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On the area of feasible solutions and its reduction by the complementarity theorem

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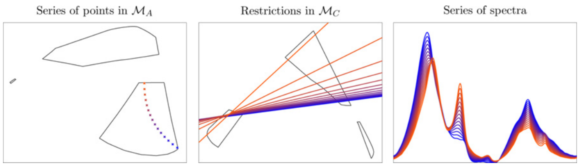
HIGHLIGHTS

- We show how the rotational ambiguity can drastically be reduced by means of the complementarity theorem.
- The results directly apply to the area of feasible solutions (AFS).
- A reduction of the rotational ambiguity up to uniqueness is possible.
- The new methods are tested for FT-IR spectroscopic data.
- A software implementation is made available in FAC-PACK.

GRAPHICAL ABSTRACT



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ABSTRACT

Multivariate curve resolution techniques in chemometrics allow to uncover the pure component information of mixed spectroscopic data. However, the so-called rotational ambiguity is a difficult hurdle in solving this factorization problem. The aim of this paper is to combine two powerful methodological approaches in order to solve the factorization problem successfully. The first approach is the simultaneous representation of all feasible nonnegative solutions in the area of feasible solutions (AFS) and the second approach is the complementarity theorem. This theorem allows to formulate serious restrictions on the factors under partial knowledge of certain pure component spectra or pure component concentration profiles.

In this paper the mathematical background of the AFS and of the complementarity theorem is introduced, their mathematical connection is analyzed and the results are applied to spectroscopic data. We consider a three-component reaction subsystem of the Rhodium-catalyzed hydroformylation process and a four-component model problem.

1. Introduction

Multivariate curve resolution (MCR) methods in chemometrics are important and successful tools to extract information on the pure components from spectroscopic data of multi-component chemical reaction systems. However, MCR methods suffer from the so-called rotational ambiguity. This means that the factorization problem for the spectral data matrix often has wide ranges of nonnegative solutions. These solutions are called feasible factors. From these solutions the "true" nonnegative concentration profiles of the pure components and their associated spectra are to be selected. For two-component systems the observation of such continua of possible solutions has been made by Lawton and Sylvestre [1]. They also gave a representation of these continua of solutions by plotting the associated expansion coefficients in the plane. Such a

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representation of range of feasible solutions by sets of expansion coefficients is called an area of feasible solutions (AFS). For three-component systems Borgen and Kowalski [2] have devised a technique for representing the AFS also in the two-dimensional plane. For details on the construction of the AFS see [3–6]. The numerical computation of the AFS is very intensive in terms of computing time. For three-component systems efficient numerical processes have been presented in [7–9]. For four-component systems Golshan, Maeder and Abdollahi [10] recently presented a technique to compute the AFS.

1.1. *Using supplemental information*

Once having computed the AFS for a given spectral data matrix, one is interested in selecting one solution from the AFS which fits best the chemical system under consideration. Any further information on the reaction system can help to decrease the ambiguity and so to reduce the AFS. Various chemometric techniques have been developed to this end. Examples are the window factor analysis [11], the evolving factor analysis [12,13], the application of unimodality conditions [14] or the use of kinetic models [15–18] and last but not least the uniqueness theorems by Manne [19]. Another approach for feeding-in partial knowledge of the factors in order to reduce the rotational ambiguity is the *complementarity and coupling theory* which have been introduced in [20].

1.2. *Aim and organization of this paper*

The aim of this paper is to combine the complementarity theorem from [20] with the AFS for systems with an arbitrary number of components; practical applications are shown for three- and four-component chemical reaction systems. It is shown how the knowledge of a single spectrum, i.e. a single point of the spectral AFS, can reduce the AFS for the concentration factor for the remaining components to a straight line in case of a three-component system and vice versa, cf. [9,21]. We also consider four-component systems where a pre-given point in the spectral AFS results in a plane in the AFS for the concentration factors. Such additional information on a chemical reaction system is sometimes accessible as the spectra of the reactants or the spectrum of the main product might be available. In other cases there are techniques to determine the concentration profiles of certain species. In Section 4 we consider experimental data from the Rhodium-catalyzed hydroformylation from which a catalytic subsystem with three components is studied.

The paper is organized as follows: after a brief introduction to the spectral recovery problem and to the AFS, the mathematical background for the application of the complementarity theorem to the AFS is discussed in Section 3. Numerical results are presented for a three-component system which is a subsystem of the Rhodium-catalyzed hydroformylation. Further a four-component model problem is studied.

2. Area of feasible solutions

2.1. *The factorization problem*

The key equation for the following analysis is the low-rank-approximation of the spectral data matrix $D \in \mathbb{R}^{k \times n}$

$$D \approx \underbrace{U\Sigma T^{-1}}_{C}\underbrace{TV^T}_{A}, \tag{1}$$

which can be computed from a singular value decomposition [22] of D. Therein U is a $k \times s$ matrix containing the first s left singular vectors of D, the $n \times s$ matrix V contains the first s right singular vectors of D and Σ is the $s \times s$ diagonal matrix with the s largest singular values on its diagonal, see [23,24] for details. The regular $s \times s$ matrix T serves to represent the rotational ambiguity. The desired approximate factors C and A of D can be computed by right-multiplication of $U\Sigma$ with T^{-1} and left multiplication of V^T by T. Spectral recovery amounts to the construction of a suitable T by using soft constraints, kinetic models or any other additional information, see e.g. [14–16,25,26].

A systematic and fundamental approach to the factorization problem is to compute and to represent the full set of all nonnegative solutions simultaneously. This complete representation is just the AFS. For an explanation of the AFS see the seminal papers of Borgen and Kowalski [2] as well as Rajkó and István [3]. Newer contributions on the numerical computation of the AFS for two-, three- and four-component systems can be found in [5–10].

2.2. *Singular vector expansions*

The representation of the AFS for the spectral factor is based on the expansion of the spectra with respect to the basis of right singular vectors given by V. In a similar way the AFS for the concentration factor rests on an expansion of the concentration profiles with respect to the basis of left singular vectors given by U.

In (1) the rows (spectra) of A are represented as linear combinations of the right singular vectors, which are the columns of V. The ith row of $A = TV^T$ reads

$$A(i,:) = (t_{i1}, \ldots, t_{is})V^T = t_{i1}\left(1, \underbrace{\frac{t_{i2}}{t_{i1}}, \ldots, \frac{t_{is}}{t_{i1}}}_{=:x}\right)V^T = t_{i1}(1,x)V^T. \tag{2}$$

Therein $t_{i1} \neq 0$ has been used, a fact which is by no means obvious, but has been proved in Theorem 2.2 of [9]. Eq. (2) shows that the ith spectrum $A(i,:)$ aside from scaling is uniquely determined by the row vector $x \in \mathbb{R}^{s-1}$ of expansion coefficients. The scaling constant t_{i1} in (2) can be written as

$$t_{i1} = (T)_{i1} = (AV)_{i1} = (AV(:,1))_i. \tag{3}$$

The construction for the factor C is similar. The jth column of $C = U\Sigma T^{-1}$ with $(T^{-1})_{ij} = \bar{t}_{ij}$ reads

$$C(:,j) = U\Sigma(\bar{t}_{1j}, \ldots, \bar{t}_{sj})^T = \bar{t}_{1j}U\Sigma\left(1, \underbrace{\frac{\bar{t}_{2j}}{\bar{t}_{1j}}, \ldots, \frac{\bar{t}_{sj}}{\bar{t}_{1j}}}_{=:y}\right)^T$$

$$= \bar{t}_{1j}U\Sigma(1,y)^T. \tag{4}$$

Once again, $\bar{t}_{1j} \neq 0$ is guaranteed by Theorem 2.2 in [9]. It holds that

$$\bar{t}_{1j} = (T^{-1})_{1j} = (\Sigma^{-1}U^TC)_{1j} = \sigma_1^{-1}U(:,1)^TC(:,j). \tag{5}$$

2.3. *The AFS*

As shown in Eq. (2) any spectrum can be represented (aside from scaling) by its vector x of expansion coefficients with respect to the right singular vectors $V(:,2), \ldots, V(:,s)$. This is the basis for a low dimensional representation of the AFS. A further argument is needed for the representation of the AFS, namely that by a permutation matrix P and its inverse P^T can be inserted between C and A in (1) and that this allows to rearrange the row of A and columns of C arbitrarily, since $CA = (CP^T)(PA) = (U\Sigma T^{-1}P^T)(PTV^T)$. Therefore only the first row of T is to be considered in order to define the AFS for the spectral factor. The delineation of the area of feasible solutions