Common and Diverse Characteristics of Three-Dimensional Fluorescence Spectra of Crude Oils

Yong Kelan[a]; Lu Jingci[b]

[a] School of Life Sciences, Shanghai University, Shanghai, P. R.China [b] College of Sciences, Shanghai University, Shanghai, P. R.China

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COMMON AND DIVERSE CHARACTERISTICS OF THREE-DIMENSIONAL FLUORESCENCE SPECTRA OF CRUDE OILS

Yong Kelan

School of Life Sciences, Shanghai University, Shanghai 201800, P. R. China

Lu Jingci

College of Sciences, Shanghai University, Shanghai 201800, P. R. China

ABSTRACT

According to the contour maps of the three-dimensional fluorescence spectra of non-quenching crude oil samples, we have found the common and diverse fluorescence characteristics of various crude oils. The common fluorescence characteristic is that the main peaks of various crude oils are located in around the position of excitation/emission wavelength pair 228nm/340nm. The diversity of fluorescence characteristics can be represented with several indexes α, K, F and R, and these indexes provide measurable parameters for division of fluorescence fingerprints of crude oils. The fluorescence fingerprints of crude oils can be divided into three models named O, B and Q that are corresponding to condensate oil, light oil, and heavy oil respectively.

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INTRODUCTION

Fluorescence spectroscopy is particularly useful for the detection of multinuclear aromatics. Because of its great sensitivity, fluorescence spectroscopy is enjoying increasing popularity as a technique for qualitative and quantitative analysis. It is becoming an important tool for the determination of crude oil [1~2] especially at low concentration levels. However, variations in composition of the complex mixture of hydrocarbons comprising crude oil are insufficient to cause marked changes in fluorescence emission spectra [3~4]. Conventional fluorescence methods suffer from low selectivity and are generally ineffective in spectral structural elucidation of various crude oils. Crude oils can not be resolved by conventional fluorescence spectroscopy which should be regarded only as an aid to identification and be limited in use as an exact diagnostic tool.

The three-dimensional fluorescence (TDF) spectroscopy overcomes the above mentioned shortcomings. This technique has been used in study on environmental contamination of crude oil and geochemical exploration [5~8]. TDF is essentially a mapping of the fluorescence intensity as the simultaneous function of excitation and emission wavelengths. There are two types of graphic patterns. One is the space graph that can be visualized as one or some small mountain range; the other is the contour map that can be called a fingerprint.

TDF spectra can provide much more information than routine scanning ones. Mason *et al.* has obtained good results in studying crude oil with TDF spectroscopy [9]. But they have not provided a method to classify various crude oils. In this paper we studied fluorescence properties of crude oils and proposed common and diversity fluorescence characteristics of various crude oils. Using a set of indexes we can divide fingerprints of various crude oils into models O, B and Q that are corresponding to condensate oil, light oil and heavy oil, respectively.

EXPERIMENTAL

Apparatus and Software

Fluorescence spectra were obtained with a Perkin Elmer LS-50 luminescence spectrophotometer. Slit widths were 5.0nm.

The luminescence spectrophotometer was interfaced to an EPSON microcomputer. FLDM and LC software packages controlled the instrument, data acquisition and data processing.

An EX800 printer and a HP 7440 color plotter were connected to the microcomputer to obtain graphical representations.

Reagents

Hexane or petroleum ether was used as solvent with further purification before use.

Samples

Crude oil samples were collected or donated by various oil fields.

Method

Contour maps of TDF spectra were obtained by measuring the emission intensity at 2nm intervals from excitation wavelengths of 200~300nm and from emission wavelengths of 300~500nm. Spectra were recorded at a scanning speed of 240nm/min.

Concentrations of the solutions of crude oil samples in hexane were chosen between 10^{-5} and 10^{-6}, so that we could control a linear response of fluorescence intensities to concentrations and avoid possible quenching effects and particular energy transfer in highly complex systems of crude oils. This technique could provide sufficiently high fluorescence intensity and a sufficient spectral resolution.

RESULTS AND DISCUSSION

TDF spectra of more than fifty crude oil samples collected from China and abroad have been detected. In order to eliminate any possible interference and avoid quenching effect, the solute must be highly diluted. According to the contour maps of non-quenching solutions of crude oil samples, we have found some fluorescence characteristics of various crude oils.

Common fluorescence characteristic of various crude oils

Some typical contour maps of crude oils were illustrated in FIG. 1. The contour maps showed that the maximum fluorescence intensity peak (i.e. the main peak) of various crude oils was located in around the position of excitation/emission wavelength pair 228nm/340nm(±2 nm), no matter whether it is condensate oil, light oil, or heavy oil.

The contour maps of samples related to fossil fuels, such as coal, natural gas, oilfield water and soil above reservoir, show the same common fluorescence characteristic. But the contour maps of non-fossil fuel samples, such as river mud and other samples, do not present this common fluorescence characteristic. Some contours of various samples are shown in FIG. 2.

The position of the maximum fluorescence intensity peak of crude oils is a problem in dispute. Kennicutt and Brooks [7] carried out experiments in which the extracts of oil rock samples were concentrated and the volumes of solutions were limited. Oil samples were treated with a similar method. He emphasized that various oils exhibit a maximum
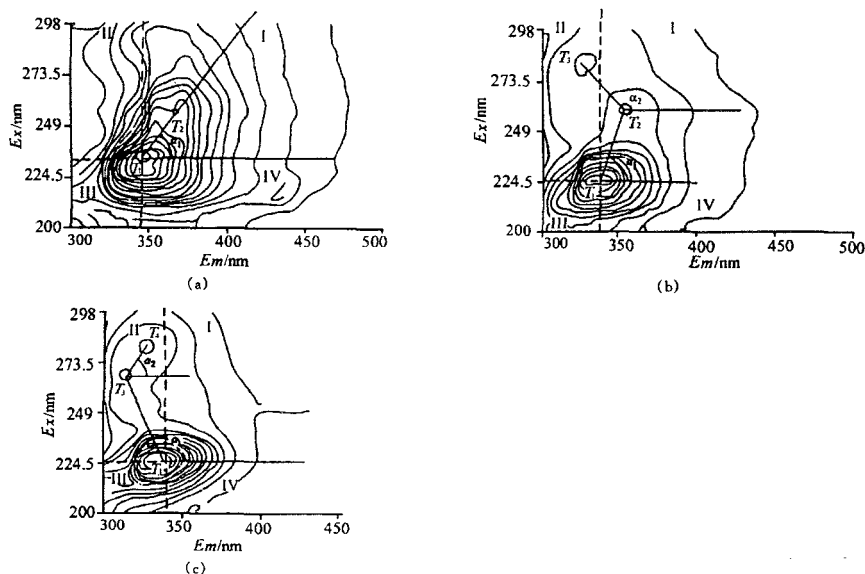
FIG. 1 Classification of typical fingerprints of crude oils
a. Crude oil from Oman, model Q,
b. Crude oil from Brunei, model B,
c. Crude oil from Xinjiang of China, model O.

fluorescence peak at different ranges of excitation/emission wavelength pairs. Dick *et al.* [8] experimented with two crude oil samples collected from offshore wells. Various steps in the $10^{-4} \sim 10^{-7}$ g/ml concentration range were used to control a linear response of fluorescence intensities to concentrations. They pointed out that maximum fluorescence peak occurs at an excitation wavelength of 230nm and corresponding emission wavelength at around 340nm for typical reservoir hydrocarbons. But they did not prove that it was the common fluorescence characteristic of various crude oils. Based on experimental results about fifty crude oil samples and one thousand samples related to fossil fuels, we came to the conclusion that the maximum fluorescence peak of various crude oils was located in the position of excitation/emission wavelength pair 228nm/340nm.

The concentration of the sample is the key to the question of whether the main peak is basically variable or not. Possible quenching effects and particular energy transfer processes
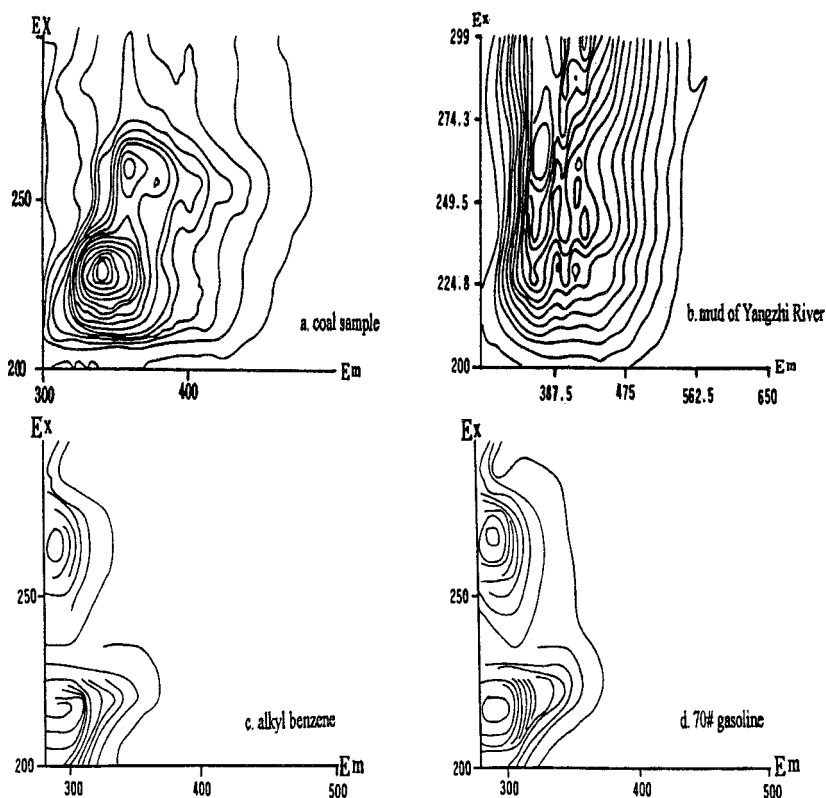
FIG. 2 Contours of various samples
a. Coal sample,　b. Mud of Yangzhi River,
c. Alkyl benzene,　d. 70# gasoline.

competing with fluorescence in highly complex aromatic systems can be found when the concentration of the solute exceeded 10^{-4}g/ml. In two-dimensional spectra, the normal spectra were distorted and exhibited marked shifts to longer wavelengths. In three-dimensional spectra, arising from spectra shift to longer wavelengths both in excitation and emission, the position of the main peak could shift to a longer excitation/emission wavelength pair. Test-runs at various steps in $10^{-2} \sim 10^{-7}$g/ml concentration ranges were monitored to check the phenomena of the main peak shift. We have found that when fluorescence intensity

is not linear with concentration, the shift can occur [10]. The higher the concentration, the farther the main peak shifts. The position of the main peak keeps changing until fluorescence intensity is linear with concentration. The fluorescence intensity can show linear response to concentration below 10^{-4}g/ml. Only in this concentration range, can the contour maps of TDF spectra provide unique information concerning the oils, and the contour maps are called real fingerprints. Because of different concentrations in non-linear ranges the samples of the same crude oils can exhibit several different contour maps with the main peaks located at different positions. These contour maps are not real fingerprints of the crude oil. Therefore it is important to obtain real fingerprints of crude oil. Only on the basis of real fingerprints of various crude oils, can the essential characteristics be presented markedly.

<u>Diversity of fluorescence characteristics of various crude oils</u>

Besides common characteristics, there is distinct diversity in fluorescence properties of various crude oils. In investigating comprehensively the space graphs and fingerprints of fifty samples of various crude oils for diversity of fluorescence characteristics, we have found that the fingerprints of crude oils can be divided into three models named O, B and Q (shown in FIG. 1). The models are corresponding to condensate oil, light oil, and heavy oil, respectively.

In order to describe this viewpoint more clearly, we take the position of the main peak as a center, and draw two lines parallel to the X and Y axes, respectively (FIG.1). The fingerprint is divided into four regions I, II, III, and IV by the two lines. The main peak is named T_1, the peak appearing in region I is named T_2, the peaks appearing in region II are named T_3 and T_4. Besides T_1, we defined the fingerprints with the peaks appearing in region II as model O, the fingerprints with the peaks appearing in regions I and II as model B, and the fingerprints with the peaks appearing in region I as model Q. Further investigating on the relation of fingerprints of various crude oils, we have found that the models of O, B and Q represent condensate oil, light oil, and heavy oil respectively.

In order to present their diversities in quantity, we proposed the following indexes.

1) α –   an index about contour strike of fingerprint

It is measured by the angle formed by the line parallel to the X-axis and the link line of peaks (link line between the points representing peaks in the contour, shown in FIG. 1.)

2)   K -   an index about the slope of the main peak

It shows the variant rate that the height of the main peak decreases with the increase of wavelengths. We can obtain the rate by this method: the fluorescence intensity of the

TABLE 1
Range of Index of Various Typical Crude Oils

Crude Oil Type	Model of Fingerprint	$\alpha(°)$		K	R
		α_1	α_2		
Condensate Oil	O	100~130	60~80	0.65~80	>6
Light Oil	B	55~65	110~70	0.55~0.70	2.5~6
Heavy Oil	Q	45~60		0.40~0.60	<2.5

main peak is divided by the numbers of equal-intensity contours in emission wavelength range from 340nm~380nm.

3)   **F -** an index of fluorescence intensity of characteristic wavelength pairs

4)   R - an index of fluorescence intensity ratio of two characteristic wavelength pairs

α, K, F and R provide measurable indexes for division of fluorescence fingerprints of crude oils. By these indexes, the fingerprints of crude oils can be divided into three models: O, B and Q. Their ranges are presented in TABLE 1.

CONCLUSION

From a number of real fingerprints of various crude oils we have observed the common characteristic, that their maximum fluorescence peak is located in the same position of excitation/emission wavelength pair 228nm/340nm($\pm$2nm). The common characteristic of crude oils in TDF spectra shows clearly that two or three ring aromatics systems are the main components in crude oils under the experimental condition described here. This characteristic exists in other fossil fuel samples, too. Non-fossil fuel samples do not appear to have this characteristic. So we can obtain an unambiguous distinction from various fluorescence pollution sources. Using a set of indexes α, K, F and R, namely, the diversities of fluorescence characteristics of various crude oils, we can divide fingerprints of various crude oils into models O, B and Q. It can be used as the scientific basis for the classification of crude oils. These results would contribute to diagnostic fluorescent abnormalities of various sources, such as natural and artificial abnormalities, and provide the solid basis for correlation of oil/oil and oil/source rock.

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