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A STUDY OF OXIDATIVE DEGRADATION OF PLASTICS BY GC AND GC-MS

Key words: plastics, oxidative degradation, gas chromatography and mass spectrometry

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ABSTRACT

The behaviour of plastics, namely, polyethylene, polypropylene, polystyrene, polyvinyl chloride, polyamide and some copolymers, was studied in a combustion chamber in which the conditions of large-scale fires were simulated. Volatile combustion products were frozen-out or analyzed directly on two columns, one packed with Porapak Q and the other capillary column coated with squalane or CP Sil 5 CB. Carbonyl compounds were determined as the 2,4-dinitrophenyl hydrazones on an OV-101 stationary phase. Thermal conductivity and flame ionization detectors were used. The decomposition products were identified either on the basis of retention data (retention indices) or by combined capillary GC-MS. The data obtained are used for the cataloguing of plastics from the point of view of their product toxicity during fires.

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INTRODUCTION

A great danger in fires is caused by toxic products formed during combustion of plastics. In addition to CO and HCN, many other toxic substances are formed that may effect the function of vitally important organs. Therefore, detailed analysis of the volatile products liberated during combustion of plastics is important.

In the laboratory, the conditions prevalent during fires can be simulated in combustion chambers. Capillary gas chromatography is advantageous in the analysis of complex mixtures of the products. To identify the compounds, the GC-MS combination is optimal, but sometimes the comparison of accurately measured retention indices with the literature values can also be used (see e.g. refs.[1-4]).

Many data on the composition of the combustion products of polymers in inert and oxygen atmosphere have been published (e.g. refs.[4-20]). However, a standard analysis method must be used for the comparison of materials with respect to the toxicity of their combustion products. The extensive published data are inhomogenous and cannot be used in cataloguing of plasticts. This is mainly caused by varying experimental conditions on which the composition of the products is strongly dependent.

A solution to the problem of the danger caused by the combustion products of plastics requires a complex approach, i.e. a combination of various analytical methods, such as DTA, GC, GC-MS, IR spectroscopy, biological tests, etc. The present paper is a part of extensive research carried out in many laboratories in Czechoslovakia. The topic of the present paper is the use of capillary GC and GC-MS for the identification of polymer combustion products, obtained under fire conditions simulated in a combustion chamber.

EXPERIMENTAL

Materials

Polymers: polyethylene Bralen RB 03-23, polypropylenes Tatren TF 411, Mosten 52 492, Mosten 52 517, polystyrene Krasten 127, polyvinyl chloride Sloviplast GC-702, polyamide Spolamid 6, copolymers of styrene with butadiene Krasten 336, with acrylonitrile Kostil SAN, and with butadiene and acrylonitrile Forsan 752, copolymer of ethylene with vinyl acetate Urlen, all produced in Czechoslovakia.

Chemicals: n-hydrocarbons C_5, C_6 - Laborchemie Apolda, GDR, C_7 - Loba Chemie, Austria, C_9 - Reakhim, USSR, C_{20}, C_{22}, C_{24}, C_{28} - Applied Sci.Lab., USA. All the other chemicals were of p.a. purity and were obtained from Lachema, Czechoslovakia.

Equipments and Methods

The studied polymers were pyrolyzed in nitrogen in a vertical tubular pyrolyzer[2] and decomposed in air in a combustion chamber[17]. The combustion chamber is depicted in Fig. 1. It consists of separate compartments for the sample combustion and the biological tests with mice. The sample is placed in a crucible that is electrically heated to the required temperature. A ventilator forces the combustion products into the smoke compartment from which the samples are taken by syringes or are drained by an inert gas into absorption vessels. The absorption vessels used were either empty and were cooled with dry ice for the sample collection for the GC-MS analysis, or contained a frit and a saturated solution of 2,4-dinitrophenyl hydrazine in 2N-HCl (the volume of solution, 4 ml). The sample weight was 200 mg, the oven temperature 600°C and the overall volume of the chamber was 4.5 l.

Standards of 2,4-dinitrophenylhydrazones were prepared by precipitation of an aqueous or alcoholic solution of the corresponding carbonyl compounds with a saturated solution of 2,4-dinitrophenylhydrazine in 2N-HCl or H_2SO_4. The contents of the carbonyl compounds in the combustion products were found using the absolute calibration method.

A Chrom 4A gas chromatograph with a flame ionization detector (Laboratorní Přístroje, Czechoslovakia) and a Carlo Erba gas

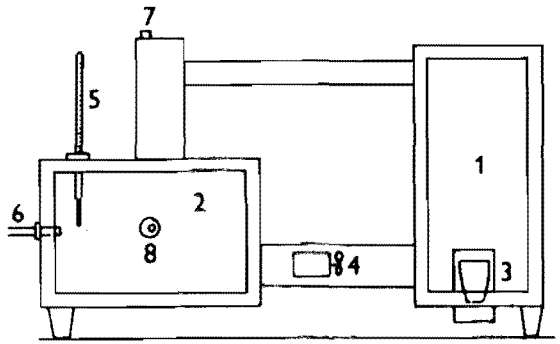


Fig. 1 Combustion chamber CAB 4.2. 1- combustion chamber, 2 - fume chamber, 3 - crucible oven, 4 - ventilator, 5 - thermometer, 6 - oxygen concentration probe, 7 - safety valve, 8 - sampling septum

chromatograph Model C with a flame-ionization and thermal-conductivity detectors (Italy) were employed. A 50 m x 0.2 mm I.D. stainless steel capillary column coated with squalane (an efficiency of 3600 plates/m for heptane) and packed columns with Porapak Q, 180 mm x 2.5 cm and with 5 % OV-101 on silanized Chromosorb W(60-80 mesh), 130cm x 3 mm I.D. Column temperatures were 60 and 80°C for squalane, with nitrogen carrier gas, ca. 0.3 ml/min, and with hydrogen and air flow-rates of 35 ml/min and 0.25 l/min, respectively. The Porapak column was operated at 25°C (TCD) and 80°C (FID), with a carrier gas (nitrogen) flow-rate of 30 ml/min. The temperatures of the OV-101 column, the injector and the detector were 232, 280 and 150°C, respectively. Nitrogen carrier gas flow rate was 30 ml/min.

A Finnigan 4000 GC/MS instrument (Finnigan MAT, USA) was used in the electron ionization (EI) mode under the following conditions: electron energy, 70 eV, electron current, 0.30 mA, ion source temperature, 250°C. A 50 m x 0.33 mm I.D. fused silica columns coated with CP Sil 5 CB was used. The flow-rate of the

carrier gas, helium, was 1 ml/min, with a split ratio of 1:100. The end of the column was directly inserted into the ion source. The interface oven was kept at 200°C. The temperature of the injector and splitter were 220 and 200°C, respectively; the column temperature was programmed as follows: 5 min at 70°, then 5°/min up to 200°C and finally isothermal regime; 1 µl samples were injected.

The molecular weights of the decomposition products of the polyamide samples were verified by positive ion chemical ionization, using ammonia as the reagent gas (at a pressure of 0.3 torr; ion source temperature, 200°C). The spectra were obtained with a Data General Nova 4/S computer system with custom-made software.

RESULTS AND DISCUSSION

Commercially available plastics were burned in the chamber depicted in Fig. 1. The degradation products were sampled by a syringe and directly injected into the gas chromatograph. For the GC-MS analysis, the products were frozen out. The most volatile products (CO, CO_2, HCN, hydrocarbons C_1-C_3) were separated on columns with Porapak Q at 25°C (TCD) and 80°C (FID) (see Fig. 2). Degradation products with carbon numbers of up to C_8-C_9 were analyzed on a capillary column coated with squalane. The products were identified on the basis of their retention indices or by combined capillary GC-MS.

The carbonyl compounds formed during combustion of plastics could not be identified when the combustion products were directly injected into the column, as their concentrations are very low and their adsorption occurs on the smoke particles and on the walls of the combustion chamber and the syringe. These compounds may also be irreversibly adsorbed or decomposed in various parts of the gas chromatograph. Therefore, the carbonyl compounds were absorbed in 2,4-dinitrophenylhydrazine and the

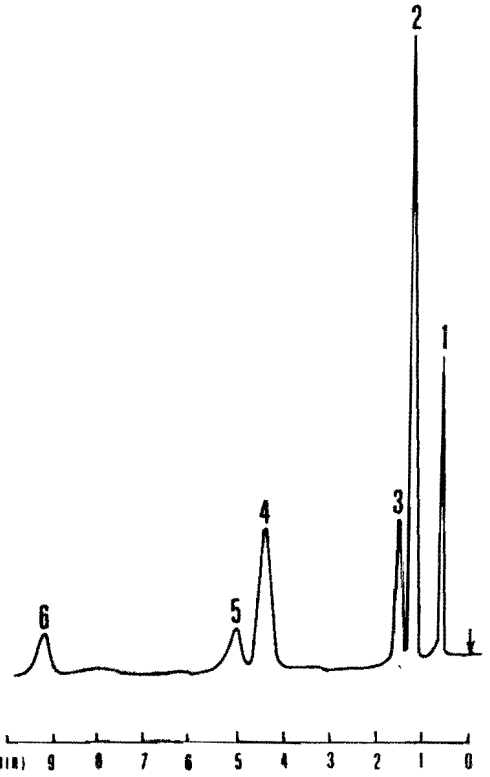


Fig. 2 Chromatogram of the combustion products of Spolamid 6 (Porapak Q, 80°C, FID). 1- Methane, 2 - ethene, 3 - ethane, 4 - propene, 5 - propane, 6 - HCN

hydrazones formed were analyzed on an OV-101 column at 232°C. The amounts of aldehydes and ketones found (in per cent), related to the weight of the burnt polymer sample, are given in Table 1.

Polyethylene and polypropylenes

From various polyethylenes, the commercial linear product Bralen 0323 was studied. A chromatogram of the thermooxidation products is given in Fig. 3. As can be seen, the main products

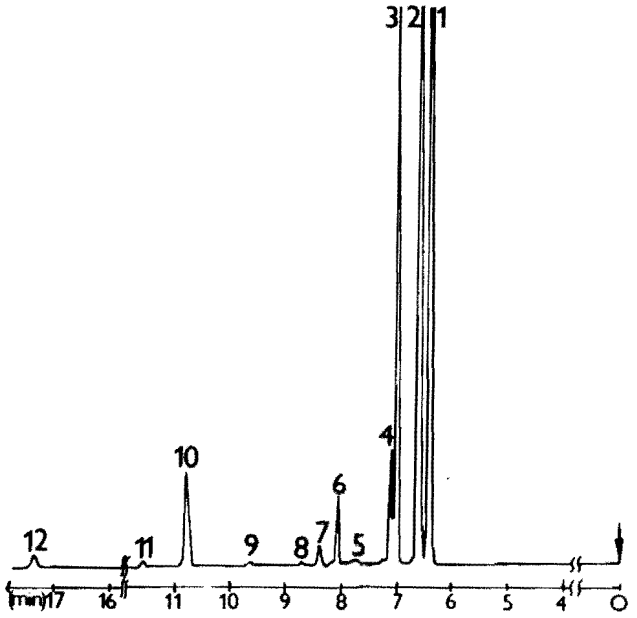


Fig. 3 Chromatogram of the combustion products of polyethylene Bralen RB0323 (squalane, 60°C). 1 - Methane, ethene, ethane, 2 - propene, propane, 3 - 1-butene, 4 - butane, 5 - 1,4-pentadiene, 6 - 1-pentene, 7 - pentane, 8 - 1-trans-3-pentadiene, 9 - 4-methyl-1-pentene, 10 - 1-hexene, 11 - hexane, 12 - 1-heptene

of the combustion of polyethylene are 1-alkenes, in addition to CO and CO_2. Alkanes and alkadienes are also present. The products are virtually the same as produced by pyrolysis in an inert atmosphere [3].

Similar results were obtained with the combustion of the polypropylenes Tatren 411, Mosten 52492 and Mosten 52517. All three polypropylenes yielded chromatograms similar to those obtained after pyrolysis at the same temperature [3] (see Fig.4). In addition to CO, CO_2, methane, ethane, ethylene and propane, the propene monomer, the 2-methyl-1-pentene dimer and the 2,4-dimethyl-1-heptene trimer were found, as well as a number of

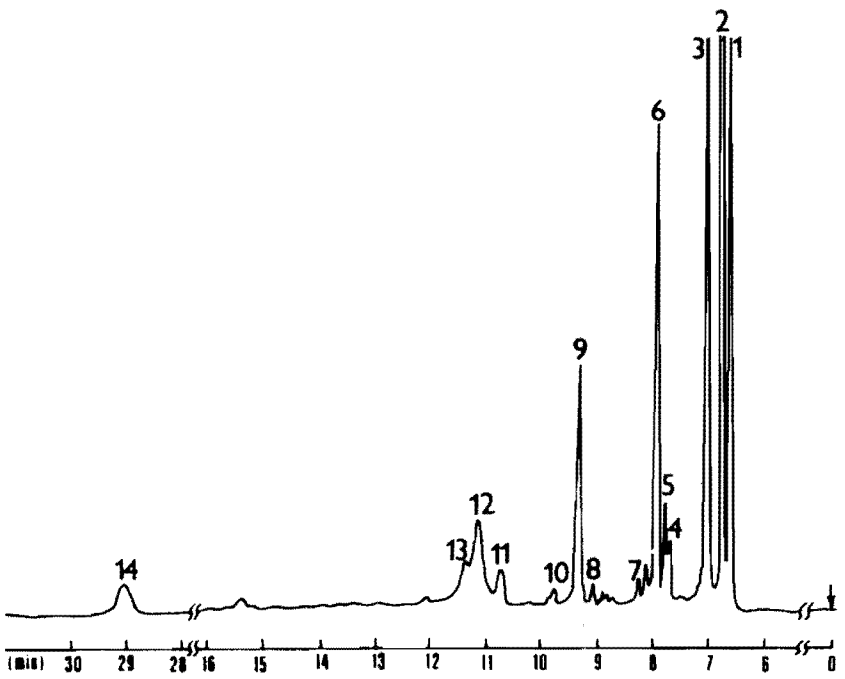


Fig. 4 Chromatogram of the combustion products of polypropylene Tatren 411 (squalane, 60°C). 1 - Methane, ethene, ethane, 2 - propene, propane, 3 - 2-methylpropene, 4 - 1-pentene, 5 - 2-methyl-1-butene, 6 - 2-methyl-1,3-butadiene, 7 - 2-methyl-2-butene, 8 - 2-methylpentane, 9 - 2-methyl-1-pentene, 10 - 2-methyl-2-pentene, 11 - 2-methyl-1-trans-3-pentadiene, 12 - not identified, 13 - 2,4-dimethyl-1-pentene, 14 - 2,4-dimethyl-1-heptene

other branched and unbranched hydrocarbons. No oxygen containing substances were found with direct injection of the combustion products of polyethylene and polypropylenes. In addition to the main product, acetaldehyde, further saturated and unsaturated aldehydes and ketones were detected in the form of 2,4-dinitrophenylhydrazones in PE and PP (see Table 1). The low concentrations found indicate that the oxidation to CO and CO_2 is prevalent in the combustion chamber under the given experimental conditions.

TABLE 1

The Content of Carbonyl Compounds (%) in the Combustion Products of Selected Polymers (+ Traces)

	Bralen	Tatren	Sloviplast	Krasten 127	Forsan	Spolamid 6
methanal	-	+	-	+	+	+
ethanal	0.164	0.067	0.032	0.004	0.029	0.077
propanal	0.033	0.007	0.006	+	0.002	0.004
2-propanone	0.010	0.002	+	+	+	0.006
butanal	0.015	+	0.002	+	0.001	0.001
pentanal	0.013	-	-	-	0.001	+
hexanal	+	-	-	-	0.001	-
heptanal	-	-	-	+	+	-
2-methylpropanal	-	-	-	-	0.002	-
4-methylpentanal	-	+	-	-	-	-
1-propenal	0.005	-	-	+	+	-
1-butenal	0.002	+	+	+	+	+
1-hexenal	-	-	-	+	-	-
2-pentanone	-	0.004	-	-	-	-
2-heptanone	-	-	-	+	-	-
6-methyl-2-heptanone	0.001	-	-	-	-	-
cyclopentanone	-	-	+	-	-	0.004
methylcyclohexanone	-	-	-	-	+	-
benzaldehyde	-	-	-	0.008	+	-

Polyvinyl chloride

Polyvinyl chloride is one of the most common plastics because of its favourable properties (resistance to alkalis, elasticity, mechanical strength). At higher temperatures (above 150°C) it is degraded with the liberation of hydrogen chloride that is dangerous to human health. The degradation can be described by the scheme (e.g. refs. [11,19])

$$-CH_2-\underset{Cl}{CH}-CH_2-\underset{Cl}{CH}- \rightarrow CH_2{=}CHCl$$

$$\downarrow (-HCl)$$

$$-CH{=}CH-CH{=}CH- \rightarrow \text{low molecular weight products}$$

$$\downarrow$$

cross-linked structure

Decomposition to the monomer virtually does not occur; dehydrochlorination proceeds first to 96 to 99 %, followed by the scission of C-C bonds. During the thermal degradation, first linear and then cross-linked three-dimensional structures are formed.

Under the combustion conditions used in this work, CO, CO_2, HCl, methane, ethane, ethene, propane and propene were detected with TCD and FID using a Porapak Q column. Among the volatile products detected using a squalane capillary column, benzene is most abundant; toluene was also present (see Fig. 5). Substance No. 12 is probably 1-octene. Benzene is formed via intramolecular cyclization involving a cyclohexadiene intermediate. Among the volatile hydrocarbons, similar triplets as during the combustion of polyethylene are obtained, i.e. 1,4-pentadiene, 1-pentene and pentane and 1,5-hexadiene, 1-hexene and hexane. By the GC-MS analysis of a frozen-out sample, some other compounds were identified: acetaldehyde, ethanol, acetone, 2-propanol, acetic acid, 1-chlorobutane and cyclopentanone. The presence of acetaldehyde and cyclopentanone was also verified by GC analysis of the corresponding 2,4-dinitrophenylhydrazones, but other carbonyl compounds were

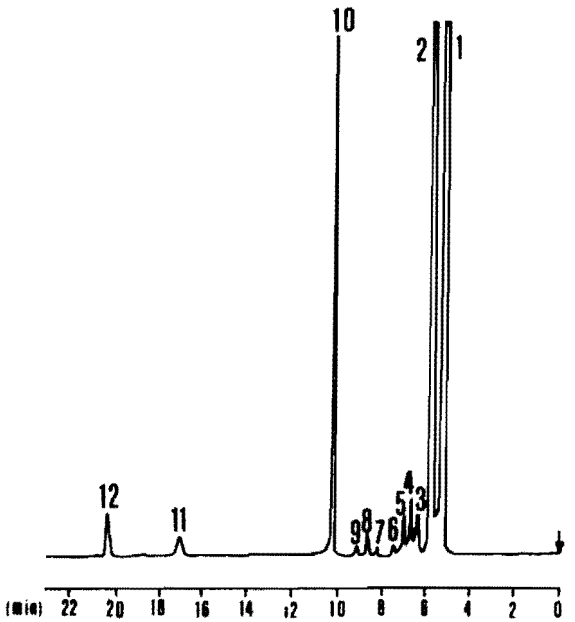


Fig. 5 Chromatogram of the combustion products of polyvinyl chloride Sloviplast SG-702 (squalane, 80°C). 1 - Methane, ethene, ethane, 2 - propane, propene, 3 - butane, 1-butene, 1,3-butadiene, 4 - 1,4-pentadiene, 5 - 1-pentene, 6 - pentane, 7 - 1,5-hexadiene, 8 - 1-hexene, 9 - hexane, 10 - benzene, 11 - toluene, 12 - probably 1-octene

also found. HCl that is produced as a main product during combustion of PVC is dangerous not only to living organism, but also destroys the column packing as well as the metallic parts of the gas chromatograph and the combustion chamber. Therefore, it was attempted to trap HCl on on a precolumn containing $CaCl_2$ but it adsorbed all components from the samples.

Polystyrenes

The products of the degradation of polystyrene and styrene copolymers in air are listed in Table 2. Similar to polyethylene and polypropylenes, the same products as those obtained during pyrolysis in nitrogen [3] were

TABLE 2

Combustion Produts of Polystyrene and Styrene Copolymers

Product	Retention index I^S_{80}	Krasten 127	Krasten 336	Kostil SAN	Forsan 752
hydrocarbons C_1-C_2	-	+	+	+	+
hydrocarbons C_3	-	+	+	+	+
1,3-butadiene	387.7	+	+	+	+
trans-2-butene	406.5	+	+	-	-
acrylonitrile	435.2	-	-	+	+
1-pentene	482.3	-	-	-	+
methacrylonitrile	535.3	-	-	+	+
cyclopentene	552.7	+	+	-	+
1-hexene	582.9	-	+	-	+
benzene	646.0	+	+	+	+
toluene	753.0	+	+	+	+
phenylacetylene	827.4	-	+	-	+
vinylcyclohexene	833.5	-	+	-	+
ethylbenzene	844.0	+	+	+	+
styrene	870.0	+	+	+	+

identified by capillary GC. CO, CO_2, low molecular weight hydrocarbons and HCN (from the copolymers Kostil SAN and Forsan 752) were identified using Porapak Q column. Benzaledhyde was formed as the main carbonyl product of the pure polystyrene Krasten 127. With a styrene-butadiene-acrylonitrile copolymer (Forsan 752) a greater number of carbonyl compounds is formed due to the oxidation of butadiene (see Table 1).

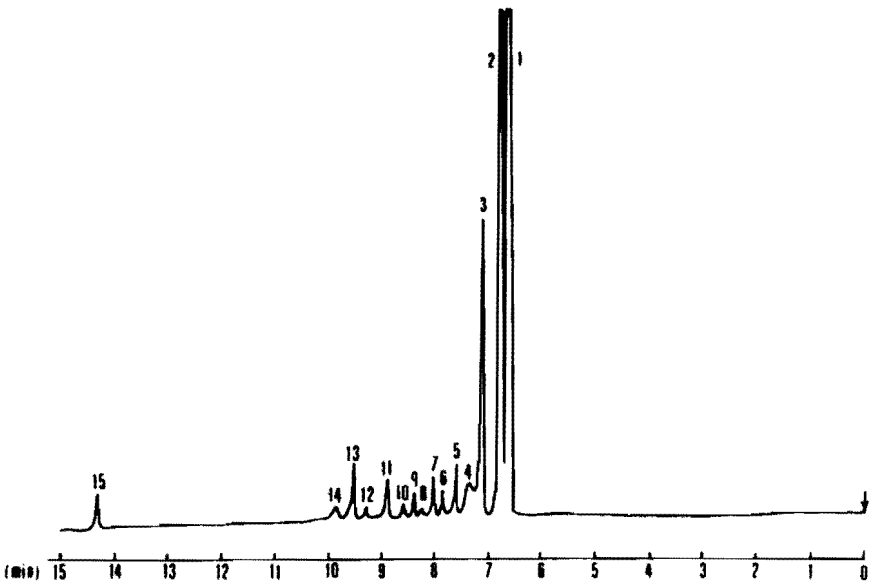
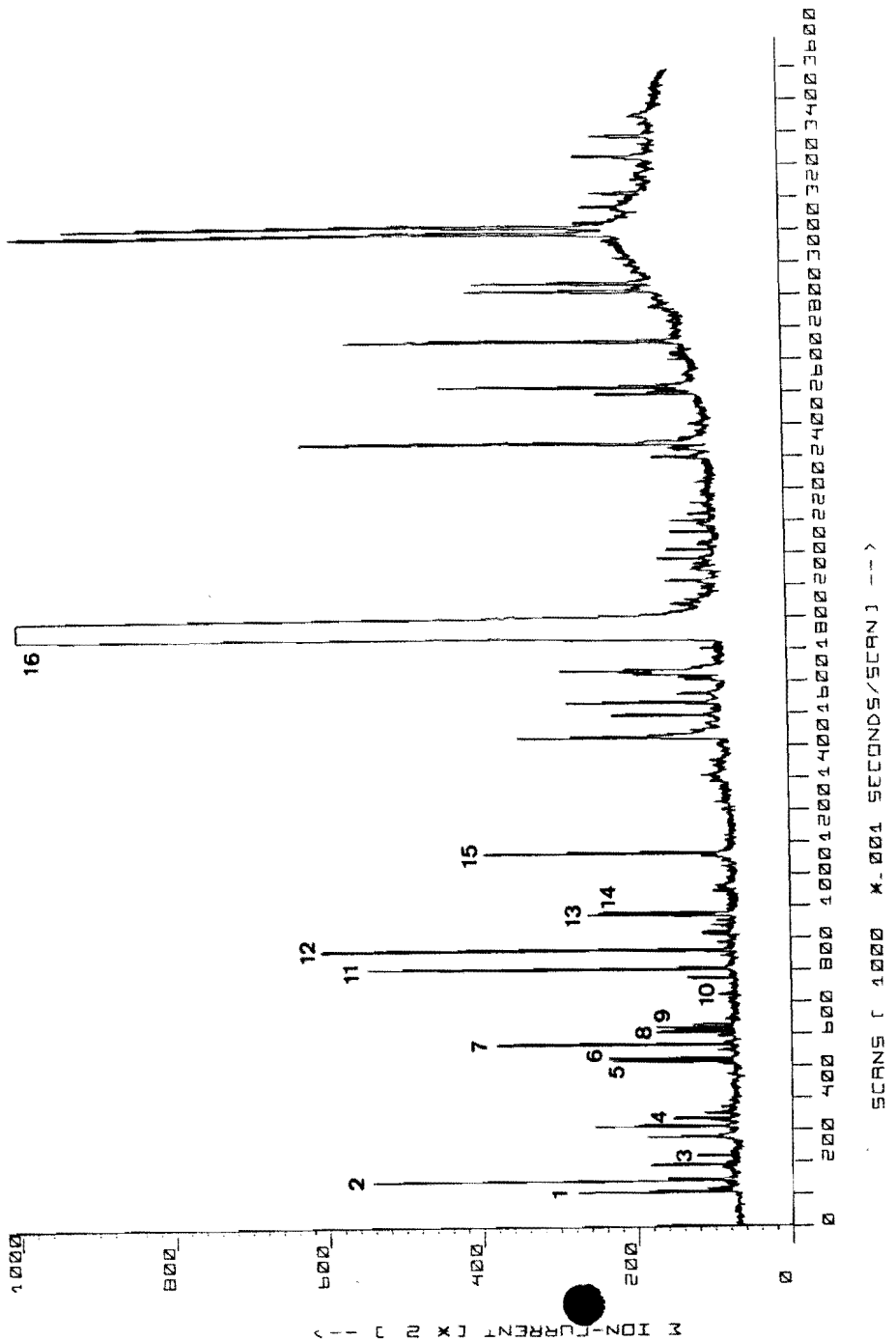


Fig. 6 Chromatogram of the pyrolytic products of polyamide Spolamid 6 (squalane, 80°C). 1- Methane, ethene, ethane, 2 - propene, propane, 3 - HCN, 1-butene, butane, 4 - acetone, 5 - 1-pentene, 6 - 2-methyl-1-butene, 7 - 3,3-dimethyl-1-butene, 8 - 1,3-pentadiene, 9 - 2,2-dimethylbutane, 10 - not identified, 11 - 1,5-hexadiene, 12 - not identified, 13 - 1-hexene, 14 - hexane, 15 - heptane

Polyamide

The anionic polycaprolactam Spolamid 6 was decomposed both in an inert and in the air atmosphere at 600°C. The pyrolysis products obtained in a quartz tubular pyrolyzer are shown in Fig. 6. Lower hydrocarbons, mostly olefins and diolefins, up to C_7 were found. The caprolactam monomer could not be eluted under the experimental conditions used in this work.

In the combustion chamber, only CO, CO_2, NH_3, HCN and low hydrocarbons were detected in the decomposition products formed



by burning of Spolamid 6 (see Fig. 2). Other products were present in negligible amounts and could not be identified on the basis of the retention indices. Therefore, the products were also frozen-out and analyzed by GC-MS. The total ion current chromatogram obtained under EI conditions is shown in Fig. 7. In addition to the main product, ε-caprolactam, the presence of saturated and α-olefinic mononitriles was demonstrated, in accordance with ref. [20]. Heterocyclic N-containing compounds (pyridine, 2-methylpyridine), aromatic compounds (benzene, toluene, aniline) and ketones (acetone, cyclopentanone) were also found.

The carbonyl compounds formed in the combustion products of polyamide include acetone and cyclopentanone that were also detected by the GC-MS analysis, as well as small amounts of propionaldehyde and butyraldehyde (see Table 1).

Ethylene-vinyl acetate copolymer

The ethylene-vinyl acetate copolymer, Urlen, was degraded in the air in the combustion chamber at 600°C in the same manner as the other plastics studied. The combustion products were identified from the chromatogram given in Fig. 8. As can be seen from the figure, the main products formed are analogous to those formed in the combustion of polyethylene, namely, the triplets consisting of alkanes, 1-alkenes and α,ω-alkadienes. The oxygen-containing substances involved acetone and propionaldehyde, in addition to CO and CO_2.

Fig. 7 GC-MS analysis of the combustion products of polyamide Spolamid 6 (for the conditions see Experimental). 1- CO_2, 2 - acetone, 3 - acrylonitrile, 4 - benzene, 5 - pyridine, 6 - 1-pentenenitrile, 7 - pentanenitrile, 8 - toluene, 9 - cyclopentanone, 10 - 2-methylpyridine, 11 - 1-hexenenitrile, 12 - hexanenitrile, 13 - N-methylpropionamide, 14 - 2-methyl-4-pentenenitrile, 15 - aniline, 16 - caprolactam

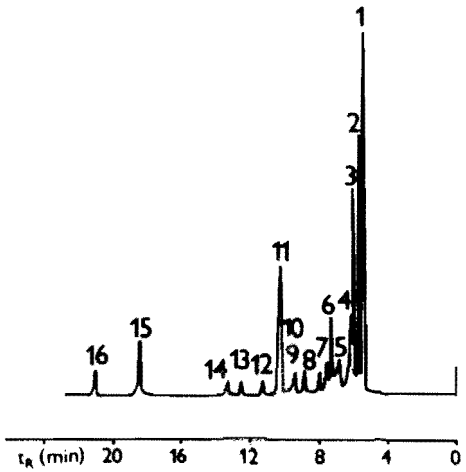


Fig. 8 Chromatogram of the combustion products of Urlen (squalane, 50°C). 1- Methane, ethene, ethine, ethane, 2 - propane, propene, 3 - 1-butene, 4 - acetone, 5 - propionaldehyde, 6 - 1-pentene, 7 -pentane, 8 - 1,3-pentadiene, 9 - 4-methyl-1-pentene, 10 - 1,5-hexadiene, 11 - 1-hexene, 12 - hexane, 13 - 1,3-pentadiene, 14 - 2,3,3-trimethyl-1-butene, 15 - 1-heptene, 16 - heptane

It can be concluded from the results obtained with polyethylene, polypropylene and polystyrene, that combustion in the air yields the main products analogous to those obtained during pyrolysis in nitrogen. O-containing compounds were identified in the combustion products of polyvinyl chloride, polyamide and of the copolymer Urlen. The carbonyl compounds are present at very low concentrations and mostly cannot be directly detected by GC; their determination is only possible after the conversion into the 2,4-dinitrophenylhydrazones.

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