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GAS CHROMATOGRAPHIC ANALYSIS OF CHLORINATED ETHANES

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SUMMARY

The separation of the products from the chlorination of ethane by temperature-programmed gas chromatography on a packed column was studied. The gas chromatographic behaviour of all nine possible components (from ethyl chloride to hexachloroethane) was characterized by the retention indices on the following stationary phases: OV-101, Halocarbon K-352, SE-30, OV-17, methyl phenyl silicone oil MFSD-5, SP-2340 and β,β'-oxydipropionitrile.

Quantitative analysis was accomplished with a flame-ionization detector, for which the correction factors of the chlorinated ethanes were determined.

INTRODUCTION

Chlorinated hydrocarbons are important as solvents, raw materials and intermediates for organic synthesis and in special applications (*e.g.*, as insecticides).

In general, the products of chlorination consist of several chlorinated hydrocarbons and often include positional isomers; other compounds such as hydrogen chloride and chlorine are usually removed before analysis. So far as we know, the gas chromatography of all nine possible chloroethanes has not been investigated. The most complete study was the work of Balandina and Subbotin[1], who described the separation of eight chloroethanes (*i.e.*, except hexachloroethane) on tricresyl phosphate. Six chloroethanes were separated on SE-30 by Hinshaw[2], higher chlorinated ethanes (from tri- to hexachloroethane) by Solomons and Ratcliffe[3] and less chlorinated ethanes by Mamedov *et al.*[4] and Kosorotov and Kolesničenko[5].

Various combinations of chloroethanes have been separated on a number of stationary phases: non- or weakly polar squalane[6,7], paraffin oil[8–13], Apiezon L[5,8,14], Halocarbon[15] and silicone oils or elastomers[2–4,7,11,16–21], polar alkyl phthalates[4,13,16,17,19–22], aryl phosphates[1,4,8,21,23–25], Carbowax 4000 and 20M[8,14], polyethylene glycol adipate[1,7,23], β,β'-oxydipropionitrile (β,β'-ODPN)[4,26] and Porapak-Q[27].

The most frequently used detectors in the chromatography of chloroethanes are the thermal conductivity detector (TCD)[1–5,7,8,11,13,16–19,21,25,27], and the flame-ionization detector (FID)[3,6,14,15,23,24,26]. The advantages of the gas density balance (GDB) were confirmed even for these compounds[15] (predictable response, non-specificity, linearity and sufficient sensitivity). A combination of an FID with a

thermionic detector (TID), which is more specific for chlorinated compounds, was also used for chloroalkanes[14]. The detection of chlorinated compounds by means of an electron-capture detector (ECD) is well known. Combinations of different types of detectors are to be preferred as additional information is provided. The different responses depend on the physico-chemical properties which are exploited for the detection, e.g., an increasing number of chlorine atoms in a molecule causes an increase in the response of the TCD, GDB and ECD and a decrease in that of the FID.

From the published data, the following problems emerge: the overlapping of the peaks of 1,1,1-trichloroethane and 1,2-dichloroethane on non-polar stationary phases, and of 1,1-dichloroethane and 1,1,1-trichloroethane on polar phases. This paper presents the results of the gas chromatography of all nine chloroethanes on seven various stationary phases. Owing to the large differences in the volatilities of these compounds, temperature-programmed gas chromatography was employed. Detection was accomplished with an FID.

EXPERIMENTAL

A Packard Model 7409 gas chromatograph equipped with a double FID and a temperature programmer was used. Glass columns (2 m × 3 mm I.D.) were used with the following column packings:

(1) 5% MFSD-5 (VÚOS, Rybitví, Czechoslovakia) on Supelcoport (80–100 mesh) (Supelco, Bellefonte, Pa., U.S.A.);

(2) 5% Halocarbon K-352 (Supelco) on Supelcoport (80–100 mesh);

(3) 3% OV-17 (Serva, Heidelberg, G.F.R.) on Chromosorb W HP (100–120 mesh) (Serva);

(4) 5% OV-101 (Serva) on Supelcoport (80–100 mesh);

(5) 5% SP-2340 (Supelco) on Supelcoport (80–100 mesh);

(6) 3% SE-30 (Becker, Delft, The Netherlands) on Chromaton N-AW-DMCS (100–120 mesh) (Lachema, Brno, Czechoslovakia);

(7) 5% β,β'-ODPN (Becker) on Supelcoport (80–100 mesh);

(8) 10% Squalane (Becker) on Chromaton N-AW-DMCS (80–100 mesh).

The following chemicals were employed: ethyl chloride (Synthesia, Kolín, Czechoslovakia), 1,1-dichloroethane (Spolana, Neratovice, Czechoslovakia), 1,1,1-trichloroethane (Dow Chem., Midland, Mich., U.S.A.), 1,2-dichloroethane (Spolana), 1,1,2-trichloroethane (Spolana), pentachloroethane (Spolana), 1,1,2,2-tetrachloroethane (Chemie, Apolda, G.D.R.), 1,1,1,2-tetrachloroethane (ÚVVVR, Prague, Czechoslovakia), hexachloroethane (ÚVVVR) and C_6–C_{17} n-alkanes (VŠCHT, Prague, Czechoslovakia).

The chromatographic behaviour of the chloroethanes was characterized by their relative retention temperatures (RRT) (relative to n-octane). Several rates of temperature increase were examined and 8°/min was found to be optimal. The initial temperature was usually 40°, except for the Halocarbon K-352 column (50°) and the β,β'-ODPN column (30° and a rate of 5°/min). The carrier gas (argon) flow-rate was 30 ml/min except for the β,β'-ODPN column (50 ml/min). The retention index, I_r, for chloroethane (x) was found by interpolation from

$$I_r = n + 100 \cdot \frac{RT_x - RT_n}{RT_{n+1} - RT_n}$$

where the retention temperatures, RT, of n and $n+1$ alkanes and chloroethane, x, are $RT_n < RT_x < RT_{n+1}$.

Correction factors, F_t, were calculated from the expression

$$F_t = \frac{G_x \, A_{STD}}{G_{STD} \, A_x}$$

where G_x and G_{STD} are the amount of chloroethane and of n-octane used as the internal standard, respectively, and A_x and A_{STD} are the peak areas of chloroethane and the internal standard, respectively. Peak areas were measured by triangulation with a high chart speed. In all instances, the chromatograms were recorded at the same sensitivity in order to eliminate any errors due to the attenuator switching.

RESULTS AND DISCUSSION

The chromatographic behaviour of all nine possible products of ethane chlorination (from ethyl chloride to hexachloroethane) was studied on the following stationary phases, with different polarities: OV-101, SE-30, K-352, OV-17, MFSD-5, SP-2340 and β,β'-ODPN. The retention temperatures and relative retention temperatures on the various stationary phases are given in Table I. The differences in the retention characteristics of the chloroethanes on these stationary phases depend mainly on the volatility and polarity of the chloroethane molecule, as well as on the polarity of the stationary phase. The differences in the gas chromatographic behaviour of the individual compounds on the stationary phases investigated are, however, more apparent from their retention indices given in Table II. The retention indices of chloroethanes are generally higher on a polar than for a non-polar stationary phase. From the retention indices shown it follows that the weak polar stationary phases (polysiloxanes) of the OV-17 type are the most suitable for the separation of the chloroethanes, which is demonstrated in Fig. 1.

If a correlation between the retention data and certain physical parameters is

TABLE I

RETENTION TEMPERATURES (RT) AND RELATIVE RETENTION TEMPERATURES (RRT) OF CHLOROETHANES ON VARIOUS STATIONARY PHASES

Compound	K-352		SE-30		OV-101		OV-17		MFSD-5		SP-2340	
	RT (°C)	RRT	RT (°C)	RRT	RT (°C)	RRT	RT (°C)	RRT	RT (°C)	RRT	RT (°C)	RRT
Ethyl chloride	65.0	0.63	45.0	0.65	53.0	0.89	54.0	0.69	56.0	0.64	56.0	0.83
1,1-Dichloroethane	72.0	0.70	47.7	0.68	54.3	0.92	61.7	0.79	67.0	0.77	74.3	1.10
1,1,1-Trichloroethane	78.7	0.77	52.0	0.75	55.3	0.93	67.0	0.86	74.0	0.85	74.3	1.10
1,2-Dichloroethane	78.7	0.77	52.0	0.75	55.3	0.93	72.3	0.92	80.0	0.92	97.7	1.44
1,1,2-Trichloroethane	94.0	0.92	62.7	0.91	59.0	0.99	94.0	1.20	102.0	1.17	123.0	1.82
n-Octane	102.7	1.00	69.0	1.00	59.3	1.00	78.3	1.00	87.0	1.00	67.0	1.00
1,1,1,2-Tetrachloroethane	107.8	1.05	73.1	1.06	63.5	1.07	105.7	1.35	115.3	1.33	121.2	1.79
1,1,2,2-Tetrachloroethane	117.0	1.14	82.0	1.19	67.0	1.13	121.7	1.55	131.0	1.51	154.0	2.27
Pentachloroethane	131.7	1.28	94.0	1.36	75.5	1.27	130.3	1.66	141.0	1.62	142.0	2.10
Hexachloroethane	153.0	1.49	110.4	1.60	83.0	1.40	145.6	1.86	150.7	1.73	140.1	2.07

TABLE II

BOILING POINTS (b.p.), CORRECTION FACTORS (F_i) AND RETENTION INDICES OF CHLOROETHANES

Compound	b.p. (°C)	F_i	Retention index						
			SE-30	OV-101	K-352	OV-17	SP-2340	MFSD-5	β,β-ODPN
Ethyl chloride	13.1	—	—	—	—	—	—	—	—
1,1-Dichloroethane	57.0	3.51	—	600.0	—	658.8	879.5	650.0	842.9
1,1,1-Trichloroethane	74.0	4.46	628.6	660.0	631.6	715.0	879.5	733.3	828.6
1,2-Dichloroethane	84.0	3.23	628.6	660.0	631.6	754.9	1077.6	753.3	1042.9
1,1,2-Trichloroethane	113.0	4.18	747.5	790.0	745.6	898.1	1275.6	888.2	—
n-Octane	125.5	1.00	800.0	800.0	800.0	800.0	800.0	800.0	800.0
1,1,1,2-Tetrachloroethane	129.5	—	827.2	870.0	829.5	959.4	1261.0	959.5	—
1,1,2,2-Tetrachloroethane	146.0	5.58	888.4	922.1	882.7	1051.1	1535.4	1047.4	—
Pentachloroethane	162.0	5.62	963.2	1025.0	965.0	1100.0	1429.2	1100.0	—
Hexachloroethane	186.0	—	1057.8	1100.0	1088.2	1176.5	1412.4	1230.6	—

established, it could facilitate the identification of unknown substances. An approximately linear correlation between the retention index for non-polar or slightly polar stationary phases and the boiling point is shown in Fig. 2. The increments of the retention indices of 1,1,1-trichloro-, penta- and hexachloroethanes decrease with increasing polarity of the stationary phase, contrary to 1,2-dichloro-, 1,1,2-trichloro- and 1,1,2,2-tetrachloroethane, for which the retention index increases.

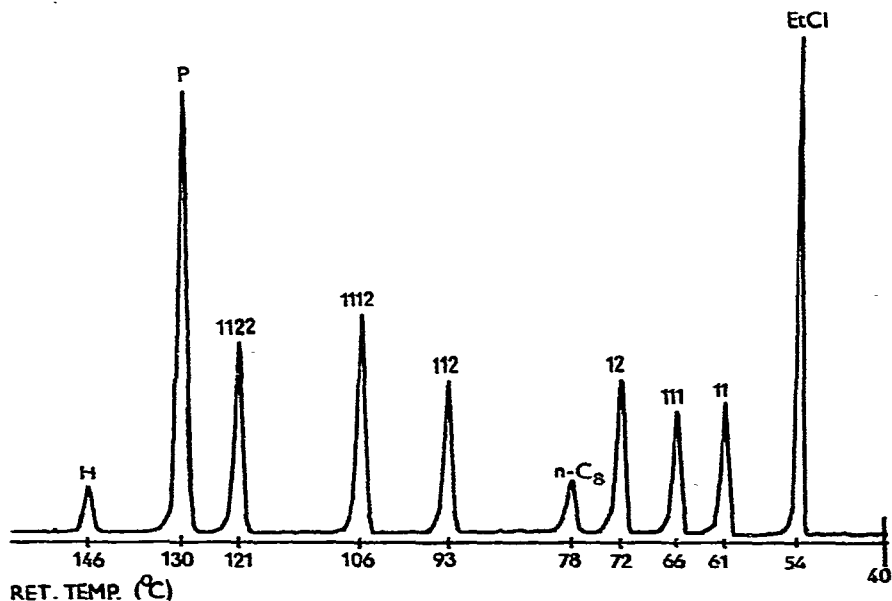In contrast to non-polar and weakly polar stationary phases, the plotted points

Fig. 1. Temperature programmed gas chromatography of chloroethanes on an OV-17 column. EtCl = ethyl chloride; 11 = 1,1-dichloroethane; 111 = 1,1,1-trichloroethane; 12 = 1,2-dichloroethane; n-C₈ = n-octane (internal standard); 112 = 1,1,2-trichloroethane; 1112 = 1,1,1,2-tetrachloroethane; 1122 = 1,1,2,2-tetrachloroethane; P = pentachloroethane; H = hexachloroethane.
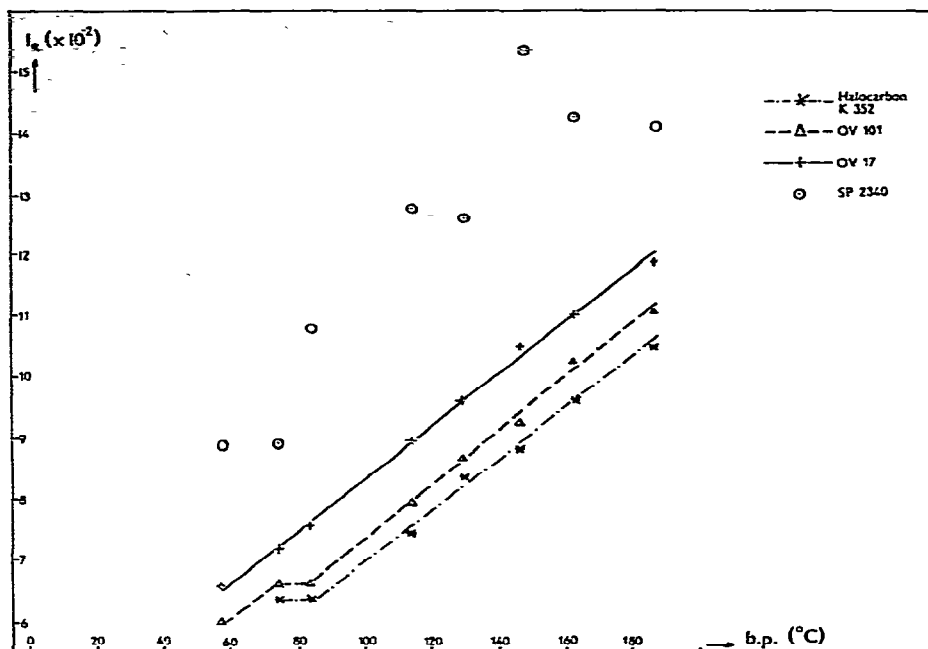
Fig. 2. Correlation between the retention index measured with columns of different polarity and the boiling point of chloroethanes (1,1-dichloroethane–hexachloroethane).

deviate from a linear correlation for the strongly polar SP-2340 phase. On the non-polar Halocarbon K-352, OV-101 and SE-30, the retention of 1,1-dichloroethane is less than that of 1,2-dichloroethane and 1,1,1-trichloroethane, for which retention times are equal. On the other hand, on the polar stationary phase SP-2340 1,1-dichloroethane and 1,1,1-trichloroethane are not separated and have lower retentions than 1,2-dichloroethane. Finally, on the strongly polar β,β'-ODPN the retention of 1,1,1-trichloroethane is lower than that of 1,1- and 1,2-dichloroethanes (Table II). Similar behaviour of the chloroethanes on polar stationary phases was reported by Urone et al.[8], Mamedov et al.[4] and Baladina and Subbotin[1] and on non-polar stationary phases by Urone et al.[8] and Kosorotov and Kolesničenko[5].

In a similar manner to the Rohrschneider characterization of stationary phases, the influence of the polarity of the stationary phase on the retention indices of chloroethanes was investigated. To compare the polarities, the increase in the retention index of 1,1,2,2-tetrachloroethane obtained with any polar stationary phase in comparison with that obtained with a non-polar stationary phase (Squalane) is given as follows[7]:

$$\Delta I_{R(CHCl_2CHCl_2)} = I_{R(CHCl_2CHCl_2)} \text{ (polar)} - I_{R(CHCl_2CHCl_2)} \text{ (non-polar)}$$

Then the value of $\Delta I_{R(CHCl_2CHCl_2)}$ obtained with a given stationary phase is presumed to indicate its polarity. The influence of the polarity of the stationary phase on the retention index is demonstrated in Fig. 3. As the retention indices on a new stationary phase can be predicted by measuring the retention index of 1,1,2,2-tetrachloroethane

on a particular stationary phase, the relationship illustrated in Fig. 3 appears to be very useful for the selection of new stationary phases and for identification purposes. It is evident that this relationship is not a simple function of one molecular property, and the influences of molecular weight, volatility, the polarity and polarizability of the molecule and steric effects must be taken into account.
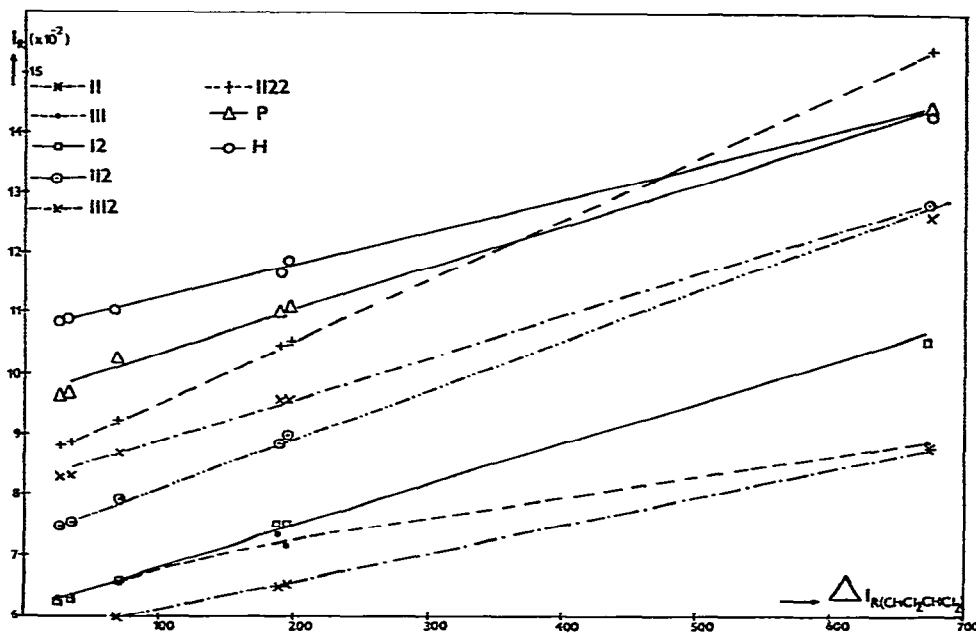

Fig. 3. Influence of the polarity of the stationary phase [measured as $\Delta I_{R(CHCl_2CHCl_2)}$] on the retention index of chloroethanes (1,1-dichloroethane–hexachloroethane).

The selection of a stationary phase is also restricted by the lower and upper temperature limits. For instance, EGSS-X could not be used for lower chloroethanes because of its lower temperature limit of 90°; on the other hand, β,β'-ODPN, the upper temperature limit of which is 70°, is not suitable for more highly chlorinated ethanes.

The correction factors for chloroethanes are given in Table II. As expected, the FID response decreases as the degree of chlorination increases. The correction factor for an FID is a complicated function of the operating conditions (carrier gas, hydrogen and air flow-rates and temperature), which must therefore be maintained constant in all analyses.

CONCLUSIONS

Temperature-programmed gas chromatography on weakly polar stationary phases of the OV-17 type is convenient for the analysis of chlorinated ethanes, for which a linear correlation between retention index and boiling point was found. The results obtained on stationary phases of different polarity could possibly be used for

identification purposes. The chromatographic behaviour of chloroethanes is influenced by several factors (molecular weight, volatility, polarity and polarizibility of the molecule). For quantitative analysis an FID can be used, the response of which decreases with increasing degree of chlorination.

REFERENCES

1 L. A. Balandina and A. I. Subbotin, *Zavod. Lab.*, 34 (1968) 154.
2 L. D. Hinshaw, *J. Gas Chromatogr.*, 8 (1966) 300.
3 D. A. Solomons and J. S. Ratcliffe, *J. Chromatogr.*, 76 (1973) 101.
4 M. A. Mamedov, T. P. Popova and N. S. Murzina, *Zh. Anal. Khim.*, 23 (1968) 1716.
5 V. I. Kosorotov and A. F. Kolesničenko, *Chim. Prum.*, 8 (1975) 571.
6 O. L. Hollis and W. V. Hayes, *Anal. Chem.*, 34 (1962) 1223.
7 R. Iwate, Y. Makide and T. Tomirage, *Bull. Chem. Soc. Jap.*, 47 (1974) 3071.
8 P. Urone, J. E. Smith and R. J. Katnik, *Anal. Chem.*, 34 (1962) 476.
9 R. R. Barefoot and J. E. Cural, *Chem. Can.*, 7 (1955) 45.
10 A. T. James and A. J. P. Martin, *Brit. Med. Bull.*, 10 (1954) 170.
11 G. W. Warren and L. J. Priestly, Jr., *Anal. Chem.*, 31 (1959) 1013.
12 I. A. German and N. Ciot, *Rev. Chim.*, 16 (1965) 382.
13 D. A. Vjachirov and L. E. Reschetnikova, *Zh. Prikl. Khim.*, 31 (1958) 802.
14 D. Jentzsch, *Z. Anal. Chem.*, 221 (1966) 377.
15 C. L. Guillemin, *J. Chromatogr. Sci.*, 7 (1969) 493.
16 J. H. Knox, *Chem. Ind. (London)*, 10 (1955) 1631.
17 T. E. Archer, A. Bevenue and G. Zweig, *J. Chromatogr.*, 6 (1961) 457.
18 K. Malinowska, *Chem. Anal. (Warsaw)*, 9 (1964) 585.
19 J. B. Evans and J. E. Willard, *J. Amer. Chem. Soc.*, 78 (1956) 2908.
20 F. H. Pollard and C. J. Hardy, *Anal. Chim. Acta*, 16 (1957) 135.
21 G. F. Harrison, in D. H. Desty (Editor), *Vapour Phase Chromatography*, Butterworths, London, 1957, p. 333.
22 C. J. Hardy, *Analyst (London)*, 79 (1954) 726.
23 A. J. Lazaris, *Neftekhimiya*, 5 (1965) 166.
24 G. M. Sassu, F. Zilic-Grandi and A. Conté, *J. Chromatogr.*, 34 (1968) 394.
25 E. Gloesener, *J. Pharm. Belg.*, 11–12 (1961) 379.
26 J. Efer, D. Quaas and W. Spichale, *Chem. Tech. (Leipzig)*, 20 (1965) 44.
27 A. Forris and J. G. Lehman, *Separ. Sci.*, 4 (1969) 225.