

# Reduction of the rotational ambiguity of curve resolution techniques under partial knowledge of the factors. Complementarity and coupling theorems.

Mathias Sawall<sup>a</sup>, Christian Fischer<sup>b</sup>, Detlef Heller<sup>b</sup>, Klaus Neymeyr<sup>\*a</sup>

<sup>a</sup>Universität Rostock, Institut für Mathematik, Ulmenstrasse 69, 18057 Rostock, Germany

<sup>b</sup>Leibniz-Institut für Katalyse, Albert-Einstein-Strasse 29a, 18059 Rostock

---

## Abstract

Multivariate curve resolution techniques allow to uncover from a series of spectra (of a chemical reaction system) the underlying spectra of the pure components and the associated concentration profiles along the time axis. Usually a range of feasible solutions exists due to the so-called rotational ambiguity. Any additional information on the system should be utilized to reduce this ambiguity.

Sometimes the pure component spectra of certain reactants or products are known or the concentration profiles of the same or other species are available. This valuable information should be used in the computational procedure of a multivariate curve resolution technique.

The aim of this paper is to show how such supplemental information on the components can be exploited. The knowledge of spectra leads to linear restrictions on the concentration profiles of the complementary species and vice versa. Further affine linear restrictions can be applied to pairs of a concentration profile and the associated spectrum of a species. These (affine) linear constraints can also be combined with the usual non-negativity restrictions. These arguments can reduce the rotational ambiguity considerably. In special cases it is possible to determine the unknown concentration profile or the spectrum of a species only from these constraints.

*Key words:* chemometrics, factor analysis, pure component decomposition, non-negative matrix factorization, spectral recovery.

---

## 1. Introduction

The aim of a model-free pure component decomposition is to extract the pure component spectra and the associated concentration profiles from the series of spectra of the (chemical reaction) system. In the best case no additional information is used for this computational procedure; even the number of reacting species is a result.

Typically the spectroscopic data is provided on a frequency  $\times$  time grid in the form of a matrix; this data matrix is denoted by  $D$ . Due to the Lambert-Beer law a factorization of  $D$  into matrix factors  $C$  and  $A$  is desired, where  $C$  column-wise contains the concentration profiles and  $A$  row-wise contains the pure component spectra (molar extinction coefficients). As  $C$  and  $A$  are non-negative matrices, the pure component decomposition can be considered as the problem of the computation of a non-negative matrix factorization. However, this mathematical problem (aside from singular exceptional cases) turns out to have a continuum of possible

solutions. Most of these solutions do not have a chemical/physical meaning or importance and should be disregarded. These (so-called) abstract factors constitute a considerable obstacle for a fast and stable (hard) model-free pure component decomposition. There is a vast literature on these methods, see e.g. [17, 18] and the references therein.

Often some additional facts on the chemical reaction system are known. Sometimes the number of starting reactants is given and/or some of their pure component spectra are available. Further the spectra of the main products might be accessible or even those of intermediary products. All these data reduce the set of the mathematically feasible factorizations to those factorizations which are consistent with the pre-given supplemental data.

The goal of this paper is a systematic analysis of the relation between such supplemental data and the resulting constraints on the set of feasible solutions in order to extract the relevant and chemically meaningful solutions. We derive the results (in the form of a couple of

---

\* Correspondence to: K. Neymeyr, Universität Rostock, Institut für Mathematik, Ulmenstrasse 69, 18057 Rostock, Germany.

theorems) by combining the Lambert-Beer law with a singular value decomposition (SVD) of the data matrix  $D$ . To this end we apply various arguments from linear algebra to the columns of the concentration matrix  $C$  and rows of the absorption matrix  $A$ .

The paper is organized as follows. In Section 2 the problem of a pure component decomposition is introduced and classical approaches to its solution are presented. Some comments on the enclosure of the range of admissible solutions follow in Section 3. Section 4 contains the main mathematical results. These results are linear constraints on “complementary species” and also affine linear constraints coupling the spectrum and the concentration profile for particular species. All these restrictions are combined with the typical non-negativity constraints. To demonstrate the usefulness of the arguments we apply the theorems to a three-component model problem in Section 5. Further a three-component reaction system which results in the formation of hafnacyclopentene is analyzed in Section 6.

## 2. Self-modeling curve resolution

The Lambert-Beer law only holds in the absence of error sources like noise and nonlinearities. Its perturbed form reads

$$D = CA + E.$$

The data matrix  $D \in \mathbb{R}^{k \times n}$  contains in its rows  $k$  spectra (taken at different times from a chemical reaction system); each spectrum is given at  $n$  frequencies (or spectral channels). If the reaction system contains  $s$  species, then the concentration matrix  $C \in \mathbb{R}^{k \times s}$  contains in its  $s$  columns the concentration profiles. The matrix  $A \in \mathbb{R}^{s \times n}$  holds the associated  $s$  pure component spectra in the rows. The error matrix  $E \in \mathbb{R}^{k \times n}$  comprises the mentioned deviations from the linear Lambert-Beer law.

The problem of a self-modeling curve resolution technique (hard model-free analysis) is to compute only from the given matrix  $D$  the number of species  $s$  together with proper matrix factors  $C$  and  $A$  in such a way that the error matrix  $D - CA$  is close to the zero matrix. For such hard model-free methods we refer to [16, 17, 18] and the references therein.

### 2.1. The mathematical factorization problem

Mathematically the (hard) model-free analysis in absence of error terms is a factorization problem for the matrix  $D$ . The factors  $C$  and  $A$  are non-negative matrices. We refer to this problem as

**Problem 2.1** (Non-negative matrix factorization). *For  $D \in \mathbb{R}_+^{k \times n}$  with  $\text{rank}(D) = s$  the problem is to find non-negative matrix factors so that*

$$D = CA \tag{1}$$

with  $C \in \mathbb{R}_+^{k \times s}$  and  $A \in \mathbb{R}_+^{s \times n}$ .

Therein the rank  $s$  of  $D$  equals the number of columns of  $C$  and the number of rows of  $A$ . Problem 2.1 is a so-called inverse problem. It is well known that an arbitrary non-negative  $k \times n$  matrix  $D$  with  $2 < \text{rank}(D) < \min(k, n)$ , and hence  $\min(k, n) > 3$ , may have no factorization of the form (1); for a discussion of the existence and uniqueness of solutions, see [5, 6, 33, 34]. For spectral data matrices  $D$  the existence of an “approximate” factorization (1) can be assumed, since  $D$  (due to the Lambert-Beer law) originates from the physical quantities which are inscribed into the matrix factors  $C$  and  $A$ . The factorization “reverses” the physics of the problem.

However, problem 2.1 usually has a continuum of possible solutions. The insertion of an invertible matrix  $T \in \mathbb{R}^{s \times s}$  and its inverse in (1) results in a further factorization

$$D = (CT^{-1})(TA). \tag{2}$$

If these transformed factors  $CT^{-1}$  and  $TA$  are non-negative matrices (which can be achieved for proper  $T$ ), then a further mathematically feasible solution is found. Typically the factorization problem does not have a unique solution due to the rotational ambiguity induced by  $T$ . We ignore the trivial non-uniqueness which originates from permuted diagonal matrices  $T$ , since such matrices correspond to positively scaled and reordered solutions. On the uniqueness question see Manne’s theorems [20], Malinowski [19] and the work of Rajkó [29] together with the references therein. For the mathematical background of this problem see e.g. [7, 31]. To find the correct and chemically relevant solution within the set of (mathematically) feasible solutions one can try to compute or to characterize the whole set of feasible solutions [9, 10, 16, 25]. Then one hopes to detect the desired solution within this set. Alternatively, one can apply proper regularizations to the factorization problem and hopes to steer the factorization procedure in the correct direction [18, 22, 23, 36].

In any case the first step of the computational process is the construction of a truncated singular value decomposition to construct a basis for the factors  $C$  and  $A$ . This is the classical approach of Lawton and Sylvester [16].

## 2.2. Factorization by the singular value decomposition

The singular value decomposition (SVD) [11] for a given  $D \in \mathbb{R}^{k \times n}$  reads

$$D = U \Sigma V^T$$

with orthogonal matrices  $U \in \mathbb{R}^{k \times k}$  and  $V \in \mathbb{R}^{n \times n}$ . The diagonal matrix  $\Sigma \in \mathbb{R}^{k \times n}$

$$\Sigma_{i,j} = \begin{cases} \sigma_i & \text{for } i = j, \\ 0 & \text{for } i \neq j, \end{cases}$$

contains the non-negative singular values  $\sigma_i$  in decreasing order with  $i$ .

If  $D$  has the rank  $s$ , then the SVD can be reduced to

$$D = \tilde{U} \tilde{\Sigma} \tilde{V}^T \quad (3)$$

where  $\tilde{U}$  is a submatrix of  $U$  which contains the  $s$  left singular vectors being associated with the non-zero singular values. Further  $\tilde{V}$  is built from the associated  $s$  right singular vectors and  $\tilde{\Sigma}$  is the leading  $s \times s$  submatrix of  $\Sigma$ .

The SVD provides a factorization of  $D$ . In the context of a self-modeling curve resolution technique  $\tilde{U} \tilde{\Sigma}$  and  $\tilde{V}^T$  are called *abstract factors*; these factors usually contain negative components and cannot be used for a chemical/physical interpretation. The trick from (2) to introduce a proper transformation matrix and its inverse is decisive for a successful solution of the reconstruction problem; see, among many others, the references [1, 10, 16, 18, 22, 35]. By means of a proper  $T \in \mathbb{R}^{s \times s}$  it is possible to recover the factors  $C$  and  $A$  as follows

$$D = \underbrace{\tilde{U} \tilde{\Sigma} T^{-1}}_C \underbrace{T \tilde{V}^T}_A. \quad (4)$$

Thus the aim of a self-modeling curve resolution (SMCR) technique is to construct just such a suitable transformation matrix  $T$ .

## 3. Enclosure of solutions

The rotational ambiguity of the factors  $C$  and  $A$  is an annoying fact which complicates the development of universal and stable SMCR algorithms. The computational (and sometimes analytical) determination of the range of feasible solutions can help in the analysis of chemical reaction systems. Here a brief overview is given on classical and more recent analytical and numerical techniques on the enclosure of feasible solutions; these techniques are essentially based on the required non-negativity of the solutions.

### 3.1. Enclosure of feasible solutions

The range of admissible solutions for a two-component ( $s = 2$ ) system has partly been analyzed analytically by Lawton and Sylvestre [16]. This work is among the earliest ‘‘chemometric’’ publications. Further Maeder and his coworkers contributed to this topic [1, 35]; see also the papers of Rajkó and István [28, 30].

For dimensions  $s > 2$  a comparable analysis gets much harder. For three-component systems Borgen et al. did pioneering work [3, 4]. Rajko et al. improved the analytical solution for three-component systems with computer geometry tools (Borgen plots), see [26, 27] and the references in these papers. A novel approach to compute the boundaries of the set (or manifold) of solutions for three-component systems has been presented by Golshan, Abdollahi and Maeder in 2011 [10].

In some of these works the Perron-Frobenius theorem [21] appears as an important tool. This theorem characterizes the largest eigenvalue (singular value) and the associated singular vector of a non-negative matrix. Boundaries for the range of possible solutions can be derived by determining all transformations of the first two (or three) right singular vectors which result in non-negative spectra. The associated inverse transformations can be applied to the left singular vectors and must also result in non-negative concentration profiles. This approach has been used e.g. in [10, 16] to construct optimal factors  $C$  and  $A$  which also fulfill  $D \approx CA$ .

However, various other hard and soft constraints can be applied. Sometimes even a pre-given kinetic model can be used for the regularization of the optimization procedure. This allows to find optimal kinetic constants by a kinetic regularization together with optimized  $C$  and  $A$  simultaneously, see [12, 14, 32].

### 3.2. Usage of supplementary information

Self-modeling curve resolution techniques are *hard model-free* methods in a sense that no a-priori information on the chemical system is needed for the construction of the factors  $C$  and  $A$ . However, sometimes certain information on the system is available, e.g., some of the pure component spectra of the starting reactants or of certain products may be known from separate measurements. Further the number of starting reactants or products may be given. Such additional information on the system should be utilized in order to reduce the range of admissible non-negative factorizations. This data can be used as a hard (or even soft) constraint on  $C$  and  $A$  while minimizing the reconstruction error  $D - CA$ . A mathematical approach of how to exploit such information in the computational procedure is presented in the next section.

#### 4. Reduction of the rotational ambiguity

As explained in Section 3 any additional information on the chemical reaction system can be exploited to reduce the rotational ambiguity of the solutions of a self-modeling curve resolution technique. Next we use arguments of linear algebra to prove

1. the *complementarity theorem* 4.2 which allows to impose restrictions on the concentration profiles of complementary species if certain spectra are given (and vice versa),
2. the *coupling theorems* 4.5 and 4.6 which prove affine linear constraints for pairs of a spectrum and the associated concentration profile,
3. a *non-negativity theorem* 4.7 which provides admissible ranges for the components that can be derived from the non-negativity constraints.

In this section we assume the Lambert-Beer law to hold exactly, i.e.,  $D$  is given as the exact product of  $C$  and  $A$ . Hence we ignore any nonlinearities and error terms. Therefore the existence of a solution of Problem 2.1 is guaranteed. The results of this section can be applied to practical data (containing error terms), which is shown in Section 6. However, with a decreasing signal-to-noise ratio the application of the results gets harder.

It is worth to note that the complementarity-coupling theorems are different from the duality results as introduced by Henry [13] for multivariate receptor modeling and discussed by Rajkó [24] in the SMCR context. This duality approach uses the non-negativity constraints to find restrictions on the feasible regions and works with the "external" matrices  $\tilde{U}$  and  $\tilde{V}$  in (4). In contrast to this, the complementarity-coupling approach is based on the partial knowledge of the factors  $C$  or  $A$  and uses the coupling through the "inner" matrix pair  $T$  and  $T^{-1}$  in (4) in order to derive restrictions on the feasible regions. The mathematical arguments also rely on rank/dimension arguments which are combined with non-negativity constraints.

##### 4.1. The colon notation

A useful notation to specify a row or a column of a matrix is the *colon notation*. For a matrix  $M \in \mathbb{R}^{n \times m}$  its  $k$ th row is denoted by

$$M(k, :) = (m_{k1}, \dots, m_{km})$$

and its  $k$ th column is

$$M(:, k) = \begin{pmatrix} m_{1k} \\ \vdots \\ m_{nk} \end{pmatrix}.$$

Further, we use the colon notation to extract sub-matrices. If  $1 \leq i_1 \leq i_2 \leq n$  and  $1 \leq j_1 \leq j_2 \leq m$ , then  $M(i_1 : i_2, j_1 : j_2)$  is the submatrix of  $M$  which results from extracting the rows  $i_1$  through  $i_2$  and the columns  $j_1$  through  $j_2$ . For example one gets

$$M(3:4, 2:5) = \begin{pmatrix} m_{32} & m_{33} & m_{34} & m_{35} \\ m_{42} & m_{43} & m_{44} & m_{45} \end{pmatrix}.$$

The  $n$ -by- $n$  identity matrix is denoted by  $I_n$  with

$$I_n = (e_1, \dots, e_n)$$

where  $e_k$  is the standard basis vector

$$e_k = (\underbrace{0, \dots, 0}_{(k-1)\text{-times}}, 1, \underbrace{0, \dots, 0}_{(n-k)\text{-times}})^T. \quad (5)$$

Sub-matrices of the identity matrix can be used to extract sub-matrices of  $M$  in the following way

$$M(:, k:l) = M I(:, k:l) \quad \text{and} \quad M(k:l, :) = I(k:l, :) M.$$

In words, the right-multiplication with  $I(:, k:l)$  extracts columns from  $M$  and left-multiplication with  $I(k:l, :)$  extracts rows from  $M$ .

##### 4.2. The complementarity theorem

Next we consider the situation that one (or even more than one) of the pure component spectra are known. A typical case is that these known spectra are those of the reactants of the chemical reaction; sometimes the spectra of certain products are also given. This supplementary knowledge of the chemical system should be exploited within the computation of the pure component factorization of  $D$ . Theorem 4.2 shows that such additional information on the columns of  $A$  imposes restrictions on the *complementary* columns of the concentration matrix  $C$ . These restrictions are expressed in the form of linear equations and can be used to reduce the rotational ambiguity of the decomposition.

The special case that  $s - 1$  pure component spectra are known within an  $s$ -component system is discussed in Corollary 4.3. For this problem the complementarity principle shows that the concentration profile of the single remaining component is unique (aside from scaling). In Sec. 4.3 further theorems are proved, which characterize the concentration profiles of the same species for which the spectra are available.

Lemma 4.1 proves an auxiliary result which is required for the proof of Theorem 4.2.

**Lemma 4.1.** Let  $T \in \mathbb{R}^{s \times s}$  be a regular matrix and  $1 \leq s_0 < s$ . Then

$$T(1 : s_0, :)y = 0$$

holds if and only if  $y \in \mathbb{R}^s$  is of the form

$$y = T^{-1}(:, s_0 + 1 : s)z$$

for a proper  $z \in \mathbb{R}^{s-s_0}$ .

*Proof.* Any regular matrix  $T$  satisfies

$$TT^{-1} = I.$$

Left-multiplication of this equation with  $I(1 : s_0, :)$  extracts the first  $s_0$  rows and right-multiplication with  $I(:, s_0 + 1 : s)$  extracts the last  $s - s_0$  columns so that

$$T(1 : s_0, :)T^{-1}(:, s_0 + 1 : s) = 0 \in \mathbb{R}^{s_0 \times s - s_0}, \quad (6)$$

i.e. the  $s_0 \times s - s_0$  zero-matrix.

If  $y = T^{-1}(:, s_0 + 1 : s)z$  with  $z \in \mathbb{R}^{s-s_0}$ , then left multiplication with  $T(1 : s_0, :)$  together with (6) yield

$$T(1 : s_0, :)y = T(1 : s_0, :)T^{-1}(:, s_0 + 1 : s)z = 0z = 0.$$

To prove the other direction just observe that the columns of  $T^{-1}(:, s_0 + 1 : s)$  build a basis of the null space of  $T(1 : s_0, :)$ . This argument reads in detailed form as follows: Let  $\mathcal{N}$  be the null space (or kernel) of  $T(1 : s_0, :) \in \mathbb{R}^{s_0 \times s}$ , i.e. any  $y \in \mathcal{N}$  satisfies  $T(1 : s_0, :)y = 0$  and vice versa. As  $T$  is a regular matrix the rank of its submatrix  $T(1 : s_0, :)$  is  $s_0$  and the dimension of its null space  $\mathcal{N}$  equals  $s - s_0$ .

Further the dimension of the column space (or image)  $\mathcal{M}$  of  $T^{-1}(:, s_0 + 1 : s)$  equals  $s - s_0$  (once again due to the regularity of  $T$ ).

Equation (6) proves that  $\mathcal{M}$  is a subspace of  $\mathcal{N}$  and  $\dim \mathcal{M} = \dim \mathcal{N}$  proves that  $\mathcal{M} = \mathcal{N}$ . Thus any  $y \in \mathcal{N}$  with  $T(1 : s_0, :)y = 0$  can be represented by a  $z \in \mathbb{R}^{s-s_0}$  so that  $y = T^{-1}(:, s_0 + 1 : s)z$ .  $\square$

The central theorem is as follows; therein  $\mathbb{R}_+^{n \times m}$  denotes the set of  $n$ -by- $m$  real matrices with non-negative entries.

**Theorem 4.2.** Let  $D \in \mathbb{R}_+^{k \times n}$  with  $\text{rank}(D) = s$  be decomposable in a way that  $D = CA$  with  $C \in \mathbb{R}_+^{k \times s}$  and  $A \in \mathbb{R}_+^{s \times n}$ . The truncated singular value decomposition of  $D$ , see (3), reads  $D = \tilde{U}\tilde{\Sigma}\tilde{V}^T$  with  $\tilde{U}$  and  $\tilde{V}$  having the rank  $s$ .

We assume that  $s_0$  rows (i.e.,  $s_0$  spectra) of the factor  $A$  are known with  $s_0 < s$ . Without loss of generality these known spectra can be placed in the first  $s_0$  rows of  $A$ . Thus  $A(1 : s_0, :) \in \mathbb{R}^{s_0 \times n}$  is given.

Then the complementary columns  $C(:, i)$ ,  $i = s_0 + 1, \dots, s$ , of  $C$  are contained in the  $(s - s_0)$ -dimensional vector space

$$\{\tilde{U}\tilde{\Sigma}y : y \in \mathbb{R}^s \text{ with } A(1 : s_0, :)\tilde{V}y = 0\}, \quad (7)$$

which is a linear subspace of the  $\mathbb{R}^k$ . (In words (7) defines the set of all vectors  $\tilde{U}\tilde{\Sigma}y$ , where  $y$  is a vector in the  $\mathbb{R}^s$  satisfying  $A(1 : s_0, :)\tilde{V}y = 0$ . Alternatively, one can describe the set (7) as the kernel (null space) of the matrix  $A(1 : s_0, :)\tilde{V}$  which is multiplied from the left by  $\tilde{U}\tilde{\Sigma}$ .)

*Proof.* A regular matrix  $T \in \mathbb{R}^{s \times s}$  exists which relates the factors in  $D = CA$  to the factors in  $D = (\tilde{U}\tilde{\Sigma})\tilde{V}^T$  in a way that

$$C = \tilde{U}\tilde{\Sigma}T^{-1} \quad \text{and} \quad A = T\tilde{V}^T;$$

for a proof see, e.g., Lemma 2.1 in [22].

The pre-given first  $s_0$  rows of  $A$  can be written as

$$I(1 : s_0, :)A = A(1 : s_0, :) = T(1 : s_0, :)\tilde{V}^T.$$

Right multiplication with  $\tilde{V}$  yields

$$A(1 : s_0, :)\tilde{V} = T(1 : s_0, :)\tilde{V}^T\tilde{V} = T(1 : s_0, :), \quad (8)$$

so that the first  $s_0$  rows of  $T$  are also known.

Further from  $C = \tilde{U}\tilde{\Sigma}T^{-1}$  we get for its  $s - s_0$  last columns

$$C(:, s_0 + 1 : s) = C I(:, s_0 + 1 : s) = \tilde{U}\tilde{\Sigma}T^{-1}(:, s_0 + 1 : s).$$

The image (or column space) of this matrix is

$$\mathcal{I} = \{\tilde{U}\tilde{\Sigma}T^{-1}(:, s_0 + 1 : s)z \text{ for } z \in \mathbb{R}^{s-s_0}\}.$$

Lemma 4.1 allows to rewrite this space as

$$\mathcal{I} = \{\tilde{U}\tilde{\Sigma}y : \text{with } y \in \mathbb{R}^s \text{ so that } T(1 : s_0, :)y = 0\}.$$

Insertion of (8) allows to eliminate  $T(1 : s_0, :)$  and proves the proposition.  $\square$

Next we consider the extremal case that  $s_0 = s - 1$ . This means that only one pure component spectrum is unknown. Then Theorem 4.2 shows that the concentration profile of this single component is uniquely determined (aside from scaling).

**Corollary 4.3.** On the assumptions of Theorem 4.2 assume the first  $s - 1$  rows of  $A$  to be given. Then the complementary concentration profile  $C(:, s)$  is unique (aside from scaling).

*Proof.* The  $(s - 1 \times s)$ -matrix  $A(1 : s - 1, :)\tilde{V}$  has the maximal rank  $s - 1$  since  $\text{rank}(D) = s$ . Hence its null space is a one-dimensional space and has the form  $\{ty : t \in \mathbb{R}\}$  for a proper  $y \neq 0$ . Theorem 4.2 shows that the concentration profile reads  $C(:, s) = \tilde{U}\tilde{\Sigma}y$  with a proper scaling constant  $t \in \mathbb{R}$ .  $\square$

**Remark 4.4.** *The complementarity theorem 4.2 can also be formulated for pre-given columns of  $C$  and the resulting implications on the complementary rows of  $A$ . This means that for known concentration profiles (i.e., some of the columns of  $C$  are given) the spectra of the complementary species are characterized by a condition like (7). The direct pendant of Corollary 4.3 reads as follows: If (for some reason) the concentration profiles of  $s - 1$  components are available, then the spectrum of the single remaining species is uniquely determined (aside from non-negative scaling).*

#### 4.3. The coupling theorems

In Sec. 4.2 we have analyzed the way in which the knowledge of  $s_0$  spectra imposes restrictions on the concentration profiles of the complementary species indexed with  $s_0 + 1, \dots, s$ . Next we analyze the way in which the knowledge of certain pure component spectra affects the concentration profiles of just the same species. This analysis results in affine-linear constraints which are formulated in the *coupling theorem* 4.5. Additionally, the non-negativity constraints can be used to formulate further restrictions (in order to reduce the rotational ambiguity); this is the topic of Sec. 4.4.

The theorem (once again) exploits the relation of the pure component factorization of  $D$  with the truncated singular value decomposition (4). The key observation is that the “subtraction” of a single component from the system can be represented by

$$D - C(:, i)A(i, :),$$

where  $C(:, i)A(i, :)$  is a *dyadic product* with the rank 1. If  $A(i, :)$  is known, then the correct concentration profile  $C(:, i)$  as an element from the column space of  $D$  satisfies the constraint  $\text{rank}(D - C(:, i)A(i, :)) = s - 1$ , since the subtraction of  $C(:, i)A(i, :)$  “removes” the  $i$ th species from the system. In other words the rank reduction by 1 is a constraint on the unknown profile  $C(:, i)$ .

**Theorem 4.5.** *Let  $D \in \mathbb{R}_+^{k \times n}$  with  $\text{rank}(D) = s$  be decomposable so that  $D = CA$  with  $C \in \mathbb{R}_+^{k \times s}$  and  $A \in \mathbb{R}_+^{s \times n}$ . Let  $\tilde{U}\tilde{\Sigma}\tilde{V}^T$  be a truncated singular value decomposition of  $D$ .*

*If the  $i$ th row of  $A$  is known, then the associated column  $C(:, i)$  is an element of the  $(s - 1)$ -dimensional affine-linear space*

$$\{\tilde{U}\tilde{\Sigma}y : y \in \mathbb{R}^s \text{ with } A(i, :)\tilde{V}y - 1 = 0\} \subset \mathbb{R}^k. \quad (9)$$

*Proof.* The proof is similar to that of Theorem 4.2. The  $i$ th row of matrix  $T$  is known since  $T(i, :) = A(i, :)\tilde{V}$ . The  $i$ th diagonal element of  $TT^{-1} = I$  is  $T(i, :)\tilde{V}^{-1}(i, i) = 1$ . Hence  $A(i, :)\tilde{V}T^{-1}(i, i) = 1$ . Therefore the  $i$ th column vector  $T^{-1}(i, :)$  is an element of the affine-linear space  $\{y \in \mathbb{R}^s : A(i, :)\tilde{V}y = 1\}$  with the dimension  $s - 1$ . Since  $C(:, i) = \tilde{U}\tilde{\Sigma}T^{-1}(i, :)$  the affine space of admissible solutions  $C(:, i)$  has the form  $\{\tilde{U}\tilde{\Sigma}y : y \in \mathbb{R}^s, A(i, :)\tilde{V}y - 1 = 0\}$  which is a subset of the  $\mathbb{R}^k$ .  $\square$

This theorem can also be formulated in a form which treats the case that  $s_0 \geq 1$  pure component spectra are known. Then the space of admissible concentration profiles is an  $(s - s_0)$ -dimensional subspace. This form of the Theorem 4.5 is similar to Theorem 4.2.

**Theorem 4.6.** *Let  $D \in \mathbb{R}_+^{k \times n}$  with  $\text{rank}(D) = s$  which is decomposable in  $D = CA$  with  $C \in \mathbb{R}_+^{k \times s}$  and  $A \in \mathbb{R}_+^{s \times n}$ . Let  $\tilde{U}\tilde{\Sigma}\tilde{V}^T$  be the truncated singular value decomposition of  $D$ . We assume that the first  $s_0$  rows of  $A$  are known.*

*Then for each  $i, i = 1, \dots, s_0$ , it holds that the concentration profile  $C(:, i)$  is contained in the affine-linear vector space*

$$\{\tilde{U}\tilde{\Sigma}y : y \in \mathbb{R}^s, A(1 : s_0, :)\tilde{V}y = e_i\} \subset \mathbb{R}^k \quad (10)$$

*whose dimension is  $s - s_0$ . Therein  $e_i \in \mathbb{R}^{s_0}$  is the  $i$ th standard basis vector, see (5).*

*Proof.* We proceed as in the proof of Thm. 4.5. However, we consider  $T(j, :) = A(j, :)\tilde{V}$  and we get  $T(j, :)\tilde{V}^{-1}(j, i) = 0$  if  $j \neq i$ . Therefore,  $A(j, :)\tilde{V}T^{-1}(j, i) = 0$ . From this one gets that  $C(:, i)$  is an element of  $\{\tilde{U}\tilde{\Sigma}y : y \in \mathbb{R}^s, A(j, :)\tilde{V}y = 0\}$ . Combining this with the result of Thm. 4.5 shows that  $A(1 : s_0, :)\tilde{V}y = e_i$  with the standard basis vector  $e_i$ .  $\square$

#### 4.4. Non-negativity

Let us review what is known on the columns of  $C$  and the rows of  $A$ . First, by definition, the columns of  $C$  are vectors from the  $\mathbb{R}^k$  and the rows of  $A$  are from the  $\mathbb{R}^n$ . Second, the singular value decomposition provides  $s$ -dimensional subspaces (namely the column space of  $\tilde{U}$  and the column space of  $\tilde{V}$ ) which contain the desired concentration profiles and spectra. Third, the Theorems 4.2 and 4.5 impose additional constraints on these solutions. These constraints are valuable in order to reduce

the rotational ambiguity, i.e., to reduce the set of admissible factorizations. Sometimes (in favorable cases) certain concentration profiles or spectra are uniquely determined (as in Corollary 4.3).

Additionally, there are the *non-negativity constraints* on the factors  $C$  and  $A$ . These constraints can be merged with the spaces given in (7) and (9). Due to the nature of these non-negativity constraints (which imply bounds on the scaling factors) one gets *subsets* of admissible solutions of the linear and affine-linear spaces (7) and (9). Theorem 4.7 deals with the case of an affine-linear space; in the case of a vector space only (non-useful) lower bounds equal to 0 can be derived.

**Theorem 4.7.** *On the assumptions of Theorem 4.5 let  $\bar{c}^{(i)} \in \mathbb{R}^k$  be a vector (of upper bounds for  $C(:, i)$ ) whose components are defined as*

$$(\bar{c}^{(i)})_j := \min_{\substack{\ell=1, \dots, n, \\ A_{i\ell} > 0}} \frac{D_{j\ell}}{A_{i\ell}}, \quad \text{for } j = 1, \dots, k.$$

*Then the set (9) of admissible concentration profiles can be reduced to*

$$\{\tilde{U}\tilde{\Sigma}y : y \in \mathbb{R}^s \text{ with } A(i, :)\tilde{V}y = 1 \text{ and } 0 \leq \tilde{U}\tilde{\Sigma}y \leq \bar{c}^{(i)}\}. \quad (11)$$

*In (11) the vector inequalities are to be interpreted component-wise.*

*Proof.* The matrices  $C$  and  $A$  are component-wise non-negative. Therefore for all  $j, \ell, i$  it holds that

$$C_{ji}A_{i\ell} \leq \sum_{k=1}^s C_{jk}A_{k\ell} = D_{j\ell},$$

which implies  $C_{ji} \leq D_{j\ell}/A_{i\ell}$  if  $A_{i\ell} \neq 0$ . Thus

$$C_{ji} \leq \min_{\substack{\ell=1, \dots, n, \\ A_{i\ell} > 0}} \frac{D_{j\ell}}{A_{i\ell}}, \quad i = 1, \dots, k. \quad (12)$$

The right-hand side defines the upper bound  $(\bar{c}^{(i)})_j$ . Theorem 4.5 provides the space (9) of possible solutions for the concentration profiles  $C(:, i)$ . The combination of the bound (12) with (9) proves the proposition.  $\square$

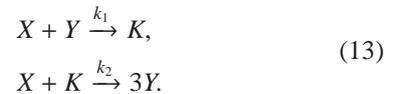
Theorem 4.7 can be generalized to the case that several spectra are known; this can be stated in a form similar to Theorem 4.6.

#### 4.5. Noisy data and perturbations

The analytical results of this section have been derived on the assumption of the idealized pure component decomposition  $D = CA$ . However, for any practical spectroscopic data matrix  $D$  nonlinearities and errors of the measurement result in a perturbed factorization problem  $D = CA + E$ . For such a problem not only the factors  $C$  and  $A$  are to be determined but also a small perturbation matrix  $E$  is desired, i.e.,  $E$  should be close to the zero-matrix. The reconstruction problem with pre-given (known) spectra is stable as long as these spectra can be well constructed from the right singular vectors, i.e., the error  $\|A(i, :) - A(i, :)\tilde{V}\tilde{V}^T\|$  is small. Moreover,  $\tilde{U}\tilde{\Sigma}\tilde{V}^T$  has to be a good approximation of  $D$ , which means that the singular value  $\sigma_{s+1}$  is small compared to  $\sigma_1, \dots, \sigma_s$ . If this is the case, then the singular vectors corresponding to the  $s$  largest singular values allow a good approximation of the linear and affine-linear subspaces which are determined in the Theorems 4.2 and 4.5. According to our experience difficulties may occur in the application of the interval restrictions (11) to noisy data. Such problems appear if for a given spectrum  $A(i, :)$  and for certain  $l$  both  $A_{ij}$  and  $D_{il}$  are close to zero.

### 5. A three-component model problem

In this section we apply the theoretical results to a three-component (artificial) catalytic model reaction. We consider the following system of second order reactions



The initial concentrations of the species  $X$ ,  $Y$  and  $K$  are the components of the column vector  $c(0)$  which is assumed as  $c(0) = (1, 0.1, 0)^T$ . The kinetic constants are taken as  $k_1 = 0.05$ ,  $k_2 = 1$ . The numerical solution of the initial value problem for  $t \in [0, 100]$  is computed by the *ode15s* multi-step solver for stiff problems of Matlab. This highly accurate solution is restricted to an equidistant grid with  $k = 101$  nodes in  $[0, 100]$ .

The absorption spectra of the three components  $X$ ,  $Y$  and  $K$  are taken as linear combinations of Gaussians in

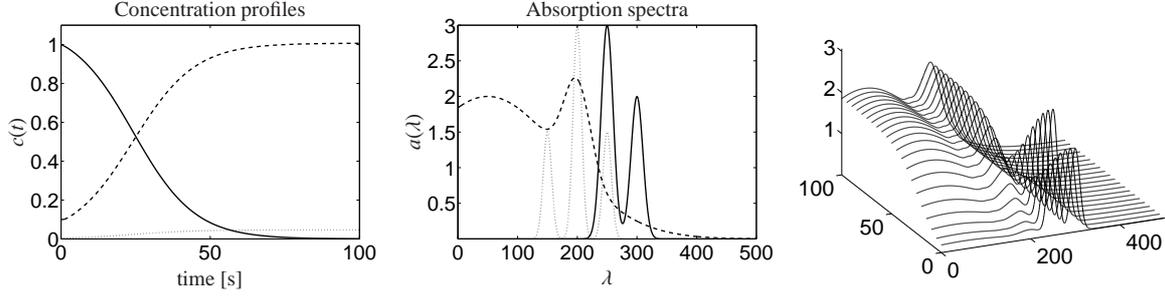


Figure 1: Model problem: concentration profiles with  $\lim_{t \rightarrow \infty} c_2(t)/c_3(t) = 21.7577$  (left), absorption spectra (center) and mixture spectra (right). Component X (solid line), component Y (dashed line) and component K (dotted line).

the form (we use the indexes 1,2,3 for X, Y, K)

$$\begin{aligned}
 a_1(\lambda) &= 3 \exp\left(-\frac{(\lambda - 250)^2}{200}\right) + 2 \exp\left(-\frac{(\lambda - 300)^2}{200}\right), \\
 a_2(\lambda) &= 2 \exp\left(-\frac{(\lambda - 50)^2}{30000}\right) + 1.3 \exp\left(-\frac{(\lambda - 200)^2}{1000}\right), \\
 a_3(\lambda) &= 3 \exp\left(-\frac{(\lambda - 200)^2}{100}\right) + \frac{3}{2} \exp\left(-\frac{(\lambda - 250)^2}{100}\right) \\
 &\quad + \frac{3}{2} \exp\left(-\frac{(\lambda - 150)^2}{100}\right)
 \end{aligned}$$

with  $\lambda \in [0, 500]$ . These spectra are evaluated on an equidistant grid with  $n = 501$  nodes.

Due to the Lambert-Beer law the absorption of the mixture at the time  $t$  and the wave-lengths  $\lambda$  reads

$$d(t, \lambda) = \sum_{i=1}^3 c_i(t) a_i(\lambda).$$

Its evaluation on the  $101 \times 501$  discrete grid defines the data matrix  $D \in \mathbb{R}^{101 \times 501}$ . Figure 1 shows the concentration profiles and the associated pure component spectra together with the mixture spectra.

From now on we only use the data matrix  $D$ . Numerically we get  $\text{rank}(D) = 3$  (singular values close to the machine precision are ignored). The next step is to recover the factors  $C \in \mathbb{R}^{101 \times 3}$  and  $A \in \mathbb{R}^{3 \times 501}$  from the given mixture data  $D \in \mathbb{R}^{101 \times 501}$ . There are many admissible (e.g. non-negative) factorizations of  $D$  and additional information on the system is required to compute the correct factors. In the following Sections 5.1 and 5.2 we make use of the knowledge on the initial concentrations  $C(1, :) = (1, 0.1, 0)$ . Further we assume that the pure component spectra of the components X and Y are given; i.e., the rows  $A(1, :)$  and  $A(2, :)$  are known. Finally the correct factors  $C$  and  $A$  are recovered in Section 5.3 due to linear and nonlinear regression with a kinetic model of (13).

The given data are summarized:

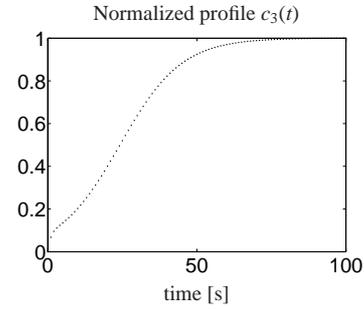


Figure 2: Normalized concentration profile  $c_3(t)$  of the unknown intermediate species K.

- The data matrix  $D \in \mathbb{R}^{101 \times 501}$ ,
- the initial concentrations  $C(1, :) = (1, 0.1, 0)$ ,
- two pure component spectra  $A(1, :)$  and  $A(2, :)$ .

Data to be recovered are:

- Three concentration profiles  $C \in \mathbb{R}_+^{101 \times 3}$ ,
- one pure component spectrum  $A(3, :) \in \mathbb{R}_+^{1 \times 501}$ .

### 5.1. The complementary concentration profile

Two spectra  $A(1, :)$  and  $A(2, :)$  of the three-component system (13) are known. Hence Theorem 4.2 and Corollary 4.3 can be used to reconstruct the complementary concentration profile  $C(:, 3)$  (which is uniquely determined aside from scaling). Therefore if  $y \neq 0$  is a vector in the null space of  $A(1 : 2, :)\tilde{V}$ , then a real constant  $\gamma$  exists so that

$$C(:, 3) = \gamma \tilde{U} \tilde{\Sigma} y.$$

This normalized (the maximum is set equal to 1) concentration profile is shown in Fig. 2.

### 5.2. The associated concentration profiles

The coupling theorems of Section 4.3 allow us to formulate restrictions on the unknown two concentration profiles  $C(:, 1 : 2)$  which correspond to the known absorption spectra  $A(1, :)$  and  $A(2, :)$ . First Theorem 4.6 allows to construct one-dimensional affine subspaces which contain the profiles  $C(:, 1)$  and  $C(:, 2)$ . Then the non-negativity constraints of Theorem 4.7 reduce these subspaces to smaller and bounded sets.

Due to Theorem 4.6 the associated concentration profiles satisfy

$$\begin{aligned} C(:, 1) &\in \{\tilde{U}\tilde{\Sigma}(v_1 + \alpha w) : \alpha \in \mathbb{R}\}, \\ C(:, 2) &\in \{\tilde{U}\tilde{\Sigma}(v_2 + \beta w) : \beta \in \mathbb{R}\}. \end{aligned}$$

Therein  $w$  is a non-zero element of the null space of  $A(1 : 2, :)\tilde{V}$ , which means that  $A(1 : 2, :)\tilde{V}w = 0$ . The vectors  $v_1$  and  $v_2$  are solutions of the under-determined linear systems

$$\begin{aligned} A(1 : 2, :)\tilde{V}v_1 &= (1, 0)^T, \\ A(1 : 2, :)\tilde{V}v_2 &= (0, 1)^T. \end{aligned} \quad (14)$$

These affine spaces can be reduced, by means of Theorem 4.7, to the bounded sets

$$\begin{aligned} C(:, 1) &\in \{\tilde{U}\tilde{\Sigma}(v_1 + \alpha w) : \alpha \in I_1\}, \\ C(:, 2) &\in \{\tilde{U}\tilde{\Sigma}(v_2 + \beta w) : \beta \in I_2\}, \end{aligned}$$

with intervals  $I_1 = [l_1, u_1]$  and  $I_2 = [l_2, u_2]$ .

Without loss of generality we can assume that  $\tilde{U}\tilde{\Sigma}w$  is a componentwise non-negative vector (i.e.  $\tilde{U}\tilde{\Sigma}w \geq 0$ ) since  $\tilde{U}\tilde{\Sigma}w = \gamma C(:, 3)$  with a real constant  $\gamma$ . With the solutions  $v_1$  and  $v_2$  of (14) we get the intervals

$$\begin{aligned} I_1 &= [-0.0221, 0.2229], \\ I_2 &= [-2.001, -0.0182]. \end{aligned} \quad (15)$$

All this allows us to represent the concentration matrix  $C$  in the form

$$\begin{aligned} C(:, 1) &= \tilde{U}\tilde{\Sigma}(v_1 + \alpha w), \\ C(:, 2) &= \tilde{U}\tilde{\Sigma}(v_2 + \beta w), \\ C(:, 3) &= \tilde{U}\tilde{\Sigma}w \end{aligned} \quad (16)$$

with  $(\alpha, \beta) \in I_1 \times I_2$  as given by (15).

This set of feasible solutions is further restricted by the constraint  $A(3, :) \geq 0$ . For the present model problem the influence of this constraint appears to be marginal. (Later for the practical problem in Section 6 the same argument appears to be more useful, see Fig. 10.)

To summarize, the factor  $C$  in (16) has a two-parametric, bounded representation. The continuum of admissible solutions is shown in Fig. 3; the separate solution  $c_3(t)$  is shown in Fig. 2.

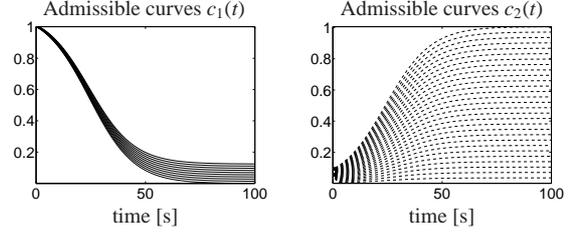


Figure 3: Continuum of admissible non-negative concentration profiles  $c_1(t)$  and  $c_2(t)$  of the components  $X$  and  $Y$ .

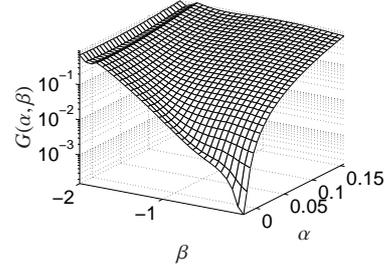


Figure 4: The function  $G(\alpha, \beta)$  on a subregion of  $I_1 \times I_2$ .

### 5.3. Best fit with the kinetic model

The set of admissible solutions (16) still depends on the two parameters  $\alpha$  and  $\beta$ . Next we apply techniques of linear and nonlinear regression in order to find optimal  $(\alpha^*, \beta^*)$  in a way that the concentration profiles of the kinetic model of (13) (with optimized kinetic constants  $(k_1, k_2)$ ) fit best the solution (16).

Our aim is to minimize the function

$$\begin{aligned} G : I_1 \times I_2 &\rightarrow \mathbb{R}, \\ (\alpha, \beta) &\mapsto \min_{(k_1, k_2) \in \mathbb{R}_+^2} \|C^{(S)}(\alpha, \beta) - C^{(\text{ode})}(k_1, k_2)\|_F^2. \end{aligned}$$

Therein  $\|\cdot\|_F^2$  is the squared Frobenius norm (sum of the squares of all components). Further  $C^{(S)}$  is given by (16) with a proper scaling of the columns. Linear least squares are used to compute these scaling constants so that the columns of  $C^{(S)}$  result in a best fit of the columns of  $C^{(\text{ode})}(k_1, k_2)$ . The matrix  $C^{(\text{ode})}(k_1, k_2)$  contains the concentration profiles which result from a numerical solution of the ordinary differential equation for (13) with the given initial values  $c(0) = (1, 0.1, 0)^T$  at  $t = 0$ . Additionally, the kinetic constants  $k_1$  and  $k_2$  are determined by a nonlinear regression so that  $G$  for given  $(\alpha, \beta)$  takes its minimum. Fig. 4 shows  $G$  on a proper subregion of  $I_1 \times I_2$ .

The numerical minimization of  $G$  shows that its minimum is attained in  $(\alpha^*, \beta^*) = (-2.0686 \cdot 10^{-2}, -1.8221 \cdot 10^{-2})$  together with the optimized kinetic constants  $(k_1^*, k_2^*) = (0.05, 0.99999)^T$ . These constants can be

accepted as very good approximations of the initial (of the model problem) kinetic constants  $(k_1^{(\text{orig})}, k_2^{(\text{orig})}) = (0.05, 1.0)^T$ . For the reconstructed columns of  $C$  we get the following relative deviations from the original data

$$\varepsilon_i = \frac{\|C^{(\text{orig})}(:, i) - C(:, i)\|_2}{\|C^{(\text{orig})}(:, i)\|_2}, \quad i = 1, 2, 3,$$

with  $\varepsilon = (8.95 \cdot 10^{-9}, 6.82 \cdot 10^{-11}, 5.33 \cdot 10^{-8})^T$ . For the single spectrum we get the error

$$\frac{\|A^{(\text{orig})}(3, :) - A(3, :)\|_2}{\|A^{(\text{orig})}(3, :)\|_2} = 1.17 \cdot 10^{-7}.$$

Therefore the reconstruction problem for the concentration profiles and the spectrum has been solved successfully. The rotational ambiguity of this three-component system has first been reduced to the two-parametric representation (16). In a second step a unique solution, which is a good approximation of the initial data, has been found by means of a least squares fit to the underlying kinetic model.

## 6. A three component catalytic system: Formation of hafnacyclopentene

A part of the catalytic cycle from ethylene to linear  $\alpha$ -olefines with a hafnium-complex as catalyst can be described kinetically as a linear consecutive reaction  $X \xrightarrow{k_1} Y \xrightarrow{k_2} Z$  with  $k_1 \gg k_2$ . This is a chemical reaction system with three dominant components; we consider the formation of hafnacyclopentene which is denoted as component Z. See [2, 8] for the details and conventional approaches to determine the kinetic constants.

Experimentally we have combined a stopped-flow instrument with a UV-VIS diode array so that each 5ms a separate spectrum can be taken. The spectral data matrix  $D$  is formed from  $k = 500$  single spectra which are recorded in the time interval  $[0, 2.495]$ s. Each spectrum contains  $n = 381$  spectral-channels which are distributed equidistantly in the interval  $[420, 800]$ nm. A 2D plot of the series of the spectra is shown in Fig. 5.

At the start of the reaction only the reactant X (*rac*-(ebthi)-Hf( $\eta^2$ -Me<sub>3</sub>SiC<sub>2</sub>SiMe<sub>3</sub>) with ebthi = 1,2-ethylen-1,1'-bis( $\eta^5$ -tetrahydroindenyl)) contributes to the absorption within the spectral range  $[420, 800]$ nm. The distribution of the singular values of  $D$  (see Fig. 6) clearly indicates that only three independent chemical components can be found. In other words the perturbation matrix  $E$  in  $D = CA + E$  seems to be close to the zero-matrix. Therefore a truncated singular value decomposition of  $D \in \mathbb{R}_+^{500 \times 381}$  is to be determined with factors  $C \in \mathbb{R}_+^{500 \times 3}$  and  $A \in \mathbb{R}_+^{3 \times 381}$ .

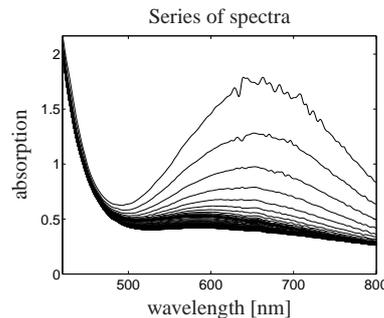


Figure 5: Series of spectra in the rows of the matrix  $D$ .

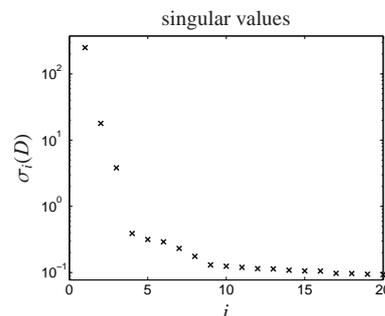


Figure 6: Semi-logarithmic plot of the 20 largest singular values of data matrix  $D$ .

The initial concentration of  $X$  is  $c_X(0) = 0.01309 \text{ mol L}^{-1}$ . Assuming that the conversion to  $Z$  at  $t = 2.495$ s is complete the last spectrum is that of the pure component  $Z$  (only traces of  $X$  and  $Y$  are present). Therefore fairly accurate spectra of the reactant  $X$  and the product  $Z$  are available, see Fig. 7. We use the following notation and plot-line-style for the three components

$$\begin{aligned} C(i, 1) &= c_X(t_i), & A(1, j) &= a_X(\lambda_j), & (\text{line: solid}), \\ C(i, 2) &= c_Y(t_i), & A(2, j) &= a_Y(\lambda_j), & (\text{line: dashed}), \\ C(i, 3) &= c_Z(t_i), & A(3, j) &= a_Z(\lambda_j), & (\text{line: dash-dotted}) \end{aligned}$$

with  $i = 1, \dots, 500$  and  $j = 1, \dots, 381$ . Hence  $A(1, :)$  and  $A(3, :)$  are known parts of the factorization  $D = CA$ .

### 6.1. The complementary concentration profile

Two spectra of the three-component system are known. Thus Theorem 4.2 and Corollary 4.3 determine the concentration profile  $C(:, 2)$  of the (unknown) intermediate  $Y$ . This concentration profile, see Fig. 8, is uniquely determined aside from (positive) scaling.

### 6.2. The associated concentration profiles

The coupling theorem 4.6 can be applied to derive affine linear representations of the unknown concentra-

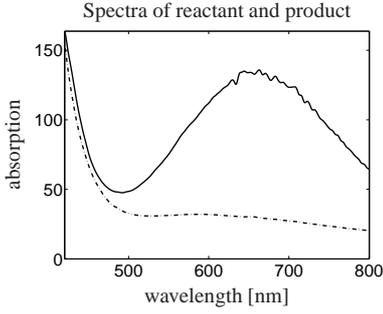


Figure 7: Spectra of *rac*-(*ebthi*)Hf(C<sub>4</sub>H<sub>8</sub>) (solid) and *rac*-(*ebthi*)Hf( $\eta^2$ -Me<sub>3</sub>SiC<sub>2</sub>SiMe<sub>3</sub>) (dash-dotted).

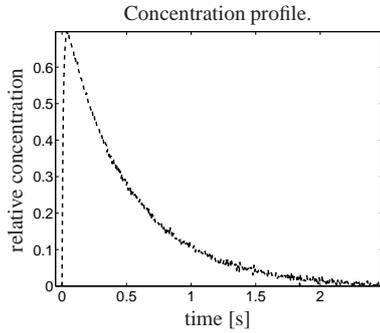


Figure 8: Concentration profile (arbitrarily scaled) of the intermediate *Y*.

tion profiles  $C(:, 1)$  and  $C(:, 3)$  in the form

$$\begin{aligned} C(:, 1) &= \tilde{U}\tilde{\Sigma}(v_1 + \alpha w), \\ C(:, 3) &= \tilde{U}\tilde{\Sigma}(v_2 + \beta w). \end{aligned}$$

The vectors  $v_1, v_2, w \in \mathbb{R}^3$  are determined as follows (cf. Theorem 4.6 and Section 5.2)

$$\begin{aligned} A([1, 3], :)\tilde{V}v_1 &= (1, 0)^T, \\ A([1, 3], :)\tilde{V}v_2 &= (0, 1)^T, \\ A([1, 3], :)\tilde{V}w &= (0, 0)^T. \end{aligned}$$

Once again the complementarity theorem 4.2 is applied. It allows to conclude from the two profiles  $C(:, 1)$  and  $C(:, 3)$  on the remaining spectrum  $A(2, :)$  of the intermediate. As  $C(:, 1)$  and  $C(:, 3)$  depend on  $\alpha$  and  $\beta$  the spectrum  $A(2, :)$  given by

$$A(2, :) = \gamma_1 \tilde{V}(:, 1) + \gamma_2 \tilde{V}(:, 2) + \gamma_3 \tilde{V}(:, 3) \quad (17)$$

also depends on these constants. Therein  $\tilde{V}(:, i)$  are right singular vectors and  $\gamma_i = \gamma_i(\alpha, \beta)$  are real constants.

This results in the following two-parametric approxi-

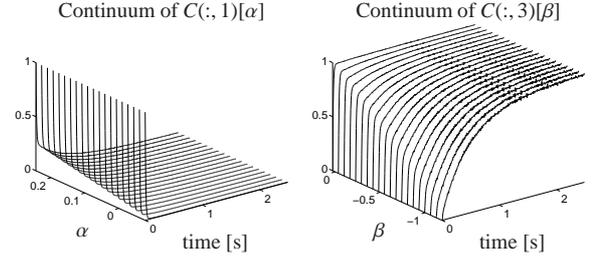


Figure 9: Continua of concentrations profiles  $C(:, 1)[\alpha]$  and  $C(:, 3)[\beta]$ .

mate factorization  $D \approx CA$  with

$$\begin{aligned} C &= (C(:, 1)[\alpha], C(:, 2), C(:, 3)[\beta]), \\ A &= \begin{pmatrix} D(1, :) \\ A(2, :)[\alpha, \beta] \\ D(k, :) \end{pmatrix}. \end{aligned} \quad (18)$$

Therein the dependence of certain columns and rows on the parameters  $\alpha$  and  $\beta$  is expressed by rectangular brackets.

### 6.3. Non-negativity constraints

Only a componentwise non-negative concentration factor  $C$  makes sense. For the vectors  $v_1, v_2, w \in \mathbb{R}^3$  and  $\tilde{V}(:, i) \in \mathbb{R}^n$  (which are known from Section 6.2) only  $\alpha \in [-0.078, 0.245]$  and  $\beta \in [-1.186, 0.0278]$  result in a non-negative matrix  $C$ , cf. Theorem 4.7. The resulting continua for the concentration profiles  $C(:, 1)$  and  $C(:, 3)$  are shown in Fig. 9.

The Cartesian product interval  $(\alpha, \beta) \in [-0.078, 0.245] \times [-1.186, 0.0278]$  can further be restricted as  $A(2, :)$  also depends on  $\alpha$  and  $\beta$ , see Equation (17). The subregion of  $[-0.078, 0.245] \times [-1.186, 0.0278]$  which guarantees non-negative spectra  $A(2, :)[\alpha, \beta]$  is shown in Fig. 10. This subregion of admissible parameters is denoted by  $\Omega$ . These further restrictions are derived in a way which is comparable to (FIRPOL in) the Borgen approach [4].

### 6.4. Best fit with a kinetic model

Up to now the rotational ambiguity of the solution matrices  $C$  and  $A$  has considerably been reduced and the remaining ambiguity, see Eq. (18), has been parametrized in the parameters  $\alpha$  and  $\beta$ . The concentration profile of the intermediate *Y* has been determined uniquely. Further the concentration profiles of the reactant and the product one-parameter representations have been derived. The spectrum  $A(2, :)$  has a two-parameter form.

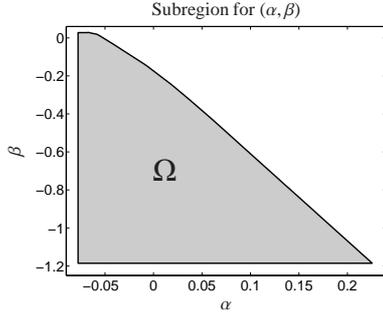


Figure 10: Region  $\Omega$  of pairs  $(\alpha, \beta)$  which guarantee non-negative concentration profiles  $C(:, 1)[\alpha]$ ,  $C(:, 3)[\beta]$  and a non-negative spectrum  $A(2, :)[\alpha, \beta]$ .

The next step is to find in the region of parameter-pairs  $(\alpha, \beta)$ , see Fig. 10, those solutions which are consistent with a kinetic model



The computational procedure is as follows: For the pairs  $(\alpha, \beta) \in \Omega$  the factors (18) are computed. Then the concentration factor  $C[\alpha, \beta]$  is fitted to the kinetic model associated with (19) and  $k_1$  and  $k_2$  are determined simultaneously. This is a hard-model-fit for each admissible pair  $(\alpha, \beta)$ . We are interested in determining those  $(\alpha, \beta) \in \Omega$  which are responsible for the best possible fit. The concentration profiles in  $C \in \mathbb{R}^{500 \times 3}$  are scaled in a way that the sum  $\sum_{i=1}^3 C(:, i)$  equals the initial concentration  $c_X(0)$  at any time (due to the mass balance). Then a nonlinear regression is used to compute the kinetic constants  $k_1$  and  $k_2$  in a way that the kinetic equations for (19) fit the concentration profiles.

The optimal kinetic constants  $k_1^*$ ,  $k_2^*$  and optimal parameters  $\alpha^*$  and  $\beta^*$  minimize the functional

$$G : \mathbb{R}_+^2 \times \Omega \rightarrow \mathbb{R}, (k_1, k_2, \alpha, \beta) \mapsto \sum_{i=1}^3 \sum_{j=1}^{500} \gamma_i^{-2} \left( C_{ji}(\alpha, \beta) - C_{ji}^{(\text{ode})}(k_1, k_2) \right)^2. \quad (20)$$

The matrix  $C^{(\text{ode})} \in \mathbb{R}^{500 \times 3}$  contains (the values on the time  $\times$  wavelength grid of) the solution of the initial value problem

$$\begin{aligned} \frac{dc_X(t)}{dt} &= -k_1 c_X(t), & c_X(0) &= 0.01309, \\ \frac{dc_Y(t)}{dt} &= k_1 c_X(t) - k_2 c_Y(t), & c_Y(0) &= 0, \\ \frac{dc_Z(t)}{dt} &= k_2 c_Y(t), & c_Z(0) &= 0. \end{aligned}$$

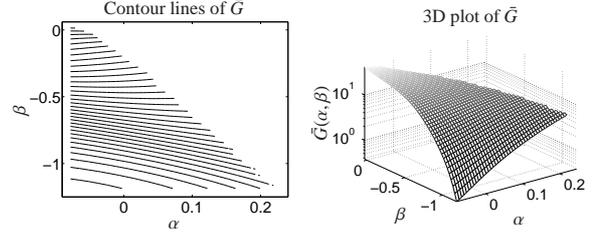


Figure 11: Error by fitting the kinetic model on the decomposition depending on  $(\alpha, \beta)$ , error plot and contour lines.

Its analytic solution reads

$$C^{(\text{ode})}(t; k_1, k_2) = \begin{pmatrix} c_X(0) \exp(-k_1 t) \\ \frac{c_X(0)k_1}{k_2 - k_1} (\exp(-k_1 t) - \exp(-k_2 t)) \\ c_X(0) \left( 1 + \frac{k_2 \exp(-k_1 t) - k_1 \exp(-k_2 t)}{k_1 - k_2} \right) \end{pmatrix}.$$

Additionally scaling factors

$$\gamma_i = \max_{l=1, \dots, 500} C_{li}, \quad i = 1, 2, 3,$$

are used in Equation (20) for a proper relative weighting of the errors for the three species  $X$ ,  $Y$  and  $Z$ .

As  $k_1$  and  $k_2$  depend on  $\alpha$  and  $\beta$  the minimization problem reads

$$\bar{G} : \Omega \rightarrow \mathbb{R}, (\alpha, \beta) \mapsto \min_{k_1, k_2 \in \mathbb{R}_+} G(k_1, k_2, \alpha, \beta). \quad (21)$$

The contour lines of  $\bar{G}$  together with a 3D plot are shown in Fig. 11. The numerical minimization results in  $\alpha^* = -0.078$  and  $\beta^* = -1.186$ . The associated optimal kinetic constants are  $k_1^* = 93.99 \text{ s}^{-1}$  (unstable result due to the poor ratio of the injection phase (5ms) and the reaction phase (45ms) with spectra taken every 5ms) and  $k_2^* = 2.152 \text{ s}^{-1}$ . The concentration profiles of the reactant  $X$ , of the intermediate  $Y$  and of the product  $Z$  are shown in Fig. 12. The solutions  $C^{(\text{ode})}(t; k_1^*, k_2^*)$  are consistent with the concentration profiles  $C(:, i)$ ,  $i = 1, 2, 3$ . The remaining small errors at  $t \approx 0$  are caused by the computational procedure which for all quantities guarantees non-negativity – a regularized SMCR approach as in [15, 22] can produce nearly accurate approximations.

### 6.5. Critical remark

The results which have been derived in this section can also be extracted by using conventional approaches: First chemometric tools allow to recover the kinetic constants from the spectroscopic data together with the knowledge of the kinetic model. This allows to construct the concentration profiles and then to compute

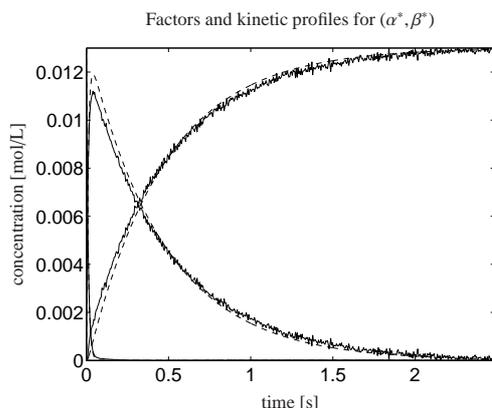


Figure 12: Concentration profiles of X, Y and Z (solid shaky line) together with the concentration profiles of the kinetic model (dashed line).

the associated pure component spectra by a linear regression. Our approach leads to the same results, but is completely different: We used the complementarity theorems to parametrize the continuum of admissible solutions, which resulted in the set  $\Omega$ . Then the concentration factor  $C[\alpha, \beta]$  is fitted to the kinetic model for each admissible pair  $(\alpha, \beta)$ . The optimal fit is attained in the minimum of the functional (21). A drawback of our approach is that it is to be adapted to each new problem. The benefit is its mathematical rigorosity which is based on a parametrization of the rotational ambiguity. We have used this simple reaction system to demonstrate the usefulness of the approach. The analysis of more complex systems (for which conventional approaches do not result in a complete analysis) is a topic for future work.

## 7. Conclusion

A couple of mathematical theorems have been introduced and proved, which allow to reduce the rotational ambiguity of the solutions of multivariate curve resolution techniques. These theorems exploit supplemental information on the chemical reaction in a rigorous way. Available information on the reaction system like concentration profiles or spectra of certain components impose (affine) linear restrictions on the remaining unknown concentration profiles and spectra. In favorable cases these restrictions can determine certain factors completely.

The usefulness of the complementarity and coupling theorems has been demonstrated for a model problem as well as for a simple catalytic reaction system. We hope that the presented new mathematical results enrich

the toolbox of chemometric methods and help to reduce the rotational ambiguity of the range of admissible solutions successfully.

## 8. Acknowledgment

The authors thank the anonymous referees for the numerous suggestions to improve the paper.

## References

- [1] H. Abdollahi, M. Maeder, and R. Tauler. Calculation and Meaning of Feasible Band Boundaries in Multivariate Curve Resolution of a Two-Component System. *Analytical Chemistry*, 81(6):2115–2122, 2009. PMID: 19216515.
- [2] T. Beweries, C. Fischer, S. Peitz, V. V. Burlakov, P. Arndt, W. Baumann, A. Spannenberg, D. Heller, and U. Rosenthal. Combination of spectroscopic methods: In situ NMR and UV/Vis measurements to understand the formation of group 4 metallacyclopentanes from the corresponding metallacycloprenes. *Journal of the American Chemical Society*, 131(12):4463–4469, 2009.
- [3] O.S. Borgen, N. Davidsen, Z. Mingyang, and Ø. Øyen. The multivariate N-Component resolution problem with minimum assumptions. *Microchimica Acta*, 89:63–73, 1986. 10.1007/BF01207309.
- [4] O.S. Borgen and B.R. Kowalski. An extension of the multivariate component-resolution method to three components. *Analytica Chimica Acta*, 174(0):1–26, 1985.
- [5] S. L. Campbell and G. D. Poole. Computing nonnegative rank factorizations. *Linear Algebra and its Applications*, 35:175–182, 1981.
- [6] J. E. Cohen and U. G. Rothblum. Nonnegative ranks, decompositions, and factorizations of nonnegative matrices. *Linear Algebra and its Applications*, 190:149–168, 1993.
- [7] D. Donoho and V. Stodden. When does non-negative matrix factorization give a correct decomposition into parts? <http://www-stat.stanford.edu/~donoho/Reports/2003/NMFCDP.pdf>, 2003.
- [8] C. Fischer, T. Beweries, A. Preetz, H.-J. Drexler, W. Baumann, S. Peitz, U. Rosenthal, and Heller D. Kinetic and mechanistic investigations in homogeneous catalysis using operando UV/Vis spectroscopy. *Catalysis Today*, 155(3–4):282–288, 2010.
- [9] P. J. Gemperline. Computation of the Range of Feasible Solutions in Self-Modeling Curve Resolution Algorithms. *Analytical Chemistry*, 71(23):5398–5404, 1999.
- [10] A. Golshan, H. Abdollahi, and M. Maeder. Resolution of Rotational Ambiguity for Three-Component Systems. *Analytical Chemistry*, 83(3):836–841, 2011.
- [11] G.H. Golub and C.F. Van Loan. *Matrix computations*. Johns Hopkins University Press, Baltimore, MD, third edition, 1996.
- [12] H. Haario and V.M. Taavitsainen. Combining soft and hard modelling in chemical kinetics. *Chemometr. Intell. Lab.*, 44:77–98, 1998.
- [13] R.C. Henry. Duality in multivariate receptor models. *Chemometrics and Intelligent Laboratory Systems*, 77(1-2):59–63, 2005.
- [14] A. Juan, M. Maeder, M. Martínez, and R. Tauler. Combining hard and soft-modelling to solve kinetic problems. *Chemometr. Intell. Lab.*, 54:123–141, 2000.
- [15] C. Kubis, D. Selent, M. Sawall, R. Ludwig, K. Neymeyr, W. Baumann, R. Franke, and A. Börner. Exploring between the extremes: Conversion dependent kinetics of phosphite-modified

- hydroformylation catalysis. Accepted for Chemistry - A European Journal, 2012.
- [16] W. H. Lawton and E. A. Sylvestre. Self modelling curve resolution. *Technometrics*, 13:617–633, 1971.
- [17] M. Maeder and Y.M. Neuhold. *Practical data analysis in chemistry*. Elsevier, Amsterdam, 2007.
- [18] E. Malinowski. *Factor analysis in chemistry*. Wiley, New York, 2002.
- [19] E. R. Malinowski. Window factor analysis: Theoretical derivation and application to flow injection analysis data. *Journal of Chemometrics*, 6(1):29–40, 1992.
- [20] R. Manne. On the resolution problem in hyphenated chromatography. *Chemometrics and Intelligent Laboratory Systems*, 27(1):89–94, 1995.
- [21] H. Minc. *Nonnegative matrices*. John Wiley & Sons, New York, 1988.
- [22] K. Neymeyr, M. Sawall, and D. Hess. Pure component spectral recovery and constrained matrix factorizations: Concepts and applications. *Journal of Chemometrics*, 24:67–74, 2010.
- [23] H. Park and H. Kim. One-sided non-negative matrix factorization and non-negative centroid dimension reduction for text classification. *Proceedings of the workshop on text mining at the 6th SIAM international conference on data mining*, 2006.
- [24] R. Rajkó. Natural duality in minimal constrained self modeling curve resolution. *Journal of Chemometrics*, 20(3-4):164–169, 2006.
- [25] R. Rajkó. Computation of the range (band boundaries) of feasible solutions and measure of the rotational ambiguity in self-modeling/multivariate curve resolution. *Analytica Chimica Acta*, 645(1–2):18–24, 2009.
- [26] R. Rajkó. Some surprising properties of multivariate curve resolution-alternating least squares (MCR-ALS) algorithms. *Journal of Chemometrics*, 23(4):172–178, 2009.
- [27] R. Rajkó. Studies on the adaptability of different Borgen norms applied in self-modeling curve resolution (SMCR) method. *Journal of Chemometrics*, 23(6):265–274, 2009.
- [28] R. Rajkó. Additional knowledge for determining and interpreting feasible band boundaries in self-modeling/multivariate curve resolution of two-component systems. *Analytica Chimica Acta*, 661(2):129–132, 2010.
- [29] R. Rajkó. Comments on "Near-Infrared Hyperspectral Unmixing Based on a Minimum Volume Criterion for Fast and Accurate Chemometric Characterization of Counterfeit Tablets"s. *Analytical Chemistry*, 82(20):8750–8752, 2010.
- [30] R. Rajkó and K. István. Analytical solution for determining feasible regions of self-modeling curve resolution (SMCR) method based on computational geometry. *Journal of Chemometrics*, 19(8):448–463, 2005.
- [31] M. Sawall. Regularisierte nichtnegative Matrixfaktorisierungen und ihre Anwendungen in der Spektroskopie. PhD thesis, Universität Rostock, 2011.
- [32] M. Sawall, A. Börner, C. Kubis, D. Selent, R. Ludwig, and K. Neymeyr. Model-free multivariate curve resolution combined with model-based kinetics: algorithm and applications. Technical Report, Universität Rostock and LIKAT Rostock, 2012.
- [33] B.S. Tam. A geometric treatment of generalized inverses and semigroups of nonnegative matrices. *Linear Algebra and its Applications*, 41:225–272, 1981.
- [34] L. B. Thomas. Rank factorization of nonnegative matrices (A. Berman). *SIAM Review*, 16(3):393–394, 1974.
- [35] M. Vosough, C. Mason, R. Tauler, M. Jalali-Heravi, and M. Maeder. On rotational ambiguity in model-free analyses of multivariate data. *Journal of Chemometrics*, 20(6-7):302–310, 2006.
- [36] E. Widjaja, C. Li, W. Chew, and M. Garland. Band-target entropy minimization. A robust algorithm for pure component spectral recovery. Application to complex randomized mixtures of six components. *Analytical Chemistry*, 75(17):4499–4507, 2003.