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Automatic generation of photochemically induced excitation-emission-kinetic four-way data for the highly selective determination of azinphos-methyl in fruit juices

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ABSTRACT

An application of four-way multivariate calibration for the quantitation of azinphos-methyl (AZM) in fruits is presented. The known photochemically induced degradation of AZM into a highly fluorescent product was exploited for the generation of third-order data with quantitative purpose. The data generation consisted in the measurement of excitation-emission fluorescence matrices at different times after UV-light irradiation. For this purpose, a reactor was built connecting an external UV-light source through an optical fiber to the sample holder. The data were modelled with two algorithms, PARAFAC and U-PLS/RTL. The second-order advantage was exploited in the analysis of samples containing un-modelled components and an improvement in the analytical figures of merit was observed as long as the data dimensions were increased. The method was successfully applied to the quantitation of AZM in apple, pear and peach juice samples with and without spiked analyte. The limits of detection were of 3.6 $\mu g\,L^{-1}$ in aqueous solution and 21–66 $\mu g\,L^{-1}$ in fruit juice samples.

1. Introduction

Although the use of pesticides provides benefits to the agriculture industry, their incorrect application may leave harmful residues, which involves possible health risks. The concentration of pesticides is regulated in many samples such as drinking waters, vegetables, juices, etc., by the European Commission [1] and the Food and Drug Administration [2], among other agencies. In Argentina, the National Service of Health and Agrifood Quality (SENASA), which is responsible for the registration, use and regulation of pesticides, sets the maximum residue levels (MRLs), i.e. the highest level of a pesticide residue that is legally tolerated in or on food or feed when pesticides are applied correctly [1,3].

Azinphos-methyl (AZM) is an organophosphate insecticide and acaricide, widely and efficiently used to protect pomes (apple and pear), drupe (peach, plum and cherry) and nut trees from a variety of insects. AZM presents a weak natural fluorescence in aqueous solution, which can be enhanced in a variety of ways, including UV photolysis, inclusion into cyclodextrins, and base hydrolysis [4]. There are previous studies related to the photochemistry of this important pesticide, in which different mechanisms have been proposed [4–6]. L. Yeasmin et al. have described a detailed UV-A photolysis mechanism involving two pathways, the major one leading to benzazimide as the stable photoproduct, and the other to N-methylanthranilic acid as an intermediate and aniline as a final stable photoproduct [7]. On the other hand, a base-catalysed conversion of AZM to anthranilic acid has been used to its detection in a fluorescence-based trace analysis [8].

A comprehensive search and the analysis of the reported methods for the determination of AZM evidenced a variety of techniques requiring, in their majority, highly sophisticated equipment. Among them, high performance liquid chromatography-diode array detector (HPLC-DAD) [9], liquid chromatography triple quadrupole tandem mass spectrometry (LC-QqQ-MS/MS) [10], gas chromatography-tandem mass spectrometry (GC–MS/MS) [11,12], gas chromatography-nitrogen phosphorous detection (GC-NPD) [13,14] and micellar electrokinetic chromatography (MEKC) [15] can be mentioned. Considering these techniques provide good and reliable results, the aim was to achieve such satisfactory performance but using a simpler and more accessible technique, as it is fluorescence spectroscopy, and to make an extra contribution to the method outcome by using higher dimension data and multiway calibration.

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In analytical chemistry, the use of higher order data has been increased due to the current technological development. There is an improvement in the selectivity and sensitivity of the analysis when the data dimension is augmented, which provides additional sample information. Furthermore, the second-order advantage is achieved with second- and higher-order data and enables the accurate quantitation of the calibrated analytes in the presence of non-modelled substances [16].

Introducing an extra data dimension to a second-order data leads to third-order data, and the mathematical object obtained by grouping third-order data for several samples into the fourth dimension is known as a four-way array [17]. Fluorescence spectroscopy, a technique widely applied in chemical and biological sciences, is highly sensitive and allows obtaining four-way data by introducing additional dimensions [18]. Different strategies, such as recording the excitation–emission fluorescence matrix (EEFM) as a function of pH [18,19] or volume of quencher [20], and time evolution of EEFM data while following the kinetics of a reaction [21–27], have been reported.

Several algorithms, such as parallel factor analysis (PARAFAC) [28,29], multivariate curve resolution alternating least squares (MCR-ALS) [29], unfolded partial least squares and multi-way partial least squares combined with residual trilinearization (U-PLS/RTL, N-PLS/RTL) [24,28–30], alternating quadrilinear decomposition (AQLD) and alternating weighted residue constraint quadrilinear decomposition (AWRCQLD) [31], among others, are available for the analysis of four-way data tensors.

In the present work, we report a fluorescent kinetic method for the determination of AZM in fruit juice samples based on third-order data generation. The data were obtained by following the time evolution, with an especially designed dispositive, of the EEFMs of the photolysis of AZM in alkaline medium. Then they were analysed with two well-known algorithms for second- and third-order data, PARAFAC and U-PLS/RBL-RTL. As will be shown, important findings regarding the second- and third-order advantages were observed and discussed.

2. Theory

2.1. Parafac

Four-way data arrays ($\boldsymbol{X}$) are obtained by arranging the third-order data of size $J \times K \times L$ for a set of I calibration samples, whose dimensions are $[(I+1) \times J \times K \times L]$. For PARAFAC modelling, it is of extreme importance that $\boldsymbol{X}$ follows a quadrilinear structure, which can be represented by Eq. (1) [32]:

$$X_{ijkl} = \sum_{n=1}^{N} a_{in} b_{jn} c_{kn} d_{\mathrm{ln}} + e_{ijkl} \quad (1)$$

where x_{ijkl} is an element of the four-way array of kinetic-excitation-emission fluorescence signals, a_{in} is the score of component n in sample i, N is the total number of responsive components, b_{jn}, c_{kn} and d_{ln} are the loading elements in the excitation, emission and time dimensions, respectively, and e_{ijkl} is an element of the array of errors not fitted by the model.

The model described by Eq. (1) defines a decomposition of $\boldsymbol{X}$ which provides access to excitation ($\mathbf{B}$) and emission spectral profiles ($\mathbf{C}$), kinetic profiles ($\mathbf{D}$) and relative concentrations ($\mathbf{A}$) of individual components in the $(I+1)$ samples, whether they are chemically known or not. An alternating least-squares minimization scheme is usually implemented for decomposition [33].

The initialization for the study of four-way arrays can be done using singular value decomposition (SVD) vectors, spectral data which are known in advance for pure components, or by the loadings giving the best fit after small PARAFAC runs involving both SVD vectors and several sets of orthogonal random loadings, options which can be implemented in the PARAFAC package.

PARAFAC performs a similar modelling for three-way data arrays ($\mathbf{X}$), which are obtained by arranging the second-order data of size $J \times K$ for a set of I calibration samples, whose dimensions are $[(I+1) \times J \times K]$.

2.2. U-PLS

U-PLS is an extended version of PLS algorithm, developed for first order data, which is capable of operating with higher orders. The cube-structured data for each sample are transformed into unidimensional arrays (vectors) by unfolding the original three-dimensional data. In the calibration step, the concentration information included in the vector $\mathbf{y}$ $(I \times 1)$ is employed, excluding data for the unknown sample [34]. This procedure allows to obtain a set of loadings $\mathbf{P}$ and weight loadings $\mathbf{W}$ ($JKL \times A$, where A is the number of latent variables) as well as regression coefficients $\mathbf{v}$ (size $A \times 1$). The parameter A is usually selected by the leave-one-out cross-validation procedure [35]. Subsequently, analyte concentration in unknown samples can be predicted with $\mathbf{v}$ using the following equation:

$$y_{\mathrm{u}} = \mathbf{t}_{\mathrm{u}}{}^{\mathrm{T}} \mathbf{v} \quad (2)$$

where $\mathbf{t}_{\mathrm{u}}$ (size $A \times 1$) is the unknown sample score, obtained by projection of the (unfolded) data for the test sample $\boldsymbol{X}_{\mathrm{u}}$ [vec($\boldsymbol{X}_{\mathrm{u}}$)] of size ($JKL \times 1$) onto the space of the A latent factors:

$$\mathbf{t}_{\mathrm{u}} = (\mathbf{W}^{\mathrm{T}}\mathbf{P})^{-1}\, \mathbf{W}^{\mathrm{T}} \mathrm{vec}(\mathrm{X}_{\mathrm{u}}) \quad (3)$$

It should be noted that if the sample under evaluation contains unexpected components, the scores given by Eq. (3) will generate abnormally large residuals in comparison with the typical instrumental noise (assessed by replicate measurements) when the prediction is performed using Eq. (2).

The effect of unexpected components in samples can be modelled with the RTL procedure through Tucker3 decomposition [30], i.e. by minimizing the norm of the residual vector $\mathbf{e}_{\mathrm{u}}$, computed while fitting the sample data to the sum of the relevant contributions to the sample signal. The expression for a single interference can be written as:

$$\mathrm{vec}(\mathrm{X}_{\mathrm{u}}) = \mathbf{P}\mathbf{t}_{\mathrm{u}} + g_{\mathrm{int}}(\mathbf{d}_{\mathrm{int}} \otimes \mathbf{c}_{\mathrm{int}} \otimes \mathbf{b}_{\mathrm{int}}) + \mathbf{e}_{\mathrm{u}} \quad (4)$$

where $\mathbf{b}_{\mathrm{int}}$, $\mathbf{c}_{\mathrm{int}}$ and $\mathbf{d}_{\mathrm{int}}$ are normalized profiles in the three modes for the interference and g_{int} is the first core element obtained for Tucker3 analysis of $\boldsymbol{E}\mathrm{p}$ in the following way:

$$(g_{\mathrm{int}}, \mathbf{b}_{\mathrm{int}}, \mathbf{c}_{\mathrm{int}}, \mathbf{d}_{\mathrm{int}}) = \mathrm{Tucker3}(\mathrm{E_p}) \quad (5)$$

The number of interferences N_{i} can be assessed by evaluating the final residuals s_{u} as a function of N_{i}, until s_{u} stabilizes at a value compatible with the experimental noise, allowing the location of the correct number of components.

For second-order data, the procedure called residual bilinearization (RBL) is applied in a similar way than RTL, but using SVD instead of Tucker3 analysis of the residual matrix $\mathbf{E}\mathrm{p}$ [16].

3. Materials and methods

3.1. Instrument

All spectrofluorimetric measurements were acquired on a Cary Eclipse fluorescence spectrophotometer (Agilent Technologies, Waldbronn, Germany) using a xenon flash lamp. The fluorescence measurements were made using a thermostated cell holder and an O.R.L., Hornos Eléctricos S.A. (Buenos Aires, Argentina) thermostatic bath.