Characterization of coal oil using three-dimensional excitation and emission matrix fluorescence spectroscopy

Xue Xiao (肖 雪)*, Yujun Zhang (张玉钧), Zhigang Wang (王志刚), Dan Jin (金 丹), Gaofang Yin (殷高方), and Wenqing Liu (刘文清)

Key Laboratory of Environmental Optics and Technology, Anhui Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, Hefei 230031

**E-mail: xiaoxue@aiofm.ac.cn*

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Three-dimensional (3D) excitation-emission matrix (EEM) fluorescence spectroscopy is applied to characterize the coal oil. The results show that the 3D fluorescence spectra of coal oil in aqueous solution mainly have one broad peak. This peak is identified at the excitation/emission wavelengths of 270/290 nm. The relation between the fluorescence intensity and the concentration of coal oil is also studied. When the concentration lies between $2-2000$ ppm, the relation between the fluorescence intensity and the concentration of coal oil is well linear. The nature of solvents significantly affects the EEM fluorescence of coal oil.

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Fluorescence spectroscopy is a rapid, sensitive, and nondestructive analytical technique providing spectral signatures in a few seconds[1−4], which can be used as fingerprints of the oil hydrocarbon. The fluorescence behavior of crude petroleum oils is significantly dependent on chemical composition, and therefore offers a very sensitive method for analyzing different oils[5]. However, traditional fluorescence spectra are broad and featureless and therefore have limited the qualitative use. In addition, analyte spectra are often irresolvable from interference spectra or background fluorescence[6,7]. Recently, three-dimensional (3D) excitation and emission matrix (EEM) fluorescence spectroscopy has been developed, which significantly increases the selectivity. EEM fluorescence spectroscopy can be successfully adopted to determine the type of the oil[8−15]. Smith *et al.* studied the red-shift cascade phenomenon when samples of motor oil and creosote are subjected to 3D fluorescence spectroscopy[13,14]. Zhao *et al.* described the 3D characteristic of fluorescence spectroscopy and its application in oil spill identification[15].

The EEM analysis provides a "fingerprint" consisting of a 3D emission/excitation (Em/Ex) intensity contour diagram. This "fingerprint" can be used for qualitative and semi-quantitative information about the fluorescent matter in the environment. In our recent studies, we investigated the 3D Em/Ex spectroscopy of several matters in water, such as dissolved organic matter[16], colored dissolved organic matter[17,18], phytoplankton[19], etc. In this letter, the determination of coal oil via EEM fluorescence spectroscopy is discussed. The effect of solvent on the characterization of coal oil EEM fluorescence is also described primarily.

Anhydrous analytical grade ethanol (99% purity) and coal oil were purchased from the local market in Hefei, and were used without further purification. Samples were stored in the dark at room temperature before analysis. Deionized water was used to prepare the standard solutions. Stock solution (about 2000 mg/L) of the coal oil was prepared by dissolving 1.0 g of commercial coal oil in ethanol. The stock solution was diluted to 2, 4, 10, 20, 40, 100, 200, 400, 1000, and 1600 mg/L concentrations by adding the stock solution by volumetric pipette to a small volume of deionized water in a volumetric flask, filling the flasks to the point slightly below the mark with deionized water. Eleven different mixtures of ethanol and water were used as solvent in the experiment. The 1 mL stock solution was respectively diluted to each mixture of ethanol-water by adding the volume of ethanol by volumetric pipette to 100-mL volumetric flask, filling the flasks to the point slightly below the mark with deionized water.

In this letter, 3D EEM measurement was taken using the Skalar fluorescence imaging system (Skalar M-153, Skalar Company, Netherland) as described previously[17−19]. The measurement was based on the spectral fluorescent signature (SFS) principle (see Fig. 1), which was based upon the measurement of excitation spectra and fluorescent spectra. At an excitation wavelength, an emission spectrum was measured with a photomultiplier tube (PMT). Both the excitation wavelength interval and the emission wavelength interval were set at 5 nm. Each sample was determined thrice, with the average value acquired as the 3D EEM spectroscopy data. In the process, it was verified that the Raman scattering intensity of pure water (deionized water), located at

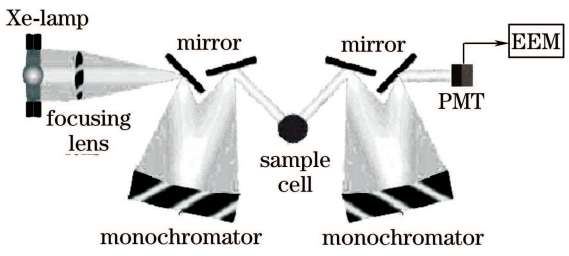

Fig. 1. Schematic diagram of fluorescence spectrum detection system.

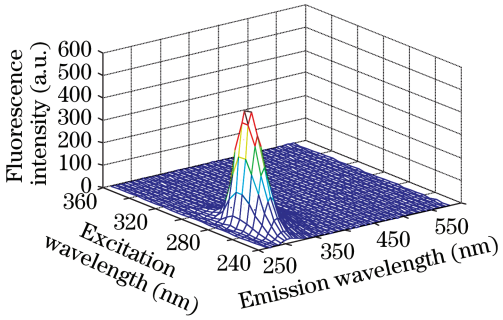

Fig. 2. EEM fluorescence spectra of coal oil.

415 nm by the excitation of 360 nm, kept stable, and the variance was less than 5%. Analysis and deconvolution of the EEM spectra were performed in the Matlab 7.0 working environment.

3D EEM spectroscopy was applied for characterizing the coal oil, as shown in Fig. 2. Spectral information about the chemical compositions of coal oil was given by the EEM. One main peak was identified from the EEM fluorescence spectra. It was identified at the excitation/emission (Ex/Em) wavelengths of 270/290 nm.

The locations of the fluorescence peaks of coal oil all showed no red shift when the concentration of coal oil varied from 2 to 2000 ppm. However, Smith *et al.* reported that petroleum and creosote samples all demonstrated the red-shift cascade phenomenon when examined by fluorescence techniques[13]. Such results suggest that the components in the coal oil in the present study were chemically different from those investigated by Smith *et al.* Further investigation is needed to quantify the fluorescence spectra of individual compounds in different oils.

Figure 3 shows the two-dimensional (2D) fluorescence spectra of coal oil derived from the 3D fluorescence spectra. The emission wavelength is 290 nm in the excitation spectrum and the excitation wavelength is 270 nm in the emission spectrum, respectively.

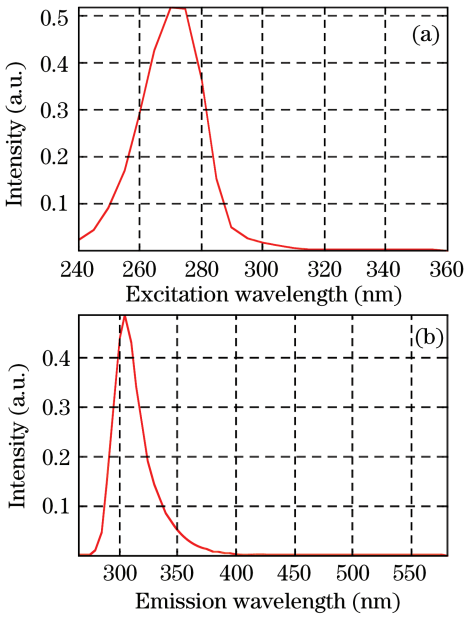

Fig. 3. (a) Excitation and (b) emission spectra of coal oil.

To investigate the relation between the fluorescence intensity and the concentration of coal oil, the EEM spectra of coal oil with the concentration varying from 2 to 2000 ppm were detected. On the basis of the 3D fluorescence spectra analysis of coal oil, excitation wavelength of 270 nm and emission wavelength of 290 nm were chosen for the quantitative analysis of coal oil.

Figure 4 shows the calibration curve for coal oil standard solution derived from the EEM spectra of coal oil. It can be seen that the relation between the fluorescence intensity and the concentration of coal oil is linear:

$$Y = 36.89855 + 9.16238X,$$

where Y responds to the fluorescence intensity, X responds to the concentration of coal oil.

The influence of the nature of solvents on the fluorescence intensity of the coal oil was evaluated using different compositions of ethanol-water mixtures. EEM spectra of the coal oil at different ethanol-water mixtures were respectively determined. The peak locations were independent of the compositions of ethanol-water mixtures, but the peak intensity depended heavily on the compositions, as shown in Fig. 5. The peak intensity increases quickly by increasing the volume of ethanol from 1 to 60 mL, and reaches a maximum with 60-mL ethanol. Keeping on increasing the volume of ethanol in the solution, the peak intensity decreases rapidly. All these results about the solution show that the proportion of ethanol in the ethanol-water solvent is closely related to the fluorescence peak intensity of coal oil. That might be attributed to the specific solvent-fluorophore interactions. There are still many questions about the effect of the solvent on EEM spectra to be further studied.

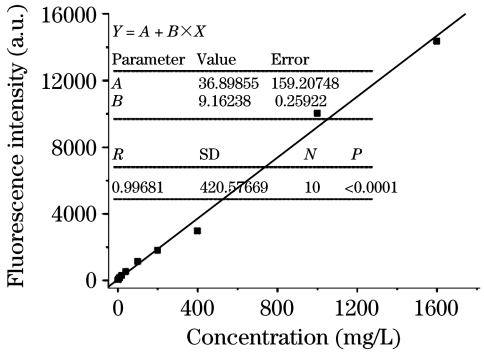

Fig. 4. Calibration curve for coal oil standard solution. The concentration range is $2 - 2000$ ppm.

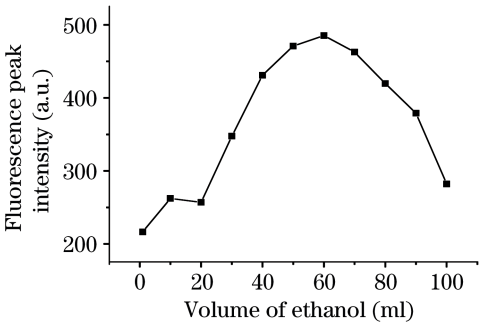

Fig. 5. Fluorescence peak intensities of coal oil at different compositions of ethanol-water mixtures.

To summarize, we have shown the potential of EEM fluorescence spectroscopy to detect coal oil. The results show that the 3D fluorescence spectra of coal oil in aqueous solution have one main peak which is identified at the Ex/Em wavelengths of 270/290 nm. When the concentration of coal oil is $2-2000$ ppm, the relation between the fluorescence intensity and the concentration of coal oil shows good linearity. The effect of the nature of solvents on EEM fluorescence of coal oil is significant. In the future work, we aim to build a robust methodology based on EEM and three-way methods for detecting complex fluorescent pollutions in water.

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