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Chemometrics-assisted high performance liquid chromatography-diode array detection strategy to solve varying interfering patterns from different chromatographic columns and sample matrices for beverage analysis

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ABSTRACT

This work reports a chemometrics-assisted high performance liquid chromatography-diode array detection (HPLC-DAD) strategy to solve varying interfering patterns from different chromatographic columns and sample matrices for the rapid simultaneous determination of six synthetic colorants in five kinds of beverages with little sample pretreatment. The investigation was performed using two types of LC columns under the same elution conditions. Although analytes using different columns have different co-elution patterns that appear more seriously in complex backgrounds, all colorants were properly resolved by alternating trilinear decomposition (ATLD) method and accurate chromatographic elution profiles, spectral profiles as well as relative concentrations were obtained. The results were confirmed by those obtained from traditional HPLC-UV method at a particular wavelength and the results of both methods were consistent with each other. All results demonstrated that the proposed chemometrics-assisted HPLC-DAD method is accurate, economical and universal, and can be promisingly applied to solve varying interfering patterns from different chromatographic columns and sample matrices for the analysis of complex food samples.

1. Introduction

Reversed-phase high performance liquid chromatography (RP-HPLC) has become an indispensable tool for the routine analysis and research in pharmaceutical, biomedical, food and environmental industries. In order to improve the selectivity and sensitivity of HPLC method, many RP-HPLC stationary phases and sample pretreatment methods have been developed. Nowadays, several hundreds of different RP-HPLC stationary phases are commercially available in the market and new ones are being introduced regularly [1,2]. Ironically, the wide range of possible stationary phases makes it difficult for the analysts to determine which would be the most suitable for a given situation. In addition, the biased chromatographic column information about their stationary phases provided by manufacturers [3] and ambiguous stationary phases information in terms of chain length, end-capping, base-deactivation, particle size and sometimes pore size and specific surface provided by some official compendia [4], such as the European Pharmacopoeia (Ph. Eur.) [5] or the United States Pharmacopoeia (USP) [6], may make it difficult to select an appropriate stationary phase or chromatographic column. Also, another fact we should realize is that common control laboratories do not usually have all available stationary phases and the column properties will change over long-term storage and/or usage in LC analysis [7]. So, it is possible that the required column is not easily available in the market or is not present at all. Thus, the analysts often resort to screen several different stationary phases to find the most appropriate one for separation.

In fact, it is a hard work to find a replacement column that can provide 'equivalent' separation efficiency as the original column described in an existing method or a paper. In order to select an appropriate column, a variety of chromatographic test methods have been developed for evaluation and characterization of columns [1–4,8,9]. These evaluations typically rely on the determination of some specific column properties such as efficiency, hydrophobicity, silanol activity, ion-exchange capacity,

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steric selectivity and the level of metal impurity. Although the test procedures seek to evaluate similar stationary phase characteristics, there are distinct differences in the methodologies used for determining those characteristics, and none of the tests is generally accepted [3]. In addition, it has never been proved that columns with similar test characteristics indeed give similar separation efficiency in practice [3,8]. For example, as reported by Dehouck et al. [8] although several types of columns belong to a class due to having a low hydrophobicity, they do not result in similar separations: one column gives a good separation for all analytes, while the other columns give co-elution of two or more peaks. Therefore, easily implemented and universal methods are urgently needed for solving varying co-elution patterns from different chromatographic columns in routine HPLC analysis.

Another common problem in chromatographic analysis is the diversity and complexity of sample matrices attributing to the wide distribution of analytes. For a given chromatographic method, complete baseline separation can be achieved in one matrix, but may not be carried out in other matrices [10]. The usual methodologies developed for solving this problem are based on sample pretreatment steps before analysis, such as solid-phase extraction (SPE) (both off-line and on-line), solid-phase micro-extraction (SPME), microwave-assisted extraction [11], which permit one chromatographic method can be applied in various complex matrices. However, extensive extraction or clean-up steps can result in the loss of a fraction of analytes and the increase of toxic solvent and labor consumption.

Synthetic colorants, widely distributed in all kinds of food, are usually added to foodstuffs and soft drinks not only to improve appearance, color and texture but also to maintain the natural color during process or storage [12]. However, many of them may exhibit adverse health effects [13], thus there is a growing need for analytical control of colorants to ensure that banned additives are not present in food and to determine those permitted by regulations [12,14]. Chromatographic techniques are the most usual alternatives to analyze a mixture of colorants, including capillary electrophoresis [15], thin-layer chromatography [16] and the most widely used high-performance liquid chromatography [12,17–19]. Nevertheless, as previously mentioned, the successful application of a certain HPLC method depends on the reasonable column selection and sample pretreatment, which is time-consuming and environmentally unfriendly. In short, it is necessary to develop a universal, high-efficiency and green method that can solve varying interfering patterns from different chromatographic columns and sample matrices.

Chemometricians have been developing diverse chemometric techniques for deconvolution and resolution of spectral and chromatographic data [20–30]. Among chemometric methodologies, the multi-way calibration methods based on “mathematical separation” are stars in the night, and have been successfully utilized in combination with second- or high-order instruments for the analysis of unresolved peaks and uncalibrated interferences in many complex samples [31–36]. HPLC-DAD coupled with second-order calibration methods is especially popular for it can rapidly and simultaneously determine multiple compounds in complex backgrounds with unknown interferences, resolve co-eluted peaks and remove baselines drifts [37–41].

The aim of this work was to develop a universal and high-efficiency HPLC-DAD strategy that can solve varying interfering patterns from different chromatographic columns and sample matrices, so as to realize the rapid and green analysis. In this paper, HPLC-DAD coupled with second-order calibration method based on the alternating trilinear decomposition (ATLD) algorithm was developed for the identification and quantification of six common synthetic colorants (see Table S1) in five kinds of beverages. This investigation was performed on two brands of C18 LC columns, a ZORBAX Eclipse XDB-C18 column and a WondaSil C18 column. The elution profiles of each sample vary significantly depending on the selected column and the types of beverage, which make the full resolution and quantification difficult in traditional HPLC analysis. Fortunately, with the help of “mathematical separation” and “second-order advantage” of second-order calibration method, the ATLD method can serve as a complementary technique to provide accurate concentrations together with reasonable chromatographic and spectral profiles for the compounds of interest, even in the presence of complex and varying interfering patterns.

2. Theory

2.1. Trilinear component model for second-order calibration

The schematic representation for second-order calibration process based on three-way HPLC-DAD data was shown in Fig. S1. If there are no obvious changes in peak positions or shapes from sample to sample, the three-way data array $\underline{\mathbf{X}}$ ($I \times J \times K$) will have an inherent mathematical structure called trilinearity, which can be depicted as follows:

$$x_{ijk} = \sum_{n=1}^{N} a_{in} b_{jn} c_{kn} + e_{ijk} \quad \text{for } i = 1, ..., I; j = 1, ..., J; k = 1, ..., K \tag{1}$$

where, x_{ijk}, the element of $\underline{\mathbf{X}}$, is the response intensity of sample k at elution time i and spectral channel j; N denotes the number of factors, which is actually the total number of detectable components including calibrated analytes of interest, uncalibrated interfering substances as well as backgrounds in the sample matrices; a_{in} is the element (i, n) of an $I \times N$ matrix $\mathbf{A}$ with normalized chromatograms of the N species; b_{jn} is the element (j, n) of a $J \times N$ matrix $\mathbf{B}$ with normalized spectra of the N species; c_{kn} is the element (k, n) of a $K \times N$ matrix $\mathbf{C}$ with relative concentrations of the N species in K samples; and e_{ijk} represents the element of the three-way residual data array, $\underline{\mathbf{E}}$ ($I \times J \times K$).

2.2. Alternating trilinear decomposition (ATLD) method

ATLD method, developed by Wu et al. in 1996 [42] without any constraints, is one of the most commonly used second-order calibration methods, and is particularly suitable for handling second-order data from hyphenated instruments, such as HPLC-DAD, LC–MS and GC–MS. It has been widely applied in quantitative analysis [43] due to the advantages of being insensitive to excessive number of components, fast convergence and fully exploiting the “second-order advantage”. ATLD alternately minimizes the following three objective functions (Eqs. (2)–(4)) to update the qualitative profiles ($\mathbf{A}$ and $\mathbf{B}$) and the relative concentrations ($\mathbf{C}$) of individual components based on the alternating least-squares principle. More details about ATLD method and its comparison with other methods can be found in our previous works [44,45].

$$\sigma_1(\mathbf{C}) = \sum_{k=1}^{K} \| \mathbf{X}_{..k} - \mathbf{A}\, diag\left(\mathbf{c}_{(k)}\right) \mathbf{B}^T \|_F^2 \tag{2}$$

$$\sigma_2(\mathbf{A}) = \sum_{i=1}^{I} \| \mathbf{X}_{i..} - \mathbf{B}\, diag\left(\mathbf{a}_{(i)}\right) \mathbf{C}^T \|_F^2 \tag{3}$$

$$\sigma_3(\mathbf{B}) = \sum_{j=1}^{J} \| \mathbf{X}_{.j.} - \mathbf{C}\, diag\left(\mathbf{b}_{(j)}\right) \mathbf{A}^T \|_F^2 \tag{4}$$

2.3. Quantitative analysis

The final quantification of target analytes was achieved based on external calibration procedures [42,43]. The first step was to establish a pseudo-univariate calibration curve by regressing the relative