On an SVD-free approach to the complementarity and coupling theory: A note on the elimination of unknowns in sums of dyadic products.

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Abstract

The partial knowledge of the factors in a multivariate curve resolution problem can simplify the factorization problem. The complementarity and coupling theory (J. Chemometrics 26 (2012), 526-537) provides precise mathematical conditions for certain unknown parts of the factors. These constraints are based on a singular value decomposition (SVD) of the data matrix; they have the form of linear or affine linear spaces which contain the unknown parts of the pure component factors.

This paper presents a new and simple SVD-free form of the complementarity and coupling theory. The derivation of these theorems is based on elementary arguments of linear algebra. The new mathematical form of the theory allows its easy and straightforward applicability.

Key words: multivariate curve resolution, nonnegative matrix factorization, complementarity and duality

1. Introduction

We consider the multivariate curve resolution problem to find for a given spectral data matrix D the nonnegative matrix factorization $D = CA^T$ into the pure component factors C and A. The following problem was discussed among some members of a recent conference on chemometrics (SSC14 in Chia, Italy):

> **Problem**: "If in an s-component system all but one pure component spectra are known and if also the spectral data matrix D is given, is then the remaining spectrum aside from scaling uniquely determined?"
>
> **Answer**: No - this is not true.

The simple numerical counterexample

$$D = \begin{pmatrix} \underline{4} & \underline{2} \\ \underline{2} & \underline{2} \end{pmatrix} = \underbrace{\begin{pmatrix} 2 & 2 \\ 0 & 2 \end{pmatrix}}_{C} \underbrace{\begin{pmatrix} \underline{1} & \underline{0} \\ 1 & 1 \end{pmatrix}}_{A^T} = \underbrace{\begin{pmatrix} 3 & 1 \\ 1 & 1 \end{pmatrix}}_{\widetilde{C}} \underbrace{\begin{pmatrix} \underline{1} & \underline{0} \\ 1 & 2 \end{pmatrix}}_{\widetilde{A}^T} \tag{1}$$

shows for a two-component system ($s = 2$) that the spectral data matrix $D \in \mathbb{R}^{2\times 2}$ has two essentially different nonnegative factorizations $D = CA^T$ even though the first rows of A^T and $\widetilde{A}^T$ are the same. Further, no scaling operation or reordering of the components exists, which allows to transform one of these factorizations into the other one. All predetermined quantities are underlined, namely the elements of D and the first rows of A^T and $\widetilde{A}^T$. The second rows of A^T and $\widetilde{A}^T$ are non-collinear vectors. Thus the remaining spectrum is not determined by the given information. This proves that the assumption is not true.

However, the equation (1) also shows that the second columns of C and $\widetilde{C}$ are the same (aside from scaling). Collinearity of these columns is not a coincidence, but is a well-understood result of the so-called complementarity theorem [16]. In fact, if all but one pure component spectra and D are known, then the complementary concentration profile, i.e. the concentration profile of the single component with an unknown spectrum, is uniquely determined aside from scaling.

1.1. Aim and overview

The aim of this paper is to present a comprehensive and easily accessible analysis of how to exploit partial knowledge of the nonnegative factors $C \in \mathbb{R}^{k\times s}$ and $A \in \mathbb{R}^{n\times s}$ in MCR factorizations $D = CA^T$ for $D \in \mathbb{R}^{k\times n}$. Implications on the remaining unknown parts of the factors are derived.

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In contrast to the complementarity and coupling theory from [16] we do not refer to a singular value decomposition of D. Thus all results are presented in an SVD-free manner. In Section 2 we start with a systematic analysis of the problem for rank-2 matrices D. For these rank-2 matrices all derivations are only based on elementary linear algebra. The simple rank-2 approach is generalized to the general problem in Section 3. The guiding line for this deepened analysis is the rank-2 approach. This analysis results in an SVD-free representation of the complementarity and coupling theory. Finally, Section 4 is devoted to the analysis of various cases of simultaneously given spectra and concentration profiles.

2. Analysis of two-component systems

First, we start with the analysis of two-component systems which are represented by rank-2 matrices. This analysis has the advantage of being very simple. Nevertheless, the rank-2 approach is capable to explain the central idea with a few lines of mathematics. Let $D \in \mathbb{R}^{k\times n}$ be the spectral data matrix of a two-component system. Assuming noise-free data, the matrix D has the rank 2 and can be written by a sum of two dyadic products

$$D = CA^T = (c_1, c_2)\,(a_1, a_2)^T = c_1 a_1^T + c_2 a_2^T. \qquad (2)$$

The $c_i \in \mathbb{R}^{k\times 1}$ are the concentration profiles and the $a_i \in \mathbb{R}^{n\times 1}$ are the spectra. For this two-component system we consider the following problem:

Problem 2.1. *For a given spectral data matrix D let additionally one of the four vectors a_1, a_2, c_1 and c_2 be known. Which information can then be derived for the remaining three vectors?*

Without loss of generality Problem 2.1 can be reduced to the case that D and the spectrum a_1 are known. This reduction can be justified as follows:

1. If a_2 is given, then the problem can be traced back to the reduced problem of given a_1 by simply exchanging the indexes 1 and 2.

2. If c_1 is given, then transposition of (2) results in

$$D^T = AC^T = a_1 c_1^T + a_2 c_2^T.$$

   Therein c_i and a_i have just changed their places. Thus all results on Problem 2.1 for given a_1 can be translated to Problem 2.1 for the case of given c_1 by simple transposition.

3. If c_2 is given, then a combination of the previous two steps transforms the problem to the reduced problem with given a_1.

All this justifies to present the problem in the following general form.

Problem 2.2. *Let a $k \times n$ rank-2 matrix D be given so that*

$$D = ab^T + cd^T \qquad (3)$$

with the column vectors $a, c \in \mathbb{R}^k$ and $b, d \in \mathbb{R}^n$. If b is given, which implications can then be drawn on a, c and d?

Problem 2.2 complies with Equation (1) and a given vector b. A solution is derived by eliminating the unknowns in (3). The details of the analysis are presented in

- Section 2.1 for implications of b on c,
- Section 2.2 for implications of b on a,
- Section 2.3 for implications of b on d.

Remark 2.3. *The vector b, whose availability is assumed in the following, must only be known up to scaling. The key point is that for a substitution $b \to \beta b$ with $\beta \neq 0$ all results are still valid if the substitution $a \to a/\beta$ is applied simultaneously. Then* (3) *turns into*

$$D = (a/\beta)(\beta b)^T + cd^T.$$

2.1. From b to c

Let the matrix D and the vector b be given, i.e. a spectrum is predetermined in the sense of (2). Next restrictions on c are derived. The complementarity theorem (Theorem 4.2 in [16]) uses a singular value decomposition (SVD) of D in order to derive restrictions on c. However, one can easily derive and formulate such restrictions without referring to an SVD. The same observation has already been made by Manne [12] where in Section 2.1 the same result has been derived for a two-component system, see also the results of Maeder [10, 9] and Malinowski [11].

1. Let $b \in \mathbb{R}^{n\times 1}$ and $D \in \mathbb{R}^{k\times n}$ be given. Multiplication of (3) with b results in

$$Db = a\|b\|^2 + c(b, d) \qquad (4)$$

   with the Euclidean inner product $(x, y) = x^T y$ and the Euclidean norm $\|x\| = (x^T x)^{1/2}$.

Next (4) is used to eliminate a in (3). One gets

$$D = \frac{Db - c(b,d)}{\|b\|^2} b^T + cd^T$$

or equivalently

$$D(I - \frac{bb^T}{\|b\|^2}) = c \underbrace{(d^T - \frac{(b,d)}{\|b\|^2} b^T)}_{=:y^T}. \qquad (5)$$

For given D and b the left-hand side of (5) can be computed. The key point is that the right-hand side of (5) says that this matrix is a rank-1 matrix because it has the form of a dyadic product cy^T for a vector $y \in \mathbb{R}^{n\times 1}$. Hence cy^T is a matrix which contains in its columns multiples of the vector c.

We express this relation with the **col** operator which extracts from the rank-1 matrix $D(I - \frac{bb^T}{\|b\|^2})$ a normalized vector which is collinear to the desired vector c. Thus

$$\widehat{c} = \mathbf{col}\left(D(I - \frac{bb^T}{\|b\|^2})\right) = c/\gamma \qquad (6)$$

with an (unknown) nonzero number γ so that $\|\widehat{c}\| = 1$.

2. Numerical example: We reconsider Equation (1) with the known matrix D and with given $b = (1,0)^T$. This yields

$$D(I - \frac{bb^T}{\|b\|^2}) = \begin{pmatrix} 4 & 2 \\ 2 & 2 \end{pmatrix}\Big(I - \begin{pmatrix} 1 \\ 0 \end{pmatrix}(1,0)\Big)$$
$$\begin{pmatrix} 4 & 2 \\ 2 & 2 \end{pmatrix}\begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix} = \begin{pmatrix} 0 & 2 \\ 0 & 2 \end{pmatrix}.$$

The columns of this matrix are multiples of the normalized column vector $(1/\sqrt{2}, 1/\sqrt{2})^T$. It holds that

$$\widehat{c} = \mathbf{col}(\begin{pmatrix} 0 & 2 \\ 0 & 2 \end{pmatrix}) = \begin{pmatrix} 1/\sqrt{2} \\ 1/\sqrt{2} \end{pmatrix}$$

and $c = \gamma\widehat{c}$ with an unknown real number γ. In other words the second columns of C and $\widetilde{C}$ in (1) have been recovered aside from scaling.

2.2. From b to a

Let the matrix D and the vector b be given. Restrictions on a are derived next. The coupling theorem (Theorem 4.5 in [16]) uses a singular value decomposition of D in order to derive information on a. Once again, all this can be done without referring to singular vectors of D.

1. For given $D \in \mathbb{R}^{k\times n}$ and $b \in \mathbb{R}^{n\times 1}$ one can write c by (6) in the form

$$c = \gamma\widehat{c} = \gamma\,\mathbf{col}(D(I - \frac{bb^T}{\|b\|^2})).$$

If $c = \gamma\widehat{c}$ with known $\widehat{c}$ and unknown γ is inserted in (3), then we get

$$D = ab^T + \gamma\widehat{c}d^T.$$

Right-multiplication with b results in

$$Db = a\|b\|^2 + \gamma\widehat{c}(b,d).$$

This equation can be solved for a, which yields

$$a = \frac{Db}{\|b\|^2} + \underbrace{(-\gamma)\frac{(b,d)}{\|b\|^2}}_{=:\alpha}\widehat{c} \qquad (7)$$

This is a representation of a in the form of an affine space where $\alpha \in \mathbb{R}$ is a single degree of freedom (and where the other quantities are known).

2. Numerical example: Taking D from Equation (1) and with $b = (1,0)^T$ we get by evaluating (7)

$$a = \frac{Db}{1} + \alpha\begin{pmatrix} 1/\sqrt{2} \\ 1/\sqrt{2} \end{pmatrix} = \begin{pmatrix} 4 \\ 2 \end{pmatrix} + \alpha\begin{pmatrix} 1/\sqrt{2} \\ 1/\sqrt{2} \end{pmatrix}.$$

In fact, setting $\alpha = -2\sqrt{2}$ results in $a = (2,0)^T$. This is the first column of C in (6). Alternatively, $\alpha = -\sqrt{2}$ gives $a = (3,1)^T$, which is the first column of $\widetilde{C}$ in the second factorization in (1).

2.3. From b to d

The non-unique factorization in Equation (1) shows that d cannot be uniquely determined from given D and b. Next the underlying equations are derived systematically.

1. Equation (3) reads in transposed form

$$D^T = ba^T + dc^T.$$

For known D and b, the vector c is determined by Equation (6) in the form $c = \gamma\widehat{c}$ with an unknown parameter γ. Hence,

$$D^T = ba^T + \gamma d\widehat{c}^T.$$

Right-multiplication with $\widehat{c}$ together with the normalization condition $\|\widehat{c}\| = 1$ yield

$$D^T\widehat{c} = b(a,\widehat{c}) + \gamma d.$$

Equation (7) allows to eliminate a. Thus

$$D^T\widehat{c} = b(\frac{Db}{||b||^2} + \alpha\widehat{c},\widehat{c}) + \gamma d.$$

Hence d satisfies

$$\gamma d = D^T\widehat{c} - \frac{b}{||b||^2}(Db,\widehat{c}) - \alpha b. \tag{8}$$

Unfortunately, this equation has two free parameters α and γ. For the given two-component system (or rank-2 system) the three vectors d, $D^T\widehat{c}$ and b are necessarily linearly dependent. In other words, the right-hand side of (8) allows to represent *any* vector in the two-dimensional plane spanned by $D^T\widehat{c}$ and b. Hence, no additional information can be derived on d.

2. Numerical example: For the factorization in Equation (1) with $b = (1,0)^T$ we have already determined $\widehat{c} = (1,1)^T/\sqrt{2}$. The two linearly independent vectors b and $\widehat{c}$ span the 2D plane. Hence, the vector $d = (1,1)^T$, i.e. the second column of A, and also the vector $d = (1,2)^T$, i.e. the second column of $\widetilde{A}$, can be represented by linear combinations of b and $\widehat{c}$. This underpins the non-uniqueness of the factorization in Equation (1).

3. General analysis for s-component systems

The results on two-component systems from Section 2 are next generalized to general s-component systems. To this end let $D \in \mathbb{R}^{k\times n}$ be a rank-s matrix, which describes an s-component system so that

$$D = CA^T = \sum_{i=1}^{s} c_i a_i^T.$$

In order to analyze the impact of partial knowledge of the factors on the remaining parts, we consider the following partitioning of C and A

$$\begin{aligned}
C_1 &= [c_1, \dots c_{s_0}] \in \mathbb{R}^{k\times s_0},\\
C_2 &= [c_{s_0+1}, \dots c_s] \in \mathbb{R}^{k\times s-s_0},\\
C &= [C_1, C_2],\\
A_1 &= [a_1, \dots a_{s_0}] \in \mathbb{R}^{n\times s_0},\\
A_2 &= [a_{s_0+1}, \dots a_s] \in \mathbb{R}^{n\times s-s_0},\\
A &= [A_1, A_2].
\end{aligned}$$

Typically we assume s_0 spectra or s_0 concentration profiles to be given, i.e. C_1 or A_1 are assumed to be given. With these matrices it holds that

$$D = \sum_{i=1}^{s} c_i a_i^T = C_1A_1^T + C_2A_2^T. \tag{9}$$

Remark 3.1. *The partitioning introduced above does not restrict the generality of the approach. If for s_0 components, either the spectra or the concentration profiles, are known, then let*

$$K = \{i_1, i_2, \dots, i_{s_0}\}$$

("K" for known) be the index set of the known components. Further, let

$$U = \{1, 2, \dots, s\} \setminus K$$

be the set of the remaining indexes of the unknown ("U" for unknown) components. With these two sets the following theory works in the same way for the matrices

$$\begin{aligned}
C_1 &= [c_i]_{i\in K}, \quad & C_2 &= [c_i]_{i\in U}, \quad & C &= [C_1, C_2],\\
A_1 &= [a_i]_{i\in K}, \quad & A_2 &= [a_i]_{i\in U}, \quad & A &= [A_1, A_2].
\end{aligned}$$

3.1. The complementarity theory

Let either A_1 or C_1 be given. Then the complementarity theorem 4.2 in [16] provides conditions on the complementary factor, i.e. either on C_2 or on A_2. The mathematical analysis in [16] is based on a singular value decomposition of D. There the restricting space is constructed as the image of the null space of the matrix A_1V, where V contains in its columns the first s_0 right singular vectors of D. For details see Equation (7) in [16]. The new theorem provides the same information without referring to an SVD of D. The new proof is a direct analog of the vectorial argumentation in Section 2.1. Moreover, this presentation of the complementarity theory is strongly related to the first theorem of Manne in [12]. Manne uses an orthonormal basis by the vectors w_m of the known parts of the factor and constructs from these basis vectors w_m a matrix W. Then $I - WW^T$ is used as an orthogonal projector from the spectral data matrix on the unknown part of the factor. The following representation of the complementarity theorem does the same; the relationship to orthogonal projectors is discussed in Section 3.1.1.

Theorem 3.2 (Complementarity theorem)**.** *Let D together with s_0 linearly independent spectra be given. These spectra form the columns of A_1. Then the $(s-s_0)$-dimensional column space of the matrix C_2, which is spanned by the concentration profiles of the complementary components, is equal to the column space of the matrix*

$$D\left(I - A_1(A_1^TA_1)^{-1}A_1^T\right). \tag{10}$$

If, alternatively, C_1 with linearly independent columns is given, then the column space of A_2, which is spanned

by the spectra of the complementary components, is equal to the $(s - s_0)$*-dimensional column space of the matrix*

$$D^T \left(I - C_1 (C_1^T C_1)^{-1} C_1^T \right). \tag{11}$$

Proof. Right-multiplication of (9) with A_1 results in

$$DA_1 = C_1 A_1^T A_1 + C_2 A_2^T A_1.$$

The s_0 given spectra are linearly independent so that A_1 is a rank-s_0 matrix. Thus $A_1^T A_1$ is an invertible $s_0 \times s_0$ matrix. Hence the last equation can be solved for C_1

$$C_1 = (DA_1 - C_2 A_2^T A_1)(A_1^T A_1)^{-1}. \tag{12}$$

Insertion of (12) in (9) yields

$$\begin{aligned} D &= C_1 A_1^T + C_2 A_2^T \\ &= (DA_1 - C_2 A_2^T A_1)(A_1^T A_1)^{-1} A_1^T + C_2 A_2^T, \end{aligned}$$

which can be written as

$$\begin{aligned} &D \left[I - A_1 (A_1^T A_1)^{-1} A_1^T \right] \\ &= C_2 \left[A_2^T - A_2^T A_1 (A_1^T A_1)^{-1} A_1^T \right]. \end{aligned} \tag{13}$$

This matrix equation says that the column space of C_2 is spanned by the columns of the matrix on the left-hand side of (13), i.e. $D[I - A_1(A_1^T A_1)^{-1} A_1^T]$.

Equation (11) follows by applying the first statement to the transposed form of (9)

$$D^T = A_1 C_1^T + A_2 C_2^T. \tag{14}$$

Thus (11) can be derived from (10) by substituting $D \to D^T$ and $A_1 \to C_1$ in (10). □

The matrix (10) can easily be computed for given D and A_1 by solving s_0 linear systems of equations within the regular $s_0 \times s_0$ matrix $A_1^T A_1$. Analogously (11) can be computed from D and C_1.

Corollary 3.3. *If all but one spectra are known, i.e.* $s_0 = s - 1$*, then the concentration profile of the last component* c_s *is uniquely determined (aside from scaling). It holds that*

$$c_s = \mathbf{col}(D(I - A_1 (A_1^T A_1)^{-1} A_1^T)),$$

with the column space operator **col** *as defined in* (6)*. Similarly, if* $s-1$ *concentration profiles are given by* C_1*, then the spectrum of the complementary component is given by*

$$a_s = \mathbf{col}(D^T [I - C_1 (C_1^T C_1)^{-1} C_1^T]).$$

Algorithm 1 Simplified complementarity.

Require: $D \in \mathbb{R}^{k \times n}$, $A \in \mathbb{R}^{n \times (s-1)}$, s.
Ensure: Complementary concentration c.

```
1: C=D*(eye(n)-A*inv(A'*A)*A');
2: c=sqrt(diag(C'*C));
3: if max(c) < -min(c), c = -c; end
4: plot(c);
```

Algorithm 2 Simplified complementarity - noisy data.

Require: $D \in \mathbb{R}^{k \times n}$, $A \in \mathbb{R}^{n \times (s-1)}$, s.
Ensure: Complementary concentration c.

```
1: C=D*(eye(n)-A*inv(A'*A)*A');
2: [c,si,v]=svds(C,1);
3: if max(c) < -min(c), c = -c; end
4: plot(c);
```

Proof. The matrix $(I - A_1(A_1^T A_1)^{-1} A_1^T)$ is a rank-1 matrix and the assertion is just a special case of Theorem 3.2 for $s_0 = s - 1$. □

In [17], see Algorithm 1, the Matlab code is provided for an implementation of the complementarity theory for the special case of $s_0 = s - 1$. With the simplified form (10) or (11) the implementation is possible without referring to the SVD of D. In line 1 of Algorithm 1 the matrix C whose columns are all multiples of the desired complementary concentration profile c is constructed by a single command. In line 2 the vector c is extracted in a numerically stable way. A possibly wrong sign of c is corrected in line 3 and finally the concentration profile is plotted.

In the case of perturbed data, that is D has a rank larger than s, the matrix $D * (eye(n, n) - A(A^T * A)^{-1} A^T)$ is no longer a rank-1 matrix. Then line 2 in Algorithm should be substituted by a better suited way to extract the vector, which generates the dominant part. The dominant left-singular vector is the optimal choice, see Algorithm 2.

3.1.1. Complementarity and projection operators

The complementarity theorem comprises a fundamental structure from linear algebra. The right-hand factors in Equations (10) and (11) are orthogonal projection operators. This is explained in the following.

Remark 3.4.

1. *In Equation* (10) *the right-hand factor*

$$P = I - A_1 (A_1^T A_1)^{-1} A_1^T$$

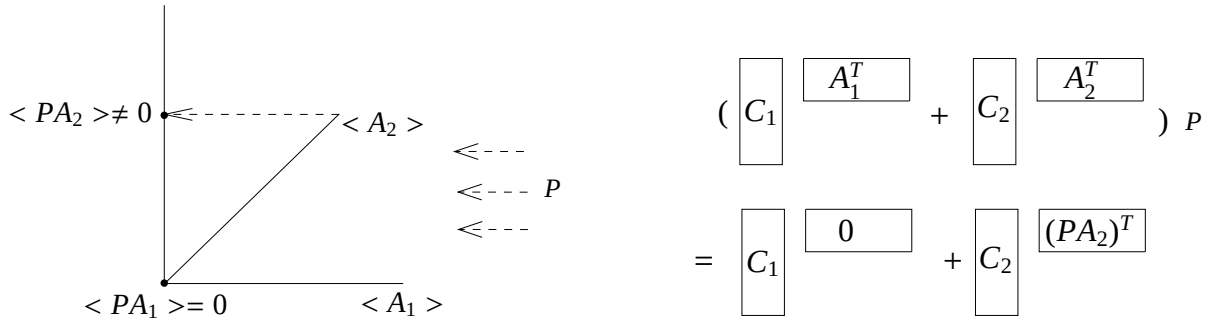

Figure 1: The geometry of the projection P. Left: P maps the column space $< A_1 >$ of the matrix A_1 to null space. It also projects the column space of A_2 to the orthogonal complement $< A_1 >^{\perp}$. Right: The same projection applied from the right-hand side to $D = C_1A_1^T + C_2A_2^T$ maps the column space of D to the desired column space of C_2.

is an orthogonal projection operator on the orthogonal complement of the column space of $A_1 \in \mathbb{R}^{n\times s_0}$. For basic properties of orthogonal projection operators see monographs on matrix algebra, e.g. Section 2.5.1 in [6] or Section 5.13 in [13]. See also Figure 1 for an illustration of the geometric properties.

Similarly, the matrix $Q = I - C_1(C_1^TC_1)^{-1}C_1^T$ is an orthogonal projection operator on the orthogonal complement of the column space of $C_1 \in \mathbb{R}^{k\times s_0}$.

2. *The fundamental functionality of the complementarity theory can be expressed with respect to the projection operator notation as follows. Equation* (10) *is rewritten as*

$$\begin{aligned} DP &= CA^TP \\ &= [C_1, C_2][A_1, A_2]^TP \\ &= [C_1, C_2]\begin{pmatrix} A_1^TP \\ A_2^TP \end{pmatrix} = [C_1, C_2]\begin{pmatrix} (PA_1)^T \\ (PA_2)^T \end{pmatrix} \\ &= [C_1, C_2]\begin{pmatrix} 0 \\ (PA_2)^T \end{pmatrix} \\ &= 0 + C_2(PA_2)^T. \end{aligned}$$

This again shows that the column space of the accessible matrix DP provides the column space of the unknown matrix C_2. The right subplot of Figure 1 illustrates the impact of the projection operator P in the sum of dyadic products $D = C_1A_1^T + C_2A_2^T$.

3.2. The coupling theory

Once again, we assume s_0 pure component spectra in the columns of A_1 to be given. We derive implications on the concentration profiles of the remaining components, i.e. C_2. The following theorem is the SVD-free counterpart of Theorem 4.6 in [16].

Theorem 3.5 (Coupling theory)**.** *Let D together with A_1 be given. Then the ith concentration profile c_i for $i = 1, \ldots, s_0$ is contained in the $(s - s_0)$-dimensional affine subspace*

$$c_i \in DA_1(A_1^TA_1)^{-1}e_i + \operatorname{span}\{Z\} \tag{15}$$

with

$$Z = D\left[I - A_1(A_1^TA_1)^{-1}A_1^T\right].$$

Therein e_i is the ith standard basis vector (the ith column of the identity matrix) and span$\{Z\}$ *is the $(s - s_0)$-dimensional column space of Z.*

Secondly, if C_1 with linearly independent columns is given, then for $i = 1, \ldots, s_0$ the ith spectrum a_i is contained in the $(s - s_0)$-dimensional affine subspace

$$a_i \in D^TC_1(C_1^TC_1)^{-1}e_i + \operatorname{span}\{Y\} \tag{16}$$

with

$$Y = D^T\left[I - C_1(C_1^TC_1)^{-1}C_1^T\right].$$

Proof. Right multiplication of (12) with the ith standard basis vector e_i an $i \in \{1, \ldots, s_0\}$ yields the ith concentration profile

$$c_i = C_1e_i = DA_1(A_1^TA_1)^{-1}e_i - C_2A_2^TA_1(A_1^TA_1)^{-1}e_i. \tag{17}$$

In this equation A_2 is unknown and thus c_i cannot be determined in a unique way. However, the $(s - s_0)$-dimensional column space of C_2 according to (13) is equal to the column space of

$$Z = D\left[I - A_1(A_1^TA_1)^{-1}A_1^T\right].$$

Hence,

$$c_i \in DA_1(A_1^TA_1)^{-1}e_i + \operatorname{span}\{Z\}.$$

A direct application of this first result to the transposed decomposition (14) results in (16). □

4. Analysis of cases of simultaneously known spectra and concentration profiles

Up to now only those cases have been analyzed in which either pure component spectra or pure component concentration profiles are known. This theory can be extended to cases of simultaneously known spectra and concentration profiles.

As in Section 3 we consider a rank-s matrix $D \in \mathbb{R}^{k\times n}$ and its dyadic-sum representation

$$D = \sum_{i=1}^{s} c_i a_i^T \tag{18}$$

with the column vectors $c_i \in \mathbb{R}^k$ and $a_i \in \mathbb{R}^n$. We analyze in

- Section 4.1 the case of simultaneously given c_ℓ and a_ℓ (same index ℓ),
- Section 4.2 the case of given c_ℓ and a_m with different indexes $\ell \neq m$.

4.1. Simultaneously given pairs (c_ℓ, a_ℓ) and matrix deflation

If for the same component, i.e. the same index ℓ, the concentration profile c_ℓ is given together with the spectrum a_ℓ, then this ℓ-th component can completely be removed from the system. Mathematically this is a subtraction of the rank-1 matrix $c_\ell a_\ell^T$. Then

$$D - c_\ell a_\ell^T = \sum_{\substack{i=1\\ i\neq\ell}}^{s} c_i a_i^T$$

is a "deflated" rank-$(s-1)$ matrix. The pure component factorization problem can then be considered for the deflated matrix. This makes the problem more simple. This problem of splitting-off certain components is well-known from the Rank Annihilation Factor Analysis (RAFA), see, e.g., [8, 1]. See also [4] on rank-1 downdates in the thematic frame of nonnegative matrix factorizations.

However, in typical applications c_ℓ and a_ℓ are only known up to scaling (as spectra from the shelf or typical assumptions on the concentration profiles are not given in absolute values). Instead of c_ℓ we consider a collinear (nonzero) vector $\widetilde{c_\ell}$ and instead of a_ℓ we consider the collinear vector $\widetilde{a_\ell}$. We assume that only $\widetilde{c_\ell}$ and $\widetilde{a_\ell}$ are known in order to express the loss of the scaling information. Then we consider the matrix

$$\widetilde{D} = D - \omega \widetilde{c_\ell}\,\widetilde{a_\ell}^T.$$

The problem is to determine the parameter ω so that $\widetilde{D}$ is a deflated rank-$(s-1)$ matrix.

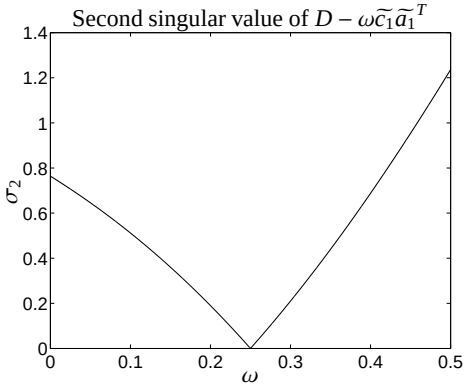

Figure 2: The second singular value of $D - \omega\widetilde{c_1}\widetilde{a_1}^T$ as a function of $\omega \in [0, 0.5]$. For $\omega = 1/4$ the second singular value is zero. Thus the matrix has the rank 1.

This problem can easily be solved numerically by computing the sth singular value of the matrix $\widetilde{D}$ as a function of ω. This is demonstrated numerically for the example problem (1). We consider the first row of Equation (1) with

$$D = \begin{pmatrix} 4 & 2 \\ 2 & 2 \end{pmatrix}$$

and $\widetilde{c_1} = (4, 0)^T$ and $\widetilde{a_1} = (2, 0)^T$. Hence

$$\widetilde{D} = D - \omega\widetilde{c_1}\widetilde{a_1}^T = \begin{pmatrix} 4 & 2 \\ 2 & 2 \end{pmatrix} - \omega\begin{pmatrix} 8 & 0 \\ 0 & 0 \end{pmatrix} = \begin{pmatrix} 4-8\omega & 2 \\ 2 & 2 \end{pmatrix}.$$

Only for $\omega = 1/4$ the matrix $\widetilde{D}$ is a rank-1 matrix and the second singular value of this matrix equals 0.

The numerical evaluation of $\sigma_2(D - \omega\widetilde{c_1}\widetilde{a_1}^T)$, where σ_2 denotes the second singular value of the ω-dependent matrix, is shown in Figure 2 for $\omega \in [0, 0.5]$. The clear minimum at $\omega = 1/4$ confirms the correctness.

4.2. Independent pairs (c_ℓ, a_m) with $\ell \neq m$

In order to illustrate that for independent indexes ℓ and m one cannot extract very much information, we reconsider the rank-2 model problem

$$D - ab^T = cd^T$$

from Section 2. We assume that D, b and c are the known quantities. It is an interesting fact that even then the factorization is not unique. Different factorizations exist, which cannot be converted into each other by trivial scaling or reordering operations. This is illustrated,

once again, by the example matrix D from (1).

$$D = \begin{pmatrix} \underline{4} & \underline{2} \\ \underline{2} & \underline{2} \end{pmatrix} = \underbrace{\begin{pmatrix} 2 & \underline{2} \\ 0 & \underline{2} \end{pmatrix}}_{C} \underbrace{\begin{pmatrix} \underline{1} & \underline{0} \\ 1 & 1 \end{pmatrix}}_{A^T} = \underbrace{\begin{pmatrix} 3 & \underline{2} \\ 1 & \underline{2} \end{pmatrix}}_{\widetilde{C}} \underbrace{\begin{pmatrix} \underline{1} & \underline{0} \\ \underline{\frac{1}{2}} & 1 \end{pmatrix}}_{\widetilde{A}^T} \tag{19}$$

Given matrix elements are underlined, namely D as well as b and c. The first columns of C and $\widetilde{C}$ are non-collinear vectors. The same holds for the second rows of A and $\widetilde{A}$. Hence c and d cannot be uniquely determined. Hence essentially different nonnegative factorizations exist.

5. Numerical studies in the literature

The complementarity and coupling theory has already successfully been applied to model and experimental FT-IR data from the hydroformylation process in [16] and to UV-VIS data from the formation of hafnacyclopentene in [18]. Aspects of its implementation in its SVD-bound form are presented in [17]. Further, implications on the Area of Feasible Solutions (AFS) are treated in [19].

Beyramysoltan et al. [3, 2] and Rajkó et al. [15] apply the complementarity theory, also called duality theory [5, 14], primarily to model data. In the recent work [7] Hemmateeneejad et al. use the theory in order to extract spectral information on methanol-water associates.

The new SVD-free approach to the complementarity and coupling theory for all these model and experimental data sets produces the same mathematical results. For perturbed experimental data for an s-component system, one can apply the theory to the rank-s approximation of the spectral data matrix.

6. Conclusion

In recent years the complementarity/duality theory with its conceptual basis by Manne, Maeder and Malinowski has increasingly gained importance as a valuable tool for extracting pure component information from systems with partially known factors. The SVD-free approach to the complementarity and coupling theory can hopefully foster the widespread application of these techniques. The results of the SVD-free complementarity theory are equivalent to the Manne theory. The SVD-free coupling theory is a new generalization. Finally, a deepened understanding of the complementarity/coupling theory is supported by its interpretation in terms of orthogonal projection operators, see Remark 3.4, due to the simple and evident geometry of a projection step.

References

[1] H. Abdollahi and F. Nazari. Rank annihilation factor analysis for spectrophotometric study of complex formation equilibria. *Anal. Chim. Acta*, 486:109–123, 2003.

[2] S. Beyramysoltan, H. Abdollahi, and R. Rajkó. Newer developments on self-modeling curve resolution implementing equality and unimodality constraints. *Anal. Chim. Acta*, 827(0):1–14, 2014.

[3] S. Beyramysoltan, R. Rajkó, and H. Abdollahi. Investigation of the equality constraint effect on the reduction of the rotational ambiguity in three-component system using a novel grid search method. *Anal. Chim. Acta*, 791(0):25–35, 2013.

[4] M. Biggs, A. Ghodsi, and S. Vavasis. Nonnegative Matrix Factorization via Rank-one Downdate. In *Proceedings of the 25th International Conference on Machine Learning*, ICML '08, pages 64–71, New York, NY, USA, 2008. ACM.

[5] P.J. Gemperline. Computation of the range of feasible solutions in self-modeling curve resolution algorithms. *Anal. Chem.*, 71(23):5398–5404, 1999.

[6] G.H. Golub and C.F. Van Loan. *Matrix Computations*. Johns Hopkins Studies in the Mathematical Sciences. Johns Hopkins University Press, 2012.

[7] B. Hemmateenejad, Z. Shojaeifard, M. Shamsipur, K. Neymeyr, M. Sawall, and A. Mohajeri. Solute-induced perturbation of methanol-water association. *RSC Adv.*, 5:71102–71108, 2015.

[8] C.-N. Ho, G.D. Christian, and E.R. Davidson. Application of the method of rank annihilation to quantitative analyses of multicomponent fluorescence data from the video fluorometer. *Anal. Chem.*, 50(8):1108–1113, 1978.

[9] M. Maeder. Evolving factor analysis for the resolution of overlapping chromatographic peaks. *Anal. Chem.*, 59(3):527–530, 1987.

[10] M. Maeder and A. D. Zuberbühler. The resolution of overlapping chromatographic peaks by evolving factor analysis. *Anal. Chim. Acta*, 181(0):287–291, 1986.

[11] E.R. Malinowski. Window factor analysis: Theoretical derivation and application to flow injection analysis data. *J. Chemom.*, 6(1):29–40, 1992.

[12] R. Manne. On the resolution problem in hyphenated chromatography. *Chemom. Intell. Lab. Syst.*, 27(1):89–94, 1995.

[13] C.D. Meyer. *Matrix Analysis and Applied Linear Algebra*. Society for Industrial and Applied Mathematics, Philadelphia, PA, USA, 2000.

[14] R. Rajkó. Natural duality in minimal constrained self modeling curve resolution. *J. Chemom.*, 20(3-4):164–169, 2006.

[15] R. Rajkó, H. Abdollahi, S. Beyramysoltan, and N. Omidikia. Definition and detection of data-based uniqueness in evaluating bilinear (two-way) chemical measurements. *Anal. Chim. Acta*, 855:21 – 33, 2015.

[16] M. Sawall, C. Fischer, D. Heller, and K. Neymeyr. Reduction of the rotational ambiguity of curve resolution technqiues under partial knowledge of the factors. Complementarity and coupling theorems. *J. Chemom.*, 26:526–537, 2012.

[17] M. Sawall, C. Kubis, R. Franke, D. Hess, D. Selent, A. Börner, and K. Neymeyr. How to apply the complementarity and coupling theorems in MCR methods: Practical implementation and

application to the Rhodium-catalyzed hydroformylation. *ACS Catal.*, 4:2836–2843, 2014.

[18] M. Sawall and K. Neymeyr. A fast polygon inflation algorithm to compute the area of feasible solutions for three-component systems. II: Theoretical foundation, inverse polygon inflation, and FAC-PACK implementation. *J. Chemom.*, 28:633–644, 2014.

[19] M. Sawall and K. Neymeyr. On the area of feasible solutions and its reduction by the complementarity theorem. *Anal. Chim. Acta*, 828:17–26, 2014.