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Short communication

## High-resolution pyrolysis–gas chromatography with a movable reaction zone

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### Abstract

A new device was constructed for pyrolysis–gas chromatography and it was laboratory tested. The device enables the thermal degradation of polymers inside a capillary pre-column and transfer of the reaction zone into a column oven. The pyrolysis procedure described protects the thermally sensitive compounds prior to pyrolysis, prevents the process of irreversible condensation of high-boiling pyrolysis products during the chromatographic process and eliminates extracolumn effects on the peak broadening. © 1997 Elsevier Science B.V.

*Keywords:* Pyrolysis; Instrumentation; Injection methods

### 1. Introduction

For over 30 years pyrolysis–gas chromatography (Py–GC) has been employed to identify and to investigate structures of high-molecular-mass organic compounds. Many technical devices have been developed to practice this analytical method. All these devices are based on the same rule of operation: rapid heating of a sample up to its decomposition temperature (350–1000°C) in the stream of an inert carrier gas before the chromatographic column followed by GC separation of the pyrolysis products. However, individual devices differ from one another in the way they provide heat to the sample, e.g., the shape of the reaction zone and the geometry of the joint between the pyrolyser and the column.

In early Py–GC studies, a sample was introduced to a hot chamber before the chromatographic column. The volatile compounds resulting from thermal

reactions were transferred in a carrier gas stream to the column [1–3]. The disadvantage of this method was that the volatile pyrolysis products were in contact with the hot environment and secondary reactions could result. Therefore, pyrolyses with impulse heating have met with more approbation. In this case a sample is deposited on a thin metal wire which is then rapidly heated up to a high temperature. The flash heating of the wire results from its electrical resistance [4] or alternatively from induction [5,6]. The second method became more popular because of its simplicity. Inductive heating of ferromagnetic material to its Curie point is a temperature self-controlling process at the Curie point, hence no sophisticated electronic controls are needed to maintain a constant level of the pyrolysis temperature.

Considering other methods, one utilising laser-based pyrolysis is worth mentioning [7,8]. Unfortunately, the use of this method is limited as complicated equipment is required.

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The basic requirement for all flash pyrolysers is that they are capable of increasing the temperature of the heating element as quickly as possible and then maintain this temperature at a constant level over a few seconds. To avoid a temperature gradient in a sample bulk, the sample should cover the heating surface in a thin and uniform film.

Initially, packed chromatographic columns were used in Py-GC but now these are replaced by capillary columns [9–11]. As regards separation of pyrolysis products in a capillary column, diffusion processes proceeding when the carrier gas passes from pyrolyser to the column are critical. The shape and size of joining elements have a great effect on the efficiency of separation. Usually, the polymer tested undergoes pyrolysis in a separate device which is then brought on-line before the column oven. This solution cannot always provide efficient separation of the pyrolysis products.

Moreover, no pyrolysis system can prevent condensation of high-boiling components of pyrolysate in the reaction zone and on its way to the column, although this phenomenon is difficult to notice during the analysis. The highest-boiling products are not recorded in the pyrogram. On the other hand, when the reaction zone is hot, the composition of a thermally sensitive sample can change before the proper pyrolysis.

In this paper, a new Py-GC method is described which avoids the above-mentioned drawbacks, i.e., extracolumn effects, irreversible condensation of the heavy pyrolysate components and decomposition of sample before pyrolysis.

## 2. Experimental

### 2.1. Construction and operation of pyrolysis device

The cross-section of the pyrolyser is shown in Fig. 1. The carrier gas flows through the tube (1) to the head (3) where there is properly sealed entry to the capillary pre-column (6). The ferromagnetic wire (2) can be introduced through a gasket in the head (3) to the uncoated capillary pre-column. The wire tip with the sample deposited on it reaches into the induction coil (5). The whole head (3) can be lifted or lowered by means of a telescopic joint (4). When power to

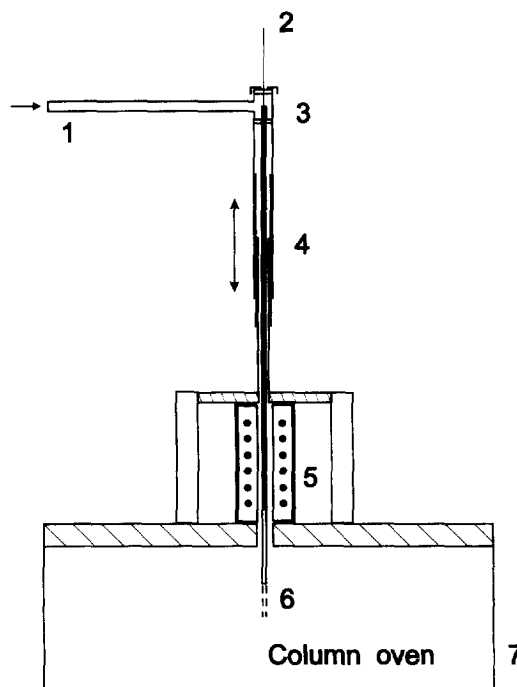


Fig. 1. Cross-section of the pyrolyser; 1=carrier gas inlet, 2=ferromagnetic wire, 3=head of pyrolyser, 4=telescopic joint, 5=induction coil, 6=capillary pre-column, 7=column oven.

the coil (5) is turned on (electrical current with the frequency of about 1 MHz), the sample on the wire (2) is pyrolysed. The pyrolysis products pass through the pre-column to the basic capillary column. Initially, the coil and the pre-column are not heated. When pyrolysis is completed, some part of pre-column with pyrolysate accumulated in it is placed in the column oven (7). Now, the pyrolysis products can be separated at a constant or programmed temperature profile. It is important that the reaction zone, which is initially cold, can be heated up in the course of analysis to the maximum temperature allowable for a given stationary phase present in a column. The performance of our resolution is similar to that of an "on-column" injector which is employed to separate high-boiling compounds. The heavy products do not evaporate completely during the chromatographic analysis and their separation can be carried out at the maximum temperature for the column utilized. It is additionally obvious, that no loss in separation efficiency results from any factors impacting from outside the column since the whole process –

including pyrolysis – takes place inside the capillary column.

## 2.2. Materials and procedures

The laboratory-made pyrolysis device as described above was employed instead of a sample injector in the Hewlett-Packard gas chromatograph, Model 5890/2, equipped with a flame ionization detector. An iron wire (Curie point 770°C), 0.18 mm in diameter, with its tip coated with a sample, was

introduced to a short fused-silica capillary pre-column (0.32 mm diameter).

High-density polyethylene ( $M_r$  about 100 000) and hen egg white were the samples for Py-GC. Polyethylene was deposited on the surface of iron wire from the solution in decaline. The egg white was introduced directly on the tip of the iron wire, and then the excess of water from the egg was evaporated using an unheated air stream.

The separation column with the same diameter was 25 m long; the column contained HP-1 siloxane

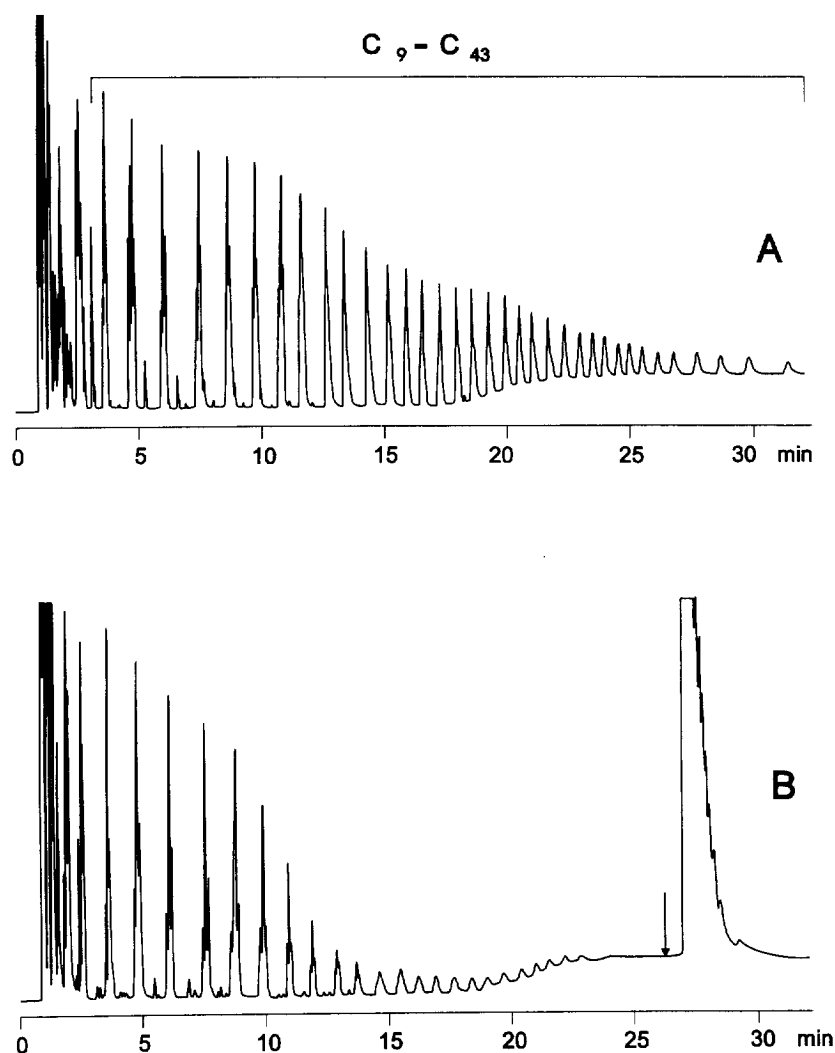


Fig. 2. Pyrograms of polyethylene. (A) Reaction zone introduced to column oven just after pyrolysis; (B) cold reaction zone introduced to column oven at 280°C.

stationary phase. Both columns were supplied by Resteck. Helium was the carrier gas. The column temperature was programmed at a rate of 10°C/min from 60 to 280°C, and with a final isotherm at 280°C. The detector temperature was 280°C.

### 3. Results and discussion

To illustrate the operation of the pyrolyser described above, two materials were selected: stable high-molecular-mass polymer (polyethylene) and

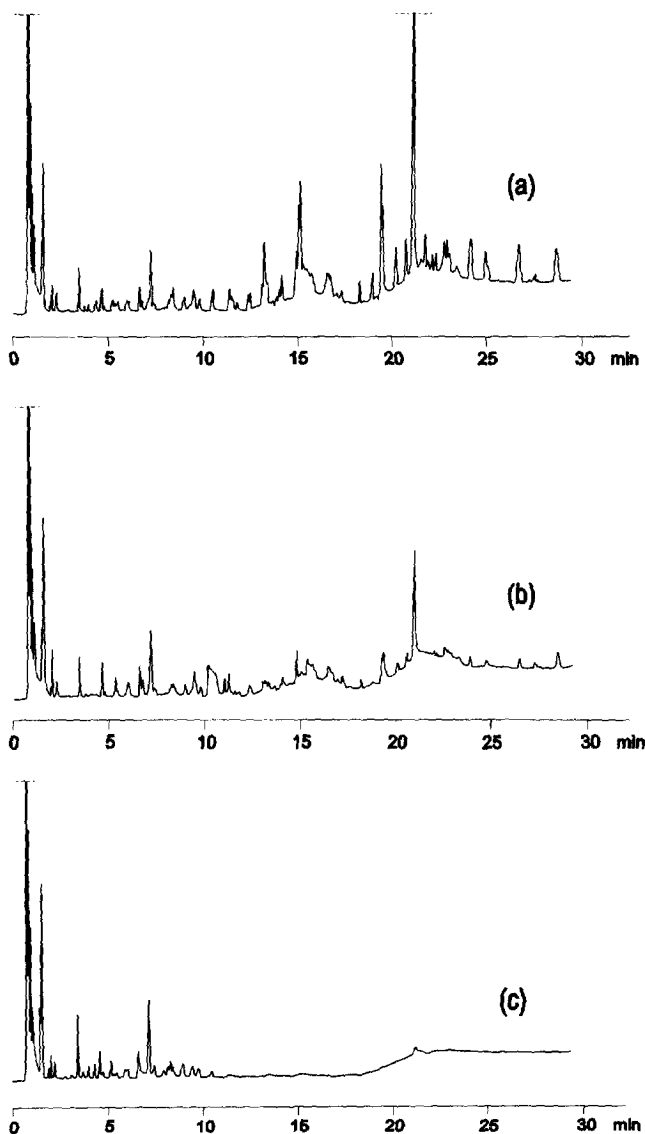


Fig. 3. Pyrograms of an egg white at the different temperatures of reaction zone: (a) 20°C before pyrolysis; (b) 150°C before pyrolysis; in both cases, the temperature was programmed in the range 60–280°C after pyrolysis; (c) 20°C before and after pyrolysis.

thermally sensitive biopolymer (egg white). In the first experiment with polyethylene (pyrogram in Fig. 2A), the reaction zone was inserted into the column oven just after pyrolysis. In the second run (Fig. 2B), the pre-column with the reaction zone was inserted into the oven not earlier than the 26th minute of analysis at 280°C.

As can be seen after comparing these two pyrograms, high-boiling hydrocarbons either are not present at all in eluate from the column or their concentrations are much lower when the reaction zone is not heated just after pyrolysis. The broad and complex peak in Fig. 2B represents the components which condensed in the cold reaction zone and did not reach the separation column. When the reaction zone and the unheated section of the pre-column are placed in the column oven at 280°C, these components can quickly move along the column. The total mass of the “delayed” components reaches about 30% of the pyrolysate mass.

In the second example the egg white was pyrolysed at different temperatures of the reaction zone before and after pyrolysis: (a) 20°C before pyrolysis and programmed in the range 60–280°C after pyrolysis (the part of pre-column with the reaction zone has immersed in the column oven after pyrolysis); (b) 150°C before pyrolysis and programmed after pyrolysis; (c) 20°C, constant before and after pyrolysis. As can be seen in Fig. 3, the three pyrograms differ from each other. The peaks of heavy products present on pyrogram (a) are absent from pyrogram (c) because of condensation of these products in the cold reaction zone, whereas (b) is the pyrogram of the pyrolysate of the denatured sample.

One possible problem in the described system results from gradual contamination of the upper part of the pre-column. Fortunately, this is not a serious problem because of the small amounts of sample (usually about a few  $\mu\text{g}$ ). Additionally, the possibility of heating of the reaction zone to extreme temperatures makes it possible to remove even very low-volatile compounds from the system. The short-lived repeated induction heating of the blank iron wire inside the pre-column in the stream of carrier

gas is usually an effective aid to remove “pyrolysable contaminants” deposited on the wall of the pre-column. After many experiments, a small section of the upper part of pre-column may be cut out, before finally the whole pre-column may be replaced by a new one.

#### 4. Conclusions

The described modification of Py-GC with a movable reaction zone prevents the sample from being affected by high temperatures before the pyrolysis reactions start. Also, it prevents irreversible condensation of heavy components in the reaction zone before the analysis. It is worth mentioning that extracolumn effects on the separation efficiency are omitted in this system similarly as in case of “on-column” injection.

Because of its advantages, this method may be recommended for the analyses of thermally unstable compounds, in particular biological materials. It can also be applicable in studying polymers which decompose to yield a range of pyrolysis products with a wide span of boiling points (polyethylene, polypropylene, etc.).

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