

NOTES

Introduction of Polymer Samples into a Microreactor

There is considerable interest in studies of the thermal degradation of polymers with increasing attention being given to analysis of the products obtained when polymers are pyrolyzed in the absence of air or oxygen. In addition the intractability of a large number of polymeric materials has led to pyrolytic methods being used for the analysis of such substances. At the present time the technique of microreactor gas chromatography (MRGC) is being increasingly exploited as a method for the rapid identification of a considerable range of complex organic materials, and in the analysis of the pyrolysis products obtained in studies of the thermal stability of polymers. In principle this method consists of directly coupling a microreactor, where the sample is pyrolyzed at 150–1000°C., to a gas chromatographic column in which the pyrolysis products are separated. These products may be identified, or the pyrogram pattern may be used, to assess the nature of the original material, and this method has been applied to the identification of such substances as polymers, barbiturates, and amino acids. The major problems that arise in the application of MRGC are the introduction of the sample into the reactor and the design of a reactor in which the sample is completely pyrolyzed at a uniform temperature. Usually, the method of admission and pyrolysis of the sample have been combined by using an electrically heated filament previously coated with sample by immersion in a solution or slurry of the polymer sample.^{1–4} This method suffers from several disadvantages, firstly that a sometimes lengthy pretreatment of the sample is required, although in one modification^{5,6} this has been overcome by placing the sample in an electrically heated boat. Secondly, these methods lead to the sample being pyrolyzed over a range of temperatures due to the time required for the electrical heating element to reach its equilibrium temperature, and even when this is very small there exist severe temperature gradients in the reaction zone.^{1,7} In addition, the sample is decomposed from the inside which can lead to sputtering of the sample, unless it is in the form of a very thin film,⁷ and consequent incomplete and nonquantitative decomposition. A few workers have separated the sample admission device from their microreactor^{8,9} which was a heated tube packed with a fibrous material. In another method¹⁰ samples mixed with metal powder are pyrolyzed by induction heating. These methods have not been applied to the complete range of physical form that a polymer sample may take, ranging through mobile liquids, viscous liquids, sticky solids, rubbers, and rigid solids, and this communication describes a simple and versatile sample admission device which can handle this range of physical form which has been used by the authors in their studies.

The reactor used, *R* in Figure 1, consists of an electrically heated 7 mm. i.d. medium wall quartz tube mounted vertically and packed in the lower 7 cm. of the 9 cm. heated zone with quartz wool. The chromatographic carrier gas enters the apparatus at *A* and flows via the reactor into the analytical column. About 200 μ g. of the polymer sample is placed on the spoon of the rod *C* and any air entrapped in the apparatus by fitting the spoon in the position shown in the diagram is gently flushed out by opening *T* and squeezing the rubber seal *D* until a small leak develops. The bore of the key of the tap *T* is adequate to permit easy passage of the spoon and sample into the carrier gas stream at *E*. When in this position, and after any residual air trapped in the sample has had time to diffuse out, the spoon is inverted and the sample allowed to fall into the microreactor at *B*, the spoon being withdrawn and *T* closed. "Sticky" samples are dusted with powdered quartz wool before admission to prevent their adhering to the

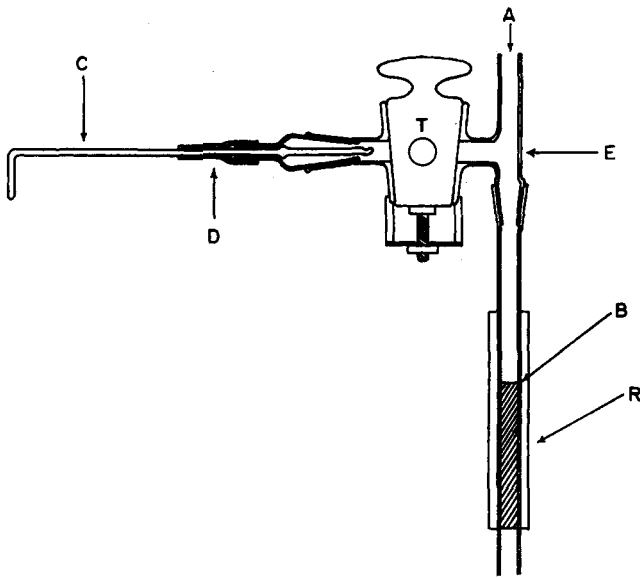


Fig. 1. Construction of the sample introduction device.

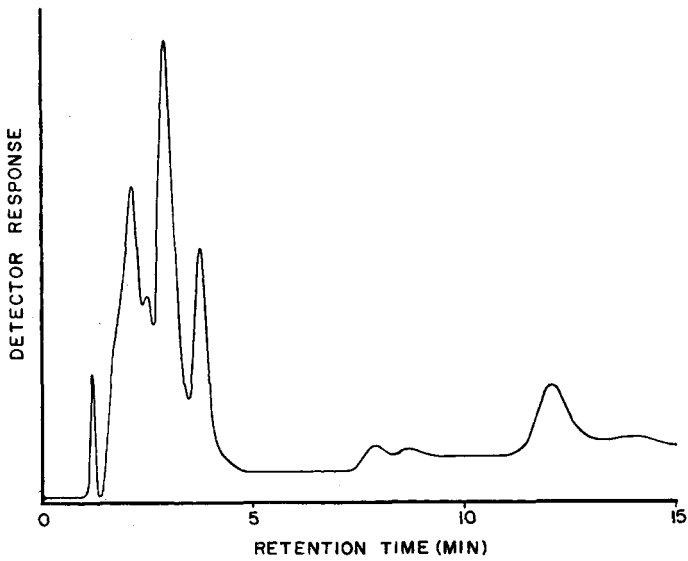


Fig. 2. 700°C. Pyrogram of a polyester resin obtained using 1 metre \times 4 mm. column of 17% M.S. 550 Silicone Oil on 80-100 mesh Celite, carrier gas Argon, 30 ml. min.⁻¹, inlet pressure 1.3 atm. 0°C.

spoon, and for the same reason very small "dry" samples of materials exhibiting electrostatic effects are wrapped in a small ball of quartz wool before being placed in the spoon. Liquid samples are admitted by wetting a piece of quartz wool with the sample and carefully rolling the wool into a ball with the liquid at its center, the ball being treated as a

solid sample. The chromatographic column is calibrated by the introduction of known gases and vapors into the carrier gas stream at *A* through a conventional serum cap fitted to a *T* junction, and an allowance made for the volume of the apparatus between *A* and *B*.

In these ways the whole range of physical form that polymer samples take can be admitted to the reactor with a minimum of preliminary treatment. That samples admitted in this manner are rapidly pyrolyzed is demonstrated by the sharpness of the peaks in the pyrogram of a sample of Bakelite polyester resin, grade SR 18995, shown in Figure 2. Pyrograms of this type may be used for the qualitative or quantitative analysis of the polymer sample, or the products identified in order to obtain information on the mode of degradation of the polymer.

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On page 519, right-hand side, line 14, the number "17,000" should be "7,000."