Analytica Chimica Acta 809 (2014) 37–46

Contents lists available at ScienceDirect

Analytica Chimica Acta

journal homepage: www.elsevier.com/locate/aca

Modeling four and three-way fast high-performance liquid chromatography with fluorescence detection data for quantitation of fluoroquinolones in water samples

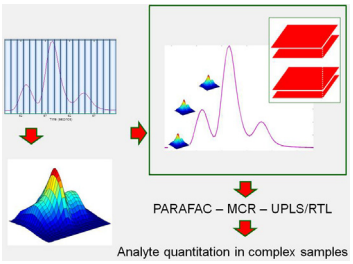
Mirta Raquel Alcaráz[a], Gabriel G. Siano[a], María Julia Culzoni[a], Arsenio Muñoz de la Peña[b], Héctor C. Goicoechea[a,*]

[a] Laboratorio de Desarrollo Analítico y Quimiometría (LADAQ), Cátedra de Química Analítica I, Facultad de Bioquímica y Ciencias Biológicas, Universidad Nacional del Litoral, Ciudad Universitaria, 3000, Santa Fe, Argentina
[b] Department of Analytical Chemistry, Faculty of Sciences, University of Extremadura, 06006, Badajoz, Spain

HIGHLIGHTS

- Four-way chromatographic-EEM data.
- Quantitation of fluoroquinolones, target analytes of the study.
- Quadrilinearity loss was observed.
- MCR-ALS allows obtaining the best results.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 12 October 2013
Received in revised form 2 December 2013
Accepted 4 December 2013
Available online 12 December 2013

Keywords:
Liquid chromatography
Third-order data
Fluoroquinolones
Water samples

ABSTRACT

This paper presents a study regarding the acquisition and analytical utilization of four and three-way data, acquired by following the excitation–emission fluorescence matrices at different elution times, in a fast liquid chromatographic HPLC procedure. This kind of data were implemented for first time for quantitative purposes, and applied to the determination of two fluoroquinolones in tap water samples, as a model to show the potentiality of the proposed strategy of four-way data generation. The data were modeled with three well-known algorithms: PARAFAC, U-PLS/RTL and MCR-ALS, the latter conveniently adapted to model third-order data. The second-order advantage was exploited when analyzing samples containing uncalibrated interferences. PARAFAC and MCR-ALS were the algorithms that better exploited the second-order advantage when no peak time shifts occurred among samples. On the other hand, when the quadrilinearity was lost due to the occurrence of temporal shifts, MCR-ALS furnished the better results. Relative error of prediction (REP%) obtained were 9.9% for ofloxacin and 14.0% for ciprofloxacin. In addition, a significant enhancement in the analytical figures of merit was observed when going from second- to third-order data (reduction of ca. 70% in LODs).

1. Introduction

In the implementation of multi-way analysis, the analytical community has found a manner to improve the quality of the results when developing analytical methods to be applied for the quantitation of target analytes in complex matrices, such as those present in environmental samples [1,2]. Using modern instrumentation, analytical laboratories can generate a variety of second- and higher-order instrumental data. Whenever these data are conveniently modeled, significant enhancement in basic analytical properties can be consequently furnished [3].

High-performance liquid chromatography (HPLC) can be combined with spectroscopic techniques such as UV–visible diode-array detection (DAD) or fast-scanning fluorescence

* Corresponding author. Tel.: +54 3424575206x190; fax: +54 3424575205.
E-mail address: hgoico@fbcb.unl.edu.ar (H.C. Goicoechea).

0003-2670/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.aca.2013.12.011

detection (FSFD), producing spectral-elution time second-order data [4]. Second-order multivariate calibration can be applied to the corresponding three-way arrays, when full selectivity in the chromatographic separation is not achieved, even in the presence of unexpected components. Additional benefits of such combination are decreasing cost and time of analysis. Recent pertinent examples can be found in the literature [5–12].

On the other hand, third-order multivariate calibration can be applied to the corresponding four-way arrays generated with chromatographic systems equipped with a proper detection way. One common example of four-way/third-order data involving chromatography is comprehensive two-dimensional gas chromatography followed by mass spectrometric detection (GC × GC-TOFMS) [13]. Another way is to record excitation–emission matrices as a function of the elution time. Very recently, this was done for the first time by performing several chromatographic runs, and recording the emission spectra of every one at a different excitation wavelength, across the excitation spectra of the compounds of interest [14].

If the latter data are registered for a group of samples, a four-way data array can be constructed, in which case the simplest model is the quadrilinear one. A four-way data array is quadrilinear if its elements comply with the following equation:

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

where a_{in} represents the relative concentration (also called *score*) of a given constituent n in the i-th sample, b_{jn}, c_{kn} and d_{ln} are the intensities in the three instrumental modes j, k and l, respectively (also called *loadings*) and e_{ijkl} collects the fitting errors. In this case, a multi-way PARAFAC model would be adequate for calibration, because this model can be applied to data with any number of ways [15].

Interestingly, multi-way data of chromatographic origin usually present multi-linearity loss owing to the variation of constituent profiles in the time mode from sample to sample. In these cases, multivariate curve resolution coupled to alternating least squares (MCR-ALS) [16] can be the algorithm of choice. MCR-ALS needs first unfolding the original third-order data into matrices, so that they could then be arranged into a bilinear augmented matrix [13,17]. On the other hand, latent structured models, as partial least squares, in its unfolded and n-way configurations (U-PLS, N-PLS) can be applied to third-order data, and when coupled to residual trilinearization (RTL) can be used to achieve the second-order advantage. These models are natural extension of residual bilinearization (RBL) to three data modes: unfolded- and n-way PLS combined with RTL (U-PLS/RTL, N-PLS/RTL) [18–20].

As regards the target analytes of the present work, fluoroquinolones (FQs), they were chosen as a model to show the potentiality of the proposed strategy of third-order data generation and pertinent modeling. FQs are highly useful antibacterial agents which are administrated in large quantities to humans and animals, and they end up in wastewater coming from hospital and municipal emissions, whereas veterinary drugs are excreted by the animals and are released in the manure. Residues of these antibiotics have been reported in the natural environment in many countries [21]. Thus, monitoring of low quantities of these compounds from different environmental matrices is essential for human health protection and environmental control. A literature search reveals that a large number of methods for the determination of FQs in environmental waters have been published, especially including liquid chromatography with fluorescence (LC-FD) or mass (LC–MS) detection [22]. Very recently, the quantitation of eight quinolones in groundwater samples, with ultrasound-assisted ionic liquid dispersive liquid–liquid microextraction, prior to high-performance liquid chromatography and fluorescence detection, has been published, reporting limits of detection between 0.8 and 13.0 ng L^{-1} [23].

In the present work, we report a method for the quantitation of FQs in water samples based on sample pre-concentration with solid phase extraction (SPE), and generation of third-order chromatographic data and their modeling with different algorithms. The procedure for generating the data was carried out collecting chromatographic fractions every 2 s. Then, EEMs were obtained for each collected fraction.

It is important to note that this is the first time that this approach is applied for quantitative purposes. Furthermore, it has the potentiality to be adapted to a high number of complex analytical applications, i.e. by obtaining the EEM at every chromatographic time more information will be available compared to the recording of the emission spectrum at one excitation wavelength (or excitation spectrum at one emission wavelength), selected as a compromise between the optimal wavelength for each analyte. Thus, optimal signal for every target analyte can be gathered exciting at all the possible different wavelengths. Additionally, the obtained information could be extremely useful for qualitative purposes, such as the identification of co-eluting compounds in highly complex samples. Consequently, the possibility of obtaining this kind of data offers two interesting advantages, independently of using chemometric modeling: (a) optimization of the couples excitation–emission wavelengths, and (b) extraction of useful information for peak identification.

2. Theory

The theory of the three algorithms used in the present report is well documented. For details see Ref. [24–26] for PARAFAC, and [18–20] and [27] for U-PLS/RTL. In the following, the theory of MCR-ALS will be presented owing to this algorithm was scarcely implemented modeling third-order data.

2.1. MCR-ALS

MCR-ALS is an algorithm capable of handling second-order data sets deviating from trilinearity, i.e., data in which time shifts or peak shape changes occur for analytes from sample to sample [16]. With this purpose, the strategy of augmenting matrices along the mode which is suspected of breaking the trilinear structure is implemented. Thus, if matrix-to-matrix variation of profiles occurs along the column direction, a column-wise augmented matrix is created. The bilinear decomposition of the augmented matrix **D** is performed according to the expression:

$$\mathbf{D} = \mathbf{C} \times \mathbf{S}^{\mathrm{T}} + \mathbf{E} \quad (2)$$

in which the rows of **D** generally contain spectra (K wavelengths) as a function of time (J times), the columns of **C** contain the time profiles of the N compounds involved in the process, the columns of **S** their related spectra, and **E** is a matrix of residuals not fitted by the model. Decomposition of **D** is achieved by iterative least-squares minimization of ||**E**|| under suitable constraining conditions, i.e., non-negativity in the spectral profiles, unimodality and non-negativity in the time profiles, correspondence among species and samples in the case of samples containing uncalibrated interferents. **D** is built by placing one on top of another the calibration submatrices and each of the test data submatrices. While the pure spectrum of each compound should be the same in all experiments and the spectral mode must be selective, the temporal profiles in the different **C** submatrices need not share a common shape; this is why this method is widely used to model second-order chromatographic data [4].