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# Automatic sampler for Curie-point pyrolysis–gas chromatography with on-column introduction of pyrolysates

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## ABSTRACT

An automatic sampler for Curie-point pyrolysis–gas chromatography (GC) to be used in connection with a packed GC column for direct (on-column) introduction of pyrolysates is described. A comparison with the conventional method for pyrolysate introduction with the on-column method is given. Good reproducibility of the results obtained for poly(acrylonitrile–co-1,3-butadiene–co-styrene–co-α-methylstyrene) and poly(methyl methacrylate) pyrolysis products was observed (relative standard deviation <5%). Examples of other applications are presented.

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## INTRODUCTION

The Curie-point pyrolysis (CPPy) method, introduced by Simon and Giacobbo [1] in 1965, is one of two different commercially available pyrolysis systems [2]. In CPPy a ferromagnetic wire is centred in a glass or quartz tube, which is connected to the inlet of a gas chromatograph and through which the carrier gas flows. A Curie-point induction coil surrounds the tube and heats the wire by introduction. The wire heats up until its Curie-point is reached. This is the temperature at which the wire becomes paramagnetic and its energy intake drops, thus holding the temperature of the wire at this point. Different pyrolysis temperatures are obtained by using wires with different Curie-points. A range of temperatures is obtained by using alloys containing differing amounts of the common ferromagnetic metals, *i.e.*, iron, cobalt, nickel and chromium.

Curie-point pyrolysis combined with gas chromatography (CPPy–GC) has developed into a well established method for research into non-volatile compounds, especially in the field of synthetic products in macromolecular chemistry such as plastics, paints, varnishes and rubber, and also of natural substances, including plant materials, soils and minerals.

Many papers have been published, particularly over the past decade, on aspects of CPPy–GC [3]. A large number of different types of apparatus have been used, on a wide range of samples [4–7]. Some information has been given about automated Curie-point pyrolysis systems [8–11].

In a previous paper [12], the Fischer 0316 A pyrolyser with a Fischer AP-6 automatic sampler for CPPy–GC–mass spectrometric–Fouriertransform IR spectro-

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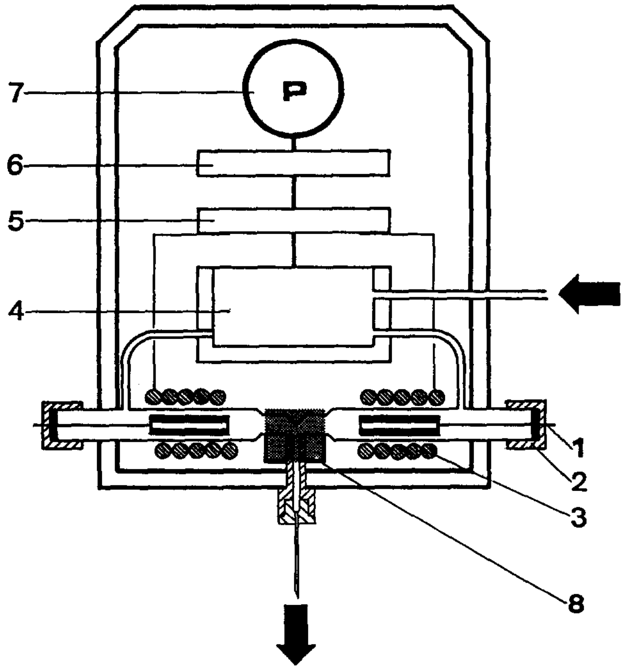

Fig. 1. Schematic sectional view of the Fischer AP-6 automatic sampler. 1 = Sample support; 2 = knurled screw-cap with septum; 3 = induction coil; 4 = carrier gas switching valve; 5 = sample switch; 6 = control switch; 7 = programmer; 8 = heating.

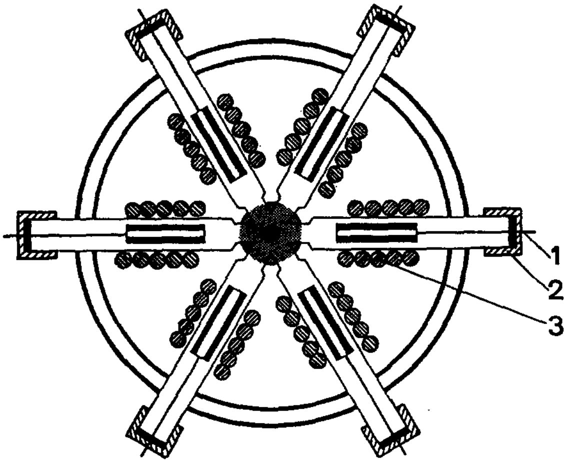

Fig. 2. Cross-section of the Fischer AP-6 automatic sampler at the level of chambers with sample supports.

metric applications was described. The most important features of the Fischer pyrolysis system are exactly reproducible temperatures of pyrolysis, "shock" heating-up within milliseconds, a wide temperature range by means of ferromagnetic filaments or tubes from 250 to 1200°C and high durability because of minor wear and tear [12]. It can be connected with any commercial gas chromatograph with horizontal or vertical injection ports.

The aim of this work was application of the Fischer automatic sampler to the direct (on-column) introduction of pyrolysates. An appropriate system and examples of applications in comparison with the conventional method of pyrolysate introduction are presented.

## EXPERIMENTAL

### *Curie-point pyrolysis*

Pyrolysis was performed using a Fischer Model 0316 A Curie-point pyrolyser of 2 kW at 1.1 MHz power supply (Fischer Labor- und Verfahrenstechnik, Meckenheim, F.R.G.), achieving a measured temperature-rise time of 20–30 ms. The pyrolyser was equipped with a digital adjuster for adjusting of pyrolysis times between 0.1 and 9.9 s and for adjusting pyrolysis sample numbers between 1 and 6 with a standby time between 1 and 99 min.

A Fischer Model AP-6 automatic sampler with six circularly arranged pyrolysis chambers made of stainless-steel with changeable glass inserts was used (Figs. 1 and 2). Removable quartz tubes (Fig. 3) were used to line the internal cavity of the pyrolysis chamber and the ferromagnetic pyrolysis tubes coated with sample. The quartz tubes also act to reduce the dead volume of the system to enable chromatographic resolution to be retained.

The central outlet of the pyrolysis chambers (see Figs. 1 and 3) was equipped with a built-in heater serving to prevent condensation of pyrolysates and to ensure a constant temperature distribution between the sample support and the GC column. The central outlet, maintained isothermally at 250°C, was directly connected to the GC column with a 1/8-in. Swagelok connection (Fig. 3).

About 1 mg of each sample was pyrolysed for 9.9 s at 700°C using ferromagnetic tubes composed of iron, nickel and cobalt (Fischer). Helium (for chromatography) from Linde (Munich, F.R.G.) was used as the carrier gas at a flow-rate of 15 cm$^3$/min.

### *Gas chromatography*

GC analyses of pyrolysates were performed using a Fraktometer F-7 gas chromatograph (Perkin-Elmer, Überlingen, F.R.G.) equipped with a flame ionization detector connected to an Linseis (Selb, F.R.G.) Model L 6512 recorder with a chart speed of 1 cm/min.

A stainless-steel column (1.5 m × 1/8 in. O.D.) packed with 10% SE-30 on Chromosorb W AW (80–100 mesh) (WGA, Griesheim, F.R.G.) was used. The column temperature was programmed from 60 to 280°C at 5°C/min. The detector temperature was 300°C. The flame ionization detector was supplied with 35 cm$^3$/min of hydrogen and 250 cm$^3$/min of air.

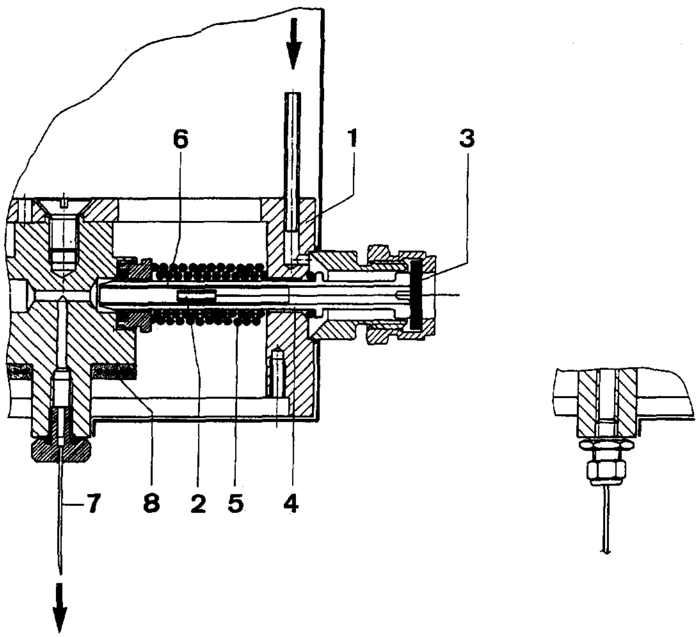

Fig. 3. Sectional enlargement of the construction of the pyrolysis chamber with the injection needle and with connected chromatographic column (right). 1 = Stainless-steel housing; 2 = ferromagnetic sample support; 3 = septum; 4 = glass tube insert; 5 = induction coil; 6 = quartz tube insert; 7 = injection needle; 8 = heater. Carrier gas flow is indicated with arrows.

### *Chemicals*

Samples of poly(acrylonitrile–co-1,3-butadiene–co-styrene–co-α-methylstyrene) (ABS–α-MS), Plexiglas [poly(methyl methacrylate)] (PMMA), PMMA of MW 200 000 in mineral oil (1:1), supplied by the Burmah Oil (Deutschland) (Hamburg, F.R.G.) and commercially available poly(ethylene) and poly(propylene) were used. 1,3-Butadiene (research purity) obtained from Matheson Gas Products (Heusenstamm, F.R.G.) and acrylonitrile, methyl methacrylate, styrene, α-methylstyrene, 4-vinylcyclohexene, toluene and ethylbenzene of analytical-reagent grade from Riedel-de Haën (Seelze, F.R.G.) were used as standards. Hydrocarbon standards obtained from PolyScience (Niles, IL, U.S.A.) were used to measure retention indices.

## RESULTS

Experimental conditions such as pyrolysis temperature, temperature-rise time, sample size, volume of pyrolysis chamber and the GC conditions should be carefully controlled in order to obtain a high reproducibility in CPPy–GC [13,14]. Figs. 4 and 5 show typical pyrograms of ABS–α-MS copolymer and PMMA, respectively, obtained at 700°C with on-column introduction of pyrolysates. The retention indices ($I_p$) of the separated components (Table I) are in agreement with values obtained for commercially available standards. The main degradation products of ABS–α-MS

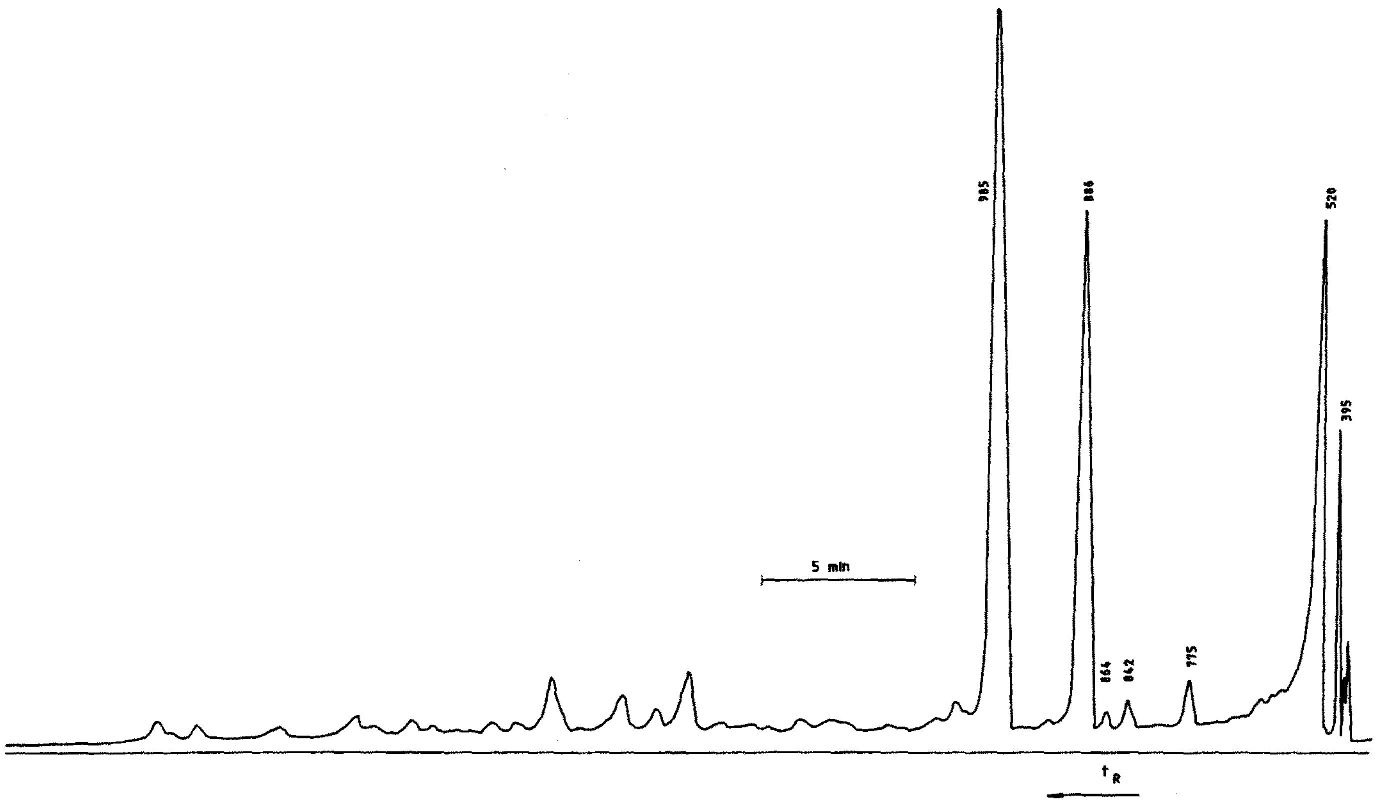

Fig. 4. Pyrogram of ABS–α-MS copolymer obtained at 700°C with the AP-6 automatic sampler and on-column introduction of pyrolysates. Analytical conditions as in Experimental. For peak identification, see Table I.

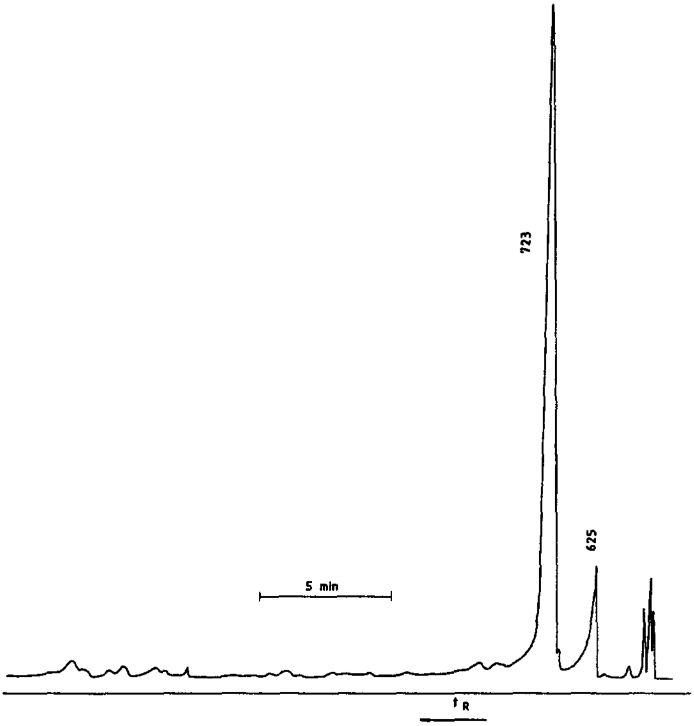

Fig. 5. Pyrogram of Plexiglas (PMMA) obtained at 700°C with the AP-6 automatic sampler and on-column introduction of pyrolysates. Analytical conditions as in Experimental. For peak identification, see Table I.

copolymer pyrolysis, with retention indices of 395, 520, 886 and 985, correspond to 1,3-butadiene, acrylonitrile, styrene and α-methylstyrene, respectively. Small amounts ($<1\%$, w/w) of toluene ($I_p = 775$), 4-vinylcyclohexene ($I_p = 842$) and ethylbenzene ($I_p = 864$) were also observed. Other peaks ($I_p > 985$) were not identified.

TABLE I

RETENTION DATA OF THE CPPy PRODUCTS FROM ABS–α-MS COPOLYMER AND PMMA

| Polymer/copolymer | CPPy product | Retention time, $t_R$ (min) | Retention index, $I_p$[a] |
|---|---|---|---|
| ABS–α-MS copolymer | 1,3-Butadiene | 0.92 | 395 |
| | Acrylonitrile | 1.50 | 520 |
| | Toluene | 5.87 | 775 |
| | 4-Vinylcyclohexene | 7.84 | 842 |
| | Ethylbenzene | 8.58 | 864 |
| | Styrene | 9.30 | 886 |
| | α-Methylstyrene | 12.38 | 985 |
| Plexiglas (PMMA) | Methyl acrylate | 2.90 | 625 |
| | Methyl methacrylate | 4.70 | 723 |

[a] $I_p$: Retention indices in temperature-programmed GC [17].

TABLE II

REPRODUCIBILITY OF CURIE-POINT PYROLYSIS OF ABS–α-MS COPOLYMER AT 700°C WITH THE AP-6 AUTOMATIC SAMPLER AND CONVENTIONAL INTRODUCTION OF PYROLYSATES

Normalized percentages of the major peaks.

| Pyrolysis chamber | Component (peak area, %) | | | |
|---|---|---|---|---|
| | Acrylonitrile | 1,3-Butadiene | Styrene | α-Methylstyrene |
| 1 | 16.70 | 3.10 | 35.01 | 45.19 |
| 2 | 15.48 | 3.40 | 34.33 | 46.79 |
| 3 | 13.41 | 3.26 | 34.71 | 48.62 |
| 4 | 16.23 | 3.62 | 33.81 | 46.34 |
| 5 | 16.30 | 3.57 | 34.88 | 45.25 |
| 6 | 17.32 | 3.61 | 33.10 | 45.97 |
| Average ($\bar{x}$) | 15.91 | 3.43 | 34.31 | 46.36 |
| $\bar{s}_x$ | 1.3639 | 0.2129 | 0.7334 | 1.2685 |
| $\bar{s}_{x,r}$ (%) | 8.57 | 6.21 | 2.14 | 2.74 |

The thermal decomposition of PMMA at temperatures >200°C yields nearly quantitatively (98%) methyl methacrylate (MMA) [15,16]. In our pyrograms the main peak obtained after PMMA pyrolysis is also monomeric MMA ($I_p = 723$). The peak with $I_p = 625$ was identified from the retention index increment ($\Delta I_p = 98$) as methyl acrylate (MA).

TABLE III

REPRODUCIBILITY OF CURIE-POINT PYROLYSIS OF ABS–α-MS COPOLYMER AT 700°C WITH THE AP-6 AUTOMATIC SAMPLER AND ON-COLUMN INTRODUCTION OF PYROLYSATES

Normalized percentages of the major peaks.

| Pyrolysis chamber | Component (peak area, %) | | | |
|---|---|---|---|---|
| | Acrylonitrile | 1,3-Butadiene | Styrene | α-Methylstyrene |
| 1 | 15.92 | 3.48 | 34.40 | 46.20 |
| 2 | 16.01 | 3.52 | 34.61 | 45.86 |
| 3 | 15.85 | 3.41 | 34.38 | 46.36 |
| 4 | 16.12 | 3.54 | 34.31 | 46.03 |
| 5 | 16.23 | 3.44 | 34.53 | 45.80 |
| 6 | 15.74 | 3.40 | 34.29 | 46.57 |
| Average ($\bar{x}$) | 15.98 | 3.46 | 34.42 | 46.14 |
| $\bar{s}_x$ | 0.1795 | 0.0578 | 0.1259 | 0.2976 |
| $\bar{s}_{x,r}$ (%) | 1.12 | 1.67 | 0.37 | 0.64 |

TABLE IV

COMPARISON OF RESULTS OBTAINED BY CPPy–GC OF PMMA AT 700°C WITH THE AP-6 AUTOMATIC SAMPLER BY CONVENTIONAL AND ON-COLUMN INTRODUCTION OF PYROLYSATES

Normalized percentages of the major peaks.

| Pyrolysis chamber | Conventional introdution of pyrolysates | | On-column introduction of pyrolysates | |
|---|---|---|---|---|
| | MA (peak area, %) | MMA (peak area, %) | MA (peak area, %) | MMA (peak area, %) |
| 1 | 6.93 | 93.07 | 7.58 | 92.42 |
| 2 | 8.40 | 91.60 | 7.95 | 92.05 |
| 3 | 8.03 | 91.97 | 7.43 | 92.57 |
| 4 | 7.30 | 92.70 | 6.97 | 93.03 |
| 5 | 9.16 | 91.84 | 7.29 | 92.71 |
| 6 | 6.86 | 93.14 | 7.49 | 92.51 |
| Average ($\bar{x}$) | 7.61 | 92.39 | 7.45 | 92.55 |
| $\bar{s}_x$ | 0.6669 | 0.66669 | 0.3240 | 0.3240 |
| $\bar{s}_{x,r}$ (%) | 8.76 | 0.72 | 4.35 | 0.35 |

Similar pyrograms for ABS–α-MS copolymers and PMMA were obtained at 700°C with conventional introduction of pyrolysates (through the injection port), but the reproducibility of analysis was lower. The results obtained for the two methods of analysis (conventional and on-column introduction of pyrolysates) with a statistical assessment are given for ABS–α-MS copolymer in Tables II and III and for PMMA in Table IV. Tables III and IV show the very good reproducibility of the results obtained by means of the automatic sampler and on-column introduction of pyrolysates. The relative standard deviations ($\bar{s}_{x,r}$, %) of the mean values of peak areas (%) obtained for ABS–α-MS copolymer and PMMA pyrolysis products are nearly 5%.

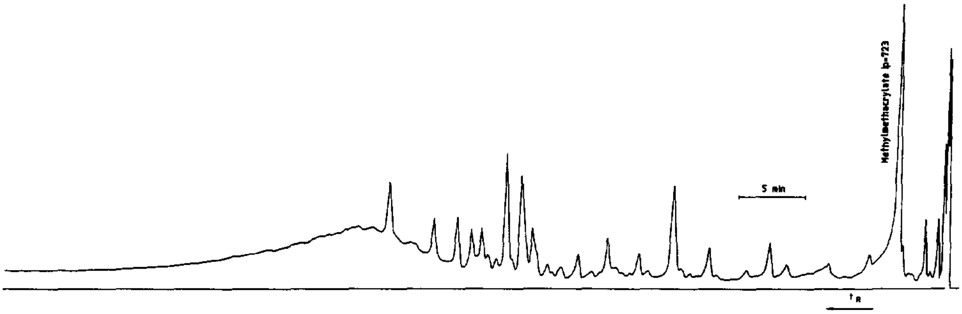

Fig. 6. Pyrogram of PMMA of MW 200 000 in mineral oil obtained at 700°C with the AP-6 automatic sampler and on-column introduction of pyrolysates. Analytical conditions as in Experimental.

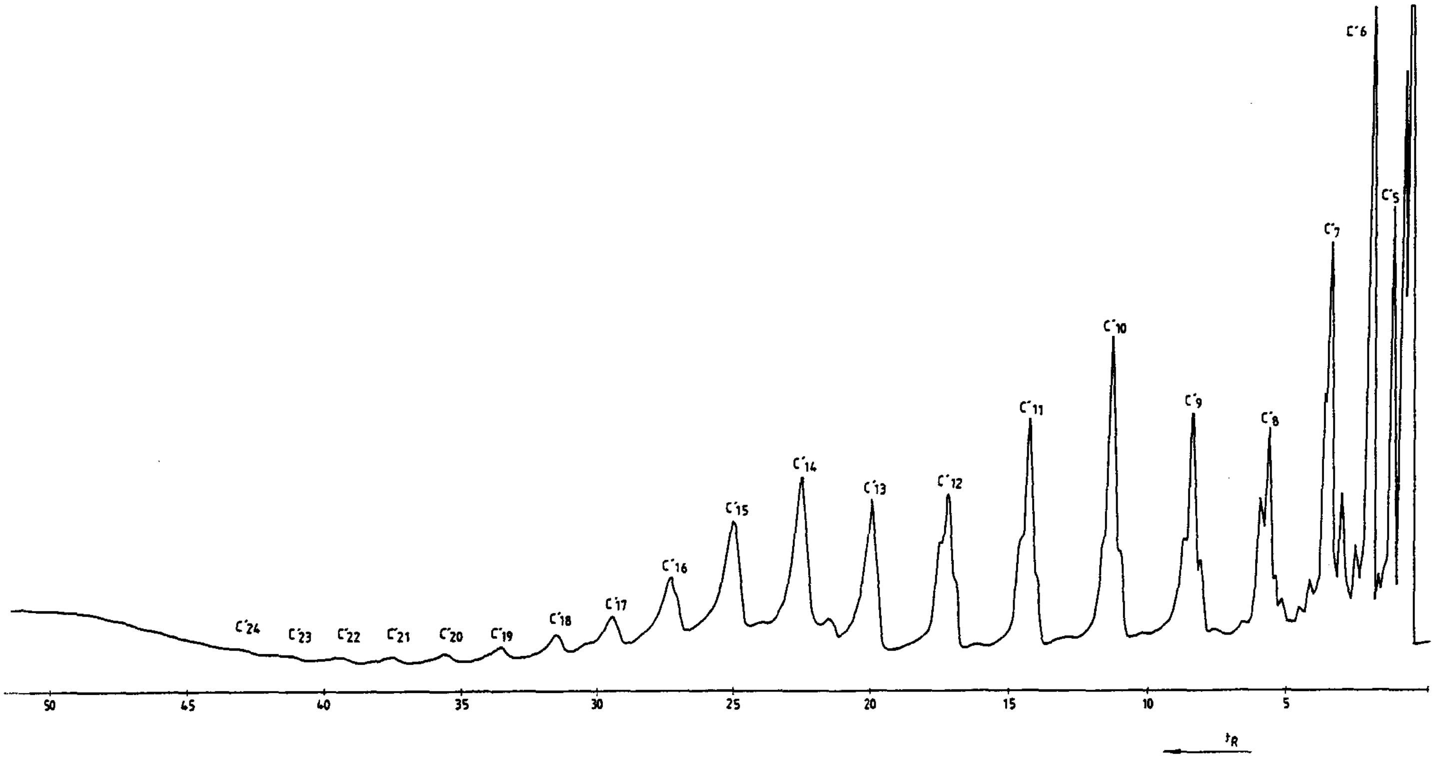

Fig. 7. Pyrogram of commercially available poly(ethylene) obtained at 700°C with the AP-6 *automatic sampler* and on-colum introduction of pyrolysates. Analytical conditions as in Experimental. Peak identification: for example, C′6 = hexane + hexene + hexadiene.

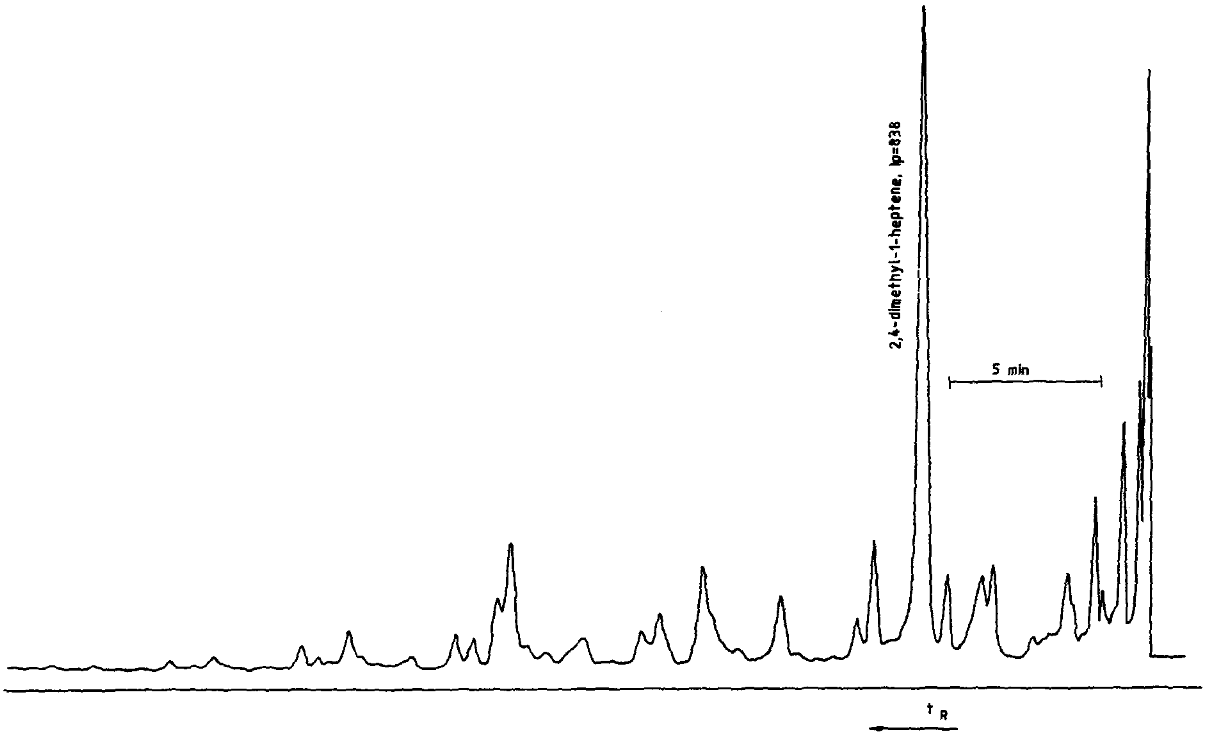

Fig. 8. Pyrogram of commercially available poly(propylene) obtained at 700°C with the AP-6 automatic sampler and on-column introduction of pyrolysates. Analytical conditions as in Experimental.

Some other examples of the application of CPPy–GC with the AP-6 automatic sampler and on-column introduction of pyrolysates are shown by the pyrograms obtained for PMMA in mineral oil (Fig. 6), commercially available poly(ethylene) (Fig. 7) and poly(propylene) (Fig. 8).

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