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Application News

No. A532

Spectrophotometric Analysis

Fluorescence Intensity Variation Due to Molecular Structure Changes

Petroleum based fuels include gasoline, diesel, kerosene, and fuel oil. These fuels are refined according to their boiling point differences and are used in various applications all around us. In Japan, the fluorescent substance coumarin is added to kerosene (and A-type fuel oil), and the Japan Petroleum Institute established standard JPI-5S-71-2010 (abbreviated to JPI method below) as a technique for quantitative analysis of coumarin. However, when the JPI method is used for gasoline, it is reported that a substance contained in gasoline exhibits fluorescence similar to coumarin [*1]. This substance is suggested to be N,N'-Bis (salicylidene)-1,2-propanediamine (abbreviated to BSPD below), and it has also been shown that performing an appropriate pretreatment could reduce the fluorescence of BSPD [*1]. Since fluorescence depends on the molecular structure of the substance, it is conceivable that the pretreatment changes the molecular structure.

This article introduces a comparison between the fluorescence intensities obtained with and without pretreatment, which changes the molecular structure of BPSD, using the RF-6000 spectrofluorophotometer and coumarin analysis kit for respective measurements.

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Sample Pretreatment and Analysis Procedure

Fig. 1 shows the RF-6000 with the coumarin analysis kit installed. Four types of commercially-available gasoline, 0.035 ppm coumarin, and 10 mg/L BSPD solution (ethanol solvent) were prepared as samples. In accordance with the pretreatment procedure for reducing BPSD fluorescence, 10 mL of 10 wt% copper sulfate solution was added to 10 mL of sample. The mixture was then shaken, left to stand, and separated according to layer [*1]. It is presumed that this process eliminates fluorescence by causing a reaction between BPSD and copper sulfate and forming a chelate compound, as shown in Fig. 2 [*1].

The fluorescence of samples for which pretreatment was performed and not performed was then measured using the JPI method to determine the difference. Fig. 3 shows a simplification of the JPI method sequence. Ultraviolet irradiation causes coumarin to isomerize and fluorescence can be observed at 500 nm. The mix rate and content of coumarin in a sample of coumarin-added oil (A-type fuel oil, kerosene) are determined according to the fluorescence intensity [*2]. For details on the coumarin analysis procedure using the JPI method and calibration curve, refer to Application News No. A494.

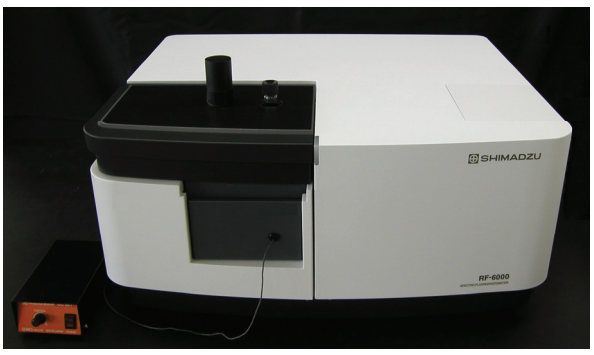

Fig. 1 RF-6000 with Coumarin Analysis Kit Installed

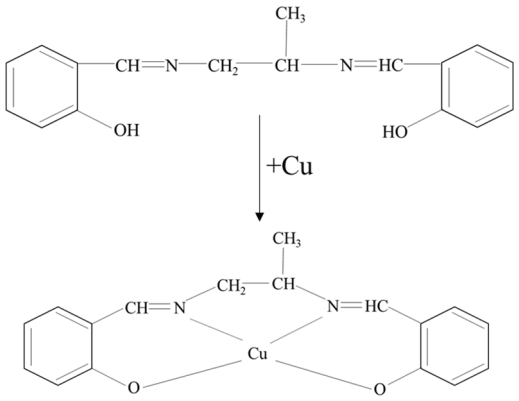

Fig. 2 BSPD and Chelate Compound

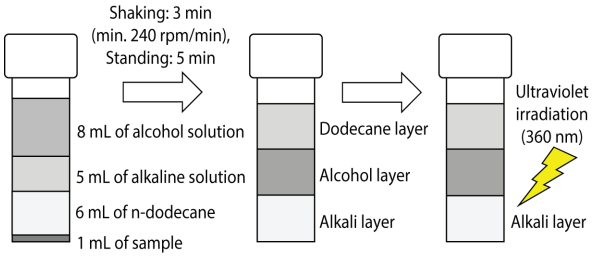

Fig. 3 Simplified JPI Method Procedure

Measurement Results

Fig. 4 shows the result of performing the JPI method without pretreatment and Fig. 5 shows the result with pretreatment. Table 1 lists the measurement conditions. For the measurement without pretreatment, we can observe that coumarin and BSPD exhibit similar fluorescence spectrum profiles. There is also fluorescence similar to coumarin for the commercially-available gasoline samples, although the fluorescence intensity differs between each sample. With pretreatment performed, on the other hand, we can see that the fluorescence of the BSPD solution was nearly eliminated. The fluorescence of the commercially-available gasoline has also significantly decreased. The reason that fluorescence was not completely eliminated may be because the amount of shaking per minute during pretreatment was insufficient and therefore the reaction was incomplete. Furthermore, the reason for the decrease in coumarin fluorescence intensity when pretreatment is performed is presumed to be due to distribution to the copper sulfate solution [*1].

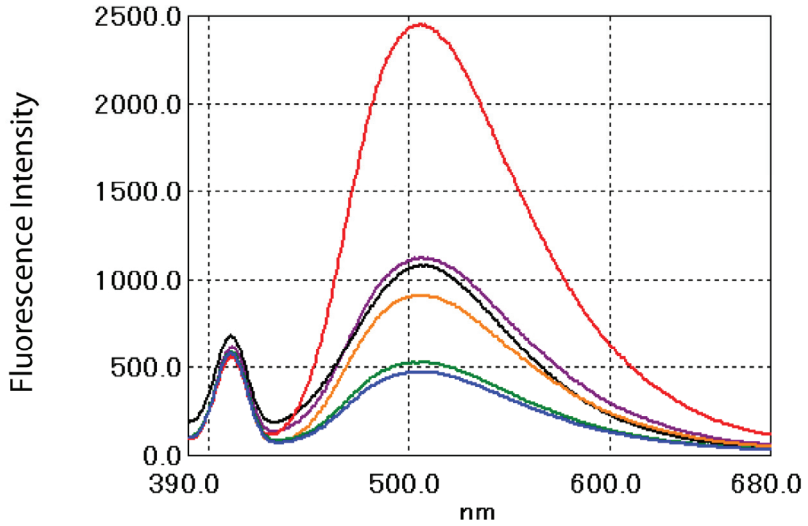

Fig. 4 Result of Performing the JPI Method Without Pretreatment
Black: 0.035 ppm Coumarin Red: 10 mg/L BSPD Solution Blue: Regular Gasoline (Company A)
Green: High Octane Gasoline (Company A) Orange: Regular Gasoline (Company B) Violet: High Octane Gasoline (Company B)

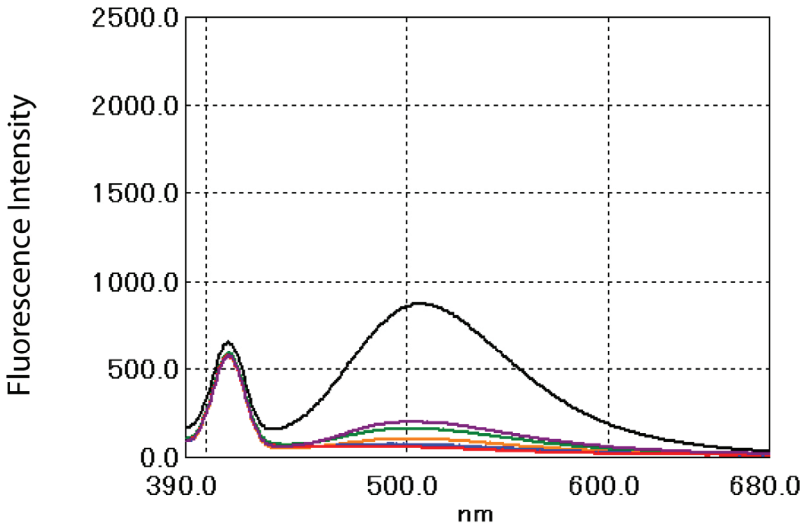

Fig. 5 Result of Performing the JPI Method With Pretreatment
Black: 0.035 ppm Coumarin Red: 10 mg/L BSPD Solution Blue: Regular Gasoline (Company A)
Green: High Octane Gasoline (Company A) Orange: Regular Gasoline (Company B) Violet: High Octane Gasoline (Company B)

Table 1 Measurement Conditions

Instrument used	:	RF-6000, coumarin analysis kit
Spectrum Type	:	Fluorescence Spectrum
Excitation Wavelength	:	360 nm
Emission Wavelength Range	:	390 to 680 nm
Scanning Speed	:	600 nm/min
Wavelength Interval	:	1.0 nm
Bandwidth	:	Ex 10.0 nm, Em 10.0 nm
Sensitivity	:	Low

Summary

In this research, we used the RF-6000 and coumarin analysis kit to measure and compare the fluorescence intensities obtained with and without pretreatment, which changes the molecular structure of BPSD. We confirmed the presence of BSPD fluorescence similar to coumarin in commercially-available gasoline. We also confirmed a reduction in fluorescence intensity by adding copper sulfate to BSPD to change its molecular structure.

References

*1 National Petroleum Association (Japan), Quality Laboratory, Takenari Sonobe, Seigo Yamazoe, Mitsuhiro Takasu: "Inferring the Origin of Kerosene Contamination in Commercially-Available Gasoline Using Coumarin Analysis", 2014 Summary Collection of Panel Discussion for Petroleum Products

*2 JPI-5S-71-2010: Petroleum products - Determination of coumarin - Fluorescence spectrometry

First Edition: Apr. 2017

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