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Simultaneous determination of naphazoline and pyridoxine in eye drops using excitation–emission matrix fluorescence coupled with second-order calibration method based on alternating trilinear decomposition algorithm

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ABSTRACT

A novel method is developed for the direct determination of naphazoline hydrochloride (NAP) and pyridoxine hydrochloride (VB6) in commercial eye drops. By using excitation–emission matrix (EEM) fluorescence coupled with second-order calibration method based on the alternating trilinear decomposition (ATLD) algorithm, the proposed approach can achieve quantitative analysis successfully even in the presence of unknown and uncalibrated interferences. The method shows good linearity for NAP and VB6 with correlation coefficients greater than 0.99. The results were in good agreement with the labeled contents. To further confirm the feasibility and reliability of the proposed method, the same batch samples were analyzed by multiple reaction monitoring (MRM) based on LC–MS/MS method. *T*-test demonstrated that there are no significant differences between the prediction results of the two methods. The satisfactory results obtained in this work indicate that the use of the second-order calibration method coupled with the EEM is a promising tool for industrial quality control and pharmaceutical analysis due to its advantages of high sensitivity, low-cost and simple implementation.
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1. Introduction

Second-order calibration methodology with attractive "second-order advantage" has become a research hotspot in current chemometric domain and has been widely accepted in many scientific fields [1–4]. Our laboratory has reported some work about the determination of multi-components in complex samples using second-order calibration methods [5–8]. Naphazoline hydrochloride (NAP, Fig. 1) [2-(naphthalene-1-yl-methyl)-4,5-dihydro-1*H*-imidazole hydrochloride] is a decongestant, which acts on α-adrenergic receptors in the arterioles of the conjunctiva to produce vasoconstriction, resulting in decreased conjunctival congestion [9]. Pyridoxine hydrochloride (VB6, Fig. 1) [5-hydroxy-6-methyl-3,4-pyridinedimethanol] is a water-soluble vitamin and primarily involved in the metabolism of amino acid carbohydrate and fat [10]. Several pharmaceuticals containing the two active ingredients are currently commercialized as eye drops in China [11]. In order to keep the quality of preparations high, it is essential to quantitatively determine NAP and VB6 in the eye drops. So far, no analytical method has been reported for the simultaneous analysis of NAP and VB6 in the eye drops. High performance liquid chromatographic (HPLC) and liquid chromatography–tandem mass spectrometry (LC–MS/MS) methods were reported for individual determination of NAP or VB6 in pharmaceutical preparations [12–14]. However, these methods are complicated and need expensive instruments. In addition, each eye drop includes various excipients that sometimes interfered with determination. This report describes a simple, sensitive and rapid method for the direct and simultaneous determination of NAP and VB6 in commercial eye drops products using excitation–emission matrix fluorescence coupled with second-order calibration based on alternating trilinear decomposition (ATLD) algorithm.

2. Experimental

NAP and VB6 were purchased from the National Institute for Control of Pharmaceutical and Biological Products (Changsha, China). The eye drop samples, Xinledun (XLD) and Shanliang (SL),

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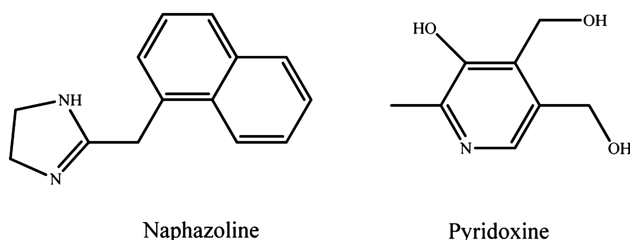

Fig. 1. The chemical structures of NAP and VB6.

were made in China and purchased from local drug stores. The active ingredients were labeled (per 10 mL) as 0.3 mg of NAP and 5.0 mg of VB6. The standard solutions of NAP (0.10 mg mL^{-1}) and VB6 (0.10 mg mL^{-1}) were prepared by dissolving corresponding standard analyte with ultra-pure water in 10 mL volumetric flasks as the stock solutions. The stock solutions were stored in a refrigerator at 4 °C. The water was prepared with a Milli-Q water purification system (Aquapro, China).

The working solutions were prepared by appropriate dilution of the stock solution in ultra-pure water. In terms of the linear analytical ranges of NAP and VB6, 14 samples (8 for calibration plus 2 for actual samples in triplicate) were prepared for the determination of NAP and VB6. The first eight samples contained NAP in the concentration range from 0.03 $\mu g\ mL^{-1}$ to 0.80 $\mu g\ mL^{-1}$ and VB6 in the concentration range from 0.2 $\mu g\ mL^{-1}$ to 3 $\mu g\ mL^{-1}$. The concentrations of the calibration sets are displayed in Table 1. 1 mL of each commercial eye drop was transferred into a 10 mL volumetric flask and diluted with ultra-pure water. Further dilution was done with ultra-pure water to reach a concentration of 0.12 $\mu g\ mL^{-1}$ of NAP and 2.0 $\mu g\ mL^{-1}$ of VB6 in triplicate.

All fluorescence measurements were performed on an F-7000 fluorescence spectrophotometer (HITACHI, Tokyo, Japan) equipped with a xenon lamp. All measurements were recorded in a 1.0 cm quartz cell. The spectra were obtained by scanning the mixture standard solutions recording at the excitation wavelengths in the range from 200 nm to 380 nm at regular steps of 2.0 nm and emission wavelengths in the range from 280 nm to 550 nm at regular steps of 3.0 nm. Excitation and emission slit widths were both set to be 5 nm, the scan rate was 12,000 nm min^{-1}, and the detector voltage was 550 V. Under the chemical conditions mentioned above, each sample can obtain a two-way data array of size 91 × 91. All computer programs were written in MATLAB, and all calculations were carried out on a personal computer with Windows 7 operating system. All glassware was rinsed with doubly distilled water before use.

3. Theory

3.1. Trilinear component model for second-order calibration

In the second-order calibration, the noted trilinear component model proposed by Harshman [15] and Carol and Chang [16] has

Table 1
Concentrations of eight calibration samples.

Sample	NAP ($\mu g\ mL^{-1}$)	VB6 ($\mu g\ mL^{-1}$)
C01	0.03	1.20
C02	0.05	3.00
C03	0.08	0.80
C04	0.10	2.50
C05	0.20	0.50
C06	0.40	2.00
C07	0.60	0.20
C08	0.80	1.60

been widely accepted, owing to its consistency with the Beer's law in chemistry. The excitation-emission matrix (EEM) fluorescence at I excitation wavelengths and J emission wavelengths for K samples can get a three-way data array $\underline{\mathbf{X}}$. This three-way data array has an internally mathematical structure called trilinear, which can be depicted as follows:

$$x_{ijk} = \sum_{n=1}^{N} a_{in} b_{jn} c_{kn} + e_{ijk}, \quad \text{for } i = 1,2,\ldots,I;\ j = 1,2,\ldots,J;\ k = 1,2,\ldots,K. \tag{1}$$

where x_{ijk}, the element of $\underline{\mathbf{X}}$, is the fluorescent intensity of sample k at excitation wavelength i and emission wavelength j, a_{in} is the element (i, n) of an $I \times N$ matrix $\mathbf{A}$ with normalized excitation spectra of the N species in K samples; b_{jn} is the element (j, n) of a $J \times N$ matrix $\mathbf{B}$ with normalized emission spectra of the N species in K sample; 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 residual element of an $I \times J \times K$ three-way residual array, $\underline{\mathbf{E}}$. N denotes the number of factors, which should be considered as the total number of fluorescing species, including the components of interest and the background as well as uncalibrated interferences.

A typical property of $\underline{\mathbf{X}}$ is that it can be uniquely decomposed, which can provide access to spectral profiles ($\mathbf{A}$ and $\mathbf{B}$) and the relative concentrations ($\mathbf{C}$) of individual components in K samples, even in the presence of chemically unknown interferences. The property is well-known as the "second-order advantage".

3.2. ATLD method

ATLD method, developed by Wu *et al.* in 1996 [17], is one of the most commonly used methods for processing second-order data. ATLD algorithm alternately minimizes the following three objective functions (2)–(4) based on an alternating least-squares principle and the Moore–Penrose generalized inverse computations with truncated singular value decomposition (SVD) to update the qualitative profiles ($\mathbf{A}$ and $\mathbf{B}$) and the relative concentration ($\mathbf{C}$) of individual components until a certain stopping criterion is satisfied, usually $\varepsilon = 10^{-6}$, calculated according to Eq. (5).

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

$$\sigma(\mathbf{B}) = \sum_{j=1}^{J} ||\mathbf{X}_{.j.} - \mathbf{C}diag(\mathbf{b}_{(j)})\mathbf{A}^T||_F^2 \tag{3}$$

$$\sigma(\mathbf{C}) = \sum_{k=1}^{K} ||\mathbf{X}_{..k} - \mathbf{A}diag(\mathbf{c}_{(k)})\mathbf{B}^T||_F^2 \tag{4}$$

$$\left|\frac{\sigma^{(m)} - \sigma^{(m-1)}}{\sigma^{(m-1)}}\right| \le \varepsilon \tag{5}$$

The ATLD method holds the advantages of fast convergence, being insensitive to excessive factors and more robust as the introduction of Moore–Penrose pseudo-inverse computation in the iterative procedures compared to the traditional PARAFAC algorithm. More details about ATLD and its comparison with other algorithms can be found in our previous works [18,19].

4. Results and discussion

The first- and second-order Rayleigh scattering that partly overlaps with the signals of NAP and VB6 and the Raman scattering that even runs throughout it make the data analysis rather difficult. When selecting a rectangular area without Rayleigh and Raman

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