Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 140 (2015) 484–488

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

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

A novel pretreatment method of three-dimensional fluorescence data for quantitative measurement of component contents in mixture

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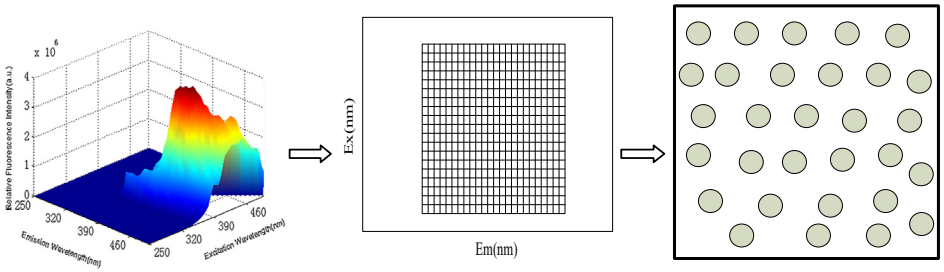
HIGHLIGHTS

- A novel pretreatment method before quantitative measurement of component contents in mixture.
- Measurement sensitivity is improved.
- Measurement slope is improved. (Amplify the slope of measurement sensitivity.)
- Random noise is reduced.
- Turn the concentration values to the solutions of nonlinear equations.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 14 July 2014
Received in revised form 4 November 2014
Accepted 28 December 2014
Available online 13 January 2015

Keywords:
Quasi Monte Carlo integral
Three dimensional fluorescence technique
Measurement sensitivity

ABSTRACT

Three-dimensional fluorescence technique is commonly used for the determination of component contents in the mixture. Fluorescence intensity data are used directly in the fluorescent spectrum data processing method. The relationship between fluorescence intensity values and concentrations is linear. Random noise is inevitable in the process of measuring due to fluorescence spectrometer. The measurement accuracy is reduced due to the existence of noise. To reduce random noise and improve the measurement sensitivity, a novel pretreatment method of three-dimensional fluorescence data is proposed. The method is based on Quasi-Monte-Carlo integral. Due to the increased slope of fluorescence intensity data during the integral, the measurement sensitivity is improved. At the same time, the sum of different exponentials of fluorescence intensity at the points reduces the random noise, so the measurement sensitivity is improved more. The recovery rates of the mixture mixed by gasoline, kerosene and diesel oil are calculated to validate the effectiveness of the method.

Introduction

Fluorescence intensity is the function of excitation wavelength and emission wavelength. Three-dimensional fluorescence spectra (3DFS) completely contain the material fluorescent information. The three dimensions of 3DFS are commonly referred to excitation wavelength, emission wavelength and fluorescence intensity.

Three-dimensional fluorescence spectroscopy is rapid, sensitive and high selective. It has been proven to be a useful technique for monitoring the changes and transformations of organic matters in natural environments [1,2], quantitative determination of butylated hydroxyanisole and *n*-propyl gallate in cosmetics [3], differentiating wines according to variety, typicality and ageing [4], classifying the different vinegars [5], determination of rice syrup adulterant concentration in honey [6], discriminating species of white chrysanthemum flowers [7] and using in other fields [8–12].

There are many data processing methods for three-dimension fluorescence data. Chemometrics methods are widely used in

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http://dx.doi.org/10.1016/j.saa.2014.12.112
1386-1425/

3DFS technique, such as hierarchical cluster analysis [13,14], principal component analysis [15], artificial neural network [16–19], parallel factor analysis [20–22], multi-way PLS [23], etc.

At present, fluorescence intensity values have a linear relation with concentrations in commonly used fluorescent method. Some tiny variables can be measured by instrument hardware. However, they are easy to be ignored in data processing. That can cause artificial low sensitivity. A method with exponential relation of fluorescence intensity values and concentrations for fluorescent data processing can effectively improve the measurement sensitivity.

Random noise often exists in a measurement process. In spite of the fact that a lot of pretreatment methods can reduce random noise, some useful information will inevitably lose at the same time. The average of reduplicative measurements is a good way to reduce random noise, but it is time-consuming and it is difficult to meet the requirements of on-site rapid measurement. Without reduced random noise, the accuracy of some model will be lower.

Due to the facts above, a novel pretreatment method of three-dimensional fluorescence data for quantitative measurement of component contents in mixture is proposed. It can reduce random noise when measurement sensitivity is improved.

Theory and calculation

The pretreatment method for quantification measurement of component contents in the mixture is based on Quasi-Monte-Carlo integral which is an effective method of computing high-dimensional integral. The integral of one area D_m on M-dimensional space is

$$I = \int \cdots \int_{D_m} g(x_1, x_2, \cdots, x_m) dx_1 dx_2 \cdots dx_m \tag{1}$$

N points are generated evenly in D_m. $\left(x_1^{(i)}, x_2^{(i)}, \cdots, x_m^{(i)}\right)$ $(i = 1, 2, \cdots, N)$

Integral approximation can be calculated by

$$\bar{I}_N = \frac{S_D}{N} \sum_{i=1}^{N} g\left(x_1^{(i)}, x_2^{(i)}, \cdots, x_m^{(i)}\right) \tag{2}$$

where S_D is the volume of D_m.

$$I_f = K \cdot I_0 (1 - 10^{-\varepsilon c l}) \tag{3}$$

Eq. (3) is deduced from Lambert–Beer law, where I_f is fluorescence intensity. K is proportional coefficient about spectrometer. I_0 is the intensity of incident light. ε is molar absorption coefficient. c is solution concentration. l is optical path length from incidence to exit.

With a low solution concentration ($\varepsilon c l \leqslant 0.05$), the higher order terms are omitted after Taylor series expansion. The relationship of fluorescence intensity values and concentrations is linear.

$$I_f = 2.3K \cdot I_0 \varepsilon c l = K' \cdot c (K' = 2.3K \cdot I_0 \varepsilon l) \tag{4}$$

Steps of pretreatment algorithm method for quantification measurement are shown as follows.

Step 1: squares and points.

The area of excitation–emission wavelength plane covered with 3DFS of the mixture is divided into small squares with areas of 10 square nanometers (more or less) (Fig. 1) numbered as $k = 1, 2, \cdots, n$.

Fig. 2 shows the schematic diagram of 10,000 (more or less) points of uniform distribution generated by Halton sequence in each small square.

Step 2: calculate integral approximations of different power of separate component.

The 3DFS data of the mixture are expressed as a matrix of power integral approximation by step 1.

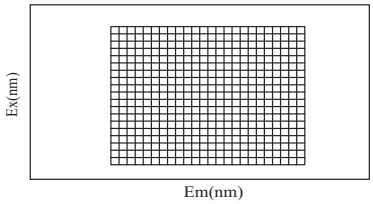

Fig. 1. Small squares in the area of excitation–emission wavelength plane covered with 3DFS.

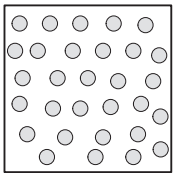

Fig. 2. Points of uniform distribution in each small square.

$$\begin{pmatrix} \bar{I}_{f_0}^{(1)} & \cdots & \\ & \cdots & \\ \cdots & \bar{I}_{f_0}^{(k)} & \cdots \\ & \cdots & \\ & \cdots & \bar{I}_{f_0}^{(n)} \end{pmatrix} \tag{5}$$

Fluorescence intensity value of mixture is the sum of component fluorescence intensity values in low concentrations.

$$I_0 = I_1 + I_2 + \cdots + I_m \tag{6}$$

Based on the linear superposition principle, the equations of third power integral approximation of mixture and integral approximations of different power of separate component in each square are shown as

$$\begin{aligned} \bar{I}_{f0}^{(k)} &= \int\int I_0^3 dxdy = \int\int (I_1 + I_2 + \cdots + I_m)^3 dxdy \\ &= \sum_{i=1}^{m} \int\int I_i^3 dxdy + 3\sum_{i=1}^{m-1}\sum_{j=i+1}^{m} \int\int I_i^2 I_j dxdy \\ &\quad + 3\sum_{i=1}^{m-1}\sum_{j=i+1}^{m} \int\int I_i I_j^2 dxdy + 6\sum_{i=1}^{m-2}\sum_{j=i+1}^{m-1}\sum_{k=i+1}^{m} \int\int I_i I_j I_k dxdy \\ &= \sum_{i=1}^{m} c_i^3 \int\int (K_i')^3 dxdy + 3\sum_{i=1}^{m-1}\sum_{j=i+1}^{m} c_i^2 \cdot c_j \int\int (K_i')^2 K_j' dxdy \\ &\quad + 3\sum_{i=1}^{m-1}\sum_{j=i+1}^{m} c_i c_j^2 \int\int K_i' \cdot (K_j')^2 dxdy + 6\sum_{i=1}^{m-2}\sum_{j=i+1}^{m-1}\sum_{k=i+1}^{m} c_i c_j c_k \int\int K_i' \cdot K_j' \cdot K_k' dxdy \end{aligned} \tag{7}$$

where $\bar{I}_{f_0}^{(k)}$ is 3rd power integral approximation of fluorescence intensity value of mixture on kth small square. Eq. (7) are the nonlinear equations ($k = 1, 2, \cdots, n$) of concentrations.

Use Eq. (2) to calculate the values below with the points generated in step 1 in each square:

$$\int\int (K_i')^3 dxdy, \int\int (K_i')^2 K_j' dxdy, \int\int K_i' \cdot (K_j')^2 dxdy, \int\int K_i' \cdot K_j' \cdot K_k' dxdy$$

Step 3: calculate power integral approximations of mixture.

The sum of third power (or more e.g., 5th power) of the fluorescence intensity values at each point generated in step 1 in one small square, multiply by the area of the small square (here the area is 10 nm^2) and divided by the number of the points in one small square (here the number is 10,000). Then we can get third