

# Development of a multifunctional pyrolyzer for evolved gas analysis, thermal desorption, and/or pyrolysis-GC of polymeric materials

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**G**as chromatography, invented as a tool for separation and analysis by Martin and James in 1952,<sup>1</sup> has advanced remarkably in regard to both hardware and software in the past 49 years. The retention time can be reproduced with a precision of less than a second in recent analyses. In addition to fused-silica capillary columns, fouling-resistant and practical-to-use metallic capillary columns with a deactivated inner wall are gaining popularity.<sup>2</sup>

Pyrolysis-gas chromatography (Py-GC), the process of thermally decomposing a nonvolatile sample before introducing it into a GC, is a simple but rapid and extremely sensitive technique for the investigation of nonvolatile materials such as polymers. It often provides unique structural information, not only for ordinary soluble polymeric materials, but also for intractable cured polymer compounds. In the early stages, however, Py-GC had some limitations, such as difficulty in attaining specific pyrolysis of the sample, complexity of the chemical reactions in pyrolysis, insufficient separation of the resultant degradation products, and poor peak identification and interpretation of the pyrograms.<sup>3</sup> Therefore, the method has long been regarded as relatively crude for the characterization of polymers, providing less reproducible results.

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However, due to recent developments such as highly specific pyrolysis devices, efficient capillary columns, and specific identification of the peaks in the pyrograms by GC-MS systems, Py-GC has made great strides toward being a powerful tool, not only in polymer identification and the compositional determination of copolymers, but also in the microstructural characterization of polymers. The structural information obtained by this high-resolution Py-GC is sometimes unique and complementary to that provided by conventional spectroscopic methods such as infrared (IR) and nuclear magnetic resonance (NMR).<sup>4</sup> This paper reports on the characteristics and performance of an improved vertical-type microfurnace with a temperature programming device (PY) and the Py-GC system utilizing the PY.

## Characteristics of various pyrolyzers

Pyrolyzers that are commercially available at present can be classified into three types: filament, Curie-point, and microfurnace. Since each of these pyrolyzers has its own characteristics and detailed reports have been made, only a brief description of each is given.

### Filament-type pyrolyzers

The majority of the pyrolyzers currently used in the U.S. are of the filament type. These pyrolyzers are typically equipped with a coil made of a very thin platinum wire of about 0.5 mm o.d., or a piece of thin

platinum foil as the heating element. The coil has an inner diameter of approx. 2 mm with a length of about 2 cm, and a quartz tube of 1/8 in. o.d. holding the sample inside is inserted into the coil. With a thin platinum foil, the solid sample or its solution is directly mounted on it. In actual use, the pyrolysis temperature in these methods is often affected by many factors, such as the shape or form of the sample, the position of the sample in the quartz sample tube, or the way in which the heating coil is wound or deformed accidentally by an external force. Good reproducibility of the pyrograms over a span of time is not easy to achieve. In addition, this type of pyrolyzer has manifold sections made of metal(s) on which polar substances tend to be adsorbed, and an undesirable diffusion takes place due to the large area of dead space in these sections. Upon introducing the sample into the heated manifold zone, air cannot be completely purged out, and adverse oxidation reactions take place. Depending on the heat of the manifold, often between 200 and 300 °C, the sample mounted there is sometimes exposed to undesirable high temperatures before final pyrolysis, and the structure and composition of the sample is often altered.

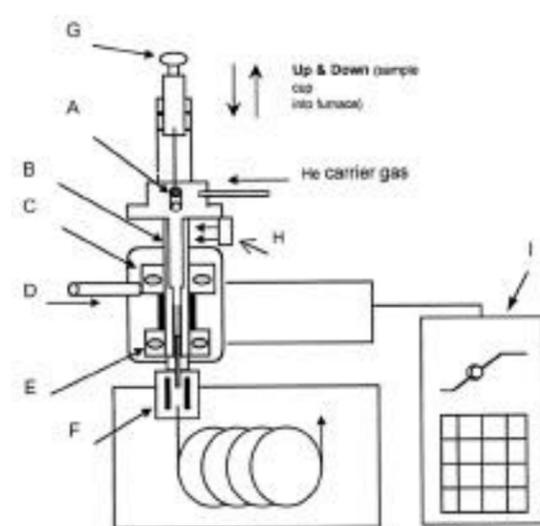
### Curie-point-type pyrolyzers

In this type of pyrolyzer, the sample is first wrapped with a piece of thin ferromagnetic foil that is inserted into the manifold furnace, which is often preheated between 200 and 300 °C. After the sample reaches the manifold temperature, the temperature of the foil is rapidly raised to its Curie-point by induction heating, and its heat is conducted to the sample to cause pyrolysis. Although a rapid increase in foil temperature is achieved with this method, the actual pyrolysis temperature of the sample might change, depending on the form of the sample or how it is wrapped, and good reproducibility of the pyrograms is therefore not necessarily attained. The problems associated with the manifold section, which are the same as those in filament-type pyrolyzers, can be alleviated by using a specially designed sample introduction system such as the Bio-probe (Japan Analytical Industry Ltd., Tokyo, Japan).

### Heating furnace-type pyrolyzers

Horizontal-type and vertical microfurnace-type pyrolyzers fall into this category. Horizontal-type units have been known throughout the world for many years. The sample is placed into a sample boat that is manually inserted into the horizontal furnace, which is controlled at a preset pyrolysis temperature. The sample is then thermally decomposed and the pyrolysis products are introduced into a separation column. Units of this type, however, are no longer widely used due to difficulties in solving the problems associated with high heat capacity of the sample boat, large dead space, and the cool section between the exit section of the pyrolyzer and the injection port of the GC.

Pyrolyzers with a vertical-type microfurnace<sup>5</sup> have a very simple structure: A sample is placed into a sample cup that is dropped by free fall, due to gravity, into the center of the vertical heating furnace, and the sample is pyrolyzed instantly with high reproducibility. The sample is kept at an ambient temperature until it is subjected to pyrolysis. This type of pyrolyzer is characterized by the fact that the pyrolysis takes place instantly, and also that the sample is never altered before final pyrolysis. Moreover, the design of the pyrolysis tube or method used to retrieve



**Figure 1** Construction of pyrolyzer: A) sample cup and its standby position, B) quartz pyrolysis tube, C) microfurnace, D) cooling air, E) heated interface, F) split injection port, G) releasing knob, H) cooling fan, and I) temperature controller.

the sample cup from the heating furnace has not been used in any other pyrolyzer.

By around 1992, commercially available pyrolyzers using this principle were not able to achieve interlaboratory reproducible results, although the method has been applied extensively to the analysis of most conventional polymers. Based on the principles of operation of these conventional systems, pyrolyzers that exhibit very high reproducibility were developed. The redesigned vertical microfurnace pyrolyzers also make it possible to acquire information on the volatile components occluded in the sample as well as on the base polymer in the sample by multistep thermal decomposition.

### Improved microfurnace-type pyrolyzer

The main components of the improved system include the Double-Shot Pyrolyzer model 2020D (Frontier Laboratories Ltd., Fukushima, Japan); Ultra ALLOY-5, 5% diphenylpolydimethylsiloxane, 30-m, 0.25-mm-i.d., 0.25- $\mu$ m film capillary column (Frontier Laboratories); model 5971 GC-MS (Agilent Technologies, Palo Alto, CA). The system configuration with the newly developed pyrolyzer is shown in Figure 1.

The sample is placed in a stainless steel sample cup with its surface deactivated by forming a multi thin layer of silicone oxide.<sup>2</sup> The cup is retained at position A via a hanger pin held in the chuck of the cup holder. The chuck opens when the knob G is pushed, and the sample cup falls down by gravity to the center of microfurnace C. The temperature there is already set at the pyrolysis condition and the sample is pyrolyzed instantly. The pyrolysis products travel through heated interface section E and split interface F to the GC and then enter the capillary column. A temperature controller independently controls the temperatures of sections C and D within  $\pm 1$  °C of the preset temperature. A cooling fan is used to cool down the chamber, where the sample cup is on standby so that the temperature there is close to ambient. In order to carry out a series of thermal desorption and pyrolysis to realize a multistep pyrolysis operation, the sample cup can be moved up and down manually from position A to the center section of microfurnace C, which can be controlled at any desired

Table 1  
Reproducibility of polystyrene pyrolysis products before and after equipping the heated interface section of the pyrolyzer\*

	SSS/S	RSD (%), n = 5
Without heated interface	0.052	13.2
With heated interface	0.139	0.63

\*Sample cup: platinum, 2 mm o.d., 3 mm high, 0.1 mm wall thickness.

temperature between 40 and 800 °C in increments of 1 °C. Moreover, the rate of temperature increase can be programmed from 1 to 60 °C/min. Before the repeated next run, the microfurnace is cooled rapidly down to ambient temperature by forced circulation of compressed air delivered from the outside. For example, the cooling time from 800 to 40 °C is about 30 min at a flow rate of 6 L/min (air). With regard to its heat capacity, the furnace was designed in such a way that the time to cool the microfurnace from its pyrolysis temperature to the initial use temperature is close to the average time it takes to obtain a pyrogram, so that loss time between runs is minimized.

### Characteristics of the microfurnace-type pyrolyzer

#### Reproducibility of pyrograms

In general, a low-temperature zone should not exist between the pyrolysis furnace and the injection port of a GC in order to prevent formation of a film from condensation and deposition of higher boiling point products or tars that cause unexpected adsorptions or interactions with the pyrolysis products in the flow path.

The pyrolyzer is supplied with interface section E and its temperature can be independently controlled to minimize the low-temperature zone. The results before and after equipping the heated interface section are shown in Table 1. The observed peak area ratio of the pyrolysis products of polystyrene at 550 °C, styrene monomer (S), and styrene trimer (SSS) (SSS/S) and its reproducibility expressed by relative standard deviation (RSD) were greatly improved using the pyrolyzer.

#### Reproducibility among different PY units (n = 100) and applicability to analysis of some polymeric materials

In order to obtain interlaboratory reproducible results, it is very important for different PY units to generate pyrograms with high reproducibility. Figure 2 is a typical example of a pyrogram for polystyrene at 550 °C, the RSD, and peak intensity ratio of SSS/S obtained using 100 different PY units produced in the authors' laboratory. Thus, observed SSS/S ratios obtained by the 100 different pyrolyzers were between 0.13 and 0.15, and RSD was a good as less than 1%.

#### Combination of thermal desorption and pyrolysis (two-step method)

In the early stage of development, a pyrolyzer equipped with two tandem connected electrically

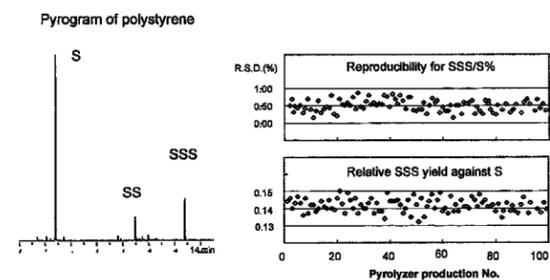


Figure 2 Reproducibility and relative peak area (ratio of SSS and S peaks) in the polystyrene pyrolysate for consecutively manufactured 100 units of pyrolyzers and its typical pyrogram using Double-Shot pyrolyzer at 550 °C. Column: Ultra ALLOY-5, 30 m × 0.25 mm i.d., 0.25 μm at 70–300 °C, 20 °C/min.

heated furnaces (thermal desorption and pyrolysis) was designed.<sup>5</sup> The instrument can provide two types of information on a polymeric material: those on the components that can be thermally desorbed, and those from the pyrolysis of the base polymer(s). The sample is first inserted into a furnace with a relatively low temperature (for example, at 200 °C) and the components desorbed are introduced into the GC column after passing quickly through the second pyrolysis furnace at a higher temperature (for example, 600 °C). However, various problems associated with the adjacent higher temperature furnace were encountered: 1) The thermal desorption temperature was often affected by the adjacent furnace, and 2) further thermal decomposition of the desorbed compounds often takes place when the compounds pass through the second furnace for pyrolysis. With the improved pyrolyzer, these problems were eliminated since only one furnace with a programmable temperature function employed both a cooling and a heating device, which enabled thermal desorption and/or pyrolysis at any desired temperature mode.

The stepwise method typically consists of thermal desorption and subsequent pyrolysis steps. In the first step for thermal desorption, the sample (a polymeric material, for example) is placed in a sample cup that is first inserted in the furnace (Figure 1c), at which temperature is programmed from near ambient to the final thermal desorption temperature. The thermally desorbed components are mainly trapped at the inlet end of the column when its temperature is thoroughly cooled down. The sample cup is then moved back to standby position A at room temperature. The thermally desorbed components are separated with the increase in column temperature, and the first thermal desorption chromatogram is obtained. In the subsequent pyrolysis step, by pushing sample-release knob G, the sample cup at position A is released for free fall to pyrolysis furnace C, at which the temperature is preheated to the desired pyrolysis temperature. The base polymer in the sample cup is then pyrolyzed instantly and the second pyrogram is obtained. The furnace is then automatically cooled to the thermal desorption temperature to prepare for the next run.

#### Evolved gas analysis

In the evolved gas analysis (EGA) technique using PY,<sup>6</sup> the detector and the split injection port attached to PY are directly connected with a deactivated metal capillary tube without coating of the GC stationary phase. The gas evolved from a given sample during the temperature increase by continuous heating is introduced into the detector, and the amount of evolved gas is plotted against the temperature, giving a thermogram.

#### Analysis of unknown rubber sample: Example of EGA/two-step method combination

In the system shown in Figure 1, a 0.15-mm-i.d., 2.5-m-long deactivated metallic capillary tube is installed in place of a GC separation column to connect the split injection port and the detector. The flow rate of the carrier gas is set at 1 mL/min, and the temperature of the GC oven is maintained at 300 °C. The unknown rubber sample mounted in the sample cup is moved from position A to the pyrolysis furnace. The furnace temperature is raised from 40 to 600 °C at a rate of 20 °C/min. The evolved gas is detected by a mass spectrometer, giving the EGA curve shown in Figure 3. For this sample, a small amount of volatile components was desorbed up to 300 °C, and then pyrolysis products of the main polymer component were observed between 300 and 600 °C.

Based on the result of the EGA curve, further detailed study with capillary GC was conducted to analyze the volatile components evolved at below 300 °C and the polymer pyrolysis products. The results are shown in Figure 4. In the chromatogram in Figure 4a, cyclic siloxane oligomers derived from a

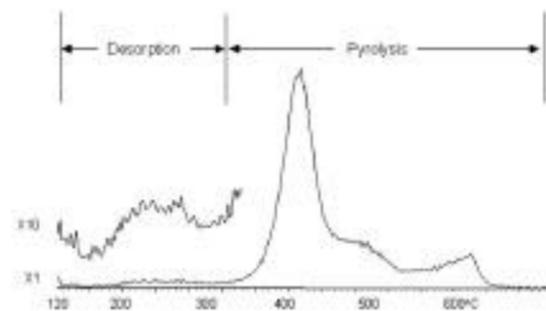


Figure 3 Evolved gas analysis of rubber impregnated additives. Sample: 20 μg, split: 1/20, heating temp: 40–600 °C (20 °C/min), MS scan range, 40–400 amu, scan speed: 100 amu/sec.

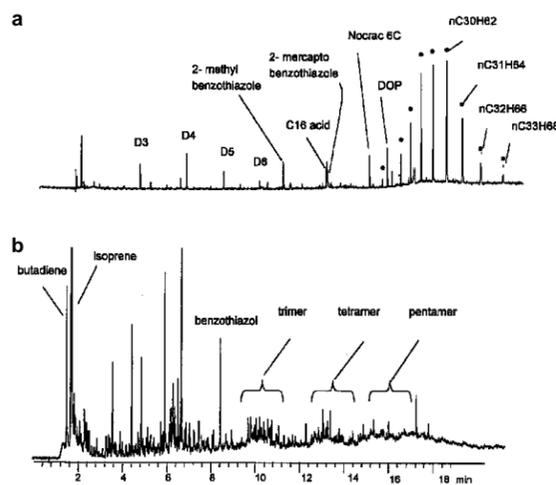


Figure 4 Thermal desorption and its consecutive pyrolysis of formulated rubber. a) Thermal desorption at 100–300 °C (20 °C/min). b) Pyrolysis at 550 °C. Column: Ultra ALLOY-5 (5% diphenylpolydimethylsiloxane, 30 m × 0.25 mm i.d., 0.25 μm film). Temp: 40–320 °C (20 °C/min), 5-μg sample using MicroJet Cryo-Trap (Frontier Laboratories, Ltd., Fukushima, Japan).

silicone coupling agent (D3, D4, D5, and D6 denote the trimer, tetramer, pentamer, and hexamer), benzothiazoles as a vulcanization promoter, long chain fatty acids as vulcanization auxiliaries, and antiaging waxes were observed. From the pyrogram in Figure 4b, polymer sample was identified as a natural rubber containing a small amount of butadiene rubber.

#### Conclusion

Using an improved pyrolyzer, it is possible to conduct an evolved gas analysis by programmed heating and a two-step pyrolyzer carrying out thermal desorption and flash pyrolysis as well as conventional flash pyrolysis. Problems frequently encountered in the past, such as poor reproducibility and trapped high-boiling species, have been resolved. A new age of polymer analysis is on the horizon, since the skills and expertise needed for traditional Py-GC are no longer required with the pyrolysis system described here.

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