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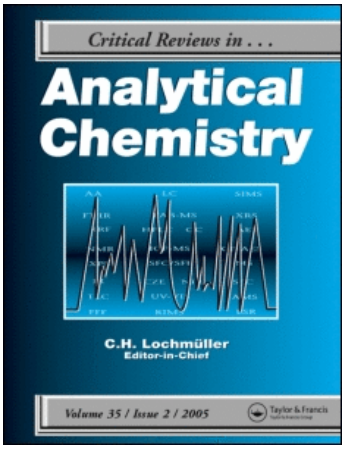

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THE DEVELOPMENT OF PYROLYSIS GAS CHROMATOGRAPHY

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I. INTRODUCTION

Pyrolysis gas chromatography (PGC) is an indirect method of investigation in which the sample is pyrolyzed, the resulting volatile products are analyzed by gas chromatography (GC), and the substance under investigation is characterized on the basis of GC of the volatile products of its pyrolysis. By qualitative and quantitative analysis of the products formed in the pyrolysis of the sample, one can determine the structure and composition of the system under study. Unlike other chemical methods widely used in PGC, pyrolysis is a complex reaction normally proceeding in many directions and involving many stages. Nevertheless, despite these difficulties, the resulting products are adequately representative of the composition and structure of the pyrolyzed samples, which is precisely what makes PGC a valuable method and provides for its development.

As a rule, pyrolysis yields a complex mixture of products. This undoubtedly renders the interpretation of the results of analyzing various substances by PGC more difficult. The difficulties involved, however, are not serious, and PGC is extensively used in the analytical practice, e.g., in analysis of polymers, nonvolatile organic compounds and microbiological objects.

Analytical pyrolysis is one of the most important methods of analytical chemistry. Thermal degradation and subsequent analysis of the degradation products have long been used for the qualitative and quantitative analysis of nonvolatile compounds and for determining their structure.[1-6] The use of GC analysis of pyrolysis products has increased the practical value of the method because only certain of the products contained in the complex mixture formed are characteristic of a particular sample.

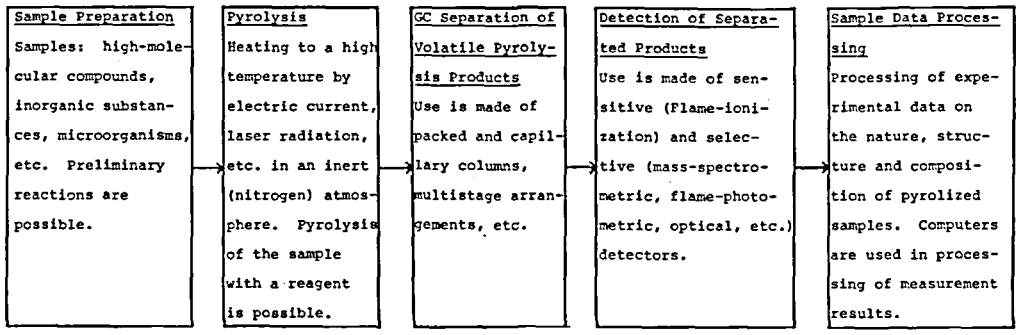

FIGURE 1. Flow chart of analytical experiment in PGC.

The use of GC for analyzing pyrolysis products is characterized by the following principal advantages of GC as an analytical method:

1. The use of sensitive detectors permits injecting small samples in volumes as low as a milligram or several tens of micrograms.
2. The high efficiency of separation on packed columns (1×10^3 to 3×10^3 theoretical plates) or capillary columns (10^4 to 10^5 theoretical plates) permits isolating "characteristic" products among the plurality of many resulting compounds.
3. The analysis time is short and ranges from several minutes to several tens of minutes.
4. Standard chromatographic equipment is used for the separation, and the pyrolysis unit is a small self-contained attachment to a standard chromatograph, its cost being only 10 to 20% of that of the chromatograph.

Figure 1 is a simplified schematic representation of a PGC analysis procedure.

In early works involving the use of GC for analysis of nonvolatile sample destruction products,[7-9] pyrolysis was conducted in a special unit, while the products were sampled and analyzed on a standard gas chromatograph. This method is recommended for the case where small samples (about 1 to 10 mg) cannot be taken because of the inhomogeneity of the substances of interest, as well as for studying the mechanism and kinetics of pyrolysis, evaluating the heat resistance of materials, determining the composition of products at low degrees of transformation, etc.[10]

In another, more widely used version, the processes of pyrolysis and chromatographic separation are integrated within a single instrument. Such a procedure for investigating polymers by pyrolyzing a sample in a special reactor upstream of the GC column in the carrier gas flow was first described by Lehrle and Robb.[11] This method features a number of advantages, namely: (1) the analysis time is drastically cut down owing to the combination of the pyrolysis and sample injection into a single short step; (2) the analysis requires small samples (in volumes as low as several milligrams or even micrograms); (3) when small samples are used (thin layer), the effect of secondary reactions is minimized; and (4) pyrolysis can be conducted under reproducible controlled conditions, and liquid as well as gaseous products can be analyzed.

An interesting intermediate version of the pyrolysis method has been proposed by Swann and Dux.[12] They pyrolyzed a polymer of interest in an evacuated sealed glass ampule (a 50-mg sample was heated for 15 min). The pyrolysis products were subjected to GC analysis after the ampule was broken in the carrier gas flow upstream of the column inlet.

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Table 1
SOME CHARACTERISTICS OF PYROLYSIS GAS CHROMATOGRAPHY

Advantages	Limitations
Universal	Complexity of the chemical reactions during the pyrolysis and the following difficulties when determining the dependence between the products of the pyrolysis
Wide field of applications	
High sensitivity of the method to the nature of the pyrolitic sample	Determination of volatile products of the pyrolysis (only)
Proximate rapid	
Possibility of automatization	Necessity of strict standardization of all experimental conditions
Standard apparatus	Indirect method

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At present, PGC is widely used in analysis of nonvolatile compounds. In general, the method and its applications are steadily developing and extending. At periodically held international conferences on analytical pyrolysis most papers deal with the development and application of PGC. For example, at the 3rd International Symposium on Analytical Pyrolysis, 80% of the papers were concerned with PGC.[13] PGC is also broadly covered in the literature. For example, according to Soviet abstract journal *Khimiya,* about 15 publications on PGC were abstracted in 1960, about 40 in 1965, and about 70 in 1970. According to McKinney,[3] more than 400 works were published over the period from 1960 to 1968. Some monographs include chapters dealing exclusively with PGC.[3-6]

The prominent position of PGC among other GC techniques is also pointed out by the data that can be obtained from the reviews periodically published in *Analytical Chemistry,* covering the development of GC over 2-year periods.[14,15] For example, 7.2% of all papers listed in the review of 1972 and 5.2% in 1974 are related to PGC. In our opinion, there are a number of reasons why investigators pay so much attention to the development of this GC technique (see Table 1). First, the method is versatile and can find a host of applications, second, it provides a wealth of data and third, other well-known simple and efficient techniques are limited insofar as the analysis of nonvolatile compounds, including polymers, is concerned. According to Wheals,[16] for example, when 190 samples of dyes were analyzed by two methods used in parallel, namely, emission spectrometry and PGC, only 53 dyes were identified by the former method and as many as 141 by the latter; i.e., for these compounds PGC is about three times as effective as emission spectrometry. There is also a fourth reason: the extensive application of PGC in analytical practice is due to the broader use over the past few years of capillary chromatography for separating pyrolysis products, which has substantially increased the potential of the method, as well as due to the wider range of substances to be analyzed (drugs, dyes, and microorganisms).

However, PGC suffers from certain drawbacks which stem from the complexity of the chemical reactions involved in pyrolysis and from the tangible effect of the secondary reactions which make it more difficult to establish correlations between the structure of the pyrolyzate and the end products of pyrolysis. In addition, the composition of the pyrolysis products depends on the specific pyrolysis conditions (temperature, duration, sample size, carrier gas flow rate, etc.). This is why to obtain meaningful results one has to strictly standardize the pyrolysis conditions.

The processes of thermal degradation of organic compounds are not yet fully known.

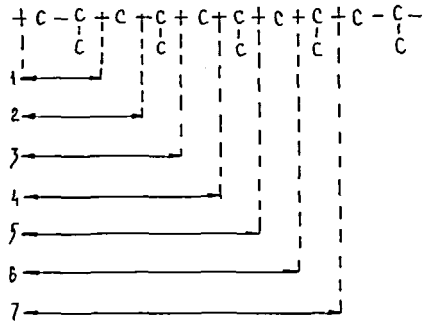

FIGURE 2. Diagram illustrating the formation of volatile polypropylene pyrolysis products as a result of rupture of certain bonds. 1, Propane; 2, isobutane; 3, 2-methylpentane; 4, 2,4-dimethylpentane; 5, 2,4-dimethylheptane; 6, 2,4,6-trimethylheptane; 7, 2,4,6-trimethylnonane.

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In the general case, it is impossible to predict the quantitative composition of the volatile decomposition products formed in pyrolysis from the sample structure and conditions of its pyrolysis. The opposite problem (establishing the structure and composition of the analyzed substance from the pyrolysis products), which is of great theoretical and practical importance, has not been solved either, although investigations aimed specifically at determining the structure of a substance from the products of its pyrolysis have been described in the literature. Therefore, in practical applications, the investigator's problem in most cases is to establish an empirical correlation between the structure of the substance of interest and the range of the pyrolysis products. In practice, different compositions of pyrolysis products are involved, depending on their nature and on pyrolysis conditions. Sometimes the composition of the volatile products may be quite simple, such as in the case of a sharply different nature of bonds in a polymer. For example, when copolymers of styrene and methyl methacrylate are pyrolyzed under certain conditions, the pyrolysis products consist primarily of the corresponding monomers.[17] However, more often, when complex organic molecules are exposed to elevated temperatures, random ruptures of chemical bonds occur and a complex mixture of volatile products is formed, representative of the structure of individual fragments of the initial molecules. This particular feature permits the structure and composition of the initial substances to be determined from the qualitative and quantitative composition of the products. For example, among the products of pyrolysis of polypropylene (after their hydrogenation), the following were identified as the main ones (in order of decreasing yield): 2,4-dimethylpentane, propane, pentane, 2-methylpentane, 2,4,6-trimethylnonane, 2,4,6-trimethylheptane, isobutane, ethane, 2,6-dimethylnonane, and 2,4-dimethylheptane. The formation of these main products is illustrated in Figure 2.[18]

It should be emphasized that PGC is often very sensitive to structural differences in polymers. Depending on the similarity of the chemical structure and selection of the pyrolysis and chromatographic separation conditions, the chromatograms of the pyrolysis products (pyrograms) from test substances may feature qualitative and in some cases only quantitative differences. For example, pyrograms of phenolformaldehyde resins obtained on the basis of 3-methylphenol and 3,5-dimethylphenol differed widely in the qualitative composition of the pyrolysis products,[19] while in the case of low-density

(Marlex 6002) and high-density (Okiten G-03) polyethylenes, only quantitative differences in the ratios of individual products were found.[20]

Owing to the extremely high sensitivity of the method to specific structural features of test substances and even to batches of received products, pyrograms are sometimes called "fingerprints" and are widely used for identifying polymers and other compounds of organic or biochemical nature. Therefore, investigations in which there is no need to identify the pyrolysis products (such investigations are predominant) are often said to be carried out by the "fingerprint" method — another indication of the empirical nature of the method. Note, however, that the number of works aimed at establishing the structure of the substance of interest from the qualitative and quantitative composition of the pyrolysis products is steadily increasing every year. While deciphering the structure of a polymer one should take into account the available data on the thermal stability of polymers.[20-23]

In most cases, pyrolysis samples are of organic substances or microorganisms. However, the application of pyrolysis to inorganic substances is as strongly recommended. For example, Getman has shown[24] that in high-temperature (1000°) pyrolysis, such elements as fluorine, chlorine, bromine, and iodine take 2 to 3 min to be released from silicate rocks and minerals. In Getman's work, the anions of these elements were determined by electrochemical methods (coulometric and polarographic). It is well known, however, that hydrogen halides may be determined gas-chromatographically as well.[25] Since the pyrolysis conditions produce a marked effect on the range of the resulting products, on the reproducibility of the obtained results, and on the relationship between the composition of the pyrolysis products and the nature (composition) of the pyrolyzed sample, a great deal of attention is given to the pyrolysis procedure and equipment in the literature.

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II. EQUIPMENT AND EXPERIMENTAL PROCEDURE

The qualitative and quantitative composition of the products of pyrolysis of various organic substances, their relation to the structure of the pyrolyzed substance, and the reproducibility of analysis are to a great extent determined by the pyrolysis conditions and hence, by the equipment and experimental procedure. Therefore, the pyrolysis equipment and techniques in PGC are given much attention, and many variations exist in the experimental arrangements. The pyrolytic cells use the same principle but are manufactured by many producers and thus differ in design parameters, a situation which accounts for some changes in the pyrolysis conditions and in some cases makes it difficult to compare the results obtained by different investigators and to standardize the measurement procedure. Further, many researchers use cells of their own design. Therefore, according to Levy,[26] there are almost as many different designs of pyrolytic devices as there are investigations involving PGC. In recent years, however, using predominantly standard industrially manufactured cells has become a trend.

According to their operating principle, pyrolysis systems can be divided into two main categories: static (enclosed)[7-9] and dynamic (continuous flow).[3,11,27-31] In a static pyrolyzer, the sample is heated in an enclosed volume for a long period of time; then all or some of the volatile pyrolysis products are introduced into the chromatograph. In practice, this principle was more widely applied in earlier works in which PGC was used in polymer analysis. In these experiments,[7-9] pyrolysis was conducted in a special unit, and the pyrolysis products were collected and analyzed on a standard gas chromatograph. It is more convenient to carry out pyrolysis of polymers in a sealed glass ampule and to analyze the pyrolysis products chromatographically after breaking the ampule in the carrier gas flow before the entrance to the column. This technique was successfully

applied under static conditions and with small samples for quantitative analysis of hydroxyethyl groups in hydroxyethyl starch.[32] A 1-mg sample of the test substance was pyrolyzed in a sealed capillary (9.0 × 0.1 cm) in a vacuum at 400° C for 10 min. The pyrolysis products were examined chromatographically. A linear relation was established between the acetaldehyde peak height and the number of hydroxyethyl groups in the sample. A properly designed ampule-breaking attachment is described in Reference 33. This pyrolysis technique was used in the analysis of copolymers of acrylonitrile with styrene in a broad range of monomer ratio variations.[34] An ampule containing a weighed amount (5 to 10 mg) of the polymer was pre-evacuated down to a residual pressure of 10^{-3} mmHg. The pyrolysis was conducted for 20 to 30 min at 500° C. The composition of the copolymers can be determined from the peaks of hydrocyanic acid and toluene which are present in the pyrolysis products in amounts proportional to those of acrylonitrile and toluene, respectively, present in the copolymer. A simple attachment for pyrolysis in an enclosed volume is described by Valkovsky et al.[35]

In considering the role of equipment in PGC, it would be appropriate to point out some general limitations of the static pyrolysis techniques. A major disadvantage of the static system is, as has been mentioned above, that because of the long duration of the pyrolysis process, the primary products of thermal degradation can enter into various inter- and intramolecular reactions with the result that it is often very difficult to tell what the possible structure of the initial polymer can be from the composition of the pyrolysis products. An important exception is, of course, polymer systems with bonds of widely different thermodynamic stability, whose pyrolysis products are, in addition, quite stable at the pyrolysis temperature. The above disadvantage of static systems can be minimized if pyrolysis is conducted in a continuous-flow system or if, for example, the volatile products are frozen out in a trap for their removal from the hot zone. Static pyrolysis is still recommended for cases where small samples cannot be used or their use is limited because of the inhomogeneity of the substance, as well as for studying the mechanism and kinetics of thermal or thermo-oxidative degradation, the composition of the volatile reaction products at low degree of conversion, etc. On the other hand, an advantage of this technique lies in the ligh reproducibility of such important pyrolysis parameters as temperature and pyrolysis time.

A good example of using PGC in studying the thermo-oxidative degradation is provided by the one-stage method of examining the thermo-oxidative stability of polymers, developed by Nemirovskaya.[36] It resides in periodic GC analysis of the volative products resulting from thermal oxidation of a polymer in a reactor (in which provision is made for periodic change of the gaseous medium) associated with the sample inlet valve of the chromatograph instead of the sampling loop. This method was used in studying the mechanism of degradation of some aromatic polyimides with different monomer unit structures and establishing a correlation between the thermo-oxidative stability of these polymers and their chemical structure.

In continuous-flow pyrolysis systems, the sample is rapidly heated in a steady carrier gas flow. The volatile pyrolysis products are diluted by the carrier gas and quickly removed from the reaction zone into the separation column. The main drawback of this method is the comparatively poor reproducibility of the heating pattern.

The pyrolyzer is usually connected directly to a standard sample injection device or in parallel to the latter. To enhance the efficiency of the subsequent chromatographic separation, the outlet of the pyrolytic cell should preferably be coupled directly to the chromatographic column.

This method features a number of advantages over static pyrolysis: (1) the experiment takes much less time owing to the sample injection and pyrolysis being combined into a single short step, and (2) when pyrolysis is conducted in the carrier gas flow, the role of secondary processes is minimized.

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According to the sample heating procedure, the most common dynamic (continuous-flow) pyrolysis systems can be divided into two major groups:[5]

1. The first group is made up of pyrolyzers with a special heating element (filament) rapidly heated to a high temperature, on which the sample to be pyrolyzed is placed. In such pyrolyzers, the pyrolysis chamber wall temperature is much lower than the pyrolysis temperature. This group includes two basic types of pyrolyzers in which the heating element is either (a) a conductor (filament) heated by the current flowing through it, or (b) a rod made of a ferromagnetic material, heated by RF currents to a temperature corresponding to the Curie point of that material.
2. The second group consists of pyrolyzers with a pyrolysis chamber of the tube-furnace type whose walls are heated to the pyrolysis temperature.

In the pyrolytic reactors of the first group, the sample is pyrolyzed on a filament (coil) rapidly heated by current. This type of pyrolytic cell is also known as a cell with a filament or a filament-type cell. The heated coil is placed in a continuous-flow chamber whose walls have a temperature normally not exceeding that of the subsequent chromatographic separation of the pyrolysis products. When working with such cells, the test substance is applied to the metal (usually platinum or nichrome) filament. After the coil with the sample has been introduced into the carrier gas flow and the cell has been rendered airtight and the instrument (chromatograph) has been set, the cell is heated in a pulsed mode. The resulting volatile products are entrained by the carrier gas into the chromatographic column, separated and detected. Cells of this type are simple in design, provide for relatively rapid heating of the sample, ensure pyrolysis in the carrier gas flow, and are characterized by a small heating surface. Pyrolysis under such conditions is marked by an insignificant effect of the secondary reactions on the pyrolysis products. Such cells must meet the following requirements: (1) the volume of the cell must be as small as possible, for a greater volume reduces the efficiency of the subsequent chromatographic separation; (2) additional heating of the cell walls is necessary to prevent the possible condensation of part of the pyrolysis product on the cold walls of the cell (or, for example, the cell must be installed inside the thermostat of the chromatograph); and (3) the coils with the sample must be rapidly and easily replaceable.

Figure 3A illustrates a typical design of a glass pyrolytic cell.[37] Similar cells are described by Janàk, Jones and Moyles, and Mlejnek[38-41] and have been used by other investigators, as well. To increase the concentration of the resulting products and use a simpler katharometer, Franc and Blaha[4] employed platinum mesh as the pyrolytic cell filament. This enabled them to increase the sample size without increasing the weight of the polymer under investigation per unit area of the heated filament surface, whereby they could use a katharometer instead of a FID.

The heating element in the filament-type cells may be in the form of a cup,[43] plate,[44] saucer,[34] or ribbon,[46,47] with the sample to be pyrolyzed being placed on its horizontal surface. Another convenient type of pyrolyzer for routine and preliminary analyses is described by Fischer.[48] It is essentially a small unit connected to the power supply and carrier gas source by flexible cables and hoses. The pyrolysis products are injected by a needle into the vaporizer of the chromatograph. The pyrolyzer is provided with sample containers and replaceable heating elements of different types, suitable for pyrolysis of various samples (powdered, liquid, viscous, soluble, insoluble, etc.).

Figure 3B shows an induction-heating pyrolyzer with a filament made of a ferromagnetic material. This arrangement provides for rapid heating of the filament with the sample to a temperature corresponding to the Curie point of the filament material,

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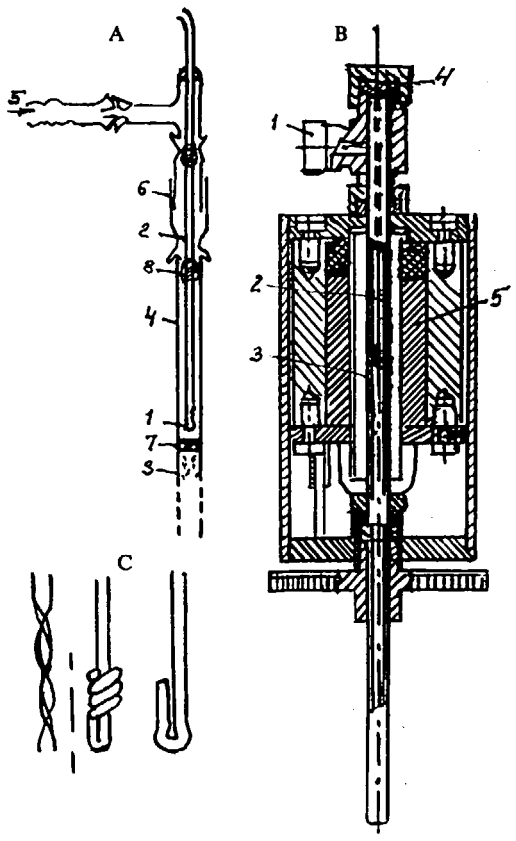

FIGURE 3. Pyrolytic cells. (A) Filament-type glass cell: (1) nichrome coil, (2) tungsten electrodes, (3) sorbent layer in GC column, (4) top of GC column, (5) carrier gas inlet, (6) ground-glass joint, (7) inert material layer, (8) insulator. (B) Curie-point of Pye design: (1) carrier gas inlet, (2) ferromagnetic wire (filament), (3) quartz tube, (4) gasket, (5) induction coil. (C) Types of ferromagnetic wire for Curie-point cells.

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which is in fact the pyrolysis temperature. Shown in Figure 3C are various types of filaments on which samples are placed and pyrolyzed.

The known methods of thermal pyrolysis by heating the analyzed sample are compared in Table 2. We compiled this table mainly on the basis of Lehrle's[49] and Crighton's[50] works. Commercially produced and widely used at present are pyrolyzers of all the above types (electrically heated filament, Curie-point filament, tube furnace), each type having an optimal area of application in which its use is advantageous over others. However, in recent years, cells with a Curie-point filament have gained the widest application. According to Alekseeva and collaborators,[51] who are primarily involved in analysis of rubbers, Curie-point induction-heating pyrolyzers are considered to be general-purpose ones and can be employed for identification of polymers determination of the composition and structure of macromolecules.

The use of metal filaments and coils (platinum, nichrome, and others) as the support for the pyrolyzed sample (film) of a polymer is not the best solution because of the possible catalytic activity of the metals. For example, as was indicated in Reference 40,

Table 2
COMPARISON OF SOME COMMONLY USED METHODS OF ANALYTICAL PYROLYSIS IN PYROLYSIS GAS CHROMATOGRAPHY

Pyrolysis	Advantages	Disadvantages
In a tube furnace	(1) Extensive application, including analysis of insoluble, infusible and fibrous samples; (2) Broad temperature range; (3) Sample size does not change within a broad range; (4) Low cost	(1) Relatively large dead volume; (2) Pyrolysis time is not controllable; (3) Temperature remains invariable throughout the experiment (the sample is pyrolyzed only at one particular temperature); (4) Relatively broad initial volatile product zone
Filament is heated directly by electric current	(1) Pyrolysis temperature can be varied during pyrolysis; (2) Simple design	(1) Method is applicable only to small samples; (2) Pyrolysis of fibrous materials is difficult; (3) Temperature control is limited
On a heated filament. Filament is heated to the Curie point by RF current	(1) Temperature and pyrolysis time can be controlled during pyrolysis. (2) Rapid heating to pyrolysis temperature; (3) Simple procedure; (4) Small dead volume of the pyrolytic cell	(1) A particular sample can be pyrolyzed only at one temperature; (2) Sample size is limited; (3) Pyrolysis of fibrous materials is difficult

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when the polymer sample size exceeds a milligram, the effect of the filament material on the composition of the resulting products is pronounced, the composition of the pyrolysis products being less complex when a gold-plated filament is used, as compared to a nichrome coil. In the case of microgram samples, the pyrograms of polystyrene and polymethyl methacrylate did not show any effect of the coil material (nichrome, platinum, gold-plated platinum). Dimbat and Eggertsen[52] succeeded in minimizing the catalytic effect of the platinum filament surface by coating it with glass from melted glass microbeads.

In some cases, the sample to be pyrolyzed should be placed not directly on the coil but in a boat made of mica, quartz, or other inert materials. Pyrolysis of rubbers in a mica boat heated by a nichrome coil yields were reproducible and characteristic (i.e., more distinct) pyrograms than when the sample is placed directly on the coil.[53]

Although it has been noted that different types of metal surfaces of heating elements affect the pyrolysis process in a different manner (which is one of the reasons why the repeatability of the results in different laboratories is poor), it should be pointed out that the effect of the metal support on analytical pyrolysis must not be always regarded as a negative factor. Consider now some possible positive aspects of the influence exerted by the metal surface on pyrolysis: (1) metal additives may improve the specificity of the pyrolysis products and enhance the selectivity of pyrolysis; and (2) metal additives may in some cases improve separation and simplify identification (as a result of the catalytic transformation of the pyrolysis products on metals). To enhance the effect of metal additives, one should use metals not only as the heating surface but also introduce them into the pyrolyzed sample, e.g., by mixing the polymer with powdered metal.

One of the most important characteristics of pyrolysis is the temperature pattern of sample heating. Therefore, the changes of the filament temperature in time is an essential characteristic of pyrolyzers. The most significant parameters are as follows: (1) filament

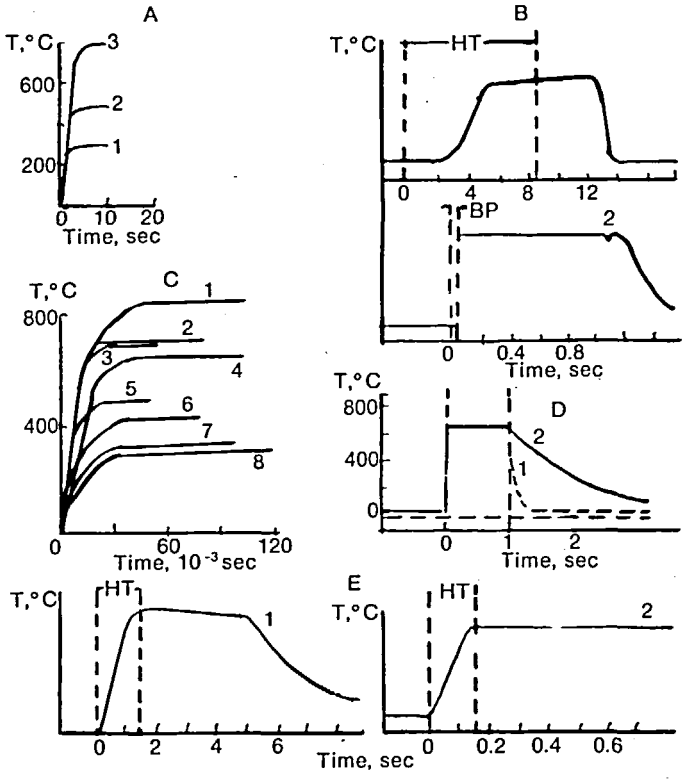

FIGURE 4. Kinetics of temperature variations in pyrolytic cells of different types. (A) In filament-type cells directly heated by electric current: (1) 300°C, (2) 500°C, (3) 800°C; pyrolysis time, 10 sec. (B) In filament-type cells directly heated by electric current: (1) With constant voltage source, heating time (HT), 10 sec; (2) with constant-voltage source and additional source of special powerful discharge for rapid heating; HT, 15 msec; diameter of heated platinum wire, 0.25 mm; pyrolysis temperature, 800°C. (C) In Curie-point cell for certain ferromagnetic materials with wire diameter of 0.5 to 0.6 mm: (1) CoNi (60:40), (2) FeZn, (3) Fe, (4) CoNi (33:67), (5) NiFe (60:40), (6) NiCrFe (51:1:48), (7) NiFe (45:55), (8) Ni; oscillator frequency, 0.45 MHz. (D) In Curie-point cell for wire 0.05 mm (1) and 0.5 mm (2) in diameter; pyrolysis time, 1 sec; HT, 0.02 and 0.1 sec. (E) In Curie-point cell for wire (filament) 0.5 mm in diameter: (1) 30-W Philips oscillator, HT, 1.3 sec; (2) 2.5-kW oscillator, HT, 120 msec.

(sample) heating time; (2) reproducibility of the kinetic heating curve; and (3) constancy and stability of the maintained temperature.

Let us first consider pyrolytic cells whose filament is heated directly by electric current. The heating time for conventional filament-type cells directly heated by electric current is usually several seconds. Represented in Figure 4A are curves for a cell described by Fischer.[48] Under such conditions, particularly in the case of microgram samples, pyrolysis of the sample is often practically completed even during heating at temperatures below the equilibrium temperature.[54] To more quickly attain the equilibrium temperature, various heating patterns have been proposed for filament-type cells, which permit reducing the heating time down to tenths[55,56] and even hundredths[57] of a second. Figure 4B represents filament temperature variation curves[57] derived when (a)

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Table 3
CURIE POINTS OF SOME FERROMAGNETIC MATERIALS

Element	Composition (%)	Curie point (°C)
Fe:Co	50:50	980
Fe	100	770
Fe:Ni	30:70	610
Fe:Ni	40:60	590
Fe:Ni	49:51	510
Fe:Ni	55:45	440
Fe:Ni:Cr	48:51:1	420
Fe:Ni:Mo	17:79:4	420
Ni:Co	40:60	900
Ni:Co	67:33	660
Ni	100	358

constant-voltage source is used, and (b) constant-voltage source is combined with an additional source of powerful discharge. As can be seen from these curves, filament-type devices can provide for shortening the heating time (down to 15 μsec) and maintaining the preset limiting filament temperature during the experiment. Note, however, that the kinetic sample heating curves are readily reproducible on the same cell but not always on different cells of the same type.[58]

In the literature, various ways of applying the test sample on the filament are described. The sample is introduced into the filament-type pyrolytic cell basically by three methods: (1) from a solution by applying it on the heated surface and evaporating the solvent (in the case of soluble substances); (2) small samples identical in shape are placed inside the coil; and (3) the sample is placed in a boat or a special container inserted in the coil.

To obtain a film on the filament, either it is dipped into a dilute solution or the polymer solution (about 1%) is applied by means of a soft brush or a microsyringe on one or two turns in the center of the coil and the solvent is evaporated. Sometimes on infrared lamp is used to speed up the drying process.[39]

A substantial advantage of conventional filament-type cells is the possibility of conducting step-by-step pyrolysis.[59,60] Unlike one-stage pyrolysis, in the step-by-step procedure the same sample is pyrolyzed at several successively increasing temperatures (e.g., at 300, 400, 500° C and so on) over the same period of time (usually 10 sec). The pyrolysis products formed at each temperature are then chromatographed. A drawback of the filament-type cells is the filament resistance varying during operation, as well as poor reproducibility of the heating pattern.

This drawback has been eliminated in the pyrolyzer designed by Simon and Giacobbo.[61,62] The test sample is applied on a ferromagnetic wire which is inserted into a quartz tube in the carrier gas flow. When a high-frequency electromagnetic field is activated, the wire is rapidly heated to the Curie point of the ferromagnetic material. At this temperature, the wire loses its ferromagnetic properties and it is no longer heated by the high-frequency field. Thus, the wire surface temperature rises rapidly to the Curie point and remains invariable at that level. The Pye pyrolyzer[62] is illustrated in Figure 3B by way of an example.

Depending on the ferromagnetic material used in the sample support, the pyrolysis temperature may be increased stepwise from 300 to 1000° C. Table 3[58] lists the compositions and Curie points of some ferromagnetic materials. The heating curves for wires made of various ferromagnetic materials are represented in Figure 4C.

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The heating time of the wire is usually from 1 sec[63] to a few tenths of a second[61,64] or even two or three hundredths of a second, depending on the pyrolysis conditions for the Curie-point pyrolyzer. The kinetics of heating or cooling of the wire depends on its diameter and the power output of the high-frequency oscillator[57,65,66] (See Figure 4D[65] and 4E.[57])

The sample is normally applied on the heated ferromagnetic wire in the form of a film from a solution by immersing the wire into the latter to a depth of 1 to 3 cm, or by means of a microsyringe. In order to deposit equal absolute amounts of the polymer, one should use a microsyringe. A better reproducibility in applying the polymer solution with the aid of a microsyringe is attained if the end of the wire on which the sample is deposited is bent, curled, or made as a helical plate.[63] In the case of bent and curled wires, the heating time is increased.[59]

A Curie-point pyrolyzer can also be used with insoluble polymers, the samples being pyrolyzed in the form of solid pieces. Such a sample, whose size may reach 0.1 to 0.5 mg, is placed in a recess specially made in the wire. To increase the amount of the sample to be pyrolyzed, which is used in the form of a piece of up to 1 mg, it has been proposed to wind a 0.5-mm wire as a tight coil around another wire of the same diameter with a piece of wire being placed on the bottom of the resulting spiral receptacle. The coil is 10 mm long. A polymer sample in the form of a thin plate is inserted into the coil.[67]

Different authors attribute the following advantages to the Curie-point cells: (1) precisely maintained and adjustable, adequately reproducible pyrolysis temperature; (2) the relatively short sample heating time (as low as hundredths of a second); (3) a very small volume of the pyrolytic cell (0.2 mℓ);[46] and (4) the possibility of standardizing the pyrolysis conditions and attaining adequate reproducibility while using commercially produced cells in different laboratories. All these factors permit minimizing the role of secondary reactions in Curie-point cells.

The drawbacks of the Curie-point cells include the necessity to work at strictly fixed temperatures, which means that step-by-step pyrolysis is impossible. Besides, until recently no provision has been made in the known Curie-point pyrolyzers for heating the cell walls to prevent possible condensation of heavy pyrolysis products on the cold walls, nor was any attention paid to ensuring conditions for rapid entry of the pyrolysis products into the chromatographic column.

Interesting conclusions have been drawn by Levy et al.[18] who tried to find an explanation for the poor reproducibility of the results when filament-type and Curie-point cells were used in pyrolysis. They contend that the use of pyrolytic cells with a filament may yield more reproducible results, to say nothing of the fact that the heating time can be cut down to 10 msec. The authors of Reference 68 criticize Curie-point pyrolyzers, pointing out the following disadvantages and operating features: (1) the heating time at different points of the heated wire (filament) is strongly dependent on its arrangement in the high-frequency coil (length- and crosswise); (2) the heating time is also dependent on the power output of the high-frequency oscillator (e.g., in the case of 1500 and 30 W oscillators, the heating time differs by one order of magnitude); (3) the heating time further depends on the composition of the alloy used (ferromagnetic materials having the same Curie point but different compositions are characterized by different heating times); and (4) the actual filament temperature is below the Curie point due to the fact that less energy is absorbed near the Curie point. The above features of the Curie-point pyrolyzers are not critical. Nevertheless they should be taken into account in practical work if more reproducible results are to be obtained.

In view of the wider application of PGC in industry and research, the development of techniques and equipment for automatic analysis by this method is of great practical interest. For Curie-type cells with a filament, an automatic PGC system was developed

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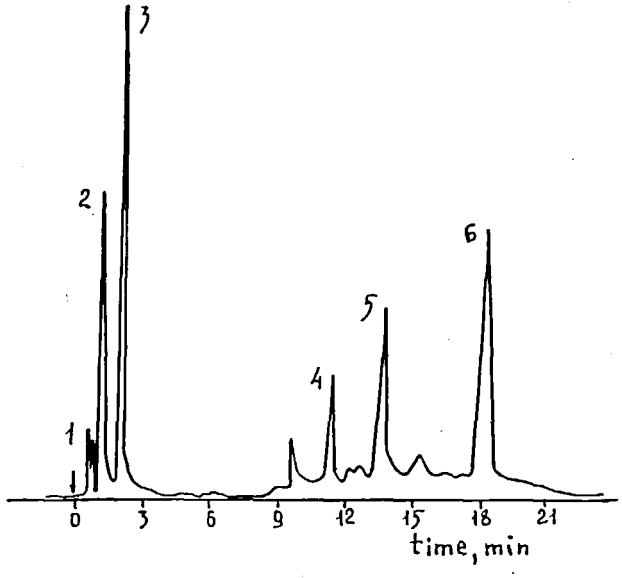

FIGURE 5. Pyrogram of a mixture of natural, butadiene-styrene, and butadiene rubbers. (1) Beginning of experiment (pyrolysis), (2) butadiene, (3) isoprene, (4) vinylcyclohexane, (5) styrene, (6) dipentene.

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by Coulter and Thompson[69] for a specific application in the tire industry. A typical analysis in this area involves identification and quantitative determination of polymers in a tire material sample. The material of a tire is essentially a mixture of polymers, most often natural rubber (polyisoprene), synthetic polyisoprene, polybutadiene, and butadiene-styrene copolymer. A tube is normally made of a material based on butyl rubber and a copolymer of isobutylene with small amounts of isoprene. In addition to the above, the material contains another 10 or 12 ingredients such as sulfur, zinc oxide, carbon black, mineral oil, pine pitch, resins, antioxidants, accelerators, and stearic acid. In analyzing very small samples of the tire material, the chemist must usually answer the following question: on the basis of which polymers is the tire made and what is their ratio? The problem is not made easier by the fact that cured rubber is not soluble in any solvent. This is why PGC seems to be the best analytical method.[7,60] Impulse pyrolysis of rubbers yields characteristic products (volatile monomers or dimers) of the analyzed polymer materials, the nature of the resulting products being but little dependent on the presence of nonpolymeric ingredients and the degree of polymerization.

In the automatic pyrolytic analyzer, Coulter and Thompson[69] used a Curie-point cell for analyzing the tire material. The heating element was made of pure iron whose characteristic heating temperature (Curie point) is 770° C. A rubber specimen was cut with a scalpel to obtain a plate-like sample weighing about 0.2 mg. It had earlier been proposed[71] to place a piece of tire inside the iron wire coil. The pyrolysis products were separated in a steel column 3 m long, packed with 10% of Apiezon L on Celite®. The initial column thermostat temperature was 50° C. After 3 min, the temperature in the thermostat was increased at a rate of 6° / min up to 150° C, and the analysis was carried out at this temperature to eluate the volatile dimers. The obtained pyrogram contained all the necessary information for polymer identification. Figure 5 represents a pyrogram of a mixture of natural, butadiene-styrene, and butadiene rubbers. It features five major

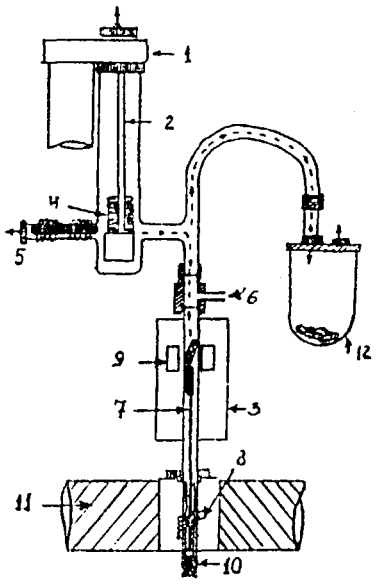

FIGURE 6. Automatic system for sample injection into pyrolyzer, pyrolysis, and GC separation of pyrolysis products. For reference numerals see text.

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peaks corresponding to (1) butadiene, (2) isoprene, (3) vinylcyclohexane, (4) styrene, and (5) dipentene. The ratio of polymers in the sample is determined with due account for the calibration data based on the areas of these peaks. The developed automatic system[69] has made it possible to increase the number of analyses performed on a single chromatograph from 50 to 200 during a week. The automation of this system essentially resided in developing an automatic sample injector. The designers of the system used an automatic device for introducing solid samples into a Pye-Unicam gas chromatograph. The automatic sample introducing device designed by Coulter and Thompson[69] is illustrated in Figure 6. Power supply unit (1) accommodates cassette (2) for storing and feeding samples into pyrolysis unit (3). Each sample is first wrapped into a piece of metal foil (14 × 4 × 0.1 mm) and placed in special glass capsule (4). It takes about 3 min to prepare a sample. The glass capsules are placed in the cassette which is inserted into the power supply unit. The cassette can hold 35 capsules. For a sample capsule to be introduced into the pyrolysis unit, an electrically actuated pusher (5) of the solenoid type is used. A capsule with a sample is fed into the pyrolysis unit (3) via a glass pipe above which carrier gas (6) (nitrogen) is supplied into the pipe. The capsule with the sample is positioned in the center of a turn of the conductor traversed by RF current (9) by means of pin the (7) controlled by a solenoid (8). Prior to pyrolysis, the conductor is energized with RF current for a certain period of time, and the sample is rapidly heated and pyrolyzed. The pyrolysis products are delivered by the nitrogen flow through the pipe into the packed column (10) in the thermostat (11). After pyrolysis the capsule with the unpyrolyzed residue is removed from the pyrolysis zone by a pin (7) and delivered to the glass collector (12).

The GC analysis results are computed automatically with the aid of a calculator. The natural rubber:butadiene—styrene rubber:butadiene rubber ratio in the analyzed material is printed out together with the initial data pyrolysis product peak retention

time, peak area, etc. This system has been successfully used by Coulter and Thompson[69] for over 2 years in industrial analysis. As a result, the quality of the end product (tires) was drastically improved. A similar device can be developed using a furnace-type pyrolyzer.

In the pyrolytic cells of the second group (with the pyrolysis chamber heated to an elevated temperature), the test sample is introduced into a tube furnace where it is pyrolized.[72] The advantages of such a reactor include better standardization of the heating pattern, and the possibility of using both small and large samples. It suffers, however, from the tangible effect of secondary reactions on the formation of pyrolysis products due to their prolonged residence in the heated zone. Increasing the polymer sample size permits using, along with GC of the volatile pyrolysis products, other physicochemical methods of analysis of both the volatile pyrolysis products and the pyrolyzed sample residue (ultimate, chemical, spectrum, and others).

Various ways of introducing a sample into a pyrolyzer of the tubular reactor (furnace) type are described in the literature. The sample can be introduced into the pyrolysis zone with the aid of a magnet,[73] directly by means of a special injector for solid samples,[74] and by gravity (free fall).[75] The latter type of furnace pyrolyzers includes a simple vertical device developed by Japanese investigators.[75] It meets the general requirements imposed on pyrolyzers of this type, namely; (1) it is made of an inert material (quartz); (2) it is easy to use; and (3) it has a small dead volume (the diameter of the tube portion in which pyrolysis takes place is 3 mm. The tube than narrows down to 1.3 mm, and the linear gas velocity at 10 mℓ/min is 2.4 cm/sec in the wider portion and 12.8 cm/sec in the narrower portion); (4) the sample is rapidly heated to the required temperature (the pyrolysis takes 0.1 sec, and it takes 0.8 sec to eluate the pyrolysis products). The authors[75] rightly assume that their pyrolyzer features characteristics similar to those of impulse filament-type pyrolyzers. The reproducibility of pyrograms taken on a vertical furnace-type pyrolyzer is three times as high as on a horizontal pyrolyzer.

In the U.S.S.R., a tubular-reactor pyrolytic cell is produced by the Dzerzhinsk affiliate of the Experimental Bureau of Designing Automatic Instrumentation.[76] The sample is placed in a quartz boat secured in a detachable holder which is introduced, with the aid of a piston rod, into a preheated quartz pyrolytic tube where the pyrolysis takes place. To reduce the residence time of the volatile pyrolysis products in the heated zone, the quartz tube portion downstream of the boat is made in the form of a capillary. During pyrolysis, the boat with the sample is positioned at the end of the tube before the capillary. Provided upstream of the pyrolysis zone in the quartz pyrolytic tube is a zone of stepwise controlled preheating of the sample, used when it is necessary to remove the volatile products contained in the sample (e.g., solvent residues). Provision is also made for annealing the boat in air, in a special electric furnace, to clean it by burning the pyrolyzed sample residue after pyrolysis. The boat is moved into the preheating zone, the pyrolysis zone, the boat annealing furnace, and the sample loading position in a simple and convenient manner without the need to remove the boat from its holder or the holder itself. The airtightness of the system and the operating conditions remain undisturbed.

It should be noted that all of the above-described pyrolytic devices suffer from a serious drawback. While relatively good reproducibility of the results can be attained on the same device, devices of the same model manufactured by the same producer often show poor reproducibility. Until about 1970 it was considered that the best reproducibility as regards the composition of the pyrolysis products could be achieved on a Curie-point pyrolyzer.[77] However, a comparative study of the results obtained in 18 laboratories on the same sample, conducted by the PGC Subgroup of the Chromatography Discussion Group at the London Institute of Petroleum, has shown that Curie-point cells are characterized by the same scatter of data as cells of the other types.[78]

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Further studies in this direction[79,80] suggest the following possible causes of poor reproducibility of data and systematic errors: (1) the presence of residual solvent in the test sample; (2) the wide range of pyrolysis temperatures; (3) contamination of the equipment by sample residues and residual products of previous pyrolyses; and (4) widely differing sample sizes. To obtain reproducible results one should give equal attention to all stages — sample preparation, pyrolysis, and GC analysis.

In general, the question of reproducibility of results obtained on the same type of polymer sample pyrolyzed in different laboratories using the same procedure unfortunately has no definite answer because in some cases the reproducibility was quite satisfactory. This gives reason to believe that a rational selection of the experimental procedure and equipment, as well as standardization of the experiment, will enable satisfactory interlaboratory reproducibility of PGC results to be attained.

The last results of Dutch investigations are in accordance with this point of view. Their investigations were carried out by Curie-point pyrolysis-mass spectrometry and also valid for pyrolysis-gas chromatography. The parameters tested — the cleaning method of the pyrolysis wires, the suspending liquid for the samples, sample size, Curie-point temperature, temperature rise time, total heating time, and the influence of the above-mentioned parameters on the spectra of some standard bipolymers (glycogen, bovine serum albumin) — are discussed quantitatively. In this paper[80a] a set of standard pyrolysis conditions producing a reasonable degree of interlaboratory reproducibility were recommended: wire cleaning method, heating in reductive atmosphere: suspending liquid, methanol: sample size, 5 to 20 ng, equilibrium temperature, 500 ± 10°C; temperature rise time, 0.1 to 1.5 g; total heating time, 0.3 to 1.2 g.

Some other methods of decomposition have been described; for instance, immersion of a U-shaped chamber with a sample into a metal melt,[81] or induction heating of a sample mixed with a ferromagnetic metal powder by means of RF currents.[72] Other described methods of producing a destructive action on a polymer, related to PGC, involve beta radiation,[88] gamma radiation,[83] decomposition in an electric discharge,[60,84] and laser-induced decomposition.[56,85] The effect of each type of radiation on a substance is marked by a number of specific features. For example, in the case of gamma irradiation (dose of about 100 Mrd) of a polymer sample in a sealed evacuated ampule, a characteristic spectrum of light radiolysis products is obtained.[83] This method is characterized by high sensitivity to hydrocarbon substitutes in the main chain of the polymer. This particular feature permits unambiguous identification of low- and high-density polyethylenes.[83]

In recent years, such attention has been given to laser PGC.[56,85-97] Lasers found their first applications in chemistry some 15 years ago. These were mostly photochemical studies making use of the unique monochromacity of laser radiation. Lasers can also be used in PGC, and substances can be subjected to "laser pyrolysis" for analytical purposes. Lasers are particularly suitable for controlled pyrolysis, bearing in mind that energy can be beamed at a definite wavelength onto a small portion of the sample to be pyrolyzed. Laser pyrolysis conditions differ considerably from those of thermal pyrolysis, which is why we can speak of a separate PGC technique — laser pyrolysis gas chromatography (LPGC). The first LPGC experiments were conducted in the late 1960s and early 1970s.[85,87-89] They were carried out to analyze polymer materials. The interaction of a laser beam with a substance is shown schematically in Figure 7.[86] A laser (e.g., ruby- or Nd-glass) beam is focused and "injected" into the sample. The pulse duration is usually about 0.001 sec, and the beam energy is about 5 J/pulse.[85] If this energy is focused on a spot 0.1 cm in diameter, the beam intensity is about 6.4×10^5 W/cm^2.[86] Initially, a certain part of this energy is absorbed by the sample. Several mechanisms of this process were discussed in the literature, the most likely being polyphoton absorption.[90] As a

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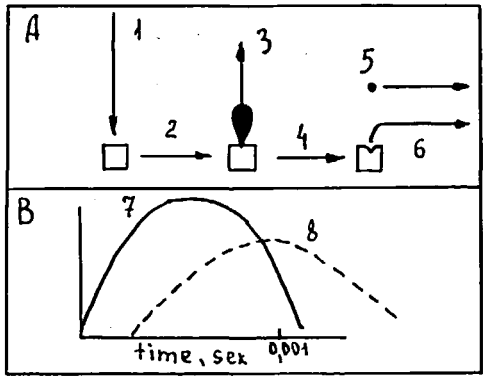

FIGURE 7. Laser pyrolysis. (1) Pulsed laser beam ("laser impact"), (2) pyrolysis, (3) initiation of plasma, (4) thermal hardening; (5) hardening of plasma; (6) thermal desorption and transport of products: (7) laser beam intensity; (8) plasma torch formation (change in height).

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result of the absorption, part of the pyrolyzed sample turns to plasma. The plasma torch grows during the interaction between the laser beam and the substance, in the direction of the laser impact. The torch grows in vacuum at a rate of about 10^5 cm/sec.[91] The high pressure occurring in the plasma gives rise to a shock wave acting upon the sample. According to the published data, the temperature of the emerging plasma exceeds 10^5 K.[92] These processes, including the growth of the torch and its "wilting", take about 0.001 sec. During this time interval and under the above conditions, the substance is chemically transformed, yielding sizable amounts of volatile products. Some of these products are formed in the plasma and others as a result of the thermal shock directly in the substance.

Figure 8[86] represents a laser pyrogram of phenanthrene. The first peak stands for a mixture of low-molecular gaseous products formed in the growing plasma. It is followed by peaks corresponding to products of greater molecular weights, but their concentration is much less than that of the previous products. They include benzene, naphthalene, methyl- and dimethylnaphthalenes, and, finally, the starting phenanthrene. The fragmentation of the initial molecule is rather simple — it permits predicting the forming products.

If the laser radiation is not absorbed by the sample (e.g., in the case of transparent materials), a substance performing the function of absorption centers (such as powdered carbon or nickel) is introduced into the sample for the latter to be pyrolyzed. For example, in Reference 93 it was proposed to decompose transparent polymers (e.g., polyethylene, polystyrene) exposed to a laser beam by placing the samples made in the form of a thin film on the flat surface of a blue cobalt glass rod. The light products are formed primarily in the plasma torch — the rapidly frozen plasma induced by the laser radiation. These products are essentially low-molecular gases whose analysis permits determining the sample composition. Such an analysis is known as plasma-stoichiometric analysis.[94]

Shown in Figure 9[86] are experimental results typical of plasma-stoichiometric analysis. The figure represents the concentration of acetylene in the gaseous products of laser pyrolysis versus the molar hydrogen/carbon ratio in the sample. As can be inferred from

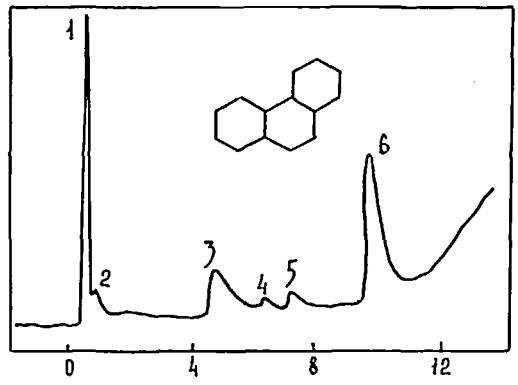

FIGURE 8. Laser pyrogram of phenanthrene. (1) Methane, ethylene, acetylene (main compounds in the light products), butadiene; (2) benzene; (3) naphthalene; (4) methylnaphthalene; (5) dimethylnaphthalene; (6) phenanthrene (initial product). The laser pyrolysis products have been separated on a column with Apiezon L.

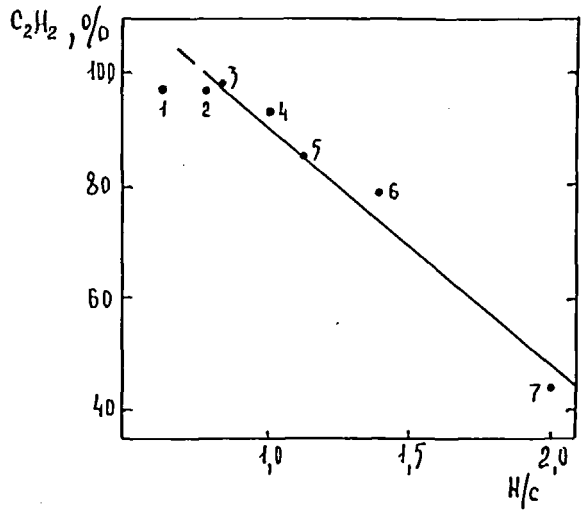

FIGURE 9. Stoichiometric analysis. Acetylene content (%) in low-molecular gases of laser pyrolysis vs. molar hydrogen/carbon ratio for different samples. Analyzed subtances: (1) phenanthrene, (2) terphenyl, (3) naphthalene, (4) 1,2-diphenylethane, (5) polystyrene, (6) durene, (7) paraffin.

these data, plasma-stoichiometric analysis can be used to evaluate the hydrogen/carbon ratio in various samples. Along with these low-molecular products heavier ones are formed as a result of degradation of the analyzed substance under the effect of the thermal shock.[56] Reference 86 gives examples of applying LPGC to determine the oil concentration in oil-bearing rocks, water content in rocks, etc. Despite the great interest in LPGC[56,85-99] the areas of rational application of this PGC method are not yet clearly

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defined and no comparative data are available on laser and thermal pyrolysis of various analytical objects, although some research has been done in this direction. For example, Reference 85 presents data on comparative analysis of the products of pyrolysis of some polymers, forming under normal thermal pyrolysis conditions and under the effect of laser radiation. The thermal degradation was carried out in cells of the filament type (pyrolysis temperature, 1000° C) and of the tubular type (pyrolysis temperature, 800° C). A ruby laser was used for laser pyrolysis. The results indicate that more specific products are yielded by LPGC. These results, however, cannot be regarded as adequately representative for (1) the thermal pyrolysis conditions were not optimized; hence, conducting the pyrolysis at extremely high temperatures might have led to a substantial decrease in its specificity; and (2) a very limited number of polymer types were analyzed. Therefore, the selection of laser or thermal PGC for analyzing different types of substances is an important problem. At present, preference is given to thermal PGC.

In PGC analysis, any type of pyrolyzer can be used with due account for the general recommendations given earlier when different types of pyrolytic cells were compared. A prerequisite for any meaningful PGC analysis is to define optimal experimental conditions with a view to obtaining specific and reproducible results. According to Levy,[100] specificity in analytical pyrolysis is defined as a measure of the relation of the composition and structure of the initial material to the characteristic pyrolysis products, whereby such materials can be differentiated.

In most cases, the analytical procedure may be outlined as follows. In comparative analysis of several samples differing in type, composition, structure, or other characteristics, the following steps are involved: (1) taking characteristic pyrograms of samples of different composition, and (2) selection of characteristic peaks (or their combinations) whose magnitudes vary with the composition (or other parameters) of the analyzed samples. Therewith, the investigator has to establish relationships of the following type from the obtained pyrograms

$$Y_i = f(X,Z_i) \qquad (1)$$

where Y_i is the peak value or a combination of peak values (for example, a ratio of the values of two peaks on the pyrograms of the polymers under investigation), X is the polymer characteristic of interest (e.g., when determining the composition of copolymers, X is the concentration of one of the monomers in the polymer), and Z_i stands for the experimental condition parameters.

Using this equation it is possible to determine the pyrolysis selectivity:

$$S_i = \left(\frac{\partial Y_i}{\partial X_c}\right)_{Z_i}$$

Cases where function (1) is variable are also considered, of course. The next step is to select one or more optimal relationships among the experimentally obtained ones, similar to Equation (1),[101] i.e., most clearly defined (specific), reproducible, and providing for maximum accuracy of calculation. This approach must be applied in considering the effect of different experimental parameters on the composition of the pyrolysis products. The possibility of using a computer at this stage was also examined by Küllik et al.[102,103] This problem was discussed in many papers and different mathematical methods were used in these studies.[103a-103e]

In order to obtain reproducible results and characteristic pyrograms, one must define the optimal experimental parameters which must then be strictly standardized, as the thermal degradation of a polymer is often sensitive to even minor changes in the pyrolysis

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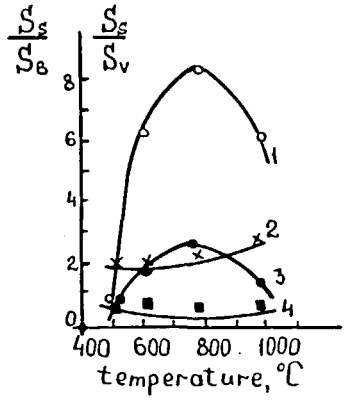

FIGURE 10. Characteristic peak area ratio vs. pyrolysis temperature for Curie-point cell. (1) and (3) Mixtures of homopolymers (polybutadiene and polystyrene); (2) and (4) statistical copolymer of styrene and butadiene (Europrene® 1500). (1) and (2) Ratio of peak areas of styrene and vinylcyclohexane; (3) and (4) ratio of peak areas of styrene and butadiene.

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conditions. Apart from the cell type, the determining experimental parameters are (1) the pyrolysis temperature and time, (2) the sample size and shape, (3) the nature and velocity of the carrier gas, and (4) the chromatographic separation conditions. Let us now consider in greater detail the effect of the above factors on the pyrolysis product yield and the specificity of pyrolysis.

The optimal pyrolysis temperature is determined by the analytical task, the nature of the polymer being investigated, and the design of the pyrolytic cell. Normally taken as the optimal pyrolysis temperature is the temperature at which the composition of the characteristic products ensures a maximum determination accuracy or is most specific. By the characteristic pyrolysis products are meant compounds whose peaks are used in quantitative measurements or in a qualitative evaluation of the pyrograms; using the parameters of characteristic peaks permits obtaining more clearly defined [specific relationships, (1) above].

In determining the composition of copolymers, the monomer peaks are generally used as the characteristic peaks. In the pyrolysis of acrylate copolymers, the relative yield of monomers passes through a maximum as the pyrolysis temperature increases.[104,105] Also studied[106] was the effect of temperature on the yield of volatile products in the pyrolysis of nonpolymer hydrocarbons, namely, 2,4,10- and 2,4-11-trimethyldodecanes on a filament-type pyrolytic cell (heating time, 15 msec) and on a Curie-point cell (heating time, 120 msec). With a few exceptions, the amount of light pyrolysis products (up to C_5 hydrocarbons) increases with temperature in both types of cells, while the amount of heavy products decreases, although the nature of changes in the amount of individual products is different depending on the cell type. The product yield also depends on the nature of the analyzed sample. Figure 10 represents a relationship, obtained by Alekseeva and Khramova,[107,108] between the yield of styrene for a statistical butadiene-styrene copolymer (Europrene 1500) and that of a mixture of polystyrene with

polydivinyl on Curie-point cells with a filament. In this case, the optimal temperature was 770° C at which the monomer yield is maximum for the mixture of homopolymers. At a lower temperature, the decomposition of the polymer yields heavier products while at a higher temperature, the decomposition is more intensive and the yield of lighter components (C_1-C_3) increases perceptibly.

As far as the temperature dependence of the product yield is concerned, pyrolysis with a particular temperature increase pattern is not only also possible in principle but also highly recommended. In this connection, it should be mentioned that Crighton[50] made an interesting comparison of two methods for analyzing nonvolatile (textile) materials: PGC and thermogravimetry (TG). PGC can be used for identifying chemical fibers, both individual and in blends. TG is applicable for qualitative and quantitative analysis of textile material samples if standard equipment and procedure are used. TG is an effective method for determining characteristic weight loss/temperature relations in a broad range of materials. According to Crighton, in order to obtain similar results in PGC, additional measurements have to be made to determine the optimal characteristic pyrolysis temperature and to define the optimal conditions for separation of the pyrolysis products. We consider this to be a somewhat one-sided conclusion because no account is taken of the large amount of data that can be obtained as a result of GC analysis and identification of the pyrolysis products. Nevertheless, Crighton's results are certainly of interest. They provide additional proof that pyrolysis with programmed temperature increase is promising. As to TG, we believe it should be combined with GC analysis of the products forming at different temperatures. A similar approach, i.e., combining analytical pyrolysis with programmed temperature control and analysis of the pyrolysis products by thin-layer chromatography (TLC), was proposed by Stahl and termed "thermorefractography".[109] In thermorefractography, a small sample of a test substance (usually a few milligrams) is heated at a constant rate (linear rise from 50 to 450°) in a nitrogen flow (30 m /min). The resulting volatile products are collected on a plate slowly moving with respect to the pyrolysis chamber outlet, whereby a sample is prepared on the starting line for TLC. Then the pyrolysis products are separated and determined by standard TLC techniques. The results differ from those obtained by PGC. The method was successfully used for analyzing various compounds (alkaloids, epoxy resins, glycosides, lignins, polyamides, polyesters, sugars, vinyl polymers, etc.).

In view of the above, the development of gas thermorefractography, in which the pyrolysis products are separated by GC, is of great interest. Step-by-step pyrolysis may be regarded as a simple analog of gas thermorefractography (see, for example, References 110 and 111).

Another important experimental parameter is the sample size. The size of the pyrolyzed sample determines the yield and composition of the pyrolysis products. This is obvious because the time of contact between volatile products and the pyrolyzed polymer depends on the thickness of the sample and its shape. Jones and Moyles[40] demonstrated the advantages of working with small, microgram samples in studying the relationship between the composition of the pyrolysis products and the sample size. They compared two pyrograms of polystyrene, produced by milligram and microgram samples. The pyrolysis was conducted under identical conditions. The appearance of additional peaks on the pyrogram in the case of the milligram sample is indicative of the increased role of secondary reactions when larger samples are pyrolyzed.

Barlow, Lehrle, and Robb[112] concluded that only in the case of very thin films (less than 0.02 mm thick at 700° C) the pyrolysis process is not dependent on the film thickness. However, the preparation of thin films is very difficult, especially when insoluble substances are involved. Therefore, investigators often pyrolyze macrosamples in the form of solid pieces, although it is only necessary to make sure that pyrolysis is carried

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out under reproducible conditions. Voight[101] established that when 2-mg samples are used, 50% variations in the sample size affect but insignificantly the composition of the pyrolysis products. The effect of the sample size in the range of 2.5 to 50 mg on the composition of the pyrolysis products in a filament-type cell was studied in Reference 113. Using a solid piece of natural rubber as the sample, it was shown that the pyrolysis of microgram samples results in a greater yield of volatile products and a higher relative content of heavy fractions than the pyrolysis of milligram samples, the effect of the sample size on the yield and composition of the pyrolysis products being more pronounced in the case of microgram samples. Therefore, in order to obtain more reproducible results when working with samples in the form of a solid piece, it is advisable to use samples of 1 mg and more, unless special limitations are imposed. The pyrolysis of several solid pieces which are not in contact with one another proceeds as several independent pyrolyses; therefore, a pyrolysis sample must be in the form of a single piece of a standard shape.

As has already been mentioned, the pyrolysis time varies within a broad range — from several tens of minutes to hundredths of a second. Unfortunately, the effect of the pyrolysis time on the composition of the products is not yet clear enough. In practice, to eliminate the effect of this factor, the experimental conditions are selected such that the sample is pyrolyzed almost completely. In this case, the area of peaks on the pyrogram does not change as the pyrolysis time increases. The time of residence of the pyrolysis products in the heated zone produces a marked effect on their composition. The carrier gas flow rate determines the time of residence of the pyrolysis products in the heated zone; hence, it may affect their composition. According to Reference 114, the carrier gas flow rate being reduced from 60 to 40 mℓ/min doubled the content of benzene in the polystyrene pyrolysis products. This effect, however, is not always observed for it depends on the thermal stability of the resulting products. When atactic polypropylene was pyrolyzed in the temperature range of 320 to 935° C, variations in the carrier gas flow rate did not affect the amounts of the resulting products.[115] Since the pyrolysis products may enter into reactions even outside the sample, the nature of the carrier gas, its reactivity, and velocity significantly influence the composition of the pyrolysis products. For example, when atactic polypropylene is pyrolyzed in nitrogen and hydrogen, the volatile pyrolysis products in nitrogen are formed at a temperature almost 200° C higher than in hydrogen.[116] The effect of the nature of the carrier gas (hydrogen, helium) in pyrolysis on a Curie-point cell was examined,[116] and it was established that the filament material (iron) produces a catalytic action. The yield of unsaturated products is lower when hydrogen is used as the carrier gas. In the case where a quartz-coated iron filament is used, the yield of products of pyrolysis of stearic acid is independent of the gas atmosphere. But when a metal-containing sample is pyrolyzed (e.g., copper phthalocyanine), the composition of the pyrolysis products is determined by the carrier gas.

Analytical pyrolysis yields a complex mixture of products providing information on the analyzed sample. This information is obtained by the investigator as a result of chromatographic separation and detection of the components of that mixture. In this connection, the importance of effective and selective chromatographic separation for identifying the sample should be emphasized.

We wish to emphasize the advisability of using, in many instances, a short precolumn arranged upstream of the separation column.[76] The precolumn may perform two main functions. First it serves for trapping heavy resinous pyrolysis products to extend the life of the separation column. In this case, the precolumn can be filled with glass wool, glass beads, and the same sorbent which is in the separation column. The precolumn must be periodically cleaned when it becomes contaminated, which is indicated by increased retention times of the pyrolysis products, more pronounced peak broadening and

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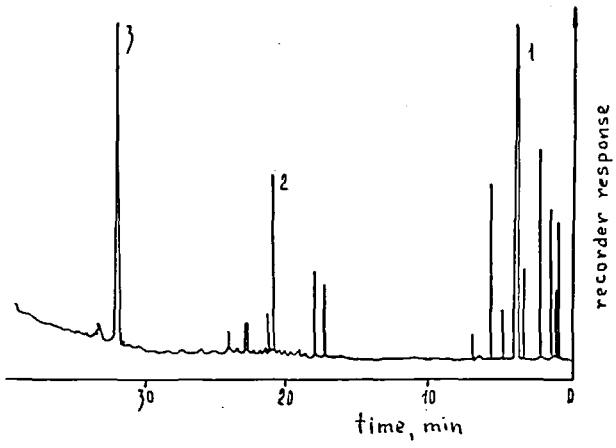

FIGURE 11. Pyrogram of polystyrene on capillary column (20 m × 0.28 mm). Experimental conditions: temperature of pyrolysis in hydrogen, 760°C; sample size, 2 mg; SLP, SE-30; temperature program, 6 deg/min from 25°C upward (1) Styrene, (2) dimer, (3) trimer.

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asymmetric shape of some peaks on the pyrogram, as well as higher pressure at the column inlet. Secondly, the precolumn can be used for separating light products from heavy ones and for purging the chromatographic system from heavy products in each experiment by reverse or semireverse flushing (see, for example, Reference 117). For instance, in determining the composition of rubbers for analytical calculations,[118] only light pyrolysis products (C_4) were used. Fifteen minutes after the pyrolysis was started, the carrier gas flow was diverted by semireverse flushing[117] and with the subsequent separation being carried out in the main chromatographic column, the heavy products were removed from the precolumn by reversing the carrier gas flow through it.

In selecting the chromatographic separation conditions, one should take into consideration the nature of the resulting pyrolysis products. With due account for the expected composition of the pyrolysis products, one should follow the recommendations generally given for selection of the SLP in analytical gas chromatography (see, for example, References 117 and 119 to 121). Since the composition of the pyrolysis products is determined by that of the analyzed sample, in investigating the composition of the products of pyrolysis of hydrocarbon polymers it is advisable to use nonpolar phases while in studying heteroatomic compounds, polar or weakly polar phases should be used. In the general case, for analysis of the volatile pyrolysis products, two or three standard chromatographic columns with phases of different polarity should preferably be used at one time. Taking into consideration the broad range of pyrolysis products with respect to boiling points and the complexity of the qualitative composition of the products, it was proposed in the past[4] to widely use capillary columns. Further developments in PGC have proved the validity of this proposal; capillary columns are extensively and successfully employed in PGC.[116,122-126] Reference 116 provides examples of using a Curie-point pyrolyzer together with glass capillary columns for identifying various nonvolatile compounds. Figure 11 is a pyrogram of polystyrene, exhibiting styrene monomer, dimer, and trimer zones. On earlier pyrograms, only the monomer[1] and dimer[2] could be seen.[127,128] The use of glass capillary columns in combination with temperature programming (6 deg/min) has made it possible to record the trimer (3) as well. The better resolution attained by combining chromatographic columns with a

Curie-point pyrolyzer in which small samples are pyrolyzed and a mass spectrometer for identifying the pyrolysis products has enabled a more definite relationship to be established between the pyrolysis products and the structure of the pyrolyzed compound.

The data obtained by PGC become more comprehensive and reliable if the pyrolysis products are identified. In this case, the chemical structure of the pyrolyzed sample may become known.[129,130] However, the identification of chromatographic zones in multicomponent mixtures is a time-consuming and complicated procedure. The efficiency and rapidity of identification are improved by a proper combination of directed physical and chemical methods (e.g., chromato-mass-spectrometry, or chromatography in combination with optical, spectrometry and chemical methods).[131] The advisability of using these methods in PGC was pointed out in an earlier monograph.[4] In some PGC works, the use of selective detectors lead to successful identification of products. For example, the molecular mass of the pyrolysis products can be determined in a much simpler way (as compared to mass spectrometry) if two gas density balances are used.[132] The pyrolysis products were analyzed on two chromatographs with density balances using two different reference gases: carbon dioxide and pentafluorochloroethane. Myers and Smith[133] showed that in identifying biological substances by PGC use should be made of a rubidium thermionic detector selective to nitrogen-containing pyrolysis products of proteins and nucleic acids, because when a conventional flame-ionization detector is employed, most characteristic structures are masked by the pyrolysis products of carbohydrates and lipids. Uden et al.[131] described an interesting procedure and device for conducting pyrolysis and identification of the pyrolysis products after GC separation. The sample to be pyrolyzed is either continuously heated with a small temperature gradient or very rapidly (about 20,000° /sec). By using an elaborate valving system, the following analytical operations can be performed:

1. Fast measurement of the radiation absorption by the pyrolysis products using the method of scanning in the infrared region
2. Ultimate analysis of the products for carbon, hydrogen, oxygen, nitrogen, sulfur, etc.
3. Functional group analysis using the "fingerprint" technique with thermal cracking in the vapor phase
4. Determination of the molecular weight by means of a gas density balance

Any one of the above methods providing important identification data can be used independently or in combination (the connection may be parallel or in series). A detailed description of the device is given in Reference 134. It provides all the necessary information on (1) the thermal stability of the sample in different media, and (2) the volatile products resulting from degradation processes. In the experiment, shale samples were analyzed and the thermal stability of chelates of metals and organometallic compounds was examined.

The applicability of PGC to samples of polymers with other components is of great practical importance. Jones and Moyles[40] showed the possibility of direct analysis of industrial samples. They obtained identical pyrograms for a sample of a pure polymer and a sample of the same polymer also containing some inert fillers. The catalytic effect of the impurities in the pyrolyzed mixture (usually inert ones) is observed only rarely. Therefore, PGC is also suitable for analysis of industrial products containing small amounts of impurities, which is an important advantage of this method over others. It should be noted, however, that the results obtained by Jones and Moyles cannot be regarded as a general regularity. The composition of the pyrolysis products can, in general, be affected

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by various ingredients and active fillers. A good example is provided by the data obtained by Alekseeva[135] in examining pyrograms of isoprene rubber and compounded rubber on its basis. The yield and ratio of the main characteristic products, isoprene and dipentene, are the same for both samples while those of other products are widely different. This can be explained by the effect of vulcanization in the presence of an active carbon filler. In some cases, the effect of ingredients, particularly their catalytic action, may be beneficial. For example, the authors of Reference 118 in analyzing trioxane copolymers, pyrolyzed a mixture of a polymer with cobalt sulfate which may act as a catalyst on the degradation of the polymer. The pyrolysis (temperature, 500° C) of the polymer mixed with cobalt sulfate yielded five products which were easy to separate chromatographically; pyrolysis at 900° C of the same samples without cobalt sulfate yielded a multicomponent mixture of products whose separation and identification was difficult. Although this investigation is not yet completed (in particular, the catalytic action cannot be considered as an established fact), it clearly demonstrated the applicability of analytical pyrolysis to mixtures of organic compounds with active solids. Also related to PGC are methods involving heating with reagents, particularly determination of oxygen in metals by reduction melting.[136] Now that we are familiar with the basic PGC procedures, let us review their main applications.

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III. IDENTIFICATION OF SUBSTANCES

In trying to identify unknown samples, the analyst has to accomplish one of the following two tasks: find a similarity between the sample and a known substance, and/or establish the nature of the pyrolyzed substance (its structure, composition, etc.). The first, more common task is easier to accomplish than the second. In PGC, its solution boils down to comparing the pyrograms of the reference and test samples. If they prove to be identical, the analyst has all reason to believe that the samples are identical, too. This technique is normally referred to as the "fingerprint" method, the implication being that pyrograms are compared just as two fingerprints would be. This identification method is an empirical one; nevertheless, it usually gives sufficiently reliable results. Its reliability can be substantially enhanced if pyrolysis is conducted at various temperatures and if stationary phases of different polarities are used for the separation of the pyrolysis products. More often than not there is no need to do that. Although the fingerprint method is widely used in polymer chemistry, biochemistry, and identification of microorganisms, its advantages become particularly useful in forensic practice where the term "fingerprints" rightly belongs.

Analytical pyrolysis is one of the most common techniques in modern forensic practice,[137] especially in analysis of paints which are essentially polymer materials.[6] Often traces of paints are left at the scene of a crime, on the criminal's clothes, or on his vehicle. Although paints contain inorganic components which are identified by various spectral methods, identifying the paints themselves is more difficult from analysis of the inorganic components. PGC enables the forensic analyst to distinguish different paints, including paints of the same grade but manufactured at different factories. For example, Table 4[16] lists the ratios of acrolein/methacrolein peak heights in pyrograms of white alkyd paints produced at two different factories (A and B) over 12 months.

In the case of Factory A, 2 out of 11 batches differ from the others while in the case of Factory B, 3 groups of paints can be distinguished. 3 batches are characterized by the following ratios of peak heights of the characteristic substance, 0.5 ± 0.1; 2 batches, 0.7 ± 0.1; 6 batches, 0.8 ± 0.1. Similar results could not be obtained by inorganic analysis.[16] Spectral analysis, for example, identified 53 paint samples out of 190, as

Table 4
RATIO OF ACROLEIN/METHACROLEIN PEAK HEIGHTS FOR DIFFERENT BATCHES OF WHITE PAINT PRODUCED AT TWO FACTORIES

Batch	Factory A	Factory B
1	0.15	0.81
2	0.15	0.64
3	0.70	0.97
4	0.15	0.47
5	0.12	0.81
6	0.12	0.99
7	0.11	0.92
8	0.13	0.62
9	0.13	0.82
10	0.14	0.54
11	0.81	0.42

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opposed to 141 identified by PGC.[16] Thus, in this example, PGC turned out to be three times as effective in identifying paints as emission spectroscopy.

The literature provides other examples illustrating the advantages of PGC over spectral methods of identifying nonvolatile substances. In his work,[138] Bélinsky demonstrated the possibility of identifying phenolic resins having comparable compositions but different degrees of curing by PGC, whereas a similar identification by IR spectroscopy is impossible. The application of PGC in forensic chemistry can be illustrated by the following example.[137] A pyrogram was obtained of a grain of a black material found on the skull of a 38-year-old woman killed by a blow on the head. The grain resembled a particle of a paint normally applied on hand tools. The pyrogram of that grain was identical to that of the paint on tools found in an abandoned car.

When identification is carried out by the PGC method, the most important factors are the presentation of the experimental results and selection of the parameters used to compare different samples. In order to simplify the evaluation of the results and increase the reliability of identification, it is advisable to limit the number of characteristics used for identification. For instance, in the above example of identification of paints produced at two factories, the characteristic value was the height ratio of only two peaks (acrolein and methacrolein) in the pyrolysis products.

The use of just one characteristic (e.g., the ratio of two components in the pyrolysis products) is, however, not always sufficient for identification by PGC. The analytical potential of PGC increases with the number of characteristics used, i.e., the number of components whose characteristics are used for identification.

Naturally, the more complex the composition of the pyrolyzed substances, the more characteristics are needed for identification. For example, in identifying isoprene rubbers (NK, SKN-3, SKIL, Natsyn, Coral, Cariflex®IR), the characteristic pyrolysis products are isoprene and dipentene, while in the case of butadiene rubbers (SKB, SKD, Budene®, Diene NF, Buna CB, Asadene NF, Cariflex® BR, Ameripol® CB), butadiene and vinylcyclohexane. In the case of copolymer rubbers, the number of characteristic products necessary for identification increases to three, namely, butadiene, vinylcyclohexene and styrene are used for butadiene-styrene rubbers (SKS-10, SKS-30, Buna S, Europrene®-1500, Solprene®) and butadiene, vinylcyclohexane and methylstyrene are used for butadiene-methylstyrene rubbers (SKMS-10, SKMS-30).[139,140] Figure

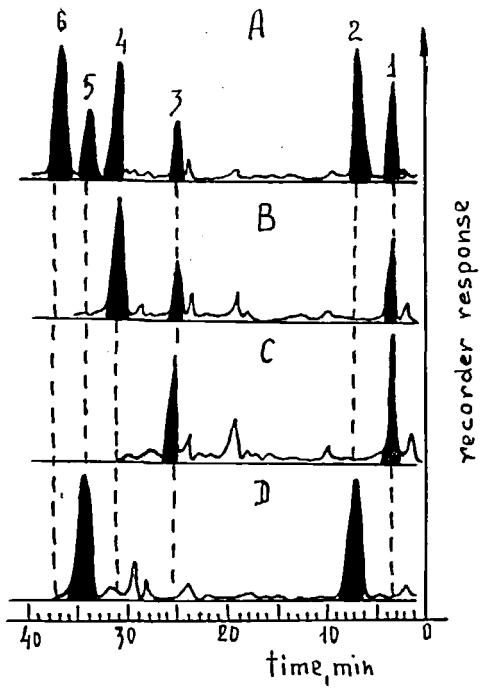

FIGURE 12. Pyrograms of some commonly used rubbers and their mixtures. (A) Pyrogram of a mixture of rubbers: isoprene (SKI), butadiene (SKD), butadiene-styrene (SKS), butadiene-methyl styrene (SKSM); (B) SKS; (C) SKD; (D) SKI. (1) butadiene, (2) isoprene, (3) vinylcyclohexane, (4) dipentene, (5) styrene, (6) methylstyrene.

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12[139,140] represents, by way of an example, pyrograms of individual general-purpose rubbers and a four-component mixture of rubbers. The hatched peaks correspond to those components in the pyrolysis products which are used for identification. The ratio of the pyrolysis products changes depending on the composition of the copolymer and structure of the polymer.

The information on the pyrolyzed sample can be most complete if the entire spectrum of the pyrolysis products is used. This information should preferably be presented in the form of bar graphs. Then, the experimental data will be presented in one of the following forms:[4,53,64,141] (1) peak height versus retention time; (2) percentage peak area with respect to the sum total of all peak areas vs. relative retention time; and (3) relative peak area vs. relative retention time (or its logarithm). When relative retention times are calculated as a standard, usually one of the peaks featured on the chromatogram is selected as the reference one. The experimental results being presented in relative values takes care of the variations caused by the inconstancies of the sample size, carrier gas velocity, separation temperature, etc. For example, when what looks like two different initial pyrograms obtained from two polymer samples of different sizes (2.3 and 4.6 mg) are presented in the form of one of the possible three bar graphs, we deal in fact with just one bar graph. Such a form of presenting experimental data is more invariant.

By now, a wealth of experimental data on PGC of polymers has been accumulated suggesting that this method can be extensively applied for identification of various

polymer systems. To identify a polymer by the fingerprint method, its pyrogram is compared with those of known substances and on the basis of this comparison, the spectrum of the test sample is identified. A sample can be identified only if a pyrogram of the substance of interest is available in advance. The method is marked by a high resolution. A good example is provided by Groten[142] who found that analysis of more than 150 various polymers had given different pyrograms for almost all samples. Clearly defined, characteristic pyrograms were obtained in the case of polymers of the vinyl series having a common formula, namely: polystyrene, polyvinyl acetate, polypropylene, and polyvinyl chloride. Sharp differences are observed in the pyrograms of cellulose esters (acetate, propionate, butyrate), natural materials (silk, wool, cotton) and polyolefins of similar structure: polyethylene, polypropylene, poly-3-methylbutene-1, and poly-4-methylpentene-1. In general, the specificity of the pyrolysis products of polymers increases with their molecular weight. This is consistent with the assumption that heavy products are more adequately representative of the test sample fragments than light products whose formation is strongly influenced by secondary reactions. Pyrograms of a great variety of plastics were examined by Nelson et al.[143] The samples (0.2 to 0.5 mg) were pyrolyzed at 650 to 750° C for 10 sec. In the case of polymers with similar structures, differences in the pyrograms could be seen only in the peaks corresponding to "heavy" products. Similar conclusions as to the high informative value of heavy products in studying the microstructure of a polymer chain were drawn by other investigators as well.[144,145] Analysis of automobile paints by PGC was described by May et al.[146] and by Levy.[147] The latter established that a shorter column improves the reproducibility of the obtained pyrograms and their selectivity which, in our opinion, is due to the "strong" involvement of heavy products in the identification of paints, which must be more informative as far as the structure and composition of the sample are concerned. In investigating inorganic and thermostable polymers, Szekely and Blazso[148] indicated that analytical pyrolysis should preferably be conducted under mild conditions in order to avoid secondary reactions; hence, to obtain more meaningful results as compared to rapid complete pyrolysis at elevated temperatures. The mild conditions for pyrolysis can be provided by using a ribbon filament at relatively low temperatures. In their work,[148] Szekely and Blazso showed that the reproducibility of pyrolysis is quite satisfactory even if a complex mixture of products is formed in a broad range of molecular weights. The reproducibility of experimental data with respect to the relative yield of pyrolysis products varied from 1.4 to 8.6% (relative RMS deviation). The studies of pyrolysis of silicon polymers, described in Reference 149, are indicative of the high structural sensitivity of this method.

PGC finds extensive application in the identification of rubbers. The results obtained in this area have been summarized by Malyshev and Pomogaibo.[150] Their book presents pyrograms of the pyrolysis products of a large number of rubbers with a detailed description of the pyrolysis procedure.

The identification of polymers in rubbers is a rather complicated task. In this connection, of particular interest are the results of international interlaboratory tests of the PGC method, aimed at assessing its practical value. Twenty samples were correctly identified out of 23, i.e., 87%. The authors of Reference 150 consider those results quite satisfactory, and PGC is most likely to become an internationally approved standard method for analyzing rubbers. A novel approach to the PGC procedure was proposed by Toth.[151] He developed a procedure and equipment based on using a microreactor for pyrolysis (a furnace-type pyrolyzer), in which different temperature programs may be run in combination with a two-channel gas chromatograph for analysis of the degradation products. In particular, the following temperature patterns were used: (1) simple short-impulse heating, (2) heating by a sequence of isothermal impulses, (3)

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heating by several sequences of impulses with the impulse temperature increasing from one sequence to another, (4) continuous isothermal heating over a long period of time, and (5) continuous increase in temperature at a preset programmed rate.

The area of application of PGC for identification is extensive. Its use is especially recommended for substances which are either difficult to identify by other techniques (e.g., insoluble polymers) or necessitate sophisticated and expensive instrumentation, which restricts their wide application. The applications of PGC are steadily increasing; we shall only name those areas in which PGC has become a traditional technique. They include PGC analysis of polymers, drugs, biochemical substances, and microorganisms. In addition to the works discussed above in connection with applying PGC for identification of polymers, we would like to mention other studies as well. The identification of acrylate, methacrylate and styrene polymers and copolymers was covered by McCormick in his work.[104] Fischer and Meuser[152,153] examined the identification of polymers in adhesive compositions. PGC is recommended for identification of such nonvolatile natural products as bitumens. It has been used not only for the identification of bitumens but also found to be more informative than direct chromatographic analysis and IR spectroscopy.[154]

Dencker and Wolf[155] demonstrated the applicability of the method in identifying methyl esters of organic acids. Every ester is characterized by a specific pyrogram of the degradation products, which is independent of the pyrolysis temperature in the range of 575 to 650° C and of the sample size if it is not less than 1 $\mu\ell$. Asphaltenes have also been analyzed by PGC.[156] High-molecular sulfur-containing compounds were identified by PGC in fractions resulting from the separation of oil by column liquid chromatograph.[157] Ortner proposed a simple method for determining sulfur-containing groups in organic compounds.[158] The method is based on conversion of these groups to sulfur-containing gases (e.g., hydrogen sulfide, carbon disulfide, sulfur dioxide, and carbon oxysulfide). The determination of these gases even chromatographically has been elaborated by Ma and Spiegel[159] who showed the possibility of quantitative determination of sulfonic acids by PGC from the amount of the formed sulfur dioxide. The authors of Reference 160 used the PGC-MS method in identifying 179 gelatin glues, as well as acrylic, cellulose, epoxy, polyether, rubber, polystyrene, polyvinyl-acetate, and urea-formaldehyde adhesives. PGC was used in the analysis of filled and unfilled samples. Different aspects of rapid identification of polymers by PGC are considered[161], as are polyamides[162] and epoxy polymers.[163] PGC has successfully been applied in analysis of ion-exchange resins,[164] surfactants,[165] and polyethylene.[166,167]

PGC is not only a method for identification of substances and their mixtures but can also be used as a functional analysis method. For example, Iglauer and Bentley[168] showed that the composition of the pyrolysis products permits determining the functional groups of polymers (polyolefins, polyesters, polyurethanes, polyacrylonitriles, polyamides, polycarbonates, phenolic, and epoxy resins, etc.). PGC is also successful in wood chemistry.[169] For example, PGC permits not only qualitative identification but also quantitative determination of the degree of etherification and esterification of polysaccharide ethers and esters. In this case, the characteristic peaks are the peaks of compounds forming as a result of thermal detachment of the alkoxy or acyl groups of respective polysaccharide esters. Descriptions can be found in the literature of methods of determining cellulose xanthates[170] and benzyl cellulose[171] of different degrees of substitution. The identification of phenolic resins is also discussed.[172,173]

An important area of application of PGC is analysis of fibers. Comprehensive studies of synthetic and natural fibers by PGC were conducted by Kirret and Kullik and others,[174-183] Crighton,[50] and other investigators.[184,185] Geochemistry and pedology are other application areas for PGC. In soil pyrolysis, the heterocyclic products are good

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indicators of the organic substances present in soil.[186] It is shown that the characteristic changes in soil pyrograms are determined by the genetic layers over the vertical sections of soil, as well as changes in soils according to humus types. Described in Reference 187 is an attempt to determine, through identification of the pyrolysis products by the PGC-GC-MS method, the structure of kerogen, an insoluble organic substance present in sedimentary rocks.

Another successful application of PGC includes investigation of organic volatile compounds forming during step-by-step heating (pyrolysis) of carboniferous meteorites, for which purpose a special device was designed. The chromatographed compounds were identified by means of a mass-spectrometer. The pyrolysis products contained *n*-alkanes, alkenes, aromatic hydrocarbons, and thioaromatic compounds.[188-190] The rapidity, high selectivity, and adequate reproducibility of PGC make it a valuable tool in biomedical research. In 1960, Janák published his first work in which PGC was used for analysis of amino acids;[191] in later years, PGC had been applied to analysis of amino acids and proteins,[192,193] fats, oils, steroids,[194] porphyrins,[195] and pyrimidines.[196] PGC has enormous possibility in qualitative analysis of drugs — nonvolatile heteroatomic organic compounds. The results obtained in this case are more reliable as compared to pyrolysis of carbon-containing polymers because the different pyrolytic stability of various chemical bonds leads to a more characteristic spectrum of pyrolysis products which are in a lesser variety. In addition, there is little difference in the pyrograms of pure substances and those with fillers. This is why the identification of nonvolatile organic substances is in this case sufficiently reliable and simple. For example, in Reference 197, a method is proposed for identifying sulfamides in pure and medicinal forms. The combined PGC-GC-MS method was used for the identification although as can be inferred from the obtained results, the mass-spectrometer is not an absolute necessity. The same results can be had when other highly sensitive detectors are employed. The pyrolysis was carried out in a Curie-point cell at a temperature of 980° C, and the pyrolysis products were separated on a column packed with Carbowax® 20M, on a KOH-treated solid support. It should be noted that all 11 sulfamides examined yielded characteristic spectra, and the compounds can be identified by one of the characteristic pyrolysis products. The pyrograms of the pure and medical forms are identical. In this application, the pyrolysis method is advantageous over the technique involving formation of volatile derivatives. The application of PGC in analysis of penicillins is described,[198,199] and in some cases pyrolysis should preferably be combined with alkylation.[200]

PGC also finds application in practical medicine. Here is a vivid illustration of how this method can be used.[191] A child was poisoned after swallowing some pills. His urine was acidified and the ester extract was pyrolyzed after the ester had been evaporated. When the pyrogram of the extract was compared with that of veronal, it appeared that the child was intoxicated by that particular compound. The correct diagnosis saved his life.

In recent years, PGC has been successfully used in analyzing microorganisms. The currently existing microbiological methods for identifying bacteria are too complicated and time-consuming. Therefore, search for simpler and faster identification methods has always been the focus of the investigators' attention. Analysis of the possibilities of GC in the identification and systematization of microorganisms is in favor of PGC.[201] In applying this method, culture extracts or simply dry cells are subjected to thermal decomposition at elevated temperatures in pyrolytic cells and the resulting products are chromatographically analyzed.

It was shown that most microorganisms yield characteristic pyrolysis products, the pyrograms being readily reproducible under standard culture growing conditions.[202-204] This enables the chromatograms obtained to be compared with those of known microorganisms without the need to establish the nature of the products of their

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pyrolysis. The first work dealing with the application of this method[205] indicated that its sensitivity is sufficient to use a single colony for obtaining a meaningful pyrogram, and the analysis takes no more time than the preparation of specimens for microscopy.

The PGC method is highly sensitive to cell types. It is interesting to note that the pyrograms of healthy and affected cells are different.[206]

One of the areas where PGC has obvious advantages over the traditional methods is the identification of "noxious" bacteria. Bacteria such as *Pseudomonas* present serious problems from the standpoint of health protection. Although generally harmless, under specific conditions (e.g., when present in dialyzer tubes or in distilled water) these bacteria may multiply rapidly and their toxic products may harm the patient. The method for analyzing such bacteria is described by Reiner.[207] Needleman and Stuchberg[208] deal with a method which permits identifying Gram-negative microorganisms by PGC. Analytically interesting results were obtained in an experiment using a glass capillary column (70 m long, 0.5 mm in diameter) with Chromosorb® W-containing Carbowax® 20M applied on its walls. The samples were pyrolyzed in a quartz tube heated by a platinum filament. Each microorganism was identified through computer-aided comparison of pyrograms with respect to the retention times and peak areas on the pyrograms of the analyzed and known microorganisms. An interesting technique is proposed by the authors of this work to enhance the efficiency of the subsequent separation of a capillary column. The pyrolysis products to be analyzed are introduced into the chromatographic column without a stream splitter and frozen out at the beginning of the column. The freezing agent is carbon dioxide. Then, after pyrolysis is over, the products are thawed out, separated on the column, and detected. Since the pyrolysis products also contain heavy components which may contaminate the analytical capillary column and destabilize its characteristics, a precolumn should preferably be used for trapping the heavy, practically nonvolatile compounds.[209] The authors[208] also proposed resorting to back flushing along with using the precolumn for this purpose.

In another work,[210] PGC was used in analysis of six species of *Bacillus* which are supposed to be important in space research. Samples (about 150 mg) of bacterial cultures grown on membrane filters were pyrolyzed at 800° C for 10 sec. The pyrolysis products were separated on a 300 × 0.3 cm column packed with a sorbent containing 10% Carbowax® 20M on Anachrom® ABS, 100-110 mesh. Different species of *Bacillus* produce different pyrograms. Bacterial cultures of different incubation ages also produce different pyrograms; therefore, only pyrograms of cultures of the same age can be compared.

An interesting and highly promising method was proposed by Andreev et al.[211,212] for analyzing microorganisms with respect to the composition of the constituent fatty acids. It is based on chromatographic analysis of methyl esters of fatty acids, forming as a result of joint pyrolysis of microorganisms and a quaternary ammonium compound. This method permits determining within 30 min, the content of fatty acids in microorganisms using only one microcolony.

The sensitivity of gas chromatography enables the amount of microorganisms to be determined by analysis of the products of their metabolism. Analysis of lethogenic clostridia has shown that the presence of bacteria in a culture medium in amounts less than 10^4 mℓ permits their identification.[213] GC may be used to check the sterility of microbiological processes. Analysis of bacteria and microorganisms is a new, promising trend in PGC of great practical interest.

In the literature, works concerning the application of PGC for analysis of volatile compounds are few. Fig. 13[214] demonstrates the possibility of applying PGC in identifying volatile hydrocarbons. It represents mass spectra and pyrograms of two compounds: 3-methylpentene-2 and 2-ethylbutene-1. It can be seen that the pyrograms of

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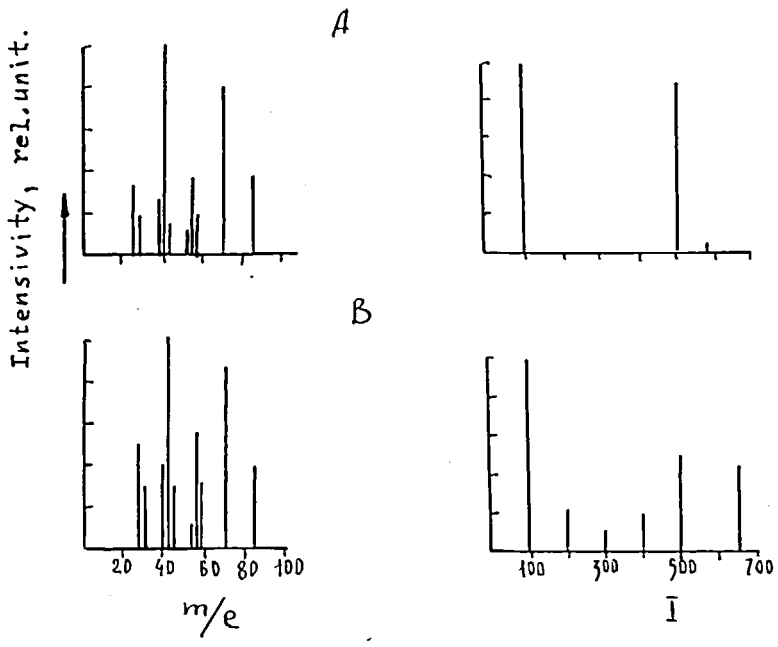

FIGURE 13. Comparison of mass spectra and bar graph GC pyrograms of two isomeric hexenes. (A) 2-Methylpentene-2; (B) 3-ethylbutene-1. Pyrolysis temperature, 600°C. The pyrolysis products were analyzed on a column with silicone DS-200 at 120°C.

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similar hydrocarbons are different while their mass spectra are almost identical, a fact which makes it practically impossible to identify them by mass spectroscopy. According to Fanter et al.,[214] the pyrograms of all 83 hydrocarbons investigated differ widely (with the exception of *cis-trans* isomers). Note that the pyrolysis products are consistent with the theory of radical reactions.[215-217] This fact is in favor of development of pyrolytic chromato-mass spectroscopy similar to conventional mass spectrometry. Optimally reproducible results are to be expected when individual chromatographic zones are used for pyrolytic identification after GC separation of the initial sample. In this case, it may be assumed with a high degree of probability that the sample to be is pure and that its concentration in gas phase is sufficiently low. Indeed, as was shown,[218] pyrograms depend on the pyrolysis temperature and the carrier gas flow rate, but not on the sample size. For practical implementation of chromato-mass spectroscopy a number of chromatographic schemes were proposed, including simple[219] and more complicated[218-221] ones with a greater analytical potential.

Although no general methods are available for determining the structure of a substance from the pyrolysis products (a task which must be approached individually and requires a great deal of experience and intuition on the analyst's part), certain recommendations can still be given. First, analytical pyrolysis should preferably be carried out under conditions when the role of secondary reactions is insignificant, in particular, seeing if it is possible to conduct pyrolysis at lower temperatures. Second, the pyrolysis products should preferably be identified using capillary flame photometry, etc.). Third, particular attention during the experiment should be paid to analysis and identification of heavy products which give a more complete picture of the sample structure. Fourth, functional groups can in some cases also be determined by pyrolysis

Table 5
COMPARISON OF THE RESULTS OF ANALYZING COPOLYMERS OF VINYL ACETATE AND VINYL CHLORIDE BY DIFFERENT METHODS

Copolymer sample (grade)	Vinyl chloride content in copolymers (%)		
	Ultimate analysis for chlorine[a]	IR spectroscopy[b]	PGC[c]
049	60.8 ± 0.6	54.7	55.8
047	69.4 ± 0.1	64.4	65.2
075	74.1 ± 0.3	72.3	72.2
076	69.1 ± 0.9	66.7	67.8
46/82	81.8 ± 4.4	84.8	83.9
51/83	87.9 ± 1.0	89.0	87.7

[a] Data from two determinations.
[b] Accuracy ± 1%.
[c] Accuracy ± 2%.

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GC. This method is especially recommended for determining the functional groups whose ultimate composition differs from other parts of the molecule under investigation by at least one element. For example, a method for determining the degree of esterification of cellulose xanthate has been described.[169] The main pyrolysis product of dithiocarbonic groups is carbon disulfide whose amount is a measure of the degree of esterification of cellulose xanthate. A similar method had been proposed for analysis of arylsulfonic acids to determine the sulfo groups from the sulfur dioxide resulting from pyrolysis. A reverse approach might also be of interest. To determine the functional groups, preliminary quantitative reactions are first conducted with respect to these groups. The derivatives resulting from subsequent pyrolysis yield characteristic products, the amount of which is a measure of the content of a particular functional group in the initial compound.

The above examples attest to the sufficiently high versatility of PGC in identifying unknown substances. The next, more complex but also successfully solved problem is quantitative analysis by PGC.

IV. DETERMINATION OF THE COMPOSITION OF POLYMER SYSTEMS AND THE STRUCTURE OF POLYMERS

The spectrum of pyrolysis products is a function of the composition and structure of the pyrolyzed sample, which accounts for the applicability of PGC in quantitative analysis and structural studies. Determining the composition of polymer systems (mixtures and copolymers) and establishing the structure of the analyzed polymers are practically important and rather complex problems. PGC is successfully used in solving these problems and is one of the few methods that can be employed in investigating insoluble polymers.

In evaluating the PGC method, it is interesting to compare the results of quantitative determinations of polymer compositions by PGC and other methods using the same samples. Such comparison has already been made in one of the earliest works[59] (see Table 5), the fit being excellent.

Thus, PGC ensures reliable results in a rapid procedure and on relatively simple equipment. Unfortunately, the calibration holds only for a particular instrument.

Two methods are normally used in PGC for determining the composition of polymer systems and structure of macromolecules. The first, indirect or comparison (substitution) method is based on comparison of the pyrogram of the analyzed (unknown) polymer system with that of a known system. The identity of the pyrograms suggests that the structure and composition of the polymer systems are identical, too. An improved version of this method involves the application of the interpolation and extrapolation methods widely used in other branches of chemistry, which makes the experiment much less time-consuming. The identification of the pyrolysis products in the indirect method is not absolutely necessary. The other, more time-consuming but more informative independent (absolute) method for determining the structure and composition of a polymer system resides in that the structure of the system of interest is derived from the pyrolysis products, the most useful for this purpose being the heavy, "high molecular" products containing several monomer chains. In this case, the pyrolysis products must be identified, which can be achieved by gas chromatography or other physicochemical methods. The identification of chromatographic zones is simplified if selective detectors and, primarily, a mass spectrometer are included in the GC system (see, for example, References 4, 5, and 222 to 224).

The analysis of the composition of polymer systems by the more common indirect method normally boils down to the following steps: (1) taking characteristic pyrograms of samples of systems of different composition; (2) selection of characteristic peaks on the pyrograms, whose magnitude varies with the composition of the polymer system; and (3) plotting a calibration curve on the basis of the obtained data (e.g., relative characteristic peak height versus monomer content in the polymer).

More stable results with respect to the experimental conditions, permitting one to disregard insignificant deviations of some parameters (sensitivity of the instrument, sample size, carrier gas flow rate), can be obtained for quantitative calculations using the relative values of characteristic peak areas (or heights) with respect to the reference (standard) peak. The reference should preferably be a peak which is characteristic for the second component[225] or a peak associated with the presence of both components in the system.[226]

In PGC, just as in other methods, an internal standard should be used (see, for example, References 223 and 224). This, however, cannot be done directly in PGC, primarily because of the possible degradation of the standard, volatility of commonly used standards and, possibly, their effect on the pyrolysis of the test sample, etc.

The PGC method involving an integral standard has been described by Esposito.[227] According to this technique, a certain amount of a standard polymer (in a solution) is added to the solution of the test polymer. Then the mixture is pyrolyzed after the solvent has been removed, and the area of the characteristic peaks of the analyzed polymer system are calculated with respect to the area of one of the standard polymer peaks. A serious limitation of this method is the necessity of using only soluble polymers. It is also necessary to provide for the separation of the characteristic peaks of the system under investigation and of the standard polymer. In addition, the introduction of a standard polymer may, in some instances, affect the composition of the pyrolysis products of the sample being analyzed.

As is known, the internal standard method offers a number of advantages, which is why it should be developed further. Particularly, polymers with a "poor" characteristic spectrum of pyrolysis products must be used. This idea was prompted by Gross.[228] He suggested using polymer products as standards and (in the case of isothermal separation of the pyrolysis products) substances yielding a small number of easily identifiable peaks,

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such as polystyrene, polymethyl methacrylate, and also (in the case of programmed separation) polyethylene whose pyrolysis results in n-paraffins, γ-olefins and γ,ω-diolefins which produce on the pyrogram characteristic groups of three peaks corresponding to compounds with the same number of carbons. It is also advisable to use monomer compounds, specifically organic complexes, as standards. The effect of the standard on the pyrolysis products of the analyzed polymer can be easily determined by comparing the pyrograms of the sample, the sample together with the standard, and the standard.

There is another possibility of using the internal standard method. The standard may also be a thermally stable volatile compound if it can be introduced into the pyrolysis zone in a sealed capillary of a low-melting alloy.[229]

When PGC is used for quantitative analysis of nonvolatile organic compounds, it is the analyst's task to establish a correlation between the structure (composition) of the samples and the composition of their volatile pyrolysis products recorded in the form of a pyrogram. Therewith, in studying a number of systems with varying compositions or structures, it is generally sufficient to discriminate without identification the most characteristic peaks, i.e., those peaks of which the area (height) variations would be quantitatively representative with a high degree of accuracy of the differences in the composition (structure) of the samples. In view of the fact that using relative values is always preferable, two peaks are normally selected for quantitative calculations: of characteristic and reference peaks. Even when analytical packed columns are employed, the total number of peaks on a chromatogram may amount to several score, out of which only some can be used for the calculations. Therefore, the selection of an optimal combination of peaks, ensuring maximum sensitivity and accuracy of analysis, involves time-consuming calculations and is often difficult.

Alishoyev et al.[230] describe a procedure involving a computer to solve this problem. It is illustrated by an example based on the results of determining the composition of mixtures of natural (NK) and butadiene-styrene (SKS-30) rubbers. Previously, this particular determination was performed by a conventional method.[226]

Of all the combinations of peaks on the chromatograms of the pyrolysis products, only 11 were selected for which the height (1) and width at half height (μ) could be determined. The calibration curve was in the form of the relative characteristic peak area Y_{KLi} vs. content X_i of one of the mixture components (SKS-30):

$$Y_{KLi} = f(X_i) = \frac{M_{Ki}\ell_{Ki}}{M_{Li}\ell_{Li}} \qquad (2)$$

where K and L are peak numbers.

Since analysis of the literature indicated that calibration curves may be expressed as functions close to parabolic ones, the regression lines sought (within the second order) were in the form

$$Y = A_1 + A_2X + A_3X^2 \qquad (3)$$

with the basic functions being 1, X and X^2. Coefficients A_1, A_2, and A_3 can be found assuming minimum total quadratic misclosure $\sum_{j=1}^{m} U_i^2$, where U_i is the misclosure and m is the number of calibration measurements made within region $\alpha \leq X \leq \beta$

$$\sum_{j=1}^{m} U_i^2 = \sum_{j=1}^{m} [Y_i - (A_1 + A_2X + A_3X^2)]^2 \qquad (4)$$

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Where conditions of the minimum are that partial derivatives in the right-hand part with respect to A_1, A_2, and A_3 must be equal to zero. This gives three first-degree equations with respect to A_1, A_2, and A_3, from which they can be defined.

The RMS error in determining X from observed Y, i.e., $\delta/[f(x)]$ (δ is the RMS error in determining Y) can be evaluated in terms of sampling RMS error η

$$\eta = \sqrt{\frac{\frac{1}{m-1}\sum_{j=1}^{m} U_i^2(\beta-\alpha)^2}{[f(\beta)-f(\alpha)]^2}} = \frac{(\beta-\alpha)}{m-1}\sqrt{\frac{\sum_{j=1}^{m} U_i^2}{[f(\beta)-f(\alpha)]^2}} \qquad (5)$$

For example, with varying K and L, the value of $(\beta-\alpha)$ for portion $[\alpha, \beta]$ and the number m of calibration measurements are constant. Then the smaller the value

$$V = \sqrt{\frac{\sum_{j=1}^{m} U_i^2}{[f(\beta)-f(\alpha)]^2}}$$

the greater the accuracy.

To find the best peak combinations for determining X use was made of a "Minsk-22" computer. The software features of the problem solution were outlined above.

The program is written in such a way as to use any functions ϕ_1 (X) and ϕ_2 (X) instead of functions X and X^2. The program calculates for each portion $[\alpha, \beta]$ the regression lines with respect to every pair of peaks K and L (i.e., the values of A_1, A_2, and A_3) and selects all pairs of peaks in increasing order of V values until V becomes a certain number of times greater than the minimum value.

The experimental data are presented in the form of tables. Each table contains a sequence of values $\mu_{L_i} l_{L_i} \ldots \mu_{S_i} l_{S_i}$ for five peaks (in this case, S = 11), corresponding to a certain value of X. Four X variation intervals were taken for the calculation: 0 to 0.3, 0.3 to 0.7, 0.7 to 1, and 0 to 1. For the best regression lines the accuracies were 1, 1, 1.5, and 5%, respectively.

Comparison of the calculated data with the results given in Reference 226 has shown that not all of the selected peak combinations are optimal, although most of them were among the ten best within the 0 to 1 interval. This was another proof that the best peak combinations are difficult to select without a computer, especially that different combinations are optimal in different regions of variations in the content of the component under analysis. For example, the calibration curve for K = 3 and L = 7 should be used only in the region of small concentrations of SKS-30, while the maximum accuracy within the 0 to 1 interval of varying SKS-30 concentrations is ensured by calculations with respect to peaks 5 and 6 which were not taken into consideration at all in this work.[226] It should be noted that the determination accuracy is to a great extent dependent on the selection of the standard peak, whereas practically no selection criteria are involved when its selection is "subjective". Note also that the calibration curves given in Reference 226 are close to those calculated from the equations for the same peaks, but do not coincide with them.

To experimentally verify the results of the above work, chromatograms were taken of the pyrolysis products of three samples of NK and SKS-30 mixtures containing 40% SKS-30. The contents in the pyrolyzed samples (mean value), determined from the calibration curves of Reference 226 for the peak area ratios of 4/7, 8/7, 9/7 and 11/7 were, respectively, 36, 42, 43, and 38.5%, while from the curves calculated for the same peaks,[230] they were 38, 41, 41, 38.5%, and, for ratio 6/5, 40.8%. Thus, the composition of

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the pyrolyzed samples can be more accurately determined if use is made of calibration curves calculated from the corresponding equations. Since the composition of a mixture under investigation can be determined using different calibration curves, the accuracy of calculating X can be improved by means of the least-squares method (see, for example, Korn and Korn[231]). For various peak combinations $y_1 = f_1(x) \ldots y_\mu = f_\mu(x)$, the observed values are, respectively, $Y_1 \ldots Y_\mu$, and the RMS errors are $\theta_1 \ldots \theta_\mu$. The quantity X can best be expressed in terms of X_o which minimizes expression

$$\theta = \sum_{j=1}^{m} (\theta_i - Y_i)^2 \frac{1}{\delta_i^2} \qquad (6)$$

At the minimum point, the derivative in the right-hand part with respect to X is equal to zero, i.e.,

$$\sum_{j=1}^{m} \frac{1}{\delta_i^2} [\theta_i \cdot f_i(X) - f_i'(X) \cdot f_i'(X)] = 0 \qquad (7)$$

which permits a more accurate evaluation of X. If X_o is the minimum point, the RMS error of the measurement is

$$\delta^2 = \frac{1}{\sum_{j=1}^{m} \frac{1}{\delta_i^2} [f_i'(X_o)]^2} \qquad (8)$$

The above-described calculation method involves a time-consuming step of manual determination of the chromatographed peak parameters. Evidently, this step can be automated if the signal from the chromatograph is recorded on a magnetic tape for subsequent direct entry of raw data into a computer.

Thus, the results obtained in the work described by Alishoyev et al.[230] attest to the possibility and advisability of using a computer in determining the composition of polymer systems by PGC. It should be noted that more recently a method for mathematical processing of pyrograms of an ethylene-propylene copolymer using factorial analysis and multiple regression analysis was described.[232] This method permits rapid determination of a peak or a group of peaks for calculating the content of the degradation products of interest.

PGC is widely used for determining the composition of binary systems (see, for example, Reference 6). As one passes from binary to three- and multicomponent polymer systems, the analytical problems become much more complicated. The possibility of determining the composition of ternary polymer systems by introducing a standard and optimizing the presentation of the experimental results has been discussed.[233]

In the experiment, ternary block copolymers of divinyl, styrene, and 2-vinylpyridine were used, which enabled mechanical mixtures of the corresponding homopolymers to be introduced as reference samples.[233] Used as the standard was *n*-nonane introduced by means of a microsyringe into the sample injector of the chromatograph prior to pyrolysis of the sample, after pyrolysis, and after recording the chromatogram of separation of the volatile products. In what follows, such a standard substance will be referred to as an external standard.

The calculation of the relative characteristic peak areas on the chromatograms of the volatile pyrolysis products, using an external standard irrespective of the pyrolysis procedure, permits taking into account the sensitivity of the detector and easy

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computation of the ratio between the peak areas of the component of interest and the standard which, under normal conditions (sample size, carrier gas flow rate, pyrolysis temperatures, etc.), are proportional to the absolute amounts of the pyrolysis products. This calculation method is essentially a modification of the absolute calibration method in gas chromatography which had never been used before in PGC. To facilitate comparison of the results obtained at different times or on different instruments, the results of individual measurements should preferably be presented in terms of specific yields (or relative characteristic peak areas); i.e., the yield of the volatile pyrolysis products must be calculated per 1 mg (g or μg) of the pyrolyzed sample with respect to 1 mg (g or μg) of the external standard. Such a calculation makes sense in the range of sample sizes which affect but insignificantly the specific yield of light pyrolysis products.

In calculating the pyrograms, one should use mean values of the retention times and peak areas of the external standard. The relative retention time of component i with respect to the external standard (t_{rel}) can be determined from formula

$$t_{rel_i} = \frac{t_i - t_o - t_h}{t_{st} - t_{o_{st}}} \tag{9}$$

where t_i is the time period from the moment the sample starts to be heated to the appearance of the maximum component peak, t_o is the dead time system with the vaporizer, and t_h is the sample heating time (from the beginning of heating to the beginning of pyrolysis) determined when the pyrolyzer is connected to the detector.

To prove the possibility of calculating the relative retention times of the pyrolysis products with respect to an external standard, polypropylene was pyrolyzed under conditions described by Berezkin et al.;[234] and the retention time of 2-methylpentene-2 on the pyrogram (with due account for the sample heating time) was compared with that of 2-methylpentene-2 introduced as an external standard. According to the experimental data, the deviation did not exceed 0.5%, which corroborated the possibility of calculating the relative retention times of the volatile pyrolysis products with respect to an external standard by this method, which is of great interest as far as the description of pyrograms and identification of nonvolatile substances by PGC are concerned.

The experimental results were used as a basis for plotting calibration curves representing relative characteristic peak areas vs. concentration of the component of interest in the mixture which permit the content of divinyl, styrene, and 2-vinylpyridine to be determined independently in their block copolymers and mechanical mixtures of homopolymers. As can be seen from Figure 14, for the system under investigation, the relation between the relative characteristic peak areas and the content of the component of interest is linear in the examined range of concentrations.

It should be pointed out for comparison that when the same experimental results are presented in the usual form (i.e., as the relative areas of the characteristic peaks of polydyvinyl and poly-2-vinylpyridine) and calculated with respect to the characteristic peaks of polystyrene vs. the content of the component of interest, this relation is not linear. Thus, it was found for the system under investigation that the relative characteristic peak areas with respect to an external standard (in other words, the absolute amounts of the volatile pyrolysis products) vary with the content of the components of interest in the system.

In this case, the relation between S_i/S_j and X_i/X_j (i and j are components of the system) must also be linear.

$$\frac{S_i}{S_j} = \frac{S_{reli}}{S_{relj}} = \frac{K_i X_i}{K_j X_j} = K_{ij} \frac{X_i}{X_j} \tag{10}$$

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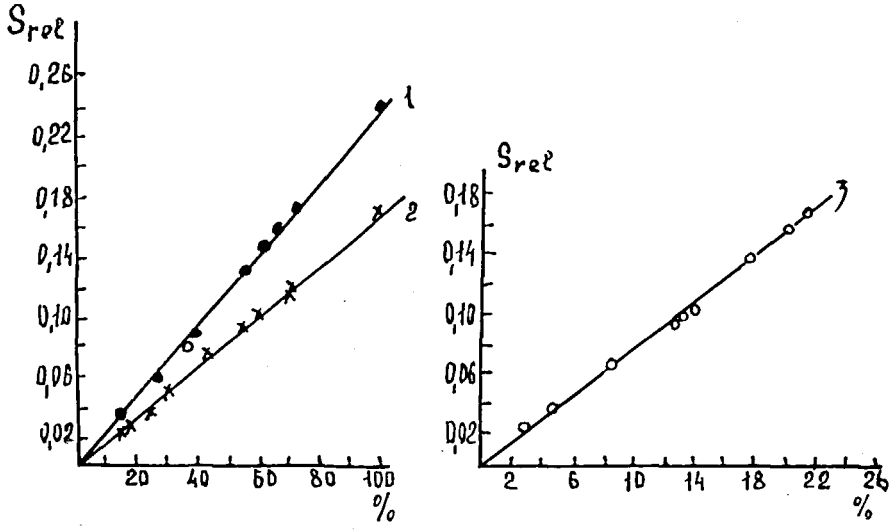

FIGURE 14. Relative characteristic peaks of (1) polydivinyl, (2) polystyrene, and (3) 2-vinylpyridine vs. analyzed components in the polymer.

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Such a form of presenting the experimental data used in some works[235] does not require the introduction of a standard and seems to be useful in determining the composition of three- and multicomponent polymer systems. The corresponding relations similar to Equation 10 for the characteristic peaks of a system under investigation are linear.

The above relation can also be used in the case of binary systems. Its application permits obtaining a linear calibration curve which is preferable in most cases. We have recalculated the nonlinear calibration curves presented in earlier works,[236-238] using Equation 10. In all cases, linear relations were derived.

As can be inferred from the experimental results published earlier, in the case of a polymer system, the specific yield of the characteristic pyrolysis product for the analyzed component is independent of the amount and nature of the other components in the system. This can be attributed to the fact that the secondary processes accompanying the pyrolysis of a system of interest are restricted mainly to intramolecular transformations of the primary pyrolysis products. Establishing such a regularity in each particular case will evidently facilitate the interpretation of the results in studying the structure of polymers by PGC.

The following advantages of the external standard method should be pointed out.[239] The use of an external standard permits obtaining a simpler relation between the content of the component of interest (particular groups or structural units) in the system and the yield of the characteristic pyrolysis products, which increases the reliability and accuracy of measurement. The introduction of an external standard with a sufficient degree of accuracy makes the selection of a standard peak unnecessary and considerably simplifies the determination of the composition. This method may be employed in qualitative and quantitative comparisons of chromatographs of the pyrolysis products of various polymer systems, particularly in developing identification methods.

As has already been mentioned, PGC is sensitive not only to the composition of a copolymer but also to its structure. This is understandable, bearing in mind that during pyrolysis, in general, chemical bonds are ruptured not only along the boundaries of the initial monomer units. Therefore, pyrograms of statistical copolymers are, in general, not

identical with those of mechanical mixtures of homopolymers, while pyrograms of graft and block copolymers correspond to those of mechanical mixtures of the same composition.[240,241] This result is not surprising because if the number of sites in the chain of the initial polymer at which grafting occurred (the number of joints in block copolymers) is small as compared to the number of units in the homochain, the high-temperature pyrolysis of such copolymers may be regarded in most cases as pyrolysis of homopolymers. For example, the calculation curves (characteristic peak area ratio vs. composition) for statistical copolymers of methyl methacrylate and ethylene and for mechanical mixtures of the corresponding homopolymers are different. The point corresponding to the graft copolymer falls on the curve for mechanical mixtures.[242]

Normally, the relative yield of monomers in the case of pyrolysis of graft and block copolymers is higher than during pyrolysis of statistical copolymers of the same composition. Proceeding from these differences, Zizin et al.[243] proposed a quantitative method for determining the degree of block linkage with respect to styrene in divinylstyrene copolymers. Similar ideas were set forth by Masagutova et al.[244]

The necessities of using reference samples of a known composition and having the same structure as the system under investigation impedes practical implementation of PGC in determining the composition of statistical copolymers to some extent. Turkova and Belenky[245] showed that for some copolymers it is possible to select a pyrolysis temperature at which the compositions of the pyrolysis products of statistical copolymers and mechanical mixtures of homopolymers coincide which permits (under given pyrolysis conditions) calibration with respect to the mechanical mixtures of homopolymers. However, because of the lack of a sufficient number of examples, this result cannot be regarded as a general regularity. As was shown by McCormick,[104] step-by-step pyrolysis can be used to distinguish statistical copolymers from mechanical mixtures of homopolymers.

The PGC procedures and equipment are applicable to ultimate analysis of polymers, as well as to analysis of copolymers if the ultimate composition of the monomers is different. Meade et al.[246] determined the oxygen content in organic compounds with the use of a carbon catalyst at 105°C. Under these conditions, methane, hydrogen, and carbon monoxide are formed; they were separated on a column with molecular sieves. The application of PGC for determining the oxygen content in polymers is also described,[247,248] as well as nitrogen component in positive photoresists.[249]

As mentioned above, two methods are used in studying the structure of organic compounds by PGC: the "substitution" or "fingerprint" and absolute methods. In general, it is difficult to say which of the two methods is preferable. The selection of an appropriate method depends largely on the nature of the substance to be analyzed and on the availability of standards, which makes it possible to use the "fingerprint" method. In the case of the absolute method, however, more stringent requirements are imposed on the chromatographic column efficiency, the sensitivity of the detector used and its selectivity, which permits the nature of the separated components to be determined individually. In this case, preference should be given to high-efficiency capillary columns and a mass spectrometer as the chromatographic detector along with other selective detectors.

In structural PGC studies, use is often made of hydrogenation pyrolysis in which the volatile pyrolysis products are hydrogenated to saturated hydrocarbons (see, for example, References 250 and 251). This procedure facilitates the elution of all volatile products and their identification. In hydrogenation pyrolysis, hydrogen is employed as the carrier gas. The use of hydrogen is also advantageous because it minimizes the effect of secondary reactions. The hydrogenation method is recommended for the following reasons: (1) when unsaturated hydrocarbons are hydrogenated, a simpler pyrogram is

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obtained because the same fragment of the polymer macromolecule often yields several different unsaturated compounds with identical carbon skeletons, and (2) saturated hydrocarbons are much easier to identify than olefinic hydrocarbons since one can use a large number of tabulated data and standard substances, to say nothing of the fact that the reproducibility of their retention values is much better. It should be noted, however, that some of the information on the structure of the initial polymer may be lost because the position of the double bond in the pyrolysis products indicates the site of rupture of the macromolecule of the polymer under study.[252]

Hydrogenation pyrolysis was applied to determine the composition of copolymers of α-olefins, the sequence of monomer units, and the manner in which they are added ("head-to-head" and "head-to-tail").[253] Mikhailov et al.[251] used PGC to investigate the structure of low- and high-density polyethylenes and copolymers of ethylene with propylene. The pyrolysis products were hydrogenated. The method made it possible to examine alkanes up to C_{50}, which facilitates the investigation of the polymer chain structure. The identified isoalkanes corresponded to the branched polyethylene structure. It has been established that the ethyl and butyl side chains occur most frequency in polyethylenes.

The PGC method was also applied in studying the structure of some phenolformaldehyde resins. The main pyrolysis products were found to correspond to individual fragments of the initial polymer molecule.[254]

PGC is sensitive to such structural features of the polymer chain as the mutual arrangement of the substituents. In a previous work,[148] various pyrograms of polypropylenes of different stereoregularity (atactic and isotactic) were obtained. Deur-Siftar[255] demonstrated that in some cases PGC permits determining the degree of crystallinity of low- and high-density polyethylenes, which is associated with the branched structure of the macromolecules of this polymer.

The yield of monomers in the pyrolysis of copolymers that decompose primarily into monomers depends on the distribution of monomer moieties in the copolymers. This is due to the fact that if the polymer decomposes by the radical mechanism with cleavage of the monomer units from the ends of the polymer molecule, the probability of cleavage of the next monomer unit depends on the nature of the nearest neighbor.

Shibasaki[256] developed a method for calculating the structure of copolymers from the number of monomers formed during pyrolysis. The respective probabilities can be determined by pyrolyzing copolymers of a known composition. The method has been verified on styrene-acrylonitrile and styrenemethyl methacrylate copolymers.

Important information on the structure of substances of interest is provided by the yield and distribution of dimer compounds, since their structure is representative of the addition of monomeric and comonomeric structural units in the polymer.[257-261] Dimbat[262] succeeded in applying PGC to determine the isotacticity and length of isotactic and syndiotactic blocks in polypropylene. This technique provides for the use of several calculation methods and does not require any calibration. It is based on the fact that the configuration of the pyrolysis products which contain asymmetrical carbons is different depending on whether they are formed from blocks (iso- or syndiotactic) or from block joints.

In their work, Tsuge and collaborators[263] showed that PGC can be used to determine the molecular weight of polycarbonates from the terminal groups. PGC is also shown to be applicable to determining the degree of cross-linking of carbon-exchange resins in the hydrogen and sodium forms on the basis of these copolymers.[264] The application of PGC in studying the structure of ion-exchange resins and porous polymers was considered.[265-267]

The dependence of the pyrolysis products on the sample structure may be used in

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applying PGC to solve various physicochemical problems. In particular, PGC was used to study the kinetics of cyclization of polyisoprene rubber; the results were later corroborated by other methods.[268,269]

V. CONCLUSION

The areas of application of pyrolysis gas chromatography are extensive. It is used to accomplish the following tasks: (1) determining the composition of copolymers and polymer systems, (2) establishing relationships between the composition of polymers and their properties (performance characteristics, physicochemical properties, etc.), (3) determining the structure of polymers, (4) identification of polymers, drugs, etc., (5) identification of microorganisms, and (6) evaluating the stability of polymers and other substances.

In conclusion, here are what we believe to be the most promising developments of the method.

First is providing conditions for specific pyrolysis. Pyrolysis is the most important stage in pyrolysis GC. The specificity of the products obtained at this stage determines the successful outcome of the analytical or physicochemical investigation as a whole. Unfortunately, this stage has not yet been systematically and comprehensively studied. All it comes to in practice is rapid pyrolysis, the only variable parameter being the pyrolysis temperature. Optimizing the temperature does produce positive results, but temperature is only one of the many factors that may be effectively utilized to obtain specific products and hence, to enhance the efficiency of the method. Among the factors of particular interest in this respect are: (1) use of different carrier gases, including chemically active ones; (2) conducting pyrolysis together with a chemically active reagent; and (3) conducting pyrolysis at lower temperatures, and others.

Second is applying a combination of chromatographic techniques to evaluate the pyrolysis products. In pyrolysis GC, use should preferably be made of column, liquid, thin-layer and capillary GC integrated into one method. Liquid chromatography is especially useful for analysis of heavy products which are more adequately representative of individual fragments of the sample, hence providing more complete information on the molecular structure.

Third is to accomplish practical tasks. Here it is necessary to standardize the procedure of analysis of industrially important substances, automate pyrolysis GC, and use computers more extensively in this area.

Fourth is the development of simple and efficient equipment for pyrolysis and subsequent chromatographic analysis.

Fifth is to increase the information content of pyrolysis GC, e.g., by using temperature programming pyrolysis[271] and cross-correlation chromatography[272] together in the same experiment.[273,274]

Sixth is the use and development of computing methods to evaluate the experimental results in pyrolysis GC.

In conclusion, we would like to draw special attention to three new and useful reviews (References 275 through 277) and a book on pyrolysis chromatography (Reference 278).

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