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The Evaluation of Two Pyrolyzers for the Analysis of Insoluble Polymers

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ABSTRACT

Two devices were evaluated in the pyrolysis-gas chromatographic analysis of a linear polyethylene standard. The Chemical Data Systems Coil Probe, a pulse-type pyrolyzer, and the Du Pont 950 Thermogravimetric Analyzer, a continuous heat-type unit, were studied. The latter was connected to the gas chromatograph using an interface designed to allow on-column collection of pyrolyzates.

It was found that the coil probe yields reproducible results in the analysis of linear polyethylene, and the distribution of pyrolysis products obtained is essentially unaffected by changes in heating rate, time, and final heating temperature, provided these parameters are above certain experimentally determined values. This behavior may be explained by the action of the quartz tube sample holder as a heat transfer barrier between the heating coil and the sample. Large size samples enhance the formation of secondary products. The most serious shortcoming of the device is the difficulty involved in quantitating sample size.

It was further found that the proposed thermogravimetric analysis-gas chromatography interface had only limited usefulness because of back-diffusion. Condensation in the

transport lines and formation of secondary products presented some problems. The results were reproducible and product distribution was not effected by changing heating rate and sample size. Isothermal operation of the thermal balance yielded satisfactory results and shortened the analysis time considerably.

INTRODUCTION

In order to further the art of pyrolysis-gas chromatographic analysis of insoluble polymers, we have evaluated the performance of two pyrolyzers, the Chemical Data Systems Coil Probe, a pulse-type unit, and the Du Pont 950 TGA, a continuous heat pyrolyzer. Both of these instruments are capable of handling genuine solid samples without the use of solution techniques, and they also allow controls over such important variables as heating rate, temperature of pyrolysis and heating time. In the course of this work, a new thermogravimetric analysis-gas chromatography (TGA-GC) interface utilizing on-column trapping rather than external traps was used and evaluated.

The technique of pyrolysis-gas chromatography has been reviewed extensively [1-3]. This method of analysis has not developed to its full potential because of lack of interlaboratory communication due to the use of nonstandardized equipment and operating methods.

The first generation of pyrolyzers were either the oven [4] or the filament type [5]. The only variables which were controlled to some extent were the final temperature and time of pyrolysis. Consequently, the technique was marked by irreproducible results. The search for an optimized pyrolyzer with improved design and operation resulted in the recognition that the method of heating, the heating rate, and the sample size and geometry are important parameters to be considered [2, 6]. A second generation of pyrolyzers was developed and characterized by pulse-type application of heat as opposed to the continuous method of heating of the oven-type pyrolyzers [2]. The pulse-type pyrolyzers are characterized by extremely rapid heating rate (rise time), accurate control of final temperature, and extremely small sample size. The Curie point pyrolyzer [7, 8] and the Chemical Data System ribbon probe [9] are examples of pulse-type pyrolyzers. It is required in the operation of these instruments that the polymers investigated be dissolved in a solvent. The aliquots of this solution are then transferred onto the pyrolyzer where, upon evaporation of the solvent, a polymer film remains which is subsequently pyrolyzed. The technique described above is obviously not applicable for cross-linked and/or insoluble polymers, but these are the materials in whose characterization pyrolysis-gas chromatographic analysis is most essential.

EXPERIMENTAL

Reagents

Linear polyethylene:	NBS Standard 1475
Polystyrene $M_w = 2,500,000$:	Waters Associates
Polystyrene $M_w = 5,000$:	Waters Associates
Hydrocarbon kits:	Polyscience Corp.

Apparatus

Chemical Data System Pyroprobe 100 equipped with ribbon and coil probe. The latter was used exclusively in the present work. It consists of a platinum coil into which a quartz tube containing the sample is placed. It is possible to control the heating rate, the final temperature of the coil, and the time of heating.

Du Pont 950 Thermogravimetric Analyzer modified to allow purge gas to enter at the back (tare weight end) of the instrument.

Perkin-Elmer 900 Gas Chromatograph equipped with dual columns and dual flame ionization detectors and without a subambient over cooling accessory.

The interface between the thermal balance and the gas chromatograph was designed for on-column collection of pyrolyzates with the use of cold traps. A Pyrex female ball joint was attached to the quartz furnace tube of the TGA with a clamp. The opposite end of the Pyrex tube was connected through a graded seal to 1/16 in. o.d. stainless steel tubing, which in turn was attached via a "swage lock" fitting to the injector insert of a Perkin-Elmer gas sampling valve. The exit portion of the furnace tube which is outside the oven and the adjoining transport lines were maintained at a temperature of 250°C with the aid of Perkin-Elmer "mass spec"-type heating tapes and variacs. Two separate tanks of helium are required: one serves as carrier gas for the GC while the other is used as the purge gas for the TGA. A schematic diagram of the TGA-GC system is shown on Fig. 1.

ProcedureCDS Coil Probe

About 500 μg of polymeric material was placed in the quartz tube which was then inserted into the platinum coil of the probe. The assembly was attached to the gas chromatograph and allowed to equilibrate for 10 min, at which point the sample was pyrolyzed and analyzed by the gas chromatograph.

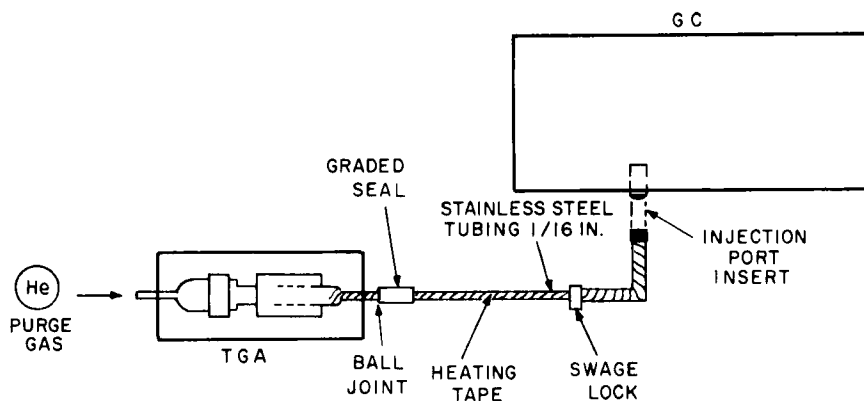


FIG. 1. Schematic representation of TGA-GC interface.

Thermogravimetric Analyzer

The sample was placed into the instrument which was then purged with 200 ml/min of helium for 30 min without being connected to the GC. Simultaneously, the gas chromatographic column was cooled to 0°C. The helium flow to the gas chromatograph was then shut off, the septum cap removed, and the injector insert of the interface was placed into the gas chromatograph. At this point the gas flow through the columns was supplied by the TGA purge gas. The sample was then heated to 900°C and the pyrolyzate collected on the GC column. Upon completion of the pyrolysis step, the injector insert was removed from the chromatograph, the septum cap was replaced, and the carrier gas flow reinstated. After the establishment of equilibrium, the pyrolyzate was analyzed gas chromatographically.

Gas Chromatograph

The operating conditions were as follows:

Column:	12 ft, 1/8 in. diameter 10% Dexsil on Chromosorb W
Detector:	Dual flame ionization
Injector port temperature:	250°C
Manifold temperature:	250°C
Column temperature:	Coil probe experiments: program 50 to 300°C at 13°C/min TGA experiments: program 0 to 300°C at 13 or 26°C/min

Qualitative identification of peaks was achieved through the use of *n*-alkane mixture calibration curves. Quantitative peak area measurements were done by multiplying the peak height by one-half of the peak width.

RESULTS AND DISCUSSION

Evaluation of CDS Coil Probe

The Chemical Data System Pyroprobe 100 [9] is a versatile instrument with a capability of controlling heating rate, final temperature, and time of heating. It is equipped with two probes. In one, a platinum ribbon is used as a sample holder, heating element, and sensing device, while in the other probe the sample is placed into a quartz tube which in turn is inserted into a platinum heating and sensing coil. The sophisticated controls available on this instrument apply mainly to the operation of the ribbon probe. In the case of the coil probe, the heating parameters of the platinum coil are well controlled, but the quartz tube sample holder represents a formidable barrier to heat transfer between the heating coil and the sample. In spite of this basic shortcoming, the coil probe was found to be a more practical device for analysis of solid samples. The ribbon probe requires that the sample be dissolved and plated out on it or be melted in the solid state. Many polymers are insoluble or decompose upon melting, thus making the use of the ribbon probe impossible. Furthermore, many polymers yield inorganic residues upon pyrolysis which may short out the platinum ribbon.

The variables studied in connection with the coil probe were heating rate, heating time, final heating temperature, and sample size. Linear polyethylene was used as a sample. A typical chromatogram is shown in Fig. 2. Experiments were carried out to study the effect of final temperature on the pyrolysis process. Samples weighing approximately 500 μg were pyrolyzed at 500, 600, 700, 800, or 900°C (these are temperatures of the platinum coil, not of the sample). The heating rate was maintained at 1°C/msec and the heating time was 10 sec. No pyrogram was obtained at 500 and 600°C settings. The distribution of pyrolysis products was quite similar and reproducible at 700, 800, and 900°C settings (Fig. 3). These results are not surprising, for the TGA analysis of polyethylene showed a single sharp decomposition step at 500°C.

Heating rates of 0.1, 1, and 10°C/msec were investigated. In these experiments the final pyrolysis temperature was 900°C and the heating time was 20 sec for 0.1°C/msec and 10 sec for the other two heating rates. Again no marked differences were observed in product distribution as a result of varying the heating rate. Similarly, the product

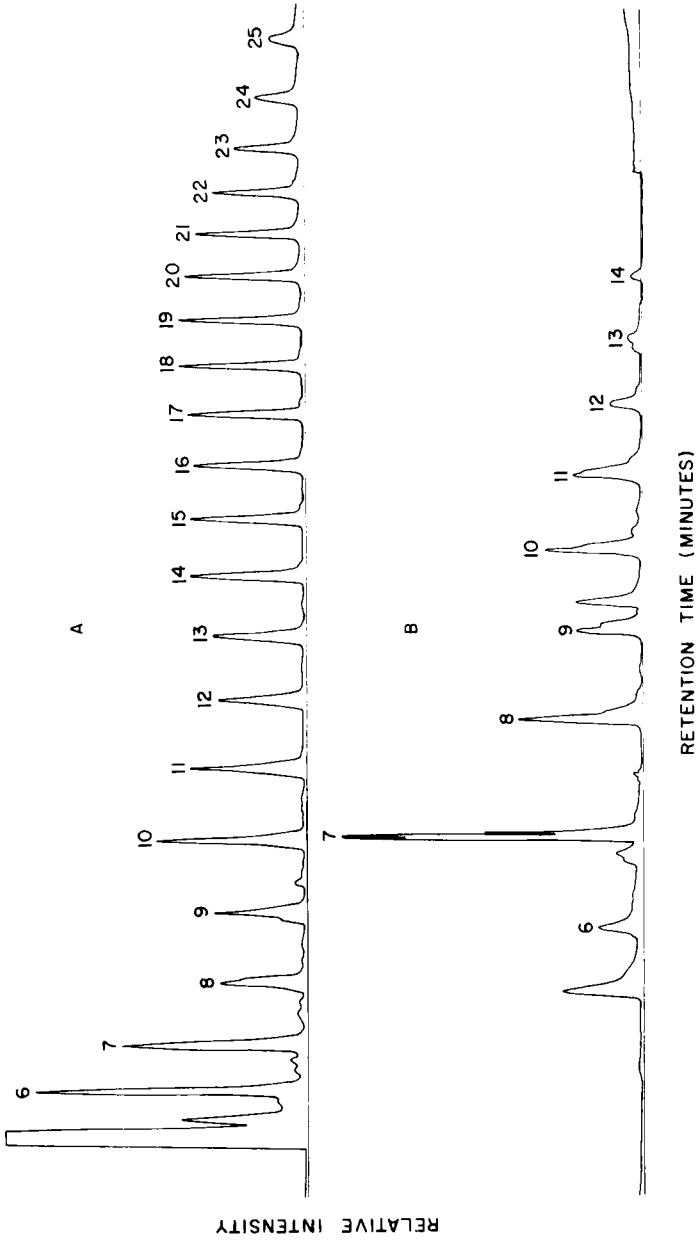


FIG. 2. Typical pyrogram of linear polyethylene using CDS coil probe (A) and TGA-GC system (B).

distribution was not seriously affected by varying the heating time between 2 to 10 sec while maintaining the heating rate at $1^{\circ}\text{C}/\text{msec}$ and the final temperature at 900°C .

Increasing the sample size from 0.5 to 5 mg resulted in the formation of secondary products as shown by the appearance of many extraneous peaks, especially at the low molecular weight section of the chromatogram.

Apparently in the pyrolysis of linear polyethylene with the coil probe, there is a definite temperature (700°C setting) and a heating time (heating time equals rise time) below which pyrolysis will not occur. Above these boundary conditions the behavior of the sample is essentially unaffected by variation in instrument settings. This situation is brought about by the presence of the quartz tube between the heating coil and the sample, and because of the relative insensitivity of polyethylene to changes in pyrolysis temperature. In the analysis of polystyrene the expected change occurred in product distribution as a function of temperature. At 500°C the products were styrene and its dimer, while at 900°C a great many additional products were also found.

Obviously, reproducibility of results requires careful quality control of the material and geometry of the quartz tube. An additional factor is that upon repeated use, the platinum coil anneals or deforms and will not heat uniformly. According to the manufacturer, this situation has been remedied on the newer models. The greatest single shortcoming of the coil probe is the difficulty involved in quantitating sample size. It requires a microbalance and tedious operation. A $500\text{-}\mu\text{g}$ sample size was found to be too great, for a condensed film of polymer was often found at the exit end of the quartz tube.

In order to alleviate some of the problems of quantization, we are presently involved in the development of an internal standard method for the coil probe. Polymethyl methacrylate upon pyrolysis yields a single major compound, the monomer, and thus can be used as an internal standard. The feasibility of this method is illustrated by the data appearing in Table 1.

Thermogravimetric Analyzer

The application of the thermogravimetric analyzer as a gas chromatographic pyrolyzer was pioneered by Chiu [10, 11]. He has pointed out the advantages of this approach as precise control over heating rate, good reproducibility, no necessity to search for optimized pyrolysis conditions, the possibility of analyzing the products of pyrolysis from each thermal degradation step separately, and the obtaining of important additional information from the thermogram regarding sample size and degradation temperatures. Subsequently, Cukor and Lanning demonstrated the usefulness of an instrument combination

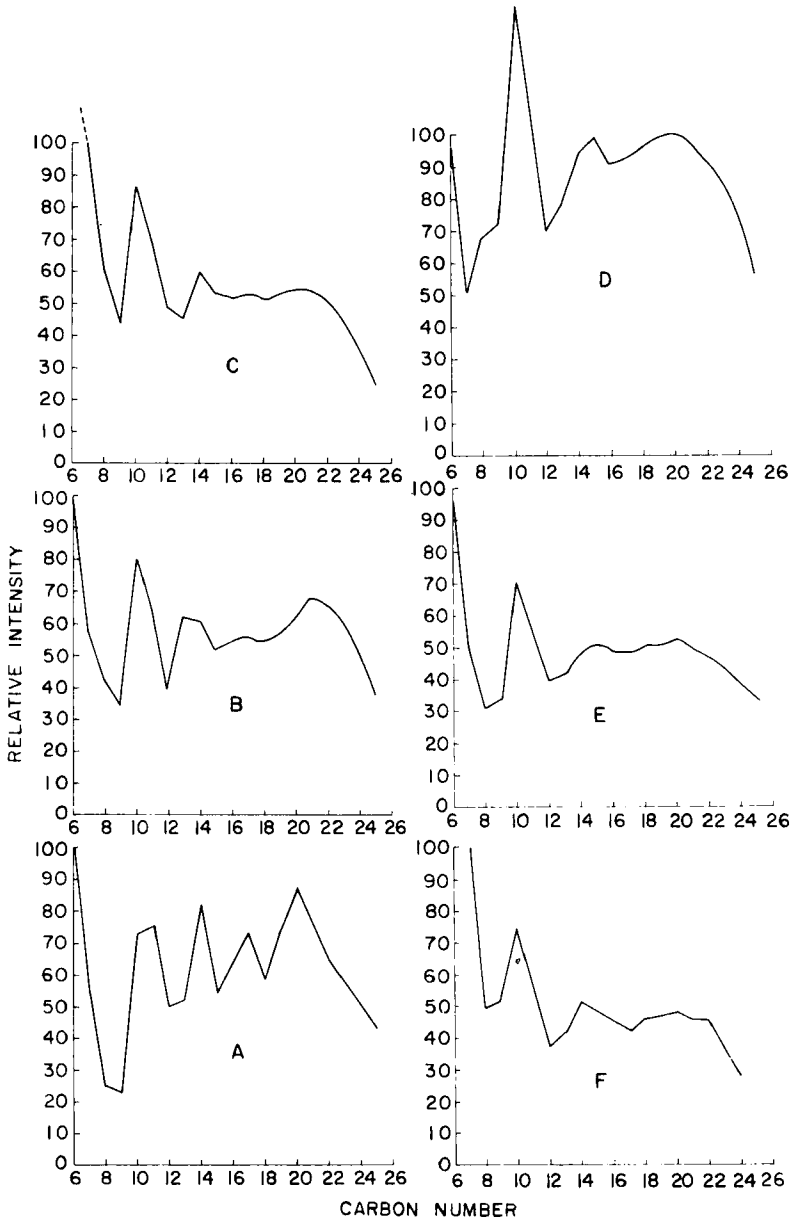


FIG. 3. Relative distribution of pyrolysis products of linear polyethylene using CDS coil probe: continued—

consisting of TGA-GC-IR for the analysis of organic mixtures [12]. Similarly, Chang and Mead combined TGA, GC, and mass spectroscopy for the analysis of polymers [13]. The present effort is aimed at continuing these developments. It is directed toward two major areas: 1) investigating the feasibility of on-column trapping with a TGA-GC system, and 2) evaluating the effect of heating rate and sample size on the performance of the TGA as a pyrolyzer.

In order to investigate the feasibility of on-column collection of the pyrolyzate, the effect of prolonged cooling and slow trapping was initially studied. A mixture of n-alkanes was chromatographed under several conditions:

1. Injection: temperature programming from 50 to 300°C at 26°C/min.
2. Injection: temperature programming from 0 to 300°C at 26°C/min.
3. Injection: hold at 0°C for 30 min, then programming to 300°C at 26°C/min.
4. Using the TGA for sample introduction employing 30°C/min heating rate, collecting on the column at 0°C, then programming to 300°C at 26°C/min.

The data obtained indicated that, with the exception of the lowest molecular weight components of the mixture (C₆ to C₉), no drastic band broadening was taking place at this rapid heating rate (26°C/min). The observed band broadening of the low molecular weight hydrocarbons could probably be eliminated by further lowering the sample collection temperature. It was also noted that repeated cycling of the Dexsil column between 0 and 300°C did not affect its performance adversely.

In the course of these experiments, the formation of condensate films was observed on the wall of the furnace tube toward the cold end

continued from opposite page

Curve	Final temperature (°C)	Heating time (sec)	Heating rate (°C/msec)
A	700	10	1
B	800	10	1
C	900	10	1
D	900	2	1
E	900	20	0.1
F	900	10	10

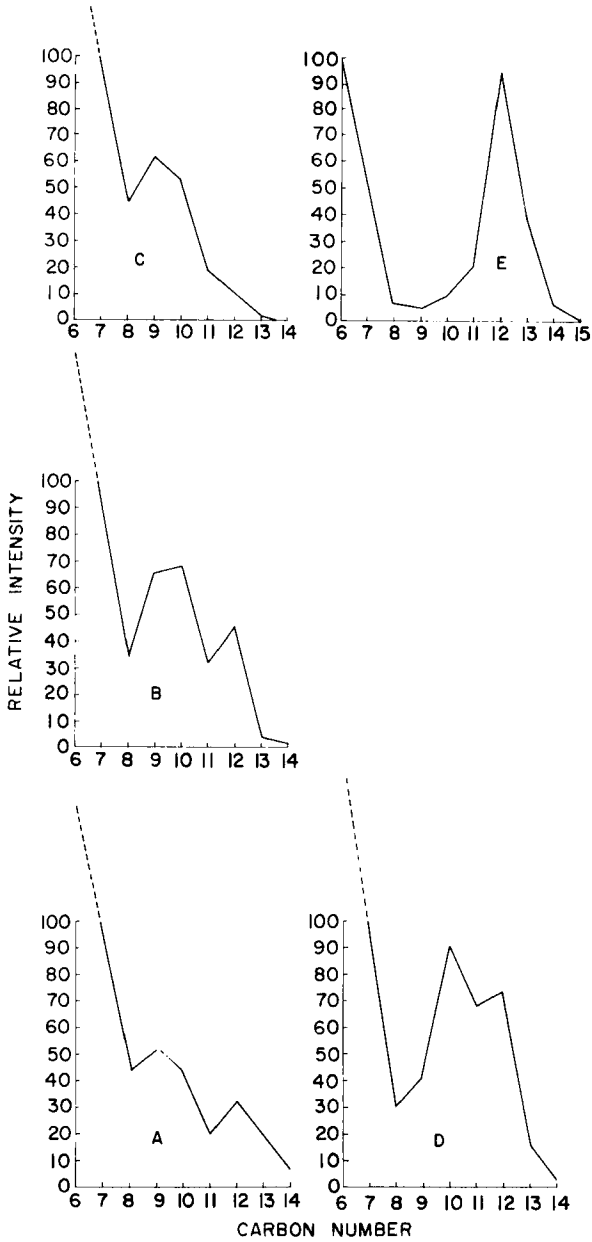


FIG. 4. Relative distribution of pyrolysis products of linear polyethylene using TGA-GC system: continued—

of the balance. The condensation was due to back-diffusion and sputtering of the pyrolyzed fragments. The geometry of the furnace tube, because of its large volume, is not ideal for use as a pyrolyzer. Rapid purging may alleviate this difficulty, but a flow rate of over 200 ml/min was found to cause a large noise signal in the operation of the balance. This back-diffusion problem is particularly serious if the thermal degradation yields gaseous corrosive products such as hydrochloric or acetic acid. In such an instance, severe damage to the balance mechanism will result.

Ideally, transport lines should be maintained at temperatures above the boiling point of the least volatile component. In the case of the pyrolysis of linear polyethylene, this would require maintaining the lines at 400°C, which is a formidable task. Instead, we chose to keep the transport lines at 250°C and allowed hydrocarbons heavier than octadecane to condense at the exit of the furnace tube, making sure all along that this condensate did not produce a memory effect.

Finally, we also noted that secondary reactions occur among the products of pyrolysis. In the pyrolysis of polystyrene, we obtained seven or eight major products instead of the anticipated styrene and its dimer. Chang and Mead reported similar results [13].

The effect of heating rate and sample size on the distribution of pyrolysis products was also investigated using linear polyethylene samples (Fig. 2). No drastic differences in the distribution of products were observed due to varying the heating rate from 10 to 30°C/min or varying sample size from 1 to 25 mg (Fig. 4). A minor difference in product distribution was observed when the TGA had been used in an isothermal manner at 800°C. It took 2 to 3 min for the sample to reach this temperature. The isothermal heating mode shortens the time of analysis considerably, and it is fairly reproducible. The data are summarized in Fig. 4.

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Curve	Heating rate (°C/min)	Sample size (mg)
A	30	1.3
B	30	5.0
C	30	25.0
D	10	4.0
E	Isothermal at 800°C	4.2

TABLE 1. Evaluation of Internal Standard Method

μE	Polyethylene		Polymethyl methacrylate		Ratios	
	Response of C_{12} fragment	Response of C_{20} fragment	μg response	Methacrylate response	C_{12} Peak/sample wt, mg	Peak/sample wt, mg
450	123	102	2	266	1.0	0.85
390	376	228	2	696	1.4	0.84
350	204	125	2	396	1.4	0.91
650	200.0	179	2	286	1.1	0.95

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