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GAS CHROMATOGRAPHIC SEPARATION OF CHLORINATED C_1 – C_3 HYDROCARBONS

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SUMMARY

A gas chromatographic method for separating mixtures of chlorinated C_1 – C_3 hydrocarbons has been developed. With temperature programming from 40 to 160°C a good separation was obtained when using 5% SP-1200 + 1.75% Bentone-34 on Supelcoport (100–120 mesh) as the column packing. A method for calculating retention indices with a column temperature programme is described. The polarity of the applied mixed stationary phase was calculated, based on McReynolds test substances.

INTRODUCTION

In the analytical monitoring of processes for the manufacture of chlorinated light (C_1 – C_3) hydrocarbons by the chlorination or chlorolysis of alkanes, alkenes and some by-products obtained in the manufacture of vinyl chloride, allyl chloride, epichlorohydrin, etc., there is often a need to define the composition of some complex mixtures containing chlorinated hydrocarbon derivatives such as chlorinated methane, ethane, ethylene, propane and propylene.

The well known separation methods^{1–7} employed for mixtures of chlorinated light hydrocarbons using conventional packed columns are suitable for the analysis of chlorinated derivatives of methane, ethane and ethylene. Popescu and Tomi⁸ separated some mixed chlorinated C_1 – C_3 hydrocarbons using a triethylene glycol dibenzoate stationary phase. Heavy fractions that contain components boiling above 120°C cannot be determined in this way because of the poor thermal stability of the stationary phase used (*ca.* 130°C).

To separate chlorinated C_1 and C_2 hydrocarbons and some of the chlorinated C_3 and C_4 hydrocarbons, in addition to conventional columns, capillary columns^{9–11} have also been used with squalane, squalene, hexadecane, didodecyl phthalate, diethylene glycol succinate, OS-138, FFAP, Carbowax 20M or a mixture of oxybis(2-ethyl benzoate) with silicone GE-96 as the stationary phase.

In this paper, a gas chromatographic (GC) method for separating mixtures of chlorinated methane, ethane, ethylene, propane, and propylene in a conventional packed column is presented.

EXPERIMENTAL

Apparatus

A ZSDO Model 577 (ZDSO, Kędzierzyn, Poland) gas chromatograph equipped with a flame-ionization detector (FID) having a sensitivity of 0.018 C/g was used, connected to an MKE-I recorder (VEB Messgerätewerk, Magdeburg, G.D.R.) having a range of 0–2 mV and a chart speed of 1 cm/min.

A Nickel-200 column (Analabs, North Haven, CT, U.S.A.) (3.6 m × 1/8 in. O.D.) was used. The column was packed with a mixture of 5% SP-1200 and 1.75% Bentone-34 on Supelcoport (100–120 mesh) (Supelco, Bellefonte, PA, U.S.A.).

The temperature of the injector and detector was 200°C. Calculations were carried out using a Hewlett-Packard Model 9830A calculator. The graphs were plotted using a Hewlett-Packard Model 9862A plotter.

Reagents

Standard mixtures of chlorinated C₁–C₃ hydrocarbons were prepared using chloromethane (purum), chloroform (puriss.), carbon tetrachloride (puriss.), 1,1,1-trichloroethane (purum), trichloroethylene (purum), 1,1,1,2-tetrachloroethane (purum), 1,1,2,2-tetrachloroethane (purum) and 2,2-dichloropropane (purum), from P.P.H. POCh (Gliwice, Poland); *cis,trans*-1,3-dichloropropene-1 (purum), supplied by Z.Ch. (Bydgoszcz, Poland); 1,1-dichloroethane (purum), 1,1,2-trichloroethane (purum), pentachloroethane (pract.), 2-chloropropane (puriss.) and 2-chloropropene-1 (purum), supplied by Fluka (Buchs, Switzerland); vinyl chloride (99.9%), 1,2-dichloropropane (pro synth.) and 1,3-dichloropropane (pro synth.), obtained from Merck-Schuchardt (Hohenbrunn, G.F.R.); dichloromethane (LiChrosolv; Merck, Darmstadt, G.F.R.); *cis,trans*-1-chloropropene-1, 1,1-dichloropropene-1 and 2,3-dichloropropene-1 (all pro synt. grade), obtained from Riedel-de Haën (Seltze-Hannover, G.F.R.); chloroethane (purum), from Ferak (Berlin, G.D.R.); 1,1-dichloroethylene (puriss.), from Koch-Light (Colnbrook, Great Britain); *cis,trans*-1,2-dichloroethylene (pract.), from Serva (Heidelberg, G.F.R.); 1,2-dichloroethane (purum), from Carlo Erba (Milan, Italy); tetrachloroethylene (puriss.), from Loba-Chemie (Vienna, Austria); allyl chloride (purum), from Reachim (U.S.S.R.); and hexachloroethane (99.9%), which was synthesized in this Institute.

To measure the retention indices of McReynolds substances and the retention times of C₄–C₁₂ hydrocarbons, McReynolds Kit No. 81C, obtained from Poly-Science Co. (Niles, IL, U.S.A.), and *n*-butane (research grade; Matheson Gas Products, Oevel, Belgium) taken from an LB-type cylinder were used.

Analytical conditions

The column was packed with 5% SP-1200 and 1.75% Bentone-34 on Supelcoport (100–120 mesh) and 160°C, for 6 h on each of five consecutive days in a stream of nitrogen flowing at 20 cm³/min.

During the analysis, the nitrogen flow-rate was 15 cm³/min. The column temperature was maintained isothermally at 40°C for 4 min, then programmed at 5°C/min up to 160°C and maintained at that temperature until the completion of the analysis. Samples of 0.5 μl were injected using a 5-μl microsyringe (S.G.E., Melbourne, Australia).

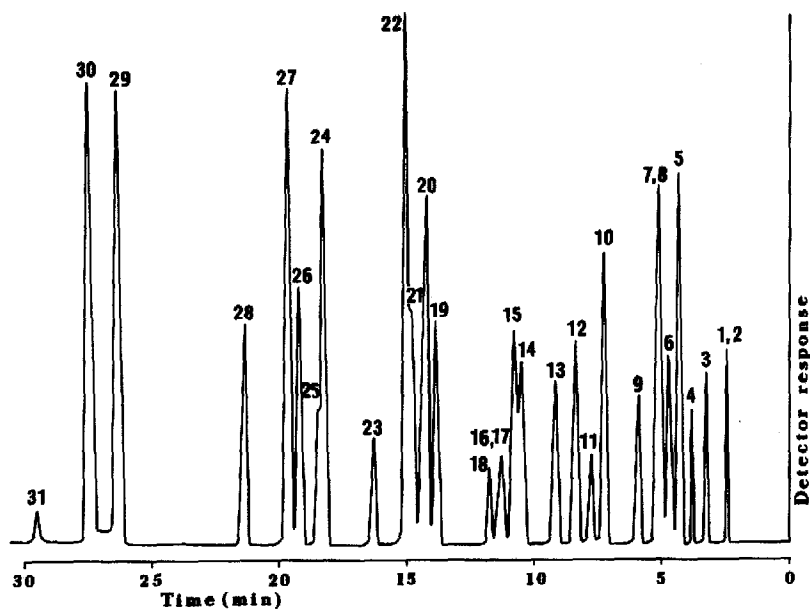


Fig. 1. Separation of the mixture of chlorinated C₁-C₃ hydrocarbon standards. Column: 3.6 m × 1/8 in. O.D. Nickel-200 tube, packed with 5% SP-1200 + 1.75% Bentone-34 on Supelcoport (100-120 mesh). Column temperature: 4 min isothermal at 40°C then programmed at 5°C/min to 160°C and kept isothermal at 160°C until the end of the analysis. Carrier gas: nitrogen at 15 cm³/min. Detector: FID, 0.018 C/g. Injector and detector temperature: 200°C. Sample size: 0.5 μl. Attenuation: 16 × 10⁻⁹. For peak identification, see Table I.

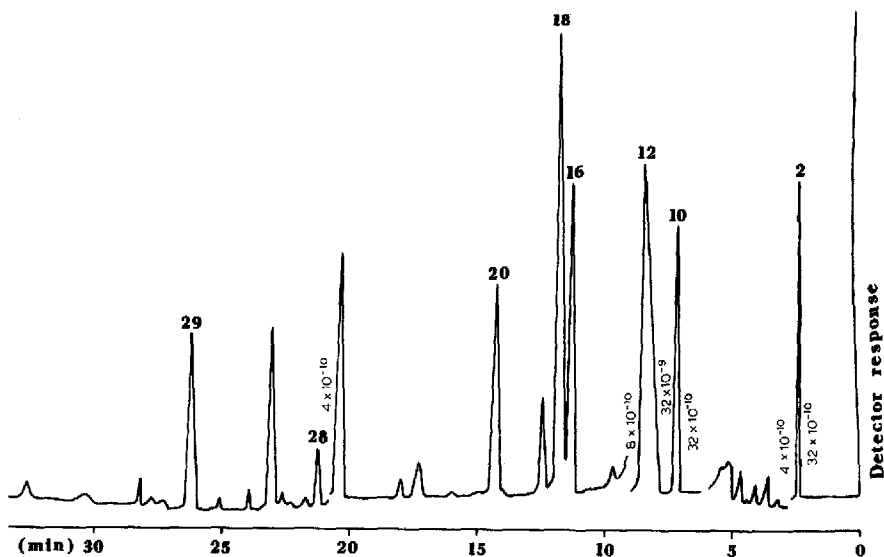


Fig. 2. Gas chromatogram of by-products taken from a vinyl chloride manufacturing plant. Conditions of analysis as in Fig. 1. For peak identification, see Table I.

RESULTS AND DISCUSSION

In preliminary experiments, stationary phases of various polarities (squalane, Apolane-87, SE-30, OV-101, OV-7, OV-17, SP-1000 and SP-2340) were examined for the separation of the chlorinated C_1 – C_3 hydrocarbons. Under the above conditions an acceptable separation could be achieved only on Apolane-87. However, even on this stationary phase no separation was achieved between (among others) *trans*-1,2-dichloroethylene and 1,1-dichloroethane. As the separation of these compounds is essential in the industrial process for which the method was developed, the use of mixed stationary phases for the separation of chlorinated C_1 – C_3 hydrocarbons was investigated.

The separation of the made-up mixture of chlorinated C_1 – C_3 hydrocarbon standards on 5% SP-1200 and 1.75% Bentone-34 on 100–120-mesh Supelcoport is shown in Fig. 1.

Fig. 2 shows a chromatogram of the by-products obtained from an industrial vinyl chloride manufacturing plant.

The total duration of conditioning of the column packing was 30 h. Such a long conditioning time was needed in order to obtain a good effect of partitioning and reasonably symmetrical peaks of 1,1,2,2-tetrachloroethane and pentachloroethane. The influence of the conditioning time of the column packing on the elution of 1,1,2,2-tetrachloroethane and pentachloroethane is shown in Fig. 3. The above behaviour of the column packing was verified for three column types of O.D. 1/8 in., having lengths of 1.5, 2.5 and 3.6 m.

The retention data of the components of the mixture of chlorinated C_1 – C_3 hydrocarbons are shown in Table I. The dead time was calculated by the method of Al-Thamir *et al.*¹² and was found to be 0.27 min.

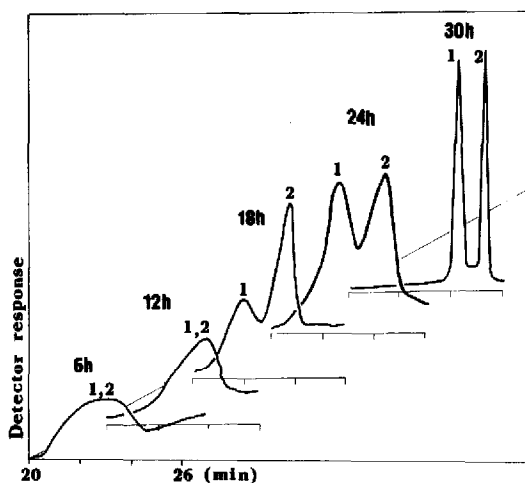


Fig. 3. Effect of conditioning time of a column (3.6 m \times 1/8 in. O.D., Nickel-200) packed with 5% SP-1200 + 1.75% Bentone-34 on Supelcoport (100–120 mesh) on the elution of 1,1,2,2-tetrachloroethane and pentachloroethane. Column conditioning temperature: 160°C. Nitrogen flow-rate: 20 cm³/min. Peaks: 1 = 1,1,2,2-tetrachloroethane; 2 = pentachloroethane.

TABLE I
RETENTION DATA AND BOILING POINTS OF CHLORINATED C₁-C₃ HYDROCARBONS

Peak No.	Compound	B.p. (°C)	<i>t</i> ' _R (min)	<i>I</i> _p * (min)
1	Chloromethane	-24	2.18	
2	Vinyl chloride	-14	2.18	
3	Chloroethane	12	2.98	
4	2-Chloropropene-1	23	3.48	
5	2-Chloropropane	35	4.03	
6	<i>cis</i> -1-Chloropropene-1	33	4.45	
7	<i>trans</i> -1-Chloropropene-1	37	4.81	
8	Vinylidene chloride	32-37	4.81	
9	3-Chloropropene-1	45	5.63	581
10	<i>trans</i> -1,2-Dichloroethylene	48.5	6.95	611
11	Dichloromethane	40	7.48	623
12	1,1-Dichloroethane	57.5	8.08	636
13	2,2-Dichloropropane	70.5	8.91	655
14	1,1,1-Trichloroethane	74	10.23	685
15	Carbon tetrachloride	76-77	10.51	691
16	Chloroform	62	11.11	705
17	1,1-Dichloropropene-1	78	11.11	705
18	<i>cis</i> -1,2-Dichloroethylene	60	11.53	714
19	Trichloroethylene	87	13.55	760
20	1,2-Dichloroethane	84	13.91	768
21	1,2-Dichloropropane	96.5	14.53	782
22	2,3-Dichloropropene-1	94	14.73	786
23	<i>trans</i> -1,3-Dichloropropene-1	104	16.01	815
24	Tetrachloroethylene	121	17.98	860
25	<i>cis</i> -1,3-Dichloropropene-1	112	18.18	864
26	1,3-Dichloropropane	120	18.91	881
27	1,1,2-Trichloroethane	114	19.28	889
28	1,1,1,2-Tetrachloroethane	130	21.03	928
29	1,1,2,2-Tetrachloroethane	146	26.03	1041
30	Pentachloroethane	162	27.13	1066
31	Hexachloroethane	185	29.18	1112

* Retention indices for the programmed column temperature. The calculation method is shown in the text.

As temperature programming of the column was used, the problem arose of what type of calculation of retention indices of the individual components in the mixture should be employed. Van den Dool and Kratz¹³ pointed out that retention indices (being not very dependent on temperature) may be used to determine the retention behaviour of substances in temperature-programmed GC. They employed the following equation:

$$I_p = 100 (t_x - t_z)/(t_{z+1} - t_z) + 100z \quad (1)$$

where $t_x - t_z$ is the distance on the strip chart between a homologous n -alkane z and the substance to be examined, and $t_{z+1} - t_z$ is the distance between the homologous n -alkane z and the next higher alkane $z + 1$. Habgood and Harris¹⁴ observed that, if the temperature coefficient of the substance is high, the isothermal retention index

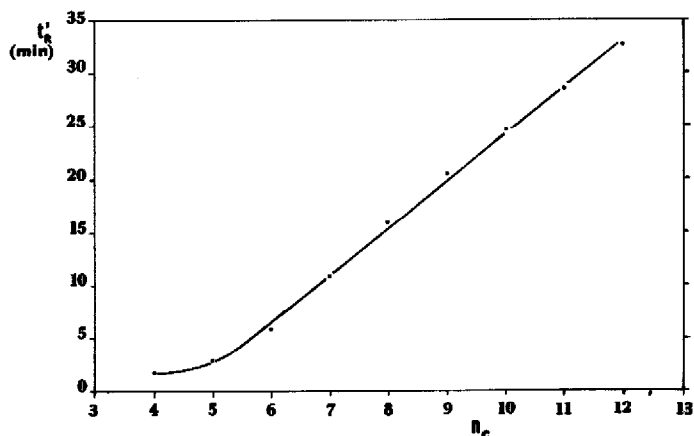


Fig. 4. Plot of reduced retention time (t'_R) versus carbon number (n_c) for C_4 - C_{12} n -alkanes. Column, temperature programming and other conditions as in Fig. 1.

cannot be converted into a linearly temperature programmed retention index (I_p).

A variety of methods have been suggested for obtaining a rough estimate of the retention index (I_p), based on the isothermal data for substances with high temperature coefficients. The best values¹⁵ can be obtained from isothermal values if the latter are measured at a temperature T' , calculated from the retention temperature T_R by means of a factor $0.92K_R^0$, where K_R^0 is T_R on an absolute scale^{16,17}. The equation $T' = T_R - 20$ also gives acceptable temperatures^{16,17}, although 20 is an approximate value and depends on the rate of the temperature programme.

Dahlmann *et al.*¹⁸ described a method for determining the retention indices for isothermal and programmed column temperatures based on a multiple correlation between the retention index and the physical and chemical behaviour of the component to be examined.

In this study, with a view to finding the retention indices of chlorinated C_1 - C_3 hydrocarbons, we examined the correlation of the reduced retention times of C_4 - C_{12} n -alkanes with the number of carbon atoms. This examination was carried out using column temperature programming as in the analysis of chlorinated hydrocarbons. This dependence is shown in Fig. 4. The experimental points in Fig. 4 are average values taken from five measurements. The sample of the regression function that most accurately approximates these values was found by the method of least squares. The function obtained is obtained by combining two functions, a quadratic one and a linear one:

$$t'_R = a_1 + b_1 n_c + c_1 n_c^2 \quad \text{for } n_c = 4, 5 \quad (2)$$

$$t'_R = a_2 + b_2 n_c \quad \text{for } n_c = 6, \dots, 12 \quad (3)$$

where $a_1 = 1.23797$, $b_1 = -9.94175$, $c_1 = 21.58945$, $a_2 = -20.1628$ and $b_2 = 4.44714$.

The quadratic function in eqn. 2 describes the values of the reduced retention times ($t'_R \leq 5.6$) for C_4 - C_5 n -alkanes, whereas the linear function in eqn. 3 describes

TABLE II
RETENTION INDICES OF McREYNOLDS TEST SUBSTANCES AT 120°C

Stationary phase	Retention index				
	Benzene	Butanol-1	Pentanone-2	1-Nitropropane	Pyridine
Squalane ¹⁹	653	590	627	652	699
SP-1200 ²⁰	720	760	730	855	865
SP-1200 + Bentone-34 (5:1.75)	738	759	752	864	875

the values of the reduced retention times ($t'_R > 5.6$) for C₆-C₁₂ *n*-alkanes. For a quadratic function, the calculated values are identical with the experimental values. On the other hand, for a linear function, the correlation coefficient is $r = 0.9984$ and the standard deviation is $\delta t'_R = 0.58772$. The dependence obtained is statistically significant at the $\alpha = 0.01$ level.

Taking the above facts in consideration, the following method for calculation of indices was used for components of the mixed chlorinated C₁-C₃ hydrocarbons for which the reduced retention times are described by the linear function in eqn. 3:

$$I_p = 100(t'_{R(x)} - a_2)/b_2 \quad (4)$$

where $t'_{R(x)}$ is the reduced retention time of the substance to be examined and a_2 and b_2 are coefficients in the equation of the straight line which defines the dependence $t'_R = f(n_c)$.

The retention index values calculated by this method for 23 components are given in Table I. In contrast to the method of Van den Dool and Kratz¹³ of retention index calculation, the above method makes it possible to estimate the precision of the I_p determination. In our case, this value (δI_p) was calculated from the following equation:

$$\delta I_p = 100 \cdot \frac{\delta t'_R}{b_2} \quad (5)$$

The precision of the retention index is 13 index units or 1.2-2.2% of the index value.

To determine the polarity of the stationary phase mixture, some measurements of retention indices were made at 120°C for benzene, butanol-1, pentanone-2, 1-nitropropane and pyridine. The values obtained are shown in Table II.

CONCLUSIONS

A mixture of chlorinated hydrocarbons such as methane, ethane, ethylene and some derivatives of chlorinated propane and propylene can be separated effectively using a column packing that contains 5% SP-1200 and 1.75% Bentone-34 as the stationary phases on Supelcoport (100-120 mesh) and suitable conditions of GC analysis. When methyl chloride and vinyl chloride are to be separated, satisfactory results are obtained if the carrier gas flow-rate is decreased to 10 cm³/min and the initial temperature of the column is decreased to 25-30°C.

The polarity of the mixture of SP-1200 and Bentone-34 is higher than that of SP-1200 alone: $\sum_{i=1}^5 (\Delta I_i^{\text{SP-1200} + \text{Bentone-34}} - \Delta I_i^{\text{SP-1200}}) = 58$.

The proposed method for the calculation of retention indices with column temperature programming is accurate if the $t'_R = f(n_c)$ dependence for the n -alkanes is linear.

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