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THE USE OF GAS CHROMATOGRAPHY IN THE STUDY OF POLYMERS

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Chromatography is a physical method for the separation of compounds, in which the substances being separated are distributed between two phases, one of which is stationary,

while the other is mobile and filters through a layer of the stationary phase[1,2].

Gas chromatography is a form of chromatography in which the mobile phase is a gas. In a gas-chromatographic separation, the molecules of a compound being analysed are moved by a stream of carrier gas, so that gas chromatography can be used for the separation of only those compounds which can be transported without decomposition in the gaseous state. Thus the gas-chromatographic method cannot be used directly to separate non-volatile macromolecular compounds, and its application is restricted to volatile compounds with vapour pressures not less than several mmHg at the temperature of the separation. Accordingly, gas chromatography is used to determine the concentration of volatile products in polymers, or in compositions based on them. A common feature of these methods is that the polymer is introduced into the chromatography either in suspension or in solution in a suitable solvent. To facilitate calculations, a standard is usually added to the mixture introduced into the chromatograph. The polymer is retained in the column (a special short initial column, which is replaced at intervals, is often used to separate the polymer) and the solvent, standard, and volatile impurities present in the polymer are separated and detected.

A method has been developed for determining residual monomer and other volatile components in polymers based on styrene[3]. Dimethylformamide is used as solvent, and toluene is used as standard. The volume of sample taken is 5 μl. The sensitivity of the method corresponds to 10^{-6} g monomer in 1 g polymer.

Wilkinson and coworkers[4] developed a method for determining residual monomers in latices. Acetic anhydride, 2,2-dimethoxypropane, and cyclohexanone can be used as solvents. The first two solvents react with water and convert it into other compounds more convenient for chromatographic study. A separate initial column containing glass wool is used to separate the latex. The volume of sample used is 0.02–0.1 ml. The sensitivity is 0.01–0.05%.

A method has also been developed for determining free phenol and formaldehyde in phenolic resins[5].

Gratsianskaya and coworkers[6] were the first to use an analogous method for the quantitative determination of polymeric substances in a reaction system, for the example of the isomerisation of α-pinene into camphene, during which polymeric ompounds are also formed. A short initial column was used to separate the polymers. Cineol and menthol were used as internal standard. The concentration of polymer was determined from a comparison of the percentage concentration of standard in the prepared mixture and that determined by chromatographic analysis.

The application of gas chromatography to the direct study of polymers is possible only with a new type of approach, since the classical version of the analysis is impossible for non-volatile substances. In the study of polymers and other non-volatile compounds by gas chromatography, two approaches are possible in principle: (1) analysis of the polymers by the recently proposed method of "reversed" gas chromatography, and (2) analysis of macromolecular compounds from the products of chemical changes.

In the new method of "reversed" gas chromatography, in contrast to the usual version, the unknown system is the stationary liquid phase, on which known volatile compounds are separated[7]. The organic compounds used as stationary liquid phases are characterised by a definite spectrum of relative retention times for standard compounds. The spectra of the standard compounds change markedly with change in the nature of the stationary phase. Polymers can also be used as unknown stationary liquid phase; this can be used, in particular, to characterise their molecular weights. If the molecules of the polymer contain functional terminal groups differing from the main chain, there should be a definite relationship between the concentration of these groups (and hence the molecular weight of the polymer) and the retention times for standard compounds. This relationship for polyethyleneglycol maleate adipate[8] is given in Fig. 1.

The method of "reversed" gas chromatography can also be used to study phase changes in polymers, for example in polyethylene[9]. In the region of a phase change (fusion) the curves giving the dependence of the retention time or peak width on the column temperature show a maximum due to the change in the distribution constant resulting from the phase change (Fig. 2).

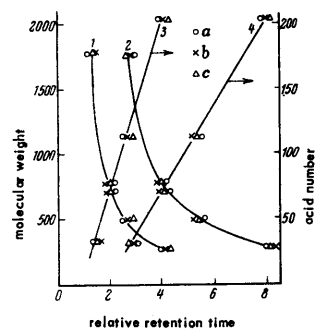


Fig. 1. Dependence of the relative retention times of ethanol (1, 3) and propanol (2, 4) on the number-average molecular weight and acid number of polyethyleneglycol maleate adipate; *a*), *b*), *c*) series of experiments.

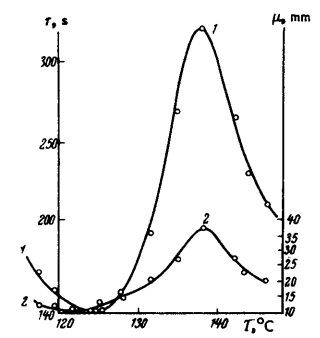


Fig. 2. Dependence of the retention time (1) and peak width (2) of n-tetradecane on the temperature of the column. The stationary phase is a mechanical mixture of polyethylene (1%) and glass beads.

The method of "reversed" gas chromatography can apparently also be used to determine the structure of polymers, the composition of copolymers, and other polymer characteristics which influence the change in the "gas–liquid" distribution constants for standard volatile compounds. An advantage of the method is that it makes possible the direct study of a polymer (without decomposing it) in small samples, but one restriction is the viscosity of the compounds being studied, which should not be too great at the temperature of the experiment[10]. "Reversed" gas chromatography can also be used to study the kinetics of chemical reactions[11], including polycondensation.

A method more widely used at present in the study of polymers characterises macromolecular substances by an indirect method—the macromolecular compound is characterised by the spectrum of volatile products formed by chemical changes. Here we must first mention the extensive application of the universal reaction of pyrolysis in the study of polymers, since the use of other chemical methods is often limited by the chemical inertness, the absence of functional groups, and the insolubility of many polymers of practical importance.

Disadvantages of the pyrolysis method include the complexity of the chemical reactions taking place during thermal degradation and the generally important part played by secondary reactions. The processes involved in the thermal degradation of polymers have as yet been insufficiently studied. Thus in general it is impossible to predict quantitatively the spectrum of volatile products from a knowledge of the structure and conditions of pyrolysis of the polymer; the opposite problem (the determination of the structure and composition of a polymer from the pyrolysis products), which is of considerable analytical interest, has not yet been solved theoretically.

The analyst's task is to establish an empirical correlation between the structure of a polymer and the spectrum of the products formed on pyrolysis. Since the composition of the pyrolysis products is determined by many factors (temperature, duration of pyrolysis, size of sample, etc.), the dependence on the structure of a polymer of the composition of the pyrolysis products becomes unambiguous only with strict standardisation of the conditions of pyrolysis, including some standardisation of the sample.

Thermal degradation followed by analysis of the degradation products has for long been used for the qualitative and quantitative analysis of macromolecular compounds and to establish their structures[12–15]. The use of the gas-chromatographic method for the analysis of the products has greatly increased the value of this method in the study of polymers, since in the complex mixture of products formed, only a few are characteristic of a given type of polymer. Thus for the analysis of volatile compounds, gas chromatography is in general a more selective method than spectroscopy and a simpler method than mass spectroscopy.

The use of gas chromatography for the analysis of pyrolysis products is due to the following fundamental advantages of gas chromatography as an analytical method: (1) the use of sensitive detectors makes it possible to carry out the analysis with small polymer samples of the order of one milligramme or several tens of microgrammes; (2) the high efficiency of separation on packed columns—1–3 thousand theoretical plates (t.p.)—or in capillary columns (20–60 thousand t.p.); (3) the time required for the analysis is short and usually varies from several minutes to several tens of minutes; and (4) standard chromatographic apparatus is used for the separation, and the pyrolysis unit consists of a small independent attachment fo the standard chromatograph.

The method of studying non-volatile compounds from the chromatographic spectrum of the volatile products is often called pyrolytic gas chromatography.

In the earliest work on the use of gas chromatography for the analysis of polymer degradation products[16–18], the pyrolysis was carried out in a special assembly, and the products were removed and analysed on a standard gas chromatograph. This method is convenient when the use of small samples (about 1–10 μg) is impossible because of the inhomogeneity of the specimen, to study the mechanism and kinetics of pyrolysis, to estimate the heat resistance of a material, when it is necessary to study the composition of the products at low degrees of conversion, etc.[19]

In a second version, the pyrolysis and the chromatographic separation are combined in a single instrument. This method for studying polymers by pyrolysis of a specimen in a special reaction vessel in front of the gas-chromatographic column in a current of carrier gas was first described by Lehrle and Robb[20]. This method has the following advantages: (1) the time required for the study is reduced considerably, since the pyrolysis and introduction of the sample are combined in a single short operation; (2) the study requires only small quantities of specimen (of the order of several milligrammes or even microgrammes); (3) for small samples (thin layers) the part played by secondary reactions is reduced; and (4) it is possible to carry out the pyrolysis under reproducible controlled conditions and to analyse both liquid and gaseous products.

An interesting intermediate version of the pyrolytic method was proposed by Swann and Dux[21]. The pyrolysis of the polymer being studied was carried out in an evacuated glass ampoule (weight of specimen 50 mg, duration of heating 15 min). The pyrolysis products were studied by gas chromatography; the ampoule was broken in a current of carrier gas in front of the column inlet.

An analogous method was used successfully for the quantitative determination of hydroxyethyl groups in hydroxyethyl–starch[22]. A sample of the substance being studied (0.001 g) was pyrolysed in a sealed capillary (9.0 × 0.1 cm) in a vacuum at 400°C for 10 min. The pyrolysis products were studied chromatographically. It was established that there is a linear relationship between the height of the acetaldehyde peak and the quantity of hydroxyethyl groups in the specimen being analysed.

A more widespread version of the pyrolytic method is that in which the cell for the pyrolysis is also the assembly for the introduction of the sample into the chromatographic column.

The layout of the apparatus in pyrolytic gas chromatography is characterised by considerable variety; the pyrolysis cells designed by foreign firms are extremely varied. The various pyrolysis cells can be divided into two design types. In pyrolytic reactors of the first type, the pyrolysis is carried out on a filament (spiral), which is heated rapidly by electric current. The heated spiral is placed in a flow chamber whose walls are at a temperature not exceeding the temperature of the subsequent chromatographic separation.

When these cells are used, the substance being studied is applied to the metallic filament (usually platinum or Nichrome). The spiral carrying the substance to be analysed is then placed in the gas stream, the cell is made airtight, the instrument is brought to operating conditions, and the spiral is heated. The resulting pyrolysis products are carried by the carrier gas into the chromatographic column, separated, and recorded by the detector. With cells of this type the design is simple, the specimen being studied can be heated rapidly to the required temperature, the pyrolysis is carried out in a stream of carrier gas, and the heating surface is small, so that the possibility of secondary reactions by the pyrolysis products is reduced. Cells of this type must satisfy the following requirements: (1) the cell colume must be as small as possible, since increase in its volume leads to a decrease in the efficiency of the subsequent chromatographic separation; (2) supplementary heating of the cell walls is required to prevent condensation of liquid pyrolysis products on the cold walls of the cell; alternatively, the cell can be placed in a thermostat; and (3) rapid and convenient replacement of the spirals carrying the substance being studied must be possible. Pyrolysis cells of this type can be used to carry out pyrolysis in various gaseous media, including reactive media, or in a vacuum.

The construction of a typical glass pyrolytic cell[23] is illustrated in Fig. 3. Cells of similar design are described by Janak[24], Jones and Moyles[25,26], and Mljenek[27]. These authors used chromatographs with an ionisation detector, since the total volume of products formed by pyrolysis on the spiral from very small samples is insufficient for detection by the simpler but less sensitive katharometer.

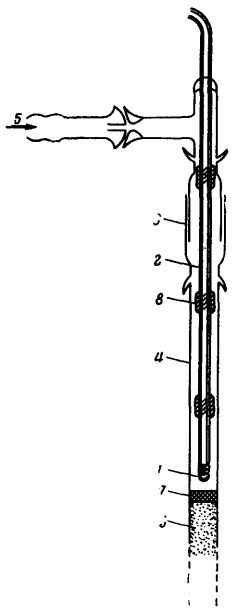


Fig.3. Glass cell for pyrolysis:
1) Nichrome spiral (0.2 Ω); 2) tungsten electrodes (diameter 1 mm); 3) sorbent; 4) column; 5) carrier gas inlet; 6) ground joint; 7) layer of asbestos; 8) glass insulation.

Franc and Blaha[28] worked with a pyrolysis cell in which platinum gauze was used instead of a spiral. This made it possible to increase the quantity of specimen being analysed, without increasing the weight of polymer per unit area of wire, so that it became possible to detect the pyrolysis products by means of a katharometer.

The temperature of the cell does not remain constant during the pyrolysis; Fig. 4 shows the change in the temperature of the cell and the concentration of volatile products with time in various experiments on the pyrolysis of a poly(propene oxide–tetrahydrofuran) copolymer. Thus the pyrolysis of the polymer actually takes place under conditions of rapidly changing temperature.

Kyryacos and coworkers[29] suggested the application of a higher voltage to the spiral at the start of pyrolysis in order to reduce the time required to heat the spiral to a given temperature.

The use of metallic filaments and spirals (platinum, Nichrome, etc.) as supports for the polymer film during pyrolysis is not the best arrangement, because of the possible catalytic activity of the metals. It has been shown[26] that for samples weighing more than one milligramme the filament material has a marked influence on the spectrum of products; the spectrum of pyrolysis products is simpler when a gold-plated filament is used than when a Nichrome filament is used. When smaller samples (20–30 μg) are used, however, the spectrum of pyrolysis products for polystyrene and poly(methyl methacrylate) are independent of the spiral material (Nichrome, platinum, gold-plated platinum). This undesirable factor for large samples can apparently be eliminated by using glass coated filaments.

It is sometimes convenient to place the sample for pyrolysis in a small boat of mica, quartz, or other more inert material, instead of directly on the spiral[30].

It has been reported[30] that when the pyrolysis of rubbers is carried out in a small mica boat heated with a Nichrome spiral, the gas-chromatographic spectra of the products are more characteristic (that is, greater differences are observed between them) than when the sample for pyrolysis is deposited directly on the spiral.

A method has also been described for studying non-volatile organic compounds by pyrolysis of a weighed specimen of the substance (5–30 μg) placed in a capillary

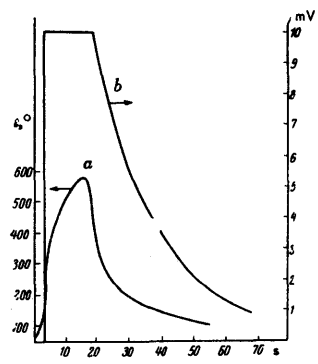


Fig.4. Change in the temperature of the spiral (*a*) and the concentration of volatile products (*b*) during pyrolysis.

(0.2 × 0.05 cm) sealed at one end[31]. The area and height of the peak were found to be linearly dependent on the size of the sample.

In pyrolysis cells of the second type, the specimen for pyrolysis is introduced into a high-temperature zone of a tubular reactor, where the thermal degradation takes place. An advantage of reactors of this type is the more effective standardisation of the thermal conditions, but a disadvantage is the possibility of secondary reactions by the pyrolysis products as a result of the increased time for which they are present in the hot zone.

Increase in the dimensions of the polymer sample being analysed makes it possible to supplement the gas-chromatographic method for the study of the degradation products with other physicochemical methods for the analysis of the residues from the pyrolysed polymer (chemical, spectroscopic, etc.).

Various methods for heating the specimen for pyrolysis have been described: (1) introduction of the small boat into a hot zone, heated to a high temperature[32]; (2) the use of an electric heater consisting of a platinum wire wound directly on to the boat or capillary[33,34]; (3) immersion of a U-shaped vessel containing the specimen in a bath of Wood's alloy (500–550°C);[35] and (4) induction heating of the specimen, mixed with a metal powder, by high-frequency currents[36].

An original assembly for the pyrolysis of polymers was proposed by Giacobbo and Simon[37,38]. The specimen for pyrolysis is deposited on a wire of ferromagnetic material (0.5 × 20 mm) and placed in a glass capillary in the stream of carrier gas. The ferromagnetic wire is heated rapidly to the Curie point in ~ 2×10^{-3} s by means of a high-frequency furnace. During pyrolysis of the polymer, the temperature of the wire remains constant at the Curie point. The temperature of pyrolysis can be varied to some extent by using different ferromagnetic materials. The method has been used to study the spectra of pyrolysis products from various amino-acids. This method of heating the specimen for pyrolysis was also used by Völlmin and coworkers[39].

Reactors using a heated filament have found wider practical application.

To obtain reproducible results and a characteristic spectrum of pyrolysis products, it is necessary to select the optimal parameters for the experiment, and these should be standardised precisely.

The thermal degradation of a polymer is sensitive to even slight changes in the conditions of pyrolysis. The decisive parameters in the rational design of a cell are as follows: (1) the size and geometric form of the specimen for pyrolysis; (2) the temperature conditions of the pyrolysis; (3) the duration of pyrolysis; and (4) the conditions of the chromatographic separation.

The polymer is deposited on the spiral of the pyrolysis cell by two main methods: (1) from solution by evaporation (for soluble substances) or from a suspension (for insoluble substances); and (2) small specimens (several milligrammes) of identical shape are placed directly inside the spiral.

A film can be obtained by immersing the spiral or filament in a dilute solution or suspension; Alternatively, a solution or suspension containing ~ 1 wt.% of polymer can be applied by means of a soft brush to one or two rings in the centre of the spiral, which is then dried; the drying can be accelerated using an infrared lamp[25].

Sometimes, the specimens for pyrolysis are first finely divided, and plasticisers and other soluble substances are removed by extraction[40]. It is sometimes recommended that the sample be deposited on the wire from alkaline or acidic solutions[38,41].

The removal of solvent and other volatile substances (gases, monomers, moisture, etc. dissolved in the polymers) can apparently be carried out conveniently by heating the polymer, before pyrolysis, at a temperature lower than that at which degradation begins.

In the study of the mechanism of pyrolysis, and sometimes in the study of the fine structural details of a polymer, the more complicated method of thin films is apparently the optimal method, since in thick films the low rate of diffusion, the increase in the part played by secondary reactions, and a number of other factors lead to distortion of the true rate of the process and a change in the qualitative composition of the pyrolysis products[25,42].

Jones and Moyles[26], in a study of the dependence of the composition of pyrolysis products on the size of the sample, demonstrated the advantages of working with small microgramme specimens. They give for comparison two chromatograms, obtained using milligramme and microgramme specimens of styrene homopolymer. The pyrolysis conditions were the same in both cases. The appearance of additional peaks on the chromatogram of the degradation products for the milligramme specimen indicates that the part played by secondary reactions is greater when large specimens are used. Since it is difficult in practice to obtain such a thin film, the degradation is usually carried out on thicker films, with the same thickness in all experiments. According to Voight[42,43], fluctuations of ±50% in the weight of sample produce no significant changes in the chromatographic spectrum of the pyrolysis products.

The structures of various amino-acids were investigated by pyrolysis of thin films of the acids[39]. The pyrolysis products were separated on capillary columns, and detected using a mass spectrometer fitted with a rapid scanning device.

A problem of practical importance concerns the possibility of applying the pyrolytic method to specimens which contain other components in addition to the polymer itself. When the polymer is insoluble in water and the other components soluble, it might be possible to prepare aqueous emulsions or suspensions of these specimens and to deposit them on a spiral and examine them in the usual way. The possibility of carrying out the direct study of industrial specimens was demonstrated by Jones and Moyles[26], who obtained identical chromatograms for the pyrolysis products from a specimen of pure polymer and a specimen containing various inert fillers. The polymer powder was mixed with the natural resin tragacanth (1 wt.%) and water, and applied to the filament in the form of a suspension for subsequent pyrolysis.

The pyrolysis may also be influenced by the carrier gas velocity, which determines the duration of contact between the pyrolysis products and the high-temperature spiral. It has been reported[44] that a decrease in the carrier gas velocity from 60 ml min^{-1} to 40 ml min^{-1} doubled the concentration of benzene in the products of the pyrolysis of polystyrene.

This effect is not always observed, however. Thus in the pyrolysis of atactic polypropylene in the range 320–935°C, the quantity of products did not change with change in the carrier gas velocity[45].

In the study of the structure of a polymer, the pyrolysis conditions should be chosen in such a way that the spectrum of polymer pyrolysis products obtained characterises unambiguously the material subjected to pyrolysis. To satisfy this requirement, it is apparently necessary that the final products be produced as a result of the minimal number of changes, that is, they should have a short "genealogy". It is then obviously easier to follow the relationship between the products of the change and the structure of the specimen being studied.

To reduce the part played by secondary reactions in the formation of the pyrolysis products, the temperatures used are usually not too high (400–800°C) and the time for which the products remain in the hot reaction zone is reduced.

An increase in the number of polystyrene pyrolysis products with increase in the temperature of pyrolysis has been demonstrated[44].

The optimal temperature of pyrolysis is determined by the nature of the analytical problem, the type of polymer studied, and the design of the pyrolysis cell. For example, in the determination of the monomeric composition of a copolymer, the optimal temperature is the temperature at which the relative yield of characteristic pyrolysis product varies most rapidly with change in the composition of the copolymer. The dependence of the percentage yield of methyl acrylate on the potential difference applied to the spiral (the voltage applied to the spiral determines its temperature) for copolymers of methyl methacrylate and methyl acrylate[46] is shown in Fig. 5.

The nature of the carrier gas also determines the conditions of pyrolysis to an appreciable extent. In the pyrolysis of atactic polypropylene, the temperature at which the gaseous pyrolysis products are liberated is about 200 deg higher in an atmosphere of nitrogen than in an atmosphere of hydrogen[47].

In the selection of conditions for the chromatographic separation, allowance must be made for the nature of the pyrolysis products. In the study of the composition of the pyrolysis products from hydrocarbon polymers, it is best to use non-polar phases, but in the study of hetero-atomic compounds it is best to use polar phases. In the analysis of volatile pyrolysis products, it is apparently best to use simultaneously two or three standard chromatographic columns containing phases with different polarities. In view of the wide range of boiling points among the pyrolysis products and also the complexity of the qualitative composition of the products, it is desirable, particularly in the study of the mechanism of thermal degradation, to use capillary columns combined with temperature programming[48]. A combination of pyrolysis in a vacuum and pyrolysis in contact with air has been used to determine the mechanism of the degradation of polystyrene and to identify the pyrolysis products in the range 300–420°C.[49]

It is convenient to express the results of the chromatographic analysis of the pyrolysis products in relative units, using the internal standard method, that is, in the form of line diagrams on coordinates S_i/S_{st} against $\lg(t_i/t_{st})$, where S_i and S_{st} are the areas of the peaks of the ith compound and the standard, and t_i and t_{st} the retention times of the ith compound and the standard. When the results are expressed in this form, it is possible to smooth out the changes due to fluctuations in the dimensions and weights of the specimens, the carrier gas velocities, temperature, etc.[30] Pyrograms obtained for various sample weights and various carrier gas velocities are given in Fig. 6. All these outwardly different pyrograms correspond to the same line diagram.

A large amount of factual material has now been obtained from the study of a wide variety of polymeric materials and non-volatile organic compounds by pyrolytic gas chromatography: Nitrocellulose, α-butyl methacrylate, poly(vinyl alcohol), poly(vinyl chloride), poly(methyl methacrylate),

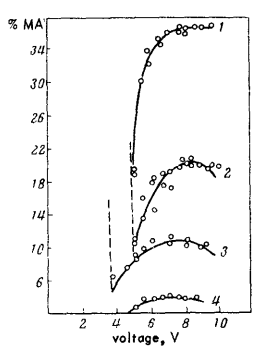


Fig.5. Dependence of the yield of methyl acrylate on the potential difference applied to the spiral for the pyrolysis of methyl methacrylate (MMA)–methyl acrylate (MA) copolymers. Polymer composition: 1) MMA : MA = 1 : 3; 2) MMA : MA = 1 : 1; 3) MMA : MA = 3 : 1; 4) MMA : MA = 9 : 1.

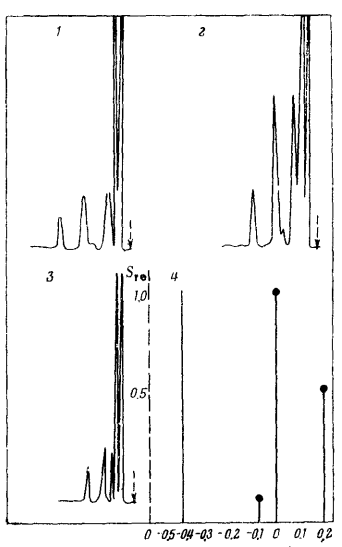


Fig.6. The use of line diagrams in pyrolytic gas chromatography: 1) pyrogram for 2.3 mg polymer specimen, carrier gas velocity 30 ml min^{-1}; 2) pyrogram for 4.6 mg polymer specimen, carrier gas velocity 30 ml min^{-1}; 3) pyrogram for 2.3 mg polymer specimen, carrier gas velocity 50 ml min^{-1}; 4) line diagram corresponding to pyrograms 1–3.

cellulose acetate, polyethylene, polypropylene, polyacrylonitrile, natural and synthetic rubbers, barbiturates, phenothiazines, amino-acids, various aromatic compounds, etc.

Let us consider the main fields of application of pyrolytic gas chromatography.

Identification of polymers. A large number of studies have shown that on pyrolysis under standard conditions various polymers give characteristic chromatographic spectra (pyrograms) of the pyrolysis products. An example is provided by the work of Groten[34], who found that almost all specimens of more than 150 different polymers tested gave different pyrograms. Distinct characteristic pyrograms were obtained for polymers with general formula $(CH_2-CHX)_n$, namely polystyrene, poly(vinyl acetate), polypropylene, and poly(vinyl chloride). Marked differences were observed in the pyrograms of cellulose esters (acetate, propionate, and butyrate), natural materials (silk, cotton, and wool), and the polyalkenes with similar structures: polyethylene, polypropylene, poly(3-methylbut-1-ene), and poly-(4-methylpent-1-ene)[34].

The pyrolytic spectra of a large number of plastics have been studied[50]. The specimens studied (0.2–0.5 mg) were subjected to pyrolysis at 650–750°C for 10 s; the pyrolysis products were separated on a column filled with a sorbent consisting of 5% silicone oil on Chromosorb W. It was noted that for polymers with similar structures, differences in the pyrograms are observed only in the peaks corresponding to the "heavy" products.

Janak[24,51] was the first to apply the method involving the identification of substances from the chromatographic spectra of the products of their pyrolysis on a heated spiral to non-volatile organic compounds (barbiturates, amino-acids, and other biochemical materials). Chromatograms for the products of the decomposition of the potassium salts of various amino-acids are given in Fig. 7. The spectrum of the decomposition products depends to a marked extent on the structure of the amino acids subjected to pyrolysis.

Interesting work on the pyrolytic study of proteins was carried out by Winter and Albro[52]. The observed differences in the pyrograms are related to differences in the structures of the materials taken for pyrolysis. For example, egg and serum albumins are characterised by different pyrograms, since the latter contains four times more cystine.

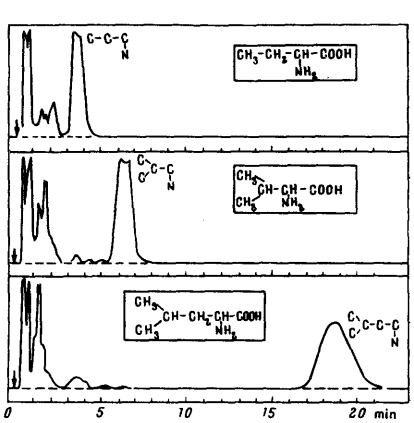


Fig.7. Pyrograms for various amino-acids (stationary phase squalane, temperature of separation 30°C).

Pyrolytic methods were subsequently developed for the identification of non-volatile aromatic compounds[28,53], benzene clathrates[54], phosphates[55], and other compounds. The results obtained indicate that it is possible to identify polymers and non-volatile compounds from the chromatographic spectra of the products of their degradation under controlled pyrolysis conditions.

The pyrograms obtained in pyrolytic gas chromatography are sometimes figuratively described as "fingerprints", emphasising the empirical nature of the method. For the identification of a polymer, it is necessary to compare its pyrograms with the pyrograms of known specimens and to identify the spectrum. The interpretation of an analysed sample is possible only if the pyrogram of this material has been previously recorded. Inert fillers do not influence the pyrogram of a polymer[26].

In certain instances, definite conclusions regarding the nature and structure of a polymer can be reached merely on the basis of the volatile products obtained. For example, identification of the acid in the products of the pyrolysis of cellulose esters established the nature of the ester being studied.

The characteristic features of the structure of condensation polymers taken for pyrolysis can also be established from the composition of the pyrolysis products, particularly if the polymer contains phenyl groups. The influence of the structure of phenol-formaldehyde resin on its pyrolysis products[56,57] is shown in Fig. 8. It has been shown possible to identify phenolic resins with similar compositions but different degrees of curing[58]. It is pointed out that this identification is impossible by infrared spectroscopy. The analysis of natural and synthetic fibres has been described in detail[59–61].

The extensive application of pyrolytic gas chromatography is being held back, in our opinion, by the lack of standard pyrolysis cells and recommendations on standard conditions of testing.

Analysis of copolymers. In the study of copolymers, it is necessary to have the following information: (1) the concentration of original monomer units in the copolymer, and (2) the structure of the polymeric macromolecule.

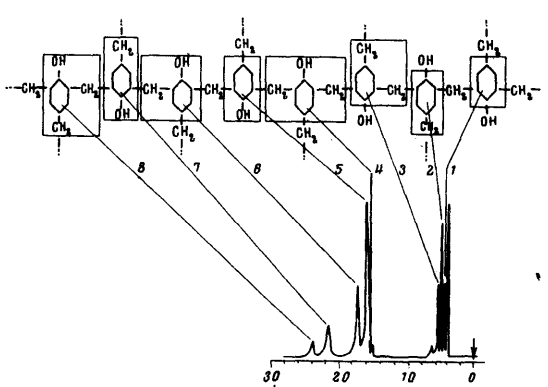


Fig.8. Correlation between the pyrolysis products and the structure of the original phenol–formaldehyde resin. Temperature of pyrolysis 900°C; capillary column [length 100 m (100 cm? Ed. of Translation), diameter 1 mm]; temperature of separation 170°C; stationary phase polypropylene glycol.
1)–8): identified pyrolysis products.

With certain limitations, pyrolytic gas chromatography can provide this information.

The development of a method for determining the composition of a copolymer usually involves the following operations: (1) the recording of characteristic pyrograms for copolymer specimens with different compositions; (2) the selection of characteristic peaks on the pyrogram, whose magnitudes depend on the composition of the copolymer; and (3) the construction of a calibration curve from the data obtained.

Various copolymers whose compositions have been determined by pyrolytic gas chromatography[57] are listed in the Table, together with the methods of calculation.

An interesting feature is that the results of the determination of the compositions of block copolymers of ethylene and propylene show satisfactory agreement with the results obtained by infrared spectroscopy, and make it possible to determine the composition of the copolymer with an absolute error of 1–3%.[43]

For styrene copolymers it is convenient to select as characteristic peak the peak due to the monomer, the quantity of which (relative to the concentration of styrene in the copolymer) is almost independent of the temperature and of the composition of the copolymer over the range 545–640°C.[71]

The pyrolytic method has been used successfully for the analysis of graft copolymers. The error in composition in the analysis of graft copolymers does not exceed 5 rel.%.[72,73]

The method of pyrolytic gas chromatography is applicable to the analysis of the composition of copolymers even when the use of the classical methods of elementary analysis are restricted by the similarity in the elementary composition of the original monomers.

Esposito[74] proposed the use of the internal standard method in pyrolytic gas chromatography. A solution of the polymer taken as internal standard is suspended with a known quantity of the sample being studied and diluted with a solvent. The resulting solution of the polymers is deposited on a spiral and the pyrolysis is carried out in the usual way (the volatile products are separated by gas chromatography). The concentration of polymer (P) is determined from the formula $P = AB/C$, where A is the corrected area of the characteristic peak, C the area of the peak due to the substance formed by pyrolysis of the internal standard, and B the concentration of internal standard. Esposito[74] used ethyl methacrylate as internal standard. This internal standard method, however, is applicable only to soluble polymers.

It should be emphasised that the method of pyrolytic gas chromatography is sensitive not only to the composition of the copolymer, but also to its structure. This is understandable, since the rupture of chemical bonds in pyrolysis, generally speaking, is not restricted to the boundaries of the original monomeric units. Thus the pyrograms for copolymers with monomeric units alternating in disordered fashion (random copolymers) are in general not identical to the pyrograms of mechanical mixtures of the pure homopolymers, whereas the pyrograms for graft copolymers often correspond to the pyrograms for artificial mixtures of homopolymers with the same composition[72,73]. This result is not unexpected, since if the number of points in the chain of the original polymer at which grafting has taken place is small compared with the number of units in the main chain, the process can be regarded as the degradation of the homopolymers. Two different calibration curves obtained for random copolymers of methyl methacrylate and ethylene and for mechanical mixtures of the corresponding homopolymers[75] are given in Fig. 9. The point corresponding to the graft copolymer lies on the curve for the mechanical mixtures.

Pyrolytic gas chromatography is sensitive to such structural characteristics of the polymer chain as the relative arrangement of the substituents. Groten[34] obtained different pyrograms for polypropylenes with different stereoregularity—atactic and isotactic; this emphasises the extensive possibilities provided by the method.

It has been shown possible[76], in the case of double copolymers of α-alkenes, to use pyrolytic hydrogenation to determine the composition of a copolymer, and also the order of arrangement of the monomer units and the nature of their attachment ("head to head" and "head to tail").

TABLE. Copolymers whose compositions have been determined from pyrograms.

Copolymer	Method of calculation	References
Methyl methacrylate–methyl acrylate	RFA*	62
Methyl methacrylate–ethyl acrylate	RPH**	63
Methyl methacrylate–ethyl methacrylate	RPA	62
Methyl methacrylate (MMA)–ethylene dimethacrylate	AP***(MMA)	62
Methyl methacrylate (MMA)–styrene	HP****(MMA)	64
Butyl methacrylate (BMA)–hexyl methacrylate	AP(BMA)	65
Vinyl chloride (VCl)–vinyl acetate (VAc)	HP(HCl or HAc)	64
Vinyl acetate (VAc)–copolymer	AP (HAc)	66
SBR–polybutadiene	RPH	34
Ethylene–vinyl acetate (VAc)	AP (HAc)	67
Ethylene (ET)–ethyl acrylate	AP (ET)	67
Ethylene–propene, block and random copolymers	RPA	43, 34
Ethylene–butene	RFA	68
Ethylene–methyl acrylate, block and random copolymers	RPA	69
Ethylene–methyl methacrylate, block and random copolymers	RFA	69
Ethylene oxide–propene oxide	RPA	8
Cellulose esters	RPH	34
Plasticisers (PI) in a polymer	HP (PL)	70
Hydroxyethyl group in hydroxyethyl–starch	HP (HCHO)	22

* RPA ratio of peak areas.

** RPH ratio of peak heights.

*** AP area of the peak due to the component indicated in parentheses.

**** HP height of the peak due to the component indicated in parentheses.

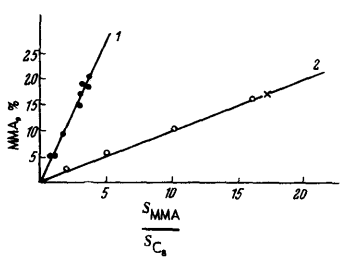


Fig. 9. Dependence of the relative area of two characteristic peaks on the pyrograms of random copolymers (1) and mixtures of polymethyl methacrylate and polyethylene homopolymers (2) on the methyl methacrylate concentration. The point × corresponds to the graft copolymer.

The yield of monomers in the pyrolysis of copolymers which decompose chiefly to the monomer depends on the distribution of the monomer molecules in the copolymer. This is due to the fact that if a polymer decomposes by a radical mechanism with removal of monomer units from the ends of the polymer molecules, the probability of removal of the next monomer unit depends on its immediate neighbour. A method has been developed for calculating the structures of copolymers from the quantity of monomers formed on pyrolysis[77]. The corresponding probabilities can be determined by pyrolysis of copolymers with known composition. The method was tested using styrene–acrylonitrile and styrene–methyl methacrylate copolymers.

In all the above applications of the method, the determination of the individual compositions of the products is not necessary. The study of the mechanism of degradation is a much more complex problem, since it is necessary to obtain as far as possible the complete spectrum of pyrolysis products and to determine their qualitative composition. In these instances it is desirable to carry out the pyrolysis in thin films, to use capillary columns with temperature programming[48], and to use specific, for example chemical, methods of peak identification[78]. Chromatography combined with mass spectroscopy will obviously be of considerable assistance in the interpretation of the chromatographic peaks.

Berton[79], for the example of a number of polymeric materials, proposed the use of selective galvanic detection of the pyrolysis products, based on the reaction of the pyrolysis products with the electrolyte of the detector. This reaction leads to a change in the polarisation of the electrode and the electric current. The nature of the electrolyte determines the classes of compounds detected. The use of a saturated solution of chromium(VI) oxide in nitric acid as electrolyte makes it possible to detect alcohols, aldehydes, and various unsaturated substances, with a high sensitivity[79]. The use of galvanic detection with the above electrolyte appears particularly promising for the analysis of the products of oxidative pyrolysis.

In some instances the identification of pyrolysis products can be carried out gas-chromatographically from their molecular weights, using a density detector and carrier gases with different molecular weights[80] or two katharometers, one of which operates as a density detector[81]. In the latter instance, when certain conditions are satisfied, the ratio of the signals from these detectors is directly proportional to the molecular weight of the substance. The study of processes which take place in polymers at elevated temperatures and are accompanied by the liberation of products volatile at the temperature of the experiment is also of interest.

Garzó and Székely[82] studied the thermal processes involved in the curing, decomposition, and depolymerisation of silicone polymers, by using a carrier gas to carry the volatile reaction products, at measured time intervals, from the micro-reactor into the chromatograph.

Finally, it may be noted that the published experimental material makes it possible to recommend the pyrolytic method for research purposes, and in some instances for technological control. A necessary condition for the extensive introduction of this method, however, is the development of standard apparatus and standardisation of the pyrolysis conditions (the size of sample, temperature of pyrolysis, conditions of chromatographic separation, etc.).

Future Prospects for the Development of Degradative Chromatographic Methods

In the study of the composition and structure of polymers, it is undoubtedly desirable, in addition to pyrolysis, to apply to polymers other, possibly more structurally sensitive, degradation methods, and also various combinations of these methods. Thus pyrolytic gas chromatography can be regarded as one version of degradative gas chromatography.

Scholz and coworkers[83] proposed the characterisation of polymers from the spectra of the products of their oxidative degradation. The polymer being studied is deposited on a solid inert carrier and placed in a short additional column placed between the device used to introduce the sample and the chromatographic separating column. The temperature of the additional steel column containing the polymer being studied can be controlled by means of a thermostat in the range 100–600°C. Oxidation of the polymer takes place on contact with oxygen (1 cm^3 of oxygen is introduced into the stream of inert carrier gas). The volatile oxidation products are carried by the stream of carrier gas into the chromatographic column for separation. The spectrum of volatile products from the oxidative degradation is characteristic for each polymer.

As noted above, a combination of thermal degradation and thermal oxidation has been used to identify pyrolysis products and to study the mechanism of pyrolysis[49]. It has been proposed[84] that the degradation of the polymer be carried out in a current of carrier gas under the conditions of the electric discharge (300 V, 1 mA). It has been shown for several polymers that the composition of the degradation products corresponds to the products formed under the conditions of pyrolysis at 600°C.

Kolbanovskii and coworkers[85], in the Institute of Petrochemical Synthesis, developed a new method of degradative gas chromatography—radiochemical chromatography.

In radiochemical chromatography, the polymer is characterised by the spectrum of volatile radiolysis products. After γ-irradiation (dose ~ 100 Mrad) of a specimen of the polymer at room temperature in an evacuated glass ampoule, the gaseous radiolysis products were analysed. About 50 specimens of different polymers were studied, and a characteristic spectrum of radiolysis products was obtained for each polymer. The method is sensitive to the structure of the polymer and the composition of the copolymer. Different line diagrams were obtained for natural rubber, gutta percha, SKD synthetic rubber, and *trans*-polybutadiene. All four specimens, which taken in pairs differ only in their spatial configuration, gave different spectra. In a study of the radiolysis of copolymers, a linear relationship was observed between the relative yield of ethylene and the concentration of acrylonitrile in its copolymer with butadiene. The method is very sensitive to branching of the carbon chain. High-pressure and low-pressure polyethylenes also give different spectra of products from radiochemical degradation.

In addition to purely analytical applications, the use of degradation methods to study the thermal stability of polymers and non-volatile compounds in various gaseous media (and also under the influence of radiation), for the rapid determination of the efficiency of various inhibitors, etc., is of particular interest. The possibility of carrying out the studies with very small quantities of substance, the simplicity of the method, and its high resolving power are opening up extensive possibilities for the application of gas chromatography for the estimation and study of non-volatile polymeric materials.

The development of new versions of degradative gas-chromatographic methods will undoubtedly open up new horizons in the study of polymeric materials.

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