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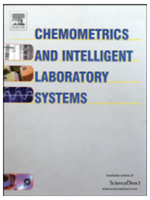

Development of a novel alternating quadrilinear decomposition algorithm for the kinetic analysis of four-way room-temperature phosphorescence data

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ABSTRACT

Four-way room-temperature phosphorescence (RTP) data recorded by following the kinetic evolution of excitation–emission phosphorescence matrices (EEPMs) have been analyzed for the first time by third-order calibration based on parallel factor analysis (PARAFAC), alternating weighted residue constraint quadrilinear decomposition (AWRCQLD) and alternating quadrilinear decomposition (AQLD) algorithms. The AQLD constructed in pseudo-fully stretched matrix forms of quadrilinear model was a new third-order calibration algorithm, which was developed as a direct extension of alternating trilinear decomposition for quadrilinear data. These methodologies were applied to investigate the hydrolysis kinetic of carbaryl even in the presence of an uncalibrated phosphorescence background and comparisons among them were done subsequently. Spectral background drift produced in measured dataset was overcome by means of modeling the drift as an additional component as well as the analyte of interest in the mathematical model. Satisfactory results were obtained for determination of carbaryl in spiked tap water samples. The spectral and kinetic time profiles resolved by these methodologies were in good agreement with experimental observations. The present work successfully faced the difficulty in investigating the hydrolysis kinetic of analyte with the RTP techniques, opening a new approach for third-order data generation and subsequent third-order calibration.

1. Introduction

There is a continuing interest in the second-order and higher-order multivariate calibration methods applied to progressively more difficult chemical scenarios in current analytical community. As the modern instrument continues to develop toward more complex arrangements, third-order data can be produced in a relatively easy way. One of the common strategies is to record full excitation–emission matrix (EEM) as a function of reaction time [1,2], pH [3,4], volume of quencher, [5] or decay time [6] using a single instrument, e.g., spectrofluorometer. The other is by resorting to hyphenated instruments, such as two-dimensional liquid or gas chromatograph (LC or GC) with time of flight mass spectrometry (TOFMS) or diode array detector (DAD) [7] and LC-DAD as a function of reaction time [8]. These types of data should, theoretically, contain the same advantages shown by second-order data, i.e., the second-order advantage [9], while offering additional advantages, such as overcoming the matrix effects, improving algorithmic resolution of serious collinear data and increasing sensitivity and selectivity [3].

Up to now, some third-order calibration algorithms for the analysis of four-way data arrays have been developed and can be generally classified into two types. The first type is based on the iterative least-squares principle, including classical parallel factor analysis (PARAFAC) [1], alternating penalty quadrilinear decomposition (APQLD) [10], alternating weighted residue constraint quadrilinear decomposition (AWRCQLD) [11], regularized self-weighted alternating quadrilinear decomposition (RSWAQLD) [4] as well as four-way self-weighted alternating normalized residue fitting (4-way SWANRF) [12]. The second type is built on a direct least-squares procedure, for example, trilinear least-squares algorithm combined with the separate procedure known as residual trilinearization (TLLS/RTL) [1], unfolded and N-way partial least-squares and unfolded principal component analysis combined with RTL (U-PLS/RTL [13], N-PLS/RTL [14] and U-PCA/RTL [15], respectively). A new toolbox, namely multivariate calibration 3 (MVC3), has recently been developed by Olivieri et al. [16] for implementing third-order multivariate calibration methodologies.

These methodologies have been successfully applied to extract the qualitative and quantitative information of single component or mixture components in complex practical samples. PARAFAC used to analyze third-order data is by far the most popular case. Pertinent examples are the simultaneous determination of methotrexate and leucovorin or folic and methotrexate in human urine [1,17], carbaryl in effluent water [18], tetracycline in tea [5], fenvalerate [2] and the polycyclic aromatic hydrocarbons in soil samples [6]. Porter et al. have presented PARAFAC-alternating least squares (ALS) for the first time to quantitatively analyze quadrilinear 2D-LC-DAD data of complex

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mixtures, including proteomic and metabolomic [19]. Two new algorithms, TLLS/RTL and UPLS/RTL, have been employed by Arancibia et al. for the quantitative analysis of methotrexate and leucovorin [13]. Xia et al. have proposed APQLD for an analysis of the hydrolyzed reaction of procaine hydrochloride embedded in a human plasma background [10]. A genuine multidimensional tool, NPLS/RTL, has been developed by Damiani et al. for simultaneous analysis of procaine and its metabolite p-aminobenzoic acid in equine serum [14]. García-Reiriz et al. have reported on a new application of classical PARAFAC and novel UPCA/RTL to quantitatively determine malonaldehyde in the complex background of olive oil samples [15]. AWRCQLD proposed by Fu et al. has been employed to predict the oxprozin concentration in the presence of high collinearity and matrix effect between the target analyte and plasma background [11]. The two latest third-order algorithms, RSWAQLD and 4-way SWANRF, have been applied to process four-way fluorescence excitation–emission–pH data, respectively [4,12].

Carbaryl (CBL), a toxic pesticide for human systems, is widely used in agriculture to control a number of insect pests on stored grain, grass lawns, fruits and vegetables [18].

It has been previously reported that fluorescence [18,20] and chromatographic methods [21] can be applied to investigate the hydrolysis kinetic of CBL (Fig. 1). However, so far none of the published papers have reported on the application of room-temperature phosphorescence (RTP) method to investigate the hydrolysis kinetic of it. RTP, firstly, is an extremely selective and very sensitive technique that shows potential for sample determination without prior separation. Secondly, many mature RTP technology, such as non-protected-RTP (NP-RTP) [22], solid substrate-RTP (SS-RTP) [23], micelle-stabilized-RTP (MS-RTP) [24] and cyclodextrin-induced-RTP (CD-RTP) [25] are developed in recent decades and all of them can provide stable and long-lasting phosphorescence signal. Thirdly, because the signal intensity of phosphorescence is directly proportional to concentration within linear ranges, excitation–emission phosphorescence matrix (EEPM) data usually follow a trilinear model. The technique in combination with second-order calibration methods have been applied to determine pyrene and benzo[α]pyrene [26], screen oil samples from the south of Argentina [27] and resolve a binary mixture of phenanthrene and 1,10-phenanthroline [28]. Moreover, the technique also provides us a new form of obtaining third-order data by introducing an additional dimension, likely, such as reaction time, pH, and volume of quencher or decay time similar to the fluorescence technique. However, the former has scarcely been employed to date for developing higher-order calibration, especially for third-order calibration methodologies. The reason is maybe that the considerable experimental difficulty is involved in the technique or the limited number of compounds to the technique can be applied. The only one reported is the application of the technique to the obtained third-order time-resolved-EEM low-temperature phosphorescence (LTP) data for the determination of 2,3,7,8-tetrachlorodibenzo-para-dioxin in highly contaminated waters [29].

In the present report, we use the RTP technique to continuously monitor the kinetics evolution of CBL by recording full EEPMs of the samples at different reaction times measured by spectrofluorometer in phosphorescence mode at room-temperature. To the best of our knowledge, this is the first time that this form of third-order data is generated. For the purpose of investigating the analytical properties of the obtained third-order data, we compare the performances of parallel factor analysis (PARAFAC), alternating weighted residue constraint quadrilinear decomposition (AWRCQLD) and a new algorithm, which is called alternating quadrilinear decomposition (AQLD), developed as an extension of alternating trilinear decomposition (ATLD) [30] for quadrilinear data and presented for the first time in this paper. These methodologies are applied to investigate the hydrolysis kinetic of CBL even in the presence of an uncalibrated phosphorescence background in complex practical samples, i.e., tap water samples. Additionally, the serious spectral background drift which is observed in all the samples are overcome by means of regarding the drift as an additional factor as well as the analyte of interest in the mathematical model.

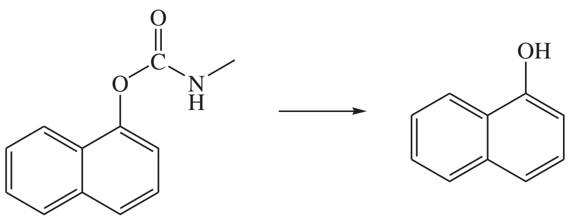

Fig. 1. The degradation process of carbaryl in alkaline medium.

2. Theory

2.1. Quadrilinear model for third-order calibration

A given sample produces third-order data when a $I \times J \times K$ data array (or third-order array) is experimentally obtained, where I, J, and K denote the number of data points in each of the three dimensions. One way of analyzing this type of data is to join the L_0 calibration sample arrays $\underline{\mathbf{X}}_{l_0,cal}$ and the L_u unknown sample arrays $\underline{\mathbf{X}}_{l_u,un}$ into a four-way data array $\underline{\mathbf{X}}$q, whose dimensions are $I \times J \times K \times L$, where $L = L_0 + L_u$. According to the quadrilinear model, each element x_{ijkl} of the data array $\underline{\mathbf{X}}$q can be represented generally as following,

$$x_{ijkl} = \sum_{n=1}^{N} a_{in} b_{jn} c_{kn} d_{ln} + e_{ijkl}, i = 1, 2\ldots, I; j = 1, 2\ldots, J; k = 1, 2\ldots, K; l = 1, 2, \ldots, L. \tag{1}$$

where N denotes the number of factors, which is really the total number of detectable physically-meaningful components of interest as well as the interferents and the background. Fig. 2 shows the graphical representation of quadrilinear model of four-way data array $\underline{\mathbf{X}}$q.

A, **B**, **C** and **D** are the four underlying profile matrices of $\underline{\mathbf{X}}$q with $I \times N$, $J \times N$, $K \times N$ and $L \times N$, respectively; $\underline{\mathbf{I}}$ is the four-way diagonal core array of size $N \times N \times N \times N$ with ones on the superdiagonal and zeros elsewhere; $\underline{\mathbf{E}}$ is the four-way residue data array of size $I \times J \times K \times L$.

Quadrilinear model can also be expressed in the following forms: (1) four fully slicewise matrices [31],

$$\mathbf{X}_{.jk.} = \mathbf{D}\mathrm{diag}(\mathbf{c}_k)\mathrm{diag}\left(\mathbf{b}_{(j)}\right)\mathbf{A}^T + \mathbf{E}_{.jk.} \tag{2}$$

$$\mathbf{X}_{..kl} = \mathbf{A}\mathrm{diag}\left(\mathbf{d}_{(l)}\right)\mathrm{diag}\left(\mathbf{c}_{(k)}\right)\mathbf{B}^T + \mathbf{E}_{..kl} \tag{3}$$

$$\mathbf{X}_{i..l} = \mathbf{B}\mathrm{diag}\left(\mathbf{a}_{(i)}\right)\mathrm{diag}\left(\mathbf{d}_{(l)}\right)\mathbf{C}^T + \mathbf{E}_{i..l} \tag{4}$$

$$\mathbf{X}_{ij..} = \mathbf{C}\mathrm{diag}\left(\mathbf{b}_{(j)}\right)\mathrm{diag}\left(\mathbf{a}_{(i)}\right)\mathbf{D}^T + \mathbf{E}_{ij..} \tag{5}$$

(2) four fully stretched matrices [31],

$$\mathbf{X}_{I\times JKL} = \mathbf{A}(\mathbf{D}\odot\mathbf{C}\odot\mathbf{B})^T + \mathbf{E}_{I\times JKL} \tag{6}$$

$$\mathbf{X}_{J\times KLI} = \mathbf{B}(\mathbf{A}\odot\mathbf{D}\odot\mathbf{C})^T + \mathbf{E}_{J\times KLI} \tag{7}$$

$$\mathbf{X}_{K\times LIJ} = \mathbf{C}(\mathbf{B}\odot\mathbf{A}\odot\mathbf{D})^T + \mathbf{E}_{K\times LIJ} \tag{8}$$

$$\mathbf{X}_{L\times IJK} = \mathbf{D}(\mathbf{C}\odot\mathbf{B}\odot\mathbf{A})^T + \mathbf{E}_{L\times IJK} \tag{9}$$