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ORIGINAL PAPER

Second-Order Data Obtained by Time-Resolved Room Temperature Phosphorescence. A New Approach for PARAFAC Multicomponent Analysis

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Abstract A second-order multivariate calibration approach, based on a combination of PARAFAC with time-resolved room temperature phosphorescence (RTP), has been applied to resolve a binary mixture of Phenanthrene and 1,10-Phenanthroline, as model compounds. The RTP signals were obtained in aqueous β-cyclodextrin solutions, in the presence of several heavy atom containing compounds. No deoxygenation was necessary to obtain the phosphorescence signals, which adds simplicity to the method. The resolution of the model compounds was possible in base to the differences in the delay-time of the RTP signals of the investigated analytes, opening a new approach for second-order data generation and subsequent second order multivariate calibration.

Keywords Second-order data · PARAFAC · Room-temperature-phosphorescence · Cyclodextrins

Introduction

Luminescence spectroscopy is used to resolve many different practical problems in modern analytical chemistry, due to its intrinsic selectivity and sensitivity, and to the easy availability of instruments [1]. A problem may arise, however, during the analysis of multi-analyte samples, namely the spectral overlapping. Spectral superposition can be circumvented by resorting to a series of multivariate chemometric procedures, designed to provide selectivity to potentially unselective signals.

When several analytes emit overlapped luminescence signals, the corresponding procedure in the first-order multivariate domain is the generalized standard addition method (GSAM) [2], which involves adding mixtures of standards to the unknown sample and scanning the emission spectra. GSAM is formally analogous to univariate standard addition, except that it demands more experimental work per sample.

The above procedure does not apply when the sample carries unexpected luminescent constituents which have not been taken into account in the calibration phase. In this case, one should resort to the second-order advantage [3], which is inherent to second-order data. Second-order multivariate algorithms such as parallel factor analysis (PARAFAC) [4], generalized annihilation (GRAM) [5] and multivariate curve resolution-alternating least-squares (MCR-ALS) [6] can be employed in the standard addition mode, and are able to obtain the second-order advantage.

To date, several approaches have been investigated to obtain second-order data, as new advanced modern instruments are available. Fluorescence spectroscopy is by far the most abundant type of data used for second-order calibration. Andersen and Bro [7] gave an overview of the use of fluorescence excitation-emission spectroscopy and how to perform valid multiway analysis of such data.

Pertinent examples are the determination of 1-naphthol, carbaryl and carbofuran [8], naphthalene, 1-naphthol and 2-naphthol [9], triphenyltin [10, 11], chlorophylls and pheopigments [12], verapamil [13], propranolol, amiloride and dipyridamole [14], naproxen, salicylic acid and salicyluric acid [15], norfloxacin, enoxacin and ofloxacin [16], doxorubicin [17], piroxicam [18], carbendazin, fuberidazole and thiabendazole [19], ibuprofen [20], ciprofloxacin [21],

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carbamazepine and carbamazepine 1,10-epoxide [22] and sulfathiazole [23].

The recording of this type of data conveys certain advantages: the measurements are carried out on a single instrument, the signals are selective and sensitive, and the obtained models are trilinear. There are, however, other methods for generating high-order data: UV-visible spectrophotometry coupled to pH or kinetic changes [24, 25], and hyphenated techniques such as chromatography coupled to mass spectrometry detection [26].

Kinetic experiments provide the opportunity of introducing an additional temporal dimension in the set of measured data, allowing to increasing the selectivity of spectroscopic-based determinations. Three-way kinetic measurements have been reported in the literature, by following the time evolution of absorption or emission spectra [27, 28].

In flow injection, three-way data often occurs. Examples are the analysis of benzoic and sorbic acids using a FIA system with pH gradient generation and diode array photometric detection [29]. Levodopa and benserazide were also analysed by modelling kinetic-spectrophotometric data, from a spectrally detected stopped-flow injection method, where the analytes react with periodate [30].

Goicoechea et al. [31] reported the first application of PARAFAC to higher-order instrumental phosphorescence data generated from Shpol'skii matrixes at liquid helium temperature. Third-order data arrays, consisting of excitation-modulated emission wavelength-delay time matrixes, were collected with the aid of a cryogenic fiber-optic probe, a tunable dye laser, and a multichannel system for phosphorescence detection. These data were applied to the analysis of 2,3,7,8-tetrachloro dibenzo-*p*-dioxin in water samples. The feasibility to directly determine parts-per-trillion concentration levels of the target compound was demonstrated with heavily contaminated samples of unknown composition.

On the other hand, it is known that cyclodextrins (CDs) have the property of forming inclusion complexes with guest molecules that have suitable characteristics of polarity and dimension [32–36]. The inclusion complex formation in the CD systems is favoured by substitution of the high-enthalpy water molecules located inside the CD cavity, with an appropriate guest molecule of low polarity. An overview of the non-chromatographic analytical uses of CDs has been presented by Szente and Szejtli [36]. As the complexation process implies an interaction producing a protection of the included species, the CDs have been used in the pharmaceutical industry to encapsulate drugs that are photosensitives.

Different room-temperature-phosphorescence (RTP) studies were made in β-cyclodextrin solution of phenanthrene [37–46] and 1-10-phenanthroline [40, 47, 48]. The cyclohexane-cyclodextrin-RTP of these phosphors and others has been demonstrated [43]. Another study of separately solutions of phenanthrene and 1-10-phenanthroline were made [49] in the investigation of six-membered carbocyclic compounds (6-MCCs) as molecular switch block of RTP in nondeoxygenated β-cyclodextrin solution. This new approach compared with other RTP methods is simple, convenient and fast.

The present reports aims at a theoretical and experimental study of the ability of PARAFAC to analyze complex samples of luminescent species, by obtaining second-order data from the time-resolved room-temperature-phosphorescence (RTP) emission of several polycyclic aromatic compounds (PACs), when included in β-cyclodextrin.

Theory

PARAFAC

A brief account of PARAFAC achieving the second-order advantage is provided. Second-order data are measured for a given sample as a $J\times K$ array, where J and K denote the number of emission wavelengths, and delay-time points in each of the two dimensions. For obtaining the second-order advantage, the I training arrays $\boldsymbol{X}_{i,\mathrm{cal}}$ are joined with the unknown sample array $\boldsymbol{X}_{\mathrm{u}}$ into a three-way data array $\boldsymbol{X}$, whose dimensions are $[(I+1)\times J\times K]$. Provided $\boldsymbol{X}$ follows a trilinear PARAFAC model, it can be written in terms of three vectors for each responsive component, designated as $\mathbf{a}_n$, $\mathbf{b}_n$, and $\mathbf{c}_n$, and collecting the relative concentrations $[(I+1)\times 1]$ for component n, and the profiles in the two modes $(J\times 1)$ and $(K\times 1)$ respectively. The specific expression is presented in Eq. (1) [50]:

$$X_{ijkl} = \sum_{n=1}^{N} a_{in} b_{jn} c_{kn} + E_{ijk} \tag{1}$$

where N is the total number of responsive components, a_{in} is the relative concentration of component n in the ith. sample, and b_{jn}, and c_{kn} are the normalized intensities at the emission wavelength j and delay-time k, respectively. The values of E_{ijk} are the elements of the array $\boldsymbol{E}$, which is a residual error term of the same dimensions as $\boldsymbol{X}$. The column vectors $\mathbf{a}_n$, $\mathbf{b}_n$, and $\mathbf{c}_n$ are collected into the corresponding loading matrices **A**, **B and C** ($\mathbf{b}_n$, and $\mathbf{c}_n$ are usually normalized to unit length).

The model described by equation (1) defines a decomposition of $\boldsymbol{X}$ which provides access to emission (**B**) and delay-time profiles (**C**) and relative concentrations (**A**) of individual components in the $(I+1)$ mixtures, whether they are chemically known or not. This constitutes the basis of the second-order advantage. The decomposition is usually accomplished through an alternating least-squares (ALS) minimization scheme [51].

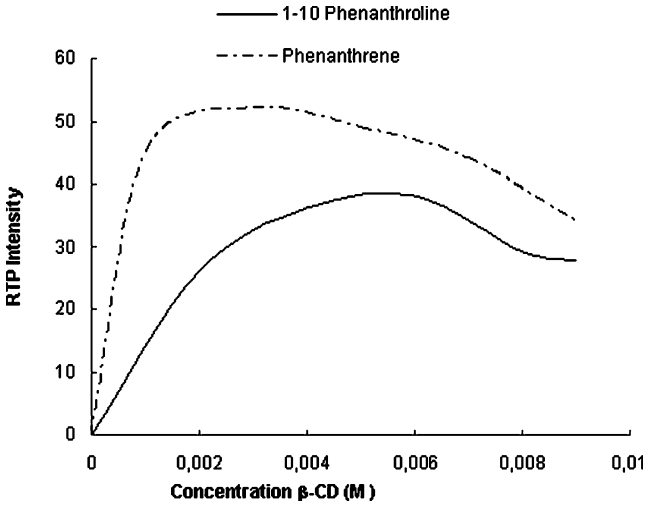

Fig. 1 Influence of β-CD concentration in the room temperature phosphorescence (RTP) intensity. pH=5.6; 1,10-Phenanthroline: λex=299 nm, λem=486 nm, 10 μL bromocyclopentane; Phenanthrene: λex=290 nm, λem=495 nm, 5 μL bromocyclohexane. Final volume 10 mL. Delay time=0.1 ms. Gate time=10 ms

Software

All routines employed to carry out the calculations described in this paper were written in MATLAB [52]. Those for applying PARAFAC are available in the internet thanks to Bro [53] and were used by employing a graphical user interface, MVC2, for data input and parameter setting, of the type already described for first-order multivariate calibration [54]. An specific Matlab routine was written to convert the raw delay-time emission data of the spectrofluorimeter to ASCII X,Y input data to MVC2.

Experimental data set

Apparatus

Luminescence spectral measurements were performed on a fast-scanning Varian Cary Eclipse luminescence spectrophotometer, equipped with two Czerny–Turner monochromators and a Xenon flash lamp, and connected to a PC microcomputer via an IEEE 488 (GPIB) serial interface. Excitation and emission band widths of 10 nm were used. Delay time and gate time of 0.1 ms and 10 ms were employed. Time-resolved-emission matrices were recorded in a 10 mm quartz cell.

Reagents and procedure

All experiments were performed with analytical reagent grade chemicals. Stock solutions of 1,10-Phenanthroline 5×10^{-3} M and Phenanthrene 1×10^{-3} M were prepared by dissolving the appropriate amount of each reagent (Merck and Aldrich) in 100 ml of ethanol. These solutions were stored in dark bottles at 4 °C. Working solutions of the analytes at different concentrations were prepared by adding the appropriate volume from stock solutions (in general, 1 mL of each analyte), drying at 70 °C, and adding the other reagents (cyclodextrin and carbocyclic compound), in 10 mL as final volume. Aqueous solutions of β- and γ-cyclodextrin (Cyclolab), 9×10^{-3} M, were prepared.

Calibration and validation sets

The time-resolved RTP matrices of these solutions were then recorded, and the data were subjected to three-way analysis, as described below. Suitable wavelength ranges for the determination were: emission from 445 nm to 555 nm at 1 nm intervals (J=110 wavelengths) and delay-times from 0 ms to 160 ms at 20 ms intervals (K=8 delay-times), making a total of 110×8=880 spectral points per sample matrix.

Results and discussion

Effects of β and γ cyclodextrin

The β-CD is the main molecular block of RTP for different lumiphors, its concentration and existence in the luminescence system plays a key role for each phosphor. Therefore, the β-CD concentration was varied from 1×10^{-3} M to 9×10^{-3} M and the concentration of other components was held constant. A temperature of 20 °C was employed for all experiments (≈ room temperature).

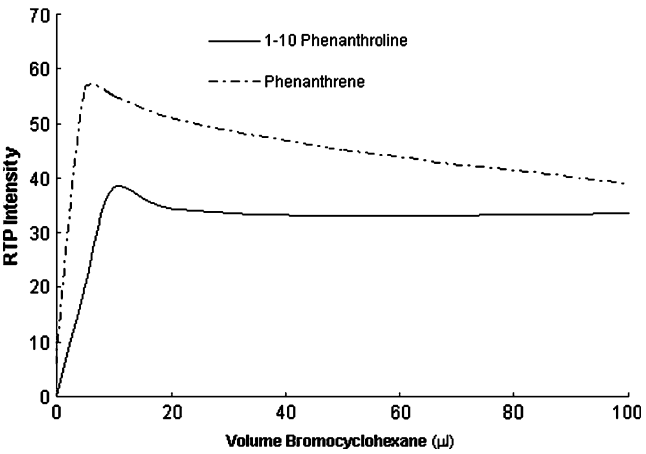

Fig. 2 Influence of bromocyclohexane concentration. pH=5.6; 1,10-Phenanthroline: λex=299 nm, λem=486 nm, 6 10^{-3} M β-CD; Phenanthrene: λex=290 nm, λem=495 nm, 3 10^{-3} M β-CD. Final volume 10 mL. Delay time=0.1 ms. Gate time=10 ms

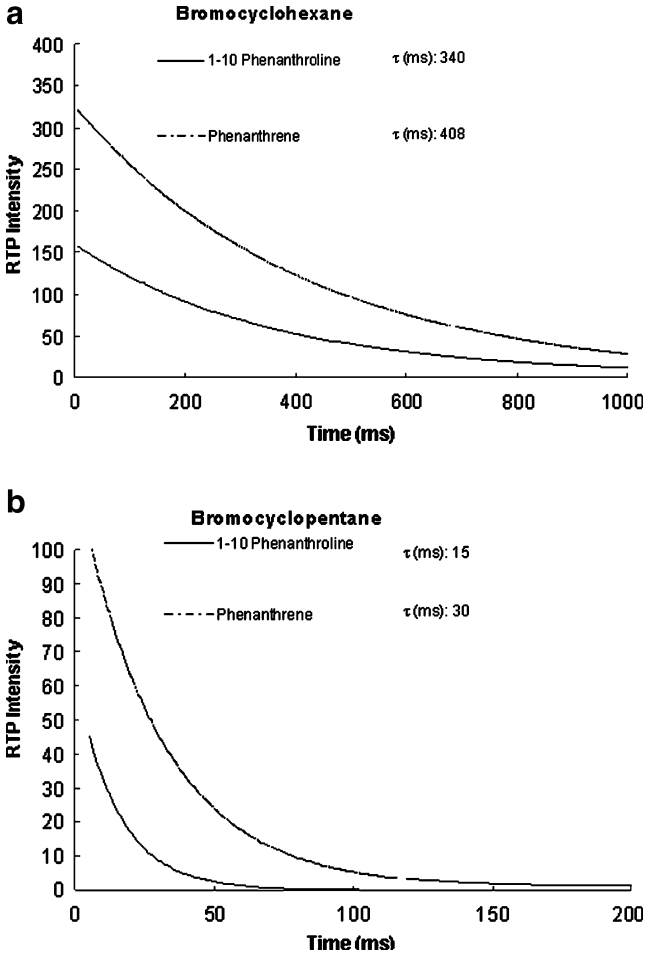

Fig. 3 Evolution of phosphorescence signal with time for each analyte by using a) bromocyclohexane and b) bromocyclopentane. pH=5.6; 1,10-Phenanthroline: λex=299 nm, λem=486 nm, 6 10^{-3} M β-CD; Phenanthrene: λex=290 nm, λem=495 nm, 3 10^{-3} M β-CD

The RTP intensity of the assayed phosphors increase with the increase of β-CD concentration, so β-CD concentration was selected when the maximum RTP signals were obtained (6×10^{-3} M and 3×10^{-3} M for 1,10-Phenanthroline and Phenanthrene, respectively) as it is shown in Fig. 1.

A comparative study between β- and γ-cyclodextrin was done by using the selected optimum cyclodextrin concentration values. The higher values for each analyte were obtained by using β-CD, then, it was the cyclodextrin selected.

Amounts of five and six-membered carbocyclic compounds

Heavy atom perturbation often induces phosphorescence emission and enhances RTP of aromatic hydrocarbons. Some compounds have been employed as external heavy atoms, for example, micro amounts of six-membered carbocyclic compounds (6-MCCs).

It was studied the influence of addition of micro amounts of five and six-membered carbocyclic compounds as bromocyclohexane, cyclohexanol, bromocyclopentane and cyclohexane. The higher RTP signals were obtained by using bromocyclohexane and bromocyclopentane.

The influence of bromocyclohexane concentration for 1,10-Phenanthroline and Phenantrene is shown in Fig. 2, where the maximum signal is obtained by adding 10 μL and 5 μL of bromocyclohexane, respectively, in a 10 mL volumetric flask.

Influence of pH

It was compared the analytical signal of the working solution (pH 5.6) and of this solution, after addition of NaOH and HCl (pH 12.2 and pH 2.2), respectively. The results show the higher phosphorescence signal at the pH of the working solution (pH 5.6).

Influence of N_2 deoxygenation

The influence of N_2 deoxygenation in the phosphoresce signal was studied with and without the presence of carbocyclic compounds. The results show that the presence of carbocyclic compounds is necessary in order to obtain phosphorescence signal of each analyte. Beside of that, it is not necessary the N_2 deoxygenation for obtaining phosphorescence, and this make experimentally easier the proposed phosphorescence procedure for determining each analyte.

Influence of stirring

It was studied the solution behaviour of each analyte during the time with and without stirring. It was observed that

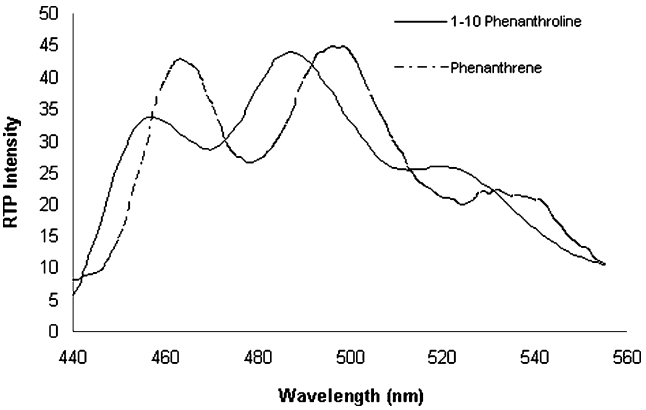

Fig. 4 Phosphorescence emission spectrum of both analytes in the optimized conditions. pH=5.6; 1,10-Phenanthroline: λex=299 nm, 10 μL bromocyclopentane, 6 10^{-3} M β-CD; Phenanthrene: λex=290 nm, 5 μL bromocyclohexane, 3 10^{-3} M β-CD. Final volume 10 mL. Delay time=0.1 ms. Gate time=10 ms

Table 1 Linear regression data

Analyte	1,10-Phenantroline	Phenantrene
Slope ± σ	0.300±0.004	0.124±0.002
Intercept ± σ	0.64±0.08	0.62±0.04
Correlation coefficient	0.995	0.995

without stirring the phosphorescence signal decreases after a while due to the lost of homogeneity. On the contrary, by stirring, the phosphoresce signal is almost constant for each analyte up to 700 s. Then, the working solutions will be stirred during the measurements.

Time-resolved phosphorescence signals. Lifetimes calculation

Some experiments were done in order to determine the decay-time phosphorescence profiles, to establish the time range where it is possible to observe the phosphorescence signals, and calculating the phosphorescence lifetime of each compound in the presence of bromocyclopentane and bromocyclohexane. Two samples were prepared for each analyte containing the optimum values of β-CD and carbocyclic compounds (bromocyclohexane and bromocyclopentane). In Figs. 3a and b it is possible to see the obtained results, when recording the decay-time curves of 1,10-Phenanthroline and Phenanthrene in the presence of bromocyclopentane and bromocyclohexane, respectively.

Taking into account the relation of lifetime (τ) by using both carbocyclic compound it is possible to see the separation of phosphorescence signals between each analyte.

In the case of bromocyclopentane: $\frac{\tau_{Fen}}{\tau_{1,10}} = 2$ and in the case of bromocyclohexane: $\frac{\tau_{Fen}}{\tau_{1,10}} = 1,2$

Then, the higher phosphorescence signal separation is obtaining by using bromocyclopentane as carbocyclic compound. For that reason, this is the carbocyclic compound selected for the simultaneous determination of Phenanthrene and 1,10-Phenanthroline.

The phosphorescence emission spectra of both analytes, in the optimized conditions, are presented in Fig. 4.

Calibration graph

The calibration graph for each analyte was obtained by registering the phosphorescence emission spectrum and measuring in their maximun (495 nm and 486 nm for Phenanthrene and 1.10-Phenanthroline, respectively) in triplicate, in the concentration range of 0–20 10^{-6} M.

The linear regression data is shown in Table 1.

Binary mixture analysis by PARAFAC calibration

The three-dimensional emission-delay time phosphorescence profile of one sample of Phenanthrene, in the established conditions, is presented in Fig. 5 as an example. The emission scan was obtained from 445 nm to 555 nm each 1 nm, exciting at 290 nm, by using different delay time (ms) in the range 0 to 160 with a gate time of 20 ms.

To apply PARAFAC in the standard addition mode, to an aliquot of the problem sample (which contains Phenanthrene and 1,10-Phenanthroline), five different amounts of Phenanthrene were added, keeping the final concentration within the linear range, and the three-dimensional emission-delay time phosphorescence profile was then registered for each of the resulting solutions. Then, to a second aliquot of

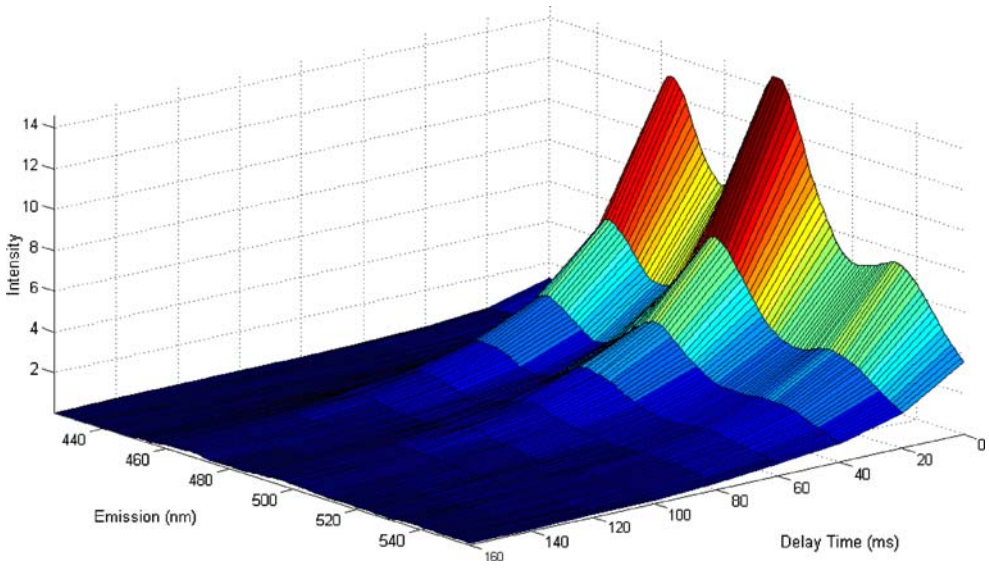

Fig. 5 Three-dimensional emission-delay time phosphorescence profile of one sample of Phenanthrene in the optimized conditions. λex=290 nm

Table 2 Composition of the calibration set of samples for the experimental system under study

Sample	μL of Phenanthrene added to cuvete	Phenanthrene /1,10-Phenanthroline (M)
Problem	–	$2.50\cdot 10^{-6}/1.25\cdot 10^{-5}$
Problem+ Adition 1	15	$2.98\cdot 10^{-6}/1.25\cdot 10^{-5}$
Problem + Adition 2	30	$3.46\cdot 10^{-6}/1.25\cdot 10^{-5}$
Problem + Adition 3	45	$3.95\cdot 10^{-6}/1.25\cdot 10^{-5}$
Problem + Adition 4	60	$4.44\cdot 10^{-6}/1.25\cdot 10^{-5}$
Problem + Adition 5	75	$4.93\cdot 10^{-6}/1.25\cdot 10^{-5}$
Sample	μL of 1,10-Phenanthroline added to cuvete	1,10-Phenanthroline/ Phenanthrene (M)
Problem	–	$1.25\cdot 10^{-5}/2.50\cdot 10^{-6}$
Problem + Adition 1	15	$1.49\cdot 10^{-5}/2.50\cdot 10^{-6}$
Problem + Adition 2	30	$1.73\cdot 10^{-5}/2.50\cdot 10^{-6}$
Problem + Adition 3	45	$1.97\cdot 10^{-5}/2.50\cdot 10^{-6}$
Problem + Adition 4	60	$2.20\cdot 10^{-5}/2.50\cdot 10^{-6}$
Problem + Adition 5	75	$2.44\cdot 10^{-5}/2.50\cdot 10^{-6}$

the problem sample, five different amounts of 1,10-Phenanthroline were added, within the linear range, and the three-dimensional emission-delay time phosphorescence profile was again registered for each of the resulting solutions (Table 2). In the standard addition mode, the calibration matrix is constructed by directly working with the problem samples, to which different standard additions of the analyte of interest are made.

The first step in processing the time-resolved data sets, with the PARAFAC second-order algorithm, is the assessment of the correct number of sample constituents. With PARAFAC, the standard procedure involves the so-called core consistency diagnostic test [55], which involves observing the changes in the core consistency parameter as the number of trial luminescent components is increased. The number of components is taken as the largest number for which the latter parameter is larger than about 50. Figure 6 shows a typical progression of core consistency values when processing a test sample, together with the calibration set of samples, as it is usual in PARAFAC modelling studies. As can be seen, the suggested number of components is two. When more components are employed, the profiles recovered by PARAFAC for the additional components are similar to those for the calibrated analytes. Therefore, two components were used for PARAFAC calculations.

Once the number of components was estimated, the array formed by joining the emission-delay time phosphorescence signals for the problem sample and those obtained by standard addition was subjected to decomposition. The identification of the chemical constituents under investigation is required before quantification by resorting to the pseudounivariate calibration graph provided by PARAFAC. This is done with the aid of the spectral and time-decay profiles extracted by this algorithm, and comparing them with those for a standard solution of the pure analyte of interest. These emission and delay-time profiles are contained in matrices B and C, respectively. The components

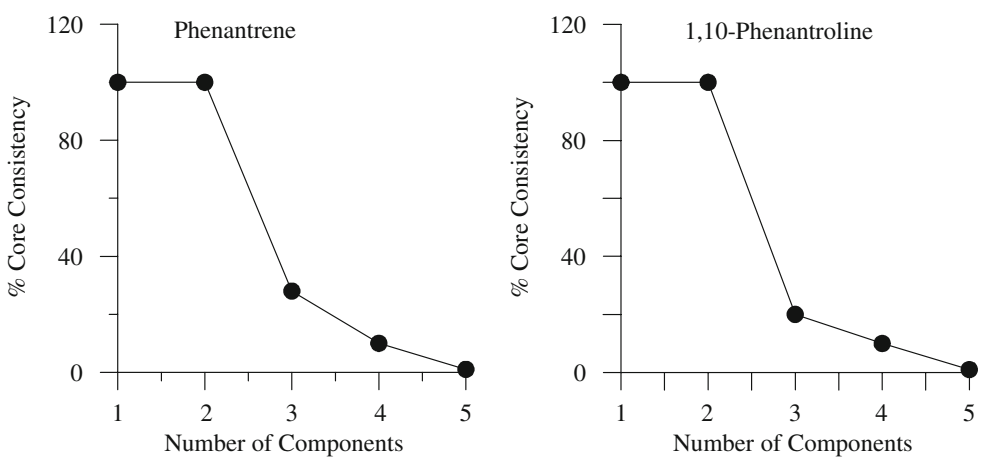

Fig. 6 PARAFAC core consistency diagnostics for a typical test sample, showing the changes in the core consistency parameter as a function of a trial number of components

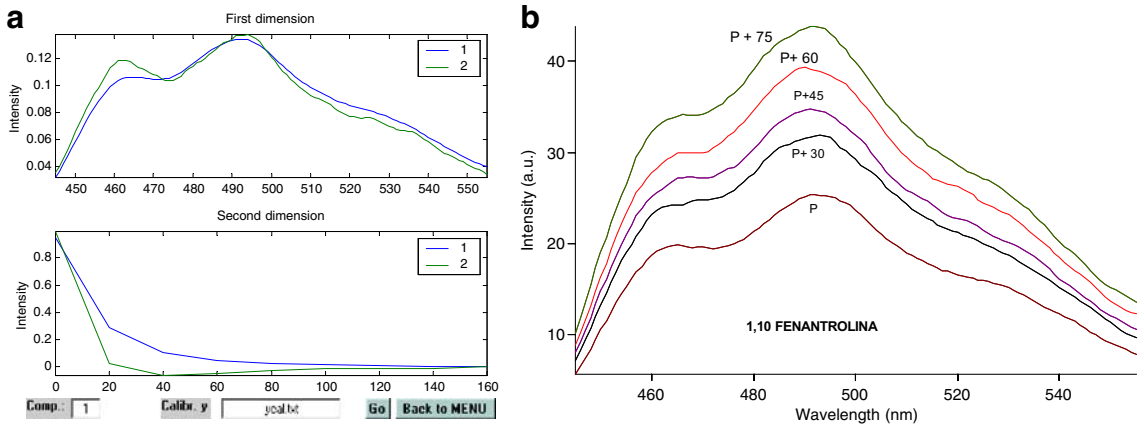

Fig. 7 Emission and delay-time profiles recovered by PARAFAC for the two components. Emission spectra of different additions of 1,10-Phenanthroline. λex=299 nm

have been labelled with the order assigned by the model, i.e., they appear in the order of their contribution to the total of the variance.

In Fig. 7, the emission and delay-time profiles recovered by PARAFAC for the two components, when it is analyzed 1,10-Phenanthroline in the problem sample, is presented. Beside of this, it is possible to see the RTP emission spectra of different additions of 1,10-Phenanthroline for a fixed delay time of 0.1 ms.

In Fig. 8, the pseudo-univariate calibration obtained after standard additions of Phenanthrene to the problem sample is shown.

In the analysis of the problem samples, a concentration of 1.32×10^{-5} M was obtained in the case of 1,10-Phenanthroline, which leads a relative error of prediction (REP) of 5.6%. Phenathrene was obtained in concentration of 2.54×10^{-6} M, which leads a REP of 1.6%.

Conclusions

The room temperature phosphorescence emisión of Phenanthrene and 1,10-Phenanthroline has been investigated in aqueous β-cyclodextrin solutions. The RTP emission is obtained, without necessity of deoxygenation, in the presence of several heavy atoms containing compounds, as bromocyclohexane and bromocyclopentane.

The recording of the time-resolved RTP signals obtained by this approach, allowed the simultaneous determination of mixtures of both compounds. The resolution was accomplished by combination of the second-order signals with PARAFAC in the standard addition mode.

As far as we know, this is the first time that time-resolved RTP signals are proposed and combined with second-order multivariate calibration for mixture resolution. In our study, the differences in the time-resolved RTP signals of the investigated analytes, increasing the information useful and disposable for the calibration model, allowed the simultaneous determination of Phenanthrene and 1,10-Phenanthroline. The approach opens new possibilities of improvement of RTP methods, by combining with different chemometric calibration schemes.

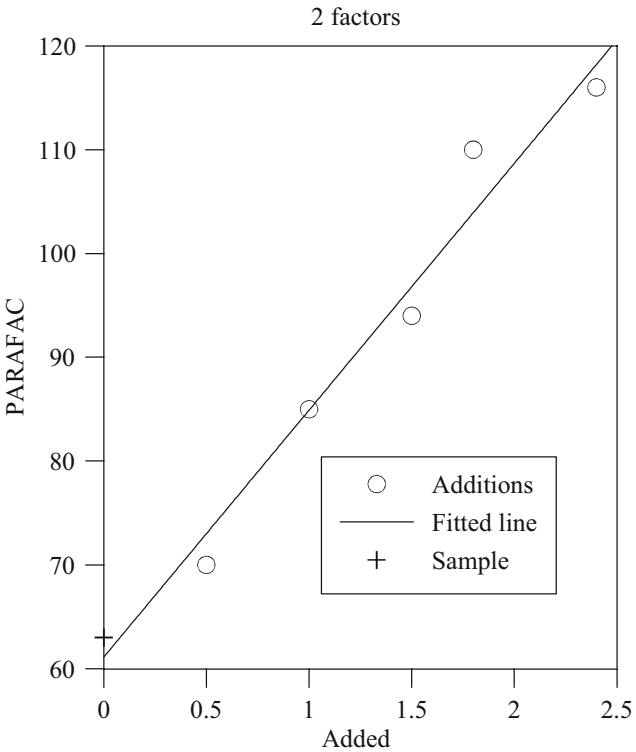

Fig. 8 Pseudo-univariate calibration obtained after standard additions of Phenanthrene

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