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# Gas chromatographic identification of complex mixtures of halomethanes and haloethanes by using the correlation between their retention and vapour pressure

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ABSTRACT

The linear correlation between relative retention values of halogenated hydrocarbons (methanes, ethanes and ethenes) having one or more identical or different halogen atoms in the molecule and their vapour pressures was used for identification purposes in gas chromatography. Absolute and relative retention values were measured at various temperatures on non-polar (OV-1) and polar (SP-1000) packed columns, and some correlations were found that permit peak identification. The calculation of retention times when the vapour pressures of the substances are known or, on the contrary, the calculation of this parameter on the basis of gas chromatographic analysis are possible.

INTRODUCTION

When very complex mixtures of halogenated compounds have to be analysed, *e.g.*, in the polluted environment, the identification of different compounds on the basis of their retention times on columns of different polarities is very useful and can avoid the use of more complex and expensive techniques that are often not suitable for routine field analysis. When standard samples are not available for the identification of less common compounds, the use of correlations between retention behaviour, physical properties and structure of these compounds can assist in tentative identification [1–8].

In a previously published paper [9], the correlation between the relative retention values, $r$, the retention index values, $I$, the retention volumes, $V_R$, and the vapour pressure, $p°$, of many halogenated hydrocarbons was investigated. For the non-polar stationary phase used, OV-1, a good linear correlation between vapour pressure and $I$ was found, which permits the separation of a complex mixture of compounds to be predicted at any temperature of the column. Further, the linear dependence of $I$ values on temperature can be used to confirm the qualitative identification of a substance, being correlated with its structure [10–12]. On the polar stationary phase SP-1000, the

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correlation was found to be non-linear and unsuitable for the calculation of retention values at different temperatures.

On the other hand, the use of an Antoine-type equation [13,14], the constants of which were calculated starting from experimental values, permitted the calculation of $I$ values at any temperature on both polar and non-polar stationary phases. The determination of $I$ values, however, by using the classical Kováts equation [15] with respect to linear alkanes, requires accurate measurements of the retention times of the compounds mixed with several linear alkane homologues. When electron capture detection (ECD) is used, the negligible response to alkanes requires the use of different homologous series of electron-absorbing compounds, e.g., linear iodoalkanes [16], and the determination of the correlation between their retention times and that of linear alkanes. The identification by means of retention index values is therefore unsuitable or very complex.

In contrast, the measurement of relative retention values, $r$, with respect to a reference compound present in the sample or added to it is much easier and does not require a complete series of reference substances. When the analyses are made on the same column and under reproducible temperature conditions, the validity of the $r$ values for identification purposes can be equivalent to the use of other retention values (the Kováts retention index or the specific retention volume, $V_g$) that are independent of many analytical parameters but whose determination is more difficult.

Of course, it is necessary to verify that the $r$ values show regular behaviour as a function of the structure, boiling point and vapour pressure of the analyte substances, similar to that shown by the $I$ and $V_g$ values, and to investigate the effect of the column polarity on the elution of the analyte compounds.

EXPERIMENTAL

Two columns of different polarity were used: non-polar OV-1 and polar SP-1000, both 10% (w/w) on Chromosorb W DMCS (80–100 mesh), with length 3 m and I.D. 2 mm. A Varian (Palo Alto, CA, U.S.A.) Model 3760 gas chromatograph was used with thermal conductivity detection (TCD), in order to permit the injection of samples with the same concentration of each component, owing to the small difference in the TCD responses to substances belonging to various homologous series (alkanes, alcohols, halogenated compounds with a different number of halogen atoms in the molecule). In fact, the use of specific detectors, which are insensitive to certain compounds, may require different amounts of each substance to be injected in order to obtain peaks of comparable area. The width and shape of some peaks may therefore change owing to column saturation and the resolution between adjacent peaks or the determination of some parameters (e.g., column efficiency) may be influenced. Obviously, the analysis of low-concentration authentic samples in the environment must be made with sensitive ECD, taking into account the possible effect of the different sensitivities of various compounds.

The samples used included chloro-, bromo- and iodo-methanes, -ethanes and -ethenes with one or more different halogen atoms in the molecule. The choice of these components permitted many different "homologous series" to be investigated, by changing the substituent halogen or increasing the number of halogen atoms in the molecule. Helium was used as the carrier gas at a flow-rate of 30 cm$^3$ min$^{-1}$. All the

samples were analysed at 50, 75, 100 and 125°C on both columns. The discussion below is based on the values at 100°C, but the results can also be applied to the retention values found at different temperatures.

THEORY

For many homologous series of compounds the following relationships were found [17,18]:

$$\log p° = K_3 + K_4 n \tag{1}$$

$$\log \gamma = K_5 + K_6 n \tag{2}$$

where $n$ is the number of structural units in the molecule (*i.e.* carbon atoms, methylene groups, chlorine atoms, etc.) and $K_3$, $K_4$, $K_5$ and $K_6$ are constants for each homologous series at a given temperature. For such compounds $\log \gamma$ and $\log p°$ are related:

$$\log \gamma = a + b \log p° \tag{3}$$

where

$$a = K_5 - (K_3 K_6 / K_4) \tag{4}$$

$$b = K_6 / K_4 \tag{5}$$

Taking into account the general equation for retention volume, $V_R$:

$$V_R = \frac{N_1 RT}{\gamma p°} \tag{6}$$

where $N_1$ is the number of moles of stationary phase in the column, the following equation is derived:

$$\log V_R = \log(N_1 RT) - a - (b + 1)\log p° \tag{7}$$

Further, as for homologous series the boiling points, $B_p$, are linearly correlated with the $p°$ values [13]:

$$\log p° = K_1 + K_2 B_p \tag{8}$$

the following relationship is obtained:

$$\log V'_R = \log(N_1 RT) - a - (b + 1)(K_1 + K_2 B_p) \tag{9}$$

showing that, on a given column at a constant temperature, $V'_R$ depends linearly on the boiling point, a readily available parameter, whereas tabulated $p°$ values are often difficult to obtain. As the $V_g$ (specific retention) values are obtained from the adjusted

retention volumes, $V'_R$, by taking into account the amount of liquid phase in the column, and therefore differ from $V'_R$ by a constant ratio, the correlation shown above is also true when $V_g$ or $I$ values are considered.

Similar results can be obtained for $r$ values [19], by starting from the equation

$$\log r_{s,q} = \log(p^\circ_q/p^\circ_s) + \log(\gamma_q/\gamma_s) \tag{10}$$

where $r_{s,q}$ is the relative retention of substance s with respect to a reference compound q. Eqn. 8 is suitable for application with very dilute solutions such as occur in gas–liquid chromatography.

By taking into account eqns. 1, 2 and 8, the following relationship is obtained:

$$\log r_{s,q} = A_1 - a_1 \log p^\circ_s = A_2 - a_2 B_p \tag{11}$$

where

$$A_1 = \log(p^\circ_q \gamma_q) - K_5 + (K_3 K_6/K_4) \tag{12}$$

$$A_2 = A_1 - a_1 K_1 \tag{13}$$

$$a_1 = 1 + (K_6/K_4) \tag{14}$$

$$a_2 = - a_1 K_2 \tag{15}$$

showing that for homologous series the behaviour of $r$ values is as linear as that of $V'_R$ values as a function both of $p^\circ$ and of $B_p$.

Fig. 1A and B show the linear dependence of $r$ and $V'_R$ values of a homologous series on $p^\circ$ and $B_p$, respectively. Further, when neither $p^\circ$ nor $B_p$ values for a given compound are available, but it belongs to a homologous series and its number of
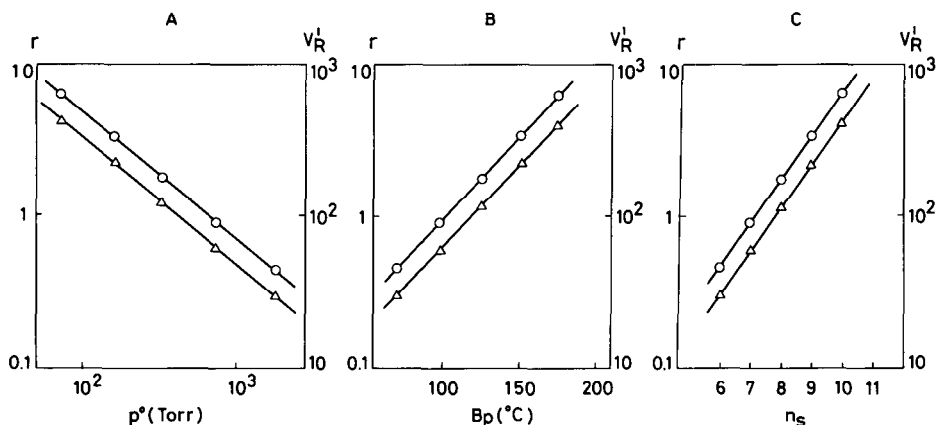


Fig. 1. Regular behaviour of (○) relative retention $r$ and (△) adjusted retention volume $V'_R$ of $C_6$–$C_{10}$ n-alkanes on non-polar OV-1 column at 100°C. Values are shown as a function of (A) vapour pressure at 100°C, $p^\circ$, (B) boiling point at 760 Torr, $B_p$ and (C) number of structural units in the molecule, $n_s$.

TABLE I

HALOGENATED COMPOUNDS ANALYSED, GROUPED BY STRUCTURE, THEIR RETEN-
TION RELATIVE TO 1-CHLORO-2-BROMOETHANE, $r$, ON NON-POLAR AND POLAR
COLUMNS AT 100°C AND, WHEN AVAILABLE, BOILING POINTS AT 760 TORR, $B_p$, AND
VAPOUR PRESSURE AT 100°C, $p°$.

Adjusted retention, $t'_R$, of reference compound: 4.28 min on OV-1, 17.33 min on SP-1000.

| No. | Compound | OV-1 | | SP-1000 | | $B_p$ (°C) | $p°$ at 100°C (Torr) |
|-----|----------|------|---|---------|---|------------|----------------------|
| | | $t'_R$ (min) | $r$ | $t'_R$ (min) | $r$ | | |
| 1 | $CH_3CHCl_2$ | 0.81 | 0.373 | 1.34 | 0.195 | 57.28 | 2303 |
| 2 | $CH_2=CCl_2$ | 0.56 | 0.258 | 0.52 | 0.076 | 37 | |
| 3 | $ClCH=CCl_2$ | 1.91 | 0.884 | 2.54 | 0.369 | 87 | |
| 4 | $Cl_2C=CCl_2$ | 4.12 | 1.898 | 3.18 | 0.462 | 121 | 412 |
| 5 | $CCl_4$ | 1.58 | 0.728 | 1.35 | 0.196 | 76.5 | 1315 |
| 6 | $ClCH_2CH_2Cl$ | 1.30 | 0.599 | 3.86 | 0.561 | 83.5 | 1129 |
| 7 | $CHCl_3$ | 1.04 | 0.479 | 2.84 | 0.413 | 61.7 | 2203 |
| 8 | $CHBr_2Cl$ | 3.40 | 1.567 | 14.57 | 2.120 | 119.5 | |
| 9 | $CHBrCl_2$ | 1.90 | 0.875 | 6.48 | 0.943 | 90 | |
| 10 | $CHBr_3$ | 6.02 | 2.774 | 32.55 | 4.730 | 149.5 | 162 |
| 11 | $CH_3CCl_3$ | 1.37 | 0.630 | 1.37 | 0.199 | 74.1 | |
| 12 | $CH_2Cl_2$ | 0.50 | 0.230 | 1.65 | 0.240 | 40 | |
| 13 | $CH_3CH_2I$ | 1.12 | 0.516 | 1.34 | 0.195 | 72.3 | |
| 14c | $BrCH=CHBr$ (cis) | 3.06 | 1.410 | 10.83 | 1.576 | 112.5 | |
| 14t | $BrCH=CHBr$ (trans) | 2.53 | 1.165 | 5.58 | 0.812 | 108 | |
| 15 | $BrCH_2CH_2Br$ | 3.69 | 1.700 | 12.13 | 1.765 | 131.4 | 339 |
| 16 | $Cl_3CCHCl_2$ | 11.15 | 5.138 | 30.02 | 4.369 | 162 | 124 |
| 17 | $CH_3I$ | 0.60 | 0.276 | 0.77 | 0.112 | 42.4 | 3378 |
| 18 | $Cl_3CCH_2Cl$ | 4.95 | 2.281 | 11.60 | 1.688 | 130.5 | 312 |
| 19 | $ClCH=CHCl$ (trans) | 0.76 | 0.350 | 1.10 | 0.160 | 47.5 | 3214 |
| 20 | $ClCH=CHCl$ (cis) | 1.00 | 0.461 | 2.41 | 0.350 | 60.3 | 2187 |
| 21 | $ClCH_2CH_2Br$ | 2.17 | 1 | 6.87 | 1 | 107 | 682 |
| 22 | $CH_2I_2$ | 7.22 | 3.327 | 44.58 | 6.489 | 182 | |
| 23 | $CBrCl_3$ | 2.97 | 1.369 | 3.92 | 0.570 | 104 | |
| 24 | $C_2H_5Br$ | 0.60 | 0.276 | 0.70 | 0.102 | 38.4 | 4248 |
| 25 | $Cl_2CHCHCl_2$ | 6.76 | 3.115 | 43.35 | 6.601 | 146 | 184 |
| 26 | $Br_2CHCHBr_2$ | 60.4 | 27.834 | – | – | 243.5 | 6 |
| 27 | $CH_2BrCl$ | 1.05 | 0.484 | 3.44 | 0.500 | 68.1 | |
| 28 | $CH_2ClI$ | 2.12 | 0.977 | 8.55 | 1.244 | 109 | |
| 29 | $CH_2Br_2$ | 1.84 | 0.848 | 7.00 | 1.018 | 97 | 833 |
| 30 | $Cl_3CCCl_3$ | 21.64 | 9.972 | 30.12 | 4.384 | 186 | 38 |
| 31 | $CBr_4$ | 18.79 | 8.659 | 112.80 | 16.419 | 190 | 47 |
| 32 | $CHI_3$ | 49.50 | 22.811 | – | – | 218 | |
| 33 | $ICH_2CH_2I$ | 14.20 | 6.543 | – | – | 200 | |
| 34 | $CH_3CH_2Cl$ | 0.33 | 0.152 | 0.33 | 0.048 | 12.3 | 9225 |

structural units, $n_s$, is known, the $B_p$ value being linearly correlated with $n_s$ [13], a linear
relationship between $r$, $V'_R$ and $n_s$ is observed (Fig. 1C):

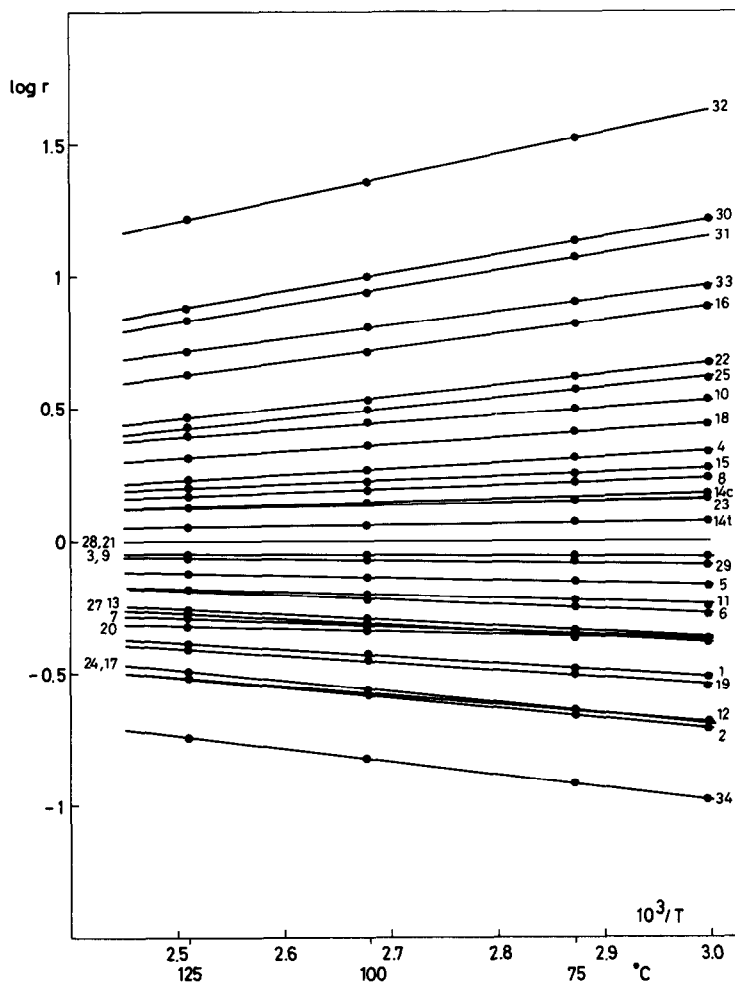$$\log r_{s,q} = \log(p°_q \gamma_q) - (K_3 + K_5) - (K_4 + K_6)n_s \tag{16}$$

Fig. 2. Retention times relative to 1-chloro-2-bromoethane of halogenated compounds listed in Table I, analysed on non-polar OV-1 column, as a function of the reciprocal of absolute temperature of the column.

The linear behaviour expressed by eqns. 11 and 16 is also found when the structural units of the molecule considered are different from methylenic groups or carbon atoms, but are halogen atoms, substituent groups, etc. [13,20].

RESULTS AND DISCUSSION

Table I lists the analytes, their adjusted retention times, $t_R'$, measured at 100°C and the r values measured with respect of 1-chloro-2-bromoethane. This substance was selected as the reference compound instead of trichloroethylene, generally used as the reference in the analysis of haloalkanes in the environment [9], because its peak showed no interference with the analyte compounds under any analytical conditions and

because its presence was never observed in authentic environmental samples, making this compound a good choice as a reference for internal standard quantitative calibration. Boiling points obtained from the literature and vapour pressures calculated by using the Antoine equation are also shown. Figs. 2 and 3 show the linear change of $r$ values with respect of 1-chloro-2-bromoethane as a function of the reciprocal of the absolute temperature of the column.

The correlation between $\log r$ on the non-polar OV-1 column and $\log p^\circ$ (both at 100°C) is shown for many haloalkanes and for $C_6$–$C_{10}$ $n$-alkanes in Fig. 4. On completely non-polar columns the retention should depend only on vapour pressure and therefore all compounds should lie on the same straight line. The experimental points are on three near-parallel lines, whose correlation coefficients are very high (>0.999); for each straight line the gas chromatographic behaviour depends only on
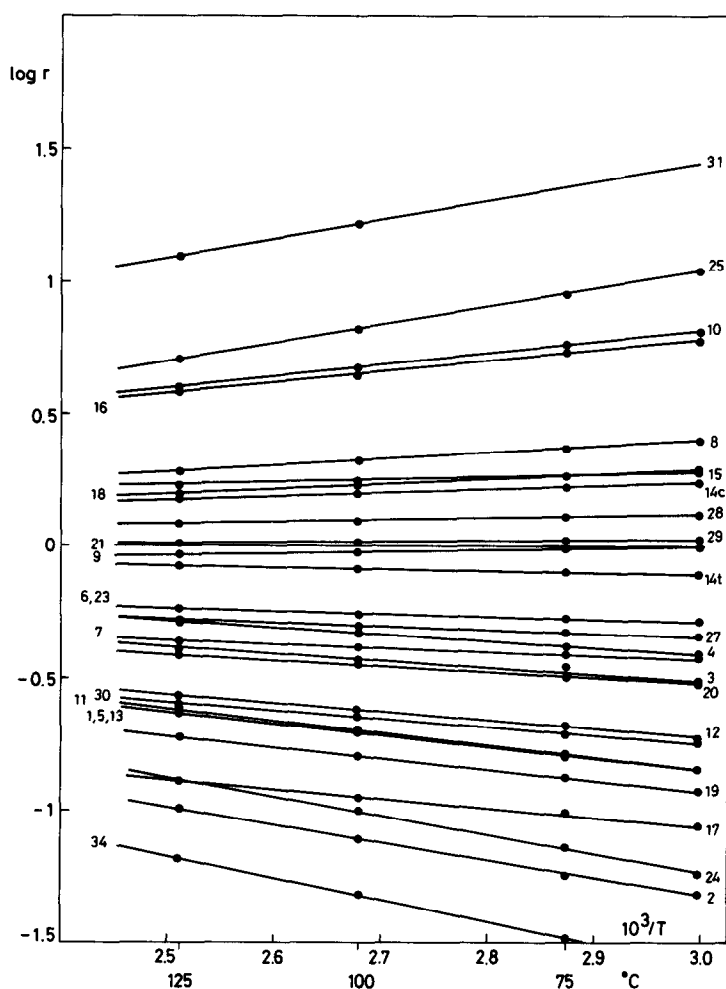


Fig. 3. Retention times relative to 1-chloro-2-bromoethane of halogenated compounds listed in Table I, analysed on polar SP-1000 column, as a function of the reciprocal of absolute temperature of the column.
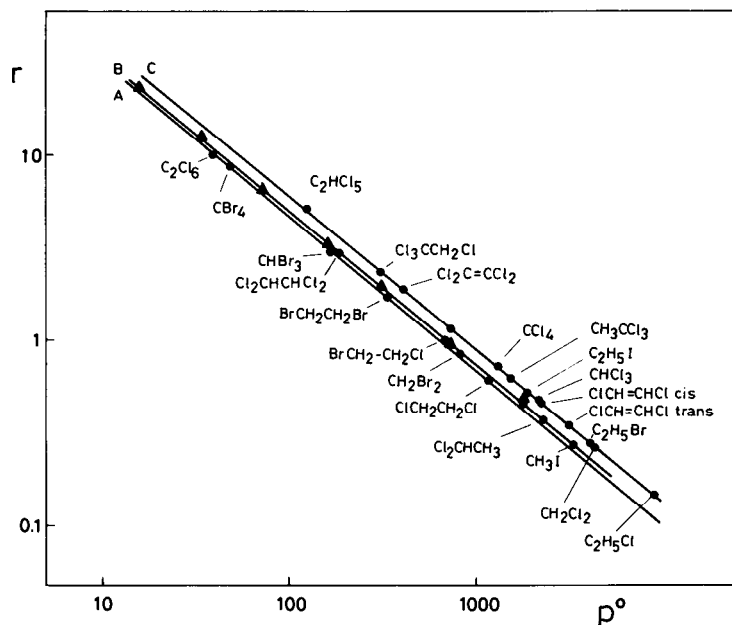
Fig. 4. Linear correlation between $r$ and $p°$ values of various halogenated compounds (●) and $C_6$–$C_{10}$ $n$-alkanes (▲) on non-polar OV-1 column. Temperature, 100°C.

the vapour pressure of the solute, the activity coefficient, $\gamma$, being constant. The lines are closely spaced, showing that the difference between $\gamma$ values for the various series of compounds is small but not negligible. On the polar SP-1000 column the interaction due to dipole moments or to hydrogen bonding can be much greater than the structural effects (e.g., symmetry or steric hindrance). Therefore, in Fig. 5 the network of straight lines connecting the compounds belonging to the same homologous series shows a fine structure.

The same behaviour, although less evident, is also shown by the log $r$ vs. log $p°$ plot on the non-polar column. It is possible to draw in Fig. 4 some straight lines that connect compounds containing the same number of hydrogen atoms or an increasing number of atoms of the same halogen.

Fig. 6 shows on an arbitrary enlarged scale this fine structure: closed circles represent the compounds, also plotted in Fig. 4, whose $r$ and $p°$ values are experimentally known. Open circles show the halomethanes whose $r$ values were measured (Table I) while $p°$ values are not available. By starting from the experimental data, the equations of the straight lines shown in Fig. 6 and the $p°$ values for other compounds can be calculated.

Table II shows the coefficients (slope and intercept) of the equation (simplified form of eqn. 11)

$$\log p° = s \log r + i \qquad (17)$$

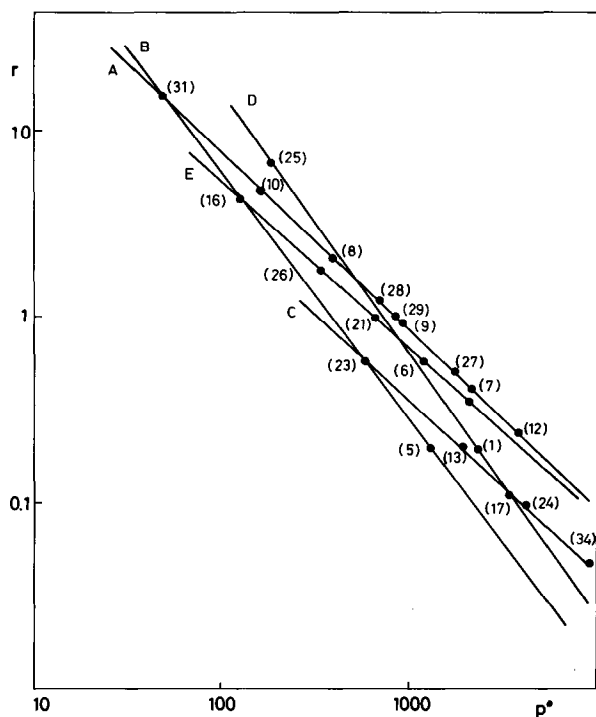calculated by using experimental $r$ values.

Fig. 5. Linear correlation between $r$ and $p°$ values of various halogenated compounds on polar SP-1000 column. Temperature, 100°C.
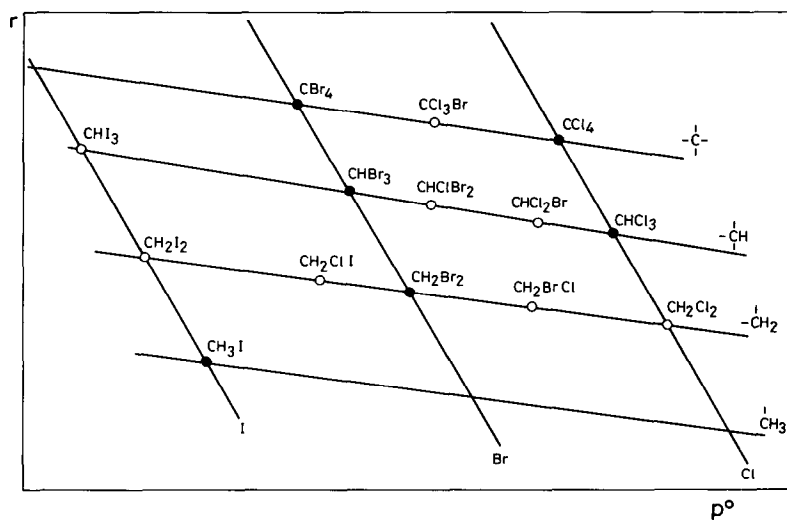


Fig. 6. Arbitrary scale enlargement of a section of Fig. 4 (OV-1, 100°C), showing the fine structure of lines where halomethanes belonging to different homologous serie lie. ●, Experimental values; ○, calculated values (see text).

TABLE II

SLOPE $s$ AND INTERCEPT $i$ OF EQN. 17 CALCULATED FROM EXPERIMENTAL VALUES ON OV-1 AND ON SP-1000 COLUMNS

Identification of lines refers to Figs. 6 and 7. Correlation coefficient for all lines >0.99.

| Column | Line | $s$ | $i$ |
|---|---|---|---|
| OV-1 | C | −1.34 | 2.93 |
| (Fig. 6) | CH | −1.48 | 2.86 |
| | CH$_2$ | −1.47 | 2.81 |
| | I | −1.36 | 2.75 |
| | Br | −1.37 | 2.82 |
| | Cl | −1.23 | 2.94 |
| SP-1000 | A | −1.04 | 2.93 |
| (Fig. 7) | B | −0.75 | 2.58 |
| | C | −0.83 | 2.77 |
| | D | −0.92 | 2.98 |
| | E | −0.82 | 2.74 |

Table III shows the $p°$ values calculated with eqn. 17 by using experimental $r$ values and the coefficients reported in Table II.

The same procedure can be applied to obtain the $r$ values when $p°$ is known. Moreover, by taking into account eqns. 11 and 16, similar fine structure plots could be obtained that permit the retention of any halomethane whose $B_p$ or $n$ values are known to be calculated by plotting log $r$ as a function of these variables.

Another method for calculating the $r$ value of a given compound follows from the constant difference, $\Delta = \log r_1 - \log r_2$, observed when a halogen atom is replaced with another halogen (Table IV). By using the $r$ values obtained from the $\Delta$ values in Table IV and the parameters of eqn. 17 shown in Table II, the $r$ and $p°$ values for some halomethanes can be predicted (Table V). The described procedure can be followed for any stationary phase. Fig. 7 shows with arbitrarily enlarged scale

TABLE III

VAPOUR PRESSURES, $p°$, AT 100°C CALCULATED WITH EQN. 17 BY USING THE COEFFICIENTS IN TABLE II AND EXPERIMENTAL $r$ VALUES IN TABLE I FOR COMPOUNDS SHOWN WITH OPEN CIRCLES IN FIGS. 6 (OV-1) AND 7 (SP-1000)

| Compound | $p°$ (Torr) | |
|---|---|---|
| | OV-1 | SP-1000 |
| CH$_2$Cl$_2$ | 4276 | 3824 |
| CH$_2$ClBr | 1905 | 1771 |
| CH$_2$ClI | 676 | 681 |
| CH$_2$I$_2$ | 111 | 120 |
| CHCl$_2$Br | 901 | 911 |
| CHClBr$_2$ | 379 | 389 |
| CCl$_3$Br | 563 | 588 |
| CHI$_3$ | 7 | |

TABLE IV

EXPERIMENTAL $\Delta$ VALUES (SEE TEXT) WITH DIFFERENT HALOGEN ATOMS (X) AS SUBSTITUENTS IN THE MOLECULE

| Column | Structure | Substitution | | $\Delta$ |
|--------|-----------|------|------|----------|
| | | of | with | |
| OV-1 | $CX_4$ | Cl | Br | 0.268 |
| | $CX_3$ | Cl | Br | 0.254 |
| | | Br | I | 0.305 |
| | | Cl | I | 0.559 |
| | $CH_2X_2$ | Cl | Br | 0.240 |
| | | Br | I | 0.296 |
| | | Cl | I | 0.537 |
| | $XCH_2\text{-}CH_2X$ | Cl | Br | 0.227 |
| | | Br | I | 0.292 |
| | | Cl | I | 0.518 |
| SP-1000 | $CX_4$ | Cl | Br | 0.478 |
| | $CHX_3$ | Cl | Br | 0.354 |
| | | Br | I | 0.543 |
| | | Cl | I | 0.896 |
| | $CH_2X_2$ | Cl | Br | 0.306 |
| | | Br | I | 0.402 |
| | | Cl | I | 0.710 |

plots A and B in Fig. 5. Closed circles represent experimental data and open circles the compounds whose $r$ values are known and that are assumed to lie on a straight line on the basis of structural characteristics.

Tetrahalomethanes belong to line B whereas tri- and dihalomethanes lie on line A (a hyperfine structure with different lines for di- and trihalo compounds is possible,

TABLE V

$r$ VALUES FOR VARIOUS COMPOUNDS CALCULATED BY USING $\Delta$ VALUES IN TABLE IV AND $p^\circ$ VALUES OBTAINED FROM EQN. 17 WITH THE PARAMETERS IN TABLE II

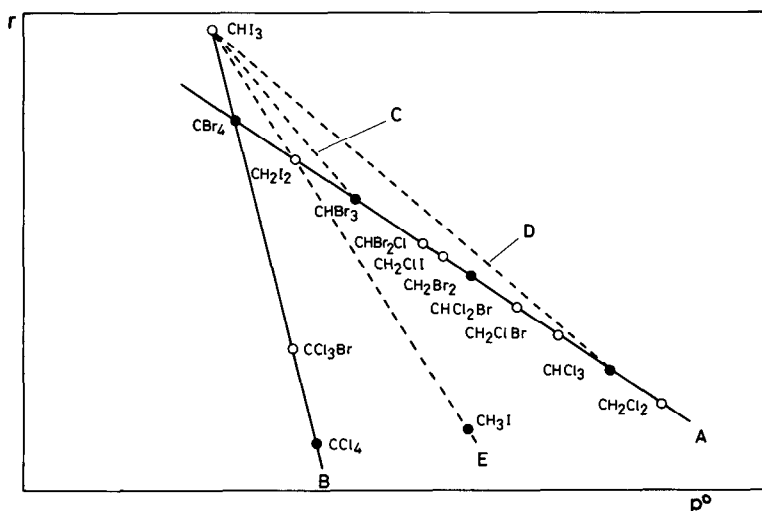| Compound | OV-1 | | SP-1000 | |
|----------|------|------|---------|------|
| | $r$ | $p^\circ$ (Torr) | $r$ | $p^\circ$ (Torr) |
| $CHCl_2I$ | 1.73 | 327 | 3.25 | 326 |
| $CHClI_2$ | 6.29 | 48 | 25.58 | 48 |
| $CHBr_2I$ | 5.59 | 57 | 16.51 | 57 |
| $CHBrI_2$ | 11.30 | 20 | 57.65 | 20 |
| $CH_2BrI$ | 1.64 | 315 | 2.56 | 320 |
| $CCl_2Br_2$ | 2.52 | 248 | 1.77 | 252 |
| $CClBr_3$ | 4.69 | 108 | 5.32 | 110 |
| $CHI_3{}^a$ | | 7 | 202 | |

$^a$ See text.

Fig. 7. Arbitrary scale enlargement of a section of Fig. 5 (SP-1000, 100°C) showing the fine structure of lines where halomethanes belonging to different homologous serie lie. ●, Experimental values; ○, calculated values that lie on a straight line (see text).

but not evident at this scale and with the obtained accuracy of retention data). Parameters of eqn. 17 for lines A and B (Table II) can be used to calculate $p°$ values shown in Table III, and $\Delta$ values (Table IV) to calculate $p°$ and $r$ values shown in Table V. The final $p°$ values obtained by following this method and using experimental data measured on polar and non-polar stationary phases are very similar, notwithstanding the great difference in retention values on the two columns.

When a compound lies on two or more straight lines, i.e., belongs to different "homologous" series, its $r$ and $p°$ values can be calculated in several ways. As an example, $CH_3I$ lies on line E (Fig. 7) (increasing number of iodine atoms in the methane molecule) and by using data in Tables II and III its calculated $r$ value on SP-1000 is 203. Fig. 7 also shows that $CH_3I$ lies on line B and by following the procedure described above the calculated $r$ value on SP-1000 is 202, in good agreement with that calculated by interpolating line E.

Mixed Br and I trihalomethanes ($CHBr_2I$, $CHBrI_2$) belong to line C and mixed Cl and I trihalomethanes ($CHCl_2I$, $CHClI_2$) to line D (Fig. 7). Parameters of eqn. 17 for lines C and D (Table II) and $\Delta$ values (Table IV) can be used to calculate both $r$ and $p°$ values shown in Table V. The $p°$ values obtained by using the experimental data measured on polar and non-polar stationary phases are very similar, although many values were calculated by starting from the $r$ value for $CH_3I$, available only on the non-polar stationary phase.

The fine structure of the $\log r$ vs. $\log p°$ plots is also shown by haloethanes and -ethenes (Fig. 8). Closed circles represent compounds whose $r$ and $p°$ values are experimentally known, and open circles compounds whose $r$ values were measured on a non-polar OV-1 column. The straight line M relates to the haloethenes and the non-symmetrical haloethanes, and line N to the symmetrical haloethanes. Lines P, Q and R connect the compounds obtained by symmetrical or non-symmetrical
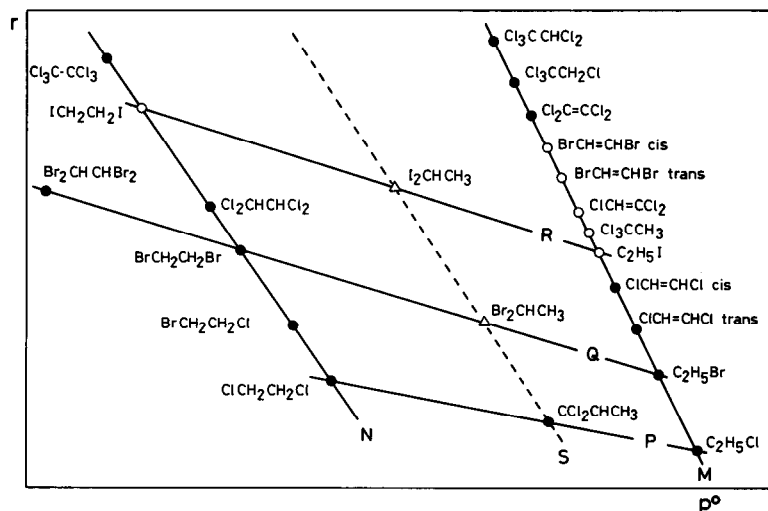
Fig. 8. Arbitrary scale enlargement of a section of Fig. 4 (OV-1, 100°C), showing the fine structure of lines where haloethanes and ethenes belonging to different homologous serie lie. ●, Experimental values; ○, calculated values. △ (Dashed line), probable position of non-symmetrical dihaloethanes (see text).

substitution of an increasing number of halogen atoms on the ethane molecule. Parameters of the straight-line equations for lines M, N, P, Q and R are shown in Table VI, and permit $p°$ values to be calculated for the compounds as listed in Table VII.

Hyperfine structure that cannot be appreciated with the experimental accuracy of $r$ values is probably present in this instance also. The empirical attribution of a compound to a given straight line on the basis of experimental data can permit the calculation of its $p°$ value. As an example, the calculation of $p°$ for $Br_2CHCHBr_2$ by using the parameters of line Q (Table VI) and experimental $r$ value (Table I) gives a value of 6.9, similar to the value of 6.3 found in the literature [21]. Other regular behaviour (e.g., the dashed line S in Fig. 8 that connects the non-symmetrical dihaloethanes) can probably be used for the calculation of $p°$ and $r$ values, but experimental data so far available do not permit this hypothesis to be verified.

TABLE VI

SLOPE $s$ AND INTERCEPT $i$ OF EQN. 17 CALCULATED FROM RETENTION DATA MEASURED ON NON-POLAR OV-1 COLUMN

Data refer to the line shown in Fig. 8. Correlation coefficients for all lines $>0.99$.

| Line | $s$ | $i$ |
|------|------|------|
| M | −1.23 | 2.94 |
| N | −1.20 | 2.81 |
| P | −1.54 | 2.69 |
| Q | −1.39 | 2.85 |
| R | −1.33 | 2.91 |

TABLE VII

$p°$ VALUES CALCULATED WITH PARAMETERS IN TABLE VI FOR VARIOUS COMPOUNDS
SHOWN IN FIG. 6, AND $p°$ AND $r$ VALUES CALCULATED BY USING $\Delta$ VALUES IN TABLE IV

| Compound | $p°$ (Torr) | $r$ |
|---|---|---|
| $C_2H_5I$ | 1987 | |
| $ClCH=CHCl$ | 1021 | |
| $BrCH=CHBr$ (*trans*) | 726 | |
| $BrCH=CHBr$ (*cis*) | 573 | |
| $ICH_2CH_2I$ | 66 | |
| $BrCH_2CH_2I$ | 152 | 3.33 |
| $ClCH_2CH_2I$ | 288 | 1.97 |

CONCLUSIONS

The suggested method permits the relative retention of a given compound not available as a standard to be predicted with an acceptable accuracy and the choice of possible identification in a complex chromatogram to be restricted to a few compounds.

When two or more compounds have very close retention times, this permits the elution order to be calculated to predict if the column efficiency is high enough for the separation of the peaks or to calculate the number of theoretical plates necessary to obtain the minimum resolution [22].

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