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Multivariate curve resolution strategy for non-quadrilinear type 4 third-order/four way liquid chromatography–excitation-emission fluorescence matrix data

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ABSTRACT

For the first time, a third-order/four-way system having instrumental modes depending on each other was experimentally generated and it was successfully resolved. Non-quadrilinear type 4 data, constituted by liquid chromatographic elution times (LC) and excitation-emission fluorescence matrices (EEFMs), were on-line measured using conventional equipment. Thus, third-order/four-way data, valuable for giving rise to highly sensitive and selective methods, were obtained minimizing significantly the experimental work and time, in comparison with the reported strategies for the acquisition of LC-EEFM data. The usefulness of MCR-ALS (multivariate curve resolution-alternating least square) for attaining reliable results from data with two mutually dependent instrumental modes, namely elution time and excitation wavelength modes, was established through the simultaneous quantitation of benz[*a*]anthracene, chrysene, benzo[*b*]fluoranthene, and benzo[*a*]pyrene. Limits of detection in the range 1.0–1.4 ng mL^{-1} were achieved for the target polycyclic aromatic hydrocarbons, allowing their determination in about 9 min per sample in leaves of different types of tea.

1. Introduction

Third-order/four-way calibration allows the development of highly sensitive and selective analytical methods, and this type of calibration has the ability to deal with strong collinearity problems which cannot be solved by second-order one [1–4].

A strategy for third-order/four-way data generation includes the measurement of excitation-emission fluorescence matrices (EEFMs) as a function of liquid chromatographic elution (LC) time [5]. Montemurro et al. [6] reported a interesting review related to the generation of reliable third-order/four-way LC-EEFM data, which includes: (1) collecting elution fractions and, then, measuring the EEFM for each collected fraction, (2) injecting consecutive aliquots of the sample, and recording the elution time-emission wavelength matrices, exciting to different wavelengths, and (3) generating third-order/four-way LC-EEFM data on-line, performing real-time chromatographic measurements at multiple excitation and emission wavelengths.

The selection of the algorithm for the correct data processing is critical and depends on the multilinearity properties of the data generated in each strategy [5,6]. According to their multilinearity characteristics, third-order/four-way data are classified in the following categories: quadrilinear data (the individual three dimensional array data is trilinear and there are no quadrilinearity-breaking modes), non-quadrilinear data of type 1, 2, or 3 (where 1, 2, or 3 modes are, respectively, responsible for the quadrilinearity loss), and non-quadrilinear data of type 4 (there is correlation between two or more modes) [2,5].

For the LC-EEFM data obtained through strategy (1), loss of quadrilinearity could be due to both lack of reproducibility in elution times and small differences between times of the fractions collection among samples (non-quadrilinear data of type 1). In this case, algorithms such APARAFAC (augmented parallel factor analysis), MCR-ALS (multivariate curve resolution-alternating least square), and U-PLS/RTL (unfolded partial least square coupled to residual trilinearization procedure) can be conveniently applied to augmented trilinear three-dimensional data arrays, bilinear data matrix or unfolded vectors, respectively [7,8].

Third-order/four-way data generated with strategy (2) are quadrilinear only if perfect reproducibility in peak times among runs is observed and the shape of the peaks remains unalterable for the set of samples. Although this ideal behavior was not observed in real systems, satisfactory results were achieved with U-PLS/RTL and MCR-ALS due to both the low degree of non-quadrilinearity of the data array and the

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internal structure flexibility of the utilized algorithms [9,10].

The strategy (3) presents a serious difficulty trying to get LC-EEFM data on-line but maintaining the quadrilinearity condition in the set of samples. In a typical chromatographic experiment, the problem arises from the time required to measure a complete EEFM with adequate numbers of excitation and emission sensors. This time is long enough to produce significant variations of the analyte local concentration as a function of excitation wavelength. The mutual dependence between excitation and time profiles leads to a non-quadrilinear type 4 data [6]. Very recently, our research group proposed an experimental procedure for on-line quadrilinear LC-EEFM data measurements based on the decrease of the linear flow rate through the increase of the flowing tube diameter which connects the column outlet with the detector [11]. This approach allowed the acquisition of EEFMs which were arranged as a four-way array complying with the quadrilinearity condition, and the system was successfully resolved with four-way PARAFAC.

Unlike this last work, in the present paper non-quadrilinear LC-EEFM data of type 4 are on-line measured in a conventional LC instrument coupled to a fast-scan spectrofluorimeter. The processing of these data with an MCR-ALS strategy to obtain reliable results is shown and discussed. Until now, this approach has never been described for LC-EEFM data of type 4, and in the present work it was applied for the determination of benz[*a*] anthracene (BaA), chrysene (CHR), benzo[*b*] fluoranthene (BbF) and benzo[*a*]pyrene (BaP) in tea samples. Tea leaves posses high surface area and, in addition to accumulating polycyclic aromatic hydrocarbons (PAHs) from air, they can adsorb these toxic compounds from the combustion gases during the drying stage [12]. Considering that, next to water, tea is the most consumed beverage worldwide, exposure to PAHs through tea results in a serious threat to human health [13]. According to the European Food Safety Authority (EFSA), the four selected analytes are suitable indicators of the occurrence of this type of contaminant in food samples [14].

2. Experimental

2.1. Reagents and solutions

PAHs were obtained from Sigma-Aldrich (Milwaukee, USA), and acetonitrile, methanol, and hexane were HPLC grade from Merck (Darmstadt, Germany). Ultrapure water was delivered by a Milli-Q apparatus (Millipore, Molsheim, France). Acetonitrile stock solutions of all the analytes of about 500 mg L^{-1} were prepared and stored in dark flasks at 4 °C. More diluted acetonitrile solutions (about 5 mg L^{-1}) were obtained. Working solutions were prepared immediately before their use in acetonitrile and water (90:10 v/v). Due to their high toxicity, all reagents were handled with extreme care, using gloves and protective clothing.

2.2. Apparatus and procedure

The chromatographic runs were performed on a Shimadzu Prominence HGE-UV liquid chromatograph equipped with an oven column compartment, and the LabSolutions V 5.82 software package to control the instrument data acquisition and data analysis. A 50 µL loop was employed to introduce each sample onto an Agilent Poroshell 120 EC-C18 column (2.7 µm average particle size, 50 mm × 4.6 mm i.d.). The column temperature was controlled by setting the oven temperature at 27 °C. The mobile phase was the same mixture of acetonitrile and water (90:10 v/v) used to prepare the samples. Samples were filtered through 0.22 µm nylon membranes before injection. The volumetric flow rate was maintained at 0.4 mL min^{-1}. An Agilent Cary-Eclipse luminescence spectrometer (Agilent Technologies, Waldbronn, Germany) was used as detector, employing an 8 µL quartz flow cell (Starna, CA, USA) of 1 mm optical path. PTFE tubing of 0.76 mm i.d. was used for all connections. The excitation and emission slit widths were 10 nm, photomultiplier sensitivity was 800 V, and spectral scanning speed of 21,999 nm min^{-1}.

Chromatographic data were collected from 2 to 7.2 min each 0.17 min, and EEFMs were recorded from 350 nm to 438 nm each 4.5 nm (emission) and from 250 to 290 nm each 5 nm (excitation). The reading of each EEFM required a time of approximately 10 s, allowing us to register 30 EEFMs for each sample. In this way, data arrays of size 30 × 20 × 9 for temporal, emission spectral and excitation spectral modes were respectively generated. The complete analysis, performed under isocratic conditions, was carried out in about 9 min.

2.3. Synthetic samples

A calibration set of 13 samples containing the four studied PAHs in acetonitrile:water (90:10 v/v) was prepared. Eight samples of the set corresponded to the concentrations provided by a half-factorial design, one sample contained all the studied PAHs at average concentrations, and the remaining four samples included each pure analyte. The tested concentrations for each PAH were in the range 0–100 ng mL^{-1} and fluorescence-concentration linearity was confirmed up to the maxima concentrations assayed and under the established working conditions.

A validation set of 20 samples was prepared with the studied PAHs at concentrations different from those used for calibration and applying a random design. Twenty additional test samples containing the analytes and other five PAHs checked as potential interferences were prepared. These additional PAHs, namely phenanthrene (PHEN), anthracene (ANT), pyrene (PYR), benzo[*k*]fluoranthene (BkF) and dibenz[*a*,*h*] anthracene (DBA), showed both time and spectral overlapping with the analytes, and they are potentially present in the analyzed real samples [12,15–17]. The latter compounds were added at variable concentrations up to a maximum value of 300 ng mL^{-1}. All samples were subjected to the chromatographic procedure and the obtained EEFMs were then analyzed with third-order/four-way multivariate calibration.

2.4. Tea leaf samples

Approximately 0.5 g of ground tea leaves were added with 5.00 mL of hexane and the mixture was mixed in a vortex for 20 s. It was sonicated for 30 min at 35 °C and then centrifugated at 2500 rpm. The supernatant was filtered through a 0.22 µm pore size nylon membrane. For the LC analysis, 3.00 mL of this solution were dried using a rotary evaporator, reconstituted with 1.00 mL of a mixture of acetonitrile:water (90:10 v/v) and subjected to the same chromatographic analysis as the synthetic samples.

For GC-MS analysis, a modified version of the GC-MS procedure suggested by Orecchio et al. was performed [18]. Thus, 1.00 mL of the filtered supernatant was evaporated to dryness, the residue was reconstituted with 0.50 mL of hexane, and 1 µL of the sample was injected into the gas chromatograph. Helium was employed as carrier at a flow of 1.4 mL min^{-1}. The injection port temperature was set at 280 °C. The ionization energy applied was 70 eV. An oven temperature gradient was employed to achieve resolution of the analytes. An initial oven temperature of 90 °C was held for 2 min, then a gradient of 5 °C min^{-1} from 90 °C to 310 °C was applied for 43 min, and finally, the oven temperature was kept at 310 °C for another 15 min. Scan mode was employed to identify the analytes, while selected ion mass monitoring mode was used for quantification (*m/z* 228 for BaA and CHR, and *m/z* 252 for BbF and BaP). Each brand of tea sample was prepared in duplicate.

2.5. Chemometric algorithm and data treatment

A brief theoretical description of MCR-ALS applied to second- and third-order data is given in Supplementary Material.

To illustrate the data structure, Fig. 1 shows a graphical representation of the analyzed super-augmented data matrix for a hypothetical system formed by two analytes in the presence of one interferent, and the MCR-ALS decomposition process.

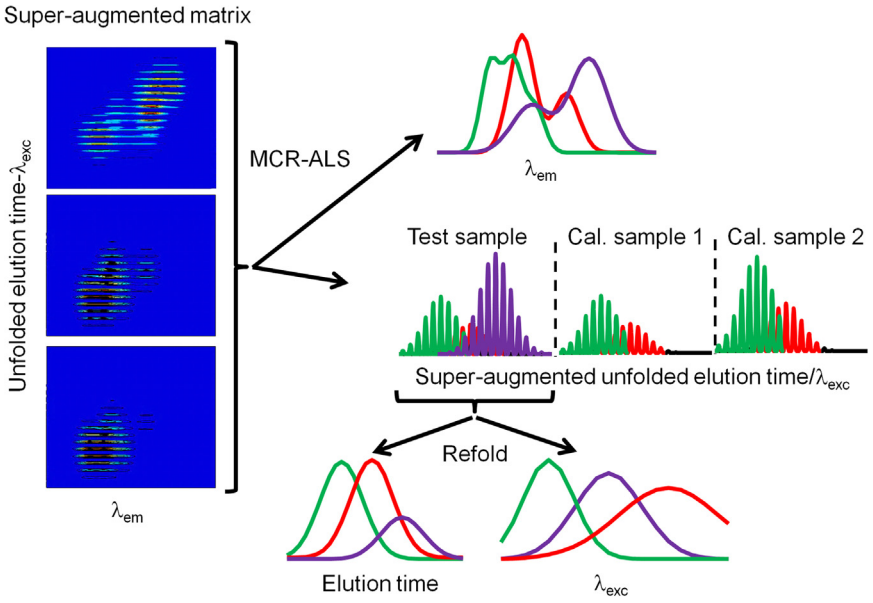

Fig. 1. Schematic illustration of the application of MCR-ALS to type 4 non-quadrilinear third-order data. Left: a super-augmented matrix is built taking the emission mode as the common mode and placing the unfolded elution time/excitation modes along the augmented direction for the samples. Right: MCR-ALS decomposition of the super-augmented matrix in emission spectra and unfolded elution time/excitation profiles for the components in all samples (one test and two calibration samples as shown as examples). For each sample, the component profiles in the super-augmented mode are refolded to give separate elution time and excitation profiles, which are useful for component identification.

2.6. Software

MCR-ALS algorithm was implemented in MATLAB R2012a, and was applied using the graphical interface MVC3 [19], which is an integrated MATLAB toolbox for third-order/four-way calibration. It is freely available on the Internet [20].

3. Results and discussion

3.1. General considerations

Fig. 2A shows the significant spectral overlap among excitation and emission spectra of BaA, CHR, BbF and BaP and their chromatographic behavior under the selected isocratic conditions. This system can potentially be solved by applying multivariate calibration, whose usefulness becomes even more evident if real samples containing unexpected components are investigated.

Particularly, third-order/four-way calibration using chromatographic measurements with fluorescence detection (Fig. 3) provides several benefits in comparing with lower-order calibrations: besides offering the advantage of allowing the determination of analytes in the presence of non-calibrated constituents (second-order advantage) [21], the selectivity and sensitivity of the method is improved [1,2].

Among the three ways to acquire LC-EEFM data [6], the most

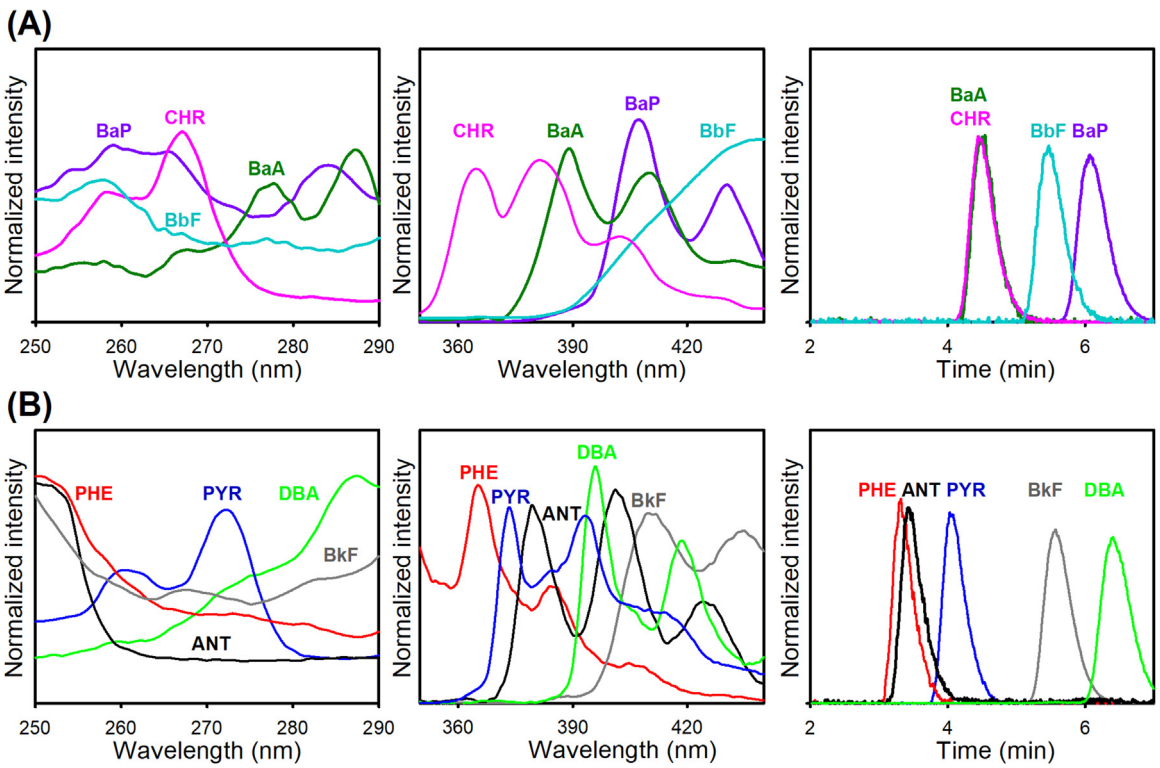

Fig. 2. From left to right: excitation, emission and time profiles for the studied analytes as indicated (A). From left to right: excitation, emission and time profiles for potential interferents investigated as indicated (B).

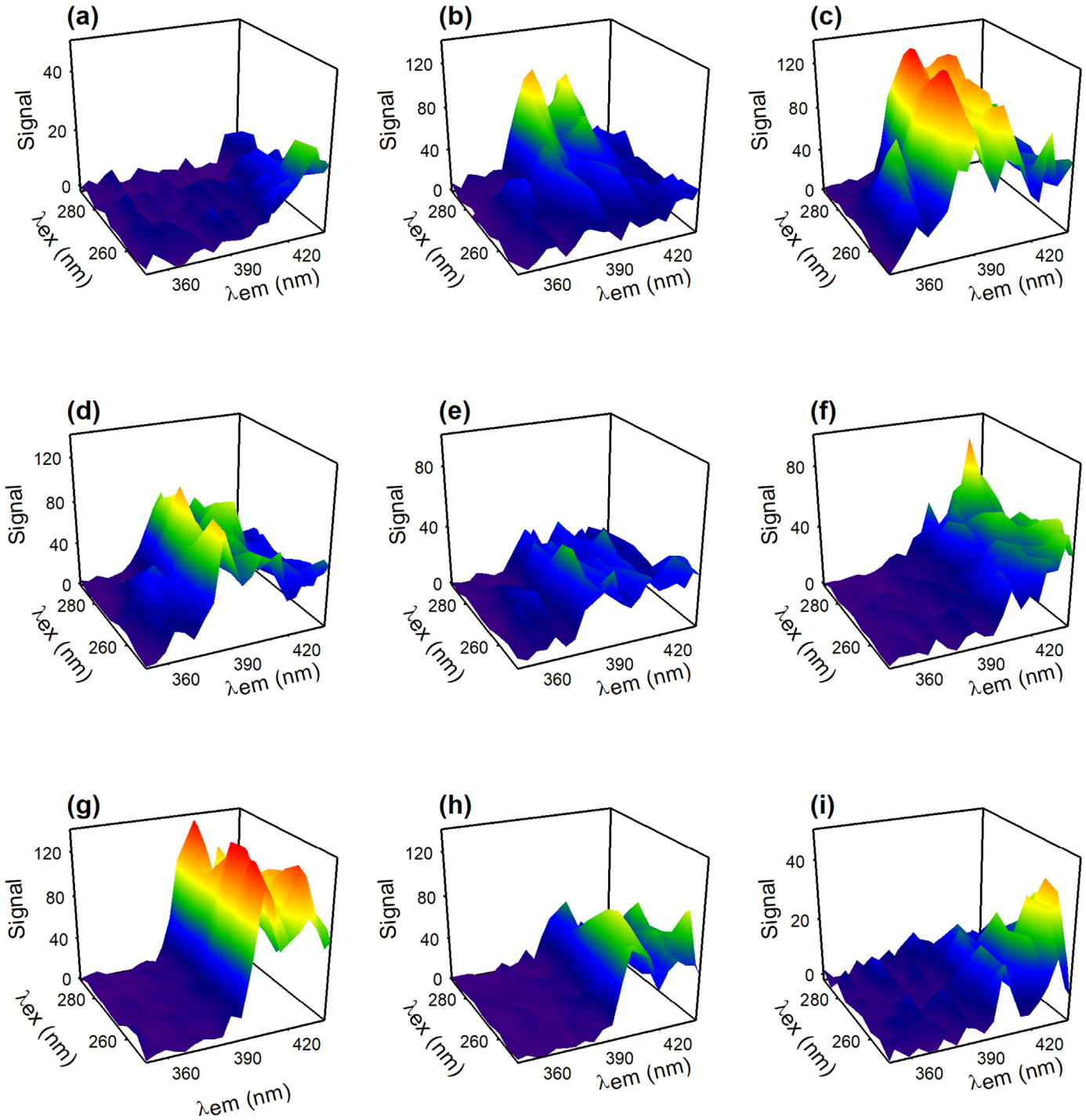

Fig. 3. EEFMs for a sample containing BaA, CHR, BbF and BaP at about 50 ng mL^{-1} measured at the following elution times: (a) 3.08, (b) 4.16, (c) 4.34, (d) 4.52, (e) 4.70, (f) 5.06, (g) 5.78, (h) 6.14, and (i) 6.50 min.

attractive and advantageous is the one based on real-time measurements, mainly because it allows to significantly reduce the total analysis time, the consumption of reagents, the complexity and cost of the equipment, and it can be a convenient alternative to study unstable or volatile analytes.

However, in a usual third-order/four-way LC-EEFM experiment, at constant linear and volumetric flow rates, while emission spectra are obtained in a time appreciably smaller than the base width of a chromatographic peak when using a fast-scanning spectrofluorimeter [22,23], the excitation spectrum of each analyte is deformed as a function of the measurement time (Fig. 4) [6]. The mutual dependence between excitation and time profiles leads to a loss of quadrilinearity of the data, giving rise to non-quadrilinear type 4 data [2,5].

Non-quadrilinear type 4 data include sub-types, depending on the number of mutually dependent instrumental and sample depending modes. In our case, in addition to the existence of two instrumental dependent modes, the elution time is sample-dependent (i.e. the elution time shifts between successive chromatographic runs).

A possible approach for processing this type of data, which is here applied for the first time, is to concatenate the two mutually dependent instrumental modes, producing a three-way array. The additional dependence of the elution time with the sample will be translated to the

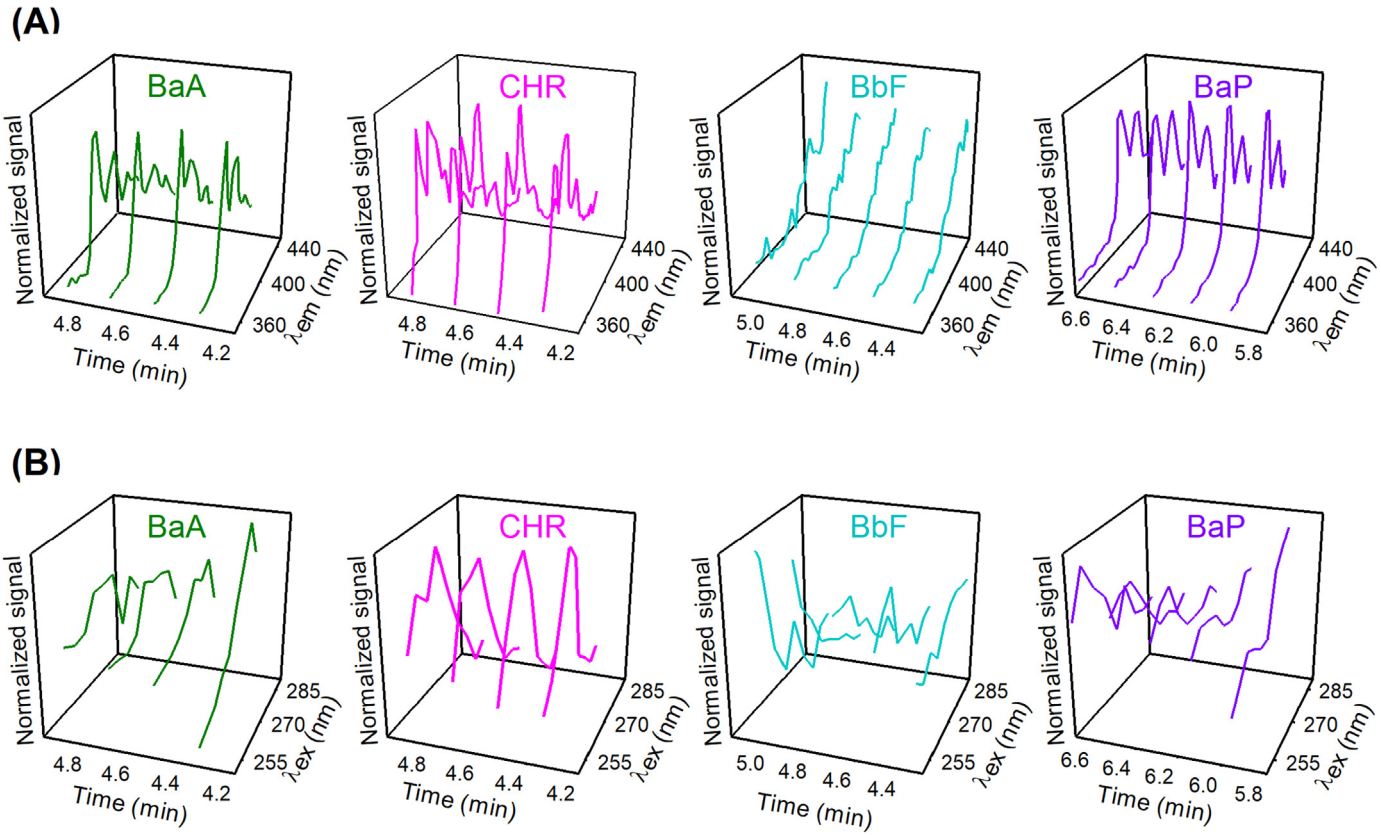

Fig. 4. Elution time-fluorescence emission wavelength matrices (A) and elution time-fluorescence excitation wavelength matrices (B) for BaA, CHR, BbF, and BaP at the corresponding maxima of excitation and emission, respectively.

concatenated elution time-excitation mode and, therefore, the resulting three-way array is classified as non-trilinear type 1 [5]. In other words, the strategy consists on building a super-augmented matrix concatenating elution time-excitation profiles on one hand (augmented mode), and the additional emission mode on the other, for each sample, and then placing the obtained matrices adjacent to each other. Assuming that the super-augmented matrix is bilinear it can be adequately processed by extended MCR-ALS [24]. To limit the number of possible bilinear solutions, and to drive the least-squares fit to a chemically meaningful one, selected constraints are applied during the MCR-ALS decomposition (see below). After decomposition of the super-augmented data matrix, a univariate calibration graph is built with the analyte scores for the calibration samples, interpolating the score for the test sample for analyte prediction. The analyte scores are estimated by integrating the area of the unfolded elution time/excitation profiles in each sample.

3.2. MCR-ALS analysis

Super-augmented data matrices for MCR-ALS treatment were built with each validation sample and all the calibration samples. Four components, corresponding to the four presently studied PAHs, were determined by principal component analysis [23]. The initial profiles used to start the MCR-ALS fitting were obtained by estimating the so-called purest variables in the emission spectral domain. Non-negativity in both augmented and non-augmented modes, area correlation and correspondence between components and samples were applied [23,25]. Unimodality constraint was applied as follows: in the augmented direction (composed by time and excitation modes), the temporal mode was separated from the excitation one and unimodality was applied to the former. Then, both modes were again concatenated. After convergence of the ALS optimization, PAHs were identified by their emission profiles and quantification was carried out through each pseudo-univariate calibration curve. The latter was built with the analyte scores (areas under the unfolded elution time/excitation profiles) for the calibration samples. The test analyte score was then interpolated in the calibration line.

Fig. 5 shows both the emission and the concatenated time/excitation profiles retrieved by MCR-ALS for a validation sample containing the analytes under study. The quality of the emission profiles recovered by MCR-ALS (Fig. 5A) was evaluated through the similarity coefficient (r) between them and those of the pure analytes (Fig. 2A) [26]. The calculated r values of 0.9600, 0.9457, 0.9230 and 0.9555 for BaA, CHR, BbF and BaP, respectively, indicate a satisfactory match between the retrieves and pure emission spectra of the studied PAHs.

Fig. 6A shows the good prediction results for validation samples for individually evaluated PAH, and Fig. 6B displays the global prediction of all analytes and the corresponding EJCR (elliptical joint confidence region) test for slope and intercept of the found vs nominal concentrations plot for a statistical evaluation of the results [27]. Because the ellipse includes the theoretically expected value of slope = 1 and intercept = 0, the accuracy of the methodology can be confirmed.

The statistical results for validation samples are completed with the parameters exposed in Table 1 [28].

In our recent work, where some of the PAHs here studied were quantified through LC-EEFMs quadrilinear data, LODs were 0.8, 1.0, 1.6, and 0.5 ng mL^{-1} for BaA, CHR, BbF and BaP, respectively [11]. These values are quite similar to those shown in Table 1, demonstrating that the sensitivity of the method is not affected by the present procedure. On the other hand, although the selectivities for the reported quadrilinear experiment, with values of 0.78; 0.77, 0.55, and 0.56 for BaA, CHR, BbF and BaP, respectively, were better than those here calculated, the current values, all higher than 0.41 (Table 1), are acceptable taking into account that a simple methodology is applied to a

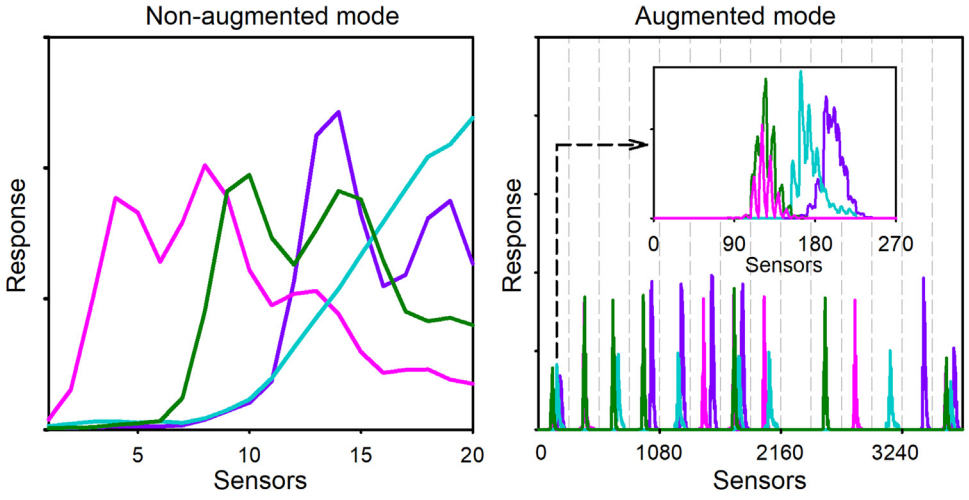

Fig. 5. Emission spectral profiles (A) and the concatenated time/excitation profiles (B) retrieved by MCR-ALS when processing a sample containing BaA (green), CHR (pink), BbF (light blue) and BaP (violet). The dotted gray lines in (B) separate, from left to right, the analyzed sample and the successive calibration samples, and the inset shows the augmented mode in the studied sample.

complex system in a shorter time. A similar conclusion is obtained for the analytical sensitivity values [11]. Finally, both the root-mean square errors and the relative errors of prediction (below 5 ng mL^{-1} and 9%, respectively) are satisfactory.

Quantification of the four analytes was also carried out in samples containing additional PAHs, namely PHE, ANT, PYR, BkF, and DBA. These compounds were selected because they are usually present in tea samples [13], and they can potentially hinder the measured signals. In fact, while the chromatographic band of PYR partially covers those of CHR and BaA, and the BbF band suffers significant overlapping from BkF and DBA, both the excitation and emission spectral overlapping between the calibrated and non-calibrated compounds is very critical (Fig. 2B). However, successful predictions were obtained when MCR-ALS was applied to these complex samples, corroborated by the EJCR test (Fig. 7).

The statistical results shown in Table 1 suggest that, as expected, the selectivity and sensibility are slightly decreased by the presence of non-calibrated PAHs. However, the RMSP and REP values are not affected by these foreign compounds.

It is well-known that the bilinear MCR-ALS solutions, even under all the applied constraints, may show a certain degree of rotational ambiguity, i.e. the presence of a feasible area of solutions which satisfy equally well the bilinear model and all the constraints [29]. In the case of the validation samples, no rotational ambiguity should remain in the bilinear decompositions achieved by MCR-ALS, since the calibration set contains four samples with each of the pure analytes. This has been shown to ensure a unique decomposition of the augmented data matrix [30]. For the test samples containing potential interferents, however, the analyte profiles may in principle show a certain area of feasible solutions. For multi-component systems such as the presently studied ones, with up to eight different constituents, the only procedure to analyze the presence of rotational ambiguity is the MCR-BANDS algorithm [31]. The latter operates by estimating the maximum and minimum contribution of each component to the total signal, using a non-linear optimization scheme under non-linear constraints. In the present case, MCR-BANDS cannot be applied in its current version, due to the need of implementing the unimodality constraint to the elution time profile, separated from the excitation time profiles, because both

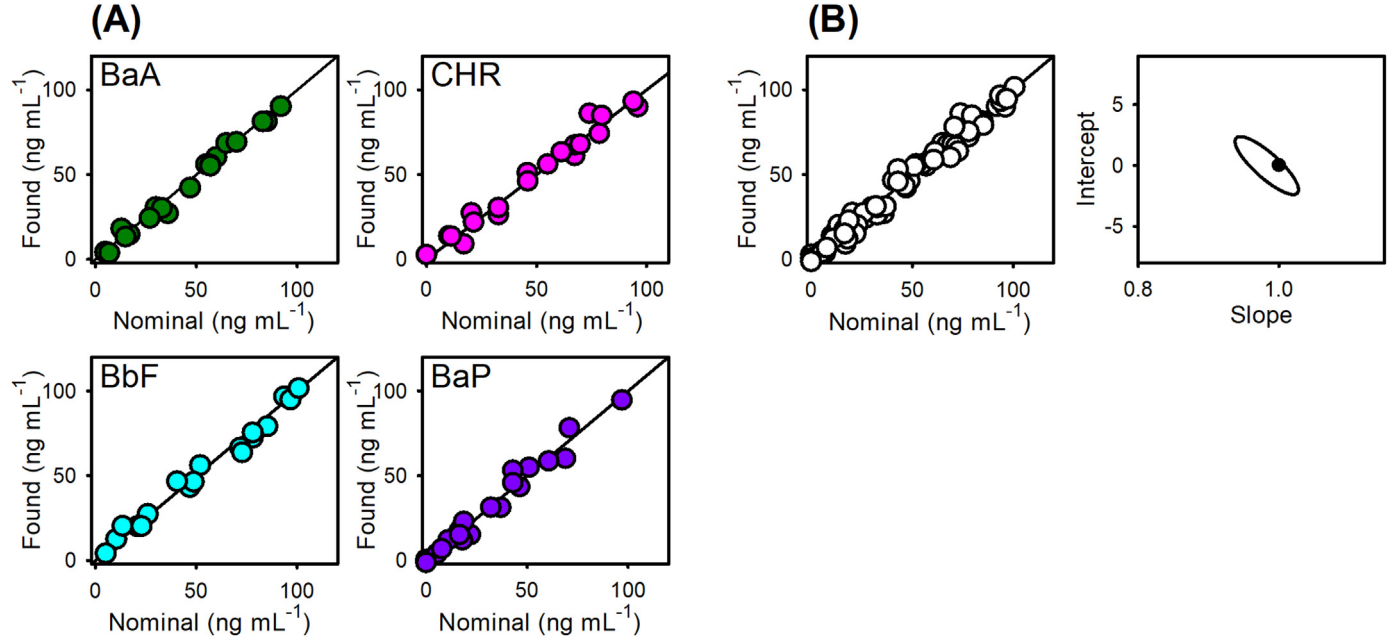

Fig. 6. Plots of individual BaA (green), CHR (pink), BbF (light blue) and BaP (violet) predicted concentrations as a function of the nominal values in validation samples (A). Plot of predicted concentrations as a function of the nominal values for all evaluated PAHs and the corresponding global elliptical joint region (at 95% confidence level) for the slope and intercept of this latter regression (B). The black circle in the elliptical plot marks the theoretical (intercept = 0, slope = 1) point.

Table 1
Statistical results for BaA, CHR, BbF and BaP in validation samples and in samples with additional PAHs.

	BaA	CHR	BbF	BaP
	Validation samples			
γ (ng^{-1} mL)[a]	2.5	3.4	3.3	2.8
SEL[a]	0.48	0.71	0.49	0.41
LOD (ng mL^{-1})[b]	1.4	1.0	1.1	1.3
LOQ (ng mL^{-1})[b]	4.3	3.1	3.2	3.8
RMSEP (ng mL^{-1})[c]	3	5	4	4
REP (%)[d]	6	9	8	9
	Samples with potential interferences			
γ (ng^{-1} mL)[a]	1.2	2.6	0.94	1.9
SEL[a]	0.33	0.46	0.24	0.31
LOD (ng mL^{-1})[b]	2.9	1.3	3.8	1.8
LOQ (ng mL^{-1})[b]	8.9	4.1	11	5.6
RMSE (ng mL^{-1})[c]	3	4	5	4
REP (%)[d]	5	8	9	8

[a] γ, analytical sensitivity and SEL, selectivity, were calculated according to Ref. [1].
[b] LOD, limit of detection, and LOQ, limit of quantitation, were calculated according to Ref. [28].
[c] RMSE, root-mean square error.
[d] REP, relative error of prediction.

define the augmented data mode in a concatenated manner. However, we are confident that no substantial rotational ambiguity remains in the bilinear decomposition of the augmented data matrices for the test samples. On one hand, the analytical prediction results are satisfactory, while a significant rotational ambiguity would lead to a substantial prediction bias. On the other, the selectivity in the common emission mode is reasonably good for all components, which should lead to a very small degree of rotational ambiguity when pure analyte standards are employed for calibration [30], as in the present research.

3.3. Tea leaf samples

With the purpose of assaying the proposed methodology, four different types of tea (red, green, black and white) of Argentine brands obtained from local retail shops were selected as real matrices. Concentrations of the four studied PAHs in each sample were first determined by gas chromatography-mass spectrometry (GC-MS) as reference method. The results of both methods (Table 2) were compared by applying a paired Student's *t*-test [32]. The experimental *t* value ($t = 0.78$) lower than the critical one ($t_{crit(0.05,25)} = 2.06$) suggests that both methods give results which are not statistically different.

Considering that the sanitary standards of BaA, CHR, BbF and BaP calculated for tea are 1000; 16,000; 3800 and 600 μg kg^{-1} respectively [12], and according to the values found in the evaluated teas, it can be stated that their content of PAHs would be in the safe range.

In comparing the proposed methodology with the reference one, it is important to remark that, in addition to using non-sophisticate equipment, the required experimental time (about 9 min per sample) is significantly shorter than that involved in GC-MS method (about 60 min per sample).

4. Conclusions

Excitation–emission fluorescence matrices for selected heavy-polycyclic aromatic hydrocarbons were acquired during a chromatographic run, rendering advantageous third-order/four-way data in a fast and simple way. The new proposal, based on MCR-ALS, for the treatment of data with a strong dependence between two instrumental modes proved to be adequate to solve the system. The method was successfully applied to the determination of these dangerous compounds in tea samples, demonstrating a new resource derived from third-order/four-way multivariate calibration to improve the quality of analytical procedures applied to complex samples.

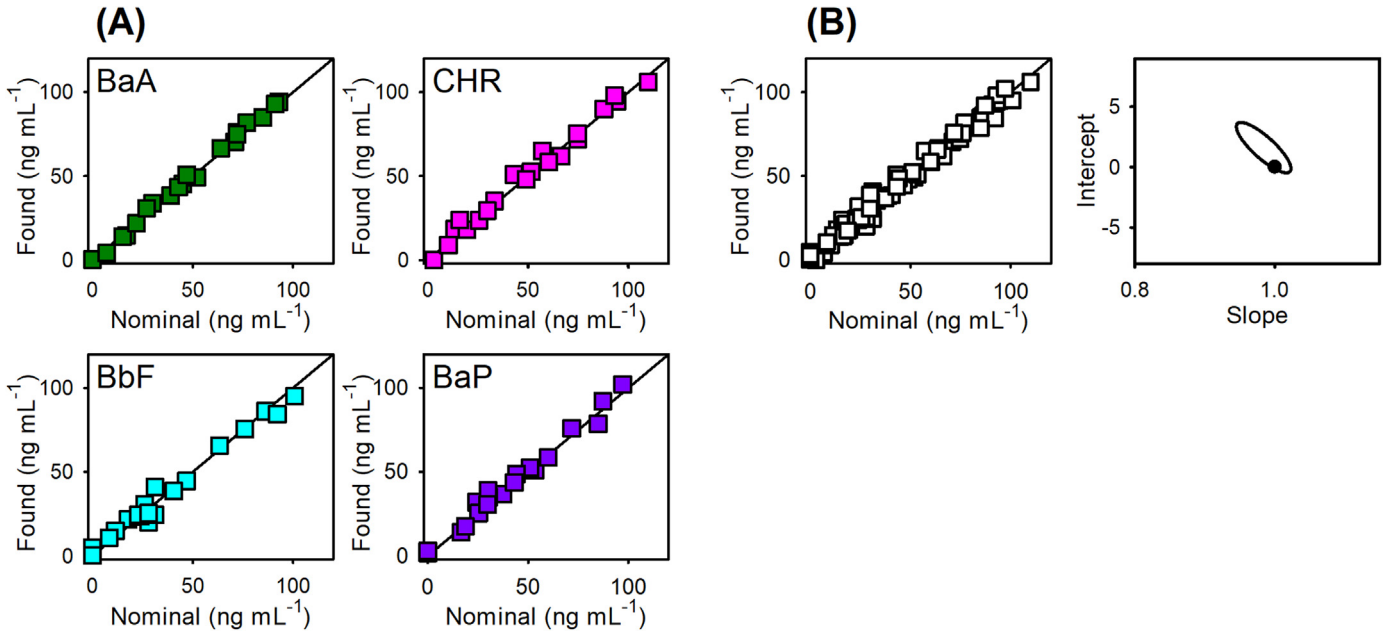

Fig. 7. Plots of individual BaA (green), CHR (pink), BbF (light blue) and BaP (violet) predicted concentrations as a function of the nominal values in samples with potential interferences (A). Plot of predicted concentrations as a function of the nominal values for all evaluated PAHs and the corresponding global elliptical joint region (at 95% confidence level) for the slope and intercept of this latter regression (B). The black circle in the elliptical plot marks the theoretical (intercept = 0, slope = 1) point.

Table 2
PAH concentrations (μg kg^{-1}) in different types of tea.[a]

	BaA		CHR		BbF		BaP	
	CG/MS	MCR-ALS[b]	CG/MS	MCR-ALS[b]	CG/MS	MCR-ALS[b]	CG/MS	MCR-ALS[b]
Red#1	69.1	67.3 (0.3)	83.2	83.0 (4)	46.1	48.8 (0.7)	ND	ND
Red#2	12.5	10.0 (0.7)	24.0	21 (5)	14.5	11 (3)	ND	ND
Green#1	11.5	11 (1)	36.7	37 (7)	39.7	35 (2)	ND	ND
Green#2	35.5	37.8 (0.7)	95.7	93.2 (0.9)	64.2	66.4 (0.7)	42.2	46 (3)
Black#1	18.9	19 (1)	57.0	64 (4)	60.8	63 (9)	35.9	39 (5)
Black#2	19.9	21 (1)	56.9	54.7 (0.8)	46.5	49 (7)	36.6	37 (2)
White#1	35.0	37 (1)	29.0	28 (2)	51.9	57 (6)	48.0	42.0 (0.9)

[a] NR = not detected.
[b] Mean of duplicates. Standard deviation between parentheses.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.talanta.2018.07.017.

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