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Interface between pyrolyzer and gas chromatograph A different configuration of pyrolysis–gas chromatography

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Abstract

In a conventional pyrolysis–gas chromatography (Py–GC) system, the pyrolyzer was interfaced on top of blocks off the normal sample injection port. In this study, a different approach has been developed. The pyrolyzer is mounted differently such that the pyrolyzer can coexist with the traditional sample injection devices, such as an autosampler. The advantages of this configuration are: (1) the pyrolyzer attachment does not interfere with sample introduction through the injection port, (2) the GC system can be converted to a Py–GC system without mounting or dismounting of the equipment and (3) when operated as a Py–GC unit, the conventional sample injection port can be used as an auxiliary sample introduction route to greatly enhance the capability of Py–GC data handling in qualitative and quantitative analysis. © 1997 Elsevier Science B.V.

Keywords: Interfaces; Pyrolysis–gas chromatography; Instrumentation; Polymers

1. Introduction

Pyrolysis incorporated with gas chromatography (GC) has been used to produce/separate pyrolysates for almost forty years [1–3]. No matter which type of pyrolysis technology is used (isothermal furnaces, inductively heated filaments, resistively heated filaments), the pyrolyzer interface has always been directly mounted on top of the GC injection port. The advantage of this top mounting configuration is that the pyrolysates are transferred immediately into the injection port, minimizing dead volume during transfer. The disadvantage of this set-up is that the GC unit has to be dedicated to pyrolysis experiments only.

In conventional GC analysis, the characterization of unknown samples depends on the interpretation of a chromatogram. Similarly, such characterization by pyrolysis–GC (Py–GC) depends on the interpretation of a pyrogram. One way to enhance the effectiveness and efficiency of the pyrogram interpretation is by retention time standardization [4,5]. Qualitative identification approaches such as (1) comparing and matching peak patterns between the unknown sample and reference pyrograms and (2) searching for the unknown peak (component) through a library of pyrograms [6] all require a standardized retention time (also called retention index). Retention time standardization typically can be accomplished by introducing a marker compound, which will serve as a reference retention time point in the chromatogram.

The retention time marker can be a single compound or multiple compounds. Usually, these compounds can be mixed with the unknown sample solutions to co-elute through the separation column. However, Py–GC analysis is not that flexible be-

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cause the sample introduction in a Py–GC is slightly different from conventional GC analysis. To ensure that the pyrolysates really come from the pyrolysis process, the sample holder (pyroprobe) is inserted into a pyrolyzer interface, which is heated at an elevated temperature (150°C or above) for a period of time. Any volatile components in the sample, such as solvents or low boiling additives, will be vaporized before being pyrolyzed. Because of this preheated sample preparation, the selection of retention time markers is limited. Although there is a pyrolyzer set-up in which the sample is kept at room temperature before pyrolysis [7], the whole sample holder block in this case is kept in the closed carrier gas flow loop. The vapor of retention time markers or the solvents of retention time markers will still create interference in the pyrogram.

In GC quantitative analyses, one way to increase the effectiveness of the analysis is to introduce an appropriate internal standard [8,9]. The identical concept can be used in Py–GC. Using an internal standard makes quantitative analysis of an unknown concentration of a pyrolysis sample simple and reliable because all uncertain factors contributed by operation and instrumentation can be cancelled. However, internal standard introduction is not easy and internal standard selection is limited in Py–GC, the reason is the same as introducing the retention markers.

In this study, a different approach was taken to connect the pyrolyzer interface to the GC. The pyrolyzer does not occupy the normal sample injection port. Instead, the pyrolyzer is mounted differently such that it can coexist with traditional sample injection devices, such as an autosampler. The advantages of this configuration are: (1) the pyrolyzer attachment does not interfere with sample introduction through the injection port, (2) the GC system can be converted to a Py–GC system without any mounting and dismounting of equipment and (3) when operated as a Py–GC unit, the conventional sample injection port can be used to inject marker compounds for retention time standardization of pyrolysates in qualitative analysis and to inject appropriate internal standards for quantitative analysis. Several polymer samples such as high density polyethylene, polybutyl acrylate and styrene–methyl methacrylate copolymer have been tested to demonstrate the advantages of this new arrangement in qualitative and quantitative analysis.

There is another type of connection between the pyrolyzer and the GC system, which is called off-line interface. This arrangement is generally used for absorption and desorption experiments [10], trapping pyrolysates into a solvent [11], multiple pyrolysis to concentrate the specific pyrolysates [12] and controlling the environment of pyrolysis [13]. This type of interface can not be categorized as a "direct on-line" connection because it separates the Py–GC procedure into two parts, pyrolysis and separation. This type of connection will not be discussed in this paper.

2. Experimental

2.1. Sample preparation

The straight chain alkanes (catalog No. 211CX and 261CX) were purchased from Polyscience (Niles, IL, USA). The styrene (catalog No. S497-2) and methyl methacrylate (catalog No. M5590-9) monomers and high density polyethylene (catalog No. 42,796-9) were purchased from Aldrich (Milwaukee, WI, USA). All chemicals were used without further purification. The internal standard solution was prepared by mixing 1.0 g of styrene and 1.0 g of methyl methacrylate with methylene chloride solvent to a total of 50 ml, and 1.0 μl was injected in the GC system. All polymeric test samples (polybutyl acrylate and styrene–methyl methacrylate copolymers) were synthesized in the laboratory [14,15].

2.2. Instrumentation

2.2.1. Pyrolyzer

The pyrolyzer used in this study was a CDS 120 pyrolysis unit. The pyroprobe used was a Pt coil for solid samples. Solid samples (approximately 100 μg) were placed into quartz tubes and equilibrated for 10 min in a 250°C interface, then pyrolyzed at a set temperature of 700°C (actual 690°C) with a maximum heating ramp (approx. 20°C/ms) for a 20 s interval. The pyrolysis products were carried by the helium carrier gas through a transfer line (heated to

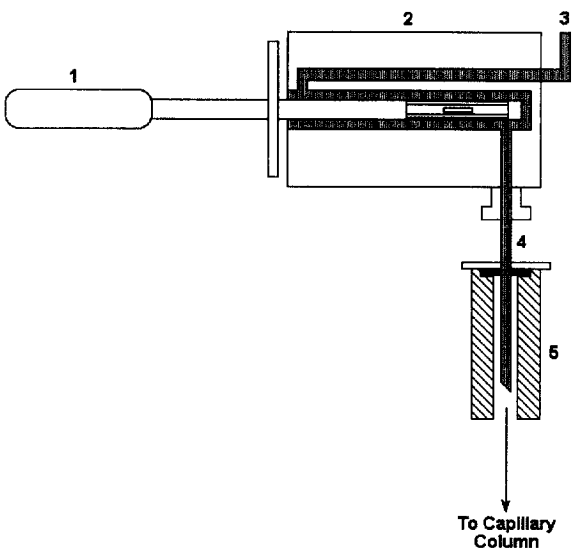

Fig. 1. Conventional Py–GC configuration. The pyrolyzer is mounted on top of the GC injection port. The output line from the pyrolyzer is directly inserted into the GC injection port. 1 = Pyroprobe; 2 = pyrolyzer interface; 3 = helium carrier gas inlet; 4 = output needle; 5 = GC injection port.

250°C) to the injection port of the GC system. The transfer line was approximately 12.5 cm long.

2.2.2. *Pyrolyzer interface*

In a Py–GC system, the pyrolyzer interface is normally mounted on top of the GC injection port. The transfer needle/line from the pyrolyzer interface output is directly inserted into the GC injection port as shown in Fig. 1. In this study, the pyrolyzer interface was inserted into the carrier gas line upstream from the GC injection port. Fig. 2 shows the position of the pyrolyzer interface and GC injection port in this set-up. The original GC carrier gas inlet line was cut to allow the connection to the pyrolyzer interface with the appropriately sized tubing. The transfer line from the pyrolyzer interface output to the GC inlet was heated to the same temperature as the pyrolyzer interface to prevent any condensation of pyrolysates before transfer to the GC. In this study, the transfer line was constructed of 1/16 in. stainless steel tubing (1 in. = 2.54 cm). If there is a concern that the pyrolysate may react with the transfer line, an inert material, such as glass lined

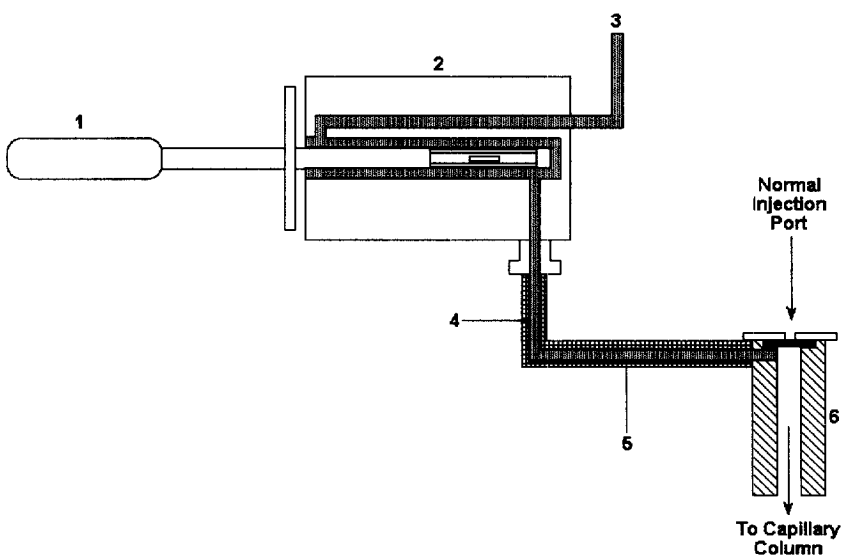

Fig. 2. Different Py–GC configuration, with the pyrolyzer attached to the carrier gas line upstream from the GC injection port. The transfer line from the pyrolyzer output to the GC inlet was heated to the same temperature as the pyrolyzer to prevent any condensation of pyrolysates before transfer to the GC. 1 = Pyroprobe; 2 = pyrolyzer interface; 3 = helium carrier gas inlet; 4 = heating jacket; 5 = transfer line; 6 = GC injection port.

stainless steel tubing or deactivated silicon capillary tubing, can be used. For Py–GC, the main advantage of this set-up is to free up the GC injection port. This extra sample introduction port can be used as an auxiliary injection port to add marker compound and internal standard introduction for qualitative and quantitative analysis by Py–GC.

2.2.3. Gas chromatography

The GC used in this study was a Hewlett–Packard (HP) 5890 gas chromatograph equipped with an HP 7673A autosampler and a flame ionization detection (FID) system. The separation was performed on a fused-silica capillary column (J&W DB-5, 30 m× 0.25 mm I.D., 0.5 μm film) using a linear temperature program (40°C for 4 min, then 10°C/min ramp to 320°C and 18 min hold), with 10 p.s.i. head pressure, and a 50:1 split ratio (1 p.s.i.=6894.76 Pa). The injection and detection area was kept at 250°C.

3. Results and discussion

The major concern when the pyrolyzer interface is not mounted directly on top of the GC injection port is the dead volume taken up by pyrolysates transfer [16]. The pyrolysates need to travel through a distance of transfer line to reach the GC inlet. During the time of transfer, the pyrolysates will spread out in the transfer line. Most of the pyrolysates will refocus in front of the capillary column because of the low-starting temperature of the oven. However, this low-temperature refocusing mechanism will only have a partial effect or no effect at all for low-boiling components in the pyrolysates. This spread of low-boiling pyrolysates in the transfer line results in a decrease in resolution in the early part of the pyrogram.

Fig. 3 is a pyrogram of high density polyethylene with the pyrolyzer interface directly mounted on the top of the injection port, and Fig. 4 is a pyrogram of

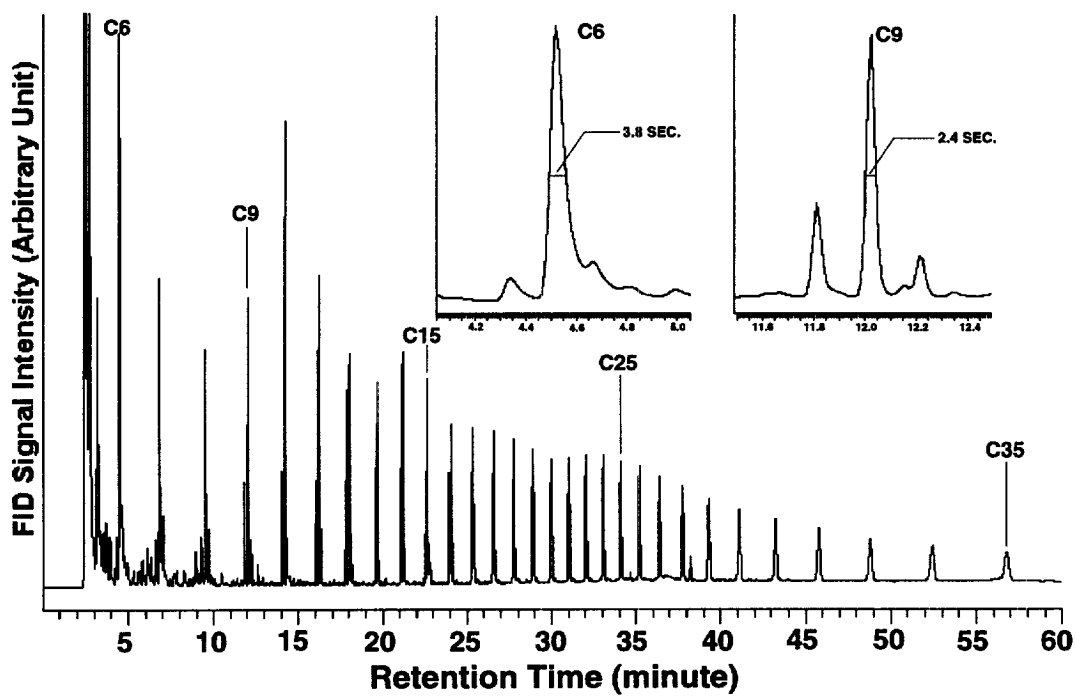

Fig. 3. Pyrogram of high density polyethylene with the pyrolyzer interface directly mounted on the top of the injection port. Oven temperature program: 40°C for 4 min, 10°C per min to 320°C for 28 min. Pyrolyzer interface, transfer line, injection port and detector were all kept at 250°C. Flow: helium at 1 cm^3 per min with head pressure 10 p.s.i. and 50:1 split.

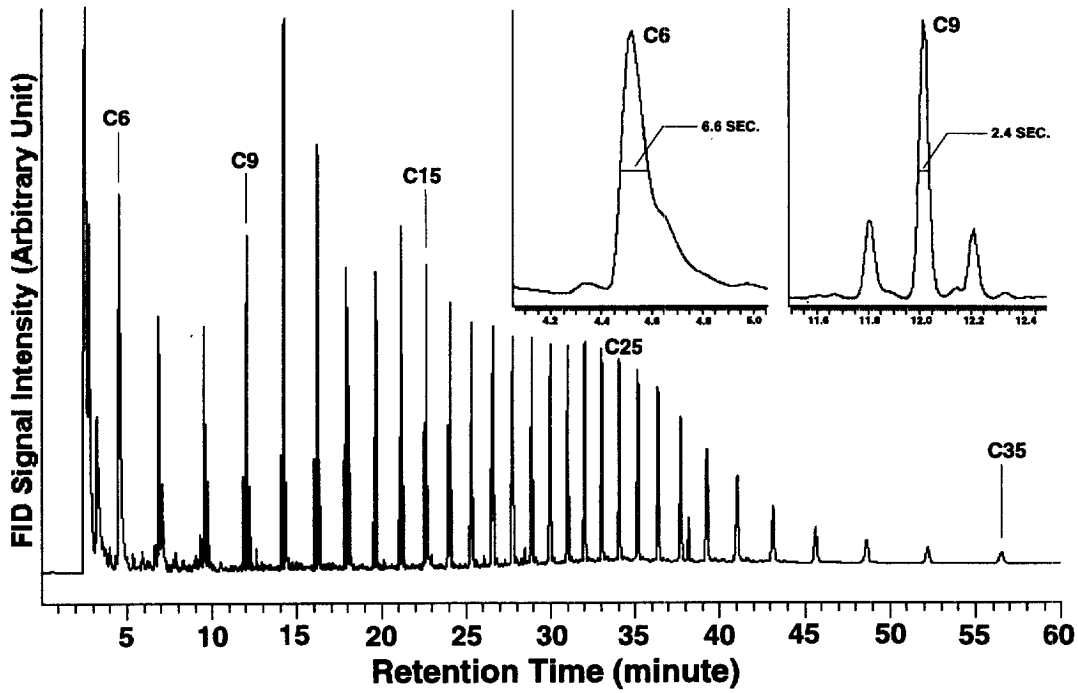

Fig. 4. Pyrogram of high density polyethylene with pyrolyzer interface mounted on the carrier gas line upstream from the injection port. Oven temperature program: 40°C for 4 min, 10°C per min to 320°C for 28 min. Pyrolyzer interface, transfer line, injection port and detector were all kept at 250°C. Flow: helium at 1 cm^3 per min with head pressure 10 p.s.i. and 50:1 split.

the same material obtained with the pyrolyzer interface mounted on the carrier gas line upstream from the injection port. The full width half maximum (FWHM) of the peak was used to demonstrate the peak broadening (spread out) effect. The C_6 peak inserts in both figures show that the FWHM of the direct mounted pyrolyzer interface was 3.8 s compared with the upstream mounted pyrolyzer interface of 6.6 s. This peak was broadened by approximately 75%. However, the C_9 peak inserts demonstrate that the peak widths, FWHM, were identical for both pyrolyzer interface set-ups (2.4 s). There was no more peak broadening in the pyrogram after this peak.

When a pyrogram is being interpreted for qualitative and quantitative analysis, the decrease in resolution in the early part of pyrogram does not have a significant effect on Py–GC information generation. The early eluting peaks in the pyrogram represents the volatile components of pyrolysates (gases), which are the results of high degree thermal degradation from pyrolyzed materials. In almost all cases, these components are not resolved under normal pyrolyzer interface set-up and GC separation conditions. Practically, these components are not useful for qualitative or quantitative analysis because there is not enough structural information. It is seldom the case that the unresolved early part of a pyrogram will be critical in a Py–GC analysis.

The peaks of semi-volatile pyrolysates (such as acrylonitrile, methyl methacrylate, ethyl acrylate, C_7, C_8 aliphatic hydrocarbons) will be broadened in the pyrogram because of this decrease in resolution. However, even with peak broadening, the shape of the peaks will still be relatively narrow and sharp. The decrease in resolution will not affect the base line resolved peaks in this region of the pyrogram. In polymer analysis, because the types of monomer are limited, it is difficult to find a polymer (even in an extreme case such as polyethylene) which contains

more than three pyrolysis products in this region. The broadened peaks in this region should be still good enough for the qualitative or quantitative analysis.

Retention time standardization (retention index) is one way to unify peak labelling, which is the base of the peak pattern comparison and matching or the minimum requirement for a database search mechanism. In this study, Kovats retention indices [17] were used as an example for nonpolar pyrolysates analyzed in a nonpolar capillary column (such as a DB-5 column). A set of straight chain alkanes were selected as markers. Regardless of the number or state (liquid or solid) of markers, they all can be properly dissolved and injected by the autosampler through the normal GC injection port along with polymers pyrolyzed through the pyrolyzer. The set of marker compounds can be run in the beginning of a series of studies or at the end of a study, or both. Sometimes, when necessary, the individual marker or several markers can be injected along with a pyrolysis sample to ensure correct retention index.

Fig. 5 shows a pyrogram of polybutyl acrylate along with six markers (C_8, C_{10}, C_{16}, C_{18}, C_{23} and C_{24} alkanes) that completely surround the four major pyrolysate peaks (butyl acrylate monomer, dimer-like, dimer and trimer) [18]. Because the markers can be injected along with the pyrolysates, the selection of markers becomes more flexible. The retention index generated from this type of marker should precisely reflect the GC conditions and elution/separation orders. The retention index will not be affected by the variation of GC operating parameters. This retention time standardization approach for Py–GC by this auxiliary port marker introduction should make the pyrogram data base creation [6] more practicable and achievable.

When using both sample injection mechanisms to introduce the sample and reference materials to the GC, the relative timing can be adjusted. The GC injection, the pyrolyzer start time and the GC data collection start time can be interconnected with a timing device to control their relative start time. This option makes the marker introduction more flexible. The markers can be presented in any region of the pyrogram, not only controlled by their elution and separation order, but also controlled by their time of injection.

Because of the availability of an auxiliary injection port for marker introduction for the Py–GC, the pyrolyzer can also be used as a marker supplier for GC experiments. The pyrolyzer can pyrolyze certain polymers to provide a set of pyrolysates which will act as a set of markers. For example, when executing high-temperature GC analysis for high-boiling compounds such as waxes, surfactants, or other high-molecular-weight polymer additives, a suitable set of pure high-boiling-point markers (or

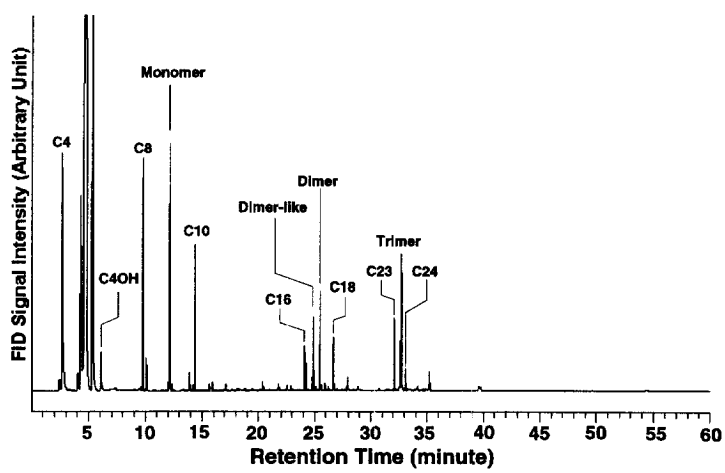

Fig. 5. Pyrogram of polybutyl acrylate along with six markers (C_8, C_{10}, C_{16}, C_{18}, C_{23} and C_{24} alkanes) that completely surround the four major peaks (butyl acrylate monomer, dimer-like, dimer and trimer).

appropriate solvents) may not be readily available. Since the pyrolysis of polyethylene will produce three peak patterns (α,ω-alkdiene, α-alkene and alkane) for every carbon number [19], any one set of them, such as the 1-alkene series, can be used to construct a retention indices system similar to Kovats retention indices.

The pyrolysis efficiency of a specific pyrolysate is important for the pyrolysis process. The pyrolysis efficiency can be defined as:

$$\text{Pyrolysis efficiency of a specific pyrolysate} = \frac{\text{Amount of specific pyrolysate produced}}{\text{Amount of sample pyrolyzed}}$$

In a Py–GC experiment, this parameter is always obtained in combination with the GC detection efficiency because all pyrolysis products are detected by the GC detector. The pyrolysis efficiency of a specific pyrolysate can be explored if a known amount of pure pyrolysate can be injected as an internal standard along with a known amount of sample pyrolyzed. The amount of pyrolysate produced from the pyrolysis process can be calculated based on the internal standard. The pyrolysis efficiency can be elucidated based on the amount of sample pyrolyzed and the amount of pyrolysate produced.

Fig. 6 shows the pyrograms of a styrene–methyl methacrylate (50:50, w/w) copolymer in addition to two internal standards (styrene and methyl methacrylate). The pyrolysis efficiency of styrene and methyl methacrylate was determined from the amount of copolymer pyrolyzed and the amount of these two monomers produced based on the calibration of internal standards. The results are listed in Table 1. The pyrolysis efficiency for styrene was 48% and the pyrolysis efficiency for methyl methacrylate was 39%.

Internal standards have been used in Py–GC quantitative analysis for a long time [20,21]. However, these standards have been limited to polymeric materials or compounds that are stable at the high pyrolyzer interface temperature. Using the set-up in this study, the internal standard selection is completely flexible. If the internal standard compound selected is the same as the compound to be quantified in the Py–GC process, the absolute amount of that compound produced by the pyrolysis can be determined. If the purpose of quantitative analysis is to determine the composition, a polymeric composition standard may still be required to calibrate the pyrolysis efficiency. Fig. 7 shows a pyrogram and Table 1 shows all calculations of a styrene and methyl methacrylate copolymer test sample (styrene–

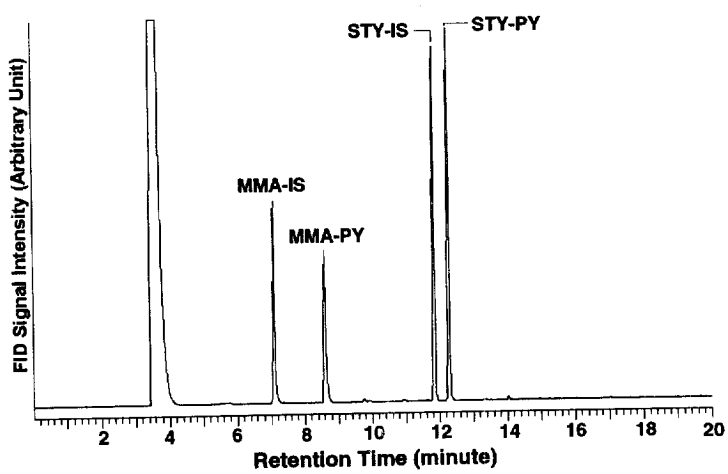

Fig. 6. Pyrograms of a styrene–methyl methacrylate (50:50, w/w) copolymer in addition to two internal standards (20 μg styrene and 20 μg methyl methacrylate). The pyrolysis was delayed 3 min. The internal standards were injected after the autosampler. The oven temperature program was 40°C for 4 min, then a 10°C/min ramp to 320°C and 18 min hold. MMA-IS = peak from methyl methacrylate internal standard. MMA-PY = peak of methyl methacrylate from pyrolysis. STY-IS = peak from styrene internal standard. STY-PY = peak of styrene from pyrolysis.

Table 1
All Py–GC quantitative analysis data and calculation results which use the internal standards injected through GC injection port

	Copolymer (50:50, w/w)	Test copolymer
Weight of sample (μg)	86	75
Peak Area of STY-IS	1 522 877	1 690 870
Peak Area of MMA-IS	897 064	1 004 256
Peak Area of STY-PY	1 572 646	874 938
Peak Area of MMA-PY	756 470	1 006 577
Amount of STY-IS (μg)	20	20
Amount of MMA-IS (μg)	20	20
Amount of STY-PY (μg)	21	10
Amount MMA-PY (μg)	17	20
PY-efficiency of STY	48%	–
PY-efficiency of MMA	39%	–
STY wt.%	50	30
MMA wt.%	50	70

MMA-IS = peak from methyl methacrylate internal standard. MMA-PY = peak of methyl methacrylate from pyrolysis. STY-IS = peak from styrene internal standard. STY-PY = peak of styrene from pyrolysis.

methyl methacrylate, 30:70, w/w) that was quantitatively analyzed by this internal standards (styrene and methyl methacrylate) method.

Table 1 lists all Py–GC pyrolysis efficiency determinations and quantitative analysis calculations of styrene and methyl methacrylate copolymer samples which utilized this technique involving internal standards injected from the GC injection port. The styrene–methyl methacrylate (50:50, w/w) copolymer was used to determine the pyrolysis efficiency of styrene and methyl methacrylate under fixed pyrolysis conditions. The internal standard not only serves as the internal quantitative measurement of the absolute amount of styrene and methyl methacrylate produced, but also performs as the reference standard to reflect the GC detection efficiency shifting. This can be seen from the internal standard peak areas detected for both copolymer pyrolysis experi-

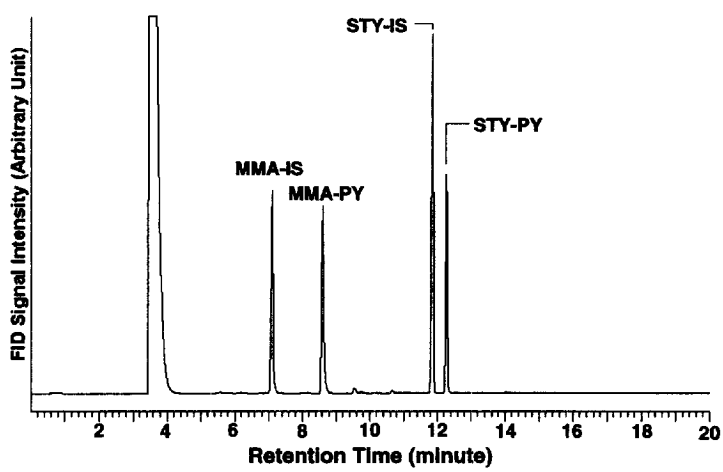

Fig. 7. Pyrograms of a styrene and methyl methacrylate copolymer with an unknown composition in addition to two internal standards (20 μg styrene and 20 μg methyl methacrylate). The pyrolysis was delayed 3 min. The internal standards were injected after the autosampler. The oven temperature program was 40°C for 4 min, then a 10°C/min ramp to 320°C and 18 min hold. MMA-IS = peak from methyl methacrylate internal standard. MMA-PY = peak of methyl methacrylate from pyrolysis. STY-IS = peak from styrene internal standard. STY-PY = peak of styrene from pyrolysis.

ments in Table 1. The composition obtained by this approach is in excellent agreement with the composition generated by other techniques. The internal standards injection through the GC injection port technique, developed from the set-up in this study, can easily be applied to Py–GC quantitative composition analysis.

4. Conclusion

The mounting of the pyrolyzer interface to the carrier gas line upstream from the GC injection port offers increased opportunities for pyrolysis technology development. The pyrolysis unit can be attached to the GC for another type of sample introduction, yet it will not affect the GC operation. This arrangement will greatly benefit those laboratories where pyrolysis work is frequently needed, but the demands are not high enough to dedicate a permanent Py–GC set-up. This set-up will also reduce the instrument down time for assembly and disassembly of the pyrolyzer interface from the GC. All Py–GC qualitative and quantitative method development can be more flexible, especially with marker injection or internal standard introduction assisted by the traditional injection port. With the set-up introduced in this study, future development of applications such as retention time standardization, data base construction and internal standard quantitative analysis by Py–GC should all be enhanced.

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