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PLASTICS ANALYSIS BY PYROLYSIS GC/MS

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Abstract

An injection head for a pyrolysis device is described which utilizes the same design for sample introduction and retrieval as the thermal desorption GC/MS device described by the authors in 1991. A commercial constant temperature furnace is used. Reproducibility of chromatograms is excellent. The pyrolysis unit does not have to be disassembled to eliminate accumulated samples. The device allows multiple reinjections of a sample. For example, thermal desorption can be done at lower temperature prior to pyrolysis. In this way pyrolysis products can be distinguished from volatile additives and components. Examples are given of analyses conducted with the new apparatus.

Introduction

In 1991 (1) the authors described an original design for a sampling device for thermal desorption gas chromatography/mass spectroscopy (TD/GC/MS). Later papers have utilized the device in a variety of analyses (2)-(6). One of its key features is the ability to remove samples from the heat to reintroduce them for further thermal desorption if results of the initial analysis warrant. Another important feature is that thermal desorption takes place in the injection port, so that volatiles are carried dynamically directly onto the GC column. Since the unit does not require a separate heater and heater controls, it is very cost effective as well as being technically excellent by reason of there being no transfer line to interfere with placement of relatively high boiling volatiles on the GC column. Gas pressure is used to eject the sample tube after thermal desorption. Gravity is the means by which the sample tube drops into the injection port.

The same design for sample introduction and retrieval has been incorporated into a pyrolytic GC/MS unit. A constant temperature commercial furnace (SGE Pyrojector) is used. Samples in quartz tubes are introduced into the middle of the furnace and can be removed for subsequent analysis. The volatiles travel to the GC column through a needle inside the injection port septum. The metal block between the furnace and the injection port is heated to ensure transport of all volatiles into the GC column.

By means of the sample retrieval feature, samples do not accumulate in the furnace, thus avoiding the necessity of dismantling the apparatus from time to time to remove pyrolyzed samples.

The temperature range of the furnace is ca. 100-1000°C, which permits thermal desorption to be conducted at the low end of the range as a separate analysis, followed by pyrolysis of the same sample. Examples of such sequential analyses are given below as well as examples of direct pyrolysis.

Pyrolysis is the method of choice for materials that do not lend themselves to identification readily by other methods. An example is copolymers, for which the identity of the comonomers can be made when they are thermally released from the copolymer and identified by GC/MS. Identification of cured thermoset resins, such as phenolic or epoxy, is aided by pyrolysis. Pyrolysis chromatograms are a function of the pyrolytic temperature. Reference materials are very helpful in identifying unknowns.

Description of the Pyrolysis Sampling Device

Figure 1 is a photograph of the device. At the top is the same sample isolation valve for controlled introduction and recovery of samples in a quartz tube as is used for TD. The heater on the injection port adaptor was added by the authors to the commercial SGE Pyrojector for transferring volatiles into the GC via the needle at the bottom of the photograph. A heat deflector separates the furnace and the sample isolation valve to minimize heating of the valve and sample by the furnace prior to placement of the sample in the furnace.

Figure 2 is a diagram of the device. No modifications were necessary for the SGE furnace or control module, which contains pressure and temperature controls for the furnace. The SGE injection port adaptor (no. 13 in Fig. 2) was modified by drilling a hole and welding a 1/16" male Swageloc fitting (no. 14) between the septum (no. 15) and bottom graphite ferrule (no. 20). This allows carrier gas to enter at the bottom of the furnace liner permitting the ejection of the sample tube.

The sample isolation valve (no. 9) used to insert samples into the furnace was modified by installing a 1/16" male Swageloc fitting (no. 6) between the top graphite ferrule (no. 20) and the sample isolation valve. This permits carrier gas to enter from the top of the furnace and drive the pyrolysis products into the injection port.

Examples of Applications

1. Adhesives for ceramic tile are mainly inorganic, with a small % (of the order of 2) of a polymeric material. Identification of the polymer has been made by pyrolysis GC/MS. Butadiene and styrene are readily identified, confirming that the polymer is styrene-butadiene rubber. Figure 4 shows these two comonomers in a pyrogram obtained at 700°C.

2. Low molecular weight polycarbonate was grafted onto glass fiber (7) via hydroxyl (OH) end groups. To prove that grafting had occurred, extraction with methylene chloride was done, followed by pyrolysis GC/MS (Fig. 5). This analysis proved that grafting had occurred.

3. Sequential thermal desorption and pyrolysis of the same sample. Figure 6 is the TD (300°C) chromatogram of a cured phenolic resin showing mainly a series of chlorinated compounds. Figure 7 is for the sample following TD, using 600°C pyrolysis temperature. Phenol and other phenolic compounds identify the resin as phenolic. The chlorinated compounds show up slightly, corresponding to the incompletely removed material from TD. Figure 8 is for direct 600°C pyrolysis of the whole resin. Using TD as a first step before pyrolysis the chlorinated material is identified as an additive, probably a flame retardant.

Figure 9 is the 300° TD of a cured phenolic/epoxy resin, showing a broad hydrocarbon peak. This peak is not seen in the direct 600°C pyrogram (Fig. 10), so that its presence would not be known if only pyrolysis was done. The epoxy resin is identified by the bisphenol A peak, and phenolic resin from the phenolic peaks.

Conclusions

The pyrolytic sample device described brings to pyrolysis GC/MS the same advantages that the design has in TD/GC/MS. Pyrolysis GC/MS is a very sensitive method of identifying resins and other materials which require thermal breakdown to permit their analysis. For formulations containing volatile material it is advantageous to perform TD before pyrolysis. The design permits such sequential analysis.

References

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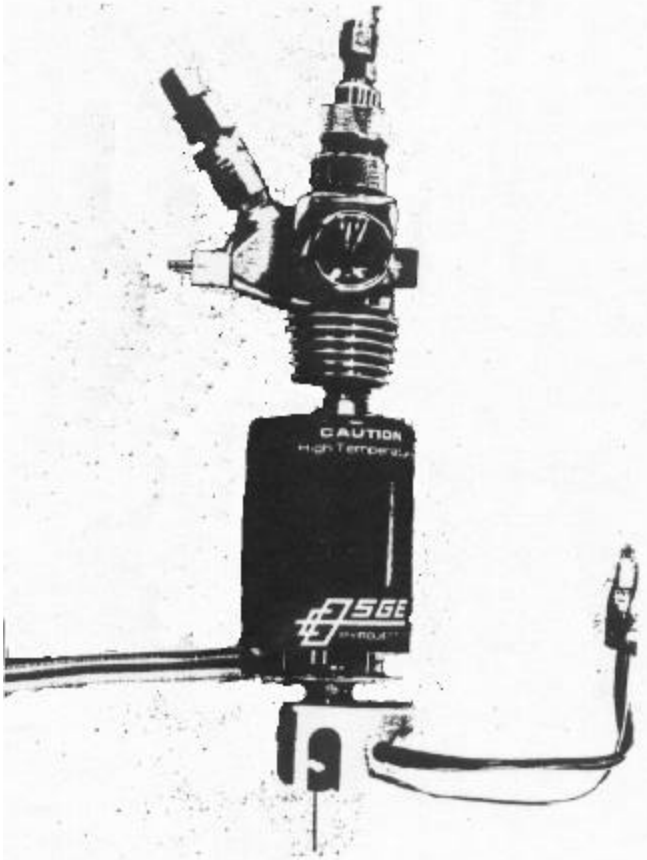

Fig. 1 - Photograph of direct dynamic pyrolytic device utilizing SGE Pyrojector furnace.

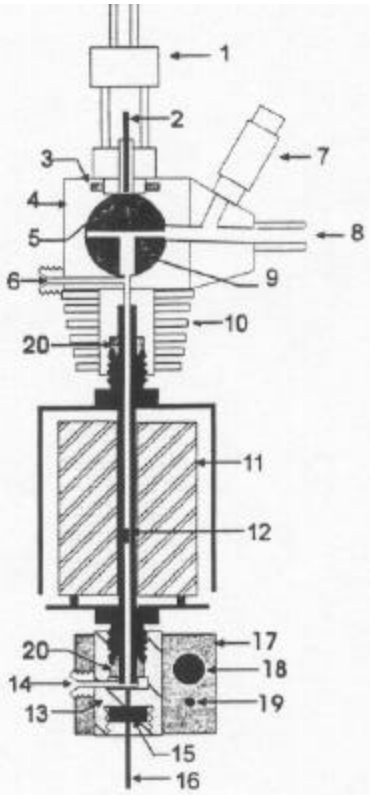

Fig. 2 - Diagram of pyrolytic device. 1. Sample loading cover, 2. Quartz sample vial, 3. Sample loading cover interlock, 4. Valve body, 5. O-Ring seal, 6. Carrier gas inlet, 7. Check valve, 8. Carrier gas outlet, 9. Sample isolation valve, 10. Heat deflectors, 11. SGE furnace, 12. Modified quartz tube and stop, 13. Modified SGE adaptor unit, 14. Carrier gas inlet, 15. Silicone septum, 16. Modified SGE needle assembly, 17. Heater block, 18. Cartridge heater, 19. Thermocouple, 20. Graphite ferrule.

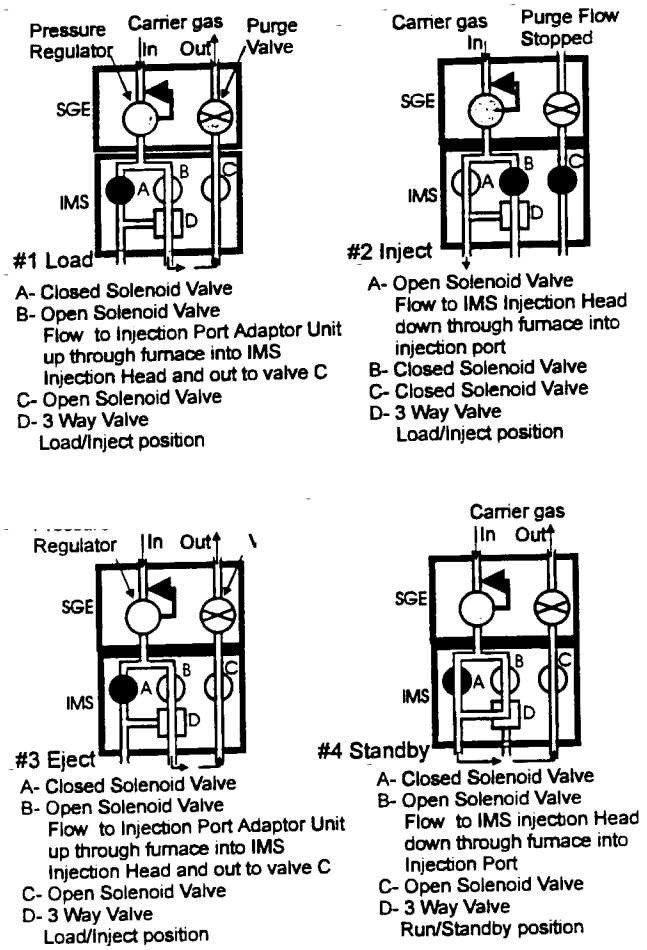

Fig. 3 - Operation of pyrolytic valve and flow control. SGE - furnished by SGE; IMS - built by Institute of Materials Science.

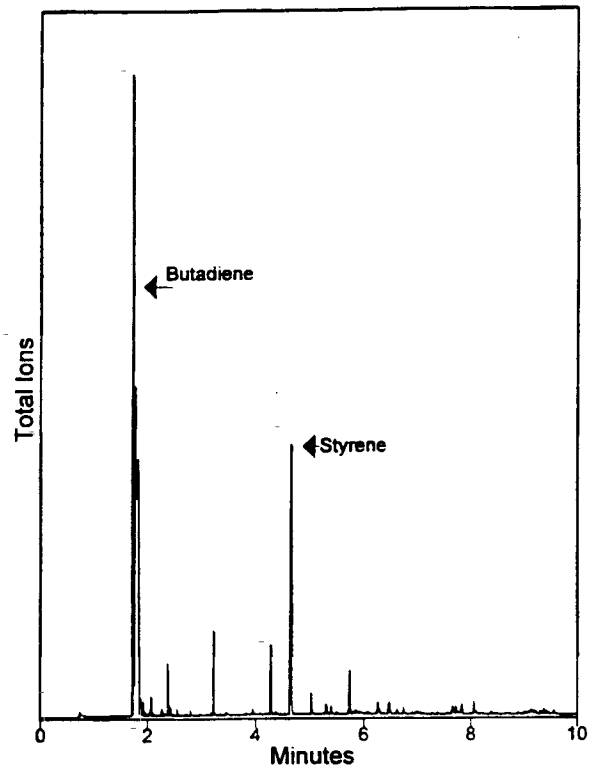

Fig. 4 - Pyrolysis chromatogram (700°C) of polymer additive in ceramic tile adhesive.

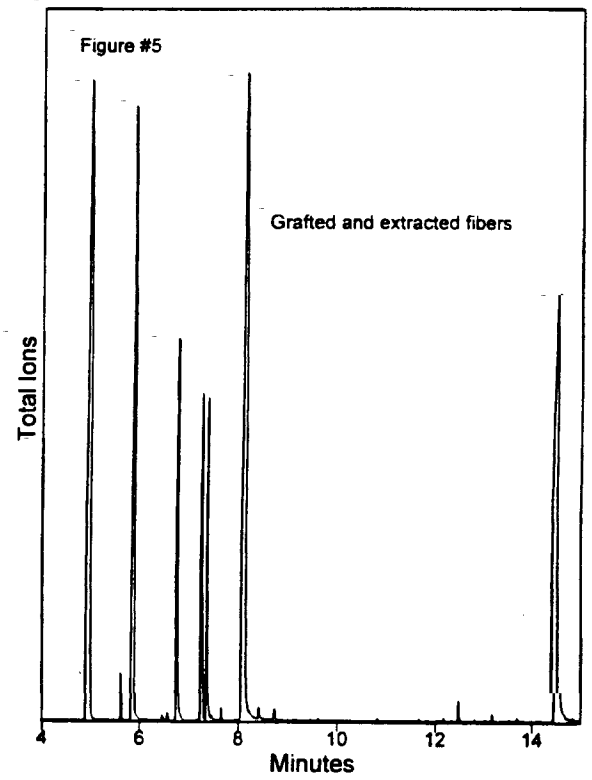

Fig. 5 - Pyrolysis chromatogram (650°C) of polycarbonate grafted onto glass fiber.

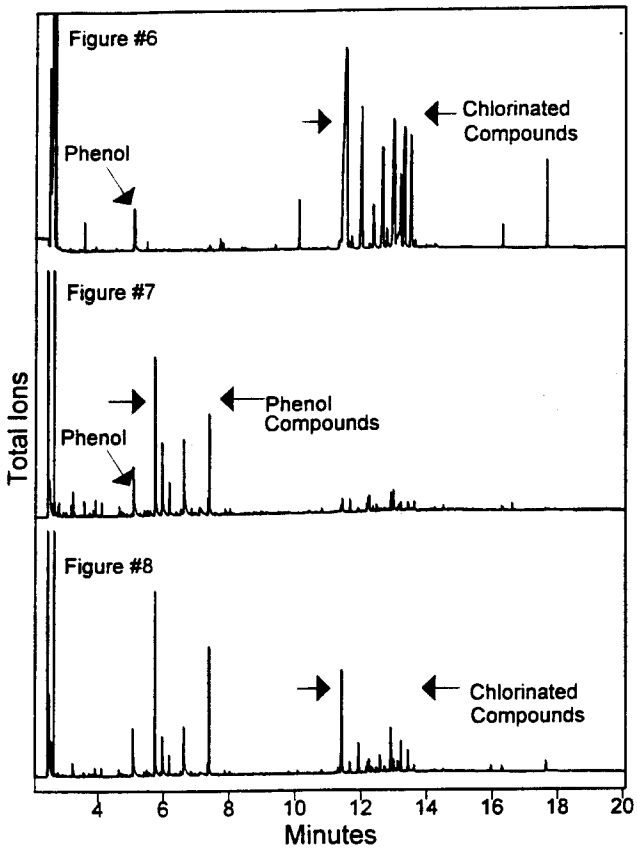

Fig. 6 - Thermal desorption GC (300°C) of a cured phenolic resin.

Fig. 7 - Pyrolytic chromatogram (600°C) following thermal desorption (Fig. 6).

Fig. 8 - Pyrolytic chromatogram (600°C) of phenolic resin of Fig. 6 and 7 without prior thermal desorption.

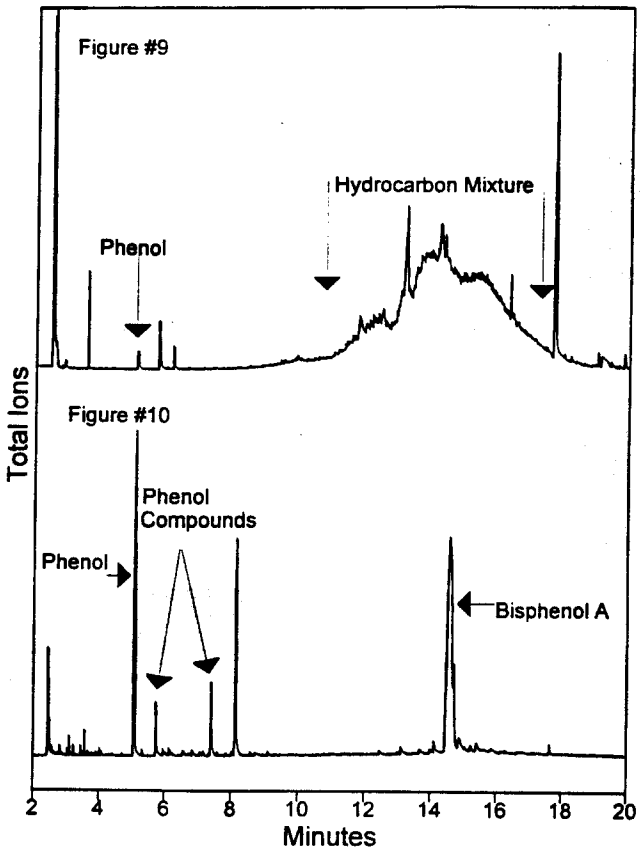

Fig. 9 - Thermal desorption (300°C) of a cured phenolic/epoxy resin.

Fig. 10 - Pyrolytic chromatogram (600°C) of a cured phenolic/ epoxy resin without prior thermal desorption.

Key Word/Phrase Index

Plastics analysis; pyrolysis GC/MS; thermal desorption GC/MS