Rapid determination of thiabendazole in orange extract using excitation-emission matrix fluorescence and second-order calibration based on alternating trilinear decomposition/alternating normalization-weighted error algorithms

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A novel approach is proposed for direct quantitative analysis of thiabendazole in the orange extract by using excitation-emission matrix fluorescence coupled with second-order calibration methods based on the alternating trilinear decomposition (ATLD) and the alternating normalization-weighted error (ANWE) algorithms, respectively. The average recoveries of thiabendazole in the orange extract by using ATLD and ANWE with an estimated component number of two were 99.7 ± 3.3% and 103.5 ± 4.1%, respectively. Furthermore, the accuracy of the two algorithms was also evaluated through elliptical joint confidence region (EJCR) tests as well as figures of merit, such as sensitivity (SEN), selectivity (SEL) and limit of detection (LOD). The experimental results demonstrate that both algorithms have been satisfactorily applied to the determination of thiabendazole in orange extract, and the performance of ANWE is slightly better than that of ATLD.

1 Introduction

Thiabendazole (TBZ) is a widely used fungicide that is applied to citrus fruits, apples, bananas and other produce in order to control pathogens. In this sense, post-harvest treatment of fruits and vegetables with fungicides is a worldwide agricultural practice, aiming to avoid rotting, and thus, elongates the shelf life of products. Because thiabendazole is a systemic pesticide, the residue of it is frequently found in agricultural commodities, which poses a threat to the health of human beings[1]. To ensure the safety of food for consumers, in the relevant laws and regulations and standards the maximum residue limits (MRL) have been established for pesticides in foodstuffs (http://postharvest.ifas.ult.edu). The tolerance levels of TBZ in citrus fruits are approved to be 6, 10, 10, and 10 mg·kg⁻¹ respectively, in Europe, Japan, America and China.

Nowadays, the used methods for the determination of TBZ in food include gas chromatography (GC)/mass spectrometry (MS)[2], high performance liquid chromatography (HPLC) with ultraviolet (UV) detection[3], HPLC-MS[4-6], micellar electrokinetic chromatography[7], thin layer chromatography[8], LC/TOFMS and LC/ion trap (IT) MS[9].

A reversed phase high performance liquid chromatograph coupled with a fluorescence detector[10], and a

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multicommented fluorescence-based optosensor\textsuperscript{[11]} can be used to determine TBZ in food; liquid-liquid extraction with the fluorimetry method has also been used for analyzing TBZ in garlic sprouts because TBZ is soluble in ethyl acetate in a basic medium but soluble in water in an acid environment\textsuperscript{[12]}. All of three methods take the advantage of the characteristic of TBZ’s fluorescence.

However, the costs of these methods are high. They involve labor-intensive sample preprocessing and usually use high volumes of toxic solvents. Fluorescence detection combined with chemometric methodologies in which “mathematical separation” replaces “chemical separation” can directly determine TBZ in mixtures. The application of a collection of parallel factor analysis (PARAFAC) and excitation-emission matrix (EEM) fluorescence spectroscopy for studying a synthesized mixture of carbendazim, fuberidazole and thiabendazole was reported recently\textsuperscript{[13]}, but no one has determined TBZ in complicated samples using three-way fluorescence with a second-order calibration algorithm.

In the present study, TBZ was directly analyzed in garlic sprouts using the alternating trilinear decomposition (ATLD)\textsuperscript{[14]} and the alternating normalization-weighted error (ANWE) algorithms\textsuperscript{[15]}, respectively, to resolve the fluorescence EEM spectra in spite of the existence of orange by using the alternating trilinear decomposition (ATLD)\textsuperscript{[14]} and the alternating normalization-weighted error (ANWE) algorithms\textsuperscript{[15]}, respectively, to resolve the EEM fluorescence spectra, in spite of the existence of many unknown interferences. The result is favorable and the second-order advantage is adequately exploited.

2 Theory

2.1 Trilinear model for second-order calibration

In the case of EEM fluorescence, a three-way data array, \( \mathbf{X} \), can be produced by stacking a series of excitation-emission matrix fluorescence spectra obtained for each of the \( K \) samples. The dimensions of such an array are \( I \times J \times K \) (\( I \) is the number of excitation wavelengths and \( J \) the number of emission wavelengths). The trilinear component model\textsuperscript{[14]} for such a three-way data array, \( \mathbf{X} \), can be given by

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

\((i = 1, 2, \ldots, I; j = 1, 2, \ldots, J; k = 1, 2, \ldots, K)\),

(1)

where \( N \) denotes the number of factors, which should be considered as a total number of fluorescent species, including the components of interest and background as well as uncalibrated interferences. \( x_{ijk} \) is the element of the three-way data array \( \mathbf{X} \) (\( I \times J \times K \)), which represents the fluorescent intensity of sample \( k \) at excitation wavelengths \( i \) and emission wavelengths \( j \). \( a_{in} \) is the element \((i, n)\) of an \( I \times N \) matrix \( \mathbf{A} \) with relative excitation spectra of the \( N \) species. \( b_{jn} \) is the element \((j, n)\) of an \( J \times N \) matrix \( \mathbf{B} \) with relative emission spectra of the \( N \) species. \( c_{kn} \) is the element \((k, n)\) of an \( K \times N \) matrix \( \mathbf{C} \) with relative concentrations of the \( N \) species in \( K \) samples, and \( e_{ijk} \) is the \( ij \)th element of the three-way residual array \( \mathbf{E} \) \((I \times J \times K)\).

2.2 ATLD algorithm\textsuperscript{[14]}

The ATLD algorithm uses the alternating least-squares principle, Moore-Penrose generalized inverse based on singular value decomposition (SVD) and an alternating iterative strategy to improve the performance of trilinear decomposition, making a loss function to reach a minimum. The loss function is defined as the sum of squares of residual errors. One can get the relative excitation concentrations matrix \( \mathbf{A} \), the relative emission matrix \( \mathbf{B} \), and the relative concentrations matrix \( \mathbf{C} \). After the appropriate processing of \( \mathbf{A} \), \( \mathbf{B} \) and \( \mathbf{C} \), the final concentration estimation of components of interest in unknown samples may be directly obtained according to the second-order calibration procedure described in ref. \cite{14}.

2.3 ANWE algorithm

The ANWE algorithm is a novel algorithm proposed by our laboratory recently\textsuperscript{[15]}. In this algorithm, one decomposes the model by alternately minimizing the following three objective functions (ANW error):

\[
S(\mathbf{C}) = \sum_{i=1}^{I} \| D_i \mathbf{B}^T (\mathbf{X}_{ik} - B \text{diag}(a_{ik}) \mathbf{C}^T) \|_F^2
\]

\[+ \sum_{j=1}^{J} \| D_j \mathbf{A}^T (\mathbf{X}_{jk} - C \text{diag}(b_{jk}) \mathbf{A}^T) \|_F^2, \tag{2}\]

\[
S(\mathbf{A}) = \sum_{j=1}^{J} \| D_j \mathbf{C}^T (\mathbf{X}_{jk} - C \text{diag}(b_{jk}) \mathbf{A}^T) \|_F^2
\]

\[+ \sum_{k=1}^{K} \| D_k \mathbf{B}^T (\mathbf{X}_{ik} - A \text{diag}(c_{ik}) \mathbf{B}^T) \|_F^2, \tag{3}\]

\[
S(\mathbf{B}) = \sum_{k=1}^{K} \| D_k \mathbf{A}^T (\mathbf{X}_{ik} - A \text{diag}(c_{ik}) \mathbf{B}^T) \|_F^2
\]

\[+ \sum_{i=1}^{I} \| D_i \mathbf{C}^T (\mathbf{X}_{ik} - B \text{diag}(a_{ik}) \mathbf{C}^T) \|_F^2, \tag{4}\]

where

\[
D_i = \text{diag} (\text{sqrt}(\text{diagm}(\mathbf{A}^T \mathbf{A}))),
\]

\[
D_j = \text{diag} (\text{sqrt}(\text{diagm}(\mathbf{B}^T \mathbf{B}))),
\]

\[
D_k = \text{diag} (\text{sqrt}(\text{diagm}(\mathbf{C}^T \mathbf{C}))),
\]