

## GAS CHROMATOGRAPHIC ANALYSIS OF A HYDROCARBON MIXTURE

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**Abstract.** Gas chromatography was used to study the products of oxidation and the following esterification of a narrow hydrocarbon fraction obtained by thermal destruction of polyethylene wastes. The dependence of retention parameters on the hydrocarbon chain length was observed for a large set of compounds – homologues with different polarity.

**Key words:** polyethylene, pyrolysis, gas chromatography, alkanes, alkenes, fatty acid esters.

### INTRODUCTION

Products of polyethylene (PE) waste pyrolysis represent a cheap secondary raw material widely used in industry for producing various oxygen-containing compounds like saturated fatty acids, alcohols, esters, etc. The aim of this work was to study chromatographic properties of a complicated mixture consisting of a full series ( $C_{12}$ – $C_{20}$ ) of linear aliphatic hydrocarbons and their oxygen-containing derivatives. It was of interest to determine the general regularities between some chromatographic parameters (retention time and index) in dependence of the hydrocarbon chain length considering the chemical nature of homologues under separation.

### EXPERIMENTAL

Complex mixtures, consisting of *n*-alkanes and 1-alkenes in varying ratios as obtained at thermal destruction of PE waste (boiling range 213–380°C) [1, 2], were oxidized and thereafter esterified. Chromatographic analysis was performed on a Chrom 5 chromatograph. For the separation of hydrocarbon homologues,

columns of different length and diameter were used. Inerton and 10% PEG-20M served as adsorbent and stationary phase enabling a steady operation of the chromatograph at high temperatures (up to 250°C). Operation conditions of columns are given in Table 1. To avoid strong noise signals caused by detector filament corrosion due to acidic medium and to obtain correct and reproducible overall chromatographic separation, the fatty acids ( $C_6$ - $C_{22}$ ) obtained by oxidation of linear hydrocarbons were converted into ethyl esters of a general formula  $RCOOC_2H_5$  [2].

## RESULTS AND DISCUSSION

A chromatogram of a narrow fraction of the PE waste pyrolysis mixture is presented in Fig. 1. The fraction consists of *n*-paraffins and  $\alpha$ -olefins with marked prevalence of unsaturated components, mainly with the number of carbon atoms ( $C_n$ ) in the range of  $C_{12}$ - $C_{20}$ . The retention time of unsaturated compounds exceeds that of the corresponding *n*-paraffins for every pair of  $C_n$  hydrocarbons eluting from the columns.

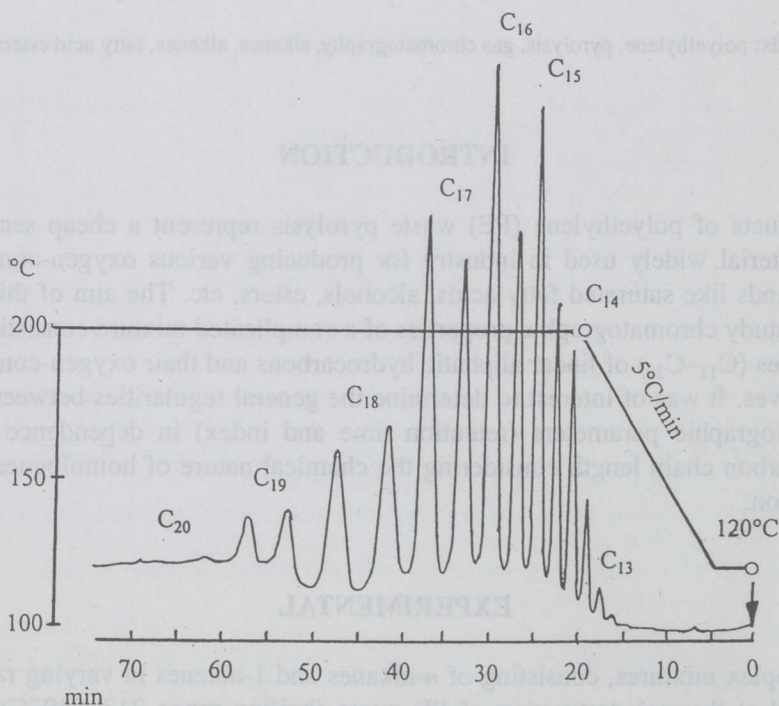


Fig. 1. Chromatogram of the hydrocarbon fraction  $C_{12}$ - $C_{20}$ .

Table 1

## Conditions of gas chromatographic analysis of pyrolysis products and their derivatives

Homologous series	Column	Temperature, °C			Flow rate of carrier gas, ml/min	Sample content in CHCl <sub>3</sub> , µl
		T <sub>col</sub>	T <sub>inj</sub>	T <sub>det</sub>		
Hydrocarbons C <sub>12</sub> -C <sub>20</sub>	<u>Steel</u> 3 m × 3 mm ID, filled with Inerton AW, 0.315-0.40 mm + 10% PEG-20M	4 min 120 → 200 (5°/min)	180	100	57.0	0.4
Hydrocarbons C <sub>12</sub> -C <sub>20</sub> Fatty acid ethyl esters C <sub>6</sub> , C <sub>9</sub> , C <sub>12</sub> , C <sub>15</sub> , C <sub>16</sub> , C <sub>18</sub> Acetates of saturated alcohols C <sub>9</sub> , C <sub>10</sub> , C <sub>12</sub> , C <sub>16</sub> Modified mixture C <sub>6</sub> -C <sub>22</sub>	<u>Glass</u> 2 m × 3 mm ID, filled with Inerton (AW) <sup>2</sup> , 0.125-0.60 mm + 10% PEG-20M	200	200	100	54.5	0.4-1.0
		a 8 min 120 → 200 (5°/min)	150	100		
		b	250	100		
Hydrocarbons C <sub>12</sub> -C <sub>20</sub> Acetates of saturated alcohols C <sub>9</sub> , C <sub>10</sub> , C <sub>12</sub> Fatty acids C <sub>3</sub> -C <sub>6</sub> , C <sub>9</sub>	<u>Quartz*</u> 25 m × 0.2 mm ID covered with PEG-20M	200	250	100	35.0	0.02-0.05
		c				

\* pressure at inlet 0.6 atm.; split ratio 150 : 1; flow rate H<sub>2</sub> - 28 ml/min, air - 250 ml/min.

The elution order of oxygen-containing compounds and some unreacted hydrocarbons is illustrated in Fig. 2. It is obvious that the liquid phase chosen is not suitable for separating aliphatic hydrocarbons from their oxygen-containing derivatives.

Functional groups (double bonds, methyl and ethyl groups) present have a strong impact on the chromatographic behaviour of the mixture on polar sorbents. Retention parameters of individual components depend strongly on the ratio and location of polar and nonpolar fragments present in long-chain molecules.

A comparison of the retention times measured for the components of the mixture with those of suitable standards – fatty acid esters (Fig. 2) – shows that  $C_n$  alkenes emerge from the column simultaneously with esters having an alkyl chain carbon number  $C_{n-6}$ .

As Fig. 2 shows, the first members of esters ( $C_6$ – $C_7$ ) and all long-chain esters starting with  $C_{14}$  give well-resolved separate peaks with the retention time being in good correlation with molecular dimensions. Towards the end of the chromatographic process, widening of the peaks occurs due to the long duration of the experiment (about 2 h).

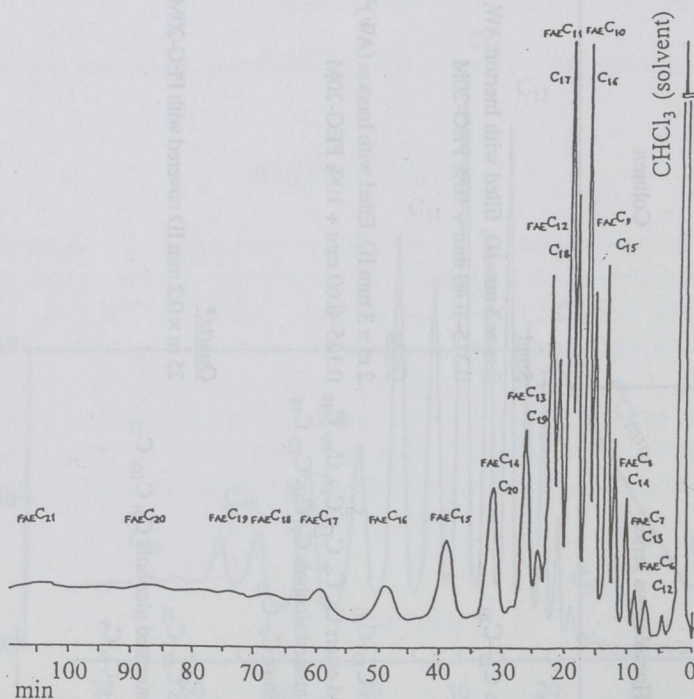


Fig. 2. Gas chromatographic separation of oxygen-containing hydrocarbon derivatives. Analytical conditions as listed in Table 1,  $T_{col}$  a.

Considering both the low degree of adsorption and low catalytic activity of the inorganic stationary phase, it can be assumed that the process of fractionation of differently substituted members of two homologous series is mainly controlled by two factors. One of them originates from the interaction between  $\pi$ -electrons of  $\alpha$ -olefins and carboxylate groups of esters, the other from the interaction of both of them with hydroxyl groups of the liquid phase (PEG).

The solid adsorbing phase plays almost no role in separation because of the concentration of the covering liquid phase. Intermolecular interaction between separable compounds prevails leading to similar chromatographic mobilities of olefins and esters present that differ in length by six methylene links. Gas chromatographic analysis of some individual oxygen-containing derivatives (Table 1, Fig. 3)

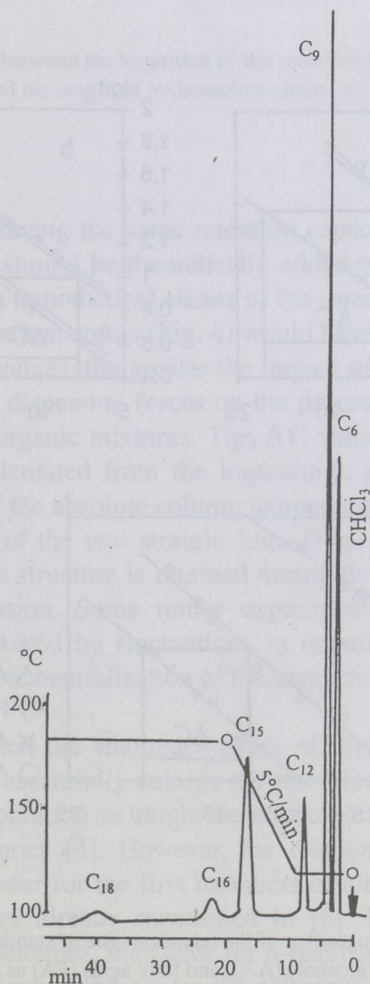


Fig. 3. Chromatogram of fatty acid ester standards (see Table 1).

as standards demonstrates that sorption and desorption processes in the columns chosen lead the separation of compounds in full accordance with the chemical nature and chain length of the molecules. As Fig. 4 demonstrates, there is linear relationship between the logarithm of the retention times of specially synthesized hydrocarbon derivatives (fatty acids, fatty acid esters, acetates of saturated alcohols) and the number of carbon atoms in the molecules. The lines for different homologous series on the same column are parallel, as previously found by Hawkes [3]. Therefore, the horizontal distance between the two parallel straight lines ( $\Delta C$ ) of every couple of an alkane and a derivative is actually a measure of the difference in chromatographic behaviour of the polar and nonpolar homologous series (Figs. 4 and 5). The  $\Delta C$  value can be considered as the difference of apparent or equivalent carbon numbers between linear alkanes and their oxygen-

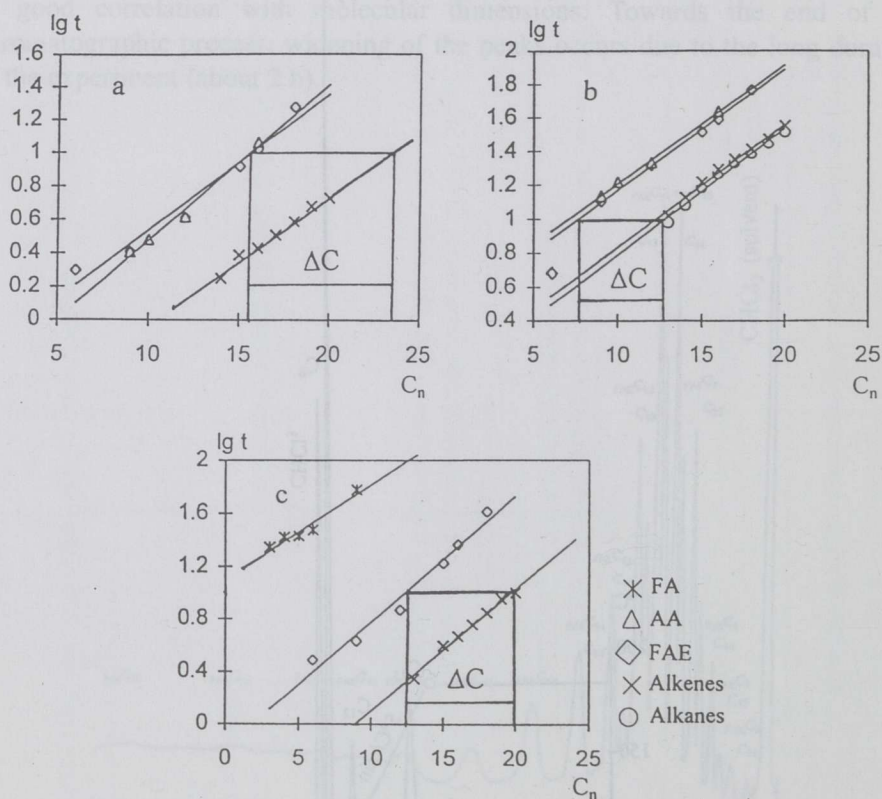


Fig. 4. Linear behaviour of the logarithm of the retention time of standard hydrocarbons, fatty acid esters (FAE), acetates of higher alcohols (AA), and fatty acids (FA) as a function of the number of carbon atoms in the molecule. Analysis conditions for *a*, *b*, and *c* are listed in Table 1.

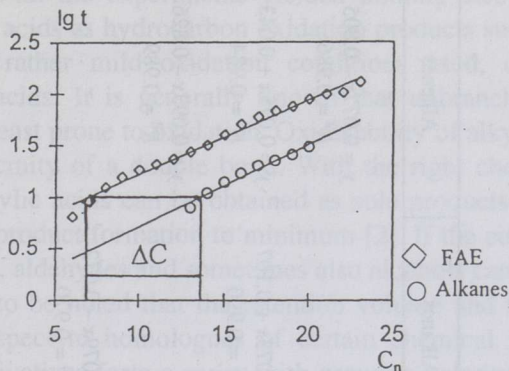


Fig. 5. The relationship between the logarithm of the retention time of oxygen-containing derivatives and the length of hydrocarbon chain (see Table 1,  $T_{col a}$ ).

containing derivatives having the same retention capacities or as the number of methylene groups that should be theoretically added to a linear alkane with  $C_n$  carbon atoms to obtain a hypothetical alkane of the same retention time as a linear ester (or acid) with  $C_n$  carbon atoms (Fig. 4) would have.

The higher the  $\Delta C$  values, the greater the impact of hydrogen bonds, dipole-dipole interactions, and dispersion forces on the process of gas chromatographic separation of complex organic mixtures. The  $\Delta C$  value as a function of column temperature may be calculated from the logarithmic plot of the retention time against the reciprocal of the absolute column temperature [4].

The parallel course of the two straight lines (Figs. 4 and 5) shows that the linearity of hydrocarbon structure is retained during the oxidation process and at the following esterification. Some minor experimental deviations in the line slopes are obviously caused by fluctuations in retention times which, in turn, result from the incomplete neutralization of the unreacted acidic compounds in the reaction mixtures.

It can be assumed that the stationary phase of higher polarity and the two-column method should essentially enlarge the retention volume of  $C_6$ - $C_{22}$  esters allowing clear peak separation as might be expected for individual members of different homologous series [5]. However, the relationship  $\lg t/C_n$ , where  $t$  is retention time, is not linear for the first members of aliphatic hydrocarbon series and their derivatives, as already mentioned in [6]. For individual classes of oxygen-containing homologues, the curve for  $n$ -paraffins (Figs. 4b and 5) can be used to find Kovats' retention indices for the column used.

Correlation equations and regression coefficients for dependencies presented in Figs. 4 and 5

Figure	Model parameters			
	FA (R·COOH)	AA (CH <sub>3</sub> ·COOR)	FAE (R·COOC <sub>2</sub> H <sub>5</sub> )	Alkanes
4a	$y = 0.082x - 0.282$ $R^2 = 0.965$	$y = 0.094x - 0.464$ $R^2 = 0.991$	—	$y = 0.077x - 0.805$ $R^2 = 0.986$
4b	—	$y = 0.072x + 0.446$ $R^2 = 0.997$	$y = 0.071x + 0.498$ $R^2 = 0.997$	$y = 0.075x + 0.043$ $R^2 = 0.984$
4c	$y = 0.071x + 1.104$ $R^2 = 0.938$	—	$y = 0.095x - 0.174$ $R^2 = 0.972$	$y = 0.093x - 0.826$ $R^2 = 0.989$
5	—	—	$y = 0.072x + 0.500$ $R^2 = 0.985$	$y = 0.079x - 0.072$ $R^2 = 0.970$



The fact that all the experiments yielded nothing else but linear saturated monocarboxylic acids as hydrocarbon oxidation products suggests the possibility that under the rather mild oxidation conditions used, only  $\alpha$ -olefins were converted into acids. It is generally known that unbranched saturated hydrocarbons are the least prone to oxidation. Oxidizability of alkyl groups is markedly higher in the vicinity of a double bond. With the right choice of the oxidation reagents, carboxylic acids can be obtained as sole products of the reaction with bringing the by-product formation to minimum [2]. If the conditions are changed to more rigorous, aldehydes and sometimes also alcohols can be obtained.

Thus, it has to be noted that the retention volume and the selectivity of the column with respect to homologues of certain chemical nature vary. All the hydrocarbon derivatives form a series with growing polarity and the strength of intermolecular interactions with the liquid phase (PEG): *n*-alkanes-1-alkenes-FAE-AA-FA.

The results of regression analysis of the experimental data are presented in Table 2. The regularities found together with equations presented might serve as a simple means for quick qualitative evaluation of the structural composition of a wide range of compound classes if analysed on that type of column without the need to use references as internal standards.

## CONCLUSION

Separation of homologous series of hydrocarbons and their oxygen-containing derivatives (fatty acids, their esters, and esters of fatty alcohols) was studied by gas chromatography using columns of various lengths. Modified Inerton-PEG-20M was used as the stationary phase. The dependence of retention times on the hydrocarbon chain length was determined for individual members of homologous series of various polarities. The chromatographic separation of the reaction mixtures of aliphatic hydrocarbons and fatty acid esters, obtained by oxidation of part of those hydrocarbons, shows that nonpolar and polar components in this mixture have identical retention times with the chain length difference of six carbons.

The experimental data allow us to suggest that in oxidizing the mixture of *n*-paraffins/ $\alpha$ -olefins, only  $\alpha$ -olefins undergo oxidation through the opening of double bonds and occasionally with breakage of hydrocarbon chains and recombination of their fractions under the oxidation conditions used.

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## SÜSIVESINIKE SEGU GAASIKROMATOGRAAFILINE ANALÜÜS

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Polüetüleenil jätmete pürolüüsil saadud kitsa süsivesinike fraktsiooni ( $C_{12}$ – $C_{20}$ ) oksüdatsiooniprodukte ja nende esterdamisprodukte on uuritud gaasikromatograafiliselt. Alkaanide/alkeenide keeruline segu lahutati 10% PEG-20M-ga modifitseeritud täidisil "Inerton". Katseandmetest järeldub, et valitud reaktsiooningimustes on süsivesinike oksüdatsiooni ainsateks produktideks monokarbok-süülhapped. Ilmselt alluvad oksüdatsioonile põhiliselt pürolüüsiproduktide segus olevad  $\alpha$ -olefiinid. On leitud suure hulga erineva polaarsusega süsivesinike homologide esindajate retentsiooniparameetrite sõltuvus molekulide ahelapikkusest  $C_n$ .