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Determination of polycyclic aromatic hydrocarbons by four-way parallel factor analysis in presence of humic acid

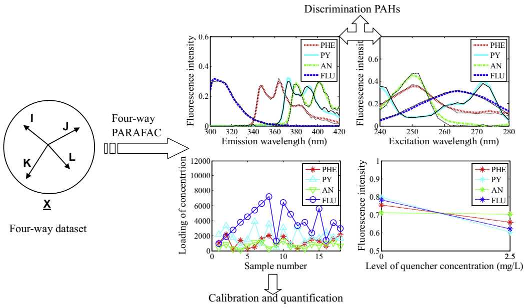
Ruifang Yang [a,b], Nanjing Zhao [a,*], Xue Xiao [a], Shaohui Yu [c], Jianguo Liu [a], Wenqing Liu [a]

[a] *Key Laboratory of Environment Optics and Technology, Anhui Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, Hefei 230031, China*
[b] *University of Science and Technology of China, Hefei 230022, China*
[c] *Hefei Normal University, School of Mathematics and Statistics, Hefei 230061, China*

HIGHLIGHTS

- Polycyclic aromatic hydrocarbons with humic acid are identified and quantified.
- Quenching effect and overlapping spectra are solved by four-way techniques.
- Each PAH concentration is predicted in the presence of matrix quencher effect.

GRAPHICAL ABSTRACT



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ABSTRACT

There is not effective method to solve the quenching effect of quencher in fluorescence spectra measurement and recognition of polycyclic aromatic hydrocarbons in aquatic environment. In this work, a four-way dataset combined with four-way parallel factor analysis is used to identify and quantify polycyclic aromatic hydrocarbons in the presence of humic acid, a fluorescent quencher and an ubiquitous substance in aquatic system, through modeling the quenching effect of humic acid by decomposing the four-way dataset into four loading matrices corresponding to relative concentration, excitation spectra, emission spectra and fluorescence quantum yield, respectively. It is found that Phenanthrene, pyrene, anthracene and fluorene can be recognized simultaneously with the similarities all above 0.980 between resolved spectra and reference spectra. Moreover, the concentrations of them ranging from 0 to 8 $\mu g\ L^{-1}$ in the test samples prepared with river water could also be predicted successfully with recovery rate of each polycyclic aromatic hydrocarbon between 100% and 120%, which were higher than those of three-way PARAFAC. These results demonstrate that the combination of four-way dataset with four-way parallel factor analysis could be a promising method to recognize the fluorescence spectra of polycyclic aromatic hydrocarbons in the presence of fluorescent quencher from both qualitative and quantitative perspective.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs), a group of chemicals containing two or more single or fused aromatic rings, are widespread in aquatic environments. It is confirmed that the long-term exposure to these chemicals will induce health problems including cancer, transgenation and deformity. So far, sixteen kinds of PAHs have been identified as priority pollutants by the US EPA [1,2]. Meanwhile, a lot of analytical techniques have been developed to recognize and monitor these PAHs effectively. Among them, gas chromatography (GC) and high performance liquid chromatography (HPLC) techniques are two of the most widely used techniques to analyze PAHs qualitatively and quantitatively

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* Corresponding author.
E-mail address: njzhao@aiofm.ac.cn (N. Zhao).

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owing to their high precision [3–5]. But they are expensive, tedious, time-consuming, and require large amounts of solvents.

Known as a sensitive, rapid and nondestructive method, fluorescence detection technique has been strongly recommended to identify and quantify PAHs [6–8], although it has dependence on environmental factors, such as temperature, ionic strength and pH value [9]. The key step to recognize individual PAH by fluorescence detection technique is accurately extracting spectra of analytes from the acquired three dimensional fluorescence spectra of PAHs mixture. However, in practical situation, a lot of chemicals coexist with PAH in aquatic system, especially the special chemical, i.e. fluorescent quencher, which will make the fluorescence spectra extraction more difficult. Taking humic acid (HA) as an example, it is ubiquitous in aquatic system as an important component of dissolved organic matter (DOM) [10,11]. HA, as a fluorescent quencher, could not only reduce the fluorescence intensity of PAHs which is called quenching, but also have the overlapped fluorescence spectra with PAHs [12]; these exert negative effect on correctly identifying and quantifying PAHs pollutants in aquatic environment. Therefore, it is urgently necessary to develop effective method to recognize the individual PAH from their fluorescence spectra in the presence of fluorescent quencher. However, this problem has seldom been investigated to the best of our knowledge.

Four-way PARAFAC has been applied in excitation and emission fluorescence spectroscopy study. In comparison with three-way PARAFAC, the additional dimension could be PH value, reaction time, quencher, etc. [9,13,14]. Analogous to the second order advantage of three-way PARAFAC, four-way PARAFAC can obtain the unique solutions and give the correct profiles of each mode [15–18], even in the presence of unknown interferents which is not included in the calibration model.

In this work, the fluorescence spectra of the mixture of four kinds of PAHs in aquatic solution in the presence of HA are analyzed via the combination of a four-way dataset with four-way parallel factor analysis (PARAFAC). The four way dataset was acquired through measuring excitation emission matrices of PAHs at different levels of HA concentration.

2. PARAFAC

2.1. Three-way PARAFAC

An excitation–emission matrix spectrofluorometer can generate a $J \times K$ data matrix, where J and K are the number of excitation wavelength and emission wavelength, respectively. By ‘stacking’ the matrixes obtained from I samples, a three-way array $\underline{\mathbf{X}}$ with dimensions $I \times J \times K$ could be produced. For this data array a trilinear model can be expressed as [9,15]:

$$x(i,j,k) = \sum_{f=1}^{F} a_{if} b_{jf} c_{kf} + \varepsilon_{ijk} \quad i = 1,\ldots,I;\ j = 1,\ldots,J;\ k = 1,\ldots,K \qquad (1)$$

where $x(i,j,k)$ is the fluorescence intensity of the i-th sample at excitation wavelength λ_j and emission wavelength λ_k. F is the number of factors, a_{if} is the relative concentration of fluorophore f in the i-th sample, and b_{jf} and c_{kf} are the excitation of fluorophore f at wavelength λ_j and the emission at the detection wavelength λ_k respectively. The column vectors a_f, b_f, and c_f are usually collected into three loading matrices A, B and C corresponding to relative concentration matrix, excitation spectra and emission spectra, respectively.

2.2. Four-way PARAFAC

When quencher effect is taken into account, only some fraction of fluorophores leads to light emission which is the fluorescence quantum yield, so applying the PARAFAC model to the four-way data array $\underline{\mathbf{X}}$ with element $x(i,j,k,l)$ requires fitting the following expression [9,15]:

$$x(i,j,k,l) = \sum_{f=1}^{F} a_{if} b_{jf} c_{kf} d_{lf} + \varepsilon_{ijkl} \quad i = 1,\ldots,I;\ j = 1,\ldots,J;$$
$$k = 1,\ldots,K;\ l = 1,\ldots,L \qquad (2)$$

where a_{if}, b_{jf} and c_{kf} are defined as previously, and d_{lf} is the fluorescence quantum yield of fluorophore f in the l-th quencher. I represents the sample number, J the excitation wavelength, K the emission wavelength and L the quencher level.

3. Experimental procedure

Phenanthrene (PHE), pyrene (PY), anthracene (AN) and fluorene (FLU), among the most abundant PAHs in the dissolved phase of natural Waters, were bought from Aladdin Co. and used without further purification. Stock solutions ($100\ \mathrm{mg\ L^{-1}}$ for each PAHs) were prepared by dissolving appropriate PAHs in HPLC-grade ethanol, and then stored in a dark flask at 4 °C for use. The working solutions of PHE, PY, AN and FLU were prepared by diluting the stock solutions to $100\ \mu\mathrm{g\ L^{-1}}$ using deionized water. Humic acid (HA) was also bought from Aladdin Co. Stock solution was prepared by dissolving appropriate HA in NaOH solution and then diluted to neutral by HCL solution. Stock solution of HA ($100\ \mathrm{mg\ L^{-1}}$) was stored under the same condition.

Two levels of quencher solution (0 and $2.5\ \mathrm{mg\ L^{-1}}$) were studied. An eighteen-sample set of PAHs mixture at each level of HA solution (0 and $2.5\ \mathrm{mg\ L^{-1}}$) were prepared with a total of thirty-six samples. The concentrations of each PAH were in the range 0–8 $\mu\mathrm{g\ L^{-1}}$. For each HA level, the first ten samples were used as calibration set; the following six samples were designed as validation set. The calibration and validation samples were prepared using deionized water. The last two samples of each level of HA concentration were used as test set and prepared with river water, which was sampled from Nanfei River in Hefei (China) and filtered through 0.45 μm filter before adding PAHs. The concentrations of each PAHs in test samples were different from calibration and validation set, and also in the range 0–8 $\mu\mathrm{g\ L^{-1}}$. All the concentrations of each sample were collected in Table 1.

Fluorescence measurements were performed on a Hitachi F-7000 spectrofluorometer equipped with a 150 W xenon lamp and connected to a PC microcomputer. The slit band widths of excitation and emission monochromators were both fixed at 5 nm, the voltage of photomultiplier detector at 700 V and the scan rate at $12{,}000\ \mathrm{nm\ min^{-1}}$. The excitation-emission fluorescence matrices were recorded with excitation wavelengths EX in ranges of 240–280 nm and emission wavelengths EM 300–420 nm at a 2-nm interval. After removing the Raman and Rayleigh scatterings by using EEMCAT under MATLAB environment [19], the acquired fluorescence matrices were arranged in a $18 \times 21 \times 61 \times 2$ four-dimensional dataset where 18 was the number of samples, 21 the excitation wavelengths, 61 the emission wavelengths and 2 the levels of quencher concentration. In addition, for comparing the performance of three- and four-way PARAFAC, all the samples of two levels of HA concentration were arranged a three-way dataset with the size of $36 \times 21 \times 61$ where 36 was the number of all the samples, 21 the excitation wavelengths and 61 the emission wavelengths.

4. Results and discussion

Fig. 1 gives the fluorescence spectra of PHE, PY, AN and FLU with HA of concentration $2.5\ \mathrm{mg\ L^{-1}}$ and without HA. From the graphs, obvious fluorescence quenching for four analytes can be observed after adding HA with concentration $2.5\ \mathrm{mg\ L^{-1}}$. Fig. 2 gives the the