Monitoring Fuel Dilution of Diesel Engine Lubricant Oil by Ultraviolet Fluorescence Spectroscopy

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Abstract—Fuel contamination is a common problem in lubricating oil contamination. Generally, methods such as gas chromatography can be used, but the experimental process is more complicated. Fluorescence spectroscopy analysis has the advantages of fast detection speed and high sensitivity. Applying it to fuel dilution analysis can simplify the analysis process and enable rapid and accurate quantitative analysis. A certain type of fluorescence spectrophotometer was used to analyze and monitor lubricating oil containing different proportions of diesel oil. The fluorescent sensitive band was found, and the corresponding relationship between different lubricating oil content and the height and peak area of the fluorescence characteristic peak was analyzed.

1. Introduction

During the combustion process, fuel will inevitably be mixed into the lubricating oil in a small amount. This situation is called fuel dilution. When the lubricating oil is diluted by the fuel, its lubricating performance will decrease, which will cause abnormal wear and affect the normal operation of the diesel engine. At present, the commonly used fuel monitoring methods include viscosity, flash point, gas chromatography [1], Fourier transform infrared spectroscopy and so on. At present, there is no mature, reliable and widely used method for quantitative monitoring of oil and fuel dilution in the field.

Fluorescence spectroscopy analysis has the advantages of fast detection speed and high sensitivity, but it has a narrow scope of application and is only for fluorescent compounds. It is currently successfully used for marine oil spill analysis, oil contaminant identification, and oil product identification in mixed oil. Scholars such as Cheng Pengfei [2] measured the three-dimensional fluorescence spectra of different concentrations of diesel, gasoline and kerosene mixed solutions prepared in the laboratory, and used a self-weighted alternating trilinear decomposition algorithm to effectively distinguish the mixed oil substances. Scholars such as Chen Zhikun [3] conducted a qualitative and quantitative analysis of oil contaminations based on the three-dimensional fluorescence spectra of carbon tetrachloride solutions with three solutes of diesel, gasoline and kerosene, combined with a combination algorithm. Yin Xiaonan and other scholars analyzed the three-dimensional fluorescence spectra of crude oil, diesel oil, ship fuel oil, and ship engine room dirty oil that are suitable for common marine oil types through wavelet analysis, spectral similarity comparison, Fisher discriminant analysis, and Bayes discriminant analysis. Data [4]. Zhou Yanlei and other scholars [5] established a crude oil and fuel oil identification method based on three-dimensional fluorescence spectroscopy using parallel
factor analysis technology. Kong Deming and other scholars combined the three-dimensional fluorescence detection technology with the alternating penalty trilinear decomposition algorithm and used it for the detection of oil components in the mixed oil \[6\], and further used the three-dimensional fluorescence spectroscopy technology and the alternating weighted residual constrained quadrilinear decomposition (AWRCQLD) algorithm Used in combination with mixed oil detection \[7\]. At present, there is no relevant application research on fluorescence spectroscopy analysis of diesel engine lubricating oil.

In this paper, fluorescence spectroscopy is applied to the quantitative monitoring of the on-site oil dilution with lubricating oil. A certain type of fluorescence spectrophotometer is used to monitor lubricating oils containing different proportions of diesel oil, find the fluorescence sensitive bands, and analyze the content and fluorescence of different lubricating oils. The previous correspondence between the height of the characteristic peak and the peak area.

2. Experimental part

2.1 Analytical instruments

A fluorescence spectrophotometer model F97XP is used. The experiment uses a quartz fluorescent sample cell of 10mm. The excitation light source is a 150W xenon lamp. The excitation wavelength range is 200nm–900nm. The emission wavelength is 200nm–900nm. Both the excitation bandwidth and emission bandwidth are 10nm.

2.2 Sample data

The lubricating oil sample is a general-purpose diesel engine lubricating oil. Under laboratory conditions, oil samples with known contaminations and concentrations are prepared and mixed with diesel oil samples with a mass percentage concentration of 1.5%, 3%, 6%, and 12%. The numbers are respectively C1, C2, C3, C4; the new oil number is A0, used as a comparison oil sample.

3. Results and discussion

3.1 Principles of fluorescence spectrum analysis and preliminary experiments

Different wavelengths of incident light produce different excitation spectra. Generally, fluorescence spectra are divided into two types. One is to fix the excitation wavelength and scan the light intensity corresponding to different emission wavelengths. This kind of spectrum is called emission spectrum. One is to fix the emission wavelength and scan the excitation wavelength. This kind of spectrum is called the excitation spectrum. Both the emission spectrum and the excitation spectrum are two-dimensional spectra. Three-dimensional fluorescence spectroscopy integrates the above two spectrograms, allows the excitation wavelength to be scanned, fixes the excitation start wavelength and end wavelength, sets the scan time and scan interval, completes the excitation wavelength scan at a fixed interval, each fixed excitation wavelength, Corresponding to an emission spectrum, after the emission spectrum is superimposed, it is a three-dimensional fluorescence spectrum. As shown in Figure 1, it is the three-dimensional fluorescence spectrum of the new oil, where the X coordinate is the wavelength value of the emitted light, the Y coordinate is the excitation wavelength value, and the Z coordinate is the fluorescence intensity value. Figure 2 shows the contour spectrum of the new oil, expressed in the form of a grayscale image. Among them, the X coordinate is the excitation wavelength value, the Y coordinate is the emission wavelength value, and the gray value of the image represents the fluorescence intensity.
3.2 Fluorescence spectrum data analysis

Fluorescence spectrophotometer was used to measure the fluorescence spectrum of No. A0 new oil and diesel oil contaminated Group C oil samples. Three-dimensional fluorescence spectrograms are shown in Figures 3. Through the two-dimensional plane contour map, the position and height of the fluorescence characteristic peak can be judged. Then select the excitation characteristic wavelength between 390nm~500nm. At the same time, it can be seen from Fig. 3 that when diesel contamination occurs, the amplitude of the Rayleigh wave and the secondary Rayleigh wave are equal to or smaller than the amplitude of the diesel characteristic peak, and the interference to the fluorescence characteristic peak is relatively small.
The analysis shows that the fluorescence characteristic peak of diesel oil and the characteristic peak position of new lubricating oil are basically coincident, and both are between the excitation wavelength

Fig.3 Three-dimensional fluorescence spectra of fuel contaminants with different concentrations

(b) 6% fuel oil

(c) 3% fuel oil

(d) 1.5% fuel oil
of 390nm–500nm. As shown in Figure 4, Figures (a) and (b) are superimposed graphs of the fluorescence spectrum data obtained from different diesel contamination when the excitation wavelength is 390nm and 430nm, respectively. It can be seen that the higher the diesel content, the lower the corresponding fluorescence peak intensity. Different excitation wavelengths have different corresponding fluorescence peak intensities, but the trend of change is the same. This is due to the phenomenon of fluorescence quenching after the diesel and lubricating oil are mixed and miscible, resulting in a decrease in the peak value. Fluorescence quenching \cite{8} refers to the physical or chemical interaction process between fluorescent substance molecules and solvent or solute molecules that causes the fluorescence intensity to decrease. The diesel substance itself does not emit light, but it has the ability to quench the fluorescence of a certain fluorescent compound in the lubricating oil. The degree of fluorescence quenching has a quantitative relationship with the concentration of diesel. The concentration of diesel contaminations can be indirectly determined by measuring the degree of fluorescence decrease of the lubricating oil at the excitation wavelength of 390nm–430nm.

According to the characteristic peak characteristics of the three-dimensional fluorescence spectrum, the characteristic parameters are defined: the highest point of the peak in the entire three-dimensional spectrum is defined as the peak height; the left and right boundary values corresponding to the emission wavelength of the characteristic peak are respectively a and b; the characteristic peak excitation wavelength corresponds to The left and right boundary values are respectively c and d; the fluorescence intensity of the absorption peak of the sample is represented by \( Z \), \( Z(x,y) \) represents the value of the fluorescence intensity \( Z \) when the emission wavelength is \( x \) and the excitation wavelength is \( y \); \((a,c,Z(a,c))\), \((a,d,Z(a,d))\), \((b,c,Z(b,c))\), \((b,d,Z(b,d))\) four boundary points, connected into a plane, called the bottom base; the bottom base, the characteristic peak excitation wavelength and the left and right boundary values of the emission wavelength, and the fluorescence intensity value surrounded by the closed figure The volume of is defined as the peak volume \( V \). The value of peak volume \( V \) is shown in formula (1).

\[
V = \int_{a}^{b} \int_{c}^{d} Z\,dx\,dy - V_{\sigma}
\]  

(a) The excitation wavelength is 390nm  
(b) The excitation wavelength is 430nm 

Fig.4 Fluorescence spectrum data of fuel contaminants with different concentrations

Among them, \( x \), \( y \), \( z \) correspond to the three coordinates of the three-dimensional fluorescence spectrum, the emission wavelength, the excitation wavelength and the fluorescence intensity value. \( V_{\sigma} \) is the volume of the closed figure enclosed by the bottom basal plane and the left and right boundary values of the characteristic peak excitation wavelength and emission wavelength.

Calculate the corresponding peak height and peak volume values when the diesel contamination proportion is 0%, 1.5%, 3%, 6%, 12%, and the boundary values \( a, b, c, d \) of emission wavelength and excitation wavelength of diesel characteristic parameters are 400nm, 700nm, 390nm and 430nm respectively.
The fitting curves of the peak height value, peak volume normalized value and diesel contamination ratio value are respectively made, as shown in Figure 5. It can be seen that the linearity of the fitting curve of the peak volume is better than the peak height value. The maximum residual mode of the linear fitting of the peak height method is 0.162, and the maximum residual mode of the linear fitting of the peak area method is 0.053. Fluorescence spectroscopy is suitable for analyzing the concentration prediction problem of diesel pollution within 12%.

![Fitting curves of peak volume-contaminants concentration and peak height-contaminants](image)

Fig.5 The Fitting curves of peak volume-contaminants concentration and peak height-contaminants

4. Conclusion
Using fluorescence spectroscopy to monitor the lubricant samples with different fuel contamination ratios prepared in the laboratory, it was found that when the excitation wavelength is between 390nm and 500nm, the sensitive peak of fluorescence intensity appears in the emission wavelength between 400nm and 550nm, and fluorescence quenching occurs Phenomenon, that is, the peak value decreases as the contamination concentration increases. The quantitative relationship between fluorescence intensity and fuel contamination concentration can be further studied.

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