reported by others. Retention volumes are affected in a regular manner by addition of methylene groups to the solute molecule and the logarithm of retention volume or relative retention volume varies linearly with carbon number.

Effect of temperature on selectivity

While the relative retention volumes of heptane with respect to benzene are lowered with a decrease in temperature, the geometrical factor for addition of a methylene group increases (as temperature decreases) and the relative retention volumes for the higher paraffins tend to be greater compared with aromatic materials. Therefore, type separations of aliphatic and aromatic compounds are not improved by decreasing operating temperature.

Separations of aromatic hydrocarbons

Typical separations of aromatic hydrocarbons on di-*n*-propyl tetrabromophthalate at 100° and di-*n*-propyl tetrachlorophthalate at 100° and 110° are shown in Figs. 2 and 3. These may be compared with separations of similar mixtures on naphthalene tetracarboxylic acid ester¹⁹ and Apiezon L²⁰. Neither substrate effected separation of

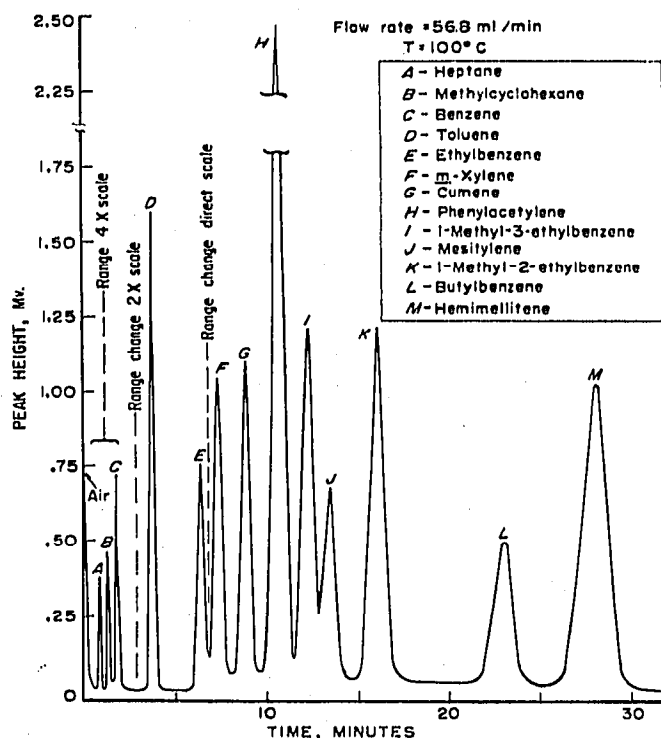


Fig. 2. Separation of hydrocarbon mixture on propyl tetrabromophthalate 10%. Column = 0.45 × 181.6 cm.

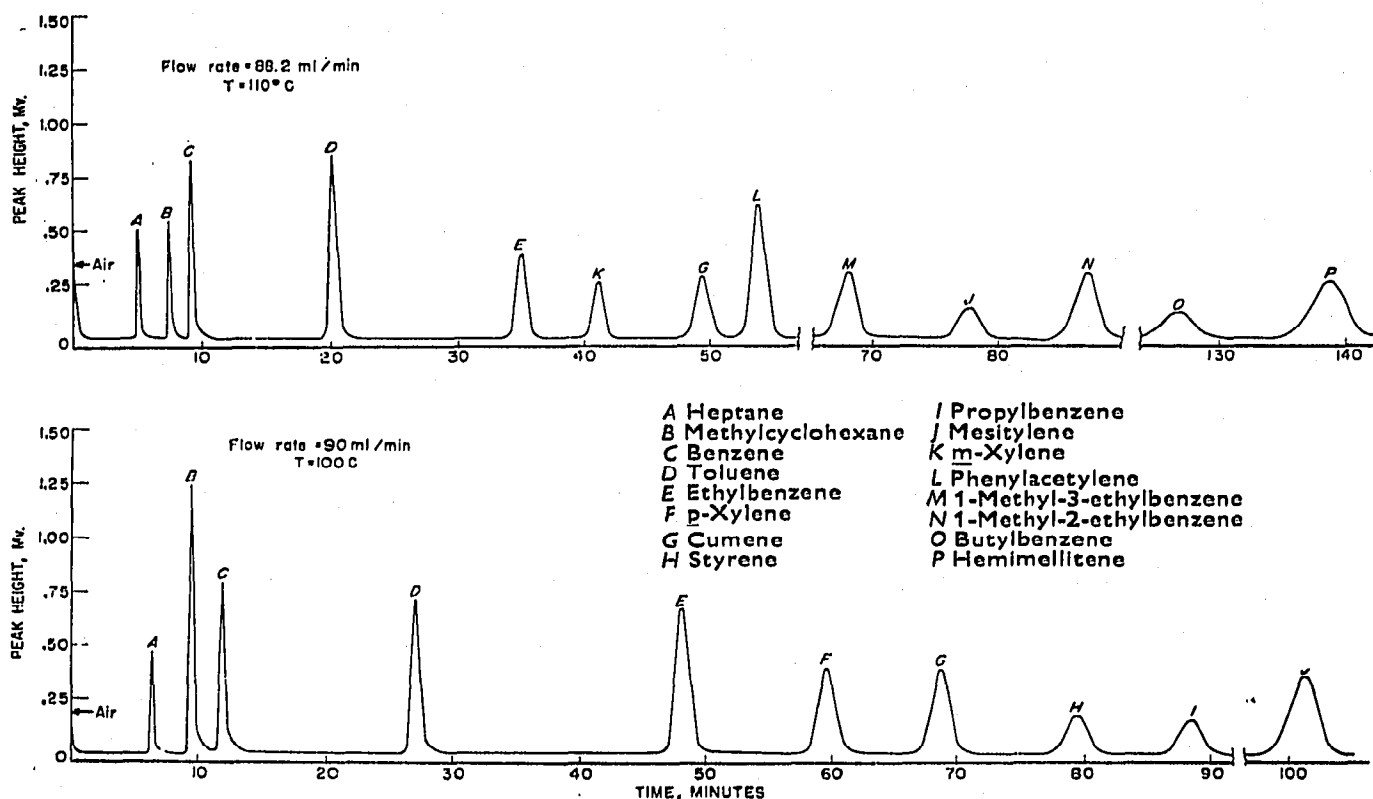


Fig. 3. Gas chromatographic separation of hydrocarbons on propyl tetrachlorophthalate. Column = 0.5×889 cm. 89.5 g packing containing 7% (w/w) liquid on 35-42 mesh firebrick.

mesitylene and 1-methyl-2-ethylbenzene. In this work, they were separated by both propyl tetrahalophthalates. In contrast to the order of elution shown in Figs. 2 and 3, retention data reported for Apiezon L²⁰ indicate mesitylene emerges after 1-methyl-2-ethylbenzene.

The data of Tables III and IV show that, although the relative retention volumes of the aromatic hydrocarbons on various tetrahalophthalates do not vary greatly, definite though sometimes minor trends exist. Thus, as the amount of alkyl group in the alkylbenzenes becomes greater, retention volumes relative to toluene increase with increasing percentage of alkoxy group in the tetrahalophthalate ester. This is not true for phenylacetylene, styrene, and benzene, where presumably activity coefficients increase (and elution times decrease) with increasing aliphatic content of the tetrahalophthalate ester. At the same time, the difference between styrene and phenylacetylene is emphasized and the separation factor is improved by going from either propyl tetrabromophthalate or propyl tetrachlorophthalate to butyl tetrachlorophthalate. Thus, a particular separation of two compounds of different type can often be achieved without upsetting the general order of elution by choosing a partitioning liquid which is a higher (or lower) member of a homologous series.

Separation of m- and p-isomers. It is readily shown^{10-13, 21} that the relative volatility, $\alpha_{1,2}$, or separation factor for two substances from the partitioning liquid may be expressed as

$$\alpha_{1,2} = \gamma_1^0 p_1^0 / \gamma_2^0 p_2^0 \quad (1)$$

where γ^0 is the activity coefficient at infinite dilution and p^0 is the vapor pressure of the pure solute.

For initial discussion purposes, the measured separation factor or relative volatility of two aromatic isomers is treated in terms of

$$\alpha_{1,2} = g_1 p_1^0 / g_2 p_2^0 \quad (2)$$

where g_1 and g_2 are "apparent activity coefficients" which may or may not include correction terms for complex formation, depending on definition of the latter. Since neither γ_1 nor g_1 have been measured g_1 and g_2 are treated relative to each other.

Vapor pressures of a number of aromatic compounds at several temperatures are presented in Table V and the separation factors for *m*- and *p*-xylene on several liquid

TABLE V
VAPOR PRESSURES OF AROMATIC COMPOUNDS*

	Vapor pressure in mm at		
	110°	100°	90°
Benzene	1756.9	1350.7	1021.7
Toluene	746.6	556.3	406.7
Ethylbenzene	355.3	257.0	181.9
<i>o</i> -Xylene	277.4	198.5	139.0
<i>m</i> -Xylene	324.5	233.6	164.6
<i>p</i> -Xylene	333.2	240.4	169.8
<i>n</i> -Propylbenzene	177.5	124.7	85.62
Cumene	218.6	155.0	107.4
1-Methyl-2-ethylbenzene	146.0	101.6	68.99
1-Methyl-3-ethylbenzene	161.4	114.6	78.18
1-Methyl-4-ethylbenzene	162.1	113.4	77.49
1,2,3-Trimethylbenzene	103.2	70.81	47.36
1,2,4-Trimethylbenzene	127.4	88.14	59.48
1,3,5-Trimethylbenzene	145.5	101.0	68.38
<i>n</i> -Butylbenzene	82.32	55.89	36.95
Styrene	268.0	191.1	133.4

* Calculated from Antoine's equation²³.

phases are given in Table VI. On the basis of vapor pressure alone it would be expected that *p*-xylene would emerge from a gas chromatographic partitioning liquid before *m*-xylene. Indeed, JAMES AND MARTIN²² found this to be true for a number of substrates including paraffin wax, a polyglycol and benzyldiphenyl. ZLATKIS and co-workers⁷ have recently confirmed this order of elution from benzyldiphenyl in a report on the xylene separation.

The emergence of *p*-xylene after *m*-xylene from the tetrahalophthalates as illustrated in Figs. 4 and 5 is additional evidence^{4, 5} that "charge transfer" forces are operative between the solute (electron donor) and the tetrahalophthalate (electron acceptor). *p*-Xylene has the lower base ionization potential and would be expected generally to interact more strongly^{8, 24, 25} (or form the more stable complex) with the tetrahalophthalate so that it would be held up in the chromatographic column.

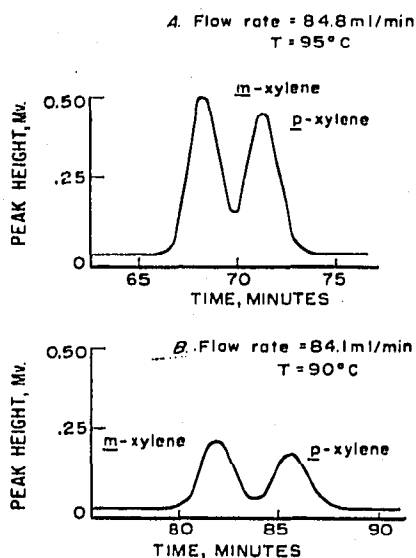


Fig. 4. Separation of *m*- and *p*-xylene on propyl tetrachlorophthalate. Column = 0.5×889 cm. 89.5 g packing containing 7% (w/w) liquid on 35-42 mesh firebrick.

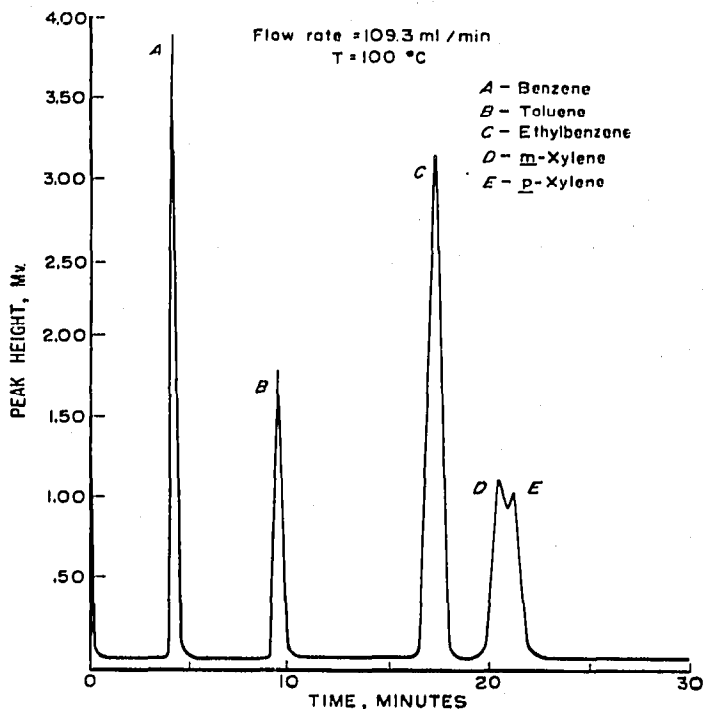


Fig. 5. Separation of aromatic hydrocarbon mixture on butyl tetrachlorophthalate. Column = 0.5×304.8 cm. 32.7 g packing with 10% (w/w) liquid on 42-48 mesh firebrick.

Since vapor pressure relationships favor emergence of the *p*-xylene before *m*-xylene, favorable separation factors based on differences in basicity of these aromatic hydrocarbons are difficult to attain, *i.e.* the effect of vapor pressures and base strengths are opposed.

From the vapor pressure data, separation factors and equation (2), g_1/g_2 is 1.067 and 1.078, for *m*- and *p*-xylene on propyl tetrachlorophthalate at 110° and 90°

TABLE VI
SEPARATION FACTORS FOR *m*- AND *p*-XYLENE ON TETRAHALOPHTHALATE ESTERS

Liquid substrate	Temperature $^\circ\text{C}$	Separation factor <i>p</i> -/ <i>m</i> -
Dimethyl tetrachlorophthalate (90%) + di- <i>n</i> -propyl tetrachlorophthalate (10%) Methyl propyl tetrachlorophthalate	97.8 110.0 95.00	1.044 1.041 1.045
Di- <i>n</i> -propyl tetrachlorophthalate	110.0 100.0 90.0	1.039* 1.043 1.045
Di- <i>n</i> -butyl tetrachlorophthalate	110.0 100.0	1.035 1.037
Di- <i>n</i> -propyl tetrabromophthalate	110.0 100.0	1.032 1.035

* This value is a revision of the earlier value of 1.042 reported in ref.⁵. This may be due to experimental error and/or the fact that the earlier value was determined on a column with 20% liquid phase.

respectively. The separation factors of Table VI indicate that separation of *m*- and *p*-xylene is favored by lower temperatures despite the fact that the ratio of vapor pressure becomes more unfavorable for separation. The increase in separation factor with decreasing temperature, therefore, is a net effect also which is dominated by the g_1/g_2 increase.

The separation of 0.7 μ l and 0.4 μ l samples of *m*- and *p*-xylene mixtures on di-*n*-propyl tetrachlorophthalate is shown in Fig. 4, A and B respectively. The peaks are separated by 4 and 4.4 standard deviations²⁶ on a 35 foot column operated at an efficiency (based on toluene) of 7,500 and 7,000 plates respectively. Separation of a 3.5 μ l aromatic mixture on a 12 foot butyl tetrachlorophthalate column is shown in Fig. 5. Although the column is somewhat overloaded a partial separation of *m*- and *p*-xylene is achieved in less than 25 min at an operating efficiency of 3,500 plates.

For the tetrachlorophthalates of Table VI, the favorable xylene separation factor apparently diminishes with increasing aliphatic content of the molecule. This is as expected since *p*-xylene emerges before *m*-xylene from an aliphatic liquid phase²². As the nature and composition of the ester molecule changes, the nature of the interaction with solute molecules changes accordingly. For the bromophthalate, the separation factor for *m*- and *p*-xylene was probably smaller than for the chlorophthalates because of the lower electronegativity of bromine. Therefore, "charge-transfer" interaction is less intense and its effect is diminished. A similar diminution in complex stability has been noted in a comparison of aromatic complexes of tetrachlorophthalic and tetrabromophthalic anhydrides²⁷.

The separation factor, *ca.* 1.048, for 1-methyl-3-ethylbenzene and 1-methyl-4-ethylbenzene on propyl tetrachlorophthalate is more than adequate for separating these previously unresolved isomers^{19, 20}. While their vapor pressure ratios (see Table V) are slightly more favorable for separation by "charge transfer" interaction, the g_1/g_2 ratio (observed) is slightly less favorable. However, the net effect permits sufficient resolution for quantitative analysis of mixtures of these materials. We have obtained a separation of 4.5 standard deviations on the propyl tetrachlorophthalate column.

Quantitative analysis. To demonstrate the usefulness of the tetrahalophthalate liquid substrates, a commercial "xylene" mixture was analyzed on the 27 foot column containing 20 % methyl propyl tetrachlorophthalate as reported previously⁵. Analysis was based on peak heights and the xylene mixture was diluted with a low boiling hydrocarbon so that the 5,900 plate column was not overloaded (maximum 0.8 μ l of either xylene isomer). Despite the fact that the xylene peaks were separated by 3.3 standard deviations, which should be adequate for analysis by peak heights²⁶, successful analysis was not possible without calibration with several mixtures because of the slight asymmetry of the *m*-xylene peak.

A calibration curve for 3.6 μ l samples containing 25 % toluene and various amounts of the xylene isomers is shown in Fig. 6. While the *m*-xylene peak heights were independent of the *p*-xylene concentration, the reverse was not true. Points A and B represent observed *p*-xylene peak heights in the presence of *m*-xylene. From such observations it was possible to correct the *p*-xylene peak height for the slight

contribution of *m*-xylene. When 20% of *m*-xylene was present in the 3.6 μ l sample, the correction to the *p*-xylene peak height was about 3% of the observed *m*-xylene peak height. After correction, analysis of the commercial mixture could be checked by means of a synthetic blend within the limits of reproducibility of our recorder, 0.003 mV.

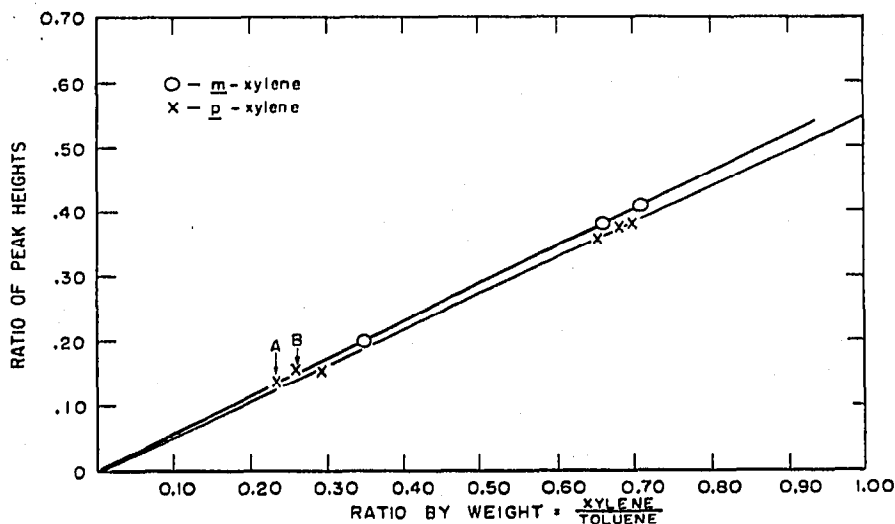


Fig. 6. Calibration curve for analysis of xylene mixtures using toluene as an internal standard.

Complexing

While solid molecular complexes of the tetrahalophthalate esters have been isolated¹⁵, the question of whether and to what extent complexes *per se* account for the abnormal retention volumes of aromatic materials on the tetrahalophthalates is difficult to answer and is greatly dependent on definition. A reasonable amount of evidence exists^{5,15} that "charge transfer" forces are involved^{1,22}, but these may be interpreted as contributing to van de Waals forces as initially suggested by MULLIKEN²⁸. The difficulties encountered in attempting to interpret spectral data, for example, in terms of "charge transfer" complexes have recently been discussed by ORGEL AND MULLIKEN²⁹. In any event, sufficient data were not obtained in this study to evaluate equilibrium constants for "complex" formation. However, these data are adequate for obtaining a qualitative picture of the tendency of some of the aromatic hydrocarbons to interact or "complex" with the tetrahalophthalate liquid phases. For convenience, this interaction will be discussed in terms of complex formation in this section.

The corrected retention volume V_R^0 , taken from the time of *emergence of the air peak* is^{11, 12, 17, 30}

$$V_R^0 = k'V_s \quad (3)$$

where V_s is the volume occupied by the liquid phase in the gas chromatographic column and k' is a pseudo solute partition coefficient defined (here) as the ratio of solute per unit volume of liquid phase, including such material as may be complexed, to solute per unit volume of the gas phase *for very dilute solutions*.

Then, defining the activity coefficient, γ , for the solute^{11, 30, 31}

$$\gamma P = \gamma x p^0 \quad (4)$$

where P is pressure of the gas phase (ideal), γ is mol fraction of solute in the gas, and x is mol fraction of *uncomplexed* solute in the liquid phase. For very dilute solutions where the concentration of liquid phase is essentially constant

$$k' = x' M_s / \gamma M_m \quad (5)$$

where M_s is moles of stationary phase per unit volume, M_m is moles of mobile gas per unit volume, and x' is total solute in solution complexed and uncomplexed.

If
$$x = (1 - c) x' \quad (6)$$

where c is the fraction of material complexed, then from eqn. (5) following others^{11, 30}

$$k' = M_s RT / (1 - c) \gamma p^0 \quad (7)$$

and the separation factor for two solutes on a column becomes

$$\alpha_{1,2} = (1 - c_1) \gamma_1 p_1^0 / (1 - c_2) \gamma_2 p_2^0 \quad (8)$$

and the g of eqn. (2) is

$$g = (1 - c) \gamma \quad (9)$$

The difficulty is in resolving γ and $1 - c$, one of which must be measured independently. However, eqn. (7) permits conclusions about relative complexing tendency or the strength of "charge transfer" interaction by considering isomeric aromatic compounds. For example, for the C_9 saturated alkylbenzenes it would seem reasonable to assume, as a first approximation, that bulk interaction (activity coefficient) with the tetrahalophthalate liquid substrate would be the same except for variation in interaction between the aromatic ring and the tetrahalophthalate nucleus. The more closely any two alkylbenzenes resemble each other, the more nearly true is this assumption.

Table VII shows an arrangement of C_9 alkylbenzenes in the order of values of $(1 - c)$ for di-*n*-propyl tetrachlorophthalate at 110°. The $(1 - c)$ values were calculated from eqn. (7), the vapor pressure values given in Table V, and the relative

TABLE VII
RELATIVE $(1 - c)$ FACTORS FOR C_9 ALKYL BENZENES (CUMENE = 1)

	Relative fraction of material not complexed (1-c)
Cumene	(1.00)
1-Methyl-3-ethylbenzene	0.99
Propylbenzene	0.97
Mesitylene	0.96
1-Methyl-4-ethylbenzene	0.94
1-Methyl-2-ethylbenzene	0.85
1,2,4-Trimethylbenzene	0.79
Hemimellitene	0.76

retention values of Table IV. The γ values are assumed to be equal for the saturated C_9 alkylbenzenes and the value of $(1 - c)$ for cumene was arbitrarily taken as 1. The arrangement then, is in the order of increasing tendency to "complex" or interact depending on definition. This order is as expected if the interaction is assumed to be between the parallel molecules. Thus, propylbenzene has a greater tendency to complex than cumene.

For the methylethylbenzenes the order of complexing (or basicity) is $o- > p- > m-$. For the three trimethylbenzenes the complexing order can be interpreted in terms of a steric factor. Molecular models show that in the di-*n*-propyl tetrachlorophthalate molecule, crowding is such that the ester groups tend to orient out of the plane of the ring with the carbonyl oxygen and alkoxy group on one side or the other. In a parallel complex there could be some steric interference from methyl groups on the aromatic donor which correspond to either of the *ortho* ester groups. The order of basicity hemimellitene (1,2,3-trimethylbenzene) $>$ 1,2,4-trimethylbenzene $>$ mesitylene gives some credence to this idea. For mesitylene, there are no two adjacent positions on the aromatic ring which are free of methyl groups; thus, the close approach and advantageous orientation of the aromatic ring relative to the tetrachlorophthalate ester which is possible for the other trimethylbenzenes appears to be excluded.

ACKNOWLEDGEMENT

We wish to express our thanks to PAUL GOLDEN and his group for construction of our apparatus and to PETER PANTAGES and MARGHARET VIAL for their assistance with this study. We are also grateful to Dr. J. HOWARD PURNELL for many helpful discussions during the course of this work.

SUMMARY

Tetrahalophthalate esters were found to be selective liquid substrates for separating aromatic hydrocarbons by gas chromatography. The tetrachlorophthalates are unusually specific in separating *meta*- and *para*-isomers, including the xylenes; this makes possible the gas chromatographic analysis of mixtures of these isomers. "Charge transfer" interaction between the volatile aromatic compounds (donors) and the tetrahalophthalates (acceptors) is apparently responsible for selectivity. Variations in the elution order of alkylaromatics may be interpreted qualitatively in terms of structure or molecular composition. Gas chromatography, in turn, provides a measure of the complexing or degree of interaction of aromatic compounds with the tetrahalophthalate esters as well as information on salient stereochemical features that effect interaction.

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