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Dealing with overlapped and unaligned chromatographic peaks by second-order multivariate calibration for complex sample analysis: Fast and green quantification of eight selected preservatives in facial masks

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ABSTRACT

The quantification of preservatives in cosmetics has attracted great attentions for their controversial and widespread use. HPLC is a prevailing method for preservatives determination among various analytical methods. However, it takes long time to fully separate these compounds because of the complexity of cosmetic matrices. In this study, a fast and green HPLC-DAD strategy assisted with second-order multivariate calibration methods based on alternating trilinear decomposition (ATLD) and multivariate curve resolution-alternating least squares (MCR-ALS) was developed for the simultaneous determination of eight selected preservatives in complex facial mask samples. This appealing strategy proved to be a useful tool for eliminating unknown interferences in complex matrices without complete separation, which benefited from the "second-order advantages" and thus made the determination of the eight analytes in facial mask samples shorten to 8.2 min under a fast elution program. In particular, for the first time, we focused on the applicability of ATLD method for modeling of HPLC-DAD data with severe signal overlapping and slight time shifts. The spiked recovery values were in the range of 71.4–124.6%, and the RMSEP and REP values ranged from 0.07 to 2.4 $\mu g\,mL^{-1}$ and 1.3–14.5%, respectively, indicating that the ATLD method could provide satisfactory prediction. The resolved spectral profiles and concentration values were compared with those obtained by the MCR-ALS method, an excellent tool for modeling of data deviating from trilinearity. Both qualitative and quantitative results from the two methods were consistent with each other, which evidenced the competence of ATLD method in handling HPLC-DAD data with severe signal overlapping and slight time shifts.

1. Introduction

The use of preservatives as essential ingredients in cosmetics and skin care products such as creams, facial masks, and deodorants is gaining momentum, both for keeping products integrity and also for catering to consumers [1]. However, in contrast to their preservative effects, the healthy damages are received more attentions because of their potential toxic effects on humans, ranging from mild skin irritation to estrogenic activity [2]. More than that, some preservatives are reported to potentially induce human breast tumours [3]. In view of the significant matter of healthy concerns, the permission and prohibition of preservatives in cosmetic products have been strictly regulated by health authorities. For example, the use of parabens including methylparaben, ethylparaben, propylparaben and butylparaben, a family of the most frequently used preservatives in cosmetic products due to their broad-spectrum antimicrobial property and low-cost [4], is restricted by the Ministry of Public Health of China [5]. What's more, some of the parabens are prohibited in cosmetic products by the European Commission [6]. As a result, the cosmetic industries are continuously looking for other new compounds that can perform the preservative function effectively and safely. Among various alternative preservatives, phenoxyethanol, salicylic acid, methylisothiazolinone and 3-iodo-2-propynyl-*n*-butylcarbamate

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are widespread in a variety of cosmetics [7]. Despite their low-toxic features, these compounds are also listed as the controlled preservatives in EU regulation (No. 1223/2009) [8]. Therefore, it is necessary that the cosmetic manufacturers have procedures to perform the analysis of these allowed and controlled preservatives, not only for quality control but also for consumer interest protection. Regrettably, there are not official methods to simultaneously quantify these target compounds in cosmetic samples yet [9].

As far as we know, several analytical methods have been reported for the determination of preservatives in cosmetics, environmental samples and food matrices, including high-performance liquid chromatography (HPLC) [10–14], gas chromatography (GC) [15–17], micellar electrokinetic chromatography [18,19] and capillary zone electrophoresis [20] coupled to UV/DAD or MS detectors. However, complicated solid or liquid extraction and clean-up steps are always needed because of the complexity of cosmetic matrices [21,22]. This implies that very long-time, tedious procedures and amount of hazardous reagents are required for the quantification of preservatives. Even so, these analytes sometimes still cannot be separated completely during the identification procedures, and, in addition, co-elution of many other cosmetic additives is very common during the quantification [22]. Thus, fast, easy and green analytical methods are desiderated to be developed for determination of preservatives in cosmetics. At this stranded moment, the increasing applications of second-order multivariate calibration methods for treating multi-way data from hyphenated chromatography caught our attentions [23–29], because this strategy could mathematically separate the contribution of individual chemical component as *a posteriori* even in the presence of unknown interferences, termed as the "second-order advantages" [30]. This means that in principle it could be possible to implement simple sample pretreatments and select fast elution program resulting in not perfect chromatographic separations, with accompanied reducing of experimental burdens and toxic organic reagents as well as analysis time and cost. In this sense, "mathematical separation" based on second-order multivariate calibration nicely caters for the goal of handling the problems derived from determination of preservatives in complex cosmetic matrices by traditional chromatography-based methods as mentioned above.

There are a large number of multivariate calibration algorithms involving the second-order advantage and can be applied to treating three-way data derived from hyphenated chromatography [31–34]. Among these algorithms, multivariate curve resolution-alternating least squares (MCR-ALS) [35] and parallel factor analysis 2 (PARAFAC2) [36] are commonly used because of their tolerances to some degree of deviations from trilinearity in three-way data array. As for those algorithms that require the data with trilinear structure, a proper data preprocessing is demanded because time shifts and/or baseline drifts often occur between different chromatographic runs. Interestingly, according to some previously published literature [37–39], alternating trilinear decomposition (ATLD) algorithm based on trilinear component model exhibits some capacities for handling baseline drifts and slight time shifts. The former property has been well-documented [37], however, none of them have conducted an in-depth study on the latter one.

Accordingly, the purpose of this work was to develop a fast and green HPLC-DAD strategy for high-quality resolution and quantification of the eight selected preservatives, i.e. methylparaben, ethylparaben, propylparaben, butylparaben, phenoxyethanol, salicylic acid, methylisothiazolinone and 3-iodo-2-propynyl-*n*-butylcarbamate in complex facial mask samples using second-order multivariate calibration methods based on ATLD and MCR-ALS algorithms. In particular, we tried to demonstrate that the ATLD method has the same ability as MCR-ALS method to deal with overlapped and unaligned chromatographic peaks. To the best of knowledge, this is the first time that the applicability of ATLD method for modeling of HPLC-DAD data with severe signal overlapping and slight time shifts has been investigated.

2. Theory

2.1. Alternating trilinear decomposition (ATLD) method

ATLD is a commonly used second-order multivariate calibration method without any constraints, which can directly decompose a three-way data array that obeys the trilinear structure [40]. In mathematical terms, if $\underline{\mathbf{X}}$ ($I \times J \times K$) is a chromatographic three-way data array obtained by stacking multiple samples including calibration samples and prediction samples, it can be decomposed into the individual component elution, spectral and concentration matrices, **A**, **B** and **C**, according to the following expression:

$$x_{ijk} = \sum_{n=1}^{N} a_{in} b_{jn} c_{kn} + e_{ijk},$$

$$\text{for} \quad i = 1, 2, \ldots, I; j = 1, 2, \ldots, J; \quad k = 1, 2, \ldots, K \tag{1}$$

where x_{ijk} is an element of the chromatographic three-way data array $\underline{\mathbf{X}}$, recording the response intensity of sample k at elution time i and spectrum channel j; N denotes the total number of responsive components; a_{in}, b_{jn} and c_{kn} are the elements of three underlying profile matrices **A** ($I \times N$), **B** ($J \times N$) and **C** ($K \times N$) of $\underline{\mathbf{X}}$; and e_{ijk} represents an element of the three-way residual data array $\underline{\mathbf{E}}$ not fitted by the model.

In ATLD, decomposition of $\underline{\mathbf{X}}$ is accomplished by alternately minimizing the following three objective functions to update the elution and spectral matrices (**A** and **B**) and the relative concentrations matrix (**C**) of individual components based on the alternating least-squares principle. More details about ATLD method were well-documented in its original literature [40].

$$S(\boldsymbol{A}) = \sum_{i=1}^{I} \| \boldsymbol{X}_{i..} - \boldsymbol{B} diag(\boldsymbol{a}_{(i)}) \boldsymbol{C}^{\mathrm{T}} \|_{\mathrm{F}}^{2} \tag{2}$$

$$S(\boldsymbol{B}) = \sum_{j=1}^{J} \| \boldsymbol{X}_{.j.} - \boldsymbol{C} diag(\boldsymbol{b}_{(j)}) \boldsymbol{A}^{\mathrm{T}} \|_{\mathrm{F}}^{2} \tag{3}$$

$$S(\boldsymbol{C}) = \sum_{k=1}^{K} \| \boldsymbol{X}_{..k} - \boldsymbol{A} diag(\boldsymbol{c}_{(k)}) \boldsymbol{B}^{\mathrm{T}} \|_{\mathrm{F}}^{2} \tag{4}$$

2.2. Multivariate curve resolution-alternating least squares (MCR-ALS)

MCR-ALS is another useful second-order multivariate calibration method for decomposing the chromatographic landscape of a sample into the contribution of elution and spectral profiles of individual components [35]. Different from the ATLD method, an augmentation step is needed for the chromatographic three-way data array along the mode which is suspected of breaking the trilinear structure, usually along the retention time direction. Then, the augmented matrix $\mathbf{D}_{aug}$, containing K calibration sample matrices and one test sample matrix, is decomposed into an augmented elution matrix $\mathbf{C}_{aug}$ and a spectral matrix **S** of individual components, according to the following expression:

$$\mathbf{D_{aug}} = \mathbf{C_{aug}} \mathbf{S}^{\mathrm{T}} + \mathbf{E_{aug}} \tag{5}$$

where $\mathbf{D}_{aug}$ is an augmented matrix containing the absorption spectra measured as a function of time with a size of [I

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