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Species identification and concentration quantification of crude oil samples in petroleum exploration using the concentration-synchronous-matrix-fluorescence spectroscopy

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ABSTRACT

In this paper, the author has developed and described a novel method for species identification and concentration quantification of crude oil sample in petroleum exploration using the concentration auxiliary parameter synchronous fluorescence technique. By introducing concentration value as a parameter, a new concentration-synchronous-matrix-fluorescence (CSMF) spectrum has been formed with a series of synchronous fluorescence spectra (SFS) at different levels of concentration. It is observed that the SFS varied with concentration level and the profiles of CSMF changed from species to species. Therefore, they can be used for species identification and concentration quantification. The CSMF of 31 crude oil samples from 20 different bore fields has been obtained to establish the database. With surface fitting, CSMF has been successfully used to discriminate the different crude oil samples from different bore fields precisely. It is also used for the quantitative analysis of concentration. Within the interesting concentration range of 10^{-4} g/L to 10 g/L, the curve fitting has been used to achieve good analytical results with the relative deviation below 3%. To evaluate the practicality and efficiency of this method in field, double-blind experiments have been carried out and the relative deviation was found to be 3 times lower than by traditional fluorescence approaches. The obtained results suggest that the newly developed method may become a more specifically applicable means in petroleum exploration.

1. Introduction

In petroleum exploration, the ability to accurately and promptly quantify the oil content of the core and rock debris samples and discriminate their oil species for oil source contrasting and tracing is among the most important and practical issues. Conventional methods including gas chromatography–mass spectroscopy (GC–MS), high-performance liquid chromatography (HPLC) with UV–vis or fluorescence detector are time consuming, expensive and require a lengthy extraction procedure before analysis [1]. Application of near infrared (NIR) spectroscopy for the determination of petroleum macromolecules content in model systems has been reported [2].

The oil bearing samples contain traces of polycyclic aromatic hydrocarbons (PAHs) that are highly fluorescent. Therefore, the fluorescence properties of petroleum products have been studied intensively for devising fluorescence-based analytical methods [3–7]. Fluorescence-based techniques feature high sensitivity, good diagnostic potential, relatively simple instrumentation and suitability for either microscopy or portable instrumentation. Unfortunately, the chemical and physical complexity of crude oils and petroleum products leads to broad spectra without fine-structures [8].

In petroleum exploration, more complex fluorescence techniques such as low temperature fluorescence (LTF) [9], and laser induced fluorescence spectroscopy (LIFS) [10] have been proposed. Unfortunately, it may incur high cost to set up and run the instruments of low temperature fluorescence in addition that sample preparation could be time-wasting. The laser induced fluorescence spectra can have a significant decrease in the fluorescence detection limit. However, since the existing wavelength tunable laser is not applicable to the field petroleum exploration, the information of the emission spectra excited by single-wavelength laser could be insufficient.

Excitation–emission matrix-fluorescence (EEMF) spectroscopy [11,12], synchronous fluorescence spectroscopy (SFS) [13,14], total synchronous fluorescence (TSF) [15,16] have gradually developed into the most important field analytic methods. However, for the petroleum exploration, the oil content of the core and rock debris samples from rich to mean ranges from 10^{-4} g/L to 10 g/L.

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The routine fluorescence techniques dilute the solutions of the fluorophore-bearing samples to the so-called linear concentration range, in which the intensity of the fluorescence changes linearly with the fluctuation of concentration value. But the dilution procedure is both solvent and time consuming and is likely to cause serious individual error and lower accuracy.

Generally, the crude oil samples have the same individual PAHs component but with different mixture ratios and the species identification techniques using fluorescence spectra are aimed at reflecting the precise composition ratios. Now that there is not any uniform linear concentration for all different individual PAHs, the dilution process inevitably makes the higher ring PAHs lose their sensitivity at lower concentration and the lower ring PAHs quenched at higher concentration. The spectra of neither EEMF, TSF nor SFS at one certain concentration level can reflect the mixture ratio of PAHs. Previous researches have reported this concentration dependent phenomenon in the spectra of multi-PAHs, which is known as the “red-shift cascade effect” [17–23].

In an attempt to obtain a more accurate and convenient analytical method of species identification and concentration quantification in petroleum exploration, concentration as a main influential factor was taken into account. The fluorescent characteristics of the crude oil from different sources at the serial concentration range with different fluorescence techniques were investigated in detail. New methods based on concentration dependent spectra have been developed and proved to be a more accurate approach than the conventional technique both in laboratory and in field in defining the source species and the oil content of the core and rock debris samples.

2. Experimental

2.1. Samples and reagents

31 crude oil samples from 20 different bore fields come from the Shengli oil field. Two types of reagent have been chosen as the extracting agent. One is normal hexane in filed double-blind experiments which has been widely used in conventional fluorescence logging. The other is isopropanol [24] for laboratory experiments owing to its high fluorescence intensities and relatively low toxicity. Considering the price for popularization in oil logging, analytically pure reagent is used without further purification. Solution of varied crude oil samples covered the concentration range from 10^{-4} g/L to 10 g/L, corresponding to the oil content of 15 grades from rich to mean in the rock core and debris samples. The binary diluting method is adopted and 18 solutions of serial reduction concentration are prepared.

2.2. Apparatus

All fluorescence measurements were carried out with a spectrofluorophotometer (Model RF5301, Shimadzu, Japan) at room temperature. The emission spectra were acquired from 260 nm to 600 nm and the excitation wavelength was 254 nm with the width of 3.0 nm. 76 emission scans from 220 nm to 600 nm at a 5-nm interval for each scan at fixed excitation wavelength were collected to form the EEMF spectra and their corresponding contours. All the synchronous fluorescence in this paper were obtained at the optimum wavelength interval $\Delta\lambda = 40$ nm [25].

3. Results and discussion

3.1. Concentration dependent spectra characteristics of different fluorescence techniques

In order to find the concentration dependent fluorescent properties of different techniques, 31 crude oil samples from 20 different bore fields in concentration range from 10^{-4} g/L to 10 g/L have been investigated by different spectral approaches.

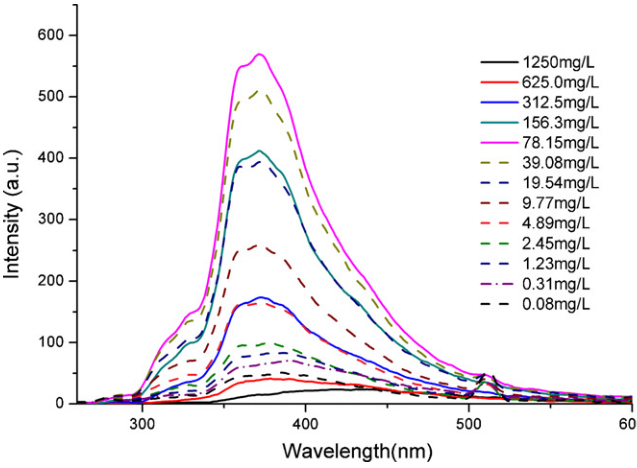

Fig. 1. The emission spectra obtained from the Xia510 sample in the concentrations range 10^{-4} g/L to 10 g/L.

For the emission spectra of the crude oil samples, 254 nm is the most widely used excitation wavelength in petroleum fluorescence logging. Fig. 1 is the results of the emission spectra of Xia510 crude oil samples obtained within the concentration range from 10^{-4} g/L to 10 g/L. Experimental results show that the fluorescence can only be detected when the concentration was below 1.0 g/L, thereafter the fluorescence intensities of principal peaks go up and down with the change of concentration value. The linear concentration range was below 4.0×10^{-3} g/L. The peak at 510 nm is the 2nd order diffraction peak of the excitation wavelength 254 nm and when the concentration increased, the peaks of 2nd order diffraction were quenched. It indicates that the single-wavelength excited fluorescence techniques can only show the fluorescence peaks of the lower ring of aromatic hydrocarbon for multi-PAHs samples.

Excitation–emission matrix-fluorescence (EEMF) spectroscopy, also known as the three-dimensional fluorescence, can be generated by collecting several emission spectra at serial excitation wavelengths and combined to 3D data. The EEMF spectra and their relevant contour graphs of the crude oil samples from the Gubei oil field at sequential concentrations were shown in Fig. 2. It is observed that the EEMF spectra have more information in terms of the number of peaks, peak location, peak intensities and peak shapes than the conventional two-dimension emission spectra. The concentration dependent “red-shift cascade” behavior of the maximum peaks is more distinct than that of the emission spectra shown in Fig. 1.

The synchronous fluorescence spectrum (SFS) is obtained by scanning both monochromators simultaneously. The most common synchronous technique is constant wavelength SFS, with which the scan rate is constant for both monochromators and therefore a constant wavelength difference $\Delta\lambda$, is kept between λ_{em} and λ_{em}. A crucial parameter in SFS is the optimum wavelength difference $\Delta\lambda$. As the crude oil is a complex multi-component system, the shape and intensity of the spectra obtained under different $\Delta\lambda$ changed distinctly and contained rich and varied information.

Six crude oil samples in a series of concentration have been investigated to define the parameters of the optimum wavelength. On the basis of the peak number and peak intensity of different concentrations and samples, 40 nm was chosen as the optimum wavelength difference and used in the subsequent experiments and analysis [25].

In Fig. 3, a series of synchronous fluorescence spectra of Xia510 crude oil sample within the interesting concentration range from

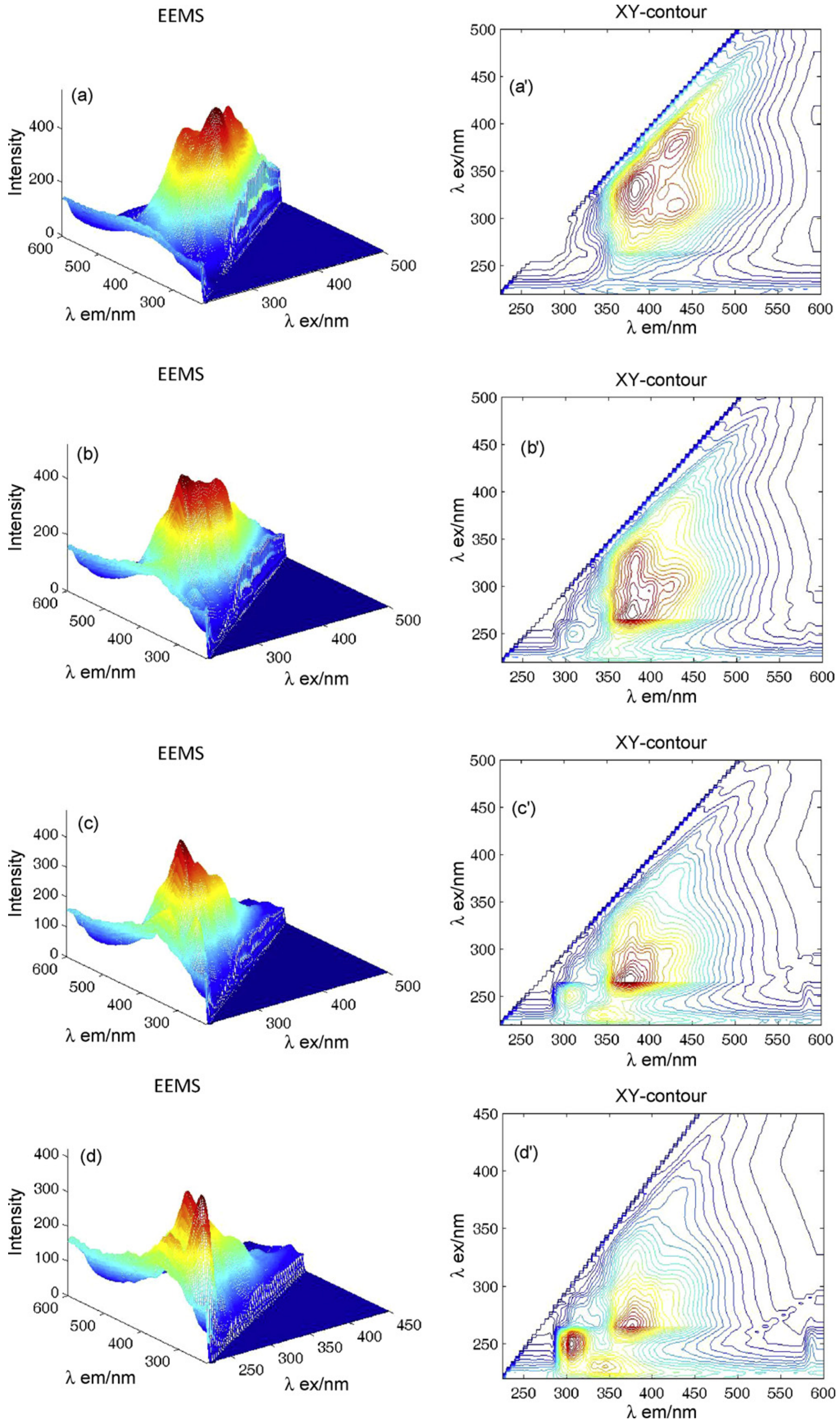

Fig. 2. The EEMS and their relevant contour graphs obtained from the Gubei sample at the respective concentration of 6.3×10^{-2} g/L (a and a′), 3.2×10^{-2} g/L (b and b′), 1.6×10^{-2} g/L (c and c′) and 7.8×10^{-3} g/L (d and d′).

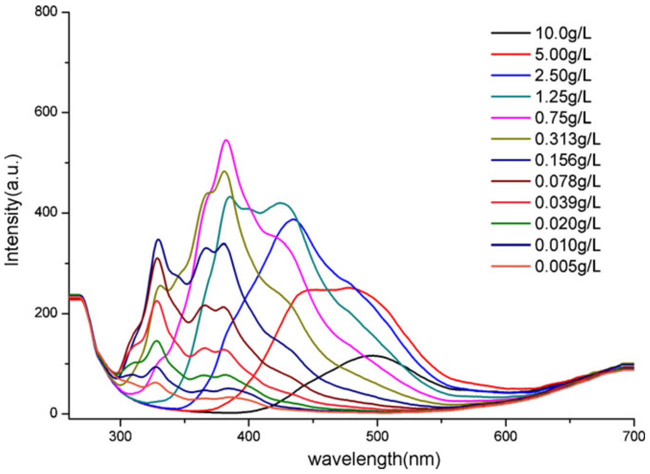

Fig. 3. The concentration dependent synchronous fluorescence spectra obtained from the Xia510 crude oil sample in the concentrations range 10^{-4} g/L to 10 g/L.

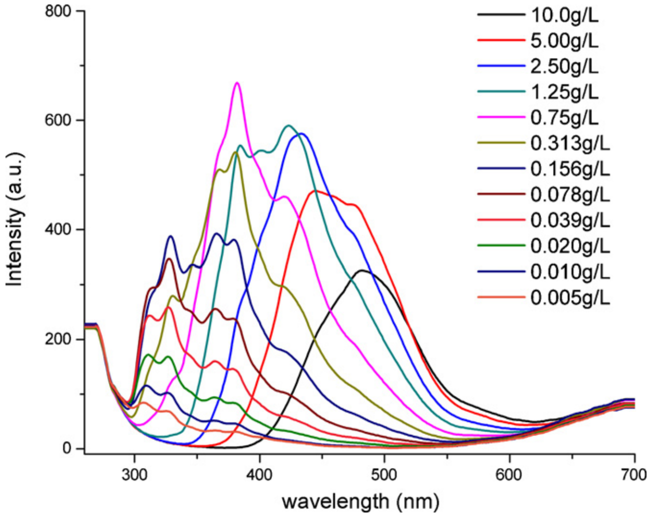

Fig. 4. The concentration dependent synchronous fluorescence spectra obtained from the Chengbei crude oil sample in the concentrations range 10^{-4} g/L to 10 g/L.

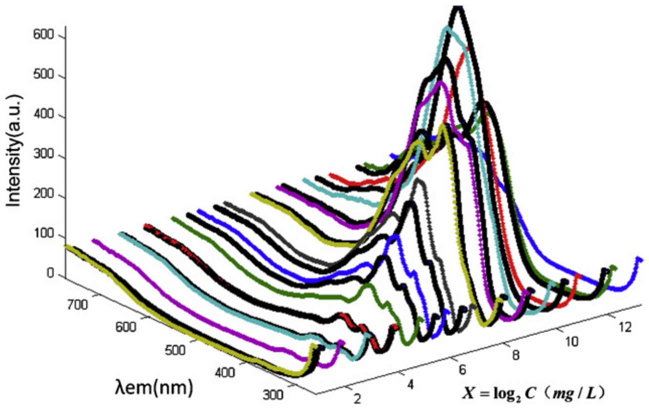

Fig. 5. The standard CSMF of the Xia510 oil sample without interpolation in the concentrations range 10^{-4} g/L to 10 g/L.

10^{-4} g/L to 10.0 g/L were obtained. Compared with the emission spectra in Fig. 1, the synchronous spectra have shown much more information: the increase of the peak number, the change of peak locations and peak intensities.

The results obtained by means of the above fluorescence techniques show that the dilution process produces a red-shift behavior of the maximum peak. The shapes of the spectra are sensitive to the concentration and the oil species. For a certain crude oil sample, it is the spectrum shape rather than the peak intensity that is one to one correspondent to its concentration.

The oil bearing samples contain a broad range of aromatic compounds that exhibit fluorescence maxima at various excitation/emission wavelengths. Two-ring aromatic hydrocarbons such as naphthalene exhibit fluorescence maxima at short emission and excitation wavelengths, while five-ring compound such as perylene has maxima high (the same question as above) emission/excitation wavelength, three and four ring compounds exhibit intermediate fluorescence characteristics [26]. For multi-PAHs systems samples at different concentrations, the presence of factors such as light attenuation, self-absorption, energy transfer, collision quenching and supermolecule aggregation [27,28] will complicate the relationship between the spectra shape and concentration. Each individual PAH responds to the concentration differently and exerts influences on each other. And choosing a narrow range of low concentration will inevitably lose the information of the high-ring aromatic compounds. The concentration dependent spectra have taken the concentration as a new dimension and the spectral information can be expanded from lower ring to higher ring PAHs.

By introducing the concentration value as a new parameter, the EEMF spectra information has increased to 4 dimensions and the great amount of information needs mathematical data extraction. In recent year, there is an increasing use of chemometrics in the petroleum products near infrared (NIR) spectra studies [29,30], and it is possible to use the math method to simplify the data. Because the EEMF spectra need more time to acquire than SFS, in this paper, the SFS obtained at the optimum $\Delta\lambda$ which represent the information of the 45° section cut through the EEMF spectra have been used as the simplified data of EEMF. And the early researches have proved that the SFS can demonstrate the main characteristic of the EEMF by a single scan [7].

3.2. Oil species discrimination based on the CSMF

EEMF and SF spectroscopies have been used to characterize or fingerprint many organic compounds rich in PAHs. However, for complex mixtures such as crude oil samples, the discrepancy of the fluorescence spectra between different concentration levels is more obvious than between the different but closely related source oil. By routine methods crude oil solutions are diluted into the linear range, whereas, for the field analysis of petroleum exploration, the species of the samples and the original concentration under test are both unknown. Past researches on species discrimination of the crude oil samples using EEMF and SFS are mainly on the

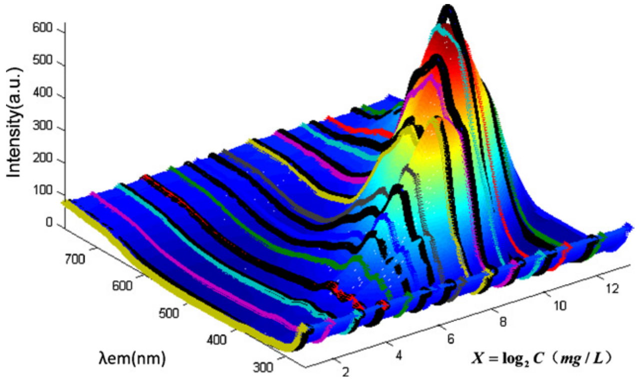

Fig. 6. The standard CSMF spectra of the Xia510 crude oil sample with 15 interpolations in the concentrations range 10^{-4} g/L to 10 g/L.

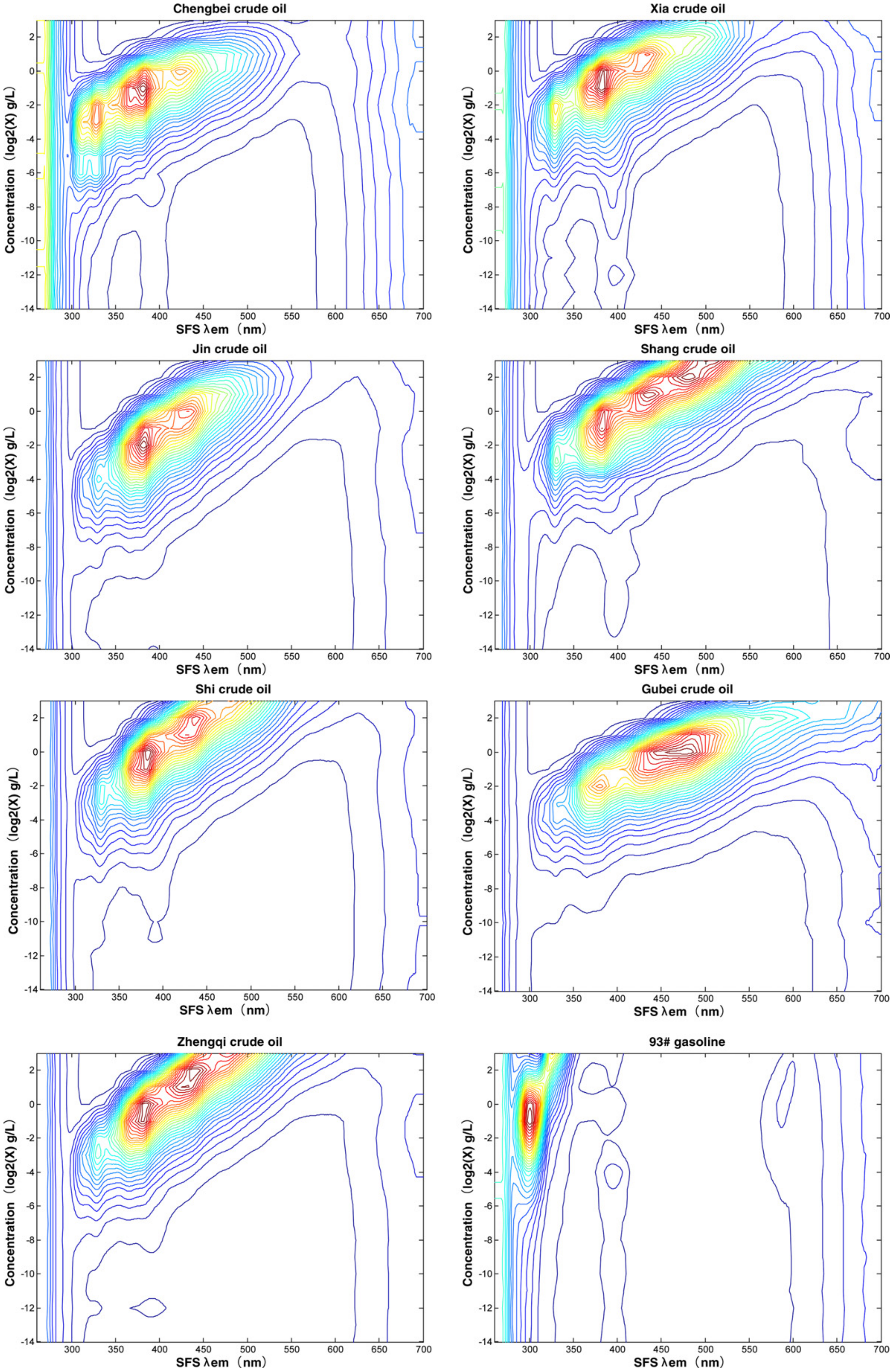

Fig. 7. The respective fingerprints of 7 crude oil samples from the different wellbore in Shengli oil field area and a sample of No. 93 gasoline.

fingerprint of different oil field or different types of petroleum production [31,32]. However, for oil source contrasting and tracing in petroleum exploration, more detailed fingerprinting is necessary to discriminate the samples of the same type and from the same oil field. It is hard to identify the species of the crude oil from different bore fields of the same oil field without knowing the concentration level even when applying the EEMF technique by means of the advanced data processing methods.

Compared with the spectra of Xia510 sample in Fig. 3, the concentration dependent SFS spectra of the Chengbei crude oil sample in Fig. 4 also demonstrate a large red-shift cascade effect. In spite of that, its location, intensities at peak, as well as the intensity ratios at different peaks are quite different from the Gubei samples. The reason is that the PAHs ingredients of the crude oil samples from the same oil field are the same but the mixture ratios of samples are diverse from bore field to bore field.

The difference in the concentration dependent SFS between the closely related oil sources is quite obvious and can be applied in the oil species discrimination. By introducing concentration parameter, the concentration dependent SFS can form new concentration-synchronous-matrix-fluorescence (CSMF) spectra which can provide the information of the precise mixture ratios of the crude oil samples.

The CSMF spectra (X: concentration, Y: excitation wavelength, Z: fluorescence intensity of SFS) were formed by the SFS at $\Delta\lambda = 40$ nm in the concentration range from 10^{-4} g/L to 10.0 g/L. As the concentration range covered 5 orders of magnitude, the binary diluting method is applied and 18 spectra at the serial solutions were acquired for one CSMF. Therefore, the concentration axis is in logarithmic form ($X = \log_2 C$ (mg/L)).

Fig. 5 shows the CSMF obtained under binary diluting method without interpolation. These SFS were measured at certain concentration level in the wide range of concentration, leaving considerably long interval. But more SFS at intervals of concentration value means much heavier burden in solution preparation. A good solution is to use the two-dimensional cubic convolution interpolation to smooth the CSMF. The increase of the number of interpolated spectra has been tested to improve the precision [33]. Fig. 6 shows the CSMF which has been interpolated 15 computing spectra data between each interval.

The CSMF of 31 crude oil samples from 20 different bore fields and 3 petroleum products have been obtained to establish the database. Fig. 7 shows the respective CSMF fingerprints of 5 crude oil samples from different wellbore areas in Shengli oil field and one sample of the typical petroleum products for comparison. The CSMFs from different bores in Shengli oil field are quite easy to differentiate. Consequently, it is natural that the spectrum of 93# gasoline is distinctive from that of crude oil samples.

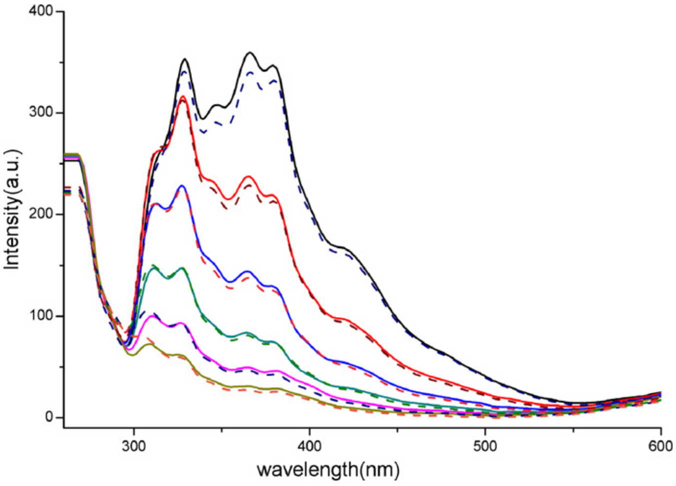

Fig. 8. Comparison between the spectra of under test sample (solid line) and its best-fitted spectra of the database (dashed line).

Surface fitting has been used to discriminate different crude oil samples. When there is an under test sample of which the concentration of solution and species is unknown, some SFS measurements can be taken at concentration levels of about 6–8 grades of doubled dilution. Comparing the spectra of the specimens tested with that of the fingerprint database generated above, the closest surface fitting spectra means the closest matching species. These multi-concentration spectra can accumulate the differences of the species and better reflect the principle information. Fig. 8 shows the high matching degree of the under test samples with the best-fitted spectra from the database. It indicates that the source of under test sample can be determined precisely and the concentration of the solution can also be quantified by the surface fitting.

As the spectra differences between different crude oils from different oil fields are always more remarkable than that from the same oil field, there is no doubt that by this method we can discriminate the crude oil samples from other oil fields more easily.

3.3. Concentration quantification based on CSMF

Since the concentration of the solution has the dramatic effect on the shapes of the SFS spectra, past researchers have developed a method to quantify the motor oil in the concentration range 5–100% (v/v) using red shift of λ_{SFS}^{Max} [14]. In this part, curve fitting has been adopted to determine the concentration level in the wide range concentration between 10^{-4} g/L and 10 g/L. The CSMF acquired

Table 1
The field double-blind experiment between the oil fluorescence analyser (OFA)-II and the proposed CSMF method.

Sample ID	Amount added (mg/L)	Amount found (mg/L)		Relative deviation (%)	
		OFA	TSF	OFA	TSF
1	3750.0	4159.0	3946.3	11	5
2	1406.3	1691.0	1385.6	20	1
3	527.4	619.0	569.1	17	8
4	263.7	312.0	276.9	18	5
5	84.0	118.0	94.6	40	13
6	84.0	106.0	94.9	26	13
7	42.0	60.0	48.4	43	15
8	14.0	17.6	14.90	26	6
9	14.0	17.4	14.80	24	6
10	7.0	8.7	7.8	24	11
11	2.0	2.5	2.2	25	10
12	0	0	0	0	0
	Average error			23	8

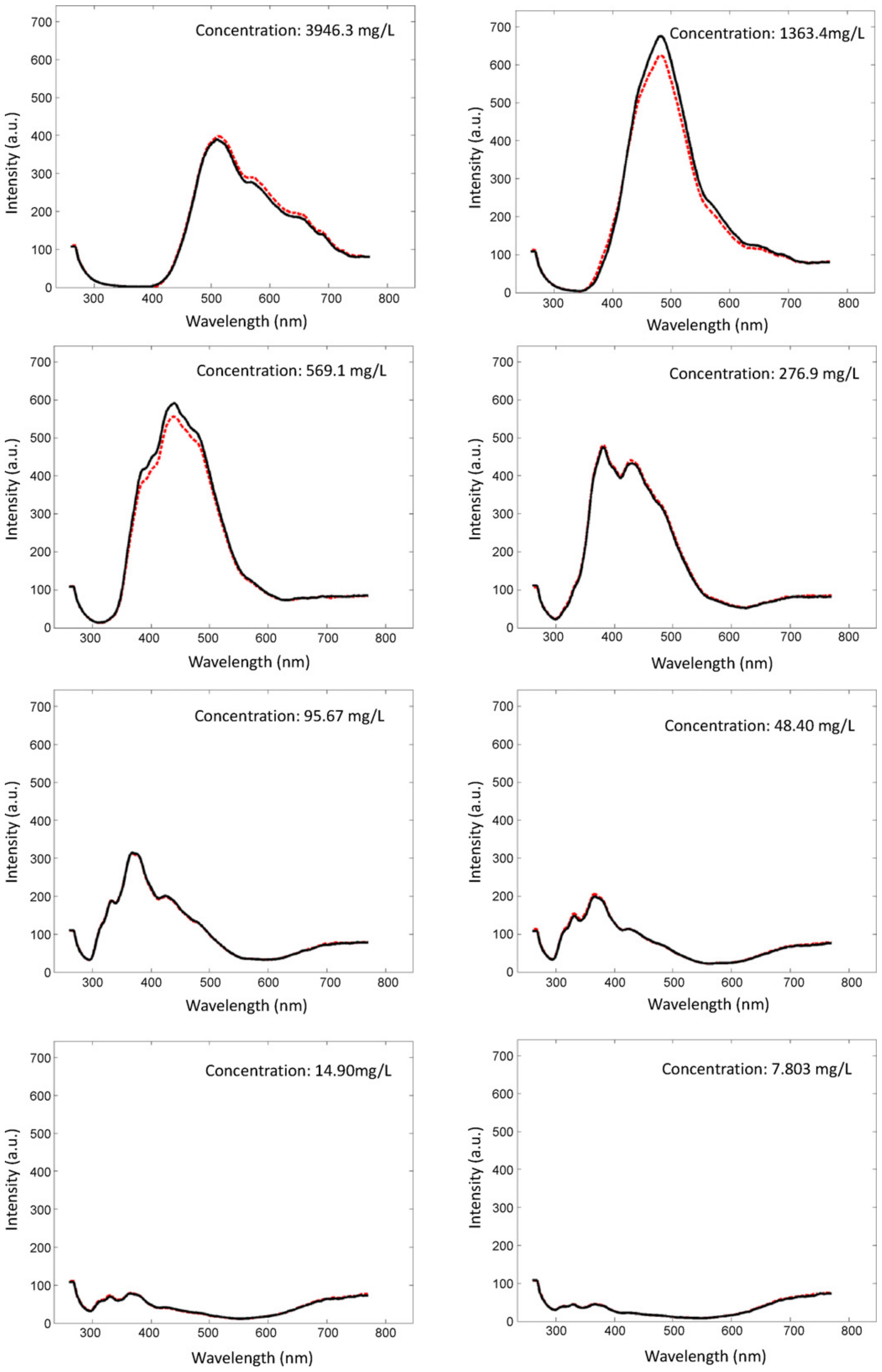

Fig. 9. Comparison between the under test sample spectra (solid line) and its best-fitted spectra (dashed line) intercepted from the standard CSMS.

above then can be used as the standard reference for concentration determination.

The SFS of the specimen tested were measured and normalized in the same condition. Comparing the SFS of the specimen tested with the spectra of the standard CSMF, the most closely fitted spectrum can stand out and the concentration value obtained from this spectrum is just the concentration level of the specimen tested. In order to get the most accurate concentration value and lessen the computing time, the successive numerical approximation method was applied to progressively approach the optimum value.

Early experiments in the laboratory indicated that the concentration value for each sample at the range between 10^{-4} g/L and 10 g/L was determined by the deviation under 3% [34].

To evaluate the field practicality and efficiency of this method, double-blind experiments were carried out between the oil fluorescence analyser (OFA)-II and the proposed CSMF method. The OFA serials products are designed and developed by Research Institute of Petroleum Exploration & Development in China, which are based on the principle and technique of emission fluorescence and excitation–emission matrix (EEM) fluorescence spectra to quantify the oil content and identify the oil species of the core and rock debris samples in the solution of linear concentration range. The results obtained in Table 1 show that this method had smaller relative deviation of 8% compared with that by the traditional fluorescence methods of 23% and the relative deviation was found to be 3 times less both for the mean and for each single value. The number of the interpolated computing spectra between each interval is 20 for these results. We also interpolated 25 and 35 spectra to find that the accuracy is close, although time consuming. Considering the high coincidence of the experimental spectra and the computation simulation spectra as shown in Fig. 9, the deviation of this method may exist during the process of the sample preparation.

Applying these CSMF-based methods in the petroleum exploration can definitely increase the accuracy in quantifying the oil content of the core and rock debris samples and minimize personal errors in the dilution procedure and other influential factors such as the intensity fluctuation of the light source in the spectrofluorophotometer. Furthermore, these methods can cut down the consumption of solvent and time in the dilution procedure.

4. Conclusion

This work shows that by introducing concentration as a variable, CSMF can be applied successfully for the quantitative analysis of the core and debris samples and discriminate their oil species for oil source contrasting and tracing. Experiments showed the newly developed method has a lower relative deviation than the traditional fluorescence approaches and can discriminate the different crude oil samples from different bore fields precisely and even from the same oil field. This method can meet the needs of convenience, rapidness and accuracy of the petroleum exploration and it is less time and solvent consuming. All the results suggest that the CSMF technique is a more suitable approach in crude oil sample analysis and this newly developed method will perhaps become a useful means in petroleum exploration. The development and implementation of this technique will help much to provide necessary data to decision-makers and analysers in field and in line.

What is more, it reflects the features of concentration dependent spectra of the crude oil bearing samples, and can also be easily applied to the analysis of other multi-PAHs or multi-fluorehore mixtures.

Acknowledgements

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