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Classification of polymeric materials by evolving factor analysis and principal component analysis of thermochromatographic data

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Abstract

Thermal decomposition of different polymeric materials was investigated by thermochromatography (ThGC), a temperature programmed pyrolysis chromatographic method. ThGC produces two-dimensional results; the co-ordinates of which are the retention time and the pyrolysis temperature at the time of sampling. Therefore, principal component analysis (PCA), on results from evolving factor analysis (EFA) successfully applied would decompose the complete data of each run into two parts: ‘thermograms’ and ‘chromatograms’. Factor analysis at this stage compresses the data, making it more convenient for further analysis of the data structure composed of a few dozen of samples. The aim of this stage of the data analysis process is to extract ‘real thermograms’ as close as possible to the corresponding ‘thermograms’ — answering the question “which products are evolved at each temperature.”

Combination of ‘chromatograms’ and related ‘thermograms’ obtained on the first stage were used as characteristic vectors in the further analysis. Sets of significant ‘thermograms’–‘chromatograms’ were subjected to PCA. Mapping of the polymeric samples onto planes defined by factors allows one to identify clusters as related to different classes of polymers, as well as different mechanisms of their thermal decomposition. The data was proven to give a very good basis for characterization of the samples by their polymer content. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Thermochromatography; Polymeric materials; Principal component analysis; Evolving factor analysis

1. Introduction

A collection of polymeric materials, consisting of five groups of rubbers and plastics and a dozen individual polymers, were analyzed using a not so common technique of pyrolysis chromatography, or thermochromatography (ThGC).

Thermochromatography is a temperature-resolved, multiple-injection gas chromatography technique [1,2]. Consecutive chromatograms are collected during pyrolysis, each at known temperature and representing the head-space gas component distribution above the pyrolyzing material. Heating rates typically used in thermogravimetry are also applicable in ThGC. It was shown earlier that, by means of thermal gravimetry (TG) and chemometrics, it is possible to gain a good deal of information about the structure of rubber blends. More specifically the formation of a new component due to the blending process used to

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produce the rubbers was detected [3]. The thermal curves of ThGC contain basically the same information as TG curves and in addition the knowledge of the chemical composition of the evolving gases that the chromatographic separation provides.

We have earlier shown the usefulness of the evolving factor analysis (EFA) in the analysis of the results of thermochromatography [4]. EFA is used to resolve overlapping, entire chromatograms based on their different origin in pyrolysis temperature. Simply, EFA deconvolutes the components of the pyrolysis process as differing thermal reactions leading to different product profiles. As a result, one obtains sets of different 'chromatograms' and their corresponding temperature-profile 'thermograms' of the evolving head-space gases. In the cases of the decomposition of inorganic materials, the chromatographic patterns are so clear that the peak shapes have also been utilized in the decomposition of thermochromatographic data [5]. In this study of polymeric materials an EFA program was used, because organic polymers produce such rich mixtures of gases that the peak shape information cannot be used. There are many other ways to do multivariate curve resolution [6]; however, EFA gave us a simple way to do the deconvolution and further study the thermal and the chromatographic factors as a basis of classification of the polymeric materials.

The main goal of the work was to study how good basis for the classification of polymeric materials the ThGC data gives. How well can different polymers be classified using principal component analysis (PCA) on thermal factors, chromatographic factors and on both decomposed from ThGC data. The chemical background of the classification is discussed concerning the differences between thermal stability and decomposition mechanisms of polymers.

2. Experimental

2.1. Equipment

The ThGC consisted of a gas chromatograph (Perkin-Elmer 2000) equipped with a pyrolysis oven, a sampling valve, a capillary column and a flame ionization detector. The pyrolysis oven was a quartz tube with an inner diameter of 3 mm and length of 250 mm,

having a centrally located, 5-mm long quartz sample vessel. The heater for pyrolysis consisted of a wire-wound, insulated cylinder surrounding the quartz tube. Temperature calibration was achieved by placing a thermocouple in sample vessel in place of a sample. The linear heating ramp could be repeated with a measured precision of $\pm 1^\circ\text{C}$. The sampling valve consisted of a Deans' type switch [7] inside the column oven run by a three-way solenoid valve outside the oven. A microcomputer was used to control both the heating of the pyrolysis oven and the timed sampling of the evolved gases in the pyrolyzer tube head-space. The temperature gradient was as follows: starting at 100°C , heat to 200°C at $50^\circ\text{C}/\text{min}$, and $200\text{--}550^\circ\text{C}$ at $5^\circ\text{C}/\text{min}$. Helium flow rate through the pyrolysis oven was 10 ml/min. One-second injection period was repeated after 2-min intervals, leading to 36 chromatograms the last 30 of which (at $260\text{--}550^\circ\text{C}$) were used in the calculations described later in Section 3. The capillary column was a combination of a $0.5\text{ m}\times 0.32\text{ mm}$ i.d. Porapak Q precolumn and a $12\text{ m}\times 0.20\text{ mm}$ i.d. methyl silicone rubber analytical column in tandem. The design permitted efficient, rapid separation of a wide boiling point range of components at the relatively high, column-oven temperature of 185°C .

3. Materials

Samples, 70 runs altogether, consisted of five groups of polymeric materials and 12 other individual samples. The groups and the samples as well as the amount of the runs are listed in Table 1. The samples were 1–2 mg of weight.

Table 1
Samples

Group	Sample specifications ^a	No. of runs
PS	$M_p=2200$	2
Polystyrenes	$M_p=4000$	3
	$M_p=9000$	1
	$M_p=47500$	1
	$M_p=140000$	2
	$M_p=300000$	1
	$M_p=1000000$	3

Table 1 (Continued)

Group	Sample specifications ^a	No. of runs
PE Polyethylenes	PE-LLDX1	1
	PE-LLDX2	1
	PE-LLDG	1
	PE-LLD	1
	PE-LDX1	1
	PE-LDX2	1
	PE/PP 72% ethylene	1
PP Polypropylenes	Isotactic polypropylene 1	2
	PP-FR 10%	2
	PP-FR 20%	1
	PP-FR 40%	1
	PP-co-PE, 90.5% PP	1
	PP-co-PE, 72.6% PP	1
Isotactic polypropylene 2	1	
EP Ethylene-propylene-rubbers	EPDM1, DCPD	1
	EPDM2, DCPD	1
	EPDM3, DCPD	1
	EPDM4, DCPD	1
	EPDM5, ENB, FR	1
	EPDM6, DCPD	1
	EPDM7, DCPD	1
	EPDM8, ENB, FR	1
	EPDM9	1
	EPDM10, ENB, FR	1
NR Nitrile rubber mixtures with chloroprene rubber	NBR	2
	NBR+CR, 80%+20%	2
	NBR+CR, 60%+40%	2
	NBR+CR, 40%+60%	2
	NBR+CR, 20%+80%	2
Other polymeric materials	Cotton	2
	Cotton, FR	2
	Polyamide 66	2
	Poly(methyl methacrylate)	2
	Chloropren rubber	2
	Polyformaldehyde	2
	Cellulose	1
	ABS	2
	Poly(phenylene oxide)	1
	Polyurethane	1
	PVC	2
Poly(ethylene terephthalate)	1	

^a ABS, acrylonitrile/butadiene/styrene; CR, chloroprene rubber; DCPD, contains dicyclopentadiene as cross-linking comonomer; ENB, contains ethylenenorbornene as cross-linking monomer; FR, contains flame retardant additive; M_p , molecular weight at peak determined by size exclusion chromatography; NBR+CR, a blend of NBR and CR; NBR, nitrile rubber; PP/PE, copolymer of polypropylene and polyethylene; PVC, poly(vinyl chloride); X, cross-linked.

4. Calculations

The data treatment is presented as a flow diagram in Fig. 1. MATLAB[®] and a data analysis toolbox by PROF-MATH. Inc. [8] were used for calculations throughout.

At first, the retention time of raw data matrices was converted to Briggsian logarithm of time. Time intervals of the signal were integrated to get 50 points at equal intervals on the logarithmic scale. The edges of the intervals were determined by interpolation. In the procedure, the number of points on the time scale was compressed by a factor of 1/3, partly by cutting areas without signal (low temperature) and partly by integration on the newly divided scale mentioned above. The effect of this conversion resembles that of changing from isothermal to temperature programmed

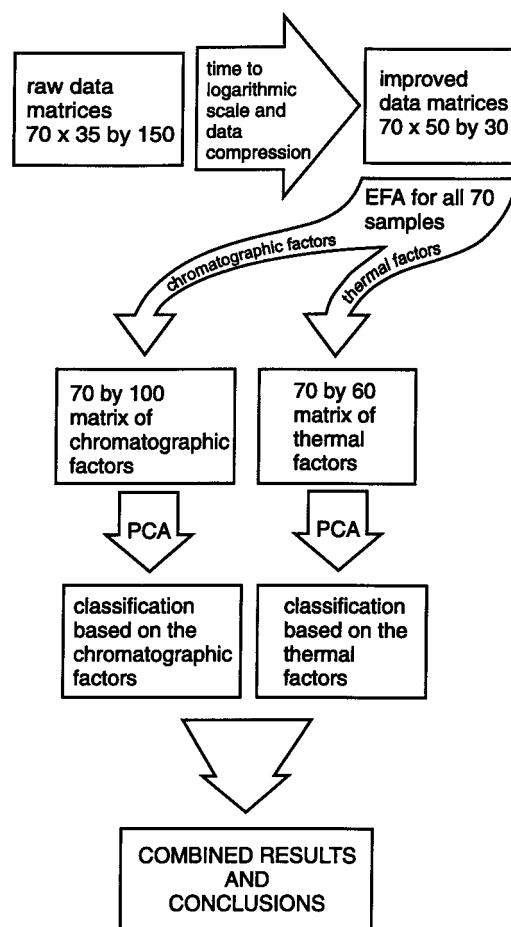


Fig. 1. Flow diagram of the data analysis.

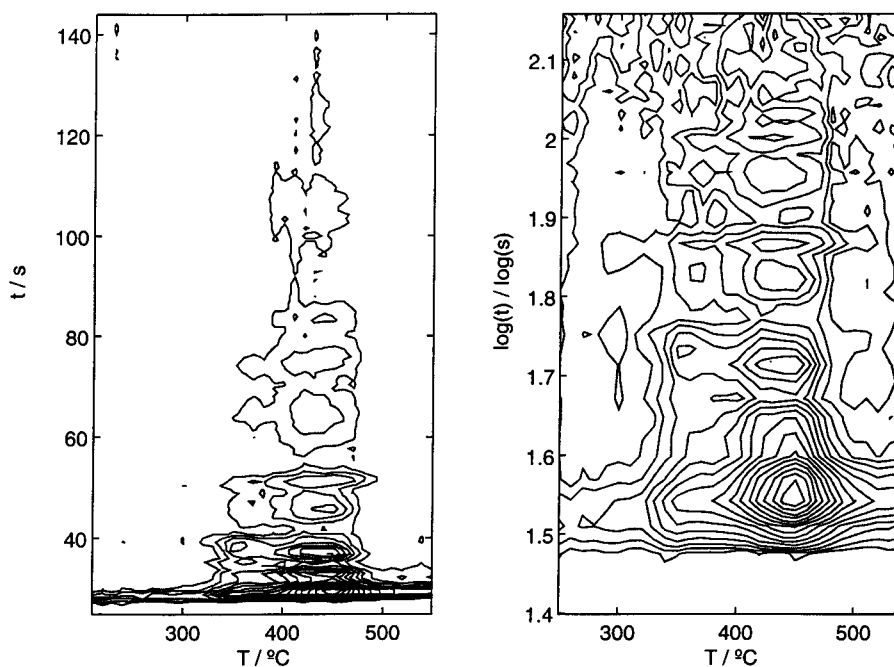


Fig. 2. Conversion of data to logarithmic time scale: Contour plots of a ThGC data matrix before (left) and after (right) the conversion.

mode in gas chromatography (Fig. 2). The peaks of low-boiling components spread and those of high-boiling components narrowed down. The conversion increased the mean variance of the chromatographic signal on an average by 25%.

Secondly, each sample (time by temperature) matrix was decomposed using EFA. In most cases a rank of two was sufficient leading to the coefficient of determination of over 99%. However, in the cases of samples highly loaded with an additive, a rank of three was used in EFA. Two thermal and two chromatographic factors were selected based on the temperature factors so that the first of them was connected to the process starting at the lower temperature and the second starting at the higher temperature, and the possibly needed third factor presenting the decomposition of the additive was rejected. Examples of the selected factors are presented in Figs. 3 and 4. Two matrixes were produced for classification of the samples, viz. ‘thermal matrix’ (70 by 60) collected from the two successive thermal factors of each of the 70 samples and ‘chromatographic matrix’ (70 by 100) collected from the chromatographic factors correspondingly.

The clustering of samples in PCA was tested by defining ellipsoids which include the samples with given 95% confidence region based on multidimensional Gaussian distributions. The functions *repres* and *classi* of the data analysis toolbox were used for this purpose.

5. Results and discussion

Clustering of different materials by PCA of both of the ‘thermal matrix’ and the ‘chromatographic matrix’ was quite clear and is shown in Figs. 5 and 6, respectively. As described in the experimental part, there were five groups of polymers and nine other polymeric materials in the data set. The cumulative percentage coefficient of determination from the PCAs of the ‘thermal’ and ‘chromatographic’ matrixes is shown in Table 2.

The clustering seen in Figs. 5 and 6, appears to be related to the thermal decomposition characteristics of the polymeric materials under investigation. The first ‘thermal’ factor is connected to the thermal stability of the material. At the lowest temperatures degrading

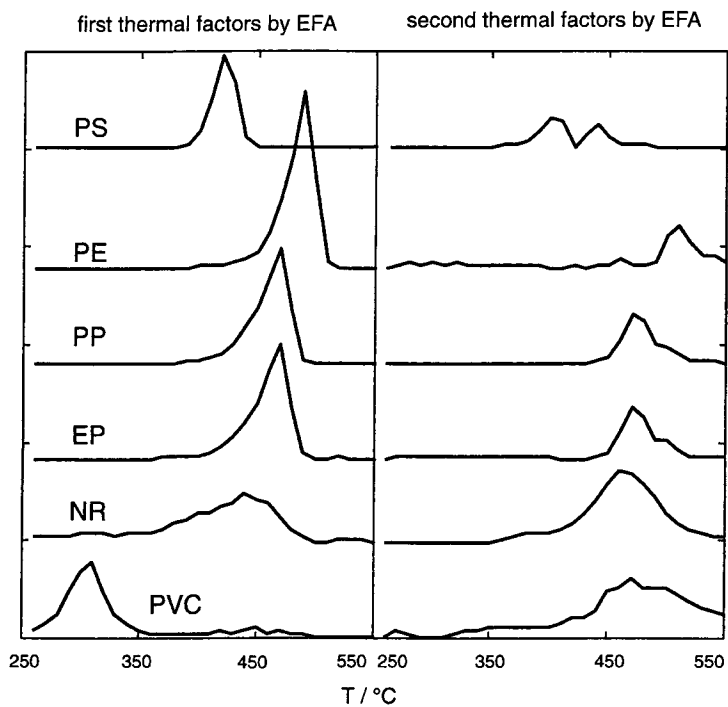


Fig. 3. Examples of typical ‘thermal’ vectors from EFA for all groups of the samples (abbreviations given in Section 2).

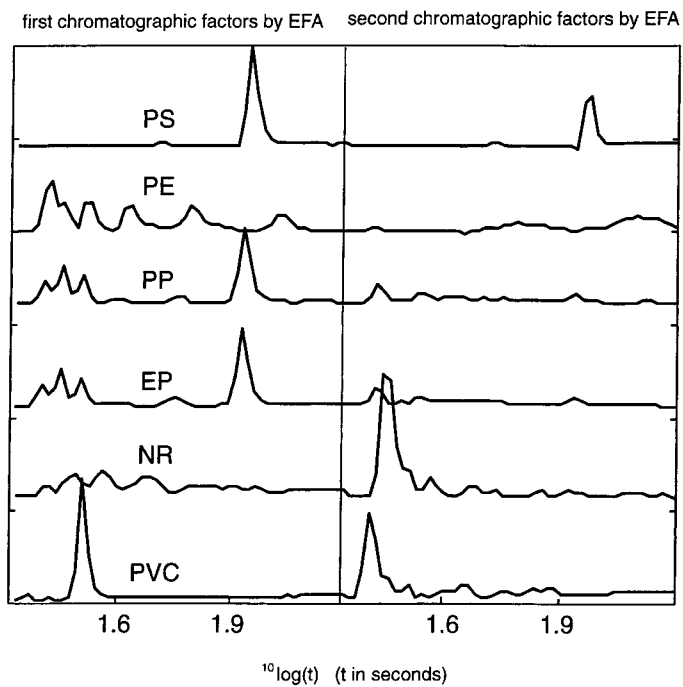


Fig. 4. Examples of typical ‘chromatographic’ vectors from EFA for all groups of the samples (abbreviations given in Section 2).

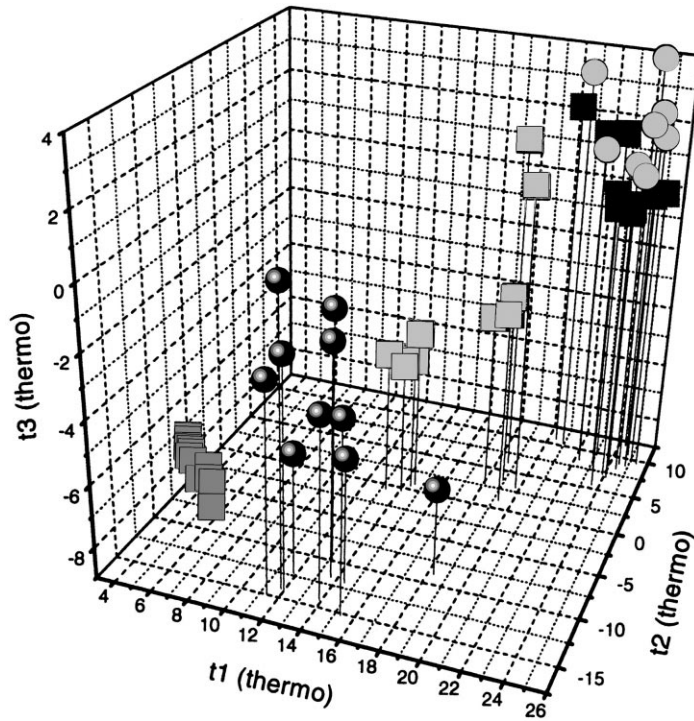


Fig. 5. Three dimensional presentation of the clustering based on the 'thermal' factors. Groups from left to right: polystyrene, nitrile rubber, polypropylene, polyethylene (black squares), ethylene-propylene rubber (gray spheres).

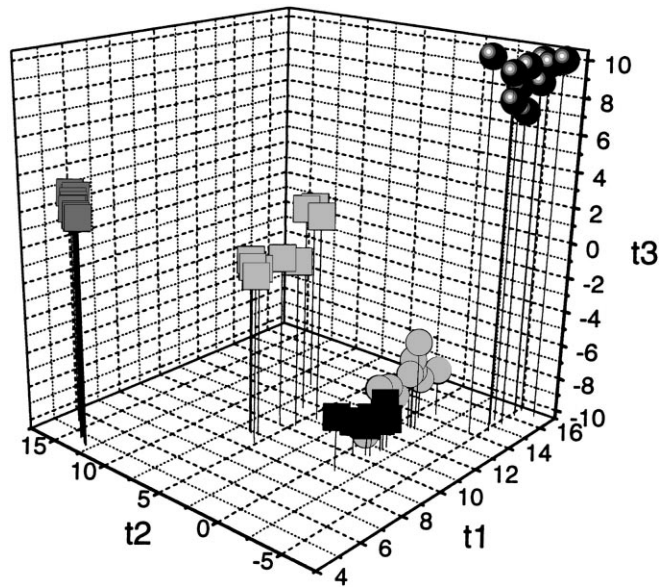


Fig. 6. Three-dimensional presentation of the clustering based on PCA on the 'chromatographic' factors. Groups from left to right: polystyrene, polypropylene, polyethylene (black squares), ethylene-propylene rubber (gray spheres), nitrile rubber.

Table 2
Coefficient of determination of the ‘thermal matrix’ and the ‘chromatographic matrix’ from PCA

Rank	Coefficient of determination	
	‘Thermal matrix’	‘Chromatographic matrix’
1	49.8	41.1
2	70.2	57.2
3	78.7	69.5
4	84.5	74.4
5	88.6	78.7
6	91.10	82.5
7	93.0	86.0
8	94.5	88.6
9	95.6	90.6
10	96.4	92.6
11	97.1	94.0
12	97.6	95.0
13	98.1	95.9
14	98.4	96.0
15	98.6	97.0

samples are on the left (low scores) and more stable materials on the right (high scores). Polystyrenes form a very tight cluster (Fig. 6) which is due to the simple chromatographic decomposition pattern consisting mostly of monomer. Similarly all polymers producing some characteristic monomer or oligomer peaks proved to be very easy to classify to their own groups. Ethylene-propylene rubbers instead are rather similar to polyethylene and their clusters are very near each other.

If the data is sufficient for classification of these materials they should be situated far enough from each other in the vector space so that their clusters do not overlap. In Table 3 is presented how well the clusters

separate when six dimensions are used in the classification. The reason for using a rank as high as six was the large number of different polymeric materials analyzed. There may occur two kinds of errors in the classification. Error of the first type is that a sample is not classified to its own group. Error of the second type occurs when a wrong type of sample is classified into a group. The first type of error was not detected in this case and only very small amounts of errors of type two were seen.

There are many methods of chemometrics available for the decomposition of bilinear matrixes like those in ThGC. EFA was selected here for simplicity. Taking always two factors from each sample means some loss of ‘the reality’ of the solutions. For instance, polystyrene decomposes at a certain temperature interval producing monomer with some minor components, and the second ‘chromatographic’ factor present mostly the noise part which is due to a chromatographic peak shift. This kind of noise appears as a double peak on the second ‘thermal’ score vector (see Fig. 3, uppermost line on the right side). In the case of PVC, two clearly different steps of thermal decomposition at different temperatures forming different products can be seen (Figs. 3 and 4). In some of the cases, for instance in the cases of some rubber blends with additives, at least three separate decomposition steps gave a more realistic figure of the process. However, by taking from each ThGC matrix two ‘thermal’ and two ‘chromatographic’ factors make it possible to treat the data of each sample similarly; furthermore, this actually was important for the clustering analysis based on different polymers in the samples. A more careful analysis inside the groups is possible and would give more information about the

Table 3
Classification of the samples using ellipsoidal representation of the groups

Group	‘Chromatographic matrix’			‘Thermal matrix’	
	No. of group members	Sample to correct group (%)	Other samples (error of second type, %)	Sample to correct group (%)	Other samples (error of second type, %)
PS	13	100	0	100	0
PE	8	100	0	100	0
PP	9	100	0	100	0
EP	10	100	5	100	2
NR	10	100	2	100	2

difference inside the groups and between the individual samples.

Further, it would be natural to try to replace the EFA-PCA by some trilinear decomposition method, such as Procrustes, Parafac, Tucker or N-way PLS regression. Thereby, the possible rotation problems between the samples' two-factor solutions may be reduced [9–13].

6. Conclusions

The data collected by ThGC is very rich in information. Despite the fact that the sample collection included rubber mixtures and plastics having high loads of additives, all the polymers (main constituents) were classified correctly. EFA and PCA combined with ThGC prove to be very useful in the analysis of polymers and could also be used for quality control of complex polymeric materials. However, trilinear decomposition methods should also be applied in the further analysis of thermochromatographic data.

References

- [1] M. Kaljurand, E. Küllik, Computerized Multiple Input Chromatography, Ellis Horwood, Chichester, UK, 1989, pp. 162–186.
- [2] M. Koel, M. Kaljurand, Crit. Rev. Anal. Chem. 26 (1996) 149.
- [3] C.H. Lochmüller, S.J. Breiner, M. Koel, M. Elomaa, Anal. Chem. 63 (1991) 1685.
- [4] M. Elomaa, C.H. Lochmüller, M. Kaljurand, M. Koel, Chemomet. Intell. Lab. Syst. 30 (1995) 129.
- [5] M. Elomaa, M. Kaljurand, M. Koel, M. Kudrjashova, Thermochm. Acta 336 (1999) 73.
- [6] R. Tauler, A. Smilde, B. Kowalski, J. Chemomet. 9 (1995) 31.
- [7] D.R. Deans, J. Chromatogr. 289 (1984) 43.
- [8] H. Haario, V.-M. Taavitsainen, Data Analysis Toolbox, PROFMATH Oy, Helsinki, 1996.
- [9] R. Bro, Chemomet. Intell. Lab. Syst. 38 (1997) 149.
- [10] R. Bro, J.J. Workman Jr., P.R. Mobley, B.R. Kowalski, Appl. Spectrosc. Rev. 32 (1997) 237.
- [11] P.K. Hopke, P. Paatero, H. Jia, R.T. Ross, R.A. Harshman, Chemomet. Intell. Lab. Syst. 43 (1998) 25.
- [12] R. Henrion, C.A. Andersson, Chemomet. Intell. Lab. Syst. 47 (1999) 189.
- [13] C. Demir, P. Hindmarch, R.G. Brereton, Analyst 121 (1996) 1443.