On the Area of Feasible Solutions for rank-deficient problems: I. Introduction of a generalized concept.

Mathias Sawall[a], Klaus Neymeyr[a,b]

[a] *Universität Rostock, Institut für Mathematik, Ulmenstraße 69, 18057 Rostock, Germany*
[b] *Leibniz-Institut für Katalyse, Albert-Einstein-Straße 29a, 18059 Rostock*

Abstract

Rank-deficiency of a spectral data matrix means that its rank is smaller than the number of the anticipated chemical components. A rank-deficiency can hide the true chemical structure of the underlying pure components and complicates the application of multivariate curve resolution and self-modeling curve resolution techniques. A new approach for the analysis of the factor ambiguities is introduced and the Area of Feasible Solutions (AFS) is generalized to rank-deficient spectral data. The extended tools are tested for the Michaelis-Menten kinetics and abstract model data.

Key words: multivariate curve resolution, self-modeling curve resolution, rank-deficiency, area of feasible solutions, polygon inflation.

1. Introduction

An elementary example for the "loss of information" in bilinear matrix modeling is the product

$$\begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} = \begin{pmatrix} 0 & 0 \\ 0 & 0 \end{pmatrix}$$

with the rank 0 whereas the factors have the ranks 1. The general law

$$\operatorname{rank}(AB) \leq \min(\operatorname{rank}(A), \operatorname{rank}(B))$$

for all matrices A and B (so that AB exists) says that matrix multiplication can delete rank - and, in fact, it does in the example above.[1] This leads us to the following problem.

> **Question:** *Assume the nonnegative matrices A or B to have a larger rank than AB and let only AB be given. How much information on the possible matrix factors A and B can be recovered from AB?*

This paper aims at giving an answer. The background of the question is the chemometric curve resolution problem to find for a given nonnegative matrix D the possible nonnegative factors C and S^T so that

$$D = CS^T. \tag{1}$$

Then D represents given spectral mixture data. We are interested in the underlying concentration profiles in time of the pure components (forming the columns of C) and the associated pure component spectra (columns of S), see [24, 23]. Equation (1) is the Lambert-Beer law in its time and frequency dependent form. Here we assume that the components of all matrices are nonnegative even though the acceptance of small negative components can be useful for noisy or biased data [37].

[1] We would like to point out that this example has no chemical background, but may serve to caricature in a compact, mathematical form the core phenomenon behind rank-deficient chemical systems and its underlying linear dependencies.

The main hurdle of the recovery problem is the intrinsic ambiguity of the factorization problem: Not only one factorization exists, but a continuum or even continua of possible factors C and S. Multivariate curve resolution methods (MCR) filter out a single solution whereas self-modeling curve resolution (SMCR) techniques in dependence of the underlying model have the potential to make any feasible solution accessible. The problem of multiple solutions is well-known under the keyword of rotational ambiguity [25, 23, 2]. More precisely it should be called a transformation ambiguity since the related matrices are in no way only orthogonal rotation matrices but general invertible matrices. The entire set of all possible profiles can be represented by the so-called Area of Feasible Solutions (AFS), see e.g. [7, 31, 35, 14, 36]. The AFS has been established as a powerful instrument to represent the bands of all possible spectra and concentration profiles that can appear in the factorization (1).

In this work we suggest a generalization of the AFS for rank-deficient spectral data. If D suffers from rank-deficiency, then at least one of the factors C and S is not of full rank and vice versa, see [4, 19, 33, 12, 9] among others. The fundamental paper of Amrhein et al. [4] systematically describes and analyzes various reaction schemes including a rank deficiency. It discusses data augmentation techniques in the context of experimental planning in order to avoid the annoying influence of rank deficiencies. The analysis of Amrhein and coauthors is of a significant mathematical nature, but also includes practical guidelines for data pretreatment. In contrast to this work, our focus is on the impact of rank deficiency on the factor ambiguity.

Rank-deficiency complicates the pure component factorization and can result in chemically meaningless matrix factors. Here we distinguish the following two situations:

1. For the given spectral data matrix D with the rank s there is no nonnegative so-called *rank or full-rank factorization* [41]. In other words, there are no nonnegative matrices C and S of rank s so that (1) holds.
2. For the given spectral data matrix D with the rank s nonnegative full-rank factorizations exist, but none of the factors has a meaningful chemical interpretation. Only if one of the factors C and S is allowed to have at least $s + 1$ columns, then chemically interpretable factors can be determined.

Here we focus on the first case, which automatically alarms the user since an empty AFS is a clear indicator that the chemometric analysis has not been successful. The second case, which is to be treated in a forthcoming publication, is somewhat harder since increasing the rank in order to attain interpretable factors is a more complex procedure. However, even the first case contains a rich structure that is analyzed here.

It is a known fact [4] that rank-deficiency can be observed if the number of independent reactions is smaller than the number of absorbing species. The simple kinetic $X + Y \to Z$ serves to explain this. The concentration factor satisfies $\operatorname{rank}(C) = 2$ (closure constraint) and if the spectra are complicated enough (no linear dependence), then $\operatorname{rank}(S) = 3$ holds. Then $D = CS^T$ has the rank 2 and is a rank-deficient matrix; see the second case above.

This paper includes a general definition of the AFS that embraces rank-deficient and non-rank-deficient problems. We call the latter problems *rank-regular*. Here the analysis focuses on rank-deficient problems. In contrast to rank-regular problems we cannot continue to use a truncated singular value decomposition (SVD) of D for a simultaneous reconstruction of C and S. Certain fundamental changes are required for the computational procedure. A further difference to rank-regular problems is that the AFS can only be computed for the factor that causes the rank-deficiency and not for the dual factor.

The paper is organized as follows: In Sec. 2 the MCR problem and the AFS are reviewed for the (classical) rank-regular problems. Then Sec. 3 explains the mathematical challenges of rank-deficient problems and introduces the generalized AFS for these problems. The underlying analysis is presented in Sec. 4. A numerical approximation method is introduced in Sec. 5. Numerical results are discussed for the Michaelis-Menten kinetics and abstract model data in Secs. 6 and 7.

2. The MCR problem and the AFS for rank-regular data

Let D be a $k \times n$-matrix containing k spectra in its rows. Each spectrum is recorded at n frequency channels. The MCR problem is to find the possible nonnegative factors C and S according to (1). If $s = \operatorname{rank}(D)$, then rank-regularity of the data implies that $C \in \mathbb{R}^{k\times s}$ and $S \in \mathbb{R}^{n\times s}$ with $D = CS^T$. A possible approach to find proper C and S is to compute a truncated singular value decomposition $D = U\Sigma V^T$ and then to form

$$C = U\Sigma T^{-1}, \qquad S^T = TV^T \tag{2}$$

with those regular matrices $T \in \mathbb{R}^{s\times s}$ that result in nonnegative C and S. See, e.g., [22, 25, 23] for more details on MCR techniques and the SVD-based construction of C and S.

Typically, many regular T exist with $C, S \geq 0$. Such solutions (C, S) can be expressed in terms of bands of possible spectra and bands of concentration profiles. The AFS pursues the concept to represent in a low-dimensional way all profiles that can be part of a nonnegative factorization of D. See the references [22, 7, 31, 15, 37, 39, 14, 35, 36, 27] and many others. Without loss of generality T can be assumed to be of the form

$$T = \begin{pmatrix} 1 & x^T \\ \mathbf{1} & W \end{pmatrix} \tag{3}$$

with $\mathbf{1} = (1, \ldots, 1)^T \in \mathbb{R}^{s-1}$ and $W \in \mathbb{R}^{(s-1)\times(s-1)}$. The vector $x \in \mathbb{R}^{s-1}$ is called *feasible* if it can be supplemented by a proper W in (3) so that T is a regular matrix and $C = U\Sigma T^{-1} \geq 0$ as well as $S^T = TV^T \geq 0$. Then the AFS is defined as

$$\mathcal{M} = \left\{ x \in \mathbb{R}^{s-1} : \quad \text{exists } W \in \mathbb{R}^{(s-1)\times(s-1)} \text{ in (3) with } \operatorname{rank}(T) = s \text{ and } C, S \geq 0 \right\}. \tag{4}$$

The AFS has a strong underlying geometric theory, see for instance [7, 31, 20, 36]. Decisive elements of this theory are the superset of the AFS (called outer polygon or FIRPOL) $\mathcal{F} = \left\{ x \in \mathbb{R}^{s-1} : \ (1, x^T)V^T \geq 0 \right\}$ as well as its subset $\mathcal{I} = \operatorname{convhull}(\{a_1, \ldots, a_k\})$ with the vectors $a_i \in \mathbb{R}^{s-1}$ given by

$$a_i = \frac{(U\Sigma)^T(2 : s, i)}{(U\Sigma)^T(1, i)}, \quad i = 1, \ldots, k. \tag{5}$$

The two sets $\mathcal{F}$ and $\mathcal{I}$ are polyhedra and polygons for $s = 3$ in the two-dimensional AFS-plane. With these polyhedra a (feasible) nonnegative matrix factorization of D can be represented by a simplex contained in $\mathcal{F}$ and which includes $\mathcal{I}$ and vice versa [7, 31, 20]. Geometrically these relations can be expressed in a way that x is feasible if and only if $x \in \mathcal{F}$ and further $s - 1$ vectors $y_1, \ldots, y_{s-1} \in \mathcal{F}$ exist so that the simplex with the vertices $x, y_1, \ldots, y_{s-1}$ encloses $\mathcal{I}$.

The computation of the AFS is a challenging task even for small dimensions. Computational methods are known for systems with two, three and four components, namely by geometric construction [22, 7, 31, 20, 36], numerical optimization-based approximations [42, 1, 15, 16, 37, 39] as well as a hybrid algorithm [36, 38].

3. Rank-deficient problems and its AFS

An MCR-problem suffers from a rank-deficiency if at least one of the chemically true factors C and S has a rank which is smaller than the number of underlying species. A rank-deficiency can be known a priori, e.g., if for a given kinetic the number of independent reactions is smaller than the number of reacting species. Not only C, but also the factor S can cause a rank-deficiency [33]. If the rank-deficiency is not known in advance, then it can be detected if no or no chemically interpretable factorization $D = CS^T$ with nonnegative factors $C \in \mathbb{R}^{k\times s}$ and $S \in \mathbb{R}^{n\times s}$ exists. Rank deficiency can often be avoided by data augmentation. Amrhein et al. [4] discuss such techniques under the keyword of *rank augmentation*, which can be gained by multiple process runs or the addition of absorbing components in the course of the chemical reaction. Nevertheless, these authors point out that rank deficiency must be expected "in many practical reaction networks". Hence techniques for rank deficient or nearly rank deficient systems appear to be necessary whenever it is too costly or even impossible to change the experimental design or to re-run the reaction under different conditions.

3.1. Rank-deficiency and the nonnegative rank of a matrix

An important characteristic number in the context of rank-deficient problems is the *nonnegative rank* of a matrix [17, 8, 13]. The notion of the nonnegative rank is the basis for several theorems on the existence or non-existence of nonnegative matrix factorizations [41, 8].

Definition 3.1 (Nonnegative rank)**.** *Let $D \in \mathbb{R}^{k\times n}$ be a nonnegative matrix. The nonnegative rank $m := \operatorname{rank}_+(D)$ of D is the least integer $m \in \mathbb{N}$ so that nonnegative matrices $C \in \mathbb{R}^{k\times m}$ and $S \in \mathbb{R}^{n\times m}$ exist with $D = CS^T$.*

According to Def. 3.1 a matrix D has a rank-deficiency if its rank is smaller than its nonnegative rank, namely $\text{rank}(D) < \text{rank}_+(D)$. Known facts, see [8], are that $\text{rank}(D) \leq \text{rank}_+(D) \leq \min(k, n)$ and $\text{rank}_+(D) = \text{rank}(D)$ for any matrix D with the rank $s = 2$. Thus $s = 3$ is the smallest rank of D for which D can be rank-deficient and $k = n = 4$ would be the associated smallest dimension. In [41] Thomas has provided the example

$$D = \begin{pmatrix} 1 & 1 & 0 & 0 \\ 1 & 0 & 1 & 0 \\ 0 & 1 & 0 & 1 \\ 0 & 0 & 1 & 1 \end{pmatrix} \in \mathbb{R}^{4\times 4} \tag{6}$$

with the rank 3, but for which no factors $C,\ S \in \mathbb{R}_+^{4\times 3}$ exist with $D = CS^T$.

Remark 3.2. *These mathematical properties from [8] have interesting implications (not only) for the simple reaction $X + Y \rightarrow Z$. The associated spectral mixture data matrix D has the rank 2. The mathematical theory predicts the existence of a nonnegative factorization of D with factors of the rank 2. However, these factors cannot represent the true chemical solution as they cannot separate the contributions from X and Y. In other words, the AFS is not empty but does not contain the chemically correct solution. Such a solution can be gained if the spectral factor is allowed to have the rank 3.*

Def. 3.1 motivates to consider the following general factorization problem in idealized, namely noise-free form.

Definition 3.3. *Let $D \in \mathbb{R}^{k\times n}$ be a nonnegative matrix with $s = \text{rank}(D)$ and $m = \text{rank}_+(D) \geq s$. The generalized nonnegative matrix factorization problem for D is to determine nonnegative factors $C \in \mathbb{R}^{k\times m}$ and $S \in \mathbb{R}^{n\times m}$ with $D = CS^T$.*

Definition 3.3 includes rank-regular problems as $m = s$ is possible. The generalized factorization problem with $m > s$ includes the difficulty that it is not possible to compute the two factors C and S simultaneously by means of a truncated SVD as in (2). Instead, it is only possible to compute the factor that causing the rank-deficiency. Only this factor with the rank s can be represented by the associated basis of the s singular vectors belonging to the s nonzero singular values. For the representation of the other factor with rank $m > s$ only s singular vectors are available. The remaining $m - s$ singular vectors are missing and are completely undetermined (aside from their orthogonality to the given s singular vectors). However, nonnegative least squares techniques (namely least squares approaches under nonnegativity constraints, NNLS) or geometric arguments can be useful to compute at least one factorization. However, no approach is available to compute the set of all nonnegative factorizations. Furthermore, if in practical computations a rank-deficiency is detected due to non-interpretable factors, then it is not clear in advance which of the two factors C and S has caused the rank-deficiency.

3.2. The AFS for rank-deficient problems

The AFS for rank-regular problems is briefly introduced in Sec. 2. Next an extension is suggested for rank-deficient problems. The basic idea remains the same, but for the construction of the factors C and S the number of required species $m = \max(\text{rank}(C), \text{rank}(S))$ is larger than the rank s of D.

For ease of representation we assume for the rest of this section and in Sec. 4 that the rank-deficiency is caused by the factor S. This assumption does not restrict the generality of the approach as the procedure can then be applied to $D^T = SC^T$. According to the definition 3.3 the aim is to compute the set of all possible spectral profiles, namely all possible first columns of the spectral factor S, that can be extended to a nonnegative pure component decomposition. This set of feasible spectral profiles reads (where $\mathbb{R}_+$ is the set of the real nonnegative numbers)

$$\mathcal{S} = \left\{ a \in \mathbb{R}^n : \text{exist } C \in \mathbb{R}_+^{k\times m},\ S \in \mathbb{R}_+^{n\times m} \text{ with } S(:,1) = a,\ \text{rank}(S) = s \text{ and } D = CS^T \right\} \tag{7}$$

with $m = \text{rank}_+(D)$ being the number of components.

Once again, a low-dimensional representation of the elements of $\mathcal{S}$ is possible by using the s expansion coefficients with respect to the basis of the s right singular vectors. And again, the factor C cannot be constructed only from the first s left singular vectors, since $m = \text{rank}(C) > \text{rank}(D) = s$. Thus the factor C has to be treated as a free variable.

In this respect, the AFS for rank-deficient problems is basically different from the AFS for rank-regular problems. In mathematical terms the generalized AFS for the spectral factor reads

$$\mathcal{N} = \left\{ x \in \mathbb{R}^{s-1} : \text{ exist } C \in \mathbb{R}_+^{k\times m},\ T \in \mathbb{R}^{m\times s} \text{ with } T(1,:) = (1, x^T),\ TV^T \geq 0 \text{ and } D = CTV^T \right\}. \tag{8}$$

This definition of the generalized AFS uses the normalization that the expansion coefficient of the first right singular vector always equals 1, cf. [30] on a study of Borgen norms in SMCR. The definitions of the two polyhedra $\mathcal{F}$ and $\mathcal{I}$, see Sec. 2, remain unchanged and by the nonnegativity constraint on $\mathcal{N}$ it holds that $\mathcal{N} \subset \mathcal{F}$. For completeness, the AFS for a rank-deficiency in C reads

$$\mathcal{N}_C = \left\{ y \in \mathbb{R}^{s-1} : \text{ exist } S \in \mathbb{R}_+^{n\times m},\ T \in \mathbb{R}^{s\times m} \text{ with } T(:,1)^T = (1, y^T),\ U\Sigma T \geq 0 \text{ and } D = U\Sigma T S^T \right\}.$$

Remark 3.4. *Formally, a rank-deficient problem can result in the two generalized AFS-sets $\mathcal{N}$ and $\mathcal{N}_C$. But only the AFS-set of the deficiency-causal factor represents meaningful profiles. If it is not known in advance which of the factors causes the deficiency, e.g., by a given kinetic model, then both generalized AFS-sets can be computed and chemical expertise can help to determine the deficiency-causal factor and the chemical meaningless profiles.*

4. Properties of the AFS for rank-deficient problems

Many of the properties of the AFS for rank-deficient problems can be shown by slight modifications of the proofs for rank-regular problems. An ingredient of the following analysis is the irreducibility of the matrix D^TD, see, e.g., [26]. In a simplified way this means that the chemical reaction system does not consist of (at least) two independent reaction subsystems with completely non-overlapping spectra. Otherwise, the measured data could be separated according to the subsystems. Then the chemometric analysis could be applied to each of the subsystems. Practically, the analytical chemist can visually recognize independent subsystems from non-overlapping (groups of) signals. An example is discussed in [28].

4.1. Boundedness of $\mathcal{N}$

The boundedness of the AFS is a necessary prerequisite for the use of numerical approximation routines for its computation. The crucial point is that an unlimited set and its unlimited boundary cannot be approximated by algorithms as grid search [42], triangle enclosure [15] or polygon inflation [37, 39]. For rank-regular problems the boundedness of the AFS is a simple, easy-to-prove property [39, 40]. This is equally valid for rank-deficient problems.

Remark 4.1. *Let $D \in \mathbb{R}^{k\times n}$ be a nonnegative matrix of the rank s and without zero-columns. If D^TD is an irreducible matrix, then the generalized AFS $\mathcal{N}$ is a bounded set as it is a subset of the bounded polyhedron $\mathcal{F}$. The boundedness of $\mathcal{F}$ is shown in Thm. 2.4 of [39].*

4.2. Geometric construction – feasible polytopes instead of feasible simplices

The geometric argument for classifying a vector x as feasible or non-feasible for rank-regular problems is well known [7, 31, 20, 36]. An $x \in \mathbb{R}^{s-1}$ is feasible if and only if $x \in \mathcal{F}$ and further $s-1$ vectors $y_1, \ldots, y_{s-1}$ can be found in $\mathcal{F}$ so that the simplex with the vertices $x, y_1, \ldots, y_{s-1}$ encloses $\mathcal{I}$. A similar geometric criterion for feasibility can be formulated for rank-deficient problems. This criterion uses polytopes with m vertices instead of simplices with s vertices. Then $m-1$ additional points in the AFS are to be determined in $\mathcal{F}$ instead of the smaller number of $s-1$ points. For example, a matrix D with $\text{rank}(D) = 3$ and $\text{rank}_+(D) = 4$ uses quadrangles for the geometric AFS construction instead of triangles. This is illustrated later by certain examples where no triangles exists with all of its vertices in $\mathcal{F}$ and that also include $\mathcal{I}$. However, quadrangles with these properties exist. The next theorem proves such a general polytope property.

Theorem 4.2. *Let $D \in \mathbb{R}^{k\times n}$ be a nonnegative matrix without an all-zero row and let D^TD as well as DD^T be irreducible matrices. Let $s = \text{rank}(D)$, $m = \text{rank}_+(D)$ and $U\Sigma V^T$ be an SVD of D with $V(:,1) > 0$. A vector $x \in \mathbb{R}^{s-1}$ is feasible if and only if further $m-1$ vectors $y_1, \ldots, y_{m-1} \in \mathbb{R}^{s-1}$ exist so that the polytope with the m vertices $x, y_1, \ldots, y_{m-1}$ is contained in $\mathcal{F}$ and also encloses $\mathcal{I}$.*

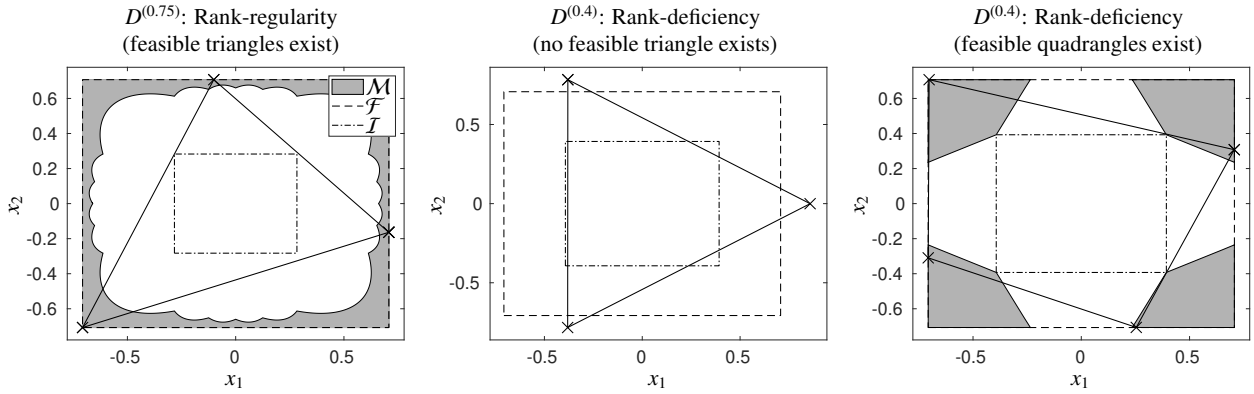

Figure 1: The AFS-sets and geometric constructions of nonnegative matrix factorizations for $D^{(z)}$ according to Example 4.3 for $z = 0.75$ (left) and $z = 0.4$ (center, right). Left: If $z = 0.75$, then D is a rank-regular matrix ($\operatorname{rank}(D^{(0.75)}) = \operatorname{rank}_+(D^{(0.75)}) = 3$). The AFS $\mathcal{M}$ (gray) is not empty. One feasible triangle is presented that is in $\mathcal{F}$ (dashed black line) and encloses $\mathcal{I}$ (dash-dotted line). Center: If $z = 0.4$, then D suffers from a rank-deficiency ($\operatorname{rank}(D^{(0.75)}) = 3 < \operatorname{rank}_+(D^{(0.75)}) = 4$). Thus the AFS $\mathcal{M}$ is empty. No triangle exists which is contained in $\mathcal{F}$ and which encloses $\mathcal{I}$. Right: The generalized AFS $\mathcal{N}$ (gray) is computed. Additionally a certain feasible quadrangle is presented that is contained in $\mathcal{F}$ and that encloses $\mathcal{I}$.

The proof in given in Appendix A. Next we illustrate Thm. 4.2 by a parameter-dependent model problem, for which parameter changes allow us to switch between rank-regularity to rank-deficiency. See Sec. 7 for the mathematical analysis of the problem and [43, 5] for the theoretical background on polytopes and convexity.

Example 4.3. *Let $z \geq 0$ and*

$$D^{(z)} = \begin{pmatrix} 1+z & 1+z & z & z \\ 1+z & z & 1+z & z \\ z & 1+z & z & 1+z \\ z & z & 1+z & 1+z \end{pmatrix}. \tag{9}$$

It holds that $\operatorname{rank}(D^{(z)}) = 3$ *for any* $z \geq 0$. *Furthermore,* $\operatorname{rank}_+(D^{(z)}) = 4$ *for* $z < 1/\sqrt{2} \approx 0.707$ *and* $\operatorname{rank}_+(D^{(z)}) = 3$ *for* $z \geq 1/\sqrt{2}$, *see Sec. 7. So for* $z < 1/\sqrt{2}$ *no triangle can be found with vertices in $\mathcal{F}$ that also encloses $\mathcal{I}$. However quadrangles with these properties exist. The AFS $\mathcal{M}$ for $D^{(0.75)}$ and the AFS $\mathcal{N}$ for $D^{(0.4)}$ are presented in Fig. 1.*

4.3. The minimal number of vertices of a feasible polytope equals the nonnegative rank

Thm. 4.2 generalizes the geometric characterization of the feasibility of a point x from rank-regular to rank-deficient problems. Therein the nonnegative rank m of D is a crucial quantity. The following theorem shows that the nonnegative rank m is the minimal number of vertices of any polytope that is contained in $\mathcal{F}$ and that encloses $\mathcal{I}$; cf. [10, 11].

Theorem 4.4. *Let the assumptions of Thm. 4.2 on D be fulfilled and let CS^T be an arbitrary nonnegative matrix factorization of D with $S(:,i)^T V(:,1) = 1$ for all i. (This means that the columns of S are scaled in a way that the first column of $T = S^T V$ is the all-ones vector.) Furthermore let $y_{i-1}^T = S(:,i)^T V(:,2:s) \in \mathbb{R}^{s-1}$ for $i = 1,\dots,m$. Then none of the vectors can be skipped, that is no index ℓ exists such that y_ℓ is a convex combination of the $m-1$ vectors $y_0,\dots,y_{\ell-1},y_{i_\ell+1},\dots,y_{m-1}$. (For ease of the proof representation we start the enumeration of the vectors with the index 0.)*

The proof in given in Appendix A.

4.4. The origin is never contained in the generalized AFS

It is a known fact that the origin, namely the all-zero vector, is never contained in the AFS if some mild assumptions on D hold [39]. This property is still valid for the generalized AFS $\mathcal{N}$.

Theorem 4.5. *On the assumptions on D as made by Thm. 4.2 the origin* $(0,\ldots,0)^T \in \mathbb{R}^{s-1}$ *is not an element of* $\mathcal{N}$ *but is contained in* $\mathcal{F}$.

Proof. Let $\mathbf{0} = (0,\ldots,0)^T \in \mathbb{R}^{s-1}$ be the origin. It belongs to $\mathcal{F}$ since $(1,\mathbf{0}^T)V^T = V(:,1) \geq 0$. Next we show that $\mathbf{0} \notin \mathcal{N}$. Let $\alpha_i = U_{i1}^2$ for $i = 1,\ldots,k$ so that $\sum_{i=1}^k \alpha_i = 1$ since the singular vectors have the Euclidean norm 1. Thus $\sum_{i=1}^k \alpha_i a_i$ is a convex combination of the vertices of $\mathcal{I}$ by (5) for which we get

$$\sum_{i=1}^k \alpha_i a_i = \sum_{i=1}^k U_{i1}^2 \frac{(U\Sigma)^T(2:s,i)}{(U\Sigma)^T(1,i)} = \sum_{i=1}^k U_{i1}^2 \frac{(\Sigma U^T)(2:s,i)}{U_{i1}\sigma_1}$$
$$= \frac{1}{\sigma_1}\sum_{i=1}^k (\Sigma U^T)(2:s,i)U_{i1} = \frac{1}{\sigma_1}\Sigma(2:s,:)\underbrace{U^T U(:,1)}_{=e_1} = \mathbf{0}.$$

Hence the origin is a convex combination of the vertices of $\mathcal{I}$. As the first left singular vector $U(:,1)$ is componentwise positive (due to the irreducibility of DD^T) we get $\alpha_i > 0$ for all i. Thus $\mathbf{0}$ is a vector in the interior of $\mathcal{I}$ and can never be an element of $\mathcal{N}$ (since at most elements from the boundary of $\mathcal{I}$ can be contained in $\mathcal{N}$ according to Thm. 4.2). □

The properties of the generalized AFS, as proved in Thms. 4.4 and 4.5, underline the key importance of the notion of the nonnegative rank with the definition of $m = \text{rank}_+(D)$ in (8). Otherwise the geometric AFS construction for rank-regular problems could not be extended to the generalized AFS for rank-deficient problems.

5. Computation of the AFS for rank-deficient problems

A new routine for the numerical computation of $\mathcal{N}$ is required. To this end we adapt the polygon inflation procedure and its algorithmic variant the inverse polygon inflation procedure [37, 39]. The idea to approximate the AFS-sets by adaptively refined, inflating polygons remains valid. What needs to be modified for rank-deficient problems is the objective function that checks the feasibility of points $x \in \mathbb{R}^{s-1}$. The new objective function works for the general case $\text{rank}_+(D) \geq \text{rank}(D)$.

5.1. The modified objective function

The feasibility check in the program code is based on a numerical optimization of an objective function. For rank-regular problems a nonlinear least squares problem is to be solved that includes various penalty terms. The degrees of freedom of this optimization are the matrix elements of T by (3). However, as (2) does not allow to represent both nonnegative factors we have to apply a different objective function for rank-deficient problems. Instead of expanding C with respect to the left singular vectors, we use the geometric arguments or a NonNegative Least Squares (NNLS) solver.

The feasibility check for x is subdivided into two steps. First the rapid and computationally cheap test $V(1,x^T)^T \geq 0$ is performed in order to decide whether $x \in \mathcal{F}$ or $x \notin \mathcal{F}$. If x is in $\mathcal{F}$, then a second, more expensive second test is applied. We suggest the following two approaches: First, the geometric construction principles can be applied directly. Then an optimization is performed that tries to extend x by $m-1$ additional points in $\mathcal{F}$ so that the resulting polygon includes $\mathcal{I}$. If such vertices exist, then x is feasible. Otherwise x is not feasible. Alternatively, one can run the optimization with an NNLS-algorithm. Then the optimization aims at computing the factor S (depending on the variables $y_1,\ldots,y_{m-1} \in \mathbb{R}^{s-1}$) and the associated factor C is computed row-wise by the NNLS-solver as

$$C(j,:) = \arg\min_{c\in\mathbb{R}_+^{1\times m}} \left\| cS^T - D(j,:)\right\|_2^2, \qquad j = 1,\ldots,k. \tag{10}$$

Possible NNLS-solvers are suggested in [21, 6, 32]. Rank deficiency of S does not raise a specific problem for the NNLS solver. The aim is to compute a nonnegative solution vector $C(j,:)$. Any non-uniqueness due to vectors from the null space of S does not interfere with the approach. A vector x is feasible if and only if $C,S \geq 0$ and $D = CS^T$. The numerical computations of this publication follow this approach and use the NNLS solver by [21].

The computational costs for the NNLS-based AFS computation are much higher than AFS computations for rank-regular problems. The main reason for this is that the factor C can no longer be computed directly from T as in (2), but necessitates the solution of a least squares problem under nonnegativity constraints.

5.2. The objective function for noisy data

Several approaches have already been published for a stable AFS-computation of rank-regular problems in the presence of noise. Next we suggest an extension to rank-deficient problems in order to deal with small negative entries. Small negative entries are often a problem if noisy, biased or background-subtracted data is considered. Here we accept small negative entries of C and S if their relative sizes are bounded from below as follows

$$\frac{C(:,\ell)}{\max\limits_{i=1,\ldots,k}|C(i,\ell)|} \geq -\varepsilon, \qquad \frac{S(:,\ell)}{\max\limits_{i=1,\ldots,n}|S(i,\ell)|} \geq -\varepsilon \quad \text{for } \ell = 1,\ldots,s \tag{11}$$

with a small control parameter $\varepsilon \geq 0$.

The handling of small negative entries is relatively easy for the construction of $\mathcal{F}$ but by no means obvious for $\mathcal{I}$. For the construction of $\mathcal{I}$ the duality principles [18, 29, 34] can help. First the outer boundaries of $\mathcal{F}$ are computed for the factor C and also for the factor S. Small negative entries are accepted according to (11). This is only done for $\ell = 1$ and without considering dual interactions. Then the inner polygons $\mathcal{I}$ for C and S are computed by duality as explained in [36, 38]. On the basis of these modified polygons the objective function can be evaluated. See [38] for more details on this approach.

The NNLS-based AFS computation needs an additional control parameter ε_f. The reason is that the factor C resulting from (10) is strictly nonnegative so that a componentwise vanishing residual $D - CS^T$ cannot always be achieved. Hence we let x pass the feasibility check if S satisfies (11) and $\|D - CS^T\| \leq \varepsilon_f$. We suggest to use $\varepsilon_f \in [10^{-8}, 10^{-3}]$ and $\varepsilon \leq 0.02$ as proper values.

5.3. How polygon inflation is used

The polygon inflation algorithm [37] and inverse polygon inflation [39] are adaptive AFS-computation methods for three-component systems. The idea is to approximate the boundary of the AFS, respectively the boundaries of all of its subsets, by series of inflating polygons. The (direct) polygon inflation method has been designed for an application to AFS-sets that consist of three clearly separated subsets. The algorithmic variant of inverse polygon inflation has been developed for a stable computation of AFS-sets that consist of either only one topologically connected subset (then necessarily with a hole around the origin) or for AFS-sets whose subsets are not clearly separated. However, inverse polygon inflation is also capable to treat the case of an AFS with three clearly separated segments, even though at somewhat higher computational costs.

For rank-deficient problems (inverse) polygon inflation uses the feasibility check as described in Sec. 5.1. The general idea of an adaptive polygon inflation remains unchanged, namely the boundary of each subset is approximated from its interior by inflating polygons. For each subset an inner point (computed from a nonnegative matrix factorization) is used to compute a starting triangle which is then recursively refined by subdividing the edges. The refinement process is stopped if a certain final accuracy has been reached. The inverse polygon inflation algorithm computes two super-sets of the AFS $\mathcal{N}$ and then computes their intersection, see [39] for the details on a rank-regular problem. Minor changes are necessary for rank-deficient problems.

6. Numerical results for a Michaelis-Menten model reaction

We consider the Michaelis-Menten kinetic

$$K + S \underset{\kappa_{-1}}{\overset{\kappa_1}{\rightleftharpoons}} [K\text{-}S] \xrightarrow{\kappa_2} K + P$$

with four reacting species but only three independent reactions. Thus the rank-loss occurs in the factor C and only for this factor the AFS can be computed. The true profiles of the factor C are determined by the Michalis-Menten model whose parameters are taken as $\kappa_1 = 30$, $\kappa_{-1} = 0.1$ and $\kappa_2 = 3$. The initial concentration values are $c_S(0) = 1$, $c_K(0) = 0.1$ and $c_{[K\text{-}S]}(0) = c_P(0) = 0$. A number of $k = 101$ nodes are selected in the time interval $[0, 7.5]$. As the concentration values of S and K-S change rapidly in $t \in [0, 0.25]$, this sub-interval gets a finer discretization

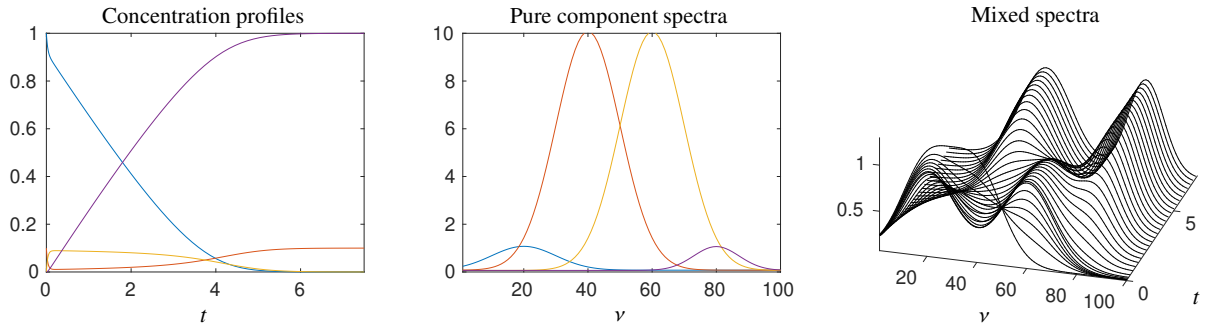

Figure 2: Spectra and concentration profiles for the model problem introduced in Sec. 6. The pure component profiles (left, center) and the mixed spectra (right, only a few spectra are plotted for a better readability). For the original factors it holds that $\operatorname{rank}(C) = 3$ and $\operatorname{rank}(S) = 4$. The spectral mixture data suffers from a rank-deficiency since $\operatorname{rank}(D) = 3$ but $\operatorname{rank}_+(D) = 4$.

with 51 equidistant nodes. The remaining, much longer interval is equidistantly discretized with 50 nodes. The pure component spectra are built from the shifted Gaussians

$$s_1(\nu) = \exp\Big(-\frac{(\nu-20)^2}{200}\Big) + 0.075, \qquad s_2(\nu) = 10\exp\Big(-\frac{(\nu-40)^2}{200}\Big) + 0.075,$$
$$s_3(\nu) = 10\exp\Big(-\frac{(\nu-60)^2}{200}\Big) + 0.065, \qquad s_4(\nu) = \exp\Big(-\frac{(\nu-80)^2}{100}\Big) + 0.065.$$

The spectra are evaluated for $\nu \in [1, 100]$ by using $n = 100$ equidistant nodes. From $C \in \mathbb{R}^{101\times 4}$ and $S \in \mathbb{R}^{100\times 4}$ we get $D = CS^T \in \mathbb{R}^{101\times 100}$. Numerical calculations show that $s = \operatorname{rank}(D) = 3$, but $m = \operatorname{rank}(S) = \operatorname{rank}_+(D) = 4$ which confirms the rank-deficiency. The profiles underlying C and S as well as the time-series of the mixture spectra forming the rows of D are shown in Fig. 2.

No nonnegative factors $C \in \mathbb{R}^{101\times 3}$ and $S \in \mathbb{R}^{100\times 3}$ with $D = CS^T$ exist since $\operatorname{rank}_+(D) = 4$. Therefore the classical AFS (for rank-regular problems) is empty. Due to Theorem 4.4 no triangles exist in $\mathcal{F}_C$ that enclose $\mathcal{I}_C$, see the left plot of Fig. 3. Assuming the Michalis-Menten model we know that C is responsible for the rank deficiency. Thus we compute the generalized AFS for the concentration factor, cf. Rem. 3.4. Only the factor C can be computed as a linear combination of the first three singular vectors since the rank-deficiency is caused by C. The AFS $\mathcal{N}_C$ is computed for $m = \operatorname{rank}_+(D) = 4$. Then the polygon inflation algorithm on the basis of feasible quadrangles is applied. This algorithm uses the modified objective function as introduced in Sec. 5 for the computation of $\mathcal{N}_C$. The AFS consists of four isolated subsets and is shown in Fig. 3. Finally, the associated bands of feasible profiles of the factor C are computed for each of the AFS-subsets. Some of these profiles are plotted in Fig. 4. We use a low profile density in order to prevent the bands from covering the internal structure of the individual profiles.

7. Rank-deficiency analysis for the model matrix

Example 4.3 generalizes the classical 4×4 example matrix (6) as suggested by Thomas in 1974, see [41, 8]. This matrix shows a rank-deficiency for the smallest possible dimension. We add to this matrix a z-multiple of the all-ones 4×4 matrix and get the parameter-dependent matrix $D^{(z)}$ given in Eq. (9). We consider only parameters $z \geq 0$. The value $z = 0$ reduces (9) to (6). The singular values of $D^{(z)}$ are $\sigma_1 = 2 + 4z$, $\sigma_2 = \sigma_3 = \sqrt{2}$ and $\sigma_4 = 0$ so that its rank equals $s = 3$ irrespective of z. As the singular value $\sqrt{2}$ has the multiplicity 2, the orientation of the AFS involves a certain non-uniqueness. In other words, a different SVD can result in a rotated AFS; nevertheless the sets of feasible profiles remain to be the same, cf. $\mathcal{S}$ by (7). The nonnegative rank of $D^{(z)}$ can be tuned by z. Next we show that $D^{(z)}$ is rank-regular for $z \geq 1/\sqrt{2}$ and rank-deficient for $0 \leq z < 1/\sqrt{2}$.

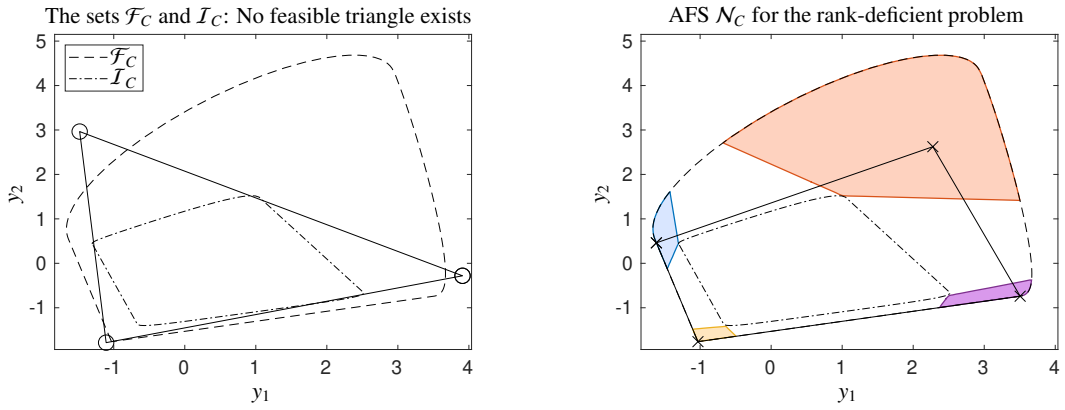

Figure 3: The AFS for the Michaelis-Menten model problem as introduced in Sec. 6 with $s = 3$ and $m = 4$. Left: The set $\mathcal{F}_C$ is marked by a dashed line and $\mathcal{I}_C$ by a dash-dotted line. No triangle with vertices in $\mathcal{F}_C$ exists which encloses $\mathcal{I}_C$ (the plotted triangle is not feasible). Hence D suffers from a rank-deficiency, see Thm. 4.2. Right: the AFS $\mathcal{N}_C$ with $m = 4$. The AFS consists of four isolated subsets. Instead of triangles (as used for Borgen plots) quadrangles are necessary for a low-dimensional construction of a complete factor C. The correct solution according to the Michaelis-Menten kinetics is added as a quadrangle (solid black lines).

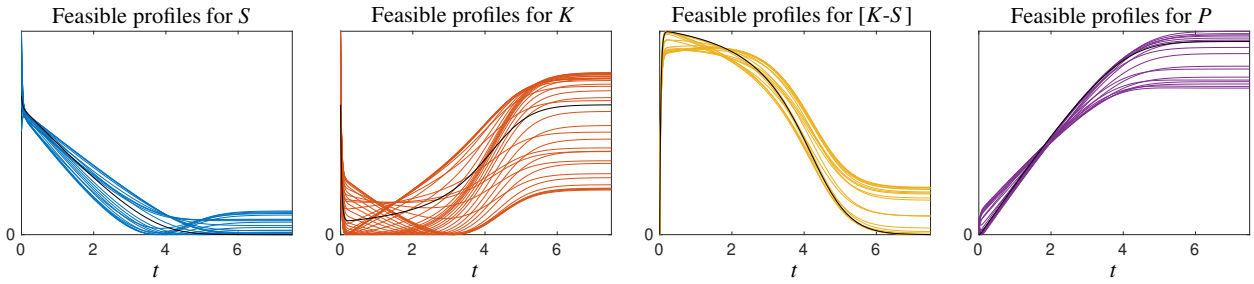

Figure 4: Feasible profiles of the factor C according to the Michaelis-Menten kinetic, see Sec. 6, with the chemical species S, K, $[K\text{-}S]$ and P. The associated generalized AFS is plotted right in Fig. 3. The four black lines are the true concentration profiles according to the Michaelis-Menten kinetic with the kinetic parameters as specified in Sec. 6.

7.1. Rank-regularity for $z \geq 1/\sqrt{2}$

For $z \geq \sqrt{2}$ it holds that $\operatorname{rank}_+(D^{(z)}) = 3$. This can easily be proved by specifying the following nonnegative factors $C, S \in \mathbb{R}^{4\times 3}$ (among others)

$$C^{(z)} = \frac{1}{2+2z}\begin{pmatrix} (1+2z)(1+z) & (1+2z)(1+z) & 0 \\ (1+2z)^2 & 0 & 1+2z \\ 0 & (1+2z)^2 & 1+2z \\ z(1+2z) & z(1+2z) & 2+4z \end{pmatrix}, \qquad S^{(z)} = \frac{1}{(1+2z)^2}\begin{pmatrix} 2(1+z)^2 & 2(1+z)z & 0 \\ 2(1+z)z & 2(1+z)^2 & 0 \\ (1+z)^2+z^2 & 2z^2-1 & 1 \\ 2z^2-1 & (1+z)^2+z^2 & 1 \end{pmatrix}.$$

Figure 5 shows the AFS (as computed by the inverse polygon inflation algorithm) for the factor S of $D^{(0.75)}$. By decreasing z towards the limit value $z = 1/\sqrt{2} \approx 0.7071$ the AFS shrinks to a finite set of isolated points. It is possible to describe the AFS for the factor S analytically. The right singular vectors of $D^{(1/\sqrt{2})}$ are

$$V(:, 1:3) = \begin{pmatrix} \frac{1}{2} & 1/\sqrt{2} & 0 \\ \frac{1}{2} & 0 & -1/\sqrt{2} \\ \frac{1}{2} & 0 & 1/\sqrt{2} \\ \frac{1}{2} & -1/\sqrt{2} & 0 \end{pmatrix},$$

and the AFS consists of 24 isolated points. The AFS is plotted in Fig. 5 and has the form

$$\mathcal{M} = \left\{(\gamma, \pm\frac{1}{\sqrt{2}}) : \gamma \in \Gamma\right\} \cup \left\{(\pm\frac{1}{\sqrt{2}}, \gamma) : \gamma \in \Gamma\right\}$$

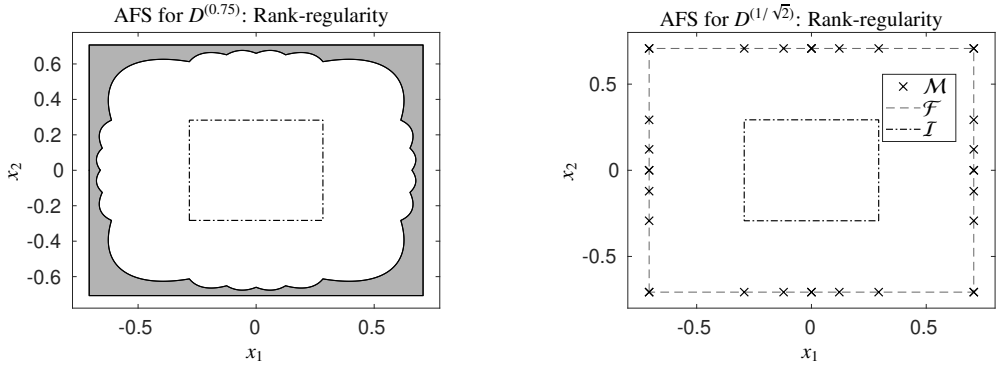

Figure 5: The AFS-sets $\mathcal{M}$ for the second (spectral) factor of $D^{(0.75)}$ (left) and $D^{(1/\sqrt{2})}$ (right). The $a_1, \ldots, a_4$ define the vertices of $\mathcal{I}$ (black dash-dotted line). The boundary of $\mathcal{F}$ is plotted by a gray dashed line in the right plot. The AFS of $D^{(1/\sqrt{2})}$ consists of 24 isolated points. The matrices do not suffer from a rank-deficiency. As two singular values are equal ($\sigma_2 = \sigma_3$) the AFS can be rotated by any angle around the origin and has still the same information content.

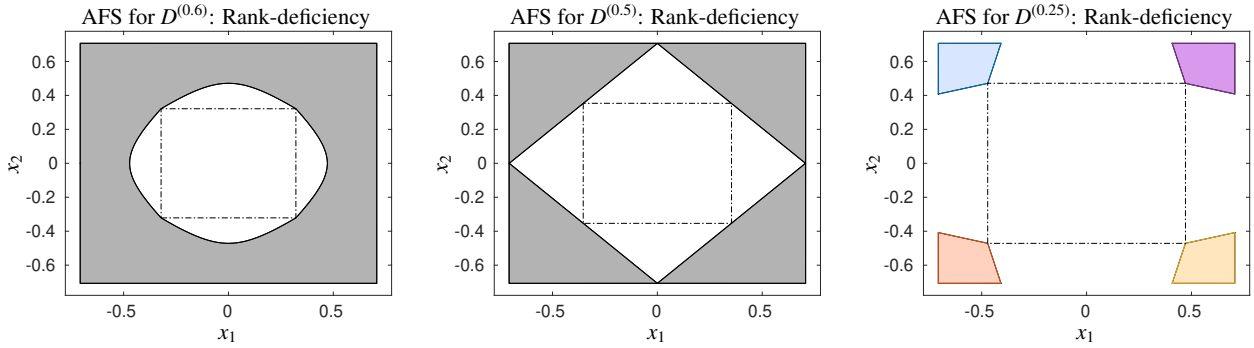

Figure 6: The AFS $\mathcal{N}$ for the rank-deficient matrices with $m = 4$ for $D^{(0.60)}$, $D^{(0.5)}$ and $D^{(0.25)}$. The inner polygon $\mathcal{I}$ (black dash-dotted line) has the vertices $a_1, \ldots, a_4$. Since two singular values are equal ($\sigma_2 = \sigma_3$) the AFS can be rotated by any angle around the origin and has still the same information content.

with

$$\Gamma = \left\{0, \pm\frac{1}{\sqrt{2}(1+\sqrt{2})^2}, \pm\frac{1}{\sqrt{2}(1+\sqrt{2})}, \pm\frac{1}{\sqrt{2}}\right\}.$$

7.2. Rank-deficiency for $z < 1/\sqrt{2}$

If $0 \leq z < 1/\sqrt{2}$, then $D^{(z)}$ is a rank-deficient matrix. Its nonnegative rank equals $m = 4$ since no nonnegative factors $C, S \in \mathbb{R}^{4\times 3}$ exist with $D^{(z)} = CS^T$. Instead, 4×4 nonnegative factors C and S exist. A trivial example is $C = I_{4\times 4}$ and $S^T = D^{(z)}$ with $\text{rank}(C) = 4$ and $\text{rank}(S) = 3$. Fig. 6 shows the AFS-sets for $z = 0.6$, $z = 0.5$ and $z = 0.25$ as computed by (inverse) polygon inflation. We used the modified objective function, introduced in Sec. 5, for these computations. The AFS for $z = 0.6$ is a topologically connected set with a hole around the origin. The AFS for $z = 0.5$ consists of four triangles so that neighboured triangles touch in one point. The AFS for $z = 0.25$ consists of four clearly separated subsets.

8. Summary and outlook

Rank-deficiency is a relatively complex phenomenon that can occur in MCR problems. Whenever the rank of the measured spectral data matrix is degenerated due to internal linear dependencies, one cannot find chemically correct pure component factors of the same rank. Instead, one of the two factors must have a larger rank - otherwise no

interpretable pure component factorization can be determined. Sometimes a workaround is possible in such cases, namely by changing the focus of the chemometric data analysis. One can either augment the given data, see Amrhein et al. [4] and others, or one can narrow the focus towards a local analysis in time and/or frequency windows, see, e.g., Lakeh et al. [3] on aspects of a local rank deficiency. Such techniques can sometimes considerably support the extraction of pure component information from multi-component systems. Nevertheless, if data augmentation or data reduction are not possible or not pursued, then the systematic approach for determining the ambiguity underlying the pure component factorization can partially be generalized from rank-regular to rank-deficient problems. However, the AFS can only be computed for the factor that causes the rank-deficiency. For the other factor the rank-deficiency implies an information gap, namely at least one singular vector for the factor reconstruction is unknown. It is not clear a priori from given D which of its factors causes the rank-deficiency. Additional information is required. Alternatively, both factors can be tested individually and the results can be evaluated concerning their chemical interpretability.

A further problem, we call it a *hidden rank-deficiency*, is not treated in this paper. For this problem it holds that $\operatorname{rank}(D) = \operatorname{rank}_+(D)$ but none of the nonnegative factorizations of D provides chemically meaningful profiles. In other words, the AFS is not empty, but does not contain the correct solution. This can arise if one factor (C or S) suffers from a rank-deficiency hidden in the interaction with the other factor. Such problems are be analyzed in a forthcoming paper.

A. Proofs of the theorems 4.2 and 4.4

Proof of Theorem 4.2:

Proof. First the direction "⇒" is shown. Let x be feasible, i.e. $x \in \mathcal{N}$ with $\mathcal{N}$ by (8). Due to the definition of $\mathcal{N}$ an $m \times s$ matrix T with the rank s exists with $T(1,:) = (1, x^T)$. Also a nonnegative matrix $C \in \mathbb{R}^{k\times m}$ exists with $D = CS^T$ and $S^T = TV^T \geq 0$. The first column of T is the all-ones vector. This factorization $D = CS^T$ is used for the rest of the proof. A number of $m-1$ vectors can be extracted from the rows of T according to $y_i^T = T(i+1, 2:s)$ for $i = 1, \ldots, m-1$. Further, the nonnegativity of $S^T = TV^T$ proves that all m vertices $x, y_1, \ldots, y_{m-1}$ of the quadrangle are contained in $\mathcal{F}$. We still have to show that this quadrangle encloses the inner polygon $\mathcal{I}$. We do this by showing that the vertices $a_1, \ldots, a_k$ by Eq. (5) are convex combinations of the $x, y_1, \ldots, y_{m-1}$.

The starting point is Eq. (5) which can be rewritten with $DV = U\Sigma$

$$a_i = \frac{(U\Sigma)^T(2:s,i)}{(U\Sigma)^T(1,i)} = \frac{(DV)^T(2:s,i)}{(DV)^T(1,i)} = \frac{(D(i,:)V(:,2:s))^T}{D(i,:)V(:,1)}. \tag{12}$$

Hence we get that

$$(1, a_i^T) = \frac{D(i,:)V}{D(i,:)V(:,1)} = \frac{C(i,:)T}{D(i,:)V(:,1)} \tag{13}$$

where for the last equality we use that

$$D(i,:) = C(i,:)S^T = C(i,:)TV^T \quad \text{and thus} \quad D(i,:)V = C(i,:)T.$$

Next we define the vectors $\alpha^{(i)} \in \mathbb{R}^m$ componentwise as

$$\alpha_j^{(i)} = \frac{C(i,j)}{D(i,:)V(:,1)}, \qquad j = 1, \ldots, m. \tag{14}$$

Next we show that $\alpha^{(i)}$ is the vector of expansion coefficients allowing to represent the a_i by (5) as a convex combination of $x, y_1, \ldots, y_{m-1}$.

First, $\alpha^{(i)} \geq 0$, since $C(i,:) \geq 0$ and $D(i,:)V(:,1) > 0$ as (the Perron eigenvector) $V(:,1)$ can be assumed componentwise positive. For each $i \in \{i = 1, \ldots, k\}$, the sum of coefficients equals 1, since

$$\sum_{j=1}^{m} \alpha_j^{(i)} = \frac{C(i,:)e}{D(i,:)V(:,1)} = \frac{C(i,:)Te_1}{D(i,:)V(:,1)} = (1, a_i^T)e_1 = 1$$

where $e = (1, \ldots, 1)^T \in \mathbb{R}^m$, $e_1 = (1, 0, \ldots, 0)^T \in \mathbb{R}^s$ and since $e = Te_1$.

Finally, by inserting (14) and by using the representation of the vectors $x, y_1, \ldots, y_{m-1}$ from the rows of T we get for the convex combination

$$\begin{aligned}
\alpha_1^{(i)} x + \sum_{j=2}^{m} \alpha_j^{(i)} y_{j-1} &= \frac{C(i,1)}{D(i,:)V(:,1)}(x^T)^T + \sum_{j=2}^{m} \frac{C(i,j)}{D(i,:)V(:,1)}(y_{j-1}^T)^T \\
&= \frac{1}{D(i,:)V(:,1)} \left(C(i,1)(T(1,2:s))^T + \sum_{j=2}^{m} C(i,j)(T(j,2:s))^T \right) \\
&= \frac{1}{D(i,:)V(:,1)} \sum_{j=1}^{m} C(i,j)(T(j,2:s))^T \\
&= \frac{1}{D(i,:)V(:,1)} \left(\sum_{j=1}^{m} C(i,j)T(j,2:s) \right)^T \\
&= \frac{1}{D(i,:)V(:,1)} (C(i,:)T(:,2:s))^T = (a_i^T)^T = a_i
\end{aligned}$$

where in the last line (13) has been applied.

The proof direction "⇐" inverts the preceding construction line-by-line. □

Proof of Thm. 4.4:

Proof. We assume that y_ℓ is a convex combination of $y_0, \ldots, y_{\ell-1}, y_{\ell+1}, \ldots, y_{m-1}$ and derive a contradiction. Without loss of generality let $\ell = 0$. Let $\beta \in \mathbb{R}^{m-1}$ be the nonnegative column vector with $\sum_{i=1}^{m-1} \beta_i = 1$ that represents the presumed convex combination $y_0 = \sum_{j=1}^{m-1} \beta_j y_j$. Next we define the auxiliary matrix $B \in \mathbb{R}^{m \times m}$ as

$$B = I - e_1(0, \beta^T)$$

where I is the $m \times m$ identity matrix and e_1 its first column. Direct computation shows that $B^{-1} = I + e_1(0, \beta^T)$ and hence $B^{-1} \geq 0$.

Then $\widetilde{C} = CB^{-1}$ and $\widetilde{S}^T = BS^T$ define a further factorization of D. In order to show the nonnegativity of the factors we first state that $B^{-1} \geq 0$ implies $\widetilde{C} = CB^{-1} \geq 0$. We still have to check that $\widetilde{S}^T = BS^T = BTV^T$ is also a nonnegative matrix. To this end we calculate

$$BT = \left(I - e_1 \begin{pmatrix} 0 \\ \beta \end{pmatrix}^T \right) \begin{pmatrix} 1 & y_0^T \\ \vdots & \vdots \\ 1 & y_{m-1}^T \end{pmatrix} = \begin{pmatrix} 1 & y_0^T \\ \vdots & \vdots \\ 1 & y_{m-1}^T \end{pmatrix} - e_1 \Big(\underbrace{\sum_{j=1}^{m-1} \beta_j}_{=1}, \underbrace{\beta_1 y_1^T + \ldots + \beta_{m-1} y_{m-1}^T}_{=y_0^T} \Big) = \begin{pmatrix} 0 & 0 \\ 1 & y_1^T \\ \vdots & \vdots \\ 1 & y_{m-1}^T \end{pmatrix}.$$

This allows us to determine $\widetilde{S}$ as

$$\widetilde{S}^T = BTV^T = (0, s_2, \ldots, s_m)^T$$

where the s_i are the columns of S. On the one hand this proves that $\widetilde{S} \geq 0$. On the other hand the sub-matrices $\widetilde{C}(:, 2:m)$ and $\widetilde{S}(:, 2:m)$ have at most the rank $m-1$ and define a further nonnegative matrix factorization of D. Hence $\text{rank}_+(D) \leq m-1$. This contradicts the assumption on the nonnegative rank of D and completes the proof. □

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. *Anal. Chem.*, 81(6):2115–2122, 2009.

[2] H. Abdollahi and R. Tauler. Uniqueness and rotation ambiguities in multivariate curve resolution methods. *Chemom. Intell. Lab. Syst.*, 108(2):100–111, 2011.

[3] M. Akbari Lakeh, R. Rajkó, and H. Abdollahi. Local rank deficiency caused problems in analyzing chemical data. *Anal. Chem.*, 89(4):2259–2266, 2017. PMID: 28192909.

[4] M. Amrhein, B. Srinivasan, D. Bonvin, and M. M. Schumacher. On the rank deficiency and rank augmentation of the spectral measurement matrix. *Chemom. Intell. Lab. Syst.*, 33(1):17–33, 1996.

[5] A. Barvinok. *A course in convexity*, volume 54 of *Grad. Stud. Math.* American Mathematical Society, Providence, 2002.

[6] Å. Björck. *Numerical methods for least squares problems*. SIAM, 1996.

[7] O.S. Borgen and B.R. Kowalski. An extension of the multivariate component-resolution method to three components. *Anal. Chim. Acta*, 174:1–26, 1985.

[8] J. E. Cohen and U. G. Rothblum. Nonnegative ranks, decompositions, and factorizations of nonnegative matrices. *Linear Algebra Appl.*, 190:149–168, 1993.

[9] A. de Juan, S. Navea, J. Diewok, and R. Tauler. Local rank exploratory analysis of evolving rank-deficient systems. *Chemom. Intell. Lab. Syst.*, 70(1):11–21, 2004.

[10] B. Dong, M. M. Lin, and M.T. Chu. Nonnegative rank factorization via rank reduction. preprint, 2008.

[11] B. Dong, M. M. Lin, and M.T. Chu. Nonnegative rank factorization-a heuristic approach via rank reduction. *Numer. Algorithms*, 65(2):251–274, 2014.

[12] M. Garrido, I. Lázaro, M. S. Larrechi, and F. X. Rius. Multivariate resolution of rank-deficient near-infrared spectroscopy data from the reaction of curing epoxy resins using the rank augmentation strategy and multivariate curve resolution alternating least squares approach. *Anal. Chim. Acta*, 515(1):65–73, 2004.

[13] N. Gillis and F. Glineur. On the geometric interpretation of the nonnegative rank. *Linear Algebra Appl.*, 437(11):2685 – 2712, 2012.

[14] A. Golshan, H. Abdollahi, S. Beyramysoltan, M. Maeder, K. Neymeyr, R. Rajkó, M. Sawall, and R. Tauler. A review of recent methods for the determination of ranges of feasible solutions resulting from soft modelling analyses of multivariate data. *Anal. Chim. Acta*, 911:1–13, 2016.

[15] A. Golshan, H. Abdollahi, and M. Maeder. Resolution of rotational ambiguity for three-component systems. *Anal. Chem.*, 83(3):836–841, 2011.

[16] A. Golshan, M. Maeder, and H. Abdollahi. Determination and visualization of rotational ambiguity in four-component systems. *Anal. Chim. Acta*, 796(0):20–26, 2013.

[17] D. A. Gregory and N. J. Pullman. Semiring rank: Boolean rank and nonnegative rank factorizations. *J. Combin. Inform. System Sci*, 8(3):223–233, 1983.

[18] R.C. Henry. Duality in multivariate receptor models. *Chemom. Intell. Lab. Syst.*, 77(1-2):59–63, 2005.

[19] A. Izquierdo-Ridorsa, J. Saurina, S. Hernández-Cassou, and R. Tauler. Second-order multivariate curve resolution applied to rank-deficient data obtained from acid-base spectrophotometric titrations of mixtures of nucleic bases. *Chemom. Intell. Lab. Syst.*, 38(2):183–196, 1997.

[20] A. Jürß, M. Sawall, and K. Neymeyr. On generalized Borgen plots. I: From convex to affine combinations and applications to spectral data. *J. Chemom.*, 29(7):420–433, 2015.

[21] C. L. Lawson and R. J. Hanson. *Solving least squares problems*, volume 15 of *Classics Appl. Math.* SIAM, Philadelphia, 1995.

[22] W.H. Lawton and E.A. Sylvestre. Self modelling curve resolution. *Technometrics*, 13:617–633, 1971.

[23] M. Maeder and Y.M. Neuhold. *Practical data analysis in chemistry*. Elsevier, Amsterdam, 2007.

[24] E. Malinowski. *Factor analysis in chemistry*. Wiley, New York, 2002.

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

[26] H. Minc. *Nonnegative matrices*. John Wiley & Sons, New York, 1988.

[27] K. Neymeyr and M. Sawall. On the set of solutions of the nonnegative matrix factorization problem. *SIAM J. Matrix Anal. Appl.*, 39:1049–1069, 2018.

[28] K. Neymeyr, M. Sawall, Z. Rasouli, and M. Maeder. On the avoidance of crossing of singular values in the evolving factor analysis. *J. Chemom.*, page e3217, 2020.

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

[30] R. Rajkó. Studies on the adaptability of different Borgen norms applied in self-modeling curve resolution (SMCR) method. *J. Chemom.*, 23(6):265–274, 2009.

[31] R. Rajkó and K. István. Analytical solution for determining feasible regions of self-modeling curve resolution (SMCR) method based on computational geometry. *J. Chemom.*, 19(8):448–463, 2005.

[32] R. Rajkó and Y. Zheng. Distance algorithm based procedure for non-negative least squares. *J. Chemom.*, 28(9):691–695, 2014.

[33] J. Saurina, S. Hernández-Cassou, R. Tauler, and A. Izquierdo-Ridorsa. Multivariate resolution of rank-deficient spectrophotometric data from first-order kinetic decomposition reactions. *J. Chemom.*, 12(3):183–203, 1998.

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

[35] M. Sawall, A. Jürß, H. Schröder, and K. Neymeyr. *On the analysis and computation of the area of feasible solutions for two-, three- and four-component systems*, volume 30 of Data Handling in Science and Technology, "Resolving Spectral Mixtures", Ed. C. Ruckebusch, chapter 5, pages 135–184. Elsevier, Cambridge, 2016.

[36] M. Sawall, A. Jürß, H. Schröder, and K. Neymeyr. Simultaneous construction of dual Borgen plots. I: The case of noise-free data. *J. Chemom.*, 31:e2954, 2017.

[37] M. Sawall, C. Kubis, D. Selent, A. Börner, and K. Neymeyr. A fast polygon inflation algorithm to compute the area of feasible solutions for three-component systems. I: Concepts and applications. *J. Chemom.*, 27:106–116, 2013.

[38] M. Sawall, A. Moog, C. Kubis, H. Schröder, D. Selent, R. Franke, A. Brächer, A. Börner, and K. Neymeyr. Simultaneous construction of dual Borgen plots. II: Algorithmic enhancement for applications to noisy spectral data. *J. Chemom.*, 32:e3012, 2018.

[39] 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.

[40] M. Sawall, H. Schröder, D. Meinhardt, and K. Neymeyr. On the ambiguity underlying multivariate curve resolution methods. In R. Tauler, editor, *Comprehensive Chemometrics, 2nd edition*, page To be published. Elsevier, 2019.
[41] L. B. Thomas. Rank factorization of nonnegative matrices (A. Berman). *SIAM Review*, 16(3):393–394, 1974.
[42] M. Vosough, C. Mason, R. Tauler, M. Jalali-Heravi, and M. Maeder. On rotational ambiguity in model-free analyses of multivariate data. *J. Chemom.*, 20(6-7):302–310, 2006.
[43] G. M. Ziegler. *Lectures on polytopes*, volume 152 of *Grad. Texts in Math.* Springer, New York, 1994.