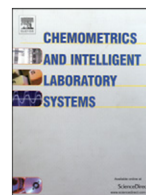
Chemometrics and Intelligent Laboratory Systems 150 (2016) 29–40

Contents lists available at ScienceDirect

Chemometrics and Intelligent Laboratory Systems

journal homepage: www.elsevier.com/locate/chemolab



Correcting inner filter effects, a non multilinear tensor decomposition method

Jeremy Emile Cohen [a,*], Pierre Comon [a], Xavier Luciani [b,c]

[a] Department of Image and Signal-processing, Gipsa-lab, CNRS, Grenoble, France
[b] Aix Marseille Université, CNRS, ENSAM, LSIS, UMR 7296, 13397 Marseille, France
[c] Université de Toulon, CNRS, LSIS, UMR 7296, 83957 La Garde, France, France

ARTICLE INFO

Article history:
Received 1 June 2015
Received in revised form 29 October 2015
Accepted 3 November 2015
Available online 12 November 2015

Keywords:
Fluorescence spectroscopy
Tensor decomposition
Inner filter effects
Identification

ABSTRACT

Among measurement used in analytical chemistry, fluorescence spectroscopy is widely spread and its applications are numerous. To recover various information on unknown components in chemical mixtures, multilinear tensor decomposition of multiway fluorescence spectra has proven extremely powerful. However, inner filter effects induce a systematic error on measurements, disturbing the decomposition. In this paper, we fully describe a non multilinear approach to include inner filter effects in the model instead of neglecting them or correcting them by linearization methods. A theoretical framework on non multilinear tensor decomposition is developed, an algorithm to recover the factors in the decomposition is detailed, and real data computer results are reported.
© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Fluorescence spectroscopy is a non invasive method for identifying components and determining their relative contribution in samples. Measurements consist of the response of the studied solution to a monochromatic source, repeated for multiple excitation wavelengths and recorded at multiple emission wavelengths [1]. The data is then stored in a Fluorescence Emission Excitation Matrix (FEEM). Because fluorescent chemical component (fluorophore) can be identified given its excitation and emission spectra, analyzing fluorescence data is typically a blind source separation problem, where the sources are the unknown fluorophores, and the observations are the mixing of their spectrum stored in the FEEM.

During the last decade, the Canonical Polyadic decomposition (CPD) [2] of tensors (seen as multiway arrays), also known in the community as CANonical DECOMPosition (CANDECOMP) [3] or PARAllel FACtor analysis (PARAFAC) [4], has proven very efficient at solving this blind source separation problem [5]. The core idea behind tensor decomposition is that using only one FEEM and without any other a priori knowledge, it is theoretically and practically impossible to recover the components linearly because usually their contribution to the FEEM overlaps. However, using multiple FEEM from different samples provides a third diversity: the fluorophore concentration profile through the sample set and hence a 3-way data tensor. This ensures that information can be obtained on each component individually. A sampling campaign is then an easy way to get a tensor whose decomposition reveals the different components in the mixture. This approach is now currently used in analytical chemistry [6] or environmental sciences, in particular for Dissolved Organic Matter (DOM) tracing and characterization purpose [7,8]. However there is a fundamental problem using the CPD to separate sources in fluorescence spectroscopy. Indeed it is well known that the suitability of the linear fluorescence model for describing a FEEM decreases with the solution absorbency [1]. Hence, in many practical situations, the gradual absorption by the solution of both exciting and fluorescent lights cannot be neglected. These effects are known as inner filter effects (IFE) [9,10]. IFE affect both FEEM magnitude and patterns and are still noticeable at quite low concentrations, since the absorbency can still be very high. For instance, this is the case for protein at low excitation wavelengths.

Most IFE correction methods consist of deducing the linear contribution from the measured FEEM, which is then called the linearized FEEM. The nonlinear contribution directly depends on the solution absorbance spectrum. Therefore a first linearization may be achieved by strongly diluting the solution until reaching a maximal absorbance threshold [11]. However the procedure can be very tedious and can lead to contamination or physico-chemical changes, thus modifying the fluorescence properties of the sample. The most common alternative is to measure the absorbance spectrum of the solution and then deduce the nonlinear contribution and finally linearize the FEEM [12,13]. However absorbance measurement is much less sensitive than fluorescence measurement and can lead to poor results [14]. In addition, it often requires another experimental device. In order to avoid these complications,

* Corresponding author.
E-mail addresses: jeremy.cohen@gipsa-lab.grenoble-inp.fr (J.E. Cohen), pierre.comon@gipsa-lab.grenoble-inp.fr (P. Comon), luciani@univ-tln.fr (X. Luciani).

http://dx.doi.org/10.1016/j.chemolab.2015.11.002
0169-7439/© 2015 Elsevier B.V. All rights reserved.

more sophisticated correction methods that require neither a strong dilution of the solution nor the absorbance spectrum knowledge have been recently proposed in Refs. [14,15].

In other words, to perform the three-way decomposition of a set of FEEM suspected to be affected by IFE, FEEM are linearized independently, one after the other. Then a tensor gathering the linearized FEEM is built and the CPD can be computed to identify individual spectra and concentration profiles. Thereby these approaches do not directly exploit the tensorial structure of the initial data set. In addition these methods require additional measurements for each solution in order to linearize the corresponding FEEM, which is time consuming and not always possible.

We show in this contribution that such a fluorescent tensor can be directly decomposed without any linearization step, and we give a complete analysis of all aspects of the resolution of the inverse problem. Following the non-linear model including inner filter effects [14], some mathematical aspects are explored, focusing on local identifiability in Section 2.3. The optimization problem and an efficient algorithm are then described in Section 3. Finally, in Sections 4 and 5 we study its assets on two real data sets.

2. A nonlinear fluorescence tensor decomposition

2.1. Modeling inner filter effect

We consider here a set of K FEEM measured from K mixtures of R fluorophores.

Each fluorophore r can be characterized by the evolution of its concentration throughout the mixture set (its concentration profile), the evolution of its molar extinction coefficient wrt (the excitation) wavelength and the evolution of its light emission probability as a function of (the emission) wavelength. In the following these values are denoted by vector $\mathbf{a}_r$ and functions $\tilde{b}_r(\lambda^{ex})$ and $\tilde{c}_r(\lambda^{em})$ respectively. Note that any function of the form $\alpha\tilde{b}_r(\lambda^{ex})$ defines the excitation spectrum of r and any function of the form $\beta\tilde{c}_r(\lambda^{em})$ defines its emission spectrum in arbitrary units. Let $x_k(\lambda^{ex}, \lambda^{em})$ be the fluorescence intensity measured from a given mixture (sample) k at a given couple $(\lambda^{ex}, \lambda^{em})$ of excitation and emission wavelengths. A classical continuous fluorescence model, taking into account IFE is then given by the following nonlinear relationship [14]:

$$x_k(\lambda^{ex},\lambda^{em}) = \sum_{r=1}^{R}(\mathrm{a}_r)_k\tilde{b}_r(\lambda^{ex})\tilde{c}_r(\lambda^{em})\nu_r\prod_{r=1}^{R}e^{-\mu\left[(\mathrm{a}_r)_k\left(\tilde{b}_r(\lambda^{ex})+\tilde{b}_r(\lambda^{em})\right)\right]} + e_k(\lambda^{ex},\lambda^{em}), \quad (1)$$

where $(\mathrm{a}_r)_k$ denotes the kth entry of $\mathbf{a}_r$, ν_r and μ are unknown values modeling non observable or experimental parameters (such as fluorophore quantum yields, optical path length…) and e is an error term. Indeed, we have to recall here that although it takes into account IFE, this model is still an approximation of the (noisy) fluorescence measurement [14,16]. Since excitation and emission spectra are unnormalized, it is then interesting to define functions $\mathrm{b}_r(\lambda^{ex})$ and $\mathrm{c}_r(\lambda^{em})$ as

$$\mathrm{b}_r(\lambda) = \mu\tilde{b}_r(\lambda), \quad (2)$$

$$\mathrm{c}_r(\lambda^{em}) = \frac{\nu_r}{\mu}\tilde{c}_r(\lambda^{em}), \quad (3)$$

yielding a simpler model:

$$x_k(\lambda^{ex},\lambda^{em}) = \sum_{r=1}^{R}(\mathrm{a}_r)_k\mathrm{b}_r(\lambda^{ex})\mathrm{c}_r(\lambda^{em})\prod_{r=1}^{R}e^{-(\mathrm{a}_r)_k\left(\mathrm{b}_r(\lambda^{ex})+\mathrm{b}_r(\lambda^{em})\right)} + e_k(\lambda^{ex},\lambda^{em}). \quad (4)$$

Now turning back to our set of FEEM, we respectively denote $[\lambda_{ex}^{min};\lambda_{ex}^{max}]$, Δ_{ex}, $[\lambda_{em}^{min};\lambda_{em}^{max}]$ and Δ_{em} as the excitation range, the excitation sampling step, the emission range and the emission sampling step used to measure each FEEM. Excitation and emission range sizes are denoted L and M respectively. We assume for the moment that excitation and emission sampling steps are equal and that in the wavelength range $[\lambda_{em}^{min};\lambda_{ex}^{max}]$ all excitation wavelengths and emission wavelengths coincide i.e. $\Delta_{ex} = \Delta_{em}$ and λ_{em}^{min} coincides with a value of λ_{ex}. At this point this assumption is fundamental but we will see in the algorithm description how it can be relaxed.

In practice, for numerical computations, excitation and emission wavelength ranges are substituted by two ranges of integer index: $[1; L]$ and $[1; M]$ respectively so that if we call $\mathcal{X}$ the fluorescence tensor of size $(K \times L \times M)$ that gathers these K FEEM we have:

$$\mathcal{X}_{klm} = x_k\left(\lambda_{ex}^{min} + (l-1)\Delta_{ex}, \lambda_{em}^{min} + (m-1)\Delta_{em}\right). \quad (5)$$

In the same way, for each fluorophore r we can define discrete version of excitation and emission spectra truncated in the considered excitation and emission ranges as vectors of sizes L and M and denoted respectively $\mathbf{b}_r$ and $\mathbf{c}_r$, whose entries are defined by:

$$(\mathrm{b}_r)_l = \mathrm{b}_r\left(\lambda_{ex}^{min} + (l-1)\Delta_{ex}\right), \quad (6)$$

$$(\mathrm{c}_r)_m = \mathrm{c}_r\left(\lambda_{em}^{min} + (m-1)\Delta_{em}\right). \quad (7)$$

We also assume that λ_{ex}^{min} and λ_{em}^{min} can be different and we define the wavelength index shift s as:

$$s = \frac{\lambda_{em}^{min} - \lambda_{ex}^{min}}{\Delta_{ex}} + 1. \quad (8)$$

Note that according to the previous hypothesis, it appears clearly that s is a strictly positive integer.

As a consequence, in order to develop a rigorous discrete version of the continuous non-linear fluorescence Model (4) we need to define a "shifted" excitation b_r' spectra of size M as:

$$(\mathrm{b}_r')_m = (\mathrm{b}_r)_{m+s-1} \ \text{ if } \ m \leq L-s+1, \quad (9)$$

$$(\mathrm{b}_r')_m = 0 \ \text{ if } \ m > L-s+1. \quad (10)$$

Finally $\mathcal{X}$ can be decomposed as:

$$\mathcal{X}_{klm} = \sum_{r=1}^{R}\mathrm{A}_{k,r}\mathrm{B}_{l,r}\mathrm{C}_{m,r}\prod_{r=1}^{R}e^{-A_{k,r}\left(\mathrm{B}_{l,r}+\mathrm{B}'_{m,r}\right)} + \mathcal{E}_{klm}, \quad (11)$$

where $\mathbf{A}$, $\mathbf{B}$, $\mathbf{B}'$ and $\mathbf{C}$ are matrices of size $(K \times R)$, $(L \times R)$, $(M \times R)$ and $(M \times R)$ respectively so that column r of $\mathbf{A}$ (respectively $\mathbf{B}$, $\mathbf{B}'$ and $\mathbf{C}$) contains vector $\mathbf{a}_r$ (respectively $\mathbf{b}_r$, $\mathbf{b}_r'$ and $\mathbf{c}_r$). This decomposition is called the Non Linear Fluorescence Decomposition (NLFD) and matrices $\mathbf{A}$, $\mathbf{B}$ and $\mathbf{C}$ are the factor matrices of the decomposition ($\mathbf{B}'$ being directly deduced from $\mathbf{B}$). We also refer to this model as non multilinear, by opposition to the usual multilinear tensor decomposition CPD.

From an algorithmic point of view, it will be useful to stack all the unknown parameters of the decomposition, i.e. all entries of $\mathbf{A}$, $\mathbf{B}$ and $\mathbf{C}$ in a unique parameter vector $\boldsymbol{\theta}$:

$$\boldsymbol{\theta} = \begin{bmatrix}\mathbf{vec}(\mathbf{A})\\ \mathbf{vec}(\mathbf{B})\\ \mathbf{vec}(\mathbf{C})\end{bmatrix}, \quad (12)$$

where $\mathbf{vec}()$ is the operator that maps a matrix or a tensor to a column vector by stacking its columns one below the other in a

Download English Version:

https://daneshyari.com/en/article/1179437

Download Persian Version:

https://daneshyari.com/article/1179437

Daneshyari.com