



Soft constraints for reducing the intrinsic rotational ambiguity of the area of feasible solutions



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ABSTRACT

The reduction of the rotational ambiguity in multivariate curve resolution problems is a central challenge in order to construct an effective chemometric method. Soft modeling is a method of choice to solve this problem.

The aim of this paper is to demonstrate the impact of soft constraints on the full set of all feasible, nonnegative solutions. To this end the starting point is the Area of Feasible Solutions (AFS) for a three-component system. Then soft constraints, namely constraints on the unimodality, monotonicity and windowing for certain concentration profiles, are used in order to reduce the AFS. This process extracts chemically meaningful solutions from the set of all feasible nonnegative factors and demonstrates the mode of action of soft constraints. Results are presented for a model problem as well as for FT-IR data for a catalytic subsystem of the rhodium-catalyzed hydroformylation process. Typically, the AFS can significantly be reduced by adding soft constraints.

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1. Introduction

Multivariate curve resolution methods aim at decomposing sequences of spectra taken from a multi-component chemical reaction system into the underlying contributions from the pure components. If these spectra are collected row-wise in a matrix D , then the Lambert–Beer law says that D can approximately be factored into a product of a matrix C containing column-wise the concentration profiles of the pure components and a matrix A containing row-wise the associated pure component spectra, that is

$$D = CA. \quad (1)$$

In general, the factorization (1) is not unique and continua of possible nonnegative solutions exist. This observation was first made by Lawton and Sylvestre in 1971 [1] for two-component systems; see also the introduction to model-free analysis and rotational ambiguity in [2]. In 1985, Borgen and Kowalski extended the approach of Lawton and

Sylvestre to three-component systems [3]. This work was continued by Abdollahi and Tauler [4] and Rajkó [5]. However, it is a main interest of chemists to find within the continuum of possible nonnegative factorizations the “true” or “chemically correct” solution. To determine a single solution is a typical trait of model-based methods. Many such curve resolution methods exist [2] which use soft constraints and/or hard models in order to compute a factorization (1) so that the factors fulfill certain conditions. The development of MCR methods is a highly active and wide research area; the references [6–9] represent only possible examples.

A fundamentally different approach is to compute the set of all possible nonnegative solutions and afterwards to reduce the set of solutions by applying various constraints. In the best case only a single and thus unique solution can be extracted. For the computation of the set of all solutions, Section 3 explains the details, we use its low-dimensional representation in the form of the Area of Feasible Solutions (AFS) [3,10–12]. An alternative way for the reduction of the rotational ambiguity by means of soft constraints is to start with a computation of the minimal and maximal band boundaries for each part of the solution [13–15]. In a second step the effect of soft constraints can be studied on changes of the minimal and maximal band boundaries. The results of the AFS and of the band boundaries approaches are similar, see [16]. Here we follow the AFS approach as it contains the detailed information on each feasible

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factorization. Furthermore, the band boundaries can always be generated from the AFS, whereas the band boundaries do not allow to reconstruct all feasible factorizations.

The aim of this paper is to demonstrate the impact of soft constraints on the solutions represented by the AFS and to present a hybrid approach which combines the conceptual rigor of an AFS computation with the successful regularization techniques underlying soft constraints. The resulting method allows to extract chemically meaningful solutions from the set of feasible nonnegative factors. Recently Beyramysoltan et al. [17,18] presented similar results in the context of equality constraints.

1.1. Organization of the paper

In Section 2 a short introduction is given to the basics of multivariate curve resolution methods. The idea behind the AFS is reviewed in Section 3. The key concept, namely how to combine soft constraints with AFS computations, is presented in Section 4. Applications to a model problem and to experimental FT-IR spectroscopic data are contained in Sections 5 and 6.

1.2. Notation

Throughout this paper, variable names for matrices are capital letters. The colon notation [19] is used to extract columns and rows from matrices. For a matrix $M \in \mathbb{R}^{m \times n}$ its i th row is

$$M(i, :) = (m_{i1}, \dots, m_{in})$$

and its i th column is

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

The (i, j) -element of the matrix M is written in the two equivalent forms $M_{ij} = M(i, j)$. Vectors are written either by using the colon notation or by lower case letters.

The pseudo-inverse of the matrix M is denoted by M^+ and the Frobenius norm $\|M\|_F$ is the square root of the sum of all squared matrix elements.

2. Multivariate curve resolution

The Lambert–Beer law in matrix form (1) poses the problem to find for a sequence of spectra, which are collected in the columns of the data matrix $D \in \mathbb{R}^{k \times n}$, the unknown factors $C \in \mathbb{R}^{k \times s}$ and $A \in \mathbb{R}^{s \times n}$. Therein s is the number of independent chemical components of the given reaction system. As already mentioned, the factors C and A are not unique but many nonnegative factorizations exist. For the actual computation of such factorizations a singular value decomposition $D = U\Sigma V^T$ of the spectral data matrix is the starting point [20,21]. Such a rank- s decomposition (or rank- s approximation if singular values smaller than a certain threshold value are ignored) has the form

$$D \approx U\Sigma V^T = \underbrace{U\Sigma T^{-1}}_{=C} \underbrace{TV^T}_{=A} \quad (2)$$

with the matrices U and V of left and right singular vectors. According to Eq. (2) the $s \times s$ regular matrix T allows to represent all possible factorizations just by linear combinations of the rows of V^T in the form $A = TV^T$. Similarly, the columns of $U\Sigma$ are used to build the concentration factor in the form $C = U\Sigma T^{-1}$. Consequently, Eq. (2) reduces the degrees of freedom of possible factorizations from $(k + n)s$ variables, that is the number of matrix elements of C and A , to only s^2 variables, namely the number of matrix elements of T .

Without loss of generality the pure component spectra can be calibrated in a way that all matrix elements in the first column of T are equal to 1 so that

$$T = \begin{pmatrix} 1 & t_{12} & \dots & t_{1s} \\ \vdots & \vdots & \dots & \vdots \\ 1 & t_{s2} & \dots & t_{ss} \end{pmatrix}. \quad (3)$$

Thus only $(s - 1)s$ degrees of freedom are remaining, see [22,3, 11,23–25]. The precise justification for this calibration is that any pure component spectrum is guaranteed to always have a contribution from the first right singular vector. This is a result of the Peron–Frobenius theory of nonnegative matrices, see [24] for the details. Nonnegativity of the factors, i.e. $C, A \geq 0$, is a basic requirement. Unfortunately, the nonnegativity constraint is in most cases not sufficient for a unique solution. Usually, there are many nonnegative solutions and many associated feasible matrices T representing these solutions. The method of choice in order to reduce these sets of feasible solutions is to formulate additional soft constraints which the solutions should fulfill, see [6,21,26]. Typical examples are constraints on

1. the unimodality of the concentration profile
2. the smoothness of the concentration profiles or spectra profiles
3. the windowing of the concentrations or the spectra.

Soft constraints are required to hold at least approximately. In contrast to this, hard modeling always forces that a certain solution completely fulfills the constraint. Typically, kinetic models for the chemical reaction are used in the form of hard models, see e.g. [6,27].

3. The area of feasible solutions

While multivariate curve resolution (MCR) methods by means of soft/hard modeling aim at computing a single factorization $D \approx CA$, the most general approach to the MCR problem is to compute the set of all possible (feasible) factorizations with componentwise nonnegative factors C and A . How to describe such a set of all possible nonnegative factorizations? For two-component systems an answer was given in 1971 by Lawton and Sylvester [1], see also [22,28]. For three-component systems this representation problem is for instance treated in [18,3,29,10,30,11,12,24]. For four-component systems a first solution has been presented in [31]. No solutions are known for systems with more than four components.

The key idea for the low dimensional representation of the set of feasible factorizations is to consider

1. only one of the factors, either A or C , as one factor also determines the other factor. Without loss of generality we consider the factor A for this discussion.
2. only the first spectrum or the first row of A , since the order of the rows of A can freely be selected (as a solution $D = CA$ always implies further solutions with row-permuted A and column-permuted C).
3. only the matrix elements $x := (t_{12}, \dots, t_{1s})$ of T as these elements according to Eq. (2) uniquely determine the first row of A , that is the first spectrum.

These three reduction steps allow to represent the set of all nonnegative spectra for an s -component system by the following set of $(s - 1)$ -dimensional row vectors

$$\mathcal{M} = \{x \in \mathbb{R}^{1 \times (s-1)} : \text{a regular matrix } T \text{ exists with } T(1, :) = (1, x) \text{ and } C, A \geq 0\} \quad (4)$$

where C , A and T are given by Eqs. (2) and (3). The set \mathcal{M} is called the AFS. In Eq. (4) the AFS is characterized for the spectral factor. Similarly the AFS can be defined for the concentration factor.

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