

Note

Increasing the reliability of the identification of polymers by pyrolysis gas chromatography*

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The interlaboratory reproducibility of gas chromatographic data for the identification of polymers by pyrolysis–gas chromatography (Py–GC) is unsatisfactory¹, although different means of improvement have been suggested. The method of hachured diagrams² can be applied only to certain polymer groups. The introduction of an internal standard in the pyrolysis products³ eliminates this limitation but this method is unsuitable in Py–GC with capillary columns because of the large injection volume. The method of simultaneous pyrolysis of an unknown polymer with poly- α -methylstyrene, in which the retention times of the characteristic pyrolysis products are defined in relation to that of α -methylstyrene, can be applied in the identification of all polymers⁴. In this method, however, the relative retention times are defined exactly only for pyrolysis products that are chromatographed near to α -methylstyrene. The use of several polymers that generate standards covering the whole pyrogram could increase the precision of the relative retention times for all pyrolysis products. In this case, polymers that disintegrate into only one or two products should be used because of the risk of peak overlap with the pyrolysis products of the unknown polymer.

The properties of columns are very important for the reproducibility of GC data, and can be better specified with the g_p parameter for packed columns introduced by Van den Dool⁵. It has been established that this method can be applied to capillary columns⁶. Good reproducibility of the data from capillary columns with a fixed length and a fixed thickness of the film of the stationary phase is achieved when the value of g_p^5 varies within narrow limits, *i.e.*, $\pm 1\%$.

EXPERIMENTAL

As polymers that are pyrolysed to only one or two basic products in over 95% yield we selected poly(methyl methacrylate), poly- α -methyl methacrylate), poly- α -methylstyrene and polycarbonate. The polymers studied and the reference compounds were pyrolysed at 770°C for 5 s, using a Curie point pyrolyser directly connected to a capillary column⁸ (Fig. 1). The capillary columns used (50 m \times 0.3 mm I.D.) were

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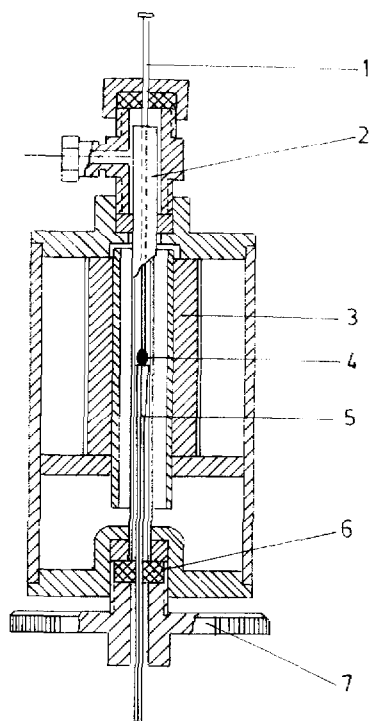


Fig. 1. Curie point pyrolyser directly connected to a capillary column: 1 = ferromagnetic wire; 2 = quartz tube; 3 = induction coil; 4 = sample; 5 = conical connecting capillary; 6 = additional gasket; 7 = connecting ring.

coated with PEG-20M or OV-101 (film thickness $0.20 - 0.26 \mu\text{m}$) and the separation number was $TZ \geq 30$ (ref. 7). With these parameters the value of g_p is about 1.250 for PEG-20M, and about 1.000 for OV-101⁶.

The flow-rate of the carrier gas (nitrogen) was adjusted to allow the C_{24} *n*-alkane to be chromatographed at $210 \pm 2^\circ\text{C}$ and $260 \pm 2^\circ\text{C}$ for PEG-20M and OV-101, respectively. *n*- C_{24} was added to pyridine at a level of 0.01 g in 10 ml. During pyrolysis *n*- C_{24} evaporates from the ferromagnetic wire and only a very small portion of it disintegrates under these conditions. The separation number for linalol-linalyl acetate and limonene-acetophenone must be less than 3 (ref. 6).

It was shown experimentally that the optimum separation of pyrolysis products is achieved with temperature programmes from 60 to 210°C at $2^\circ\text{C}/\text{min}$ for the PEG-20M capillary column and from 35 to 260°C at $3^\circ\text{C}/\text{min}$ for the OV-101 capillary column.

The experiments were performed with Pye Unicam 104 and Perkin-Elmer 910 gas chromatographs.

DISCUSSION

Methyl methacrylate has a relatively low molecular weight and a low polarity and is therefore chromatographed at the beginning of the pyrogram, which is why it

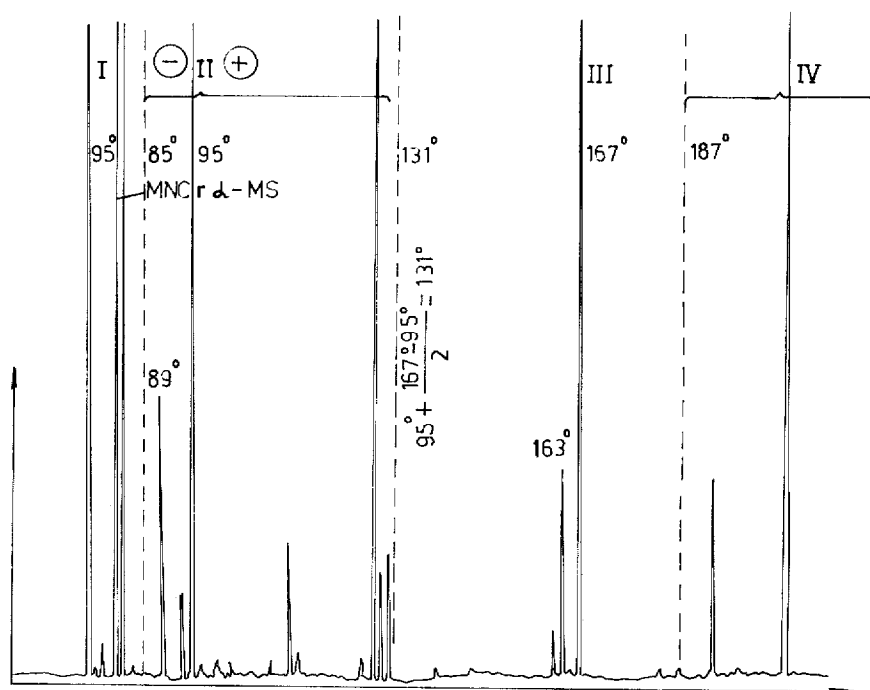


Fig. 2. Pyrogram of nylon-6,6, pyrolysed at 770°C for 5 s together with poly(methyl methacrylate), poly- α -methylstyrene and polycarbonate, obtained with a 50 m \times 0.3 mm I.D. capillary column coated with PEG-20M (film thickness 0.23 μ m), temperature programmed from 60 to 210°C at 2°C/min.

served as the first internal standard. α -Methylstyrene, because of its higher molecular weight, elutes later and is the second internal standard in the pyrogram. The polycarbonate pyrolysis products are chromatographed at higher temperatures and cover the second half of the pyrogram (Fig. 2).

These substances have an acidic character and from the form of their peaks we can estimate the absorption properties of the GC as regards this class of pyrolysis substances. In order to determine the response of the flame ionization detector to the internal standards so as to obtain peaks of comparable height, a solution of 0.02 g of poly(methyl methacrylate), 0.01 g of poly- α -methylstyrene and 0.5 g of polycarbonate in 10 ml of pyridine was injected on to the ferromagnetic wire with a microsyringe without contacting the polymer being studied. There is no need to evaporate all the pyridine because, owing to its basic properties, the form of its peak gives an indication of the behaviour of the GC system with respect to basic pyrolysis products.

In identifying polymers by Py GC, the probability (P) of two polymers with a number of characteristic peaks, k , that seem identical, although in fact they are not, can be determined using the equation

$$P_{n,m}^k = \frac{(n-k)!}{n!m!}$$

The number of strips along the abscissa of the pyrogram, n , and along the ordinate, m ,

TABLE I

VALUES OF THE CONFIDENCE INTERVAL OF THE MEAN $x = \bar{x} \pm 3\sigma$ OF THE RETENTION TEMPERATURES OF THE INTERNAL STANDARDS x

\bar{x} = arithmetic mean; σ = standard deviation, Column, PEG-20M.

Compound (x)	$x = \bar{x} \pm 3\sigma$ ($^{\circ}\text{C}$)
I. Methylmethacrylate	74.3 ± 1.4
Pyridine	83.0 ± 2.2
II. Methylstyrene	95.5 ± 1.3
III	167.4 ± 2.3
IV	208.0 ± 3.0

depend on the reproducibility of the GC data and are determined by the mean ($x \pm 3\sigma$) with 95% reliability. The values of n for the internal standards are given in Table I. On the basis of these data, the pyrograms are divided along the abscissa into strips from -3σ to $+3\sigma$ wide, using the largest value of the standard deviation for the internal standard IV:

$$\text{for a PEG-20M column } n = \frac{210 - 60}{3.0 \cdot 2} = 25$$

$$\text{for an OV-101 column } n = \frac{260 - 35}{3.6 \cdot 2} = 31$$

When calculating the strip width along the ordinate of the pyrogram, the precision of the measurement of the peak height must be taken into account. The strip width is determined from the reproducibility of the pyrolysis temperature and the homogeneity of the studied polymer. Our experience from studying different samples shows that 3σ may be up to 10% of the peak height. That is why the number of strips along the ordinate is $m = 5$ [$100\% / (2 \cdot 10\%)$].

The probability of an coincidental overlap of a polymer with a defined number of characteristic pyrolysis products, e.g., five, with another polymer having the same number of pyrolysis products in identification with a PEG-20M capillary column will be:

$$P_{25;5}^5 = \frac{(25 - 5)!}{25!5!} = 1.31 \cdot 10^{-8} \quad (k = 5, n = 25, m = 5)$$

and with an OV-101 column:

$$P_{31;5}^5 = \frac{(31 - 5)!}{31!5!} = 1.26 \cdot 10^{-9} \quad (k = 5, n = 31, m = 5)$$

The probability of coincidence of two different polymers when studied using a PEG-20M and an OV-101 capillary column is

$$P = P_{25;5}^5 \cdot P_{31;5}^5 = 1.65 \cdot 10^{-17}$$

There is another means of determining the probability of coincidental overlap, *i.e.*, by means of the relative retention time of the characteristic peaks. For this purpose, the pyrogram is divided into four sectors, the limits of which are defined as the arithmetic means of the retention temperatures of the internal standards (Fig. 2). For instance, the borderline between methyl methacrylate and α -methylstyrene will be at $75 + (95 - 75)/2 = 85^\circ\text{C}$. Using this method of calculation, the relative retention time of a peak with a retention temperature of 89°C will be $(-)^{89}_{\text{rel.}} = (95 - 89)/(95 - 85) = 0.60$ and that for a peak with a retention temperature of 127°C will be $(+)^{127}_{\text{rel.}} = (127 - 95)/(131 - 95) = 0.89$.

This method of calculation is the difficult but offers enhanced precision. Thus, the maximum value of the interval $-3\sigma \pm 3\sigma$ of the relative retention times between sectors II and III is $2 \cdot 2.4^\circ\text{C}$. The number of strips will be determined by $n = (210 - 60)/2.4 \cdot 2 = 31$, and the probability of a coincidental overlap is approximately $1.3 \cdot 10^{-8}$, *i.e.*, the identification is more reliable.

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