Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 190 (2018) 342–346

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

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

Feasibility of the simultaneous determination of polycyclic aromatic hydrocarbons based on two-dimensional fluorescence correlation spectroscopy

Renjie Yang [a], Guimei Dong [a], Xueshan Sun [a], Yanrong Yang [a], Yaping Yu [a], Haixue Liu [b,*], Weiyu Zhang [a,*]

[a] College of Engineering and Technology, Tianjin Agricultural University, 22 Jinjing Road, Tianjin 300384, China
[b] Laboratory of Agricultural Analysis, Tianjin Agricultural University, 22 Jinjing Road, Tianjin 300384, China

ARTICLE INFO

Article history:
Received 19 March 2017
Received in revised form 16 September 2017
Accepted 20 September 2017
Available online 21 September 2017

Keywords:
Polycyclic aromatic hydrocarbons (PAHS)
Two-dimensional fluorescence correlation spectroscopy
Environment contamination
Anthracene
Pyrene

ABSTRACT

A new approach for quantitative determination of polycyclic aromatic hydrocarbons (PAHs) in environment was proposed based on two-dimensional (2D) fluorescence correlation spectroscopy in conjunction with multivariate method. 40 mixture solutions of anthracene and pyrene were prepared in the laboratory. Excitation-emission matrix (EEM) fluorescence spectra of all samples were collected. And 2D fluorescence correlation spectra were calculated under the excitation perturbation. The N-way partial least squares (N-PLS) models were developed based on 2D fluorescence correlation spectra, showing a root mean square error of calibration (RMSEC) of 3.50 μg L^{-1} and root mean square error of prediction (RMSEP) of 4.42 μg L^{-1} for anthracene and of 3.61 μg L^{-1} and 4.29 μg L^{-1} for pyrene, respectively. Also, the N-PLS models were developed for quantitative analysis of anthracene and pyrene using EEM fluorescence spectra. The RMSEC and RMSEP were 3.97 μg L^{-1} and 4.63 μg L^{-1} for anthracene, 4.46 μg L^{-1} and 4.52 μg L^{-1} for pyrene, respectively. It was found that the N-PLS model using 2D fluorescence correlation spectra could provide better results comparing with EEM fluorescence spectra because of its low RMSEC and RMSEP. The methodology proposed has the potential to be an alternative method for detection of PAHs in environment.

© 2017 Published by Elsevier B.V.

1. Introduction

The polycyclic aromatic hydrocarbons (PAHs) are ubiquitous in air, water and soil environment, in which can stay in the environment for a long time. Many PAHs are carcinogenic, mutagenic, mutagenicity, with biological accumulation. Due to the health risks to humans and ecosystems, some PAHs pollutants have been listed as priority pollutants by United States Environmental Protection Agency (USEPA) [1]. The polluted environment demands appropriate methods for remediation. Prior to the remediation, a full assessment of PAHs concentration and compositional distribution in the environment is necessary to provide decision support on the proper remedial strategy to employ to clean up PAHs in the environments [2]. Therefore, it is urgent to develop a rapid, widely available and cost-effective method to detect the trace PAHs in the environment for the local government and public authorities.

Some conventional methods have been employed for the determination of PAHs in environment, such as gas chromatography [3–4], high performance liquid chromatography [5–6], and gas chromatography–mass spectrometry [7–8], et al. But, these methods require sampling, clean-up, separation, which are relatively costly and time consuming. Spectroscopic methods have been used to detect PAHs in enviroments due to their speed, simplicity and low costs [9–12]. Fluorescence spectroscopy, as a sensitive and selective analytical method, has been used to detect PAHs in environment. Okparanma and Mouazen pointed out, comparing with the conventional methods, that the fluorescence spectroscopic method had the best performance from the perspectives of operational time, analytical costs, accuracy, and operator's health and safety [2]. Especially, excitation-emission matrix (EEM) fluorescence spectroscopy can provide entire fluorescence information of PAHs in complex environment by covering a wide broad of different excitation and emission wavelength. Jin et al. quantified successfully the concentration of four PAHs components in water by means of EEM fluorescence spectroscopy and parallel factor analysis (PARAFAC) model [13]. Nahorniak and Booksh determined several PAHs at sub part per billion level in various matrices of using EEM fluorescence spectroscopy and PARAFAC, implying that EEM analyses was a good screening method for detecting pollutants in environment [14]. Ferretto et al. conducted a similar study using EEM fluorescence spectroscopy in conjunction with PARAFAC analysis to discriminate and quantify nine PAHs in aquatic environments, and detection limits from 0.02 to 1.29 μg L^{-1} [15]. Nevertheless, due to the diversity and trace of

* Corresponding authors.
E-mail addresses: liuhaixue@tjau.edu.cn (H. Liu), zhangweiyu@tjau.edu.cn (W. Zhang).

https://doi.org/10.1016/j.saa.2017.09.061
1386-1425/© 2017 Published by Elsevier B.V.

PAHs in environment, it is impossible to extract characteristic fluorescence information from heavily overlapped peaks between PAHs pollutants using EEM fluorescence spectroscopy and multivariate methods. To overcome the above-mentioned problems, in present work, a new approach for the simultaneous determination of PAHs in environment is proposed using two-dimensional (2D) fluorescence correlation spectroscopy and N-way partial least squares.

2D correlation spectroscopy was first introduced by Noda in the field of mid-infrared spectroscopy, and was extended other spectroscopic technologies such as near-infrared, fluorescence, and Raman spectroscopy [16–19]. Comparing with traditional EEM fluorescence spectroscopy, 2D fluorescence correlation spectroscopy can significantly improve spectral resolution and interpretive ability, and has been used to identify overlapping peaks in complex system [20–26]. It is noteworthy that 2D fluorescence correlation spectroscopy is different from EEM fluorescence spectroscopy. The former shows the correlation between fluorescence peaks under the perturbation, and enables the assignment of peaks origin. The latter only shows the changes of fluorescence intensities at different excitation and emission wavelengths. Therefore, 2D fluorescence correlation spectroscopy can extract more information of measured sample comparing with EEM fluorescence spectroscopy. Roselli et al. initially used 2D fluorescence correlation spectroscopy to investigate metal binding sites of protein under the perturbation of excitation wavelength [22]. Lei et al. presented the generalized theory and experimental factors of 2D fluorescence correlation spectroscopy, and pointed that the technology could resolve overlapping peaks of multicomponent chemical system [23]. Nakashima et al. reported the potential use of 2D fluorescence correlation spectroscopy for identifying overlapping PAHs peaks in cyclohexane solution under the change of concentration, excitation wavelength, quenching, and polarization as perturbation, respectively [24–26]. Nakashima et al. also investigated the feasibility of resolving fluorescence bands of tryptophan and humic acids using 2D fluorescence correlation spectroscopy [27]. Huang et al. reported the application of 2D fluorescence correlation spectroscopy for probing fluorescence energy transfer [28]. Meanwhile, the technology of 2D fluorescence correlation spectroscopy has also been used to investigate the interaction of between bovine serum albumin and prulifloxacin, paeonolum. The results showed that the structure change of prulifloxacin and paeonolum could be observed because of spectral resolution enhancement [29–30]. Su et al. used 2D fluorescence correlation spectroscopy for revealing compositional change of dissolved organic matter with hydrophobicity and polarity [31]. However, there is no report related to the quantification of PAHs in environment based on 2D fluorescence correlation spectroscopy and multivariate methods.

In present work, 2D fluorescence correlation spectroscopy was employed to determine the concentration of PAHs in water. The objectives of this research are (1) to evaluate the feasibility of determination the concentration of PAHs in environment using 2D fluorescence correlation spectroscopy combined with multivariate methods; (2) to demonstrate the better predictive ability of quantitative analytical model using the proposed method, comparing with EEM fluorescence spectroscopy and multivariate calibration; (3) to provide an alternative method for detection of PAHs in environment.

2. Theory

2.1. Synchronous two-dimensional fluorescence correlation spectroscopy

The theory of 2D correlation spectroscopy was proposed by Noda and has been applied in various fields of science and technology [16–19,32–36]. The synchronous 2D fluorescence correlation spectra can be calculated in terms of Noda's theory. A series of dynamic one-dimensional fluorescence spectra are collected for a sample (with fixed PAHs concentration) under excitation wavelength perturbation. The dynamic fluorescence spectra can be formed into a data matrix S of m by n dimensions, where m represents the total numbers of fluorescence spectra under different excitation wavelengths, and n represents the number of data points (wavelengths) per fluorescence spectrum.

The synchronous 2D fluorescence correlation spectrum matrix $\Phi(\lambda_1,\lambda_2)$ for dynamic spectra S can be expressed as [16,37]:

$$\Phi(\lambda_1,\lambda_2)=\frac{1}{m-1}S^TS \tag{1}$$

Where the superscript T indicates transposition and $(m-1)$ indicates the degree of freedom. $\Phi(\lambda_1,\lambda_2)$ represents the overall similarities of the excitation-dependent behavior of spectral intensity variations measured at the corresponding wavelength coordinates λ_1 and λ_2. The 2D correlation contour maps presented in this paper were accomplished using algorithms developed by our laboratory with MATLAB.

3. Experimental

3.1. Sample preparation

Anthracene and pyrene used in this study were purchased from Tianjin Heowns biochemical technology Co., Ltd. Anhydrous reagent grade ethanol was used for making stock-solutions without further purification. Water was purified with a Millipore Milli Q purification system. It is well known that anthracene and pyrene are partially soluble in water, but soluble in ethanol. Therefore, in present work, ethanol was selected to make stock-solutions of anthracene and pyrene. Firstly, the stock solutions of anthracene ($1.0\ g\ L^{-1}$) and pyrene ($1.0\ g\ L^{-1}$) were prepared by dissolving anthracene and pyrene in ethanol, respectively. Then, from stock solutions, individually neat solutions with final concentrations of between $10.0\ \mu g\ L^{-1}$ to $1000\ \mu g\ L^{-1}$ were prepared in ultra-pure water through serial dilutions. Finally, the mixtures of anthracene and pyrene were prepared from these individually neat solutions. In total 40 mixture solutions of anthracene and pyrene were prepared. The concentrations of anthracene and pyrene in these mixtures were between $1.0\ \mu g\ L^{-1}$ and $100\ \mu g\ L^{-1}$.

3.2. Apparatus and data collection

In this experimentation, fluorescence spectra of all samples were obtained using LS-55 fluorescence spectrophotometer (PerkinElmer, USA), with a pulsed xenon lamp as excitation source. A standard 10 mm quartz cuvette was used for EEM fluorescence measurement. The scan speed was 1000 nm min^{-1} and lamp voltage was kept at 750 V in all the measurements. EEM fluorescence spectra were acquired in the excitation wavelength range of 260–340 nm within an interval of 5 nm (excitation slit width = 3.0) and in the emission wavelength range of 350–500 nm within an interval of 1 nm(emission slit width = 2.5), respectively. Prior to EEM spectral collection, all mixture solution samples were manually stirred to ensure homogeneity.

3.3. Data processing

Firstly, in order to enhance signal-to-noise, all fluorescence spectra were pretreated using 5 point smoothing based on Savitzky-Golay method. Then, 2D fluorescence correlation spectra were calculated under the excitation perturbation using the software of MATLAB. Finally, the N-PLS quantitative models of anthracene and pyrene in water were constructed based on 2D fluorescence correlation spectra and EEM spectra, respectively. N-PLS regression was performed using "nway310" (available at http://www.models.kvl.dk).

Download English Version:

https://daneshyari.com/en/article/5139353

Download Persian Version:

https://daneshyari.com/article/5139353

Daneshyari.com