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## **Probability method for pyrolysis gas chromatographic data treatment and elaboration of a computer system for the identification of polymers**

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### ABSTRACT

In order to develop a computer-based retrieval system for polymer identification by pyrolysis gas chromatography (Py-GC), a method for the presentation of the pyrolysis chromatograms in the form of numerical parameters is proposed in accordance with a previously described procedure. The essence of the method is the calculation of  $n_p$  value,  $(t_{Ri}^p)_s$ , the sum of retention times for the significant peaks. The intensity of the peaks is taken into account by the parameters  $a_1$  and  $a_1/a_2$  of a single mathematical function for the whole pyrolysis chromatogram  $F-S_i^p$ , which where  $F$  characterizes the probability of the occurrence of a peak with a standard area  $S_i^p$ . An algorithm was developed and a set of pyrolysis chromatograms in FORTRAN-4 was created. The algorithm is based on the calculation results for pyrolysis chromatograms for reference polymers and includes an interval evaluation of the parameters of polymer identification calculated from representative selections.

This method for the treatment of Py-GC results characterized by low inter-laboratory reproducibility allows the preparation of a data bank in the form of a set of pyrolysis chromatograms and computer-based retrieval for polymer identification by users based on set procedures on available chromatographs and pyrolytic devices and on minicomputers or personal computers.

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### INTRODUCTION

Automated retrieval systems for treating the results of IR spectroscopic, mass spectrometric chromatographic-spectroscopic and gas chromatographic experiments are now widely used [1-4]. However, systems for identifying polymers and organic compounds from pyrolysis gas chromatographic (Py-GC) data have hardly been treated in the literature, except for papers on computer-based searches for the type of polymer according to the pyrolytic products by the use of IR or mass spectrometers as detectors in Py-GC [4-6].

In this paper a procedure is proposed for reducing all the information obtained from Py-GC to four numerical parameters. A new computer-based retrieval system for polymer identification using Py-GC data was developed on the basis of this procedure.

## EXPERIMENTAL

For the mathematical treatment of data, under the conditions of the previously developed procedure [7], pyrolysis gas chromatograms were obtained for the following polymers: high-density polyethylene (HDPE), polypropylene (PP), poly(4-methyl-1-pentene) (PMP), polystyrene (PS), polycarbonate (PC), acrylonitrile-butadiene-styrene copolymer (ABS-IOM), an ABS-PC (40:60)-based polymer composition (ABS-PC) and styrene-methyl methacrylate copolymer (40:60 and 80:20) (St-MMA).

The pyrolysis of 1.5–2-mg portions was carried out at 600°C for 1 min in a P-75 pyrolysis adapter of the oven type, which was connected to a Tsvet-104 chromatograph (both from Dzerzhinsk OKBA, U.S.S.R.), equipped with a thermal conductivity detector. Pyrolytic products were separated on a 300 × 0.3 cm I.D. stainless-steel column with 8% E-301 on Inerton AW (Lachema, Czechoslovakia) (0.16–0.20 mm) with temperature programming from 50 to 250°C at 11°C/min. The carrier gas (helium) flow-rate was 2 l/h, the chart speed was 600 mm/h and the evolution of peaks of the pyrolytic products did not exceed 30 min. The relative error of the retention times of peaks, determined for 1 year on the products of HDPE pyrolysis, was ± 3.5%.

All calculations were carried out with an EC 1055 computer (Robotron, G.D.R.).

## RESULTS AND DISCUSSION

We have previously demonstrated the identification of a polymer matrix of compositions, based on polyolefins, styrenic polymers, fluoroplastics, poly(vinyl acetate) plastics, polyacrylates and some other polymers by Py-GC [8–10]. The results obtained formed the basis for the development of a comprehensive procedure for identifying unknown polymer materials by Py-GC regardless of their chemical origin [7]. A comprehensive data bank was created for this procedure. However, the comparison of a pyrolysis chromatogram of an unknown polymer with the most popular "fingerprint" method by the use of a reference chromatogram, obtained under the same conditions, or by comparing diagrams of peak height *vs.* retention time, is laborious with over 100 different pyrolysis chromatograms in the data bank.

In our opinion, for the final stage of polymer identification by Py-GC using this method, it is expedient to apply a computer for treating the Py-GC data and arranging a retrieval system. The principal task in the design of a computer-based retrieval system was to rearrange a complicated phenomenon, the pyrolysis chromatogram, into a system of numerical values that could be easily recognized by the computer, *i.e.*, to reduce Py-GC data. In choosing a suitable data treatment method, it was assumed that an individual peak on the pyrolysis chromatogram is only a part of the complex characteristics of the polymer. The polymer could be described by a system of peaks (by their number,  $n$ , their retention times,  $t_{R_i}$ , and their intensities,  $S_i$ ). Therefore, the coding of Py-GC data could be based on the calculation of the overall mathematical function for the whole pyrolysis chromatogram, for which an integral distribution function could be used [11].

An analysis of the pyrolysis chromatograms from the data bank carried out previously [7] showed that for almost every homo- and copolymer the number of

significant peaks,  $n_p$ , and the corresponding sum of their retention times,  $\sum_{i=1}^{n_p} t_{R_i}^p = (t_{R_i}^p)_\Sigma$ , are specific values. The significant peaks include those with areas not less than a certain  $\alpha$  value (level of significance) with regard to the total sum of the areas of all peaks in the pyrolysis chromatogram,  $\sum_{i=1}^n S_i$ . The choice of an  $\alpha$  value is determined by the following conditions: its minimum value should never be less than the error of the procedure used, and at the given  $\alpha$  value  $n_p$  should include the peaks that are characteristic of the given polymer. When comparing the results of calculations on a statistically significant number of pyrolysis chromatograms of the same polymer with different  $\alpha$  values (3.4 and 5%), that level of significance must be selected at which the calculation of most pyrolysis chromatograms would provide closely similar results for the  $(t_{R_i}^p)_\Sigma$  and  $n_p$  parameters (levelling principle). An example of the calculation of the pyrolysis chromatograms of PE and PP (Table I) shows that  $\alpha = 4\%$  most closely corresponds to this principle. Moreover, the correctness of the level of significance selected ( $\alpha = 4\%$ ) is confirmed by the fact that with an increase in  $\alpha$  up to 5% the calculations fail to include a part of characteristic peak of smaller area for some polymers. At  $\alpha < 4\%$ , the  $n_p$  value includes those peaks which are most characteristic of artifacts of Py-GC.

The  $n_p$  and  $(t_{R_i}^p)_\Sigma$  parameters are related to a certain extent to peak intensities, as their values change with the share of  $\sum_{i=1}^n S_i$  (the total sum of peak areas in a pyrolysis chromatogram) involved in the calculation, *i.e.*, with the level of significance ( $\alpha$ ). The intensities ( $S_i$ ) are the principal quantitative characteristics of the peaks. For Py-GC data treatment these characteristics should be considered more closely. The contribu-

TABLE I

SUM OF RETENTION TIMES,  $(t_{R_i}^p)_\Sigma$ , AND NUMBER OF PEAKS,  $n_p$ , AT VARIOUS LEVELS OF SIGNIFICANCE

Polymer	Pyrolysis chromatogram No.	Level of significance					
		3%		4%		5%	
		$n_p$	$(t_{R_i}^p)_\Sigma$	$n_p$	$(t_{R_i}^p)_\Sigma$	$n_p$	$(t_{R_i}^p)_\Sigma$
Polyethylene	1	13	204.6	12	177.1	10	150.5
	2	13	196.6	11	145.6	8	89.6
	3	13	195.7	12	168.9	8	98.7
	4	13	196.5	11	144.9	9	100.3
	5	14	177.7	11	146.9	7	69.2
	6	12	180.7	11	154.5	10	130.1
Polypropylene	1	7	46.9	7	46.9	7	46.9
	2	7	47.2	7	47.2	6	45.8
	3	7	49.2	7	49.2	7	49.2
	4	8	48.5	8	48.5	7	46.4
	5	8	49.5	7	47.3	7	57.3
	6	8	49.8	7	47.5	7	47.5

tion of the intensity could be taken into account with the help of the parameters of the integral distribution function. For the calculation of this function a pyrolysis chromatogram is presented as a product of events  $A = \prod_{i=1}^{n_p} (A_i)$ , where  $A_i$  is the event which involves the appearance of the significant peak with an area  $S_i^p$ . At the time of the beginning of this event  $A_i = t_{R_i}^p$  is the retention time of the  $i$ th significant peak. The probability of the appearance of event  $A$  for the pyrolysis of a given polymer  $P(A) = 1$  or

$$P(A) = P\left(\prod_{i=1}^{n_p} A_i\right) = \sum_{i=1}^{n_p} P(A_i) = 1 \quad (1)$$

where

$$P(A_i) = P_i = t_{R_i}^p / \sum_{i=1}^{n_p} t_{R_i}^p = t_{R_i}^p / (t_{R_i}^p)_{\Sigma} \quad (2)$$

The standardized area of the significant peak is calculated as

$$S_i' = S_i^p / (S_i^p)_{\Sigma} \quad (3)$$

where  $(S_i^p)_{\Sigma} = \sum_{i=1}^{n_p} S_i^p$  is the total sum of all significant peak areas in the pyrolysis chromatogram. This would allow a comparison of the peak distribution of one type of polymer, regardless of the amount of sample.

From estimates of the  $S_i'$  and  $P_i$  values, the pyrolysis chromatogram of each of the analysed polymers could be described by the distribution function  $F = f(S_i')$ , which characterizes the probability of the appearance of a peak with standardized area  $S_i'$ , parameters  $a_1$  and  $a_2$  being calculated together with the first and the second initial moments and their ratio:

$$a_1 = \sum_{i=1}^{n_p} S_i' P_i = \frac{\sum_{i=1}^{n_p} (S_i^p t_{R_i}^p)}{(S_i^p)_{\Sigma} (t_{R_i}^p)_{\Sigma}} \quad (4)$$

$$a_2 = \sum_{i=1}^{n_p} [(S_i')^2 P_i] = \frac{\sum_{i=1}^{n_p} [(S_i^p)^2 t_{R_i}^p]}{(S_i^p)_{\Sigma}^2 (t_{R_i}^p)_{\Sigma}} \quad (5)$$

$$\frac{a_1}{a_2} = \frac{\sum_{i=1}^{n_p} (S_i' P_i)}{\sum_{i=1}^{n_p} [(S_i')^2 P_i]} = \frac{(S_i^p)_{\Sigma} \sum_{i=1}^{n_p} (S_i^p t_{R_i}^p)}{\sum_{i=1}^{n_p} [(S_i^p)^2 t_{R_i}^p]} \quad (6)$$

For drawing a curve  $F = f(S_i')$ , the experimental points (apices of stepwise

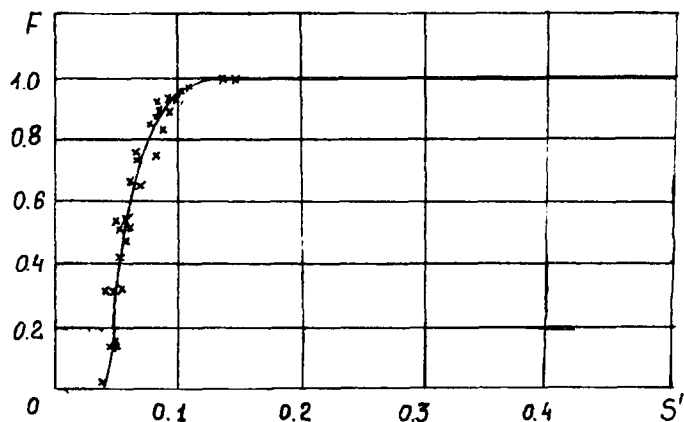


Fig. 1. Integral distribution functions for standardized peak areas in pyrolysis chromatograms of PE.  $\times$  = Experimental points.

distribution functions) were marked for each pyrolysis chromatogram from the selection (Fig. 1).

The curves of the distribution functions were drawn in such a way that the minimum sum of squares of distances from these curves to corresponding experimental points was obtained (least-squares method). The curves of the distribution functions shown in Figs. 2 and 3 indicate that the probability of the appearance of a peak with the same  $S'_i$  in the pyrolysis chromatogram of polymers is not uniform. Moreover, any changes in this probability take place individually for each individual polymer; these changes are determined to a considerable extent by the nature of the thermal degradation of the polymer chain, which, in turn, determines the composition of volatile pyrolysis products. For polymers which undergo degradation randomly with the formation of numerous fragments having various numbers of C-units

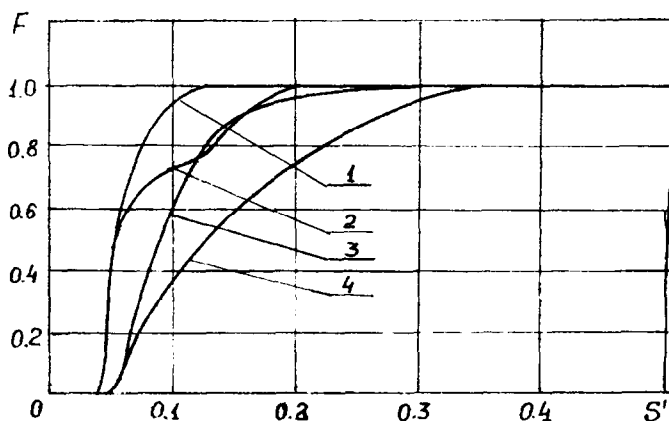


Fig. 2. Integral distribution functions for standardized peak areas in pyrolysis chromatograms for (1) PE, (2) PMP, (3) PP and (4) PS.

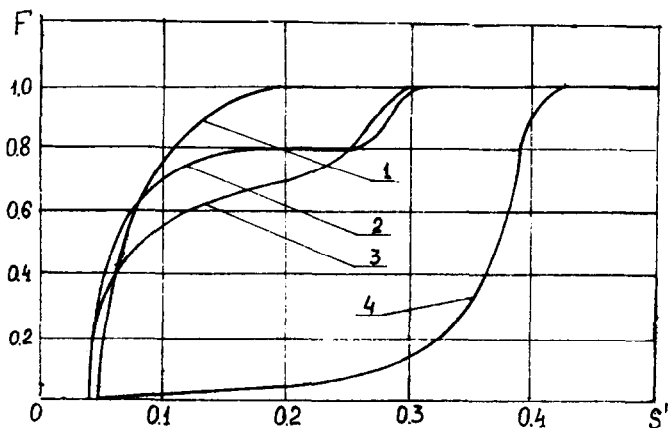


Fig. 3. Integral distribution functions for standardized peak areas in pyrolysis chromatograms for (1) styrene-methyl methacrylate copolymer, (2) ABS; (3) ABS-PC and (4) PC.

(polyolefins) [12], the probability of the  $S'_i$  value of any peak in the pyrolysis chromatogram being 0,1 (10%) is 0.95 for PE, 0.7 for PMP and 0.6 for PP. At  $F = 1$ ,  $S'_{i_{PE}} (= 0.15) < S'_{i_{PMP}} (= 0.22) < S'_{i_{PP}} (= 0.3)$ , *i.e.*, the probability of the appearance of peaks with a larger standardized area in pyrolysis chromatograms for polyolefins is zero (Fig. 2, curves 1-3).

For polystyrene and copolymers of styrene with methyl methacrylate (thermal degradation of these polymers is substantially determined by the mechanism of depolymerization [12]), the curves of the distribution functions differ from those for polyolefins (Fig. 2, curve 4 and Fig. 3, curve 1). The curve of the distribution function of ABS in the initial region is close to the curve for polyolefins (Figs. 3, curve 3). Butadiene and acrylonitrile contribute to the process of thermal degradation of this copolymer to smaller fragments [12].

The shape of the curve of the distribution function for the ABS-PC blend is influenced by the curve shapes of the two components of the blend.

From Figs. 2 and 3, it is clear that the shape of the curves gives an indication of the difference in their  $a_1$ ,  $a_2$  and  $a_1/a_2$  parameters (eqns. 4-6) for the different polymers, which is illustrated by data shown in Table II. The analysis of the parameters shows that for adequate characterization of the polymer by Py-GC it is sufficient to have  $n_p$ ,  $(t_{R_i}^p)_\Sigma$ ,  $a_1$  and  $a_1/a_2$  (Table III). It should be noted that for copolymers of different compositions the thermal degradation of which largely depends on depolymerization and the formation of the initial chemicals (*e.g.*, copolymer of styrene and methyl methacrylate, ABS plastic) the structure of the macrochains hardly influences the range of chemicals formed. A change in composition changes  $a_1$  and  $a_1/a_2$  when  $n_p$  and  $(t_{R_i}^p)_\Sigma$  are constant for the whole range of changes of composition (Table III). In thermal degradation hybrid chemicals are evolved together with the initial monomers, and their appearance or disappearance in the pyrolysis products depends on the composition and alternation of different monomer chains (*e.g.*, copolymer of tetrafluoroethylene, ethylene and hexafluoropropylene [13]), all four identification parameters being changed. This should be taken into account in the selection of reference pyrolysis

TABLE II

VALUES OF  $a_1$ ,  $a_2$  AND  $a_1/a_2$  CALCULATED FOR THE EXPERIMENTAL DATA AT  $\alpha = 4\%$ 

Polymer	Pyrolysis chromatogram No.	$a_1$	$a_2$	$a_1/a_2$
Polyethylene	1	0.074	0.006	11.79
	2	0.079	0.008	10.48
	3	0.073	0.006	11.93
	4	0.080	0.007	11.08
	5	0.077	0.007	11.08
	6	0.075	0.006	11.71
Polypropylene	1	0.149	0.026	5.78
	2	0.159	0.030	5.36
	3	0.147	0.026	5.59
	4	0.128	0.022	5.77
	5	0.139	0.024	5.79
	6	0.133	0.023	5.76
Polystyrene	1	0.194	0.047	4.13
	2	0.172	0.039	4.38
	3	0.207	0.052	4.02
	4	0.188	0.041	4.57
	5	0.176	0.042	4.22
	6	0.177	0.042	4.21

chromatograms. For the reliable identification of homopolymers, copolymers and mechanical mixtures of various compositions, preliminary work is necessary to establish the influence of different factors (polymerization method, molecular weight, additives and fillers, macrochain structure, etc.) on the form of the pyrolysis

TABLE III

VALUES OF POLYMER IDENTIFICATION PARAMETERS CALCULATED FROM EXPERIMENTAL DATA AT  $\alpha = 4\%$ 

Number of pyrolysis chromatograms in the selection = 10.

Polymer	Parameter			
	$n_p$	$(t_{R_i}^p)_x$	$a_1$	$a_1/a_2$
PE	11-12	159.5 ± 15.4	0.076 ± 0.003	11.35 ± 0.56
PP	8-8	47.8 ± 0.9	0.143 ± 0.011	5.68 ± 0.17
PMP	7-8	70.8 ± 2.0	0.127 ± 0.008	5.84 ± 0.36
PS	5-6	107.7 ± 9.6	0.187 ± 0.013	4.25 ± 0.19
PC	5-6	87.9 ± 11.1	0.170 ± 0.011	4.25 ± 0.05
ABS	6-9	74.7 ± 16.1	0.134 ± 0.033	5.85 ± 1.59
ABS-PC (40:60)	6-7	76.2 ± 8.0	0.138 ± 0.011	4.25 ± 0.34
Styrene-methyl methacrylate copolymer (40:60)	3-4	25.5 ± 1.0	0.385 ± 0.035	2.54 ± 0.22
Styrene-methyl methacrylate copolymer (80:20)	3-4	25.5 ± 1.0	0.470 ± 0.030	1.53 ± 0.21

chromatogram under the specified conditions of pyrolysis and GC separation of volatile chemicals. Identification parameters were calculated using pyrolysis chromatograms prepared on the basis of our procedure [7]. The possibilities and limitations of this procedure for different classes of polymers were studied previously [8–10].

An algorithm and some programs in FORTRAN-4 were developed on the basis of this work. The algorithm includes a program for calculating the  $n_p$ ,  $(t_{R_i}^k)_s$ ,  $a_1$  and  $a_1/a_2$  parameters from pyrolysis chromatographic data and search programs for the identification of the parameters of a given pyrolysis chromatogram by a combination of chromatographic parameters from the computer data bank. The computer data bank is compiled on the basis of the results of calculations on the pyrolysis chromatograms for reference polymers. It includes the interval evaluations of identification parameters, calculated from representative selections. The computer data bank can be supplemented by parameters for new reference pyrograms. It can accept the identification parameters calculated from the pyrolysis chromatograms obtained under various conditions of pyrolysis and GC separation of volatile products. This should be considered in the retrieval program, and the identification of any unknown sample should be carried out only from parameters of the pyrolysis chromatograms obtained under the same experimental conditions as for the reference chromatograms.

The retrieval programs could be used in two modifications. (1) In the dialogue mode, the computer gives information on the data bank, the rules to be observed for the search, the scope of the required initial information and the rules of its input. This information is sent in sequence to the computer display upon the user's request. The form of the request is shown in the display when the program is initiated. (2) In the mode of initial assignment of the pyrolysis chromatographic data for the polymer being identified, one should introduce the series of peak numbers, their retention times and their areas. In this case, the computer carries out the calculations for the chromatogram of the polymer sample, obtains the numerical value of the identification parameters and automatically initiates the search in the data bank. The efficiency of the algorithms and the software was confirmed by a number of reference calculations with the EC 1055 computer for various polymers (Table III).

In some instances the computer can give an answer that indicates two polymers having similar parameters when the identification of the unknown polymer sample by the identification parameters is carried out. For further identification in that event the sample chromatogram should be compared with the chromatograms of reference polymers in the data bank marked with the same numbers. This does not significantly reduce the merit of the computer search, because in any case the search is made faster.

In view of the specific feature of Py-GC of low inter-laboratory reproducibility, such an approach to the treatment of results allows each user to create a data bank in the form of a computer file and to carry out a computer search for the identification of organic substances and polymers by Py-GC, provided that suitable chromatographs, units for pyrolysis and a minicomputer or personal computer are available.

## CONCLUSIONS

For adequate characterization of polymers by Py-GC with a computer-based



retrieval system of identification, we propose to use  $n_p$  and  $(t_{R_i}^p)_\Sigma$ , the sum of the retention times for the significant peaks. The intensities of these peaks are taken into account by the parameters of the integral distribution functions for standardized peak areas,  $a_1$  and  $a_1/a_2$ . A series of programs in FORTRAN-4 have been developed for pyrolysis chromatogram calculations and for a search by the identification parameters  $n_p$ ,  $(t_{R_i}^p)_\Sigma$ ,  $a_1$  and  $a_1/a_2$ . The reference calculations, carried out with an EC 1055 computer, have been shown. These calculations confirm the efficiency of the algorithm and the software. Operations with the computer data bank can be in both automatic and dialogue (with messages for the operator) modes.

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