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CHEMOMETRIC METHODS IN PROCESSING THERMOCHROMATOGRAPHIC DATA

Kaire IVASK

Eesti Teaduste Akadeemia Keemia Instituut (Institute of Chemistry, Estonian Academy of Sciences), Akadeemia tee 15, EE-0026 Tallinn, Eesti (Estonia)

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Abstract. Thermochromatography of a series of rubber blends was performed. Three-dimensional thermochromatographic data were analysed by using chemometric methods.

The method of principal component analysis (PCA) used in this study is appropriate for finding the minimum number of factors needed to describe the obtained data. PCA gave a result that the shape of the thermochromatogram was mostly describable using two factors. This means that the decomposition of rubber blends proceeded as two independent processes.

Key words: thermochromatography, principal component analysis.

INTRODUCTION

Thermochromatography is an original method in thermal analysis, in which the substance analysed is heated according to a linear temperature program and the volatilized products are analysed [1] applying gas chromatography.

As the same sample is analysed at several different temperatures, the result is a series of chromatograms formed after equal time periods. This kind of data presentation gives a good survey of the thermal behaviour of the substance over the temperature interval applied. Changes in the quantity of the volatilized products can be easily registrated and, at the same time, the second dimension of the thermochromatogram gives a possibility to identify reaction products. This kind of presentation is called a mesh plot (Fig. 1).

An irreplaceable component of the thermochromatographic apparatus is a computer, which in addition to controlling the experiment saves the detector signal in the computer memory. A thermochromatogram is essentially a data matrix, where the elements have the values of the detector signal [2].

For processing large data masses the methods of chemometrics are indispensable.

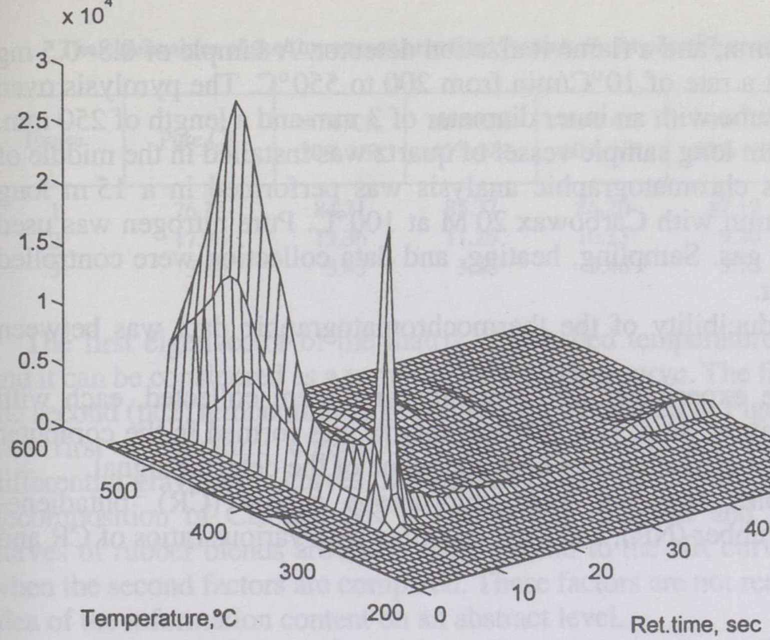

Fig. 1. Mesh plot of polychloroprene.

Elomaa used the principal component analysis (PCA) for the investigation of the thermochromatograms of different polymers [3]. He found that the decomposition of polymers proceeded as two or three independent processes. Factor analytical methods are very powerful in the analysis of complex chemical phenomena, such as pyrolysis of rubber blends [4].

Evolving factor analysis (EFA) is a general method for the analysis of multivariate data, which uses the additional information of the data matrix [5]. It has been successfully applied in different fields of chemistry, also in thermochromatographic analysis [6]. EFA helps recognize the thermal steps and elucidate which evolving compounds will dominate at those temperatures. It provides a standard procedure for the comparison of a set of thermochromatographic data. A clear separation of thermal vaporization and thermal degradation processes was obtained by Koel et al. [7].

Heuristic evolving latent projections (HELP) add some useful features in resolving multidimensional data into the pure constituents [8]. HELP is a useful method in thermochromatographic analysis making it possible to estimate the number of distinct stages in thermolysis and to establish which evolving compounds are related to these stages.

PCA and partial least square regression can perform the multivariate calibration of thermochromatographic data [9].

EXPERIMENTAL

The equipment used in thermochromatography consists of a gas chromatograph equipped with a pyrolysis oven, a sampling valve, a capillary column, and a flame ionization detector. A sample of 0.3–0.5 mg was heated at a rate of 10 °C/min from 200 to 550 °C. The pyrolysis oven was a quartz tube with an inner diameter of 3 mm and a length of 250 mm. An about 5 mm long sample vessel of quartz was installed in the middle of the tube. Gas chromatographic analysis was performed in a 15 m long capillary column with Carbowax 20 M at 100 °C. Pure nitrogen was used as the carrier gas. Sampling, heating, and data collection were controlled by a computer.

The reproducibility of the thermochromatographic data was between 10–15%.

During the experiment 37 chromatograms were collected, each with 256 digital points. So a 37×256 data matrix was formed in the computer memory. The matrix elements have the value of the detector signal.

The samples analysed were chloroprene rubber (CR), butadiene-acrylonitrile rubber (NR), and their mixtures with various ratios of CR and NR.

RESULTS AND DISCUSSION

In the case of a single thermochromatographic analysis the retention time–pyrolysis temperature pair can be considered as matrix designees. In the sense of PCA they form a property–property pair.

The data matrix is constructed with each row containing a chromatogram initiated at a certain temperature. Each column then collects the detector signal at a certain retention time over the whole temperature range.

The idea of PCA is to ascertain the important factors, actually the minimum number of factors needed to reproduce the data. In this study it is demonstrated how the data can be decomposed to temperature- and time-dependent parts by means of PCA.

There are several methods for the calculation of principal components. In this study the algorithm of singular value decomposition (SVD) was used. The SVD algorithm is a very powerful method for calculating sets of eigenvectors for the row and column spaces. The algorithm decomposes a data matrix (X) into three matrices as follows:

$$\underset{}{(X)} = \underset{37\times37}{(U)} \quad \underset{37\times256}{(S)} \quad \underset{256\times256}{(V)^{T}}$$

The data below the matrices give the matrix dimensions in the present work.

The PCA gives eigenvalues and eigenvectors, which are useful in the interpretation of the results. As three first eigenvalues formed 95% of all the eigenvalues, they were normalized to 100% (Table). The first eigenvector of the matrix V is called retention time eigenvector. It can be considered as a summarized chromatogram.

The eigenvalues of the three most principal factors, % for six different samples

Factor	Pure CR	80% CR 20% NR	60% CR 40% NR	40% CR 60% NR	20% CR 80% NR	Pure NR
1	76.38	84.21	85.37	86.20	87.12	87.52
2	17.96	12.36	11.26	10.33	9.36	7.94
3	5.66	3.43	3.38	3.46	3.52	4.54

The first eigenvector of the matrix *U* is called temperature eigenvector and it can be considered as a summarized evolving curve. The first (pc1) and the second (pc2) temperature eigenvectors are presented in Figs. 2, 3, and 4. The first temperature eigenvectors for the rubbers are comparable to differential gravimetric curves of these materials. The figures show that the decomposition of CR and NR is completely different and the evolving curves of rubber blends are much more similar to the NR curve, especially when the second factors are compared. These factors are not real but give an idea of the information content on an abstract level.

Several ideas how to convert abstract factors into real ones have been put forward. One of them is the method of Kvalheim [8]. This method gives a general projection of the first and second temperature eigenvectors on the axis (Figs. 5, 6, and 7). It presumes that the curves for pure processes can be estimated from the areas where the points are on the straight line that passes zero and further use them to deconvolute the thermochromatogram.

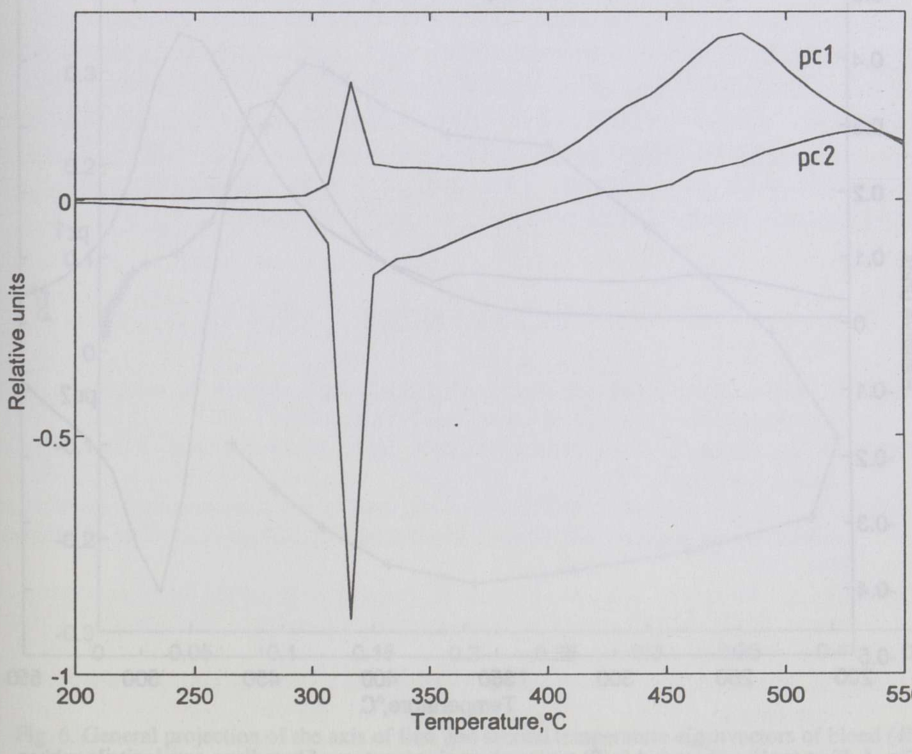

Fig. 2. First (pc1) and second (pc2) temperature eigenvectors of chloroprene rubber.

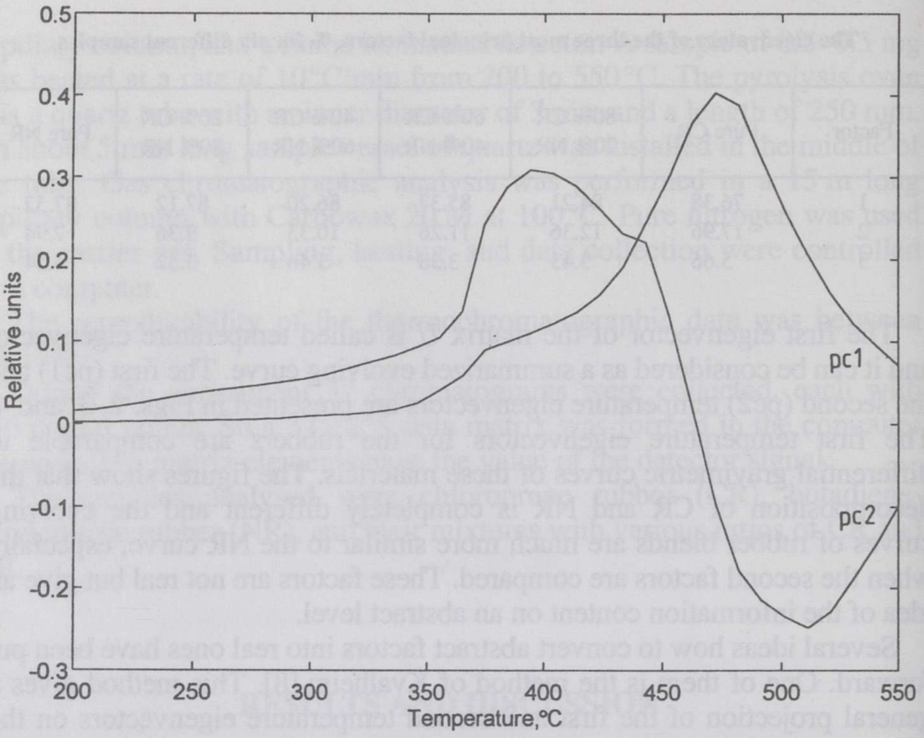

Fig. 3. First (pc1) and second (pc2) temperature eigenvectors of the butadiene-acrylonitrile and chloroprene rubber blend (40 and 60%, respectively).

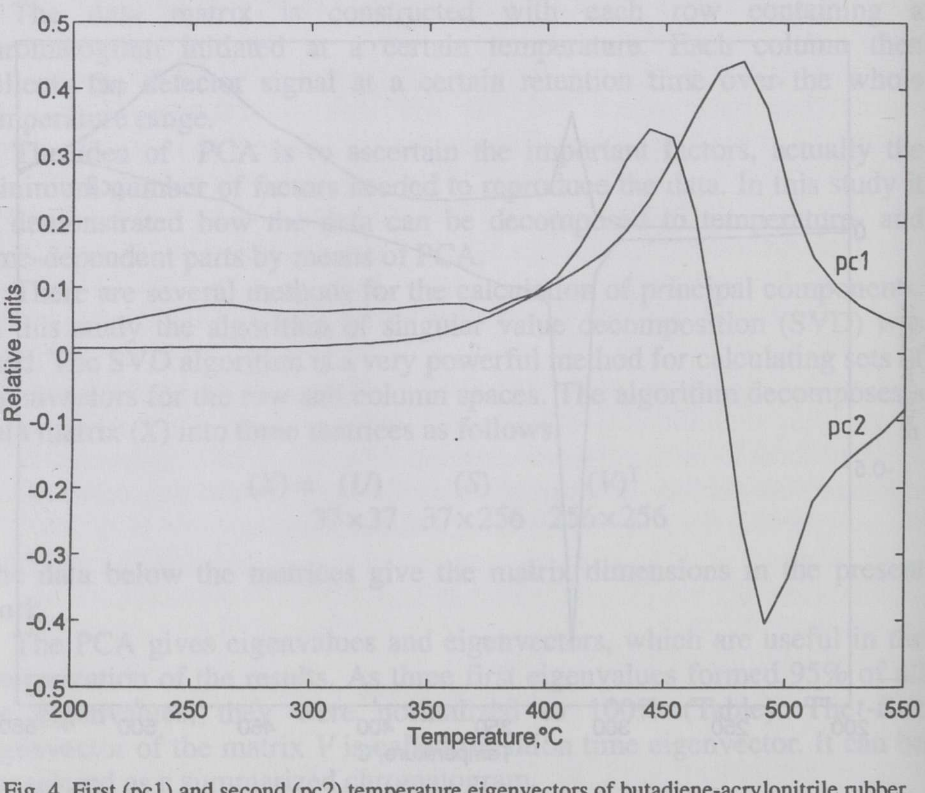

Fig. 4. First (pc1) and second (pc2) temperature eigenvectors of butadiene-acrylonitrile rubber.

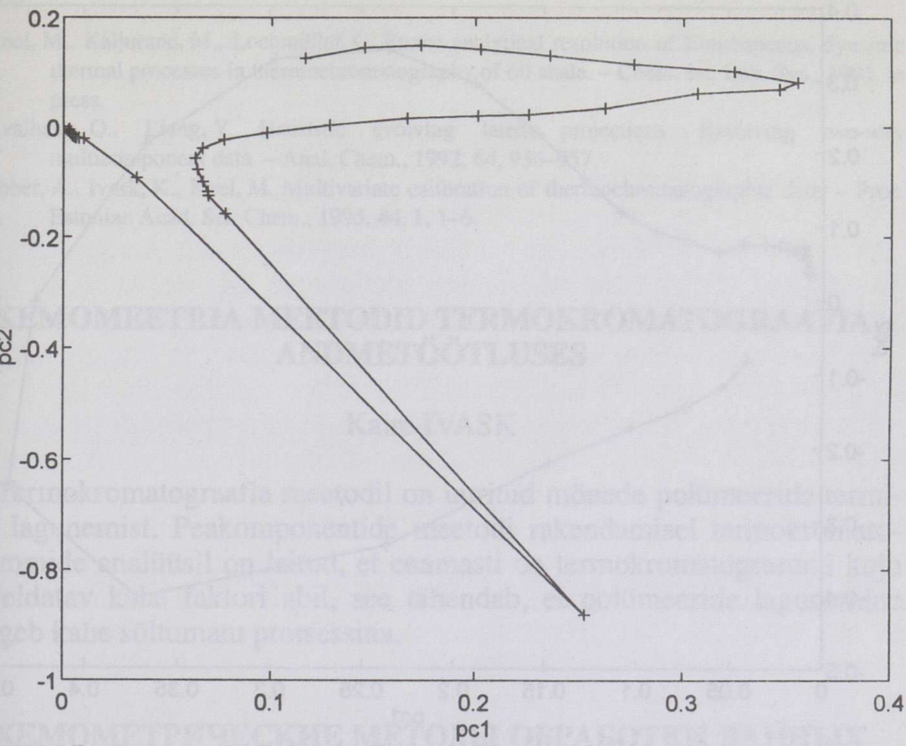

Fig. 5. General projection of the axis of first (pc1) and second (pc2) temperature eigenvectors of chloroprene rubber.

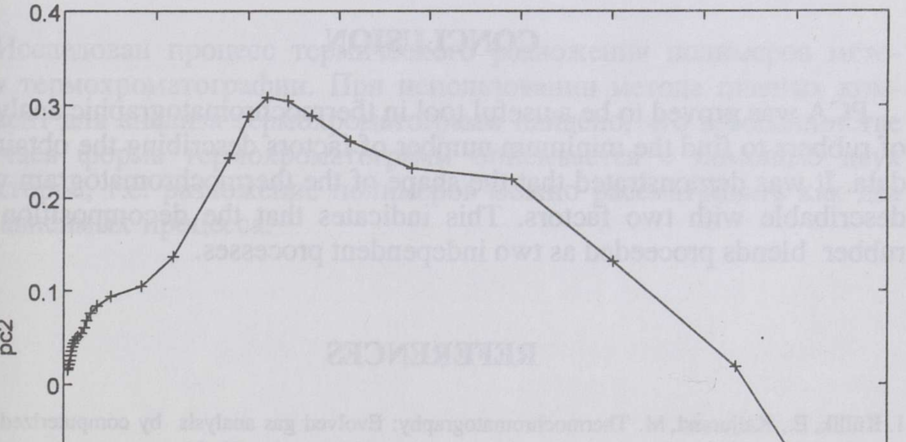

Fig. 6. General projection of the axis of first and second temperature eigenvectors of blend (40 and 60%, respectively).

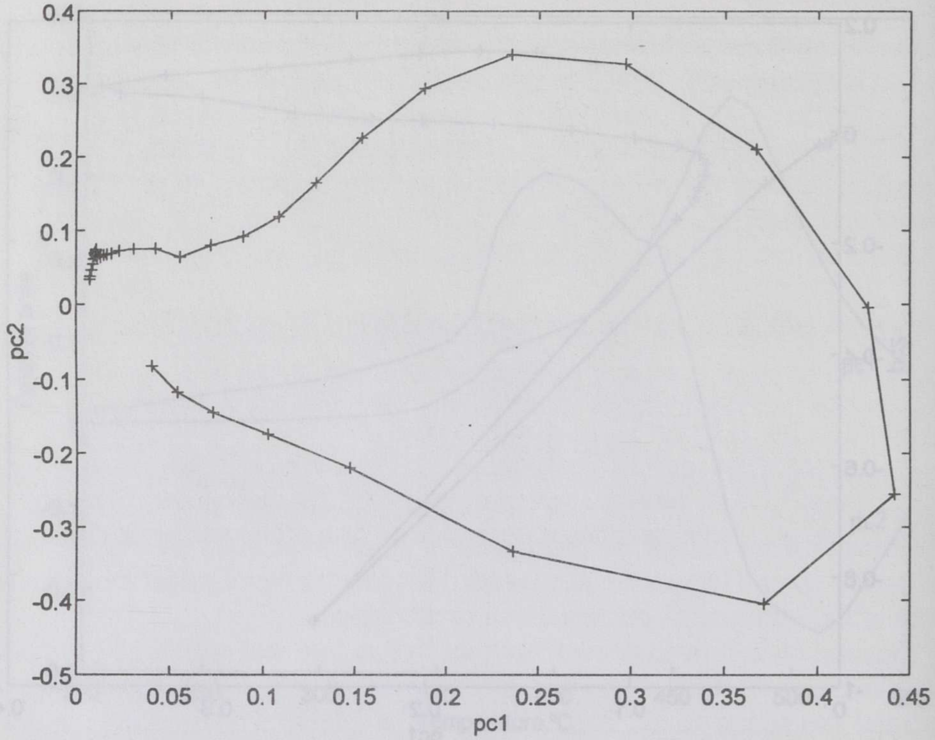

Fig. 7. General projection of the axis of first and second temperature eigenvectors of butadiene-acrylonitrile rubber.

CONCLUSION

PCA was proved to be a useful tool in thermochromatographic analysis of rubbers to find the minimum number of factors describing the obtained data. It was demonstrated that the shape of the thermochromatogram was describable with two factors. This indicates that the decomposition of rubber blends proceeded as two independent processes.

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KEMOMEETRIA MEETODID TERMOKROMATOGRAAFIA ANDMETÖÖTLUSES

Kaire IVASK

Termokromatograafia meetodil on uuritud mõnede polümeeride termilist lagunemist. Peakomponentide meetodi rakendamisel termokromatogrammide analüüsil on leitud, et enamasti on termokromatogrammi kuju kirjeldatav kahe faktori abil, see tähendab, et polümeeride lagunemine kulgeb kahe sõltumatu protsessina.

ХЕМОМЕТРИЧЕСКИЕ МЕТОДЫ ОБРАБОТКИ ДАННЫХ ТЕРМОХРОМАТОГРАФИИ

Кайре ИВАСК

Исследован процесс термического разложения полимеров методом термохроматографии. При использовании метода главных компонент для анализа термохроматограмм найдено, что в большинстве случаев форма термохроматограмм описывается с помощью двух факторов, т.е. разложение полимеров можно рассматривать как два независимых процесса.