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PRE-CALCULATION OF RETENTION INDICES OF AROMATIC COMPOUNDS BY COMPUTER ON THE BASIS OF THEIR MOLECULAR STRUCTURES AND THERMODYNAMICS IN TEMPERATURE-PROGRAMMED GAS CHROMATOGRAPHY

I. FISCH, I. OLÁCSI, M. RICHTER, A. P. SINKA, E. C. TAKÁCS and I. M. TAKÁCS

OGIL, Research Laboratory for the Oil and Gas Industry, Budapest (Hungary)

J. VÖRÖS

OKGT, Hungarian Oil and Gas Trust, Budapest (Hungary)

and

G. TARJÁN

REANAL, Fine Chemicals Factory, Budapest (Hungary)

SUMMARY

Theoretical and practical problems involved in the pre-calculation of retention indices for benzene derivatives are considered in terms of similar problems with alkanes. The determination of increment values on the basis of thermodynamic data (bond energy and bond distance), the determination of increment codes by means of a computer and the pre-calculation of retention indices in classical gas-liquid and temperature-programmed gas chromatography are discussed.

INTRODUCTION

Gas-liquid chromatography (GLC) is widely applied in the petrochemicals industry. As a consequence of the increasing demand for aromatic compounds, their production has increased considerably in recent years. The composition of the end-products of refineries can be analysed by GLC methods, with special particular emphasis on the C_{9+} aromatic compounds.

The basis of the method is that the stationary phase, polyethylene glycol adipate (PEGA), produces large differences in the retentions of aromatic and non-aromatic compounds, especially when temperature programming is applied. The gas chromatographic peaks were identified by means of retention indices¹ and standard materials based on the work of Chang and Karr².

The parameters that are suitable for application to experimental data obtained in different laboratories are the specific retention volume, the net retention volume, the relative retention and the retention index. Of these, we considered further the retention index, as proposed by Kováts³, as this is the only retention parameter in GLC in which the two mostly fundamental properties, namely the net retention vol-

ume and the relative volatility (relative retention expressed in terms of reduced retention times) combined.

There have been three main turning points in the development of this field: (a) the comprehensive paper by Ettre⁴, (b) the influence of the lectures and discussions delivered at the 5th International Conference on Column Chromatography in Lausanne (1969), and (c) the production of a chemically homogeneous apolar stationary phase⁵, that ensured the availability of a standard stationary phase over a relatively large temperature range. Benzene derivatives have been studied by Janák and co-workers^{6,7}, Schomburg^{8,9}, Hively and Hinton¹⁰, Schulz and Reitemeyer¹¹, Bonastre *et al.*¹², Hatch¹³, Krupčík *et al.*¹⁴, Karasek and co-workers^{15,16}, Louis^{17,18}, Robinson and Odell¹⁹, Wallaert²⁰, Dimov and Schopov²¹, Cook and Raushel²², Soják and Hrivnák²³, Fuchs²⁴, Vernon²⁵, Mitra *et al.*²⁶, Engewald *et al.*²⁷, Švob *et al.*²⁸, Hartigan and Purcell²⁹, West and Hall³⁰, Soják and Rijks³¹, Ryba^{32,33} and Engewald and Wennrich³⁴.

In considering the various theoretical and practical problems of the retention index system³⁵⁻³⁸ and similar questions with alkanes³⁹, our attention was turned to benzene derivatives⁴⁰. Relying on data from the literature mentioned above and our work on alkanes, extended studies were made with benzene derivatives. In this paper, the results obtained with methyl-, ethyl- and isopropylbenzenes are presented.

THEORETICAL

As we pointed out previously³⁹, applying the additive property of retention indices, we can write

$$I = I_a + I_b + I_i \quad (1)$$

where

I = retention index under isothermal conditions, in index units (i.u.);

I_a = atomic index contribution (i.u.);

I_b = bond index contribution (i.u.);

I_i = interaction index contribution (i.u.).

The atomic index contribution was established by definition:

$$I_a = \frac{\text{molecular weight}}{10} \quad (2)$$

The bond index contribution is given by the sum of individual bond increment values.

For an accurate description of the increments, the following code system was introduced for the methyl-, ethyl- and isopropylbenzenes:

(1) C-C bonds are denoted by C.

(2) C-H bonds are denoted by H.

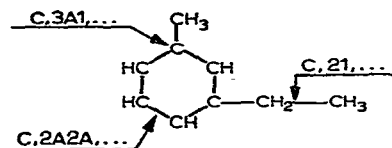
(3) C, H and every independent piece of information are followed by a comma.

(4) After the comma following C, the orders of the two carbon atoms between which the bond has been formed are given in order of decreasing values. The designation of the order of carbon atoms is as follows:

in the ring: order of carbon atom and A;

in a substituted chain: only order of carbon atom;
between the ring and the chain: combination of the two symbols.

For example:



(5) Following the orders of the carbon atoms between which the bond is formed, the orders of the neighbouring carbon atoms (primary environment) are given in increasing order. For example, in the example given in paragraph (4), the code of the carbon-carbon bond between the methyl group and the ring is as follows:

C,3A1,02A2A,000.

(6) The basic code of a carbon-carbon bond:

C,00,000,000.

(7) If all of the places in the basic code are not taken by order values, then the 0 values must remain in the untaken places of the basic code.

(8) An increment code is terminated by a full point.

(9) If two carbon atoms of the same order are bound to each other, then the code of the neighbour of the higher order will be given first.

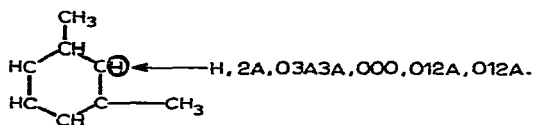
(10) The basic code of a carbon-hydrogen bond:

H,0,000,000,000,000.

(11) After the comma following H, the order of the carbon atom to which the hydrogen atom is bound is given.

(12) Following the order of the carbon atom bound to the hydrogen atom, the orders of the carbon atoms next to the carbon atom to which the hydrogen in question is bound (primary environment) are given.

(13) After coding of the primary environment, the orders of the carbon atoms bound directly to carbon atoms bound to the former are given (secondary environment), in increasing order. For example, the code of the carbon-hydrogen bond in the molecule of *m*-xylene is as follows:



The known fundamental thermodynamic data (bond energies, bond distances, etc.) of the molecule being examined should be combined with the increments or with similar gas chromatographic data such as bond index contributions. Following this, the mean value of the index unit/bond energy unit factor can be calculated by means of corresponding data for 3, 5 and 11 compounds. Then, from the thermodynamic data and the molecular structure, the increment values are determined by means of a computer. In connection with the determination of increment values, it should be noted that while there are many comprehensive works on thermodynamics, *e.g.*, by

Bartell⁴¹⁻⁴³, Herzberg and Sticheff^{44,45} and others^{46,47}, there are few data available for individual compounds and their derivatives.

From the above considerations, benzene, toluene, *m*-xylene and 1,3,5-trimethylbenzene were selected as examples, as their thermodynamic data were available. For the determination of the increment values, the simplest compound, benzene, is considered.

As the carbon-carbon π -bonds are represented by A, there are two bond types in the benzene molecule:

(a) C,2A2A,002A,002A.

(b) H,2A,02A2A,000,002A,002A.

There are six bonds of each type in the molecule. The atomization energy, taken from the literature, is 1319.4 kcal/mole and is distributed between the two different bond types as follows: each C-C bond, 122.60 kcal/mole, and each C-H bond, 97.30 kcal/mole. Hence, the distribution of the bond index contribution of the molecule is as follows: increment value of each C-C bond, 14.39 i.u., and that of each C-H bond, 11.42 i.u. If there are more than two bond types in the molecule, the value of the index unit/energy unit factor has to be determined by division, by means of the atomization energy and bond index contribution.

When the latter factor and the energy values of the increments are known, then by multiplication the increment values (index units) can be obtained. In Table I, the increment values used in the calculations are presented.

TABLE I

BOND INCREMENT VALUES APPLIED IN CALCULATIONS WITH 1,3,5-TRIMETHYLBENZENE

<i>Increment code</i>	<i>Bond increment value (i.u.)</i>
H,1,003A,000,000,02A2A	11.03
H,2A,03A3A,000,012A,012A	9.74
C,3A1,02A2A,000	9.49
C,3A2A,012A,003A	12.28

Assuming that interactions developed on squalane as a stationary phase do not contain individual interaction factors (this is only approximately true, of course) the ΔI values, published in McReynold's paper⁴⁸, give the individual interaction index contributions. These data give the possibility of making several other comparisons. A continuous curve can be obtained that represents the interaction contributions *versus* the retention polarity of stationary phases⁴⁹, as is shown in Fig. 1.

As the bond and interaction index contributions are determined on the same thermodynamic bases and in the same way, their values can be summed, in certain circumstances. The dependence of the increment (bond + interactions) values for ethylbenzene on different stationary phases is shown in Table II, and the dependence of the increment values for *n*-propylbenzene on column temperature on a standard apolar stationary phase according to Riedo *et al.*⁵ is presented in Table III.

The regular increase (95.90 i.u.) in the retention indices for the homologous series of *n*-alkylbenzenes after *n*-hexylbenzene on extending the alkyl chain length by

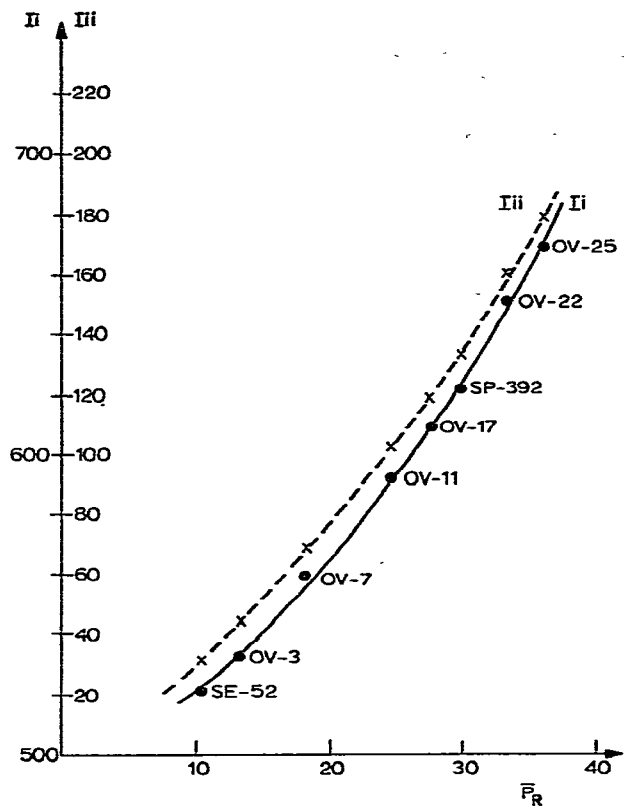


Fig. 1. Interaction contributions *versus* retention polarity of different stationary phases.

TABLE II

DEPENDENCE OF THE INCREMENT VALUES FOR ETHYLBENZENE ON THE TYPE OF STATIONARY PHASE AT 120 °C

Increment code	Stationary phase				
	Standard apolar ⁵	APL	PEG 20M	DEGA	DEGS
C,21,003A,000	39.33	39.37	51.45	54.79	62.50
C,3A2,02A2A,001	40.09	40.13	52.45	55.85	63.71
C,3A2A,02A2,002A	54.87	54.93	71.78	76.44	87.19
C,2A2A,003A,002A	55.45	55.51	72.54	77.25	88.11
C,2A2A,002A,002A	62.42	62.49	81.66	86.96	99.19
H,2A,02A2A,000,003A,002A	46.38	46.43	60.68	64.61	73.70
H,2A,02A3A,000,002A,02A2	41.39	41.44	54.15	57.66	65.77
H,2,013A,000,000,02A2A	37.05	37.09	48.47	51.61	58.88
H,1,002,000,000,003A	45.92	45.97	60.08	63.97	72.97
H,2A,02A2A,000,002A,002A	49.54	49.59	64.81	69.01	78.72

TABLE III

DEPENDENCE OF THE INCREMENT VALUES FOR *n*-PROPYLBENZENE OF COLUMN TEMPERATURE ON STANDARD APOLAR STATIONARY PHASE⁵

Increment code	Column temperature (°C)		
	70.0	130.0	190.0
C,21,002,000	31.55	32.29	33.04
C,22,003A,001	34.26	35.07	35.88
C,3A2,02A2A,002	40.34	41.30	42.25
C,3A2A,02A2,002A	53.86	55.14	56.41
C,2A2A,003A,002A	54.43	55.71	57.00
C,2A2A,002A,002A	61.27	62.72	64.17
H,2A,02A2A,000,003A,002A	45.53	46.60	47.68
H,2A,02A3A,000,002A,02A2	40.63	41.59	42.55
H,2,012,000,000,003A	39.26	40.19	41.12
H,2A,02A2A,000,002A,002A	48.63	49.78	50.93
H,2,012,000,000,003A	37.83	38.73	39.62
H,1,002,000,000,002	36.86	37.73	38.60

TABLE IV

DEPENDENCE OF THE INTERACTION FACTOR ON HEATING RATE IN TPGC APPLYING PPG (UCON LB-550X) AS THE STATIONARY PHASE, AFTER SCHULZ AND REITEMEYER'S¹¹ MEASUREMENTS

Heating rate (°C/min)	Interaction factor
0.5	4.408
1.0	4.422
1.5	4.426
2.0	4.440

one carbon atom on a standard apolar stationary phase at 190° C should be noted.

In the following, the pre-calculation of retention indices for benzene derivatives in temperature-programmed gas chromatography (TPGC) is considered⁵⁰. In recent years, many researchers have dealt with various problems connected with this

TABLE V

INFLUENCE OF THE AMOUNT OF STATIONARY PHASE ON THE INTERACTION FACTOR ON PEG 20M STATIONARY PHASE ON CHROMOSORB P (60-80 MESH) AT 140 °C, AFTER MEASUREMENTS OF BONASTRE *et al.*¹²

Compound	Stationary phase (% w/w)					
	2.5	5.0	10.0	15.0	20.0	30.0
Benzene	5.202	5.552	5.768	5.860	5.964	6.014
Toluene	4.936	5.210	5.431	5.510	5.583	5.646
Ethylbenzene	4.791	5.082	5.247	5.336	5.393	5.464
<i>n</i> -Propylbenzene	4.682	4.930	5.070	5.156	5.211	5.275
<i>n</i> -Butylbenzene	4.614	4.815	4.946	5.023	5.089	5.147

system. Van den Dool and Kratz's work⁵¹ and also the book by Harris and Habgood⁵² are particularly important in TPGC. In TPGC^{54,55}

$$I(\text{TPGC}) = I_M \cdot \pi(\text{TPGC}) \quad (3)$$

$$\pi(T) = A + \frac{B}{T + C} \quad (4)$$

$$\pi(\text{TPGC}) = \frac{\int_{T_o}^{T_R} \pi dT}{T_R - T_o} = A + \frac{B \ln\left(\frac{T_R + C}{T_o + C}\right)}{T_R - T_o} \quad (5)$$

where

T_R = retention temperature (°K);

T_o = initial temperature (°K) (TPGC);

A , B and C = constants.

The dependence of the interaction factor on heating rate (°C/min) in TPGC, applying polypropylene glycol (Ucon LB-550X) as the stationary phase, based on the work of Schulz and Reitemeyer¹¹, is presented in Table IV.

The influence of the amount of PEG 20M stationary phase (% w/w) on the interaction factor on Chromosorb P (60–80 mesh) at 140°C, based on measurements by Bonastre *et al.*¹², is shown in Table V.

Determination of the codes and calculation of the increment values were effected by means of a computer⁵³. The computer program for benzene derivatives is shown in Fig. 2.

The coding and pre-calculation of the retention index of ethylbenzene made by means of a computer is illustrated as an example in Fig. 3.

EXPERIMENTAL

The measurements were performed by means of Perkin-Elmer 900, Erba Science 2300, GI-452, Perkin-Elmer F11 instruments. In each instance flame-ionization detectors were used, together with nitrogen or helium as the carrier gas.

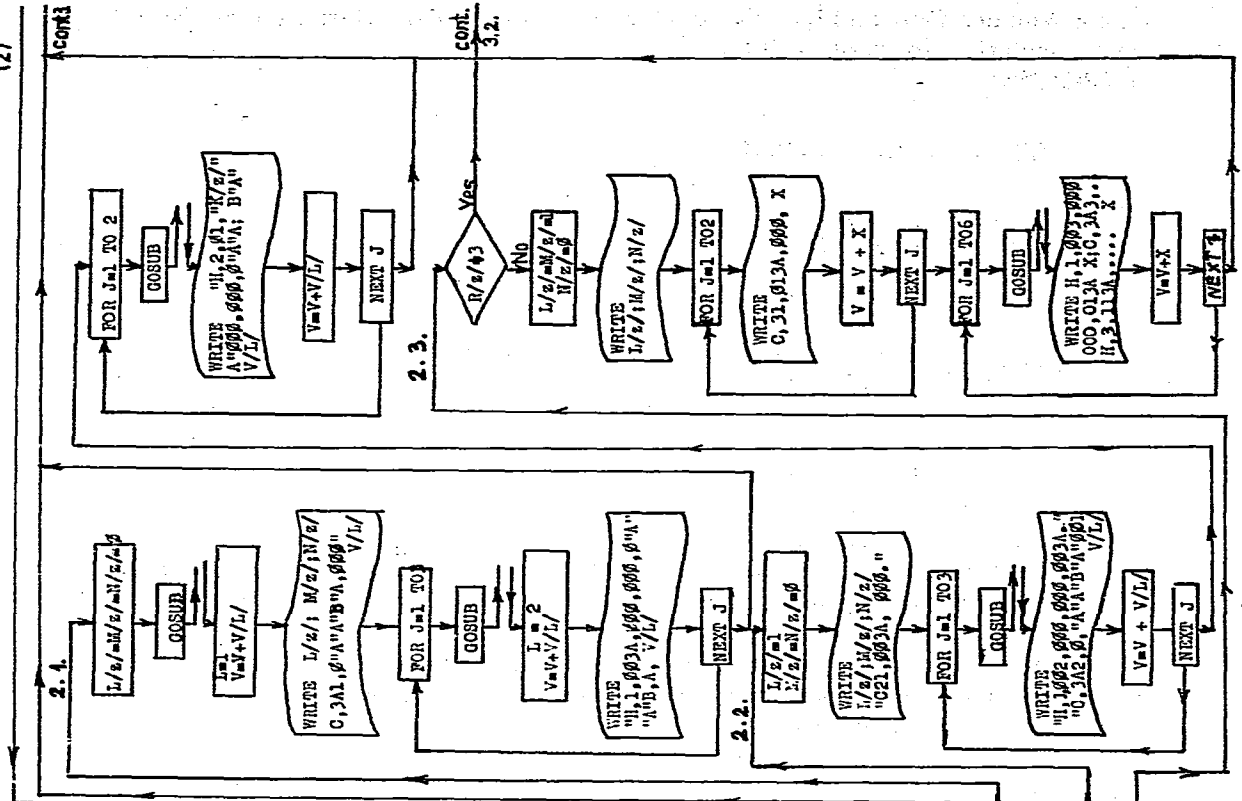
Calculations were performed by means of a Hewlett-Packard 9830A computer fitted with a Hewlett-Packard 9866A printer. Programs were written in BASIC computer language.

Pre-calculations of retention indices made by computer for alkylbenzene derivatives on a standard apolar stationary phase at 100 °C are presented in Table VI.

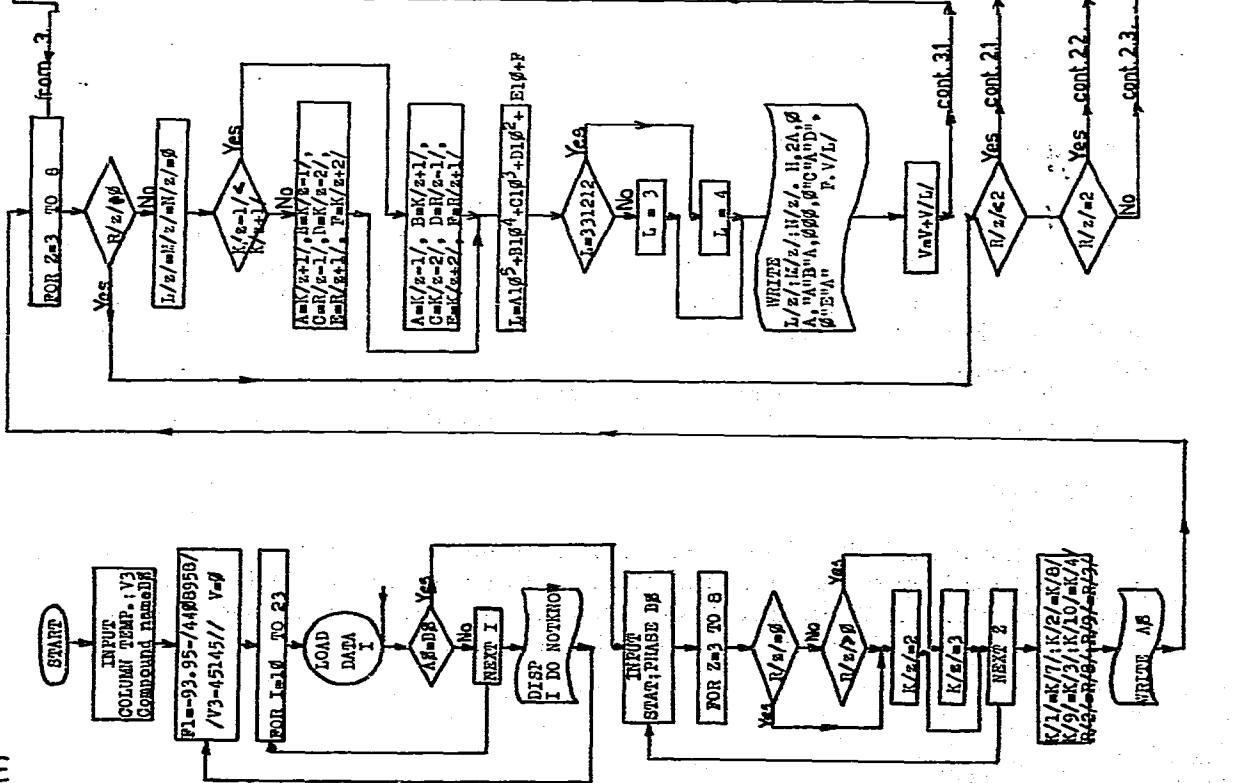
CONCLUSION

In the pre-calculation of retention data by means of increments the initial problems have been overcome and a method with good practical applicability has been developed. The determination of increment codes by computer should make possible the wider application of the pre-calculation of retention data.

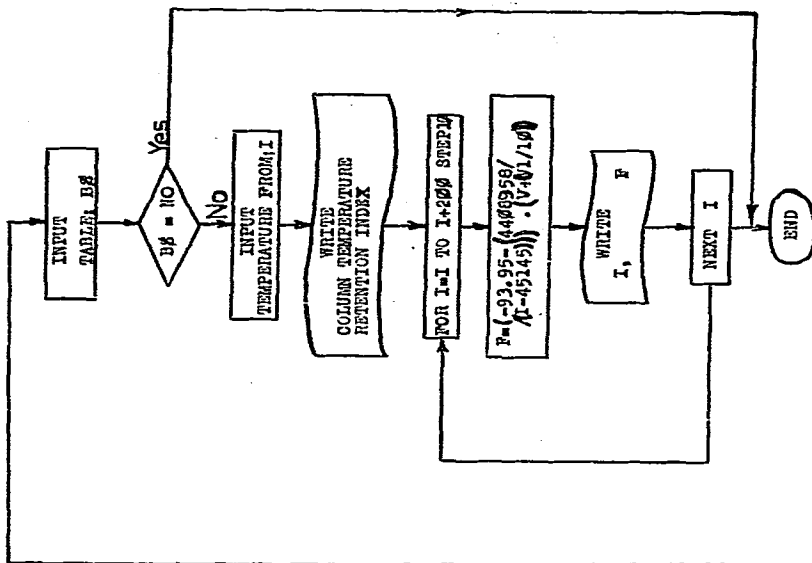
(2)



(1)



(4)



(3)

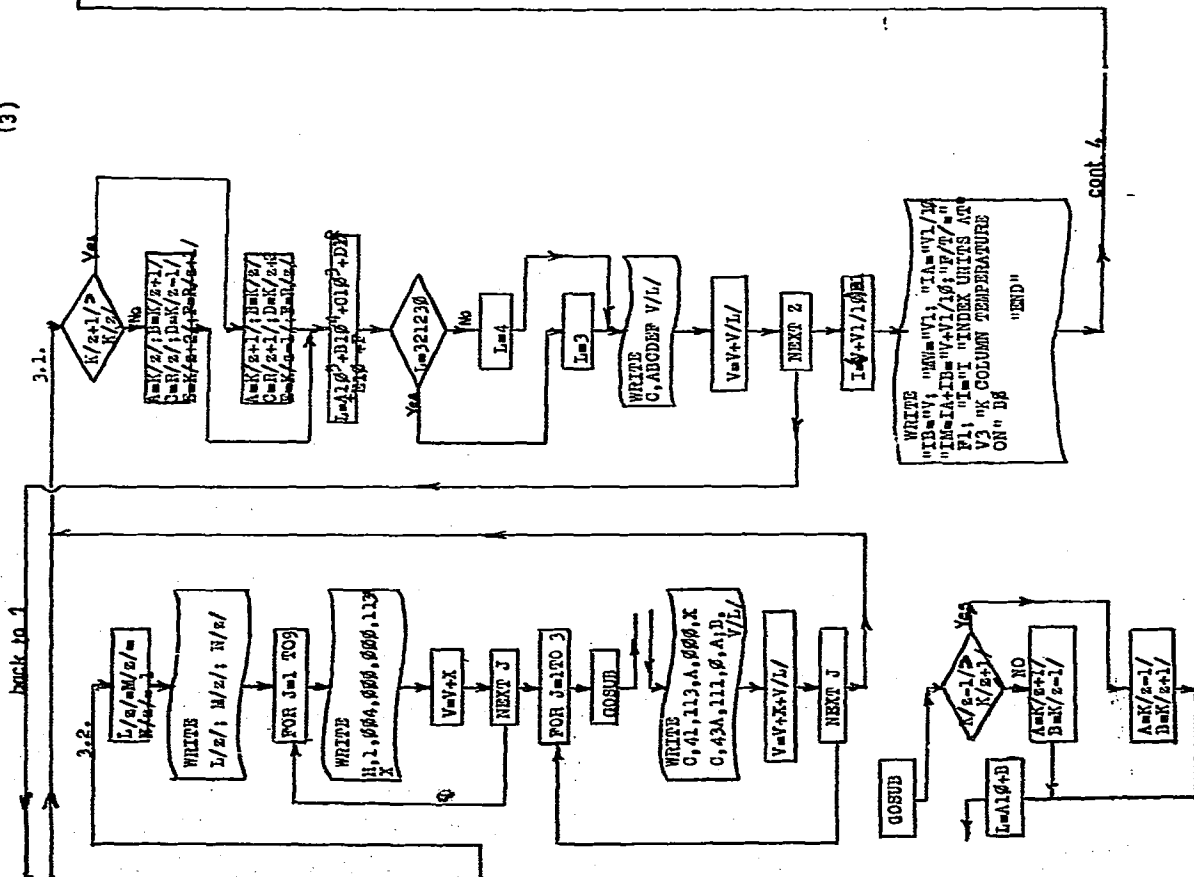


Fig. 2. Computer program for methyl, ethyl and isopropyl benzene derivatives.

ETHYLBENZENE

L3 = 1	M3 = 0	N3 = 0	
C, 21, 003A, 000.			39.33
H, 1, 002, 000, 000, 003A.			45.92
H, 1, 002, 000, 000, 003A.			45.92
H, 1, 002, 000, 000, 003A.			45.92
C, 3A2, 02A2A, 001.			40.09
H, 2, 013A, 000, 000, 02A2A.			37.05
H, 2, 013A, 000, 000, 02A2A.			37.05
C, 3A2A, 02A2, 002A.			54.87
L4 = 0	M4 = 0	N4 = 0	
H, 2A, 02A3A, 000, 002A, 02A2.			41.39
C, 2A2A, 003A, 002A.			55.45
L5 = 0	M5 = 0	N5 = 0	
H, 2A, 02A2A, 000, 003A, 002A.			46.38
C, 2A2A, 002A, 002A.			62.42
L6 = 0	M6 = 0	N6 = 0	
H, 2A, 02A2A, 000, 002A, 002A.			49.54
C, 2A2A, 002A, 002A.			62.42
L7 = 0	M7 = 0	N7 = 0	
H, 2A, 02A2A, 000, 003A, 002A.			46.38
C, 2A2A, 003A, 002A.			55.45
L8 = 0	M8 = 0	N8 = 0	
H, 2A, 02A3A, 000, 002A, 02A2.			41.39
C, 3A2A, 02A2, 002A.			54.87

		IB + II =	861.84

MW = 106

IA = 10.60

STANDARD APOLAR STATIONARY PHASE ACCORDING TO KOVATS

AND CO-WORKERS

I = IA + IB + II = 872.4 IU.

AT 393.16 K COLUMN TEMPERATURE

ETHYLBENZENE END

Fig. 3. Pre-calculation of retention index for ethylbenzene by increments using a computer.

TABLE VI

PRE-CALCULATION OF RETENTION INDICES OF ALKYL BENZENES ON STANDARD APOLAR STATIONARY PHASE AT 100.0 °C ACCORDING TO RIEDO *et al.*⁵

<i>Compound</i>	<i>Retention index (i.u.)</i>	<i>Compound</i>	<i>Retention index (i.u.)</i>
Benzene	663	1,2,3,5-Tetramethylbenzene	1134
Toluene	774	1,3-Diisopropylbenzene	1141
Ethylbenzene	866	1-Ethyl-4- <i>n</i> -propylbenzene	1147
1,4-Dimethylbenzene	881	<i>n</i> -Pentylbenzene	1154
1,3-Dimethylbenzene	881	1-Methyl-4- <i>n</i> -butylbenzene	1160
1,2-Dimethylbenzene	902	1,2,3,4-Tetramethylbenzene	1160
Isopropylbenzene	925	1,3-Dimethyl-5- <i>tert.</i> -butylbenzene	1172
<i>n</i> -Propylbenzene	955	1,4-Diisopropylbenzene	1176
1-Methyl-3-ethylbenzene	967	1-Isopropyl-4- <i>n</i> -propylbenzene	1204
1-Methyl-4-ethylbenzene	972	1,2-Di- <i>n</i> -propylbenzene	1213
1-Methyl-2-ethylbenzene	984	1,3-Di- <i>n</i> -propylbenzene	1218
1,3,5-Trimethylbenzene	987	1,3,5-Triethylbenzene	1220
<i>tert.</i> -Butylbenzene	990	1-Ethyl-2- <i>n</i> -butylbenzene	1234
1,2,4-Trimethylbenzene	1005	1,4-Di- <i>n</i> -propylbenzene	1235
<i>sec.</i> -Butylbenzene	1009	1-Ethyl-4- <i>n</i> -butylbenzene	1250
Isobutylbenzene	1010	<i>n</i> -Hexylbenzene	1254
1-Methyl-3-isopropylbenzene	1029	1-Methyl-4- <i>n</i> -pentylbenzene	1259
1-Methyl-4-isopropylbenzene	1031	1-Methyl-2- <i>n</i> -pentylbenzene	1262
1,2,3-Trimethylbenzene	1032	1,4-Di- <i>tert.</i> -butylbenzene	1305
1-Methyl-2-isopropylbenzene	1038	1- <i>tert.</i> -Butyl-4-isobutylbenzene	1315
1,3-Diethylbenzene	1046	1- <i>tert.</i> -Butyl-4- <i>sec.</i> -butylbenzene	1315
1-Methyl-3- <i>n</i> -propylbenzene	1055	1,3,5-Triisopropylbenzene	1317
<i>n</i> -Butylbenzene	1056	1,4-Di- <i>sec.</i> -butylbenzene	1329
1,2-Diethylbenzene	1058	1- <i>sec.</i> -Butyl-4-isobutylbenzene	1330
1-Methyl-4- <i>n</i> -propylbenzene	1060	1,4-Diisobutylbenzene	1332
1,4-Diethylbenzene	1060	1- <i>n</i> -Propyl-4- <i>n</i> -butylbenzene	1335
1-Methyl-2- <i>n</i> -propylbenzene	1065	1-Ethyl-4- <i>n</i> -pentylbenzene	1347
1,3-Dimethyl-5-ethylbenzene	1068	1-Methyl-4- <i>n</i> -hexylbenzene	1358
1,4-Dimethyl-3-ethylbenzene	1080	1- <i>tert.</i> -Butyl-4- <i>n</i> -butylbenzene	1370
1,4-Dimethyl-2-ethylbenzene	1082	1- <i>sec.</i> -Butyl-4- <i>n</i> -butylbenzene	1384
1-Methyl-3- <i>tert.</i> -butylbenzene	1085	1-Iso-butyl-4- <i>n</i> -butylbenzene	1385
1,3-Dimethyl-4-ethylbenzene	1086	1- <i>n</i> -Propyl-4- <i>n</i> -heptylbenzene	1406
<i>tert.</i> -Pentylbenzene	1091	1,2,4,5-Tetraisopropylbenzene	1432
1,2-Dimethyl-4-ethylbenzene	1093	1,4-Di- <i>n</i> -butylbenzene	1437
1,3-Dimethyl-2-ethylbenzene	1094	Hexamethylbenzene	1441
<i>sec.</i> -Pentylbenzene	1098	1- <i>n</i> -Propyl-4- <i>n</i> -pentylbenzene	1445
1-Methyl-4- <i>tert.</i> -butylbenzene	1098	1-Ethyl-4- <i>n</i> -hexylbenzene	1447
1,2-Dimethyl-3-ethylbenzene	1110	1-Methyl-4- <i>n</i> -heptylbenzene	1461
1,2,4,5-Tetramethylbenzene	1128		

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