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Determination of triphenyltin in sea-water by excitation–emission matrix fluorescence and multivariate curve resolution

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In memoriam: we wish to dedicate this paper to our good friend and excellent colleague Anna Izquierdo Ridorsa, who will always be remembered by us

Abstract

A new method for the determination of triphenyltin (TPhT) in sea-water is proposed. The method is based on solid-phase extraction (SPE), reaction with flavonol in a Triton X-100 micellar medium to yield a fluorimetrically active derivative and excitation–emission fluorescence measurements. TPhT was quantified by an alternating least squares (ALS)-multivariate curve resolution (MCR) procedure and a single synthetic standard. In order to select the optimum conditions for the analysis, the procedure was assessed using synthetic samples. With the proposed method, TPhT was quantified in sea-water samples at low ng l^{-1} level with an overall prediction error of around 12%. ©2000 Elsevier Science B.V. All rights reserved.

Keywords: Triphenyltin; Excitation–emission fluorescence; Second-order data; Three-way analysis; Multivariate curve resolution

1. Introduction

Triphenyltin (TPhT) is mainly used in agriculture as fungicide and in antifouling paints as biocide agent. Thus, TPhT is directly introduced into aquatic systems via runoff from agricultural fields and leaching from vessel antifouling paints [1]. The high toxicity of TPhT has stimulated the development of analytical methods for its environmental monitoring. Most methods are based on chromatographic separation, by either gas or liquid chromatography, and sensitive detection, which provide the required selectivity and sensitivity for effective environmental control.

Chromatographic separation can be avoided if a very selective detection system is used. Flavonol has been proposed as fluorogenic reagent for the fluorimetric determination of TPhT in sea-water samples after a solid-phase extraction (SPE) [2]. If a univariate calibration system at a single emission wavelength is used, the detection capability of the method is sometimes limited by the native fluorescence of the samples, mainly due to the presence of fulvic acids. An alternative to overcome this drawback is based on multiple excitation–emission matrix (EEM) fluorescence and multivariate calibration methods.

EEM fluorescence provides data consisting of emission spectra registered at different excitation wavelengths. Therefore, the excitation–emission spectra obtained for each sample can be arranged either in data vector arrays or in data matrices for further analysis.

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Arrangements of fluorescence data in arrays (i.e. first-order data) can be analyzed with first-order calibration methods such as partial-least squares (PLS) regression. This approach has been successfully applied to determine TPhT in sea-water samples [3]. However, first-order calibration methods require that both unknown and standard samples have the same chemical and physical characteristics, i.e. all detectable species present in the unknown samples, including analytes and interferences, must also be present in the standard samples. This means that standards for calibration must be real samples analyzed beforehand by an independent method. Therefore, the most expensive step in first-order multivariate calibration methods is the preparation and analysis of the large number of standards that have to be used for calibration.

Alternatively, fluorimetric data can be arranged in data matrices (i.e. second-order data) for analysis with second-order calibration methods, which may take advantage of features of both excitation and emission spectra of the compounds studied. An important advantage of second-order calibration methods is that the analyte can be quantitatively determined using synthetic standard samples that contain only the analyte of interest, i.e. the interferences in the unknown sample do not need to be present in the standards [4,5]. Three-way EEM have been analyzed with multivariate curve resolution (MCR) [6,7] and PARAFAC [8–10] methods.

In the present study, a second-order MCR procedure based on an alternating least-squares optimization (MCR-ALS) [11–15] was applied to the fluorimetric determination of TPhT in sea-water samples. The method consisted of an SPE and a subsequent reaction with flavonol in a Triton X-100 micellar medium; the EEM were monitored from 430 to 580 nm at various excitation wavelengths in the range 375–415 nm. Besides the analyte, there were other fluorescent contributions, such as those from the excess of flavonol and the intrinsically fluorescent compounds present in the sea-water matrix. The MCR-ALS chemometric method enabled TPhT in samples to be determined on the basis of differences in both excitation and emission spectra of the compounds involved.

Firstly, the method was applied to synthetic samples containing TPhT and fulvic acids in order to find the best calibration strategy. Next, TPhT was quantified in natural sea-water samples at low $ng\,l^{-1}$ concentrations.

2. Experimental

2.1. Apparatus

The EEM fluorescence spectra were obtained with an Aminco-Bowman Series 2 spectrofluorimeter equipped with 10 mm silica cells and operating in the ratio mode. A tetraphenylbutadiene standard from Perkin–Elmer was measured each working session to control the response of the spectrofluorimeter. A Gilson peristaltic pump, Model Minipuls 3, was used in SPE experiments.

2.2. Reagents and solutions

A TPhT stock solution ($500\,mg\,l^{-1}$ as tin) was prepared by dissolving TPhT chloride (Fluka, Buchs, Switzerland) in HPLC-grade methanol (Baker, Deventer, The Netherlands). This solution was stored in dark glass bottles at 4°C. $10\,mg\,l^{-1}$ standard solutions were prepared weekly by dilution with methanol and stored at 4°C. Appropriate dilutions were freshly prepared.

The fluorogenic reagent solution for EEM fluorescence was 10^{-5} M flavonol (Aldrich, Milwaukee, WI), 0.024 M Triton X-100 (Merck, Darmstad, Germany) and 0.067 M succinic acid–sodium succinate buffer (pH = 5.6) (Fluka, Buchs, Switzerland).

Aqueous solutions of fulvic acid (N 1.12%; C 46.12%; H 6.33%; O 46.43%; C/N 41.18; C/H 7.29) were prepared in the range 4–10 $mg\,l^{-1}$.

For SPE, 100 mg octadecylsilane SPE disposable cartridges, 40 μm particle size, Bond-Elut (Varian, Harbor City, CA), were used.

Milli-Q-plus deionized water (Millipore, Molsheim, France) of resistivity $18.2\,M\Omega\,cm^{-1}$ was used throughout.

All glassware used was previously soaked in 10% v/v HNO_3 for 24 h and rinsed with deionized water.

2.3. Samples

Sea-water from El Masnou marina, on the north-west Mediterranean Coast (Catalonia, Spain)

was collected in 2.5 l glass bottles, filtered through 1.6 μm particle retention GF/A filters (Whatman, Maidstone, England), acidified to pH 2 with concentrated hydrochloric acid and stored at 4°C until analysis. TPhT concentration was determined by SPE-LC-fluorimetry [16] and was found to be below the detection limit (i.e. $<0.2\,ng\,l^{-1}$). Aliquots of this sea-water sample were spiked with known amounts of TPhT, the final TPhT concentration ranging between 4.2 and $34.2\,ng\,l^{-1}$.

2.4. Procedure

Condition the SPE cartridge by rinsing successively with 5 ml of methanol, 5 ml of water and 5 ml of an aqueous solution containing 10^{-2} M hydrochloric acid and $35\,g\,l^{-1}$ sodium chloride. Pump 500 ml of the sea-water sample through the cartridge at a flow rate of about $5\,ml\,min^{-1}$. Wash the cartridge with 10 ml of water and dry it by drawing air. Elute with 2 ml of methanol at a flow rate of $0.5\,ml\,min^{-1}$ in the back-flush mode and collect the eluate in dark glass vials. Evaporate the methanol under a gentle stream of nitrogen and add 2 ml of the fluorogenic solution. Set the excitation and emission monochromator slit widths to 8 nm and record the excitation–emission spectra from 430 to 580 nm (every 1 nm), with excitation wavelengths from 400 to 415 nm (every 5 nm) at an emission-scanning velocity of $900\,nm\,min^{-1}$.

2.5. Data sets under study

The EEM spectra were recorded at excitation wavelengths (λ_{ex}) from 375 to 415 nm at regular steps of 5 nm; the emission wavelengths (λ_{em}) ranged from 430 to 580 nm at steps of 1 nm. Therefore, for each sample, the excitation–emission raw data matrix measured $151\lambda_{em}$ by $9\lambda_{ex}$. As an example, Fig. 1 shows a three-dimensional plot of the fluorescence of a sea-water sample.

For quantification, the data matrix of the unknown sample has to be simultaneously analyzed with that of the synthetic standard. However, in order to improve resolution and quantification, additional matrices providing information about the reagent and the sample background fluorescence can be included in the model. Thus, the determination of TPhT in each unknown sample involved the simultaneous analysis of the data matrix of each unknown sample together with the standard and two blank matrices (for the reagent and the background). For this purpose, all these matrices were arranged in a new augmented data matrix

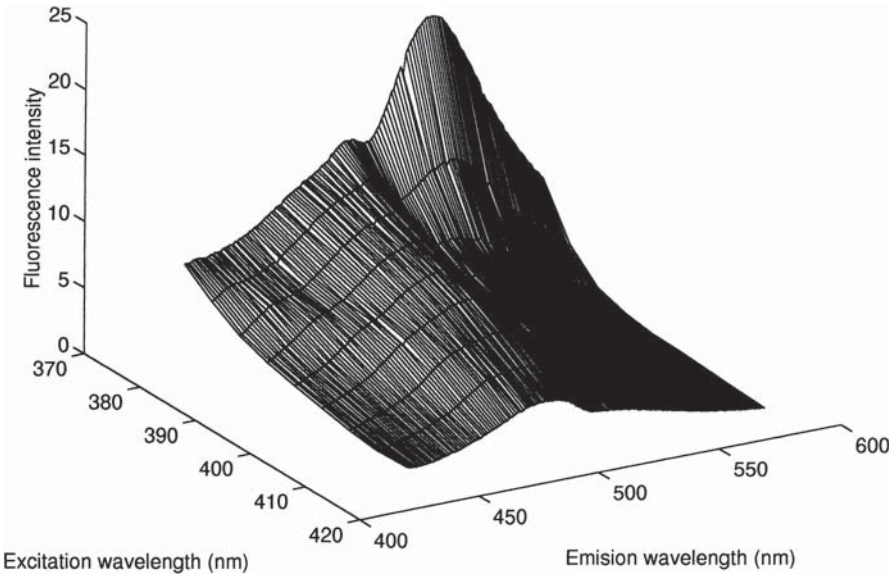

Fig. 1. Three-dimensional excitation–emission fluorescence plot for a sea-water sample containing $20.6\,ng\,l^{-1}$ TPhT.

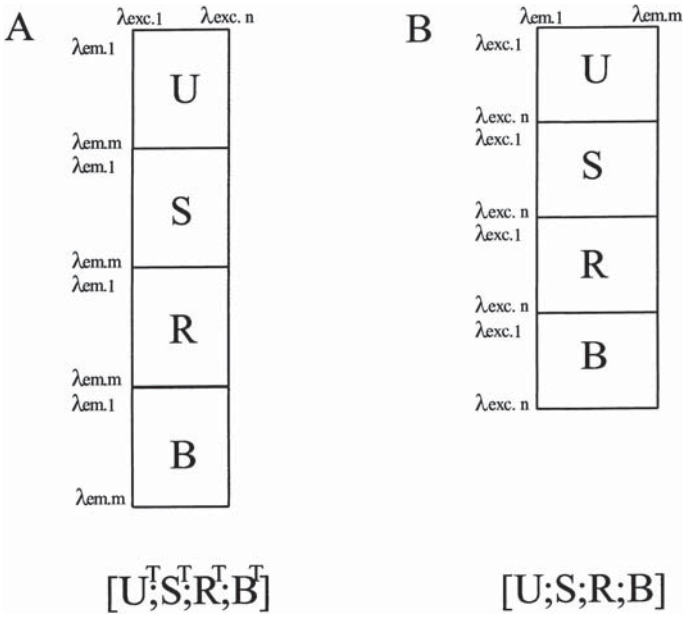

Fig. 2. Excitation-wise [$\boldsymbol{U}^{\mathrm{T}};\boldsymbol{S}^{\mathrm{T}};\boldsymbol{R}^{\mathrm{T}};\boldsymbol{B}^{\mathrm{T}}$] and emission-wise [$\boldsymbol{U};\boldsymbol{S};\boldsymbol{R};\boldsymbol{B}$] augmented data matrices built from the individual matrices $\boldsymbol{U}$ (unknown sample), $\boldsymbol{S}$ (standard), $\boldsymbol{R}$ (reagent) and $\boldsymbol{B}$ (sea-water background).

(see below). A particular and important feature of fluorimetry is that each species can be defined by its characteristic excitation and emission spectra in all data matrices studied simultaneously, so that the data obtained can be assumed to be trilinear [17]. This meant that the second-order data structure could be used to obtain more accurate predictions.

Both excitation-wise and emission-wise matrix augmentations are possible in fluorescence. In the excitation-wise augmentation, matrices are arranged by setting one matrix on top of the others and keeping the common excitation wavelengths in the same column. In the emission-wise augmentation, each emission wavelength is kept in common. Both types of augmentation are shown in Fig. 2. For an easy reference to the excitation-wise and emission-wise matrix augmentations, the MATLAB notation was used. As an example, [$\boldsymbol{U}^{\mathrm{T}};\boldsymbol{S}^{\mathrm{T}};\boldsymbol{R}^{\mathrm{T}};\boldsymbol{B}^{\mathrm{T}}$] was an excitation-column-wise augmented data matrix built with the unknown $\boldsymbol{U}$, the standard $\boldsymbol{S}$, the reagent $\boldsymbol{R}$ and the sample background $\boldsymbol{B}$ individual matrices. Conversely, [$\boldsymbol{U};\boldsymbol{S};\boldsymbol{R};\boldsymbol{B}$] was an emission-column-wise augmented matrix built with the same individual matrices as above. For any determination, the standard, reagent and background matrices were the same and the unknown matrix was of each different sample.

3. Data treatment

3.1. Rank analysis

The number of chemical species present in each EEM was first estimated by singular value decomposition, since it was assumed that chemical components were associated with the largest singular values. The number of species finally chosen was checked to provide a chemically reliable resolution of the system.

3.2. Application of the MCR-ALS method

The determination of TPhT in sea-water samples was performed with an MCR method based on ALS. For each particular quantitative determination, an augmented matrix was defined, as described in Section 2. The resolution of each augmented-data matrix gave an estimation of the excitation and emission spectra of the species included in the model. The method is

based on a linear model (similar to the generalized Beer's law), which assumes the additivity of the fluorescence of all active compounds. In excitation-wise augmentation the model was as follows:

$$\boldsymbol{D}_{\text{aug}}^{\text{ex}} = \boldsymbol{Y}_{\text{aug}}\boldsymbol{X}^{\text{T}} + \boldsymbol{E} \quad (1)$$

where $\boldsymbol{D}_{\text{aug}}^{\text{ex}}$ was the excitation-wise augmented data matrix, $\boldsymbol{Y}_{\text{aug}}$ was the augmented matrix of emission spectra, $\boldsymbol{X}^{\text{T}}$ was the transposed matrix of excitation spectra and $\boldsymbol{E}$ was the matrix of residuals. The quantitative information was contained in the relative intensities of the emission spectra $\boldsymbol{Y}_{\text{aug}}$ (see below).

A similar model can be written for emission-wise augmentation:

$$\boldsymbol{D}_{\text{aug}}^{\text{em}} = \boldsymbol{X}_{\text{aug}}\boldsymbol{Y}^{\text{T}} + \boldsymbol{E} \quad (2)$$

$\boldsymbol{D}_{\text{aug}}^{\text{em}}$ being the emission-wise augmented data matrix, $\boldsymbol{X}_{\text{aug}}$ the augmented matrix of excitation spectra and $\boldsymbol{Y}^{\text{T}}$ the transposed matrix of emission spectra. The quantitative information was, thus, contained in the relative intensities of the excitation spectra $\boldsymbol{X}_{\text{aug}}$ (see below). Fig. 3 shows both modeling alternatives in detail.

Four different analysis strategies were defined and tested in order to find the optimum resolution (Table 2).

3.3. ALS optimization

In the particular case of an excitation-wise augmented data matrix using excitation spectra as initial estimates, $\boldsymbol{X}^{\text{T}}$, the iterative optimization started as follows:

$$\boldsymbol{Y}_{\text{aug}} = \boldsymbol{D}_{\text{aug}}^{\text{ex}*}(\boldsymbol{X}^{\text{T}})^{+} \quad (3)$$

where $\boldsymbol{D}_{\text{aug}}^{\text{ex}*}$ was the PCA-reproduced data matrix for the number of components considered, $(\boldsymbol{X}^{\text{T}})^{+}$ was the pseudo-inverse of $\boldsymbol{X}^{\text{T}}$, and $\boldsymbol{Y}_{\text{aug}}$ was the augmented matrix of emission spectra updated.

Initial estimates were obtained from the analysis of standard matrices with techniques based on the detection of the 'purest' variables [18,19] as follows: for the excitation spectra of flavonol, the first purest variable of reagent matrix $\boldsymbol{R}$ was used; for the excitation spectra of TPhT derivative, the second purest variable found in the standard matrix $\boldsymbol{S}$ was used (the first purest variable corresponded to flavonol, since this made the greatest contribution to the fluorescence observed); for the excitation spectra of fulvic acids (or sea-water background), the first purest variable of the background matrix $\boldsymbol{B}$ was taken.

In a second step, the emission spectra matrix was updated ($\boldsymbol{X}^{\text{T}}$) using the equation

$$\boldsymbol{X}^{\text{T}} = (\boldsymbol{Y}_{\text{aug}})^{+}\boldsymbol{D}_{\text{aug}}^{\text{ex}*} \quad (4)$$

where $(\boldsymbol{Y}_{\text{aug}})^{+}$ was the pseudo-inverse of the $\boldsymbol{Y}_{\text{aug}}$ matrix.

These two steps were repeated until convergence was achieved. The constraints applied to get physically meaningful solutions during the ALS optimization were: (a) the excitation and emission spectra had to be non-negative, (b) there was correspondence between common species in the different data matrices, (c) the excitation spectrum of each species had to be the same in all matrices where that species was present and (d) the emission spectrum of each species had to be the same in all runs where that species was present.

When excitation spectra were used as initial estimates, the iteration procedure started with Eq. (4), and Eq. (3) was applied in the second stage. A similar procedure was applied to the emission-wise augmentation. In such a case, $\boldsymbol{D}_{\text{aug}}^{\text{ex}*}$ was the corresponding augmented matrix, and $\boldsymbol{X}_{\text{aug}}$ and $\boldsymbol{Y}$ referred to excitation and emission spectra, respectively.

Depending on the data augmentation, the quantification was performed by comparing the areas below either excitation or emission spectra of the analyte in the standard and in the unknown sample:

$$C_{\text{unk}} = \left(\frac{A_{\text{unk}}}{A_{\text{std}}}\right) C_{\text{std}} \quad (5)$$

where C_{unk} and C_{std} were the concentrations of the analyte in the unknown and standard samples, respectively; A_{unk} and A_{std} were the areas below the excitation or emission spectra profiles in the unknown and in the standard samples, respectively.

The overall prediction error was calculated using the expression

$$\text{Error}(\%) = \frac{\sqrt{\sum_{i=1}^{\text{sample}}(C_{i\text{true}} - C_{i\text{calc.}})^2}}{\sqrt{\sum_{i=1}^{\text{sample}}(C_{i\text{calc.}})^2}} \times 100 \quad (6)$$

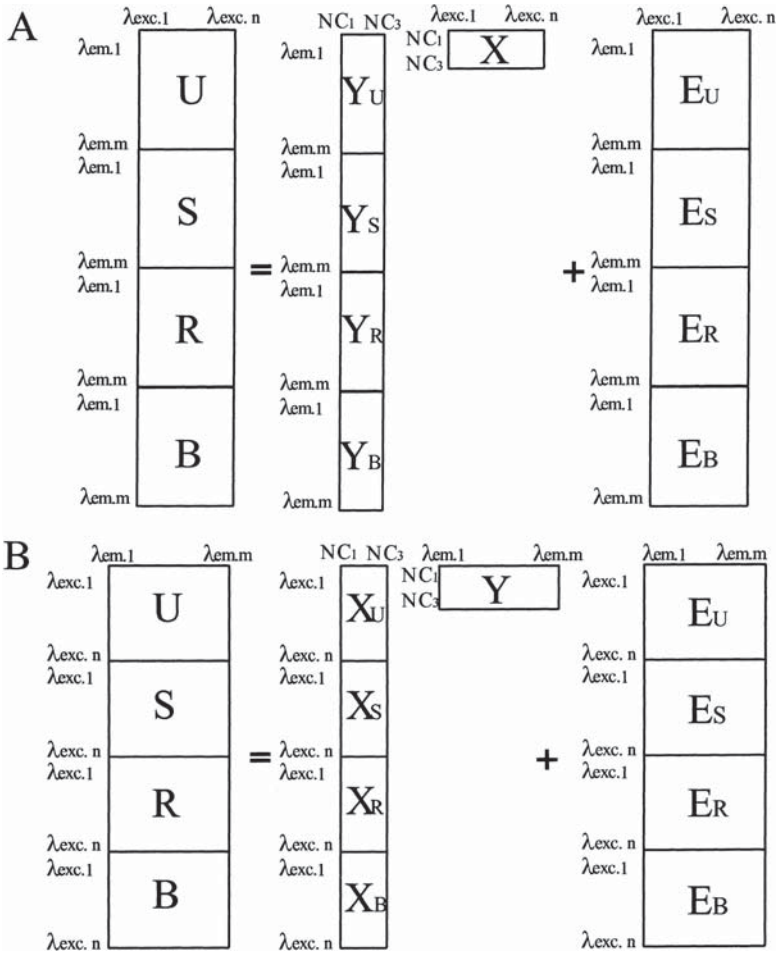

Fig. 3. Strategies for the decomposition of the augmented data matrices into the excitation and emission spectral contributions of the components. (A) Decomposition of the excitation-wise augmented data matrix; (B) decomposition of the emission-wise augmented data matrix. $\boldsymbol{U}$, unknown matrix; $\boldsymbol{S}$, standard matrix; $\boldsymbol{R}$, reagent matrix; $\boldsymbol{B}$, background matrix; $\boldsymbol{Y}$, matrices of emission spectra; $\boldsymbol{X}$, matrices of excitation spectra; $\boldsymbol{E}$, matrices of residual error. Subindices $\boldsymbol{U}$, $\boldsymbol{S}$, $\boldsymbol{R}$, and $\boldsymbol{B}$ refer to unknown, standard, reagent and background matrices, respectively. NC_1–NC_3 indicate the number of components.

where $C_{i\,\mathrm{true}}$ was the true concentration of analyte in the sample i and $C_{i\,\mathrm{calc}}$. was the concentration calculated by the method proposed.

4. Results and discussion

4.1. Rank analysis

Three chemical species were found in the rank analysis of the unknown synthetic and sea-water samples (matrix $\boldsymbol{U}$), which were attributed to TPhT derivative, flavonol and fulvic acids. The chemical rank of the standard matrix, $\boldsymbol{S}$, was found to be 2. In this case, the background fluorescence (fulvic acids) from the sample matrix was absent. Note that it was not possible to prepare a standard providing only a pure analyte response, since there was always a contribution from the excess of the flavonol reagent to the fluorescence signal. Indeed, this made it more difficult to obtain a good initial estimation of the excitation or emission spectrum of the analyte since they always overlapped

Table 1
Composition of the synthetic samples

Sample	Triphenyltin ($\mu g\,l^{-1}$)	Fulvic acids ($mg\,l^{-1}$)
U1/6	1.03	6
U2/8	2.07	8
U3/5	3.10	5
U3/7	3.10	7
U3/10	3.10	10
U4/6	4.14	6
U5/8	5.17	8
U6/4	6.20	4
U7/4	7.24	4
U7/10	7.24	10
U8/6	8.27	6
U9/8	9.31	8
U10/4	10.30	4

considerably with the spectrum of the reagent. The reagent data matrix, $\boldsymbol{R}$, gave one single main contribution to data variance since flavonol was the only fluorescent compound in this case. Background fluorescence data variance in synthetic and sea-water samples (matrix $\boldsymbol{B}$) was due to fulvic acids and only a single component was considered to account for it.

4.2. Study of synthetic samples

The MCR-ALS method was applied to TPhT quantitation in synthetic samples containing fulvic acids as interference (see Table 1 for their compositions). Since TPhT concentrations were in the $\mu g\,l^{-1}$ level, no SPE was carried out before the fluorimetric measurements. TPhT quantitation was studied using the strategies referred to as A, B, C and D (see Table 2). Fig. 4 shows the variation of prediction error against the wavelength excitation range for three samples chosen as examples of strategy A. When the whole λ_{ex} range was used, the prediction errors were maximum. Quantitative predictions improved as the number of λ_{ex} decreased, which was especially noticeable at the lowest TPhT concentrations assayed. The minimum error was achieved when the λ_{ex} range was limited to between 400 and 415 nm. This behavior could be explained by the fact that fluorescence at the lowest excitation wavelengths was mainly produced by the excess of flavonol. In this range, the flavonol fluorescence was much higher than the TPhT contribution, and it could be neither efficiently modelled nor removed during the data analysis. Removing the lowest excitation wavelengths minimized this reagent contribution, which improved significantly the TPhT quantification. However, shortening the excitation range too much caused the loss of some relevant information concerning the analyte; for instance, predictions worsened for the excitation range from 405 to 415 nm. Similar conclusions were obtained for strategies C and D, while strategy B did not require any reduction in the λ_{ex} range. The overall prediction error for each strategy, calculated using Eq. (6), showed that strategy A provided the lowest overall prediction error (Table 2). However, strategy B was also able to determine TPhT without any further data pre-treatment with a prediction error lower than 5%.

4.3. Study of sea-water samples

The quantification of TPhT in real sea-water samples was performed using a single synthetic standard. Additional information about the reagent response and the sea-water fluorescence background was also included to improve the resolution. The emission-wise arrangement (as in strategy A) was also optimal in the study of the sea-water samples and again superior to the excitation-wise augmentation. As for synthetic samples, in order to decrease the influence of the

Table 2
Overall prediction error for the determination of triphenyltin in the synthetic unknown mixtures with the MCR-ALS method using various strategies

Strategy	Matrix augmentation	Initial estimates	Data preprocessing	Overall prediction error (%)
A	excitation-wise [$\boldsymbol{U}^T;\boldsymbol{S}^T;\boldsymbol{R}^T;\boldsymbol{B}^T$]	excitation spectra	excitation range 400–415 nm	3.9
B	emission-wise [$\boldsymbol{U};\boldsymbol{S};\boldsymbol{R};\boldsymbol{B}$]	emission spectra	none; whole excitation range 375–415 nm	4.7
C	excitation-wise [$\boldsymbol{U}^T;\boldsymbol{S}^T;\boldsymbol{R}^T;\boldsymbol{B}^T$]	emission spectra	excitation range 400–415 nm	5.2
D	emission-wise [$\boldsymbol{U};\boldsymbol{S};\boldsymbol{R};\boldsymbol{B}$]	excitation spectra	excitation range 400–415 nm	7.6

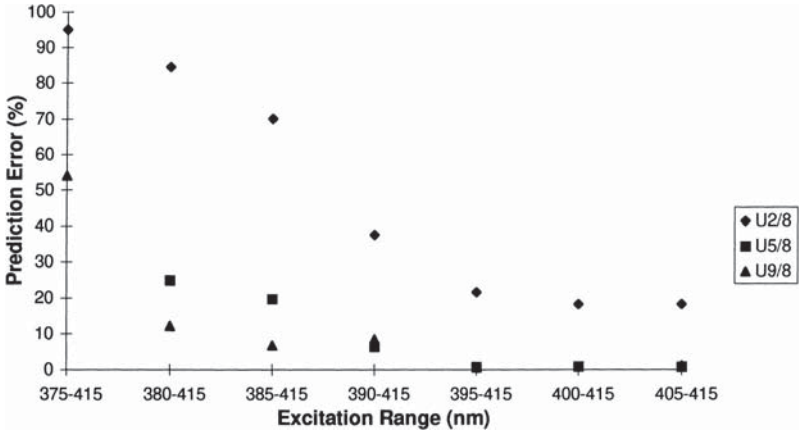

Fig. 4. Variation of the prediction error vs. the excitation range.

excess of flavonol in the model, the best λ_{ex} range was from 400 to 415 nm.

Fig. 5 shows the results of the MCR-ALS resolution of one excitation-wise augmented data matrix $[\boldsymbol{U}^T;\boldsymbol{S}^T;\boldsymbol{R}^T;\boldsymbol{B}^T]$ composed of the unknown sample ($\boldsymbol{U}$), 8 ng l^{-1} TPhT standard ($\boldsymbol{S}$), reagent ($\boldsymbol{R}$) and sea-water background ($\boldsymbol{B}$). The method allowed the emission spectra of TPhT, of the reagent and of fulvic

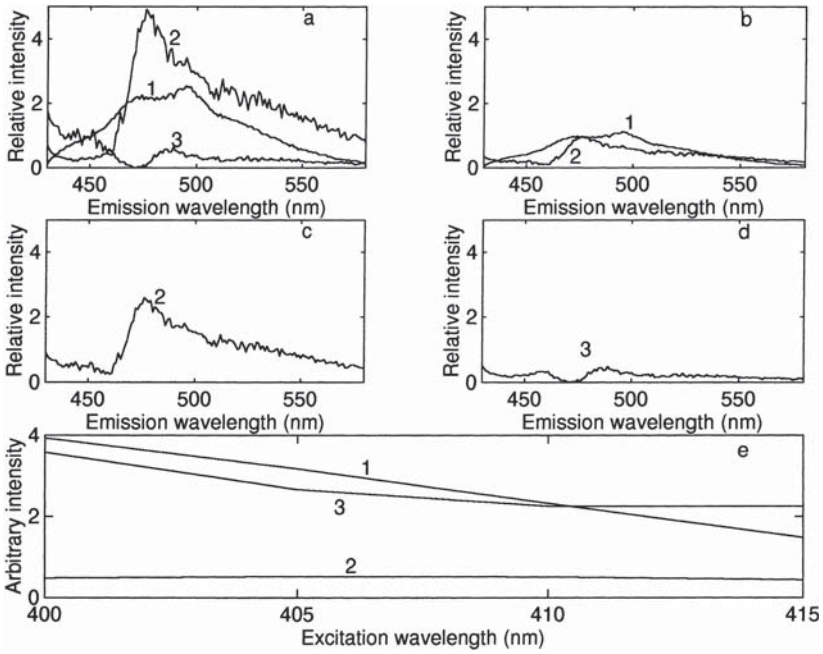

Fig. 5. Excitation and emission spectra recovered in the resolution of the excitation-wise augmented matrix $[\boldsymbol{U}^T;\boldsymbol{S}^T;\boldsymbol{R}^T;\boldsymbol{B}^T]$ using the ALS-MCR method. Species assignment: 1. TPhT derivative; 2. flavonol; 3. fulvic acids. (a) Emission spectra for the unknown sea-water sample (matrix $\boldsymbol{U}$); (b) emission spectra for the standard sample (matrix $\boldsymbol{S}$); (c) emission spectra for the reagent sample (matrix $\boldsymbol{R}$); (d) emission spectra for the background of fulvic acids (matrix $\boldsymbol{F}$); (e) excitation spectra. TPhT is quantified by comparison of the areas under the excitation profiles of the analyte in the unknown sample (a) and in the standard (b) according to Eq. (5).

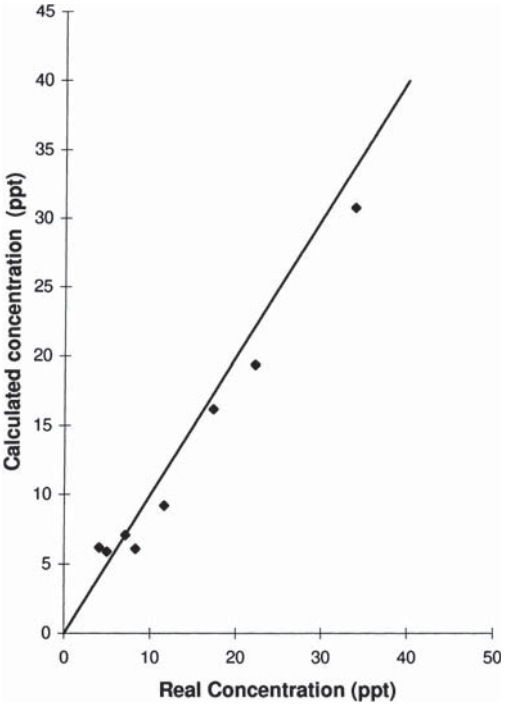

Fig. 6. Comparison between real and calculated concentration of TPhT in the sea-water samples using the MCR-ALS method.

acids to be estimated, as well as the estimation of their excitation spectra. Note that, in this case, the quantitative information was contained in the emission spectra and that TPhT in the unknown sample was determined by comparing the areas below the emission spectrum of the analyte for the standard and for the sample. The shape of the emission spectra recovered for each species in the different matrices was exactly the same, as a consequence of the trilinear structure of data and of the application of trilinearity constraints during the ALS optimization [7,12] (see constraints (c) and (d) in Section 3). Indeed, the application of the trilinearity constraints was crucial to obtain good spectral resolution and quantitation of TPhT in the sea-water samples.

Results of the determination of TPhT at low ng l^{-1} levels in 12 sea-water samples using the proposed MCR-ALS method were in accordance with the real values (Fig. 6), with an overall prediction error of 12.3 % (see Eq. (6)).

5. Conclusions

Second-order excitation–emission fluorimetric data were successfully used to determine TPhT using flavonol as reagent. The MCR method based on ALS could resolve and determine quantitatively TPhT in sea-water samples by using a single synthetic standard for the analyte. The method was successfully applied to the determination of TPhT in sea-water samples at the low ng l^{-1} level, with an overall prediction error of about 12%.

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