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Application of factor analysis for resolving thermogravimetric–mass spectrometric analysis spectra

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Abstract

Factor Analysis was used for extracting information out of the mixture mass spectra recorded in a thermogravimetric–mass spectrometric analysis. Principal component analysis (PCA) and a special diagram, the contour variance diagram (ContVarDia), were used for performing the factor analysis. The method was applied for studying the thermal decomposition of Kraton 1107 copolymer. Pyrolysis–gas chromatography–mass spectrometry (Py–GC–MS) was used for identification of the pyrolysis products of Kraton 1107. The application of factor analysis resulted in the determination of the main thermal decomposition steps and the prediction of the mass spectrum corresponding to each step. Those mass spectra were either pure spectra corresponding to main evolved gases or average spectra corresponding to multiple gases evolved in one decomposition step. The advantages and the limitations of the chemometric approach were discussed. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: TG–MS; Py–GC–MS; Chemometrics; Factor analysis; Curve resolution; Kraton 1107

1. Introduction

Thermogravimetry–mass spectrometry (TG–MS) has been a well established technique for the analysis of evolved gases since the late 1970s [1]. The main advantage of the technique is the acquisition of multiple information during one run such as, the weight loss of the sample as a function of the temperature, the type of the volatile products as a function of the temperature and the quantitative analysis of the evolved gases. Generally, most of the applications of the TG–MS analysis concern the investigation of the thermal decomposition pathways of a material through observation of the evolution profile of specific pyrolysis products.

A wide range of commercial and home-made systems are used for the analysis of inorganic materials and natural or synthetic polymers. The application of TG–MS analysis in the study of inorganic materials [2,3] seems to have no problems in the identification of the evolved gases, since the main pyrolysis products are limited in number and they consist of light gases like CO₂, H₂O, SO₃, SO₂, NO_x and volatile oxides, which can be easily identified through characteristic masses. TG–MS analysis has become increasingly popular in the study of natural [4] or synthetic polymers [5]. However, it has the limitation, that not all the evolved gases can be readily identified. Usually, mixture mass spectra are recorded by the mass spectrometry (MS) as a result of the multiple gases simultaneous evolution. To overcome this limitation TG–MS analysis can be combined with pyrolysis–gas chromatography–mass spectrometry (Py–GC–MS) [6]. As a first step, the Py–GC–MS analysis is used

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for the resolution and the identification of the evolved gases. Next, characteristic masses are selected for each one of the evolved gases of interest. The characteristic masses, usually, correspond to the molecular ions of the volatiles and are used in the TG–MS analysis to monitor the evolution of the respective gases as a function of temperature or time. However, there are cases where no characteristic masses can be found for a gas because of the numerous gases which evolve simultaneously or because of the low abundance of the molecular ion.

One approach for facilitating the identification of the coevolved species in the TG–MS analysis of synthetic or natural polymers is the discontinuous TG–MS analysis [7] which includes a chromatographic separation step; TG–GC–MS analysis. This approach is already practiced but it seems that it is generally difficult and time-consuming to operate multiple hyphenated techniques. Another approach is the use of tandem TG–MS–MS [8,9]. GC–MS is preferred when a large number of unknown components in a mixture are to be identified and MS–MS is preferred for the analysis of targeted compounds in a mixture. A third approach appears to be the development and application of chemometric techniques for resolving the mixture mass spectra and predicting the pure spectra of the coevolved gases. Application of this approach has been reported in another evolved gas analysis technique, that is the thermochromatography (ThGC) for providing information about the independent thermal processes which occurred during the sample heating of inorganic salts [10].

The objective of this work is to investigate if the application of a chemometric technique to the TG–MS data can contribute to the identification of the coevolved species and if it can improve the quality and quantity of information extracted by the data. More specifically, it is examined if the mixture mass spectra recorded at a TG–MS analysis can be resolved into the pure mass spectra of the main evolved gases. Moreover, it is investigated if the total ion current curve (TIC) can be resolved into curves that correspond to the evolution profiles of the main volatile pyrolysis products. The chemometric technique used in this work is factor analysis. Principal component analysis (PCA) and a special diagram the contour variance diagram (ContVarDia) are used for performing the factor analysis. The ContVarDia is used for

the transformation of the abstract PCA solution into physically meaningful factors. The polymer material selected for this study is Kraton 1107 which is a styrene–isoprene–styrene copolymer.

2. Theoretical

The chemometric method used for extracting the mass spectra of the main pyrolysis products and for resolving the TIC is based on factor analysis [11]. The factor analysis model is developed by combining PCA with a special kind of diagram the ContVarDia.

PCA [12] which is in principle, a data reduction technique is applied on the experimental data matrix ($D_{s \times m}$) for finding the intrinsic dimensionality of the data and for decomposing it into the abstract matrices of the scores (matrix S) and the loadings (matrix L) (Eq. (1)):

$$\bar{D}_{s \times m} = S_{s \times f} L_{f \times m} \quad (1)$$

The size of the matrices is denoted in the subscript. In Eq. (1), s is the number of the mass spectra, m the number of the mass variables and f the number of the significant PCs which denote the intrinsic dimensionality of the data. The overhead bar (·) on matrix \bar{D} indicates the reconstructed matrix of the experimental data which differs from matrix D since the non-significant PCs are ignored in Eq. (1).

The abstract solution of Eq. (1) is next transformed into a physically meaningful solution by using an appropriate transformation matrix $T_{f \times f}$. The matrix $T_{f \times f}$ transforms the scores into the relative concentrations of the chemical components. The inverse of matrix T (T^{-1}) transforms the loadings into the mass spectra of the components. This transformation is expressed by Eqs. (2a) and (2b):

$$\bar{D}_{s \times m} = (S_{s \times f} T_{f \times f})(T_{f \times f}^{-1} L_{f \times m}) \quad (2a)$$

$$\bar{D}_{s \times m} = C_{s \times f} M_{f \times m} \quad (2b)$$

where C is the matrix with the evolution profiles (relative concentrations) of the chemical components in the columns and M the matrix with the spectra of the chemical components in the rows. The elements in the columns of the matrix T represent the coordinates of the *component axes* in a geometrical approach. The

component axis of a chemical component is the axis in the PC space on which the projections of the objects (spectra) are highly correlated with the quantities of the chemical component in the associated mixtures.

In this work, the determination of the component axes and the calculation of the transformation matrix are carried out by a special type of diagram, the ContVarDia, which is an extension of the variance diagram (VarDia) [13] in three dimensions. Both diagrams are based on the same assumption; mass variables which are “typical” for a chemical component will show a correlated behavior. Due to this behavior, the vectors of the mass variables in the PC space will tend to cluster in specific directions. These are the directions of the component axes. The ContVarDia is a contour diagram in spherical coordinates which visualizes the clustering of the mass variables in a three-dimensional PC subspace. A region which shows a maximum in the ContVarDia indicates a cluster of variables with the same behavior. The direction of the cluster indicates the direction of a component axis and the respective coordinates are used as the elements of a column of the matrix T . Details about the ContVarDia and an application of the technique in GC–MS data can be found elsewhere [14]. The calculation of the transformation matrix T is selected to be done by the technique of ContVarDia instead of a technique based on pure variables because in TG–MS data of natural or synthetic polymers such as Kraton 1107, it is unlikely to have pure variables.

It should be emphasized that the columns of matrix $C_{s \times f}$ represent the unscaled evolution profiles of the chemical substances. This means that only the shapes of the evolution profiles are accurate but not the absolute values in every scan. In this work, in order to get the scaled evolution profiles (TICs) the sum of the intensities of the respective mass spectra (matrix $M_{f \times m}$) is used as a scaling factor. This means that every column of matrix $C_{s \times f}$ is multiplied by the sum of the respective row of matrix $M_{f \times m}$. The quality of prediction of the TICs by this way of scaling, which is rather simple, is depended on the quality of the prediction of the mass spectra; the more accurate the prediction of the spectra is, the more efficient the prediction of the TICs would be. If for example large negative intensities are present in the predicted spectra then the earlier way of scaling would result into poor prediction for the TICs.

3. Experimental

3.1. Material

The styrene–isoprene–styrene copolymer, Kraton 1107 was provided by the CDS Analytical Inc., as a reference material for setting up a pyrolysis system.

3.2. Instruments-methods

The TG–MS analysis was carried out by a system consisting of a thermogravimetric analyzer (TA instrument, TGA 2050) and a mass selective detector (HP-5972). An in-house interface [15] was used for the combination of the mentioned instruments. The transfer line of the TG–MS interface was a Chrompack uncoated column (2.17 m, 0.15 mm i.d.). The temperature of the TG–MS interface was 200 °C and the temperature of the transfer line was kept at 220 °C. The inert gas used was helium with a flow rate of 100 ml/min in the thermobalance. The sample of Kraton 1107, approximately 1.5 mg, was heated in the thermobalance from 50 to 650 °C with a rate of 50 °C/min. The MS interface was heated at 280 °C. The electron impact source was tuned at 70 eV and the scan duration was 0.5 s. The mass range for the MS data acquisition was 2–220 amu.

The Py–GC–MS analysis was carried out by a gas chromatograph (HP-5890 series II) equipped with an electron impact mass selective detector (HP-5972). The pyrolysis unit was a CDS instrument, model Pyroprobe 1000. The chromatographic column used was a HP 5 MS capillary (30 m \times 0.25 mm i.d., 0.25 μ m film thickness). The pyroprobe interface was heated at 250 °C. A sample of Kraton 1107, approximately 3 mg, was inserted in the pyroprobe quartz tube and it was heated with a rate of 20 °C/ms up to 700 °C for 10 s. The carrier gas was helium with a column head pressure of 15 psi and the split ratio was 1/100. The GC injector temperature was 250 °C and the MS interface temperature was 280 °C. The electron impact source was tuned at 70 eV and the scan duration was 0.7 s. The mass range for the MS data acquisition was 18–550 amu. The GC oven was set to 50 °C for 2 min and then heated with a rate of 5 °C/min up to 200 °C for 10 min.

3.3. Software

The software used for the application of the chemometric technique to the TG–MS data was in-house written in Matlab. It consists of subroutines for data preprocessing (baseline correction, spike removal), PCA application, ContVarDia construction, mass spectra resolution and curve resolution. In this work, the colour shades of the ContVarDia are replaced by shades of gray for printing purposes.

4. Results and discussion

In Fig. 1, the Py–GC–MS chromatogram of Kraton 1107 is presented. The main pyrolysis products which were identified by the library search system of

the MS software with similarity index greater than 80 are presented in Table 1 together with the eight most abundant masses derived from the eight peak index (Mass Spectrometry Data Center). The Py–GC–MS mass spectra of isoprene monomer (2-methyl-1,3-butadiene), styrene monomer (ethenylbenzene), 1,4-dimethyl-4-ethenyl-cyclohexene and 1-methyl-4-(1-methylethenyl)-cyclohexene which are the most abundant pyrolysis products are given in Fig. 2.

In Fig. 3 the TG, DTG, temperature and TICs of the TG–MS analysis of Kraton 1107 are presented. The thermal degradation of Kraton 1107 seems to take place at two different temperature regions, one with a maximum at 391 °C and another with a maximum at 445 °C. The mass spectra which correspond to the maxima are presented in Fig. 4. The first mass spectrum (Fig. 4a) seems to have great similarity with

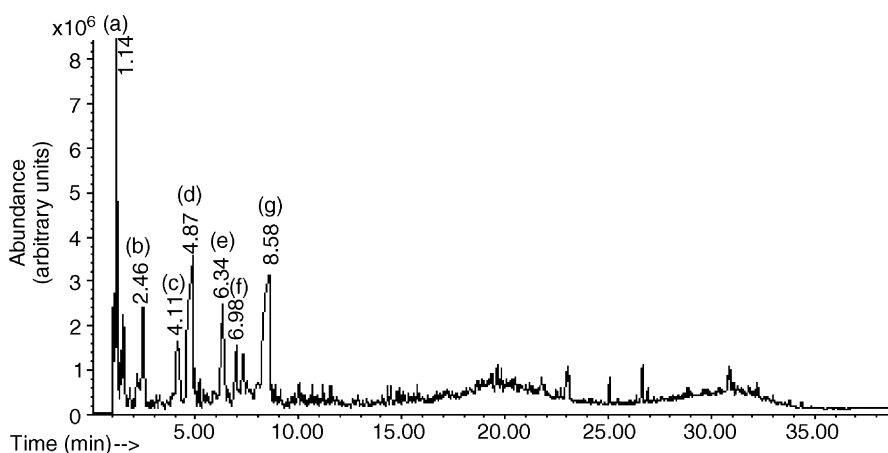


Fig. 1. Py–GC–MS chromatogram of Kraton 1107 copolymer (a) isoprene, (b) methyl-benzene, (c) isomers of dimethyl-benzene, (d) styrene, (e) 1,4-dimethyl-4-ethenyl-cyclohexene, (f) isopropenyl-benzene and (g) 1-methyl-4-(1-methylethenyl)-cyclohexene.

Table 1

Identified substances by the electronic library (Wiley) in the Py–GC–MS analysis of Kraton 1107 with the eight most abundant masses and their relative intensities according to the eight peak index (Mass Spectrometry Data Center)

Retention time (min)	Substance	Eight most abundant masses (relative intensities)
1.14	Isoprene (2-methyl-1,3-butadiene)	67, 53, 68, 39, 27, 40, 41, 42 (100, 86, 83, 71, 48, 45, 40, 22)
2.46	Methyl-benzene	91, 92, 65, 39, 63, 51, 45, 89 (100, 60, 12, 9, 6, 6, 5, 3)
4.11	Isomers of dimethyl-benzene	–
4.87	Styrene (ethenylbenzene)	104, 103, 78, 51, 77, 105, 50, 52 (100, 45, 32, 21, 17, 9, 7, 7)
6.34	1,4-Dimethyl-4-ethenyl-cyclohexene	68, 67, 93, 107, 136, 121, 53, 41 (100, 35, 29, 22, 17, 15, 15, 15)
6.98	Alpha-methylstyrene (isopropenyl-benzene)	118, 117, 103, 78, 51, 77, 39, 91 (100, 64, 58, 37, 29, 26, 25, 22)
8.58	1-Methyl-4-(1-methylethenyl)-cyclohexene	68, 93, 67, 39, 41, 27, 53, 79 (100, 47, 42, 33, 32, 28, 23, 22)

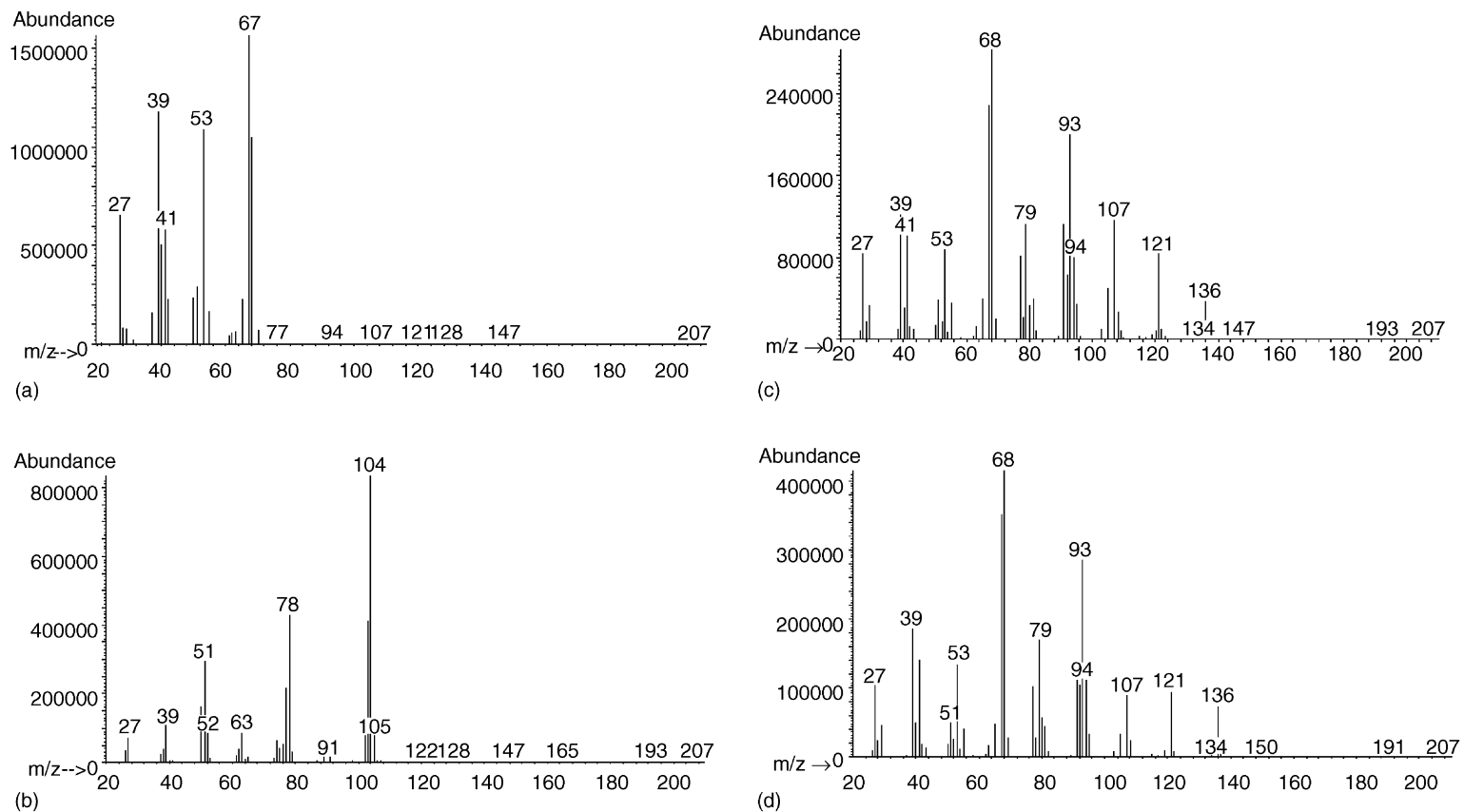


Fig. 2. Py-GC-MS mass spectra of the four most abundant pyrolysis products of Kraton 1107: (a) isoprene (retention time = 1.14 min), (b) styrene (retention time = 4.87 min), (c) 1,4-dimethyl-4-ethenyl-cyclohexene (retention time = 6.34 min) and (d) 1-methyl-4-(1-methylethenyl)-cyclohexene (retention time = 8.58 min).

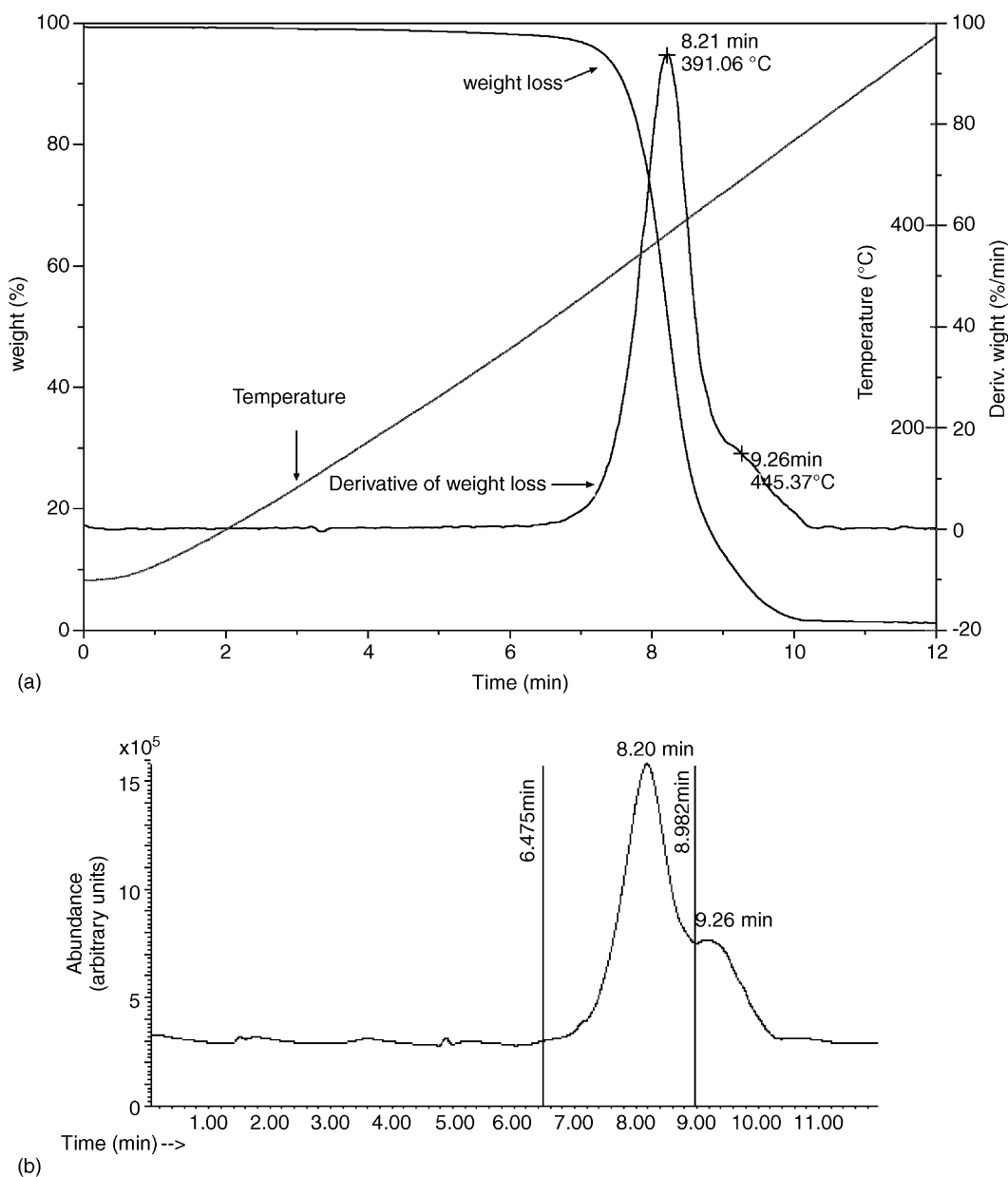


Fig. 3. (a) The weight loss (TG), the derivative of the weight loss (DTG) and the temperature curves (TG response) and (b) the TIC curve (MS response) of the TG–MS analysis of Kraton 1107.

those of 1-methyl-4-(1-methylethenyl)-cyclohexene (Fig. 2d) and 1,4-dimethyl-4-ethenyl-cyclohexene (Fig. 2c) while the second one (Fig. 4b) seems to be similar to that of styrene (Fig. 2b). For studying the evolution of the various pyrolysis products as a func-

tion of temperature, it is very common to identify the products by Py–GC–MS analysis and then plot the extracted ion chromatograms, in the TG–MS analysis, of characteristic masses for each product. In Fig. 5, the extracted ion chromatograms of characteristic

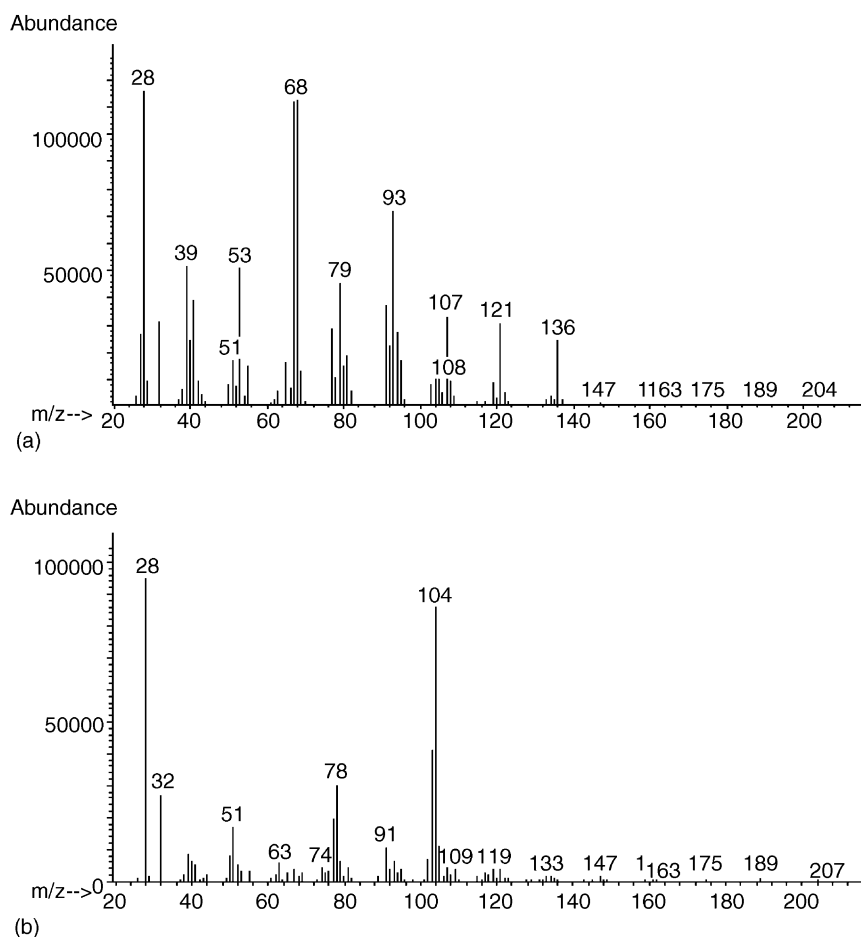


Fig. 4. The TG-MS mass spectrum at 8.20 min (391 °C) corresponding to the maximum of the first peak (a) and at 9.26 min (445 °C) corresponding to the maximum of the second peak (b) of the TIC.

masses which have been used in a previous indirect pyrolysis study of the thermal degradation of Kraton 1107 [16] are shown. Mass 68 was chosen as characteristic of isoprene monomer. However, mass 68 can be also attributed to other pyrolysis products of Kraton 1107 like 1-methyl-4-(1-methylethenyl)-cyclohexene and 1,4-dimethyl-4-ethenyl-cyclohexene. Mass 78 can originate both from benzene and styrene. A solid way to identify the pyrolysis products would be to examine the relative intensities of the most abundant masses for each product (Table 1). The extracted ion chromatograms of the six most abundant masses (Table 1) for isoprene and styrene monomers are given in Fig. 6a and b, respectively. Only the evo-

lution of styrene in the second stage of the thermal degradation can be reconfirmed (Fig. 6b) in this way.

In order to investigate if more information can be extracted for the first decomposition step (time range 6.475–8.982 min in Fig. 3b) of the TG-MS analysis, the mixture mass spectra corresponding to that step were processed by PCA. Prior to application of PCA, the number of scans were reduced by averaging them in groups of nine. In this way, smoothing of the data was achieved. Moreover, the masses that were treated by PCA were chosen to have a variance/mean ratio greater than 200 in order to avoid background masses. The raw data matrix consisted of 75 scans in the rows and 88 masses in the columns. The scree plot of the

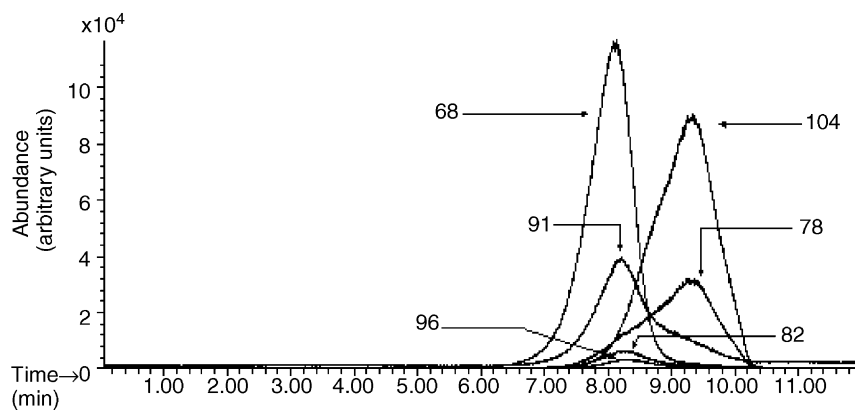


Fig. 5. Extracted ion chromatograms of some characteristic masses observed during the TG–MS analysis of Kraton 1107. Mass 68 corresponds to isoprene, mass 104 to styrene, mass 91 to toluene, mass 78 (molecular ion) to benzene, mass 82 to $C_5H_7-CH_3$ and mass 96 to $C_6H_9-CH_3$.

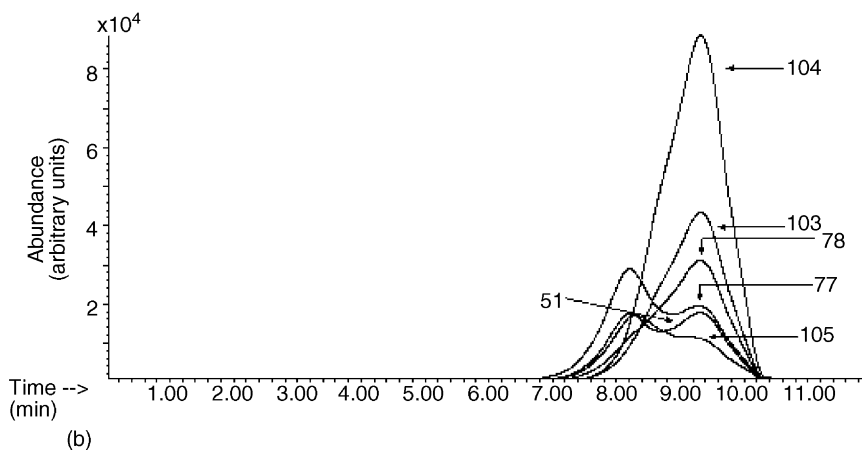
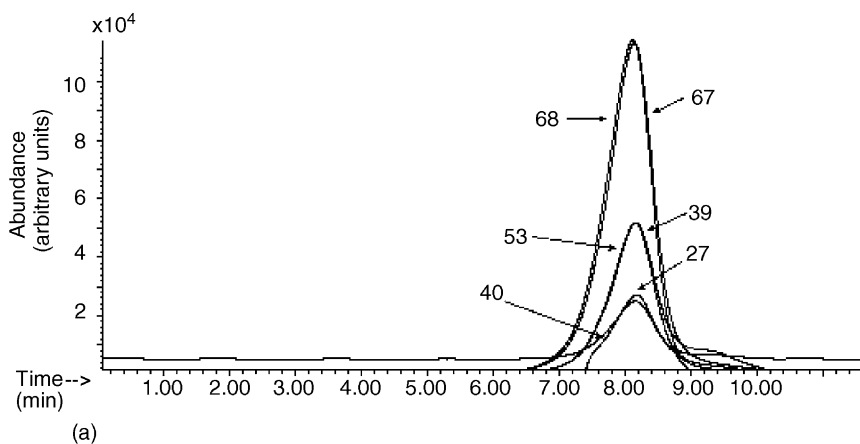


Fig. 6. TG–MS extracted ion chromatograms of the six most abundant masses of (a) isoprene and (b) styrene.

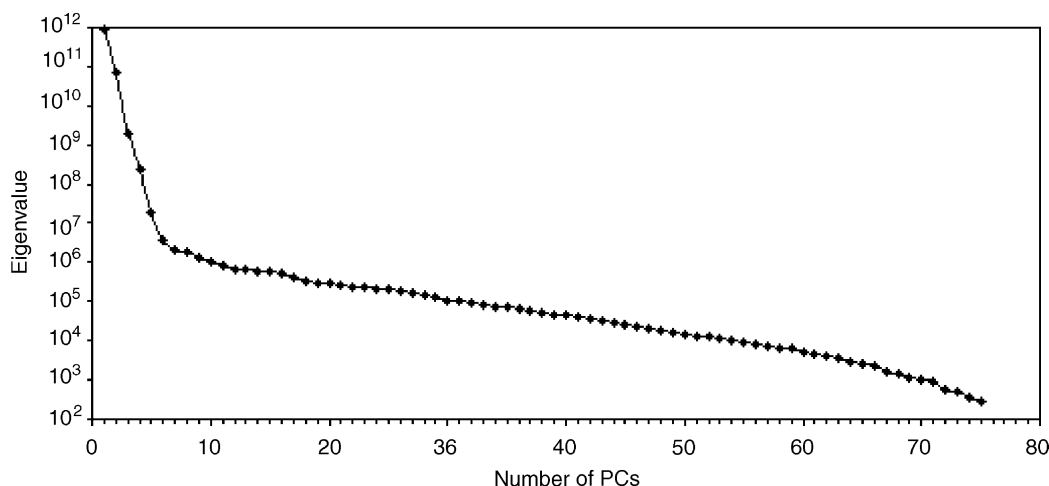


Fig. 7. Scree plot of the eigenvalues in logarithmic scale.

Table 2

The eigenvalues, the variance and the cumulative variance of the first six PCs

Number	Eigenvalues	Variance (%)	Cumulative variance (%)
1	9.107E+11	92.8231	92.8231
2	6.832E+10	6.9633	99.7864
3	1.826E+09	0.1861	99.9725
4	2.325E+08	0.0237	99.9962
5	1.850E+07	0.0019	99.9981
6	3.570E+06	0.0004	99.9985

eigenvalues in logarithmic scale is presented in Fig. 7. According to the scree plot criterion [12] for describing successfully the data, six PCs can be selected. However, there is only a small increase in the cumula-

tive variance (Table 2) after the fourth PC and this is the reason for finally selecting four PCs to represent the data. These four PCs extract 99.99% of the total variance. The ContVarDia in the PC2/PC3/PC4 space is presented in Fig. 8. The four regions of the higher variance are shown in dashed circles. The masses which participate in each one of these regions are presented in Table 3. It should be emphasized that the clustering of the masses in a region of the ContVarDia indicates a highly correlated relation among them. The direction of each cluster indicates the direction of a *component axis*. The directions of the component axes were used to construct the transformation matrix T of Eq. (2a) and (2b). Next, the resolved unscaled TICs (evolution profiles) corresponding to

Table 3

Details about the regions of high variance shown by the ContVarDia in the PC2/PC3/PC4 subspace

Region (component)	Cluster	θ (°)	φ (°)	Masses present in the cluster	Variance
1	a	30	80	102, 103, 104	0.8342
1	b	10	80	74, 75, 78	0.0766
2	a	110	100	68	0.3127
2	b	101	120	136	0.0282
3	a	285	140	69, 81, 83, 97, 107, 108, 122, 123, 133, 148	0.2087
3	b	304	120	91, 119	0.1583
3	c	281	120	15, 55, 56, 95, 96, 110, 124, 134, 150	0.1419
4	a	285	40	26, 39, 65	0.1939
4	b	270	20	37, 38, 53	0.1892
4	c	210	20	67	0.1236

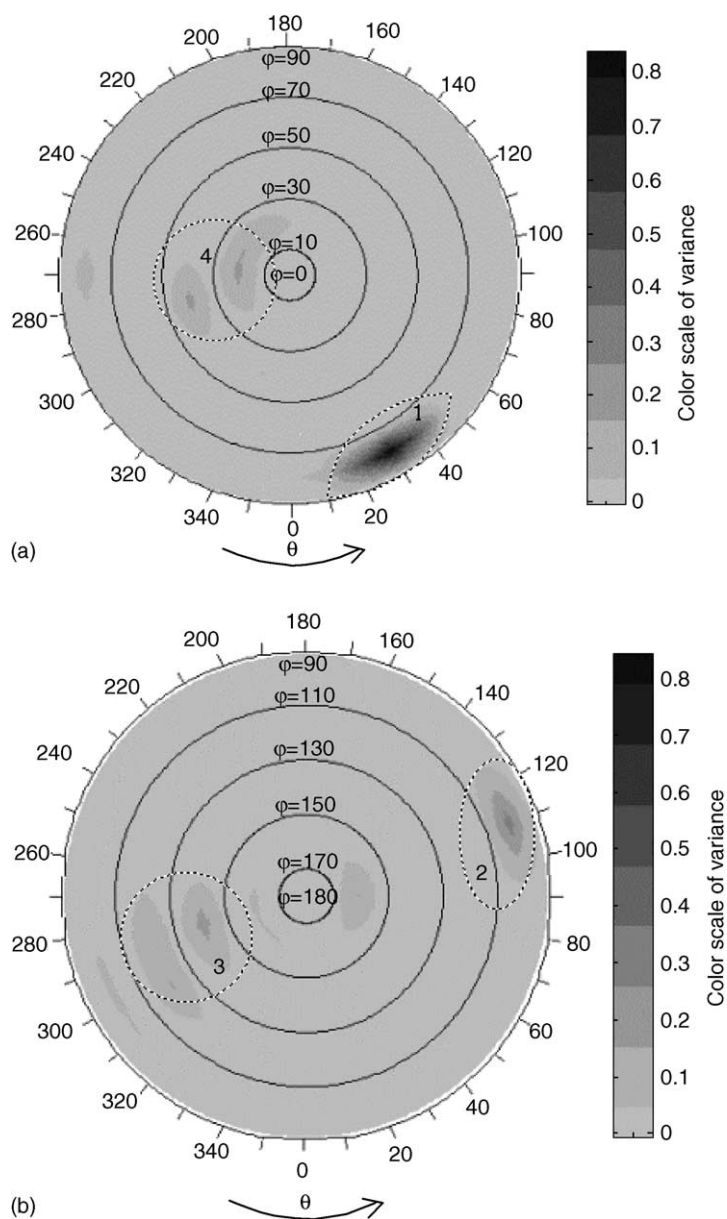


Fig. 8. ContVarDia in the PC2/PC3/PC4 subspace (a) upper hemisphere (b) lower hemisphere. Dashed circles indicate regions of high variance.

each component and the respective mass spectra were calculated (Fig. 9). In Fig. 10, the unresolved TIC and the resolved scaled TICs are presented. Comparing the predicted mass spectra of Fig. 9 with the mass spectra of the main pyrolysis products of Kraton 1107 identified by the Py-GC-MS analysis (Fig. 2)

it appears that the predicted mass spectrum of Fig. 9a shows similarity with the mass spectrum of styrene monomer (Fig. 2b). The mass spectrum of Fig. 9b is similar to that of cyclohexene-4ethenyl-1,4-dimethyl and 1-methyl-4-(1-methylethenyl)-cyclohexene (Fig. 2c and d) and the mass spectrum of Fig. 9d is

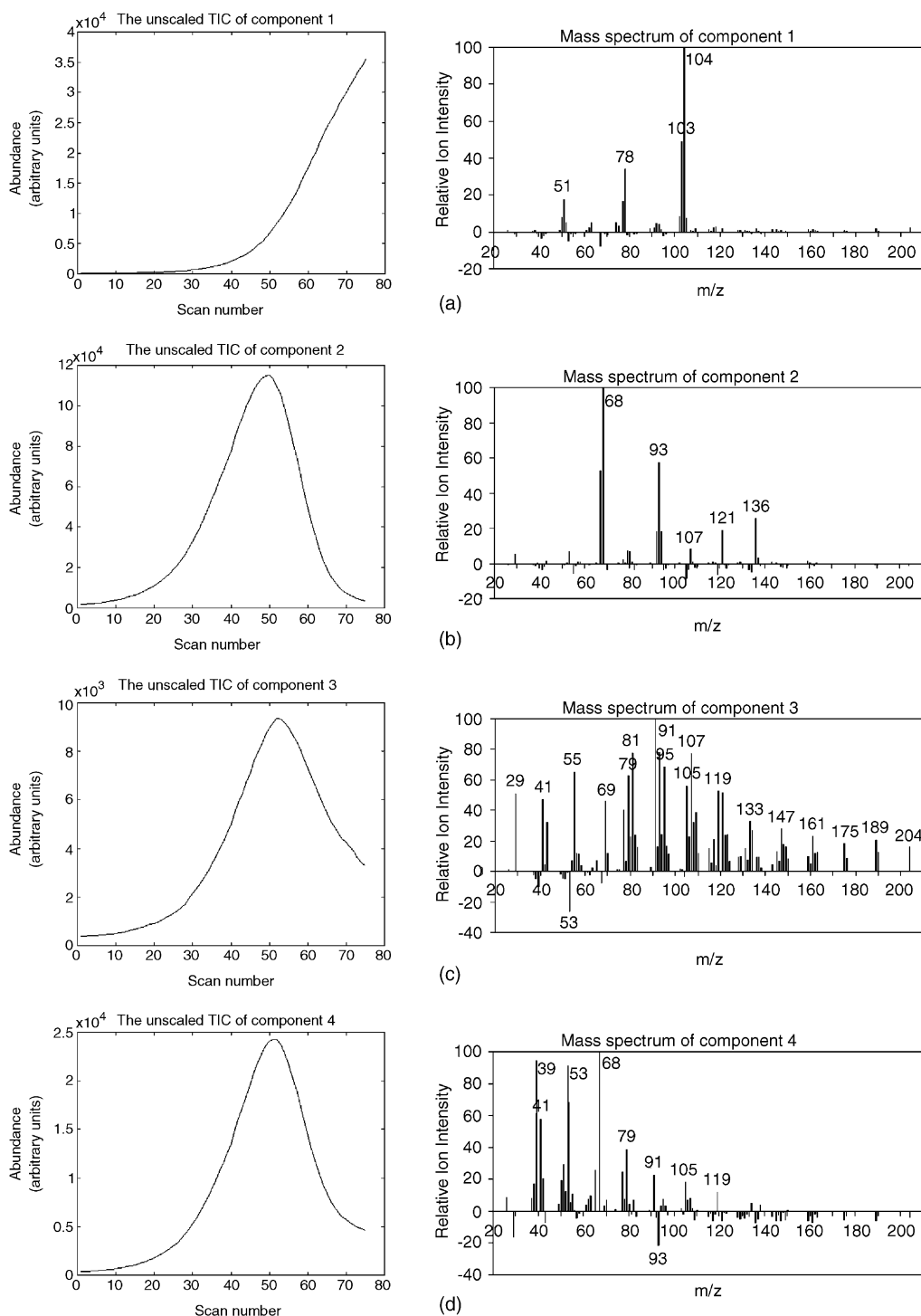


Fig. 9. The predicted unscaled TICs and the predicted mass spectra of the pyrolysis products of Kraton 1107 as estimated after applying PCA to the time range 6.475–8.982 min of the TG–MS data. Scan numbers 1 and 75 correspond to 6.475 and 8.982 min, respectively.

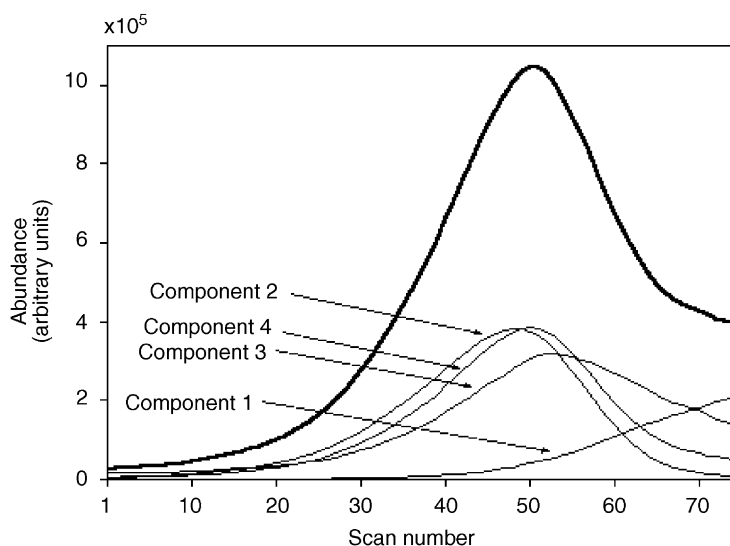


Fig. 10. The original (unresolved) TIC after subtraction of some background masses (in bold line) and the predicted scaled TICs of the pyrolysis products of Kraton 1107 in the time range 6.475–8.982 min of the TG–MS analysis.

associated with that of isoprene monomer (Fig. 2a). The predicted mass spectrum of Fig. 9c is not attributed to a single pyrolysis product but it seems to be similar to the average spectrum of the Py–GC–MS analysis in the time range 9–35 min. This average spectrum is presented in Fig. 11. Consequently, the mass spectrum of Fig. 9c seems to be attributed to a mixture of alkylbenzenes (ion series 63, 77, 91, 105,

119, 133, 147, 161, ...), cycloalkenes (ion series 81, 95, 109, 123, ...) and cycloalcadienes or saturated polycyclic hydrocarbons (ion series 79, 93, 107, 121, 135, 149, 163, ...) [17]. According to the resolved scaled TICs (Fig. 10) the first decomposition step (time range 6.475–8.982 min in Fig. 3b) of the Kraton 1107 seems to consist of four overlapped decomposition steps. In the first step,

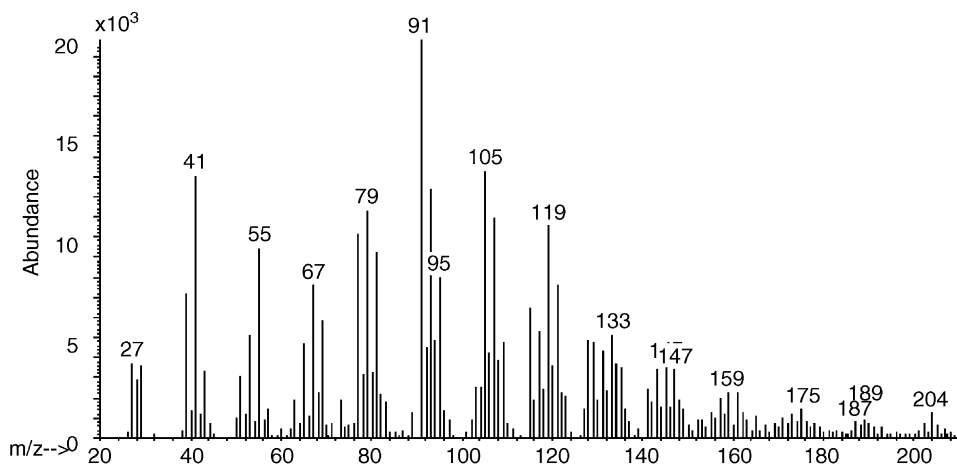


Fig. 11. The average mass spectrum corresponding to the time range 9–35 min of the Py–GC–MS analysis of Kraton 1107.

1-methyl-4-(1-methylethenyl)-cyclohexene and 1,4-dimethyl-4-ethenyl-cyclohexene start to evolve. In the second step, the evolution of isoprene monomer is taking place. In the third step, a mixture of alkyl-benzens, cycloalkenes, cycloalcadienes and saturated polycyclic hydrocarbons evolves whilst the evolution of styrene monomer (fourth step) is starting later when the pyrolysis of polyisoprene has already reached its maximum.

Another analytical question apart from revealing the decomposition steps and identifying the main pyrolysis products would be the estimation of the absolute concentrations of the pyrolysis products. This can be done by translating the areas below the predicted TICs into concentrations using standards and calibration curves. This is possible only in the case that the predicted TICs are associated with one product. It should be noted that the accuracy of the prediction of the TICs is a limiting factor for the quantitative determination.

5. Conclusions

The chemometric approach applied in this work proved to be a useful tool in extracting information out of the complex data recorded in the TG–MS analysis of a synthetic polymer. More specifically, it was shown that the main thermal decomposition steps of the sample can be revealed and the mass spectrum of each decomposition step can be predicted. The mass spectrum of each step might either correspond to the pure spectrum of a pyrolysis product or might be the average spectrum of many pyrolysis products. It should be emphasized that the technique described in this work can resolve coevolved pyrolysis products with not identical evolution profiles.

The chemometric technique described in this work has the advantage of extracting the aforementioned information out of the data without requiring any knowledge of the pyrolysis products. Moreover, it does not presuppose the existence of a pure mass for each product. In general, it can be concluded that the application of the chemometric approach to the TG–MS data of

polymers cannot substitute the information derived by the Py–GC–MS analysis, as far as the identification of the numerous pyrolysis products is concerned. In this sense, the chromatographic resolution is indispensable. But it proved to be useful in revealing the various decomposition steps and in identifying the main pyrolysis products or groups of products that evolve in each step by means of the pure or average spectra respectively. The examined approach seems to be more reliable compared to the technique of studying the evolution of the various pyrolysis products through the extracted ion chromatograms of characteristic masses, since it provides the full mass spectra.

References

- [1] R. Giovanoli, H.G. Wiedemann, *Helv. Chim. Acta* 51 (1968) 1134.
- [2] E.L. Charsley, S.B. Warrington, *Thermochim. Acta* 114 (1987) 47.
- [3] J. Wang, B. Mc Enaney, *Thermochim. Acta* 190 (1991) 143.
- [4] M. Statheropoulos, S.A. Kyriakou, *Anal. Chim. Acta* 409 (2000) 203.
- [5] K.G.H. Raemaekers, J.C.J. Bart, *Thermochim. Acta* 295 (1997) 1.
- [6] L.H. Perng, *Polym. Degrad. Stab.* 69 (2000) 323.
- [7] L.F. Whiting, P.W. Langvardt, *Anal. Chem.* 56 (1984) 1755.
- [8] B. Shushan, B. Davidson, R.B. Prime, *Anal. Calorimet.* 5 (1984) 105.
- [9] R.B. Prime, B. Shushan, *Anal. Chem.* 61 (1989) 1195.
- [10] M. Elomaa, M. Kaljurand, M. Koel, M. Kudrjashova, *Thermochim. Acta* 336 (1999) 73.
- [11] E.R. Malinowski, *Factor Analysis in Chemistry*, Wiley, New York, 1991.
- [12] I.T. Jolliffe, *Principal Component Analysis*, Springer, New York, 1986.
- [13] W. Windig, H.L.C. Meuzelaar, *Anal. Chem.* 56 (1984) 2297.
- [14] M. Statheropoulos, K. Mikedi, *Anal. Chim. Acta* 446 (2001) 353.
- [15] M. Statheropoulos, S.A. Kyriakou, N. Tzamtzis, *Thermochim. Acta* 322 (1998) 167.
- [16] J. Hacaloglu, M.M. Fares, S. Suzer, *Eur. Polym. J.* 35 (1999) 939.
- [17] E. Pretsch, T. Clerc, J. Seibl, W. Simon, *Tables of Spectral Data for Structure Determination of Organic Compounds*, 2nd Edition, Springer, Berlin, 1983.