

# Retention indices as identification tool in pyrolysis-capillary gas chromatography

Monika Ádámová<sup>a</sup>, Andrej Oriňák<sup>a,\*</sup>, Ladislav Halás<sup>b</sup>

<sup>a</sup> University of P.J. Šafárik, Institute of Chemical Sciences, Department of Physical and Analytical Chemistry, Moyzesova 11, 04013 Košice, Slovakia

<sup>b</sup> Technical University Zvolen, Faculty of Ecology and Environmental Sciences, Department of Environmental Engineering, Kolpašská 9B, 969 01 Banská Štiavnica, Slovakia

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## Abstract

Pyrolysis-capillary gas chromatography (Py-cGC) represents important method to identify the analytes in the mixture after thermal degradation. This combines high effective analyte separation on-line coupled with thermal degradation process that depends on analyte structure. System of retention indices has been used for identification of the analytes after on-line pyrolysis and chromatographic separation. The pyrolysate composition has been studied during thermal degradation of polymethylmethacrylate (PMMA) at different pyrolysis temperatures and chromatographic column conditions. Homologues series of *n*-alkanes have been used for calculation of pyrolysate Kováts retention indices (*I*) and compared with mass spectrometric (MS) data of pyrolysate model mixture. To identify PMMA thermal degradation products the high density polyethylene (HDPE) as additive standard producing triplets of the olefin homologous series during co-pyrolysis has been used. These homologous series enable to calculate programmed temperature retention indices (*I*<sub>TPGC</sub>) to identify the analytes present in the pyrolysate. Calculated *I* values were compared with published *I* values databases to identify analytes yielded at different pyrolysis temperatures. © 2005 Elsevier B.V. All rights reserved.

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## 1. Introduction

Analytical pyrolysis by breaking large molecules into characteristic smaller fragments extends the use of gas chromatography to the analysis of polymeric materials [1–5], including natural polymers such as cellulose [6–8] as well as synthetics. In Py-cGC, the non-volatile, liquid or solid sample is very fast heated and thermally decomposed at 500–1400 °C in non-oxidative atmosphere. The resulting (semi-) volatile degradation products are on-line transferred to the capillary column for gas chromatographic analysis. The coupling Py-cGC with MS (Py-cGC–MS) makes pyrolysate analyte identification more simple and accurate. The availability of different and specialized commercial libraries render available number of MS spectra, that should facilitate the identification of unknown components by comparison of the spectra

obtained during the analysis of our sample with that reported in the library, selecting those spectra that are most similar or very close to that of the “unknown”. The identification performed by Py-cGC–MS using commercial libraries can be limited for various reasons: the similarity of the spectra of many different compounds; the inaccurate experimental conditions used for the acquisition of the library spectra; the presence of different spectra in the same library reported for the same component, or the same spectra reported relatively to the same component but with different common names or systematic name. The obvious solution to the problem with MS identification is to incorporate additional tool into the process of identifying unknowns, either as the spectral matches are generated, or in the data review process. In fact, it is possible to determine the relative retention time of target components by analyzing these under identical analytical conditions used for a reference solute, usually a solution of the homologous series of hydrocarbons. This approach was first used by Kováts [9] for isothermal analy-

\* Corresponding author. Tel.: +421 556222605; fax: +421 556222124.  
E-mail address: [orinak@kosice.upjs.sk](mailto:orinak@kosice.upjs.sk) (A. Oriňák).

sis. The concept of retention indices was defined and its basic relationships derived. Isothermal  $I$  are established by the relationship [9]:

$$I_s^{\text{st,ph}}(T) = 100 \left[ \frac{\log t'_{R,s} - \log t'_{R,z}}{\log t'_{R,(z+1)} - \log t'_{R,z}} \right] + 100z \quad (1)$$

where  $t'_{R,s}$  = retention time of unknown substrate,  $t'_{R,z}$  = retention time of  $n$ -alkane with  $z$  carbon atoms,  $t'_{R,(z+1)}$  = retention time of  $n$ -alkane with  $z+1$  carbon atoms.

As these indices, within a small margin of error are a function only of the GC column and the operating temperature (in contrast with the simple retention time),  $I$  value can be appropriately reproduced in various laboratories by using modern capillary columns. In the case of temperature programming GC the relationship is linear, therefore, by applying the linear equation developed by Van den Dool and Kratz [10]:

$$I_{\text{TPGC},s}^{\text{st,ph}} = 100n \left[ \frac{T_R(s) - T_R(z)}{T_R(z+1) - T_R(z)} \right] + 100z \quad (2)$$

or equation developed by Golovnya and Uraletz [11]:

$$I_{T_0/\beta} = I_{T_0} + \frac{\beta \tau_n}{2} \frac{dI}{dT} \quad (3)$$

by which have been obtained the satisfactory results in comparison with Van den Dool and Kratz. Also numerous workers dealt with temperatures-programmed retention indices ( $I_{\text{TPGC}}$ ) i.e. Giddings [12], Guiochon [13] and Erdey et al. [14]. The direct use of hydrocarbon homologous series copyrolysis cannot be applied for  $I$  calculation regarding to their decomposition at higher pyrolysis temperatures. To overcome this problem some polymer standards addition to the pyrolysed sample has already been described. Predominantly HDPE [15–19] was co-pyrolysed to yield homologous series of  $n$ -alkane,  $n$ -alkene and  $n$ -alkadiene. In our paper the use of  $I_{\text{TPGC}}$  for identification of PMMA or cellulose pyrolysate analytes composition has been described at different pyrolysis temperatures and polymer internal standards applied. Appreciation of these research and utilization of  $I_{\text{TPGC}}$  in analytes identification is the conditions optimization in waste thermal degradation and generous fuels as well hydrogen production (often with direct addition of novel solid materials [20–21] as the conversion catalysts). In this process is necessary to obtain immediate information about pyrolysis product contents without use of expensive and time consuming MS analysis.

## 2. Experimental methods

### 2.1. Standards and chemicals

The compounds used in this study have been purchased from the following companies: PMMA (M.W. 102,600) certified reference material with p.a. purity, Acros Organics (Belgium); hexane, heptane, benzene, toluene, all of analyt-

ical grade of purity, purchased from Slavus s.r.o (Bratislava, Slovakia); octane–decane, dodecane of chromatographic purity purchased from Roth GmbH (Karlsruhe, Germany); nonane–eicosane with chromatographic purity supplied by Reanal (Budapest, Hungary); MMA (M.W. 100.12) standard purchased from Sigma–Aldrich GmbH (Taufkirchen, Germany); naphthalene supplied by Lachema a.s. (Brno, Czech Republic); both of analytical grade of purity; HDPE (density 0.95) reference material purchased from Alfa Aesar (Karlsruhe, Germany). Special low volume micro syringe (0.5  $\mu$ l) and solid sample pelletizer application unit from SGE Europe (Milton Keynes, UK) have been used for samples injection. Balance AE 240 purchased from Mettler-Toledo (Switzerland) has been used for precision sample weighting. 0.5 mg of PMMA was applied in Py-cGC–MS analysis and for  $I$  determination 0.2  $\mu$ l of  $n$ -alkanes were applied.

### 2.2. Instrumentation and methods

The instruments and the conditions used in presented experiments are listed in the Table 1.

### 2.3. Retention index calculation methods

The Kováts retention indices were calculated using procedures outlined for isothermal gas chromatography with  $n$ -alkanes ( $C_6$ – $C_{20}$ ) as reference compounds under isothermal conditions at 60 °C, 80 °C, 100 °C and 120 °C. Homologous series were injected five times before and after analysis of real sample. The retention index average was determined from five experiments. The values for retention indices were calculated according to the Eq. (1). Hold-up time was determined by mathematical equations proposed by Peterson and Hirsch [22], Toth [23] and Furr [24]. The retention indices at programmed temperature  $I_{\text{TPGC}}$  were calculated according to the Eq. (2) by Van den Dool and Kratz [10].  $n$ -Alkanes were used as homologous series produced during pyrolysis of HDPE. The calculated  $I_{\text{TPGC}}$  values were compared with those given in the used databases [25,26].

## 3. Results and discussion

### 3.1. The results from Py-cGC–MS and cGC-FID analysis of pyrolysate analyte model mixture

PMMA is known to depolymerize to give back the monomeric units in the case of moderate pyrolysis temperatures (450–800 °C) [27–30]. PMMA was pyrolysed under the Py-GC–MS-1 conditions shown in Table 1. Temperature at what the maximum MMA-yields ranged between 550 and 600 °C. At lower pyrolysis temperatures (500 °C) were obtained more complicated pyrograms with MMA as a main product and a lot of the intermediates. At higher pyrolysis temperatures the formation of MMA slowly decreased, but simpler pyrograms allowed us to prepare pyrolysate model

Table 1  
Operating conditions of Py-GC and Py-GC–MS PMMA pyrolysate analysis

	Py-GC–MS-1	GC-2	Py-GC-3
Pyrolysis reactor	SGE Pyrojector II	–	SGE Pyrojector II
Pyrolysis temperature (°C)	500–850	–	400–900
Pyrolysis reactor volume (cm <sup>3</sup> )	0.43	–	0.43
Furnace nitrogen pressure (kPa)	137.93	–	137.93
Gas chromatograph	Varian Saturn 2100T	GC 9000 Fisons Instr.	GC 9000 Fisons Instr.
Detector	MSD	FID	FID
Pre-column length (m)	–	2.0	2.0
Pre-column i.d. (mm)	–	0.32	0.32
Column length (m)	30	30	30
Column i.d. (mm)	0.25	0.25	0.25
Stationary phase	DB-5	RTX-5	RTX-5
Stat. phase film thickness (μm)	0.25	0.25	0.25
Carrier gas	Helium	Nitrogen	Nitrogen
Inlet pressure (kPa)	120.0	60.0	60.0
Air (kPa)	100.0	100.0	100.0
Hydrogen (kPa)	50.0	50.0	50.0
Make up gas	Nitrogen	Nitrogen	Nitrogen
Initial temperature (°C)	70.0	–	40.0
Time at initial temperature (min)	2.0	–	2.0
$\beta$ (°C min <sup>-1</sup> )	10.0	–	5.0
Stand by temperature (°C)	170.0	–	300.0
Stand by final temperature (min)	2.0	–	10.0
Injector temperature (°C)	150.0	220.0	220.0
Detector temperature (°C)	150.0	220.0	220.0

$\beta$ , linear heating rate.

Table 2  
Degradation products from PMMA pyrolysis (Py-GC–MS at 800 °C) with their retention times  $t_R$  (min)

Analyte in pyrolysate	$t_R$
Benzene	1.024
Methyl methacrylate	1.048
Toluene	1.364
Benzene 1,2-dimethyl	2.134
Styrene	2.372
Benzene 1,3,5-trimethyl	3.359
Indene	4.483
Naphthalene	7.191

$t_R$ , retention time.

mixture on the base of MS identification results. The model mixture was prepared from benzene, MMA, toluene and naphthalene standards. Elution of them has been established in the order: benzene, MMA, toluene and naphthalene. Pyrolysate contained also another analytes that were not in-

cluded in this model mixture (Table 2). As an example of analytes separated is presented pyrogram of PMMA, obtained at pyrolysis temperature 800 °C (Fig. 1), where MMA is the main degradation product. For application of  $I$  the model mixture was analyzed at different isothermal column temperatures 60 °C, 80 °C, 100 °C and 120 °C and under GC-2 conditions (Table 1). Retention data–retention time and calculated  $I$  values are given in Table 3. The calculated  $I_{TPGC}$  values were compared with the values from databases [25,26], and good conformance between measured and calculated values was obtained.

### 3.2. The results of HDPE analysis by Py-cGC

The previous approach of  $I$  determination required primary MS identification and it is not always possible to obtain sample of pure standard compound. Direct application of  $I$  in

Table 3  
Retention characteristics—retention times (min) and retention indices (i.u.) for compounds of model mixture at different column temperatures: 60 °C, 80 °C, 100 °C and 120 °C, on RTX-5 column

Compound	$t_R$				$I$			
	60 °C	80 °C	100 °C	120 °C	60 °C	80 °C	100 °C	120 °C
Benzene	4.480	4.056	3.936	3.906	672.74	674.03	685.00	694.74
Methyl methacrylate	5.066	4.319	4.053	3.959	716.28	713.44	714.30	717.33
Toluene	6.246	4.950	4.423	4.186	774.14	778.14	785.29	792.81
Naphthalene	–	36.914	18.724	10.720	–	1189.91	1194.25	1210.48

$t_R$ , retention time;  $I$ , Kovats retention indices.

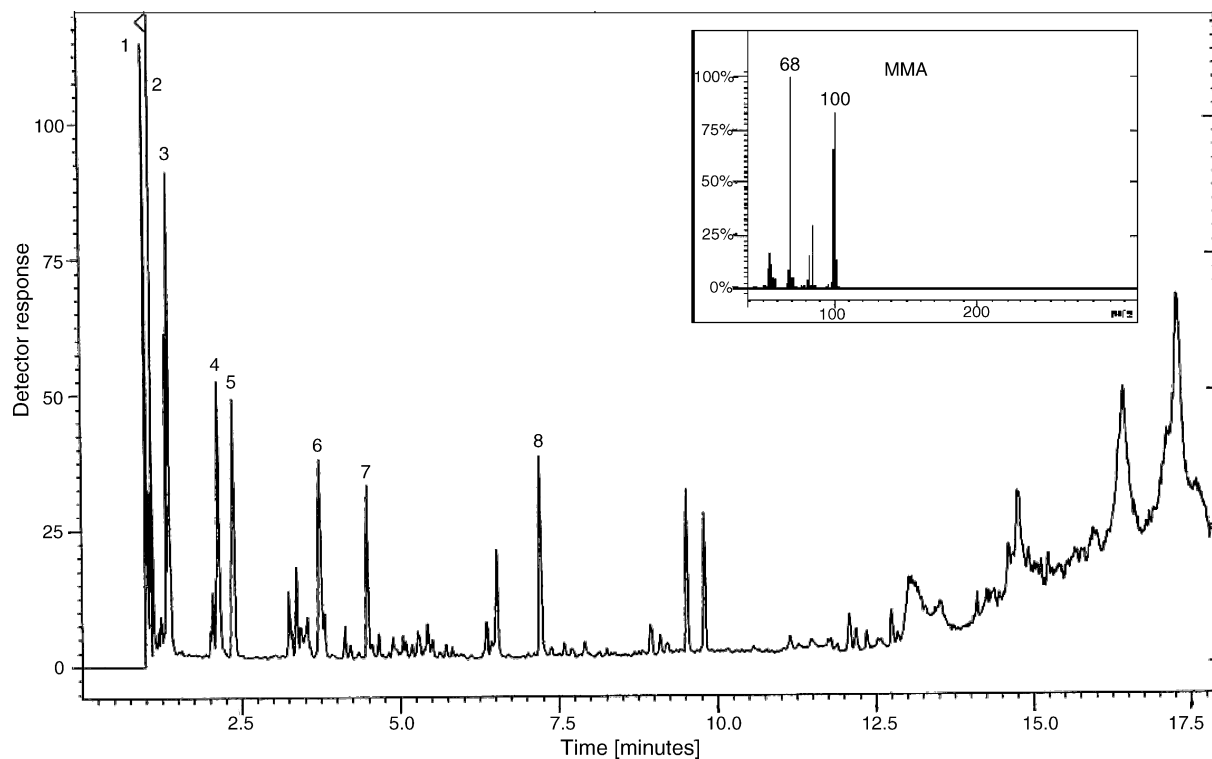


Fig. 1. Pyrogram of PMMA at 800°C. Chromatographic separation on DB-5 column. MMA identified with MS detector on-line: 1. benzene, 2. MMA, 3. toluene, 4. benzene 1,2-dimethyl, 5. styrene, 6. benzene 1,3,5-trimethyl, 7. indene, 8. naphthalene. MS spectrum of MMA. For conditions, see Table 1.

Py-cGC is not possible due to thermal degradation of the hydrocarbon homologous series at high pyrolysis temperatures. The retention indices can be calculated in the case when the sample is co-pyrolysed with appropriate material generating a homologous series of reference standards during pyrolysis. From known polymers the polyolefins degrade through a ran-

dom scission mechanism and polyethylene is a good example of this behavior and can be used for this application. When a free radical is formed along the chain of polyethylene, chain scission occurs; producing a molecule with an unsaturated end and another with a terminal free radical may take hydrogen from a neighboring carbon, producing a saturated end and

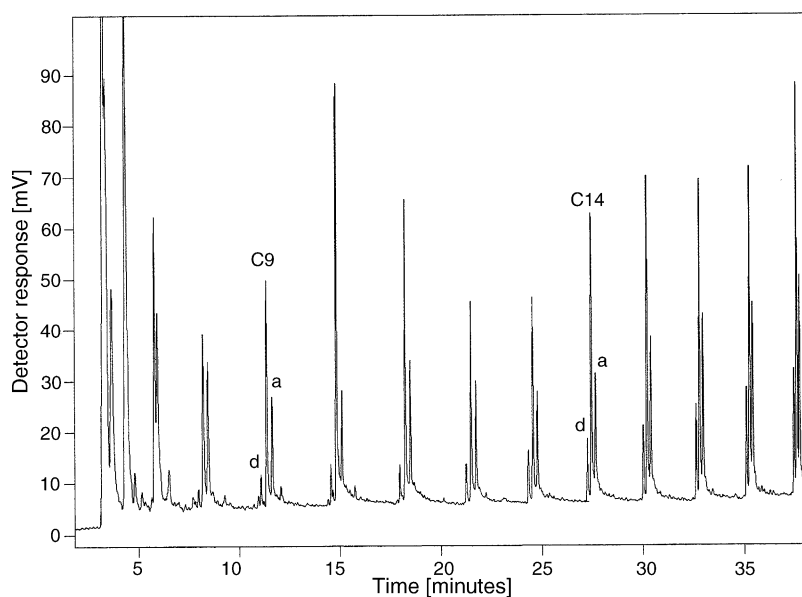


Fig. 2. Pyrogram of high density polyethylene at pyrolysis temperature 550°C, *n*-alkanes with carbon number 9 and 14 are shown. Nonane—marked a; nonadiene—marked d. For conditions, see Table 1.

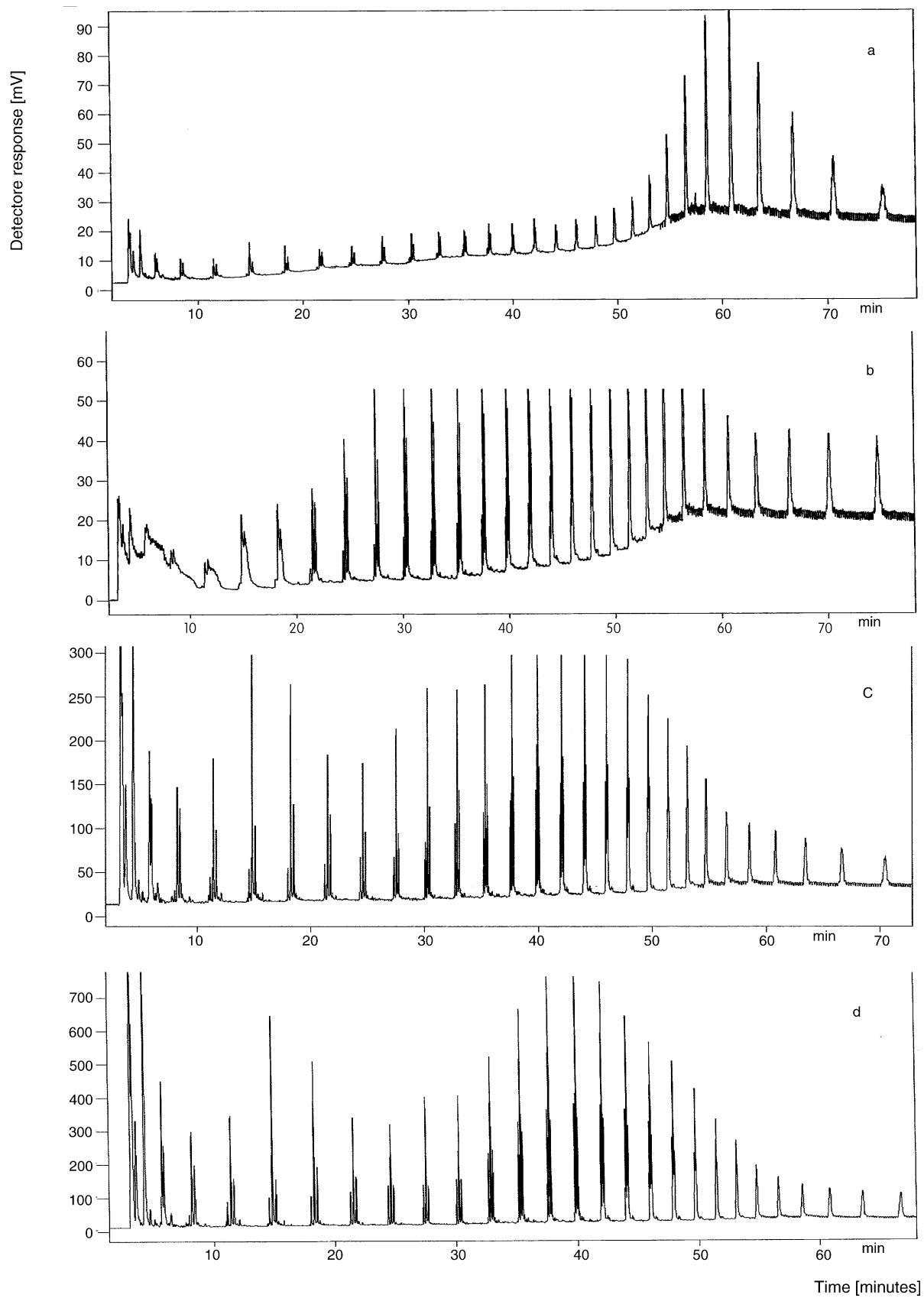


Fig. 3. Temperature dependence of HDPE decomposition at different pyrolysis temperatures: (a) 500 °C; (b) 600 °C; (c) 700 °C and (d) 800 °C. For conditions, see Table 1.

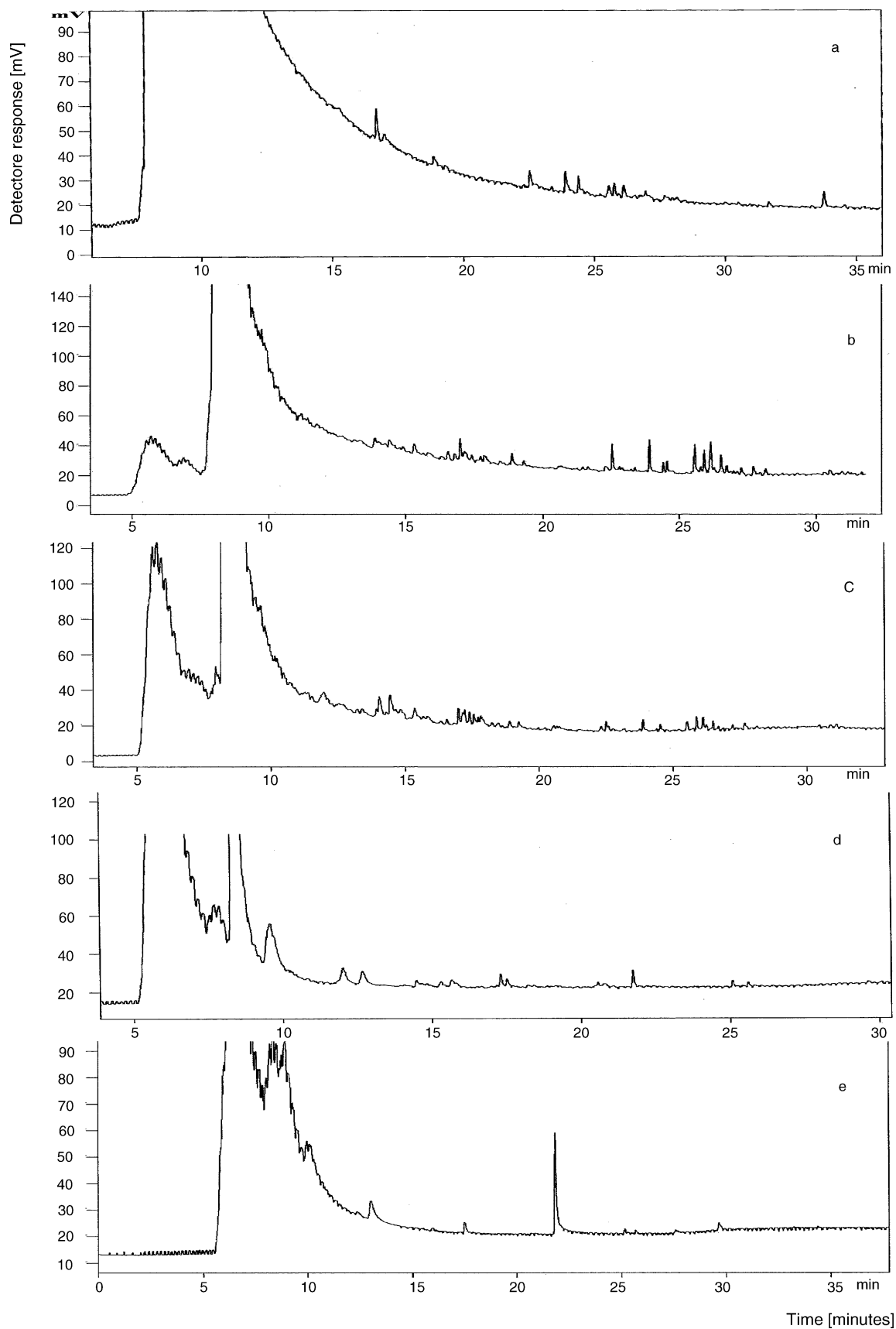


Fig. 4. Temperature dependence of PMMA decomposition at different pyrolysis temperatures: (a) 400 °C; (b) 500 °C; (c) 600 °C; (d) 700 °C and (e) 800 °C. For conditions, see Table 1.

a new radical, or combine with another free radical to form an alkane. Multiple cleavages produce molecules small enough to be volatile, with double bonds at ends, one end or neither. Since the scission was random, molecules are made with a wide variety of chain lengths. These appear in the pyrogram as a series of triplet peaks (Fig. 2). Each triplet consists of an alkane, an alkene and an alkadiene of a specific chain length. The next set of three peaks contains one more carbon than the triplet before [31]. On a RTX-5 column such as the one used here, the major peak in the center is *n*-alkene and *n*-alkane is eluted last of the three (nonene and tetradecene have been marked). As can be seen, pyrolysis of HDPE produces the series of *n*-alkenes limited only by the upper temperature of pyrolytical cell (Fig. 3). The pyrolysis temperature have been changed from 300 °C to 900 °C but only at temperatures ranging from 500 °C to 800 °C were observed mentioned triplets. This temperature range is only suitable for  $I_{TPGC}$  use in pyrolysate identification. It was also confirmed that production of the alkanes and the dienes decreases with an increase of the pyrolysis temperature. This effect has not been observed for *n*-alkenes and this fact designates them for identification at the higher temperatures when pyrogram is usually more simple. Optimal amount of HDPE sample co-pyrolysed depends on the sample behaviour and structure. This usually ranges from 0.5 to 0.1 mg.

### 3.3. The results of PMMA thermal degradation products analysis

PMMA sample was pyrolysed under different pyrolysis temperatures and separated under Py-cGC-3 conditions

(Table 1). Pyrolysis temperature effect on pyrolysate analytes distribution is given on Fig. 4. Maximum number of the compounds formed during pyrolysis has been established at temperature 600 °C (over 50) while at 800 °C it was just 11. This situation is frequent used for fingerprint determination. As mentioned above, PMMA is the polymer which depolymerizes to monomeric units. The most complicated pyrograms were obtained at pyrolysis temperatures ranged between 500 and 700 °C. The PMMA pyrogram at 400–500 °C documents uncomplete degradation with intermediates presence. Pyrogram makes simpler at 700–800 °C of pyrolysis temperatures. Now, at these temperatures the ions re-combination occurs and characteristic analytes were formed (benzene, cyclohexane, naphthalene, toluene, cresols, etc.).

### 3.4. The results of PMMA-HDPE co-pyrolysis and the products identification

Fig. 5 is an overlay of PMMA pyrogram at 700 °C and HDPE sample (each pyrolysed separately) at the same pyrolysis temperature. It is evident that HDPE provides hydrocarbon standard homologous series and  $I_{TPGC}$  values for each peak can be calculated. Over 60 constituents of the volatiles were preliminary identified by cGC-MS and Py-cGC-MS methods, which amounted to 83% of the total peak separated areas. The majority of all these compounds were further verified by measuring their temperature-programmed retention indices (this amounted 62% of the total peak area). The analytes in pyrolysate were verified by making comparison with the data from two  $I$  or  $I_{TPGC}$  values databases [25,26]. Pyrogram from co-pyrolysis of PMMA with HDPE mixture

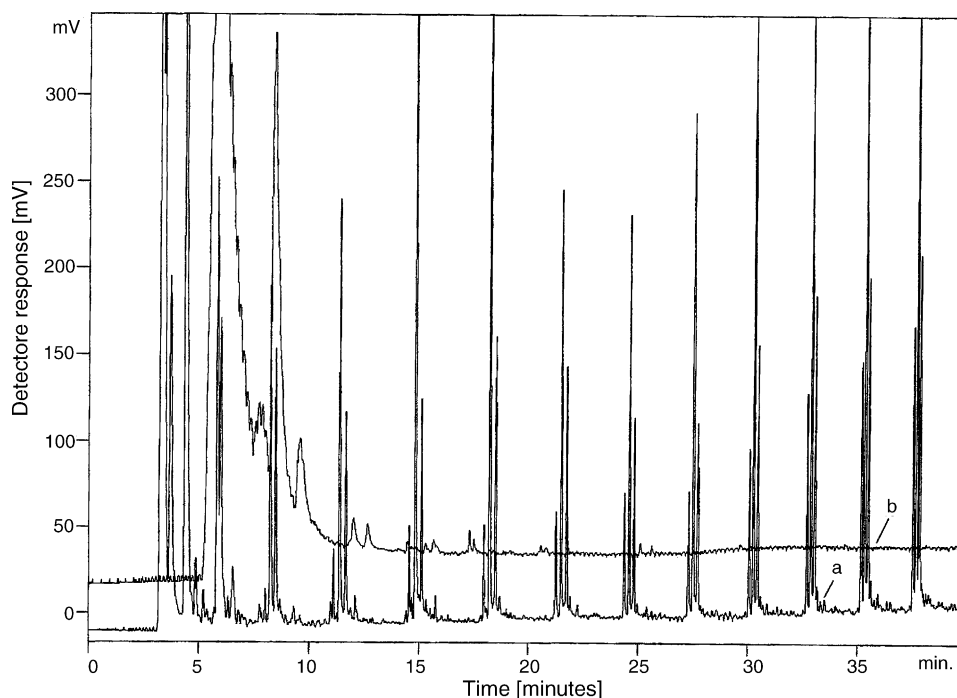


Fig. 5. Overlay of PMMA and HDPE pyrograms at pyrolysis temperature 700 °C: (a) HDPE; (b) PMMA. For conditions, see Table 1.

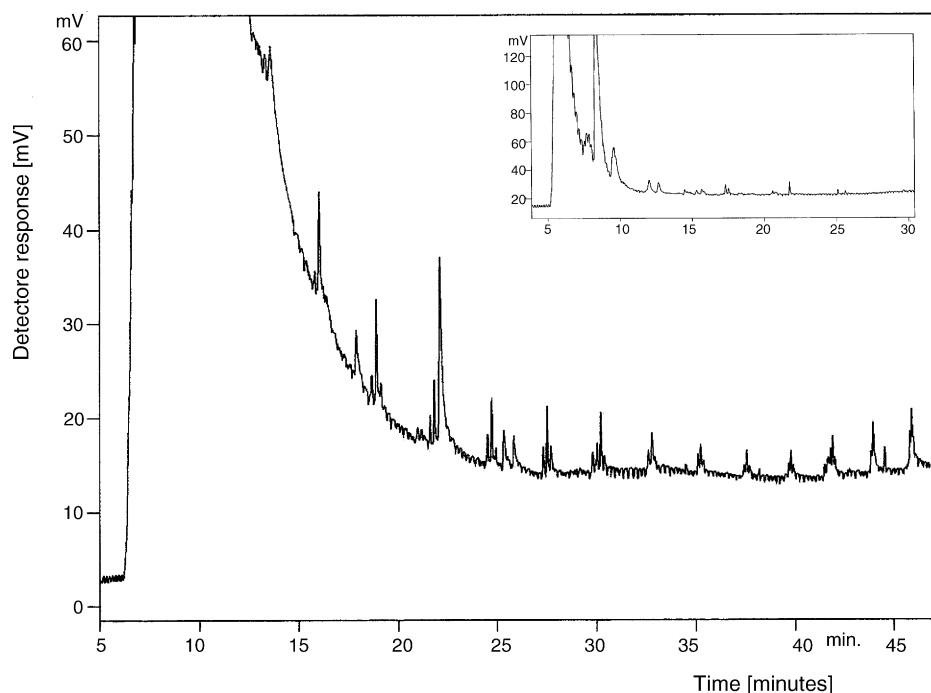


Fig. 6. Real pyrogram of PMMA and HDPE co-pyrolysis at temperature 700 °C. PMMA pyrogram shown at right upper corner. For conditions, see Table 1.

Table 4  
Comparison of  $I_{\text{TPGC}}$  data with data taken from two databases

Retention time (min)	Retention index, $I_{\text{TPGC}}$		Compound	$I_{\text{TPGC}}^{\text{meas.}} - I_{\text{TPGC}}^{\text{dat.}}$
	Measured (i.u.)	From database (i.u.)		
6.88	734.7	730 <sup>a</sup>	Methyl-2-pentanone,4-	-4.7
		<b>730<sup>b</sup></b>	<b>Trimethyl-2-pentane,2,4,4-</b>	<b>-4.7</b>
8.15	785.6	779 <sup>b</sup>	Methyl-2-butenol	-6.6
		<b>780<sup>a</sup></b>	<b>Toluene</b>	<b>-5.6</b>
		789 <sup>b</sup>	1-Hexenol	3.4
15.33	1005.1	1015 <sup>a</sup>	Cycloheptanone	9.9
		1000 <sup>b</sup>	2,4-Heptadienal	-5.1
		1006 <sup>b</sup>	Octanal	0.9
17.00	1054.1	1052 <sup>a</sup>	Isomethheptene	-2.1
		<b>1056<sup>b</sup></b>	<b>Dimethylheptenal</b>	<b>1.9</b>
18.90	1110.3	1110 <sup>a</sup>	Phenylpropanone	-0.3
		<b>1110<sup>b</sup></b>	<b>2,4-Octadienal</b>	<b>-0.3</b>
22.55	1223.9	1225 <sup>a</sup>	Ethylphenylacetate	1.1
23.92	1268.7	1270 <sup>a</sup>	Thymol	1.3
24.43	1285.2	1285 <sup>a</sup>	Dibutoxyethyl adipate	-0.2
24.56	1289.5	1290 <sup>a</sup>	Tridecene,1-	0.5
25.59	1325.1	1324 <sup>b</sup>	Methyl decanoate	-3.1
25.93	1337.4	<b>1338<sup>b</sup></b>	<b>p-Methoxystyrene</b>	<b>0.6</b>
26.16	1345.5	1344 <sup>a</sup>	Diethyl adipate	-1.5
		1343 <sup>b</sup>	Butyl benzoate	-2.5
26.55	1359.2		Unknown	

Pyrolysis temperature: 500 °C, RTX-5 stationary phase column. In bold letters are assigned characteristic compounds.

<sup>a</sup> Reference [16].

<sup>b</sup> Reference [15].



Table 5  
Comparison of  $I_{\text{TPGC}}$  data with data taken from two databases

Retention time (min)	Retention index, $I_{\text{TPGC}}$		Compound	$I_{\text{TPGC}}^{\text{meas.}} - I_{\text{TPGC}}^{\text{dat.}}$
	Measured (i.u.)	From database (i.u.)		
5.75	687.4	<b>700</b> <sup>a</sup>	<b>Cyclohexene</b>	<b>12.6</b>
		700 <sup>b</sup>	2,3-Pentandione	12.6
6.93	738.2	736 <sup>b</sup>	3-Methyl-1-butanol	-2.2
		739 <sup>b</sup>	2-Methyl-1-butanol	0.8
7.93	779.2	<b>780</b> <sup>a</sup>	<b>Toluene</b>	<b>0.8</b>
		773 <sup>b</sup>	Toluene	-6.2
8.27	792.9	790 <sup>a</sup>	Octene, 1-	-2.9
		792 <sup>b</sup>	Hexanone	-0.9
14.03	968.6	965 <sup>a</sup>	Benzaldehyde	-3.6
		968 <sup>b</sup>	Benzaldehyde	-0.6
14.43	980.2	982 <sup>b</sup>	6-Methyl-5-hepten-2-one	1.8
		<b>980</b> <sup>b</sup>	<b>Phenol</b>	<b>-0.2</b>
		981 <sup>b</sup>	Octanol	0.8
15.36	1007.5		Unknown	
15.68	1016.9	1015 <sup>a</sup>	Ethyl-1-hexanol, 2-	-1.9
		1012 <sup>b</sup>	3-Octanol	-4.9
15.83	1021.2		Unknown	
16.32	1035.7		Unknown	
16.56	1042.7	1040 <sup>a</sup>	<b>Cresol, o-</b>	<b>-2.7</b>
17.00	1055.7	1052 <sup>a</sup>	Isometheptene	-3.7
17.23	1062.4	<b>1060</b> <sup>a</sup>	<b>Cresol, p-</b>	<b>-2.4</b>
		<b>1060</b> <sup>a</sup>	<b>Indene</b>	<b>-2.4</b>
		<b>1065</b> <sup>a</sup>	<b>Acetophenone</b>	<b>2.6</b>
		<b>1065</b> <sup>a</sup>	<b>Cresol, m-</b>	<b>2.6</b>
17.41	1067.9		Unknown	
17.56	1072.2		Unknown	
		<b>1075</b> <sup>b</sup>	<b>p-Cresol</b>	<b>2.8</b>
17.73	1077.3	1081 <sup>a</sup>	Diethylmaleate	3.7
22.52	1224.9	1225 <sup>a</sup>	Ethyl phenylacetate	0.1
23.88	1269.4		Unknown	
24.52	1290.4		Unknown	
25.53	1325	<b>1330</b> <sup>a</sup>	<b>Dimethoxytoluene</b>	<b>5.0</b>
		1324 <sup>b</sup>	Methyl decanoate	-1.0
25.88	1337.1		Unknown	
		<b>1338</b> <sup>b</sup>	<b>p-Methoxystyrene</b>	<b>0.9</b>
26.12	1345.4		Unknown	
26.49	1358.3		Unknown	
27.66	1399.1	1398 <sup>b</sup>	Ethyl decanoate	-1.1
		1400 <sup>b</sup>	Tetradecane	0.9

Pyrolysis temperature: 600 °C, RTX-5 stationary phase column. In bold letters are assigned characteristic compounds.

<sup>a</sup> Reference [16].

<sup>b</sup> Reference [15].

(50/50, w/w) is given at Fig. 6. Characteristic is the structure of homologous series of n-alkanes and other hydrocarbons and between them the peaks of PMMA degradation products. The  $I_{\text{TPGC}}$  values were calculated for all analytes formed during PMMA pyrolysis at pyrolysis temperatures: 500 °C, 600 °C, 700 °C and 800 °C. The use of GC retention indexes, particularly in combination with MS can provide substantial information about trace amounts of unknowns. Comparison of  $I$  or  $I_{\text{TPGC}}$  of an unknown with those of the standards gives

an unambiguous identification, or at least, limit the number of possible structures to a few compounds. At 500 °C pyrolysis temperature there were verified compound as toluene, hexanol, cycloheptanone, octadienal and others intermediates (see Table 4). Pyrolysate does not contain characteristic degradation products as mentioned in the Table 2. Increasing pyrolysis temperature to 600 °C the pyrolysate composition get more dominant, containing cyclohexene, toluene, phenol, benzaldehyde, cresols and indole (Table 5). There is

Table 6  
Comparison of  $I_{TPGC}$  data with data taken from two databases

Retention time (min)	Retention index, $I_{TPGC}$		Compound	$I_{TPGC}^{meas.} - I_{TPGC}^{dat.}$
	Measured (i.u.)	From database (i.u.)		
5.85	701.1	<b>700<sup>a</sup></b>	<b>Cyclohexene</b>	<b>-1.1</b>
		700 <sup>b</sup>	2,3-Pentandione	-1.1
8.40	796.8	<b>780<sup>a</sup></b>	<b>Toluene</b>	<b>-16.8</b>
		798 <sup>b</sup>	4-Methyl-3-penten-2-one	1.2
12.01	909.7	<b>905<sup>a</sup></b>	<b>Xylene</b>	<b>-4.7</b>
		910 <sup>a</sup>	Ethyl acetoacetate	0.3
		914 <sup>b</sup>	Cyclohexen-3-one	4.3
12.65	928.3		Unknown	
14.48	981.4	<b>980<sup>b</sup></b>	<b>Phenol</b>	<b>-1.4</b>
		981 <sup>b</sup>	Octanol	-0.4
15.31	1005.6		Unknown	
15.65	1015.5	1015 <sup>a</sup>	Cycloheptanone	-0.5
		1012 <sup>b</sup>	3-Octanol	-3.5
17.31	1064.1	<b>1060<sup>a</sup></b>	<b>Cresol,<i>p</i>-</b>	<b>-4.1</b>
		<b>1060<sup>a</sup></b>	<b>Indene</b>	<b>-4.1</b>
		<b>1065<sup>a</sup></b>	<b>Acetophenone</b>	<b>0.9</b>
17.56	1072.2		Unknown	
		<b>1075<sup>b</sup></b>	<b><i>p</i>-Cresol</b>	<b>2.8</b>
21.75	1199.2	<b>1190<sup>a</sup></b>	<b>Naphthalene</b>	<b>-9.2</b>

Pyrolysis temperature: 700 °C, RTX-5 stationary phase column. In bold letters are assigned characteristic compounds.

<sup>a</sup> Reference [16].

<sup>b</sup> Reference [15].

also evident the increase of the analytes number presented in the pyrolysate as well the contents of unknown constituents. Number of analytes separated at 700 °C decreased and naphthalene was identified the first time (Table 6). Styrene deriva-

tives were identified in the pyrolysate at 800 °C (Table 7). From the results obtained it was found that high pyrolysis temperature effects re-combination of the ions in gaseous phase. The MMA dimers, trimers, tetramers and pentamers

Table 7  
Comparison of  $I_{TPGC}$  data with data taken from two databases

Retention time (min)	Retention index, $I_{TPGC}$		Compound	$I_{TPGC}^{meas.} - I_{TPGC}^{dat.}$
	Measured (i.u.)	From database (i.u.)		
6.61	729.6	730 <sup>a</sup>	Methyl-2-pentanone,4-	0.4
		<b>730<sup>a</sup></b>	<b>Trimethyl-2-pentene,2,4,4-</b>	<b>0.4</b>
8.36	799.0	805 <sup>a</sup>	Octane,2-	8.2
		792 <sup>b</sup>	Hexanone	-4.8
		798 <sup>b</sup>	4-Methyl-3-penten-2-one	-1.0
9.95	848.2	845 <sup>a</sup>	Butanediol,1,3-	-3.2
		846 <sup>b</sup>	Ethyl,methyl butyrate	-2.2
13.01	940.0	940 <sup>a</sup>	Diethyl oxalate	0
		945 <sup>b</sup>	Methyl- <i>p</i> -xylene	5.0
17.49	1070.6	1072 <sup>b</sup>	Octanol	1.4
		1069 <sup>b</sup>	<i>p,a</i> -Dimethylstyrol	-1.6
21.84	1203.0	1203 <sup>b</sup>	6-Decanal	0
25.16	1312.0	1312 <sup>a</sup>	<b>2-Methylnaphthalene</b>	<b>0</b>
25.70	1330.0		Unknown	
29.67	1471.7	1470 <sup>a</sup>	Isophenyl phenyl acetate	-1.7
		1469 <sup>b</sup>	Butyl decanoate	-2.7

Pyrolysis temperature: 800 °C, RTX-5 stationary phase column. In bold letters are assigned characteristic compounds.

<sup>a</sup> Reference [16].

<sup>b</sup> Reference [15].

were identified by Py-cGC–MS unit. The concentration of these analytes was determined at the trace levels and  $I$  or  $I_{TPGC}$  values were not calculated for them. MMA monomer that is relatively polar species and from this reasons it is eluted as the first from DB-5 column, before first member of homologous series. Thus, its  $I$  or  $I_{TPGC}$  values could not be calculated without the error. In the view of the complexity of many samples it is often impossible to add or produce the complete nor-alkane series to the sample without creating interferences with the sample itself. To avoid this drawback and to gain in precision nonlinear interpolations (natural cubic splines; polynomials of different orders) have been used to compute  $I_{TPGC}$  values [32]. Retention index  $I$  or  $I_{TPGC}$  values for MMA can be calculated from retention data obtained at more polar stationary phase column (e.g. polyethylene glycol).

#### 4. Conclusion

The addition of HDPE has been used in Py-cGC of PMMA pyrolysate identification by system of retention indices. The problem associated with  $n$ -alkanes homologous series thermal degradation during solid-state pyrolysis can be overcome by a simple co-pyrolysis procedure using HDPE to produce an entire spectrum of different homologous series as reference materials. This produces the homologous series of  $n$ -alkanes,  $n$ -alkenes and dienes that can be used for retention indices calculation and analyte identification. The  $I_{TPGC}$  values were calculated for all analytes formed during PMMA pyrolysis at pyrolysis temperatures: 500 °C, 600 °C, 700 °C and 800 °C. The use of GC retention indexes, particularly in combination with MS can provide substantial information about trace amounts of unknowns. Comparison of  $I$  or  $I_{TPGC}$  of an unknown with those of the tabulated standards gives an unambiguous identification, or at least, limits the number of possible structures to a few compounds. The general use of this method for analyte identification requires optimization of ratio between HDPE added and real sample. The use of chromatographic column with different stationary phase polarity is recommended to get precious results. Also application of polyisobuthylene that also forms another series of polyolefins can be of help at analytes identification to the future (Table 7).

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