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APPLICATION OF A COMPUTER AND AN EXTERNAL STANDARD IN THE DETERMINATION OF THE COMPOSITION OF POLYMER SYSTEMS BY PYROLYSIS GAS CHROMATOGRAPHY

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SUMMARY

The determination of the composition of polymer mixtures and copolymers with high precision is discussed. A method has been developed for selecting the optimum combination of peaks for plotting a calibration graph with the use of a computer. The method provides very accurate measurements. The use of an external standard in pyrolysis gas chromatography is proposed and its advantages are considered. The possibility of determining the composition of three-component polymer systems with the use of an external standard is demonstrated. Methods of representing experimental results leading to linear calibration graphs in the determination of the composition of polymer systems are discussed.

INTRODUCTION

A common application of pyrolysis gas chromatography is the determination of the composition of polymer systems (copolymers and mechanical polymer mixtures)¹⁻⁵. In order to obtain more reproducible results (with respect to the experimental conditions) in calculations, use is made of the relative values of the areas of the characteristic peaks (relative to a reference peak). For two components, the standard peak adopted is usually the peak characteristic of the second component⁶ or the peak due to the presence of the two components in the system⁷. The use of an internal standard has also been described^{8,9}, but this method is seldom used because of its limitations.

As the total number of peaks in a pyrogram may be as great as several tens¹⁰, the choice of the optimum combination of peaks (*i.e.*, the combination that ensures the maximum accuracy in the determination) involves tedious calculations and is often difficult.

In the general form, the method for the determination of polymer compositions has been worked out only for two-component systems, and for multicomponent systems the task is much more complicated. Some workers have suggested that, under the conditions of pyrolysis, the primary products form a mixture with the secondary products^{11,12}. For a two-component system, the relative area of the characteristic

peak of component 1, $S_{rel.1}$, can be regarded as a function exclusively of X_1 , *i.e.*, part of component 1 ($X_1 + X_2 = 1$) and of a term characteristic of the structure of the macromolecule, β . In the general case of an n -component system, the relative area of the characteristic peak of component i , $S_{rel.i}$, may be a function of $n - 1$ dependent variables of the composition and of β , *i.e.* $S_{rel.i} = f(X_1, X_2 \dots X_{n-1})$, and therefore the solution of the problem becomes difficult even for a three-component system.

In this work, an attempt was made to use a computer for selecting the optimum combination of the characteristic and standard peaks, which would ensure the maximum accuracy of calculation in determining the composition of two-component systems, and it is shown with the use of three-component copolymers that it is possible to determine the composition of multicomponent systems by using the new method of introduction of a standard substance. Methods of representing the experimental results are also discussed.

USE OF A COMPUTER IN SELECTING OPTIMUM COMBINATIONS OF PEAKS AND IN PLOTTING CALIBRATION GRAPHS

As an example, consider the problem of determining the composition of mixtures of natural rubber (NR) and butadiene-styrene (70:30) rubber (BSR). Previously, a method for determining the composition of these mixtures was developed and calibration graphs were plotted for an independent determination of the composition of the components⁷. The choice of characteristic and standard peaks, however, was made on the basis of a qualitative evaluation of chromatograms. In the present work, we have used in the calculations pyrograms obtained experimentally in the earlier work⁷.

A pyrogram of a 1:1 mixture of NR and BSR is given in Fig. 1. Eleven of the peaks were chosen for quantitative calculations; for these peaks, it was possible to determine the height, l , and the width at half-height, μ .

A calibration graph was sought in the form of the dependence of the relative area of the characteristic peak, Y_{KLi} , on the content, X_i , of one of the components of the mixture (BSR).

$$Y_{KLi} = f(X_i) = \frac{\mu_{Kl} l_{Kl}}{\mu_{Ll} l_{Ll}} \quad (1)$$

where K and L are the numbers of the peaks in the pyrogram of the mixture i . An analysis of published data¹³⁻¹⁵ and our earlier results⁷ showed that calibration graphs can be expressed as near-parabolic functions. In accordance with this, regression lines¹⁶ (restricted to the second order) were sought in the form

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

adopting 1, X and X^2 as the base functions. The factors A_1 , A_2 and A_3 can be found from the condition of the minimum of the total square discrepancy, $\sum_{j=1}^m U_j^2$ where U_j is the discrepancy (the deviation from the experimental calibration curve) and m is the number of calibration measurements made from the segment $\alpha \leq X \leq \beta$:

$$\sum_{j=1}^m U_j^2 = \sum_{j=1}^m [Y_j - (A_1 + A_2X + A_3X^2)]^2 \quad (3)$$

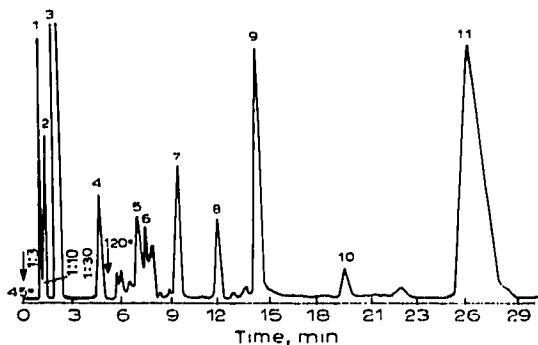


Fig. 1. Chromatogram of pyrolysis products of a 1:1 mixture of NR and BSR. 1-11: Numbers of main peaks.

The condition for the minimum is that the partial derivatives of the right-hand side with respect to A_1 , A_2 and A_3 must be zero. This yields three first-degree equations in A_1 , A_2 and A_3 from which they can be determined. The mean square error in determining X from the observed Y , *i.e.* $\sigma/f'(X)$ (σ is the mean square error in determining Y) can be estimated from the selective mean square error, η :

$$\eta = \sqrt{\frac{1}{m-1} \frac{\sum_{j=1}^m U_j^2 (\beta - \alpha)^2}{[f(\beta) - f(\alpha)]^2}} = \frac{(\beta - \alpha)}{\sqrt{m-1}} \sqrt{\frac{\sum_{j=1}^m U_j^2}{[f(\beta) - f(\alpha)]^2}} \quad (4)$$

When K and L for the segment (α, β) vary, the value of $(\beta - \alpha)$ and the number of calibration measurements, m , remain constant, so that the lower is the value of

$$V = \sqrt{\frac{\sum_{j=1}^m U_j^2}{[f(\beta) - f(\alpha)]^2}} \quad (5)$$

the higher is the accuracy.

In order to find the optimum combinations of peaks, a Minsk-22 computer was used in determining X . The main points of the program for the solution of the problem have been formulated above. The program is compiled so that it is possible to take any arbitrary functions, $q_1(X)$ and $q_2(X)$, in place of the base functions X and X^2 . For each segment (α, β) , the program calculates the regression lines for each pair of K and L peaks, *i.e.*, the values of A_1 , A_2 and A_3 , and selects, in order of increasing V , all pairs of peaks until V exceeds the minimum value of V by a definite factor.

Experimental data are presented as a set of tables. Each table contains a succession of values $\mu_{L1} l_{L1} \dots \mu_{S1} l_{S1}$ for S peaks (in this case $S = 11$) corresponding to a definite value of X . Four ranges of X values were taken for calculations: 0-0.3; 0.3-0.7; 0.7-1.0; 0-1.0. For the best regression lines, the accuracies were 1:1; 1.5 and 5%, respectively.

A comparison of the calculated data with our earlier results⁷ showed that not all of the combinations of peaks selected are optimal, although most of them are among the ten best ones in the range 0-1. This confirms the fact that it is difficult to choose

the best combinations of peaks without the use of a computer, especially as different combinations will be optimal for different contents of a particular component. Thus, it is expedient to use the calibration graph for $K = 3$, $L = 7$ only for low contents of BSR rubber, while the best accuracy in the range 0–100% of BSR is ensured by calculation from peaks 5 and 6, which were not considered earlier⁷. It should be noted that the choice of a standard peak greatly influences the accuracy of a determination, whereas there are virtually no selection criteria in a "subjective" choice. Note that the calibration curves presented earlier⁷ and calculated from equations for the same peaks are similar, but not identical.

As the composition of a mixture can be determined from different calibration graphs, the accuracy of the calculation of X can be improved by using the least-squares method¹⁶. For different combinations of the peaks $Y_1 = f_1(X) \dots Y_M = f_M(X)$, the observed values of $Y_1 \dots Y_M$ are equal to $\theta_1 \dots \theta_M$, respectively, and the mean square errors are equal to $\sigma_1 \dots \sigma_M$. The best estimate of the parameter X is the value of X_0 which minimizes the expression

$$Q = \sum_{j=1}^m (\theta_j - Y_j)^2 \frac{1}{\sigma_j^2} \quad (6)$$

At the minimum point, the derivative of the right-hand side with respect to X is zero, *i.e.*

$$\sum_{j=1}^m \frac{1}{\sigma_j^2} [\theta_j f'_j(X) - f'_j(X) f_j(X)] = 0 \quad (7)$$

which enables the value of X to be improved. If X_0 is the minimum, the mean square error of measurement is

$$\sigma^2 = \frac{1}{\sum_{j=1}^m \frac{1}{\sigma_j^2} [f'_j(X_0)]^2} \quad (8)$$

The calculation method described involves a laborious manual operation in order to determine the parameters of the chromatographic peaks. This stage can evidently be automated if the chromatographic signal is recorded on magnetic tape with the aim of introducing the input data directly into a computer.

DETERMINATION OF THE COMPOSITION OF THREE-COMPONENT POLYMER SYSTEMS BY PYROLYSIS GAS CHROMATOGRAPHY

Experimental

The materials under investigation were bulk ternary copolymers of divinyl, styrene and 2-vinylpyridine; this enabled us to use mechanical mixtures of the corresponding homopolymers as reference specimens¹⁴. These copolymers possess some valuable properties, and the development of a method for determining their composition was of practical interest, especially because other methods of analysis, including spectral methods, involve considerable difficulties. Of practical importance was the composition range 0–100% divinyl, 0–100% styrene and 0–20% 2-vinyl-

pyridine. The work was carried out on a Tsvet-1 chromatograph equipped with a Soviet-made pyrolysis attachment. With the aid of a switching valve, the pyrolysis cell was switched parallel to the sample feeder. The sample was pyrolyzed out in a quartz trough inserted into the heated pyrolysis zone (620°). The most effective separation of volatile pyrolysis products was achieved at 100° on a composite 100 × 0.4 cm column, the sorbent being β, β' -thiodipropionitrile (8%) on Spherochrome modified with 2% potassium hydroxide, and on a 100 × 0.4 cm column, the sorbent being 5% squalane on the same carrier. The carrier gas was helium and the detector was of the flame ionization type.

The standard substance used was *n*-nonane, which was introduced into the sample port of the chromatograph before pyrolysis of the sample and after the pyrolysis and recording of the volatile product separation chromatograph. In subsequent discussion, such a standard substance is conventionally called an external standard.

In calculations, it is advisable to use the retention times and peak areas of the external standard. The retention time of component *i* relative to the external standard, $t_{rel,i}$, can be obtained from the equation

$$t_{rel,i} = \frac{t_i - t_0 - t_{heat.}}{t_{st.} - t_{evap.}} \quad (9)$$

where t_i = the time from the beginning of sample heating to the appearance of the component peak maximum, t_0 = the dead time in the use of the pyrolysis reactor, $t_{evap.}$ = the dead time in the use of the evaporator, $t_{heat.}$ = the sample heating time (from the beginning of heating to the beginning of pyrolysis), which is determined when the pyrolysis reactor is connected to the detector¹⁷, and $t_{st.}$ = the retention time of the external standard. If thin connecting tubes are used, $t_0 \approx t_{evap.}$

In order to substantiate the possibility of calculating the retention times of pyrolysis products relative to an external standard, we carried out the pyrolysis of polypropylene under the conditions described earlier¹⁸ and compared the retention time of 2-methylpentene-2 in the pyrolysis product chromatogram¹⁹ (taking into account the sample heating time) with the retention time of 2-methylpentene-2 introduced as an external standard. The discrepancy did not exceed 0.5%, which confirmed the possibility of calculating the retention times of volatile pyrolysis products relative to an external standard by the method described.

Calculation of the relative areas of characteristic peaks on chromatograms of volatile pyrolysis products with the use of an external standard introduced independently into the pyrolysis process makes it possible to take into account the sensitivity of the detector and to compute by a simple method the values of $S_i/S_{st.}$ (relative peak areas of component *i* and the standard), under standard conditions (batch size, carrier gas velocity, pyrolysis temperature, etc.), and to calculate the absolute amounts of the pyrolysis products formed. Some of the advantages of the method for representing the experimental data are explained below. The calculation method described is actually a version of the absolute calibration method used in gas chromatography²⁰, and we have no knowledge of the proposed method being applied in pyrolysis gas chromatography. In order to simplify the comparison of the results obtained at different times or with different equipment, it is expedient to represent the results of

separate measurements also as values of specific yields (or in the form of relative characteristic peak areas), *i.e.*, to calculate the yield of volatile pyrolysis products per milligram (or gram or microgram) of the pyrolyzed sample with reference to 1 mg (or 1 g or 1 μg) of the external standard. This conversion is legitimate in the range where the sample size has a negligible effect on the specific yield of volatile pyrolysis products. This condition is met in work with very thin films²¹ or in the pyrolysis of a sample taken in the form of milligram-level batches¹⁷. For this reason, when an external standard is introduced, stricter requirements are imposed on the measurement of the sample size and on the amount of the standard substance introduced, which should be within a definite range.

In this investigation, the external standard (*n*-nonane) was introduced with a micrometer-screw microsyringe (piston diameter 0.8 mm), making allowance for the evaporation of the liquid from the syringe needle²². The deviation of the absolute values of the peak areas of *n*-nonane from the mean value did not exceed $\pm 3\%$. The accuracy of the introduction of the standard was $\pm 0.05\mu\text{l}$.

The chromatogram of the volatile pyrolysis products of the bulk ternary copolymer is presented in Fig. 2. Peaks 1-3 were used as characteristic peaks. Peaks 2 and 3 correspond to styrene and 2-vinylpyridine, and peak 1 is due to the presence of divinyl in the system and corresponds to light pyrolysis products of polydivinyl.

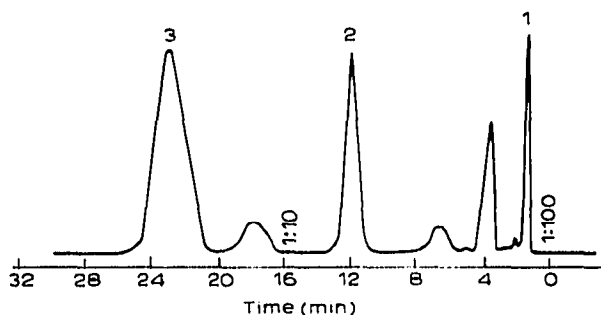


Fig. 2. Chromatogram of volatile pyrolysis products of a bulk copolymer of divinyl (37%), styrene (42%) and 2-vinylpyridine (21%). 1, 2 and 3: Characteristic peaks for polydivinyl, polystyrene and poly-2-vinylpyridine, respectively.

In order to select a reasonable batch size and the type of sample (solid or solution) to be placed in the trough for pyrolysis, we investigated the effect of the batch size on the ratio between the light and heavy pyrolysis products (from the ratio between the area of peak 1 and those of peaks 2 and 3) for samples taken in the form of a solid and samples obtained from solution by evaporating the solvent directly in the pyrolysis trough. Fig. 3 shows the respective dependences for S_1/S_2 in the pyrolysis of one of the copolymers (approximate composition: 60% divinyl, 30% styrene and 10% 2-vinylpyridine). Similar dependences were obtained for the ratio of the area of peak 1 to that of peak 3.

The shape of the graphs (Fig. 3) agrees with the results obtained earlier¹⁷ as regards the effect of the batch size of the sample on the ratio between the light and heavy pyrolysis products of natural rubber. From the results obtained, it follows that when

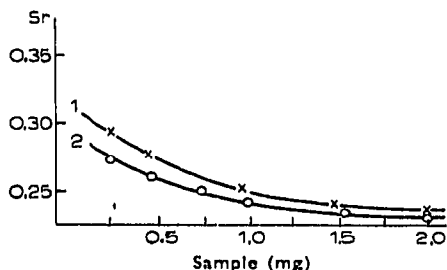


Fig. 3. Effect of sample size on ratio of peak areas of characteristic pyrolysis products of polydivinyl and polystyrene. 1, Sample in the form of a solid; 2, sample obtained from solution.

working with batches of 1 mg or more, the ratio of the characteristic pyrolysis products for divinyl, styrene and 2-vinylpyridine is virtually independent of the batch size and the type of sample used. A calibration graph constructed from data for samples inserted into the pyrolysis trough as a solution can be used for work with batches in the form of solids.

In plotting calibration graphs, we used solutions of mixtures of homopolymers in benzene (total concentration of polymers = 2%, w/w). The batch size was 1.5 mg and the solution was introduced into the pyrolysis trough with a microsyringe. As polyvinyl in bulk and in solution readily becomes cross-linked, the batch was introduced from freshly prepared calibration solutions prepared from re-deposited polydivinyl.

Results and discussion

The results of the calculation of the chromatograms of pyrolysis products of calibration mixtures of homopolymers were used for plotting calibration dependences of the relative areas of the characteristic peaks, $S_i/S_{i.t.}$, on the content of the component being analyzed in the mixture, which permits an independent determination of the contents of divinyl, styrene and 2-vinylpyridine in their bulk copolymers and mechanical mixtures of homopolymers to be made (Fig. 4). As can be seen from Fig. 4, for the system under investigation the dependence of the relative areas of the char-

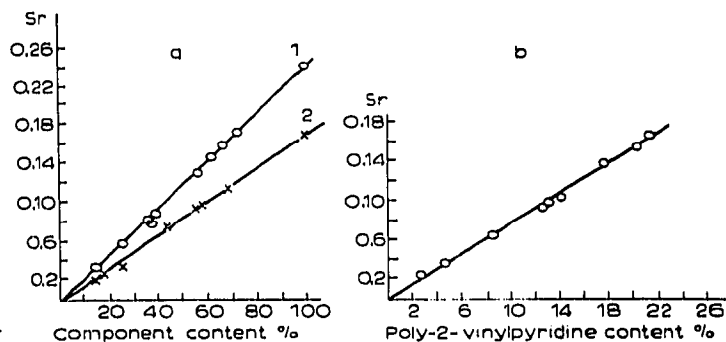


Fig. 4. Dependence of relative characteristic peak areas of (a) polydivinyl (1) and polystyrene (2) and (b) poly-2-vinylpyridine (standard: *n*-nonane) on content of components being analyzed in calibration mixtures of homopolymers.

acteristic peaks, $S_i/S_{st.}$, on the content of the component under study within the concentration range investigated is linear. For comparison, Fig. 5 exhibits the most frequently published¹⁷ dependences of the relative areas of the characteristic peaks of polydivinyl and poly-2-vinylpyridine calculated with reference to the characteristic peak of polystyrene. In this case, it was impossible to use the peak common to all three components and suitable for calculations as the standard peak.

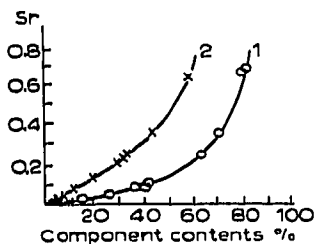


Fig. 5. Dependence of relative characteristic peak areas of polydivinyl (1) and poly-2-vinylpyridine (2) on content of corresponding component for conventional two-component mixtures of polydivinyl and poly-2-vinylpyridine with polystyrene (standard: characteristic peak of polystyrene).

Thus, for the system studied, it was found that $S_{rel.i} = f(X_i) = K_i X_i$, *i.e.*, the relative areas of the characteristic peaks with respect to the external standard substance (in other words, the absolute amounts of the volatile pyrolysis products formed) are proportional to the content of the respective components in the system. In this case, the dependence of S_i/S_j on X_i/X_j (where *i* and *j* are the components of the system) should also be linear:

$$\frac{S_i}{S_j} = \frac{S_{rel.i}}{S_{rel.j}} = \frac{K_i X_i}{K_j X_j} = K_{ij} \cdot \frac{X_i}{X_j} \quad (10)$$

This form of representation of experimental data, which has been used in some other work (see, for instance, ref. 24), does not require the introduction of a standard substance and should be useful in determining the composition of polymer systems with three or more components. Fig. 6 depicts the corresponding dependences for the characteristic peaks of the system under study.

The proportional dependence of the specific yield of characteristic pyrolytic

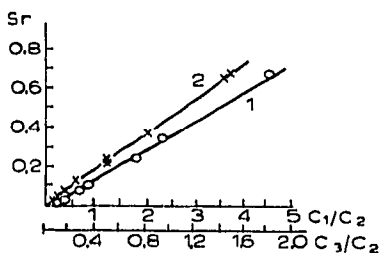


Fig. 6. Dependence of ratio of characteristic peak areas of polydivinyl and polystyrene (S_1/S_2) (1) and poly-2-vinylpyridine and polystyrene (S_3/S_2) (2) on the ratio of the corresponding components in calibration mixtures (c_1/c_2 and c_3/c_2).

products on the corresponding sample components has been described⁵. The use of the above dependence is also advisable for two-component systems, as it permits a calibration graph to be obtained, which is usually preferable. Thus, we recalculated by means of eqn. 10 the data for the non-linear calibration graphs given in previously published papers^{13,25,26}. In all instances, we obtained linear dependences. As an example, Fig. 7 shows the calibration graphs from ref. 13 plotted in the indicated coordinates by conversion using eqn. 10.



Fig. 7. (a) Calibration graph from ref. 7 for copolymers of vinyl acetate with butyl maleinate (1) and copolymers of vinyl acetate with butyl acrylate (2). (b) Calibration graph plotted from the data in graph (a) by re-calculation with the aid of eqn. 1. A, content of butyl ether; B, ratio of components in copolymer (vinyl acetate/butyl maleinate and vinyl acetate/butyl acrylate).

From the results, it follows that for the polymer system under consideration, the specific yield of the characteristic pyrolysis product for the component analyzed is independent of the amount and nature of the other components of the system. This can be attributed to the fact that the secondary processes involved in the pyrolysis of the system are essentially limited by intramolecular transformations of the primary pyrolysis products. Finding this rule in each specific case will probably facilitate the interpretation of the results when studying the structures of polymers with the aid of pyrolysis gas chromatography.

The application of the external standard method in pyrolysis gas chromatography has the following advantages. The use of an external standard permits a simpler relationship to be obtained between the content of a component (with definite groups or structural units) being analyzed in the polymer system and the yield of characteristic pyrolysis products (the relative areas of the corresponding peaks), and thus improves the reliability and accuracy of the measurements. When this dependence is linear, the relative areas of characteristic peaks can be used directly as a measure of the content of the test component (with certain groups or structural units) of the polymer system in investigating, for example, the chemical processes in polymers by means of pyrolysis gas chromatography²⁷.

When there are many peaks in the chromatogram of the volatile pyrolysis products, the choice of the optimum combination of the characteristic and standard

peaks in order to ensure the highest sensitivity and accuracy as regards the polymer characteristic under study (for instance, a change in content) involves cumbersome calculations and may be difficult. The use of an external standard, introduced with sufficient accuracy, makes the selection of a standard peak unnecessary and greatly simplifies the task.

The application of an external standard introduced independently into the pyrolysis process permits the peak areas and retention times of the volatile pyrolysis products of any polymer to be calculated with reference to the standard substance. This method may serve as a basis for quantitative and qualitative comparisons of the chromatograms of the pyrolysis products of different polymer systems.

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