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Chemometrics on thermochromatography of inorganic salts: decomposition of thermochromatograms to chromatograms and thermograms using EFA and peak shape constraints

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Abstract

A low volume thermal furnace, interfaced to a capillary gas chromatograph (GC) via a computer controlled, pneumatic sample inlet device, permits temperature resolved high speed GC analysis of the evolved components. The method is called thermochromatography (ThGC). The results of such an evolved gas analysis (EGA) can be conveniently represented as a thermochromatogram: a two-way detector response surface in the axes of sample temperature and chromatographic retention time. It is demonstrated that such thermochromatograms, if subjected to the specific chemometrics analysis — evolving factor analysis (EFA) — provide information about independent thermal processes that happened during the sample heating. The data is decomposed to matrixes of chromatograms and thermal evolution curves, thermograms, in a manner which connects each thermal decomposition step to the products evolved at that temperature region. Chromatographic peak shapes of the evolved gases are used as additional constraints in the analysis. The EFA performance is evaluated by ThGC of several inorganic salts and apatites. As a reference to EFA the direct deconvolution of thermochromatograms to the gas chromatograms and temperature dependent thermograms was performed. This comparison demonstrated that EFA gives confident results if essential constraints of non-negativity to chromatograms and thermograms have been applied. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Inorganic salts; Thermochromatography; Evolving factor analysis; Thermograms

1. Introduction

Evolved gas analysis (EGA) has been used as a common name for various techniques of thermal analysis measuring the amounts of gaseous products of thermally induced reactions [1]. Various approaches, some of historical interest alone, have been proposed for the detection and identification of evolved compounds over last few decades. An ideal EGA instrument would provide a record of all the evolved compounds as a function of time and temperature. The record should be resolved both qualitatively and quantitatively. Several hyphenated techniques like thermogravimetry–mass spectrometry (TG/MS) and thermogravimetry–infrared spectrometry (TG/IR) instruments have become available [2,3].

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Even better resolution might be achieved by a TG/GC/MS/IR system [4].

Although the current instruments can continuously monitor the evolved products with scan speeds of fractions of a second, their complete capability may only be required, when the evolved gas composition is a truly complex mixture [4]. Many EGA applications — especially those for inorganic samples — have relatively simple and predictable evolved gas composition and the necessity for sophisticated spectrometric identification tools is not justifiable. Besides the high cost per sample such approaches raise several technical problems associated with the furnace volume, connecting lines, automatic injection and detection. In practice many goals of EGA can be approached by using relatively simple and economical equipment. The method has a long history and little progress seems to have been made since the first attempts in 1960s. Even in the latest systems the approach is rather straightforward e.g. like in reference [5] where gas outlet from a common thermograph was connected to a manually operated mechanical sampling valve and packed column GC.

It was recently demonstrated that most of EGA problems can be easily solved by interfacing a small volume thermal reactor to a common capillary gas chromatograph via a computer controlled pneumatic sampling valve [6]. Such a sampler operates on the principle of the careful balancing of the pressures between the evolved gas flow and the carrier gas flow. The principle was first described by Deans [7]. A possible construction of such sampler for EGA is also described by Arnold et al. [8]. In this work thermal decomposition reactions are analyzed by computerized sampling of gases evolving from a gradually heated sample by rapid isothermal gas chromatography. By analogy with the other hyphenated analytical techniques and due to the names of the axis of the measured two way data, it is convenient to call this EGA method thermochromatography (ThGC) and the corresponding three-dimensional data as thermochromatograms. The 'information content' of this inherently simpler and cheaper device is often comparable with that of TG/GC/MS and TG/GC/IR.

The separation of total thermochromatograms into components which correspond to individual processes is of obvious use in thermal analysis and can be accomplished using a chemometrics technique known as factor analysis. It considers a thermochromatogram as a mathematical object — matrix — and it determines a rank of this matrix as well as abstract factors and factor loadings by the standard mathematical procedure: singular value decomposition (svd). Considering further a thermochromatogram as a bilinear object [9] it is assumed at first that the rank of the thermochromatogram matrix is equal to the number of independent thermal processes in the sample [10,11]. Then, using several chemically appropriate assumptions the abstract factors and factor loadings can be transformed to real EGA curves, thermograms, of the individual components released during the heating of the sample. The determination of the real ThGC matrix rank relies completely on the interpretation of the user in spite of the fact that the first action — svd — is a straightforward mathematical procedure. Moreover, finding EGA curves suffers from the subjectivity of the researcher in making assumptions and interpreting thermochromatograms. This is due to the rotational ambiguity of the process of the finding of the genuine thermograms because, strictly speaking, an infinite number of solutions can be found. Thus, chemometrics can help a lot in data interpretation but it does not provide an automatic answer and conclusions should be made by the researcher himself. Recent developments of the chemometrics data processing have provided a procedure known as evolving factor analysis [12] (EFA — do not confuse with EGA!) which greatly facilitates removing of the rotational ambiguity and in many cases results in a unique solution. This is achieved by using proper and essential pre-information about the appearance of the thermograms and the chromatograms in the form of constraints.

In this paper we would like to give a straightforward proof that the number of independent thermal processes is indeed equal to the thermochromatogram rank by demonstrating that a thermochromatogram can be factorised to a product of two matrices: a chromatogram matrix and a thermogram matrix. Both matrices have a number of columns which are equal to the number of thermal processes. Further, it is demonstrated that due to the relatively simple form of several thermochromatograms of inorganic salts, a chromatogram shape matrix can be built in a straightforward way which enables one to remove the rotational ambiguity completely. This fact makes it possible to build reference data against which the performance of the EFA procedure can be evaluated.

2. Theoretical

2.1. Representation of thermochromatogram as matrix

Assume that gases evolved during heating are generated by n independent thermal reactions each generating a total amount of gas as a function of the temperatures T used as follows: $c_1(T), c_2(T), \ldots c_n(T)$. A normalized chromatogram shape of evolved compounds can be associated with each process as a function of time, t, as follows $h_1(t)$, $h_2(t)$, $\ldots$ $h_n(t)$.

Let us assume further that the reaction media has been sampled with a temperature interval ΔT. Then the following set of chromatograms can be recorded at sampling temperatures T_1, T_2, $\ldots$ T_p, where $T_i - T_{i-1} = \Delta T$ and p sample introductions have been performed

$$\begin{array}{l} d_1(t) = c_1(T_1)h_1(t) + c_2(T_1)h_2(t) + \ldots + c_n(T_1)h_n(t) \\ d_2(t) = c_1(T_2)h_1(t) + c_2(T_2)h_2(t) + \ldots + c_n(T_2)h_n(t) \\ \hline d_p(t) = c_1(T_p)h_1(t) + c_2(T_p)h_2(t) + \ldots + c_n(T_p)h_n(t) \end{array} \quad (1)$$

If a common computerized chromatogram recording is performed then each of the chromatograms d_i is digitized to q points to form a chromatogram vector as follows: $d_i(t_1), d_i(t), \ldots, d_i(t_q)$ where $t_{i+1} - t_i = \Delta t$ is a digitation interval and the whole thermochromatogram is recorded as a data table $\boldsymbol{D}$ then — according to the well known matrix multiplication definition — it follows from the set of Eq. (1) that it, can be written as a matrix multiplication of the concentration functions, thermograms, and chromatograms as follows

$$\boldsymbol{D} = \begin{bmatrix} c_1(T_1) & c_2(T_1) & \ldots & c_n(T_1) \\ c_1(T_2) & c_2(T_2)c & \ldots & c_n(T_2) \\ \vdots & \vdots & \cdots & \vdots \\ c_1(T_p) & c_2(T_p) & \ldots & c_n(T_p) \end{bmatrix} \times \begin{bmatrix} h_1(t_1) & h_1(t_2) & \ldots & h_1(t_q) \\ h_2(t_1) & h_2(t_2) & \ldots & h_2(t_q) \\ \cdots & \cdots & \cdots & \cdots \\ h_n(t_1) & h_n(t_2) & \ldots & h_n(t_q) \end{bmatrix}$$

or simply

$$\boldsymbol{D} = \boldsymbol{c}\boldsymbol{h}^{\mathrm{T}} \quad (2)$$

where superscript $^{\mathrm{T}}$ means transpose. It follows from matrix algebra [13] that the rank of a product of two matrices can not be larger than the smallest rank of factor matrices which in our case is n. This proves our statement that rank of the thermochromatogram matrix determines the number of independent thermal processes that occour in the sample during the heating.

The aim of the chemometrics data processing is to find n and both $\boldsymbol{c}$ and $\boldsymbol{h}$ matrices from experimentally recorded data matrix $\boldsymbol{D}$. In finding n linear algebra provides an easy solution of the rank problem via singular value decomposition procedure [14] which decomposes $\boldsymbol{D}$ into a product of three matrices as follows $\boldsymbol{D} = \boldsymbol{u}\boldsymbol{\Lambda}\boldsymbol{v}^{\mathrm{T}}$ where $\boldsymbol{u}$ is a $p \times p$ matrix, $\boldsymbol{v}$ is a $q \times q$ matrix and $\boldsymbol{\Lambda}$ is a $p \times q$ diagonal matrix with n non-zero elements on diagonal. Those elements are called matrix $\boldsymbol{D}$ singular values. Although, due to experimental noise, matrix $\boldsymbol{D}$ has a full rank equal to p, however, frequently n dominant singular values can be determined and other diagonal elements can be set to zero. Thus by singular value decomposition procedure $\boldsymbol{D}$ can be decomposed to a product of two matrices as follows $\boldsymbol{D} = (\boldsymbol{u}\boldsymbol{\Lambda})\boldsymbol{v}^{\mathrm{T}}$. However, those factors have no chemical meaning and can be considered as abstract thermograms and abstract chromatogram shapes. The whole procedure is known as abstract factor analysis [15]. On the other hand, since $\boldsymbol{D} = \boldsymbol{c}\boldsymbol{h}^{\mathrm{T}}$ there must exist an orthogonal transform matrix $\boldsymbol{R}$ such that $\boldsymbol{c}\boldsymbol{h}^{\mathrm{T}} = (\boldsymbol{u}\boldsymbol{\Lambda})\boldsymbol{R}\boldsymbol{R}^{\mathrm{T}}\boldsymbol{v}^{\mathrm{T}}$ and EGA thermograms and chromatogram shapes can be calculated as follows:

$$\boldsymbol{c} = (\boldsymbol{u}\boldsymbol{\Lambda})\boldsymbol{R} \qquad \boldsymbol{h} = \boldsymbol{R}\boldsymbol{v} \quad (3)$$

Representation of thermochromatogram data matrix $\boldsymbol{D}$ deserves a few words. In ThGC the result is a set of chromatograms of the gases released at the corresponding (sampling) temperatures i.e. a particular sample temperature can be associated with each chromatogram. If the set of recorded chromatograms consists of many chromatograms with small temperature intervals between successive chromatograms, it is natural to arrange all of the chromatograms according to temperature thus forming a response surface of the evolved gases in dimensions of sample temperature and chromatographic runtime. Contemporary compu-

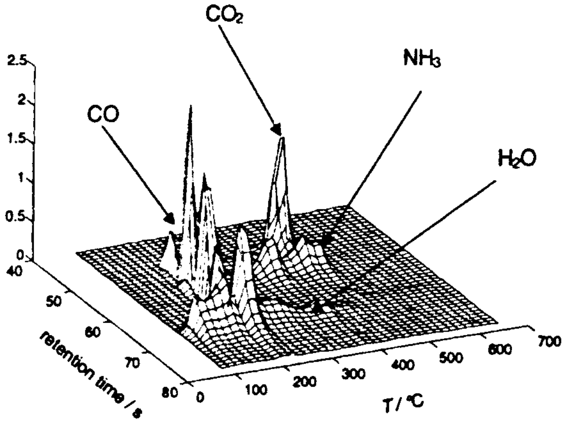

Fig. 1. Total thermochromatogram. Example of thermochromatogram of thermal decomposition products of inorganic salts as a sum of corresponding thermochromatograms of individual compounds.

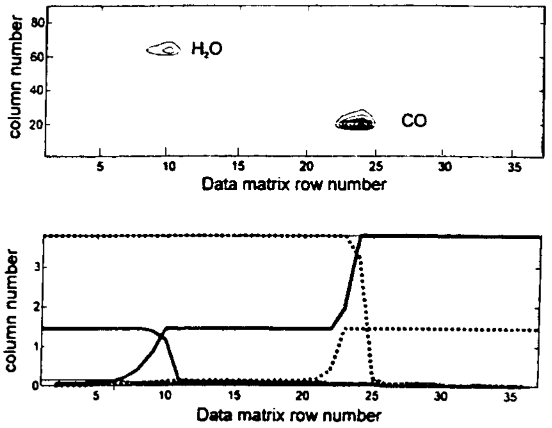

Fig. 2. Contour plot of calcium oxalate thermochromatogram (above) and evolution of singular values during evolving factor analysis of this thermochromatogram (below).

terized image processing methods enable many possibilities of representing such three-dimensional objects on a two-dimensional plane. The best known of those projections are contour and mesh plots. As a visualization of the measured data they give a convenient overview of the thermal events occurring in the sample. The evolving rates of individual released gas components, as a functions of sample temperature, may be difficult to read from such figures. However, the mesh plots of thermochromatograms have, as data matrixes, an obvious meaning as an input for chemometrics data processing. A typical thermochromatogram that is encountered in the thermal analysis of inorganic salts is represented in Fig. 1. For demonstration purposes only, it was constructed to look 'crowded' as a sum of the all individual thermochromatograms of the samples used in this study. As one can see the evolution of inorganic gases can be easily observed.

2.2. *Evolving factor analysis*

Evolving factor analysis is a procedure that first aims, to help correct determination of the number of non-zero factors and secondly, to provide a procedure for finding a unique solution of (2). EFA provides a 'cumulative' singular value decomposition of the part of the data matrix starting from the first and last row. In the next step singular value decomposition procedure is performed with the first two and the last two rows and so on going further and backwards in row numbers until all the data matrix rows are involved in the calculation. Singular values are plotted as a function of row number. In Fig. 2 such a plot is demonstrated for a simple example of thermal decomposition of calcium oxalate. The solid curves represent the growth of the first significant singular value calculated starting from the left and the second singular values calculated backwards which indicate together the first peak position for the thermograms. Similarly, the dashed curves represent the second forwards calculated evolving singular value and the first backwards calculated evolving singular value which show the position of the second thermal event. As one can see, the intersepts of corresponding forward and backward curves locate the intervals where one single process dominates. Thus, the first forward singular value plot intercepts the second backwards singular value plot around row number 10 (around 100°C) determining the region where water is detected. Second forward singular value plot crosses with the first backwards singular value plot around row number 24 (around 450°C) determining the carbon monoxide evolution temperature region. Since calcium oxalate thermal decomposition consists of well defined and separated processes, the application of EFA in this case serves as a demonstration only. If the evolution of single compounds overlap due to the overlapping of different reactions EFA becomes a powerful deconvolution tool.

3. Experimental

3.1. Furnace, sampler and chromatograph

A thorough description of the experimental set up is given in [6] and only a brief description is given here. The ThGC apparatus consists of a small, about 4 ml by volume, quartz tube furnace where the sample is located, replacing the gas chromatograph injector port, and a sampling valve before the capillary column in the chromatograph oven. The reactor temperature is controlled by a separate controller to produce a linear heating program in a temperature range from 70°C to 600°C with heating rate between 1 and 25°C/min. Aliquots of evolved gas sample are introduced to a capillary column using a pneumatic sampling valve operating by balancing pressure between the sample flow and the column carrier gas flow. At the moments of injection the balance is abruptly changed between different channels of the pneumatic switch by a solenoid valve controlled by a computer. The chromatograph used in the present study was Carlo Erba 4200 GC with an NSW-Plot capillary column (HNU Nordion Oy, Finland) 0.53 mm i.d. and 25 m in length.

3.2. Sampling control, data acquisition and EFA

The sampling and data acquisition were controlled by an Apple II computer via a laboratory made interface card. The detector signal was recorded via a 23 bit analogue-to-digital converter (Ecta Ltd, Estonia) using a digitization rate of 0.5 points/s. The digital detector signal was transformed by a Pentium type PC via an RS232 interface for further processing.

Chromatogram pre-processing (base line correction, spike removal, digital filtering etc.) software was written in house in MATLAB (MathWorks, Natic, MA USA). Abstract factor analysis and EFA procedures of thermochromatograms were done using MATLAB singular value decomposition function (SVD). In the EFA calculations first forward/backward singular value plots were obtained as a function of the row number. Then deconvolution was done by an iteration procedure using three constraints. Firstly, the chromatogram shapes intensities must always be non-negative. Secondly, the thermograms must be positive in the temperature interval where the curve, composed from the corresponding two singular value plot curves is positive, and thirdly, outside these intervals the thermogram goes to zero.

3.3. Samples

These consisted of inorganic salts (Aldrich) and synthetic carbonate apatite, synthesized by the precipitation method at Tallinn Technical University, Department of General and Inorganic Chemistry. No extraordinary precautions were taken, and the samples were kept isolated from environments contaminated with organic and inorganic vapors. For the ThGC analysis, the samples were placed into a quartz vial inside the reactor. The weight of each sample was about 20 mg.

4. Results and discussion

4.1. Characterization of decomposition of inorganic salts by ThGC

Thermochromatographic characterization of inorganic salts and apatite with detailed discussion of reactions that occur during the heating of the samples are given elsewhere [6,16,17]. The main results are summarized in Table 1 below.

Once again when interpreting the data in Table 1 it should be drawn to the readers attention that only the temperature interval of 100–600°C was investigated, due to the maximum obtainable temperature of our present ThGC equipment.

4.1.1. EFA of thermochromatograms

The analysis of the data presented in Table 1 leads to the conclusion that a maximum of number of compounds that evolve is equal to four in other words that in maximum four chromatographic peaks can be expected. Corresponding chromatographic peaks can be identified in the order of increasing retention time as follows: CO (or O_2 which retention time coincides with the CO peak), CO_2, NH_3, and H_2O. The shapes of these peaks can be easily extracted from the thermochromatograms of different salts where they appear as single peaks not overlapping with the others (except the NH_3 peak shape which was found from NH_4VO_3 thermochromatogram by separation of overlapping peaks by least squares fitting

Table 1
EGA data on inorganic salts

No.	Compound	Formula	Interval (°C)	Decomposition reactions	Evolved gases
1	Calcium oxalate	$Ca(CO_2)_2{\cdot}H_2O$	145–240	$CaC_2O_4{\cdot}H_2O \Rightarrow CaC_2O_4 + H_2O\uparrow$	H_2O
			430–500	$CaC_2O_4 \Rightarrow CaCO_3 + CO\uparrow$ $2CO \Rightarrow C + CO_2\uparrow$	CO, CO_2
2	Magnesium ammonium phosphate hexahydrate	$MgNH_4PO_4{\cdot}6H_2O$	90–190	$MgNH_4PO_4{\cdot}6H_2O => MgNH_4PO_4{\cdot}H_2O + 6H_2O$	H_2O
			240–320	$MgNH_4PO_4 => MgHPO_4 + NH_3$	NH_3 H_2O
			450– 570	$2Mg\ HPO_4 => Mg_2P_2O_7 + H_2O$	H_2O
3	Magnesium carbonate hydroxide hydrate	$4MgCO_3{\cdot}Mg(OH)_2{\cdot}5H_2O$	220–335	$4MgCO_3{\cdot}Mg(OH)_2{\cdot}5H_2O \Rightarrow 4MgCO_3{\cdot}Mg(OH)_2 + H_2O\uparrow$	H_2O, CO_2
			350–450	$4MgCO_3{\cdot}Mg(OH)_2 \Rightarrow 2MgCO_3{\cdot}2MgO + H_2O\uparrow + 2CO_2\uparrow$	CO_2, H_2O
			450–550	$2MgCO_3{\cdot}2MgO \Rightarrow 4MgO + 2CO_2\uparrow$	CO_2
4	Ammonium metavanadate	NH_4VO_3	165–240	$2NH_4VO_3 \Rightarrow 2NH_3\uparrow + H_2O\uparrow + V_2O_5$	NH_3, H_2O NH_3
			280–350	$VO_3^{-} + 4NH_4^{+} \Rightarrow VO^{2+} + 4NH_3 + 2H_2O$ $VO^{2+} + 2OH^{-} \Rightarrow VO(OH)_2$ $2VO(OH)_2 \Rightarrow 2VO_2 + 2H_2O + O_2$	O_2, H_2O
5	Ammonium oxalate	$2NH_4(CO_2){\cdot}H_2O$	200–240	$NH_4(CO_2){\cdot}H_2O \Rightarrow 2NH_3\uparrow + 2H_2O\uparrow + CO\uparrow + CO_2\uparrow$	$CO, CO_2 NH_3, H_2O$
6	Syntetic apatite	$Ca_{6.38}Mg_{2.64}$ $(NH_4)_{0.94}$ $(PO_4)_{4.98}$ $(CO_3)_{0.38}$ $(HPO_4)_{0.64}$ $(OH)_{0.53}$	210–220	$2HPO_4^{2-} = P_2O_7^{4-} + H_2O$	H_2O
			275–280	$2NH_4^{+} + 2HPO_4^{2-} = 2NH_3 + H_2O + H_2P_2O_7^{2-}$	NH_3, H_2O
			365–375	$H_2P_2O_7^{2-} + 2CO_3^{2-} = 2PO_4^{3-} + 2CO_2 + H_2O$	CO_2, H_2O

procedure). Using the existing peak shapes a matrix, $\boldsymbol{h}$, of normalized peak shapes was build up. This reference matrix enabled us to find EGA thermograms of pure individual compounds by a direct least squares solution for (2) by its pseudo-inverse as follows

$$\boldsymbol{c} = \boldsymbol{D}\boldsymbol{h}(\boldsymbol{h}^{\mathrm{T}}\boldsymbol{h})^{-1} \tag{4}$$

This solution, because of rotational ambiguity, is only one of the possible solutions. Nevertheless it proved to be very useful as a reference against which the EFA results could be evaluated.

For determination of the number of independent processes which occur during the heating of the samples, the number of non-zero factors was at first taken to be formally equal to maximum possible number 4, since there are four compounds that may evolve in the given conditions. The actual possible number of independent processes was ignored. Applying Eq. (2) demonstrated that thermograms corresponding to some of the resulting chromatograms were equal to zero as it might be expected since the corresponding compounds did not evolve. In this case the number of factors was reduced. Also, some of the chromatograms corresponding to different factors coincided. Here, the number of factors was also reduced by one. The actual number of independent factors in each of the thermochromatograms is given in Table 2. It appeared to be in most cases equal to two. For comparison two 'subjective' methods of data matrix rank determination were applied, namely visual inspection of the plot of the cumulative sum of singular values for the specific jumps and another which was just the cut-off point for the same cumulative plot at the 95% level (95% cumulative percent variance). More sophisticated methods are known [18] (which as we believe) are more or less as subjective as those simple methods we used.

Table 2 shows that the noise real thermochromatograms obviously generate an increased number of significant factors, and both the '95%' criteria or just investigation of a singular value cumulative sum plot for characteristic line breaks results in rather formal and unrealistically big number of significant factors. Only the calcium oxalate results are more or less straightforward and unambiguous because of the extremely well separated processes which occur during its thermal decomposition. On the other hand, EFA together with the scrutiny of the resulting chromatogram shapes and EGA curves gives much smaller numbers. In turn, this illustrates once again the subjectivity of the factor rotation procedure, the result of which is completely subject to human judgments and decision. In this case the final conclusion relies not only on the formal numerical evaluation of the EFA plots but also on the inspection of chromatogram shapes and corresponding thermogram curves in respect to their correspondence to what is considered a 'normal' chromatogram.

The results are represented in Figs. 3–8. The peak shapes of individual compounds are represented in the lower left part of all these figures. They are the same for all samples in all the figures. The thermograms calculated using (3) are represented in the lower right part. This set of chromatograms and thermograms is referred to as 'REF'. In the upper left part the shapes found by EFA are represented and in the upper right part the thermograms found by EFA are represented. This set of chromatograms and thermograms is referred as 'EFA'. The same number on a chromatographic peak shape and on a thermogram corresponds to one factor.

Table 2
Determination of number of significant factors

Compound	Cumsum[a]	95%[b]	% of first four factors				EFA
Calcium oxalate	2	3	0.67	0.93	0.95	0.97	2
Magnesium ammonium phosphate hexahydrate	3	10	0.63	0.74	0.88	0.91	2
Magnesium carbonate hydroxy hydrate	5	10	0.58	0.80	0.85	0.88	2
Ammonium metavanadate	5	9	0.54	0.71	0.81	0.86	2
Ammonium oxalate	4	4	0.77	0.89	0.93	0.96	2
synthetic apatite	3	25	0.65	0.76	0.82	0.85	3

[a] Number of factors determined from the singular values cumulative plot jump.

[b] Number of factors needed to describe 95% data variance.

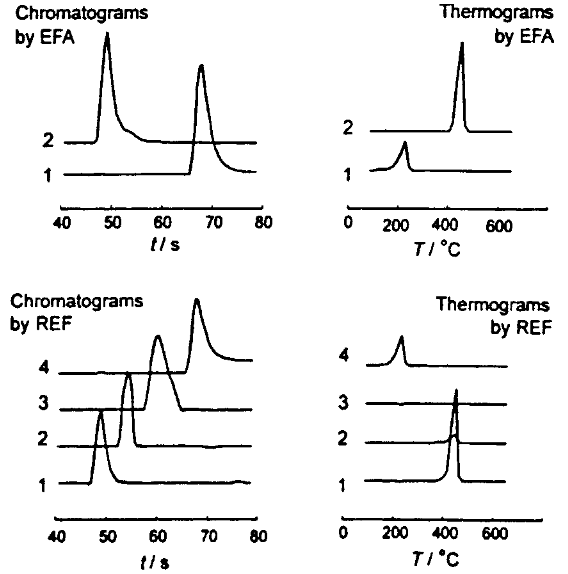

Fig. 3. EFA of thermochromatograms of calcium oxalate. Chromatogram peak shapes at ‘REF’ correspond to the following compounds: (1) CO, (2) CO_2, (3) NH_3, (4) H_2O.

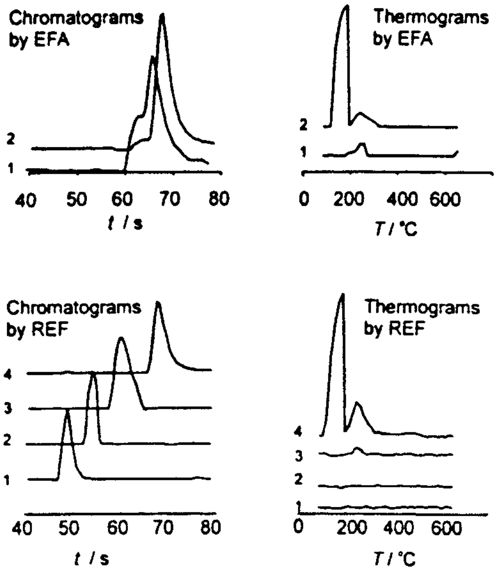

Fig. 4. EFA of thermochromatograms of magnesium ammonium phosphate hexahydrate. Chromatogram peak shapes at ‘REF’ correspond to the following compounds: (1) CO, (2) CO_2, (3) NH_3, (4) H_2O.

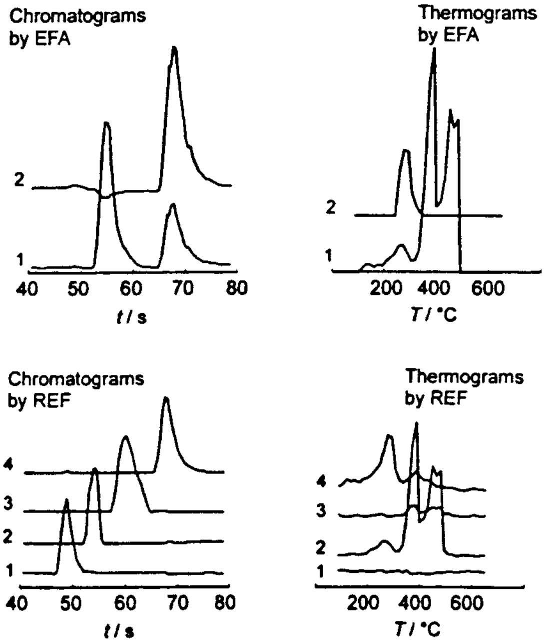

Fig. 5. EFA of thermochromatograms of magnesium carbonate hydroxy hydrate. Chromatogram peak shapes at ‘REF’ correspond to the following compounds: (1) CO, (2) CO_2, (3) NH_3, (4) H_2O.

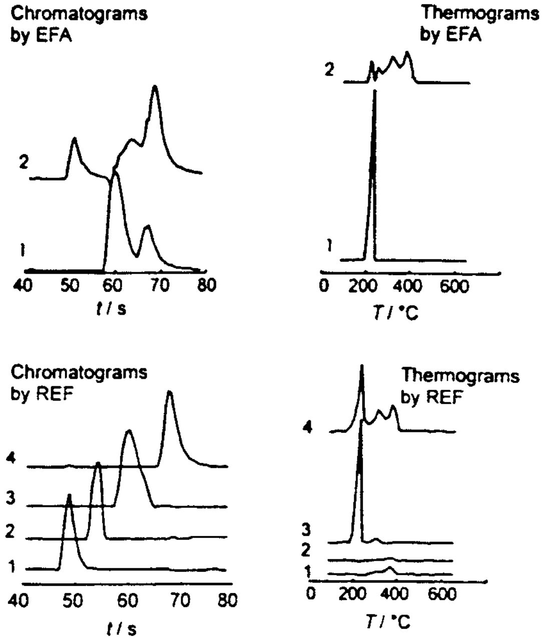

Fig. 6. EFA of thermochromatograms of ammonium metavanadate. Chromatogram peak shapes at ‘REF’ correspond to the following compounds: (1) CO, (2) CO_2, (3) NH_3, (4) H_2O.

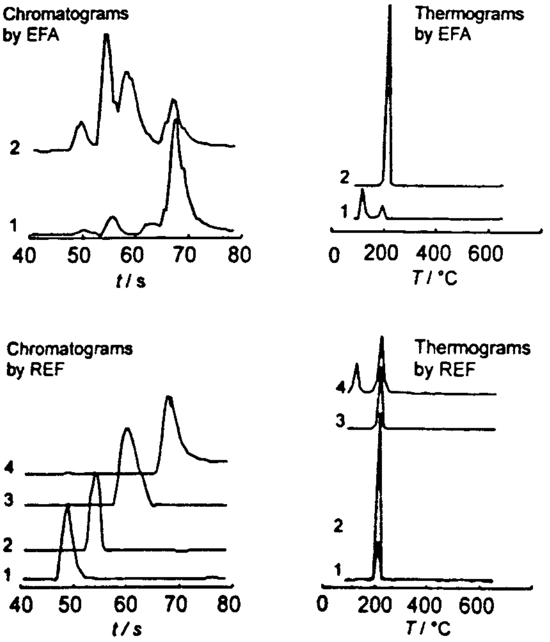

Fig. 7. EFA of thermochromatograms of ammonium oxalate. Chromatogram peak shapes at 'REF' correspond to the following compounds: (1) CO, (2) CO_2, (3) NH_3, (4) H_2O.

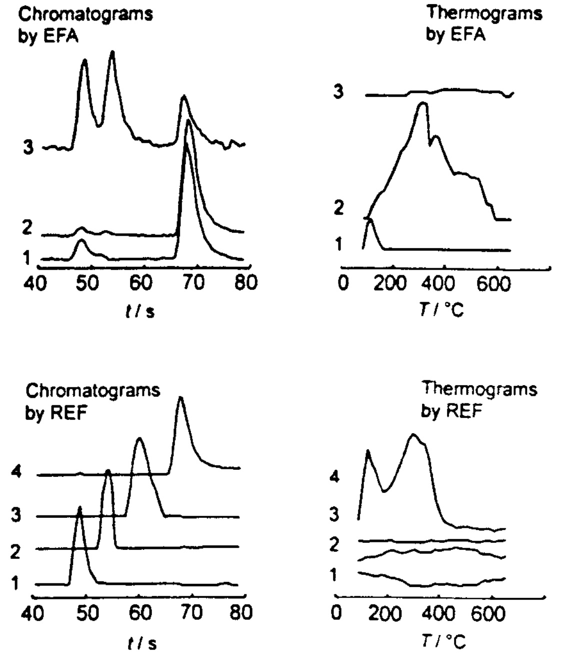

Fig. 8. EFA of thermochromatograms of synthetic apatite. Chromatogram peak shapes at 'REF' correspond to the following compounds: (1) CO, (2) CO_2, (3) NH_3, (4) H_2O.

4.1.2. Calcium oxalate

As it follows from the REF thermograms, NH_4 thermogram is trivially equal to zero in all temperature intervals as it should be since no ammonia is supposed to evolve (Fig. 3). Water evolves as a single peak according to both the REF and EFA sets. CO and CO_2 evolve simultaneously around 400°C according to the REF set. On an EFA set CO and CO_2 chromatograms merge into a single chromatogram — the main peak corresponding to CO and its shoulder corresponding to CO_2. The thermogram on EFA set found for this chromatogram shape is the sum of the CO and CO_2 thermograms found by the REF set.

4.1.3. Magnesium ammonium phosphate hexahydrate

EFA indicates two independent reactions: in both processes water is a dominating decomposition product accompanied with some extent ammonia evolution (Fig. 4). The REF curves however, indicate that the evolution of ammonia is rather insignificant.

4.1.4. Magnesium carbonate hydroxide hydrate

Two compounds — carbon dioxide and water — evolve during the heating according to a complicated pattern (Fig. 5). EFA points out that water evolves through two processes: at first, approximately at 250–300°C, as a single component (loss of crystallohydrate water) and then, in a temperature interval of 200–450°C, together with CO_2 when the thermal decomposition of magnesium carbonate basic salt ($MgCO_3 \cdot Mg(OH)$) takes place. REF curves for pure compounds essentially make no differences between different processes so EFA and REF solutions differ to some extent.

4.1.5. Ammonium metavanadate

The dominating process is the evolution of ammonia and water within narrow temperature interval around 200°C (Fig. 6). These compounds evolve also in another process at higher temperatures, but now there is a third component which was identified as oxygen [11] (like CO, it is not retarded in the GC column used in this work so its shape function was used for all calculations. As in the case of magnesium carbonate hydroxide hydrate the REF curves for pure compounds essentially make no differences between different processes so EFA and REF solutions differ to some extent.

4.1.6. Ammonium oxalate

All four compounds evolve in a narrow region around 200°C (Fig. 7). This example is a good demonstration of how the EFA solution is a sum of EGA curves of individual compounds if all compounds are released by the same process. Also the independent water evolution can be observed.

4.1.7. Synthetic apatite

This is the case of a comparatively complex example of an inorganic material for which is difficult to exactly describe the chemical reactions occurring during its heating (Fig. 8). We attempted to describe a thermochromatogram matrix by EFA using three factors. As it might be expected from the chemical structure of synthetic apatite (see Table 1), all four inorganic gases studied in this work could evolve from this sample during its thermal decomposition. Water evolution dominates and, as it follows from REF thermograms, this lost water is of different origins — adsorbed water, constitutional water and a product of reactions of thermal decomposition of apatite [16,17]. Some rudimentary evolution of other compound combinations were also recorded.

5. Discussion

Since the aim of this paper is rather a demonstration of the capabilities of EFA than an investigation of thermal behavior of the relatively simple reactions that occur during sample heating these reactions are discussed in detail elsewhere. [16,17,19]. As demonstrated by the results of EFA, the data processing method is useful for determining the possible number of reactions and deconvolution of thermochromatogram surfaces to chromatografic shapes. An important aspect of this deconvolution is that all components that participate in the corresponding reaction will generate a common single thermogram with a chromatogram which contains all the peaks (with relevant intensities) of the compounds that participate in this reaction. In contrast, using peak shapes that are determined beforehand, it is possible to obtain thermograms for each of the pure compounds evolving through different processes mixed in the results. Thus, both methods together greatly facilitate the complete understanding of the thermal decomposition processes which are going on due to heating.

Using the peak shapes for calculations requires identification of the evolved compounds. For inorganic samples the composition of evolved gases is usually simple and frequently the nature of evolved gases can be predicted beforehand. Thus, there is no necessity for broad-range spectral detectors for identification and common and cheap GC detectors (like a thermal conductivity one having response to most of the compounds) can be used instead. Due to the limited number of evolved compounds the interpretation of the chromatogram is straightforward and follows from a general understanding of the retention mechanisms of these compounds. Weight loss curves can be easily reconstructed from EGA curves (taking care that all evolved components are detected and detector responses to all components are known).

On the contrary, if the evolved gas consists of many components — e.g. in thermal decomposition analysis of polymers — then the interpretation of the chromatogram is complicated when only chromatographic means are ued. The identification of the products may be a problem. However, EFA can still be used for the analysis. EFA of thermochromatograms give two types of characteristic information for a polymer: (1) the main decomposition temperatures, (2) chromatographic patterns of the products connected to those temperatures. Careful study of those data makes it possible for a polymer chemist to classify the polymer by its type of decomposition. Perhaps, development of the empirical mathematical models (chemometrics), that relate the properties of interest of a material under study to the evolved gas patterns, would be more valuable than a simple listing of the names of hundreds of decomposition products. This fact might justify the implementation of the GC as EGA detector instead of spectral detectors in polymer analysis.

Talking about thermogravimetry of the common EGA analyses, from the present work it follows that weight loss curve reconstruction is easy using evolving rate versus temperature of digitally recorded curves. However, if quantitative conclusions must be made then EGA curves must be corrected for the detector response to individual components. Using different selective detectors adds extra flexibility of identification.

A thermochromatogram can be used as a characteristic 'fingerprint' of an object. This can then be subjected to chemometric treatment to find characteristics of interest for the studied samples. In this work it was demonstrated how abstract factor analysis of thermochromatograms as 2D objects makes it possible to determine a number of distinct thermal stages of decomposition.

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References

[1] H.H. Willard, L.L. Merritt, Jr., J.A. Dean, F.A. Settle, Jr., Instrumental Methods of Analysis, 7th ed., Wadsworth, CA 1988, p. 761.
[2] C.M. Earnest, Anal. Chem. 56 (1984) 1471A.
[3] W.J. Young, X.X. Quan, J.T. Zheng, Thermochim. Acta 111 (1987) 325.
[4] W.H. McClennen, R.M. Buchanan, N.S. Arnold, J.P. Dworzanski, H.L.C. Meuzelaar, Anal. Chem. 65 (1993) 2819.
[5] Y. Doi, T. Koda, M. Adachi, N. Wakamatsu, T. Goto, H. Kamemizu, Y. Moriwaki, Y. Suwa, J. Biomed. Mater. Res. 29 (1995) 1451.
[6] M. Koel, M. Kaljurand, C.H. Lochmüller, Anal. Chem. 69 (1997) 4586.
[7] D.R. Deans, J. Chromatogr. 289 (1987) 43.
[8] N.S. Arnold, W.H. McClennen, H.L. Meuzelaar, Anal. Chem. 63 (1991) 299.
[9] K.S. Books, B. Kowalski, Anal. Chem. 66 (1994) 782A.
[10] M. Elomaa, C.H. Lochmüller, M. Kaljurand, M. Koel, Chem. Int. Lab. Syst. 30 (1995) 129.
[11] M. Koel, M. Kaljurand, C.H. Lochmüller, M. Moebius, Chem. Int. Lab. Syst. 30 (1995) 173.
[12] M. Maeder, Anal. Chem. 59 (1987) 527.
[13] D. Zwillinger (Ed.), CRC Standard Mathematical Tables and Formulae, 30th ed., CRC Press, Boca Raton, 1996, p. 125.
[14] D. Zwillinger (Ed.), CRC Standard Mathematical Tables and Formulae, 30th ed., CRC Press, Boca Raton, 1996, p. 134.
[15] E.R. Malinowski, D.G. Howery, Factor Analysis in Chemistry, 2nd ed., Wiley, New York, 1991.
[16] M. Koel, M. Kudrjashova, K. Tõnsuaadu, M. Veiderma, J. Chromatogr. 819(1-2) (1998) 75.
[17] M. Koel, M. Kudrjashova, K. Tõnsuaadu, M. Peld, M. Veiderma, Thermochim. Acta 322(1) (1998) 25.
[18] E.R. Malinowski, D.G. Howery, Factor Analysis in Chemistry, 2nd ed., Wiley, New York, 1991, p. 110.
[19] M. Koel, Proc. Est. Acad. Sci. Chem. 46(3) (1997) 112.