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COMPARISON OF ISOTHERMAL AND NON-LINEAR TEMPERATURE PROGRAMMED GAS CHROMATOGRAPHY

THE TEMPERATURE DEPENDENCE OF THE RETENTION INDICES OF A NUMBER OF HYDROCARBONS ON SQUALANE AND SE-30

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SUMMARY

The concept of an "average temperature of elution" of a compound is proposed and used to show that a correlation may be made between retention indices determined under non-linear temperature programmed conditions and those found from plots of retention index against column temperature. The plots of I *vs.* T for a number of hydrocarbons on squalane and SE-30 are given.

INTRODUCTION

Little has so far been published about the use of retention indices[1] with non-linear temperature programming (NLTP) in gas chromatography. The fact that the value of a retention index is dependent on the temperature at which it is determined was first mentioned by KOVATS[1]. ETTRE AND BILLEB[2] have produced plots of retention index *vs.* column temperature for a number of compounds on squalane and poly(ethylene glycol)400. These plots enable the retention index of a compound to be determined at any column temperature.

In this work we have extended the data on temperature effects on retention indices and attempted to demonstrate that the results obtained under NLTP conditions may be correlated with those obtained from isothermal analysis by using the concept of the "average temperature of elution". This is the average temperature to which a compound is subjected while in the GLC column and is calculated as follows.

The non-linear temperature program is divided into isothermal steps and linear temperature programmed steps. For isothermal steps the time–temperature product is obtained by multiplying the temperature at which the step occurs by the time for which it lasts. For linear temperature programmed steps the time–temperature product is given by the product of the mean temperature for the step and the time for which the step lasts. If elution occurs during a step then the time interval is terminated when the compound is eluted and the mean temperature is adjusted accordingly. The total time–temperature product, summed over all steps until elution, of a product is divided by the total retention time for that product to give the average temperature of elution.

EXPERIMENTAL

The columns used were as follows. Squalane: A 10 ft. × 1/4 in. column containing 5 % squalane on 60/100 mesh Embacel of 2000 theoretical plates. SE-30: A 20 ft. × 3/8 in. column containing 30 % SE-30 on Chrom W, having 2900 theoretical plates.

Both columns were operated under isothermal and non-linear temperature

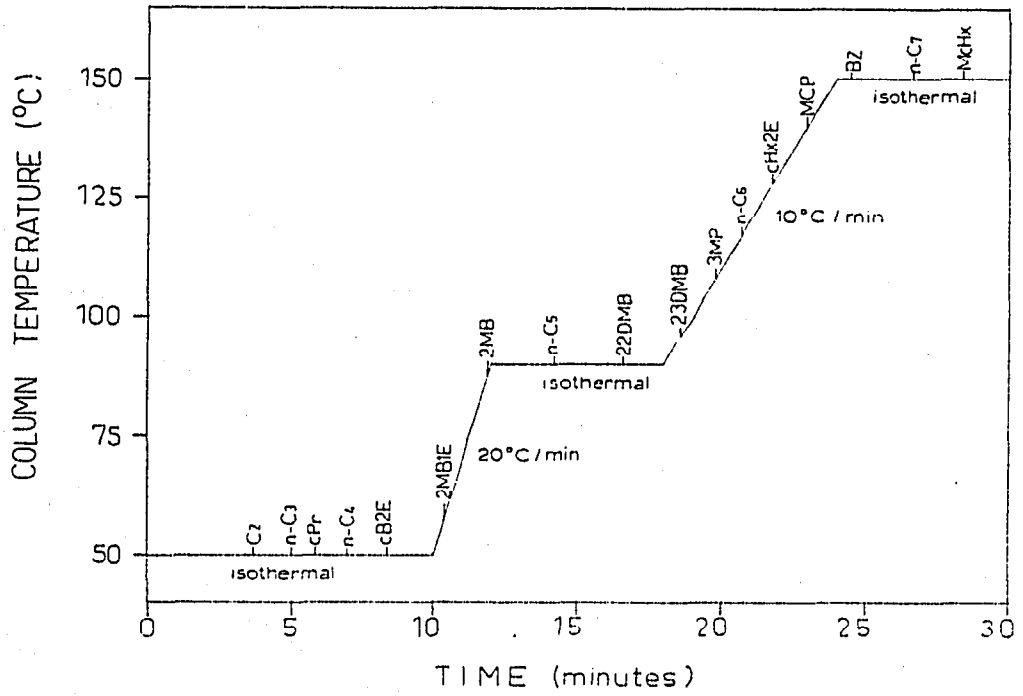

Fig. 1. Schematic representation of the non-linear temperature program used with SE-30 as the stationary phase. The positions of elution of some of the hydrocarbons are indicated.

TABLE I

ABBREVIATIONS USED IN Figs. 1–5

Symbol	*Meaning*
M	Methyl-, *meta*-
Et	ethyl-
Pr	propyl-, propane
B	butane
P	pentane
H(x)	hexane
Hp	heptane
OC	octane
BZ	benzene
TOL	toluene
XYL	xylene
D	di-
T	tri-, *trans*-
C	cyclo, *cis*-, carbon
I	iso-
E	indicates alkene

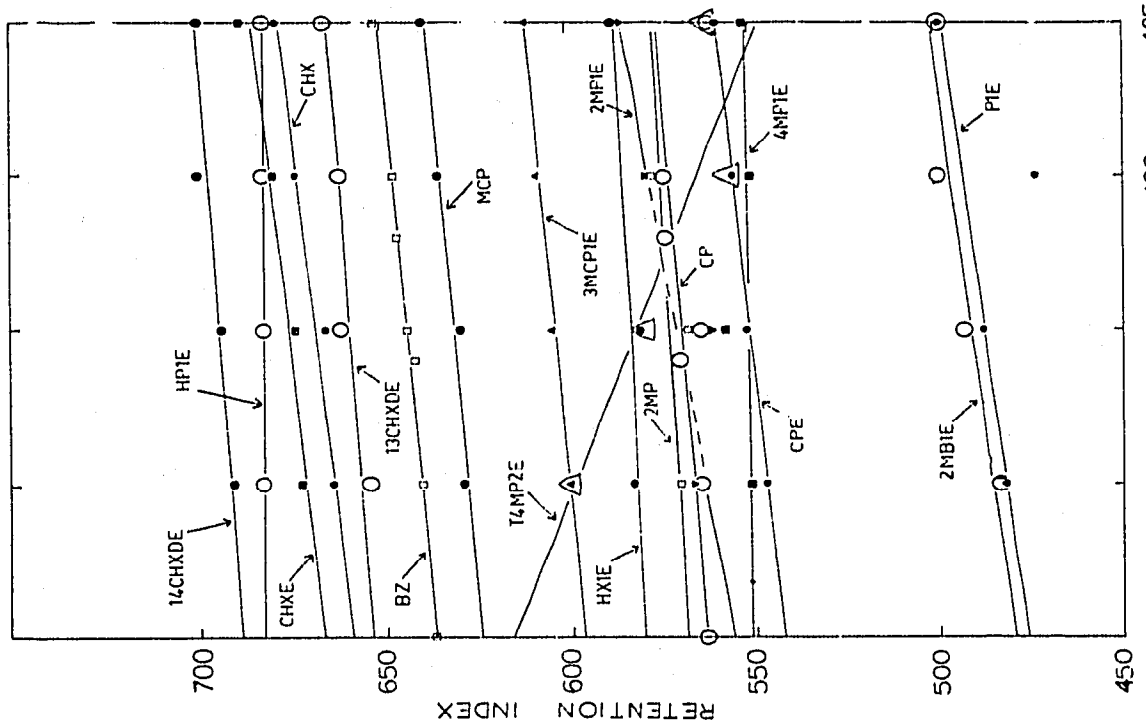

Fig. 2. Plot of retention index values of hydrocarbons obtained on squalane liquid phase against column temperature. Retention index range 450–700. The meanings of the abbreviations is given in Table I.

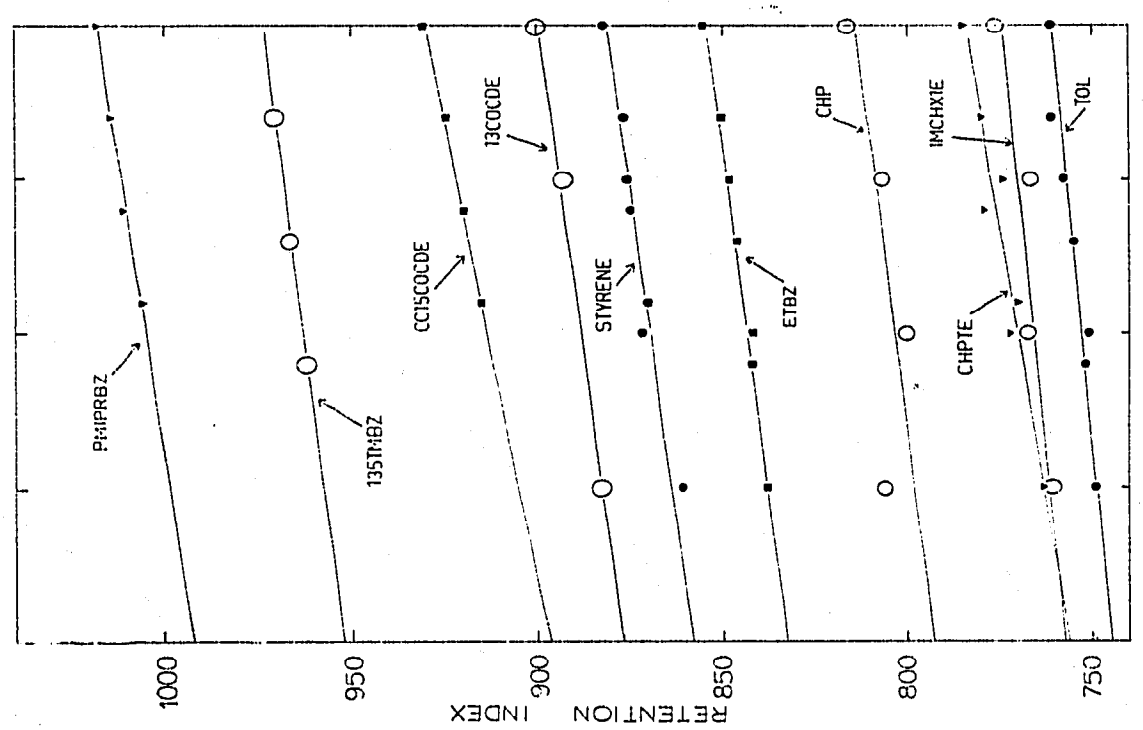

Fig. 3. Plot of retention index values of hydrocarbons obtained on squalane liquid phase against column temperature. Retention index range 750–1020.

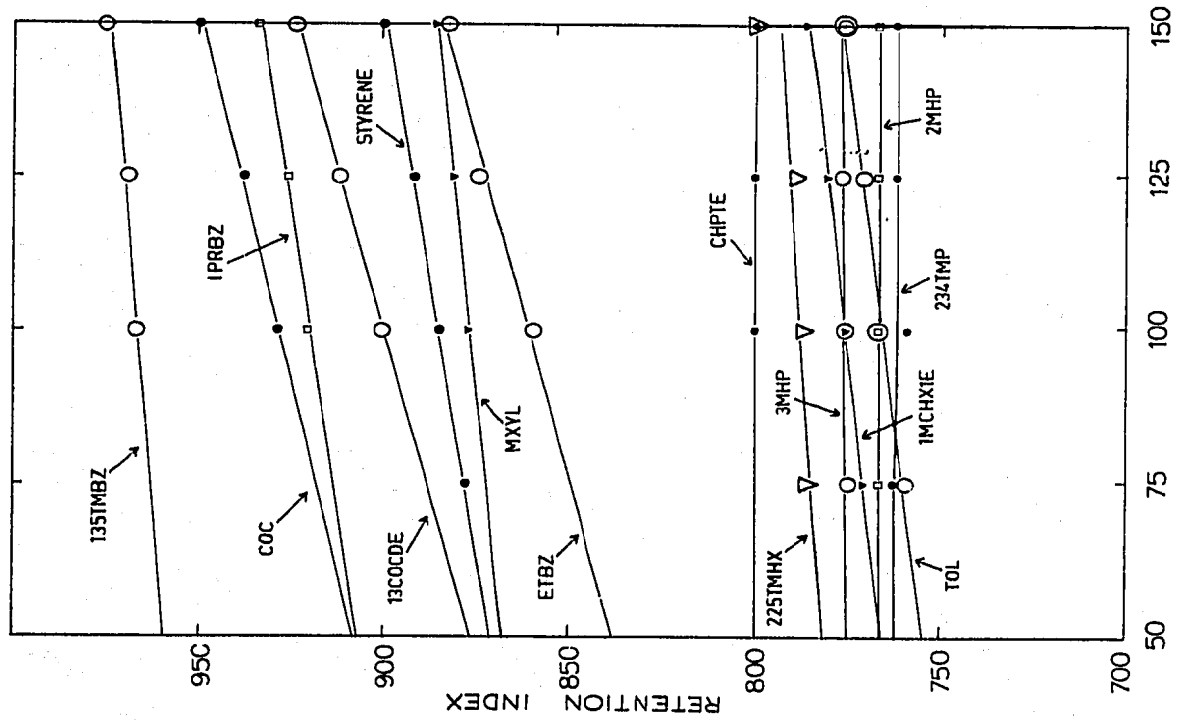

Fig. 4. Plot of retention index values of hydrocarbons obtained on SE-30 liquid phase against column temperature. Retention index range 450–720.

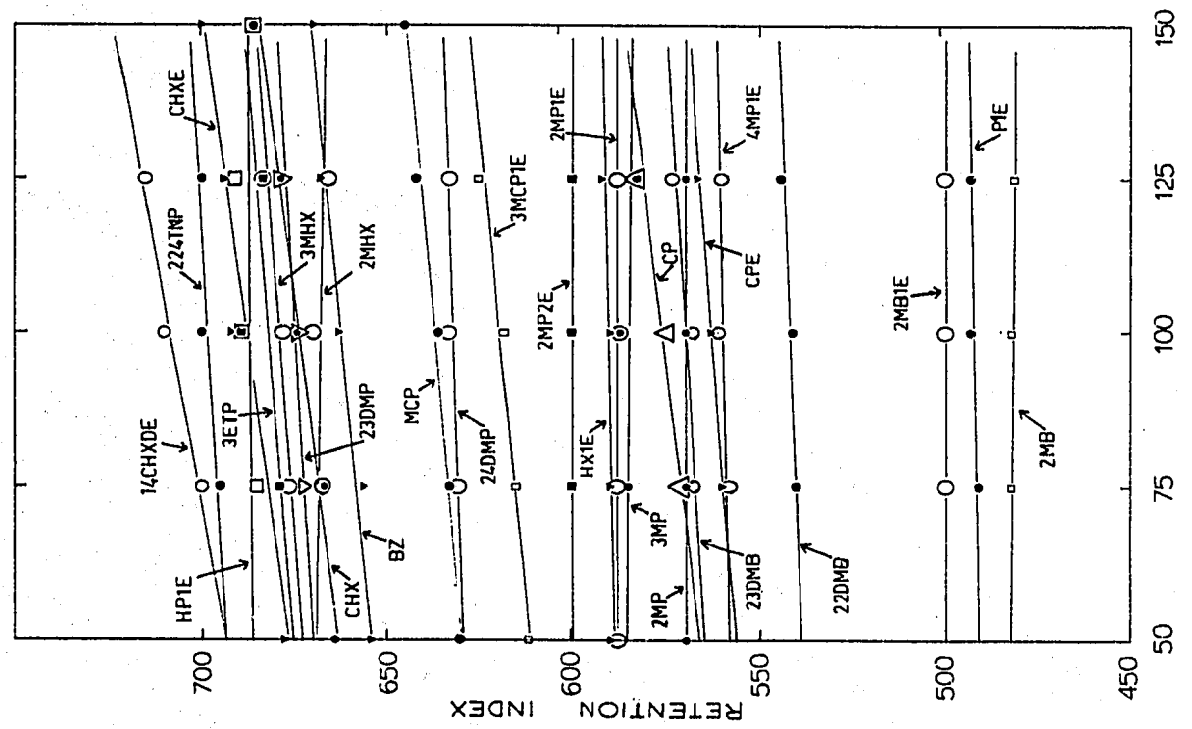

Fig. 5. Plot of retention index values of hydrocarbons obtained on SE-30 liquid phase against column temperature. Retention index range 700–970.

programmed conditions. The temperature programs used were as follows. Squalane: 5 min at 25°, 5 min at 2°/min, 15 min at 4°/min, hold at 95°. SE-30: 10 min at 50°, 2 min at 20°/min, 6 min at 90°, 6 min at 10°/min, hold at 150°.

The program used with SE-30 is illustrated in Fig. 1 and the times at which

TABLE II

COMPARISON OF RETENTION INDICES OBTAINED FROM TEMPERATURE DEPENDENCE PLOTS WITH THE NLTP VALUES ON A SQUALANE STATIONARY PHASE

The first 27 values of I_{est} were obtained from Fig. 2. The rest are from ref. 2.

Compound	*Average temperature of elution*	I_{est}	I_{NLTP}	$I_{NLTP} - I_{est}$
Pent-1-ene	25.0	476	479	3
2-Methylbut-1-ene	25.0	480	487	7
Cyclopentene	26.0	543	547	4
4-Methylpent-1-ene	26.1	551	551	0
Cyclopentane	26.7	563	564	1
2-Methylpent-1-ene	26.1	556	551	−5
2-Methylpentane	27.0	568	569	1
Hex-1-ene	27.8	580	582	2
trans-4-Methylpent-2-ene	31.2	613	619	6
3-Methylcyclopent-1-ene	29.1	597	598	1
Methylcyclopentane	32.5	625	635	10
Benzene	33.7	638	645	7
1,4-Cyclohexadiene	41.2	690	692	2
Cyclohexane	37.1	661	669	8
Cyclohexene	38.8	669	679	10
Hept-1-ene	34.5	683	681	−2
Toluene	48.7	749	755	6
1-Methylcyclohex-1-ene	50.8	762	772	10
Cycloheptatriene	50.8	764	772	8
Cycloheptane	54.3	799	800	1
Ethylbenzene	58.2	840	843	3
Styrene	60.6	866	871	5
1,3-Cyclooctadiene	62.2	887	892	5
cis,cis-1,5-Cyclooctadiene	64.3	910	917	7
1,3,5-Trimethylbenzene	68.3	962	968	6
p-Methyl-isopropylbenzene	70.9	1004	1011	7
Undec-1-ene	72.8	1083	1083	0
2-Methylbutane	25.0	474	476	2
2,2-Dimethylbutane	25.6	535	537	2
2,3-Dimethylbutane	27.1	566	571	5
3-Methylpentane	27.9	583	584	1
2,2-Dimethylpentane	32.3	625	633	8
2,4-Dimethylpentane	33.2	630	641	11
2,2,3-Trimethylbutane	34.5	638	651	13
3,3-Dimethylpentane	37.1	657	669	12
2-Methylhexane	37.9	667	674	7
2,3-Dimethylpentane	39.0	671	680	9
3-Methylhexane	39.9	676	685	9
3-Ethylpentane	41.0	685	691	6
2,3,4-Trimethylpentane	49.3	753	760	7
2-Methylheptane	50.8	765	772	7
4-Methylheptane	51.2	767	775	8
3-Methylheptane	51.7	772	779	7

TABLE III

COMPARISON OF RETENTION INDICES OBTAINED FROM Fig. 3 WITH THE NLTP VALUES ON AN SE-30 STATIONARY PHASE

Compound	*Average temperature of elution*	I_{est}	I_{NLTP}	$I_{NLTP} - I_{est}$
2-Methylbutane	51.9	481	476	−5
Pent-1-ene	56.6	491	492	1
2-Methylbut-1-ene	56.9	499	493	−6
2,2-Dimethylbutane	63.9	538	542	4
4-Methylpent-1-ene	65.9	560	561	1
Cyclopentene	65.3	558	555	−3
2,3-Dimethylbutane	66.9	566	571	5
2-Methylpentane	67.5	570	576	6
Cyclopentane	67.2	570	573	3
3-Methylpentane	69.0	586	588	2
2-Methylpent-1-ene	69.9	588	594	6
Hex-1-ene	69.6	589	592	3
2-Methylpent-2-ene	74.5	600	627	27
3-Methylcyclopent-1-ene	73.3	615	619	4
Methylcyclopentane	76.4	633	640	7
2,4-Dimethylpentane	76.4	631	640	9
Benzene	80.8	659	665	6
Cyclohexane	82.7	670	675	5
2-Methylhexane	82.9	668	676	8
2,3-Dimethylpentane	82.3	673	673	0
3-Methylhexane	84.2	677	683	6
Cyclohexene	85.3	684	689	5
3-Ethylpentane	85.8	680	692	12
Hept-1-ene	85.8	687	692	5
2,2,4-Trimethylpentane	87.2	697	700	3
1,4-Cyclohexadiene	88.1	705	708	3
Toluene	94.5	765	770	5
2,3,4-Trimethylpentane	93.6	762	761	−1
2-Methylheptane	95.0	767	770	3
1-Methylcyclohex-1-ene	95.4	775	779	4
3-Methylheptane	95.2	776	777	1
Cycloheptatriene	97.4	800	800	0
Ethylbenzene	102.3	859	864	5
m-Xylene	103.0	867	874	7
Styrene	104.8	886	900	14
1,3-Cyclooctadiene	106.5	903	920	17
Isopropylbenzene	107.2	922	929	7
Cyclooctane	108.6	932	947	15
1,3,5-Trimethylbenzene	110.5	967	973	6

some of the compounds were eluted are indicated. The meaning of the symbols used in the figures is given in Table I.

RESULTS AND DISCUSSION

The plots of retention index against column temperature are given in Figs. 2 and 3 for squalane and Figs. 4 and 5 for SE-30.

The average temperature of elution for each compound was determined and the estimated retention index was obtained from it using the appropriate plot. This

index was compared with the value found under NLTP conditions and the results are summarised in Table II (for squalane) and Table III (for SE-30).

The majority of experimental results were slightly higher than the values estimated from retention index *vs.* column temperature plots. Some 90 % of the values for $I_{NLTP} - I_{est}$ on squalane lie within a range of 10 units and nearly 80 % of the values on SE-30 lie within the same range. The accepted value for the reproducibility of retention indices is ± 5 units.

The agreement between estimated and observed NLTP values, seen above, indicates that, when I and the average temperature of elution for an unknown compound are found under NLTP conditions the compound may be identified by comparing I_{NLTP} with isothermal values using the average temperature of elution and plots such as those in Figs. 2–5. For instance, if a compound was found to have a retention index of 665 and an average temperature of elution of 80.8° on SE-30 it could be identified, from Fig. 4, as benzene, 2-methylhexane or cyclohexane. The same unknown, on squalane, had a retention index of 645 and an average temperature of elution of 33.7°. Inspection of Fig. 2 (or Fig. 3, ref. 2) shows the unknown compound to be benzene.

REFERENCES

1 E. Kovats, *Helv. Chim. Acta*, 41 (1958) 1915.
2 L. S. Ettre and K. Billeb, *J. Chromatogr.*, 30 (1967) 1.