Spectrophotometric Analysis

Measurement of Soot Content in Engine Oil by ATR Method of Fourier Transform Infrared (FTIR) Spectroscopy

Engine oil is a type of lubricant which is used in engines. The parts in an engine operate at high speeds, and metal-to-metal wear and seizing (phenomenon causing damage to cylinders or pistons) can occur under these conditions. Internal engine parts are lubricated with engine oil to alleviate these problems. In addition, combustion and rotational motion cause various types of sludge (soiling, burnt residue) that reduce the performance and shorten the life of engines. Engine oil also plays a role in adsorbing and dispersing sludge.

Soot is generated in engines by incomplete combustion of fuel. Because an increased soot content in engine oil may reduce lubrication performance and form an abrasive substance that can damage plastic parts, the soot content in engine is an indicator of the timing of engine oil changes.

ASTM E2412-10 provides a method for condition monitoring of the soot content in lubricants by Fourier transform infrared (FTIR) spectroscopy. The ASTM standard describes a method of transmission measurement using a liquid cell with an optical path length of 0.1 mm (allowable range: 0.08 to 0.12 mm), and measurement of the soot content from the absorbance value at 2,000 cm^{-1}. Although the accuracy and stability of this technique are excellent, time is required to clean the liquid cell.

Here, we introduce a soot content measurement technique using an ATR measurement attachment that allows simple cleaning of the sample stage to enable efficient measurement work.

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■ Instruments Used

A system consisting of a Shimadzu QATR™-S ATR measurement attachment with an integrated sample compartment attached to an IRSpirit™ Fourier transform infrared spectrophotometer. Fig. 1 shows the appearance of the system, and Fig. 2 shows an enlarged view of the prism plate of the QATR-S.

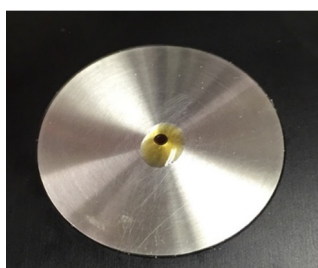**Fig. 1 Appearance of IRSpirit™ + QATR™-S**

Fig. 2 Enlarged View of Prism Plate (with Drop of Engine Oil in Center)

Fig. 3 shows the principle of the ATR (Attenuated Total Reflection) method. In this technique, the sample is placed in tight contact with the surface of a prism made of a high-refractive index substance that transmits infrared light, and a spectrum is obtained by detecting the light reflected through the minute surface of the sample.
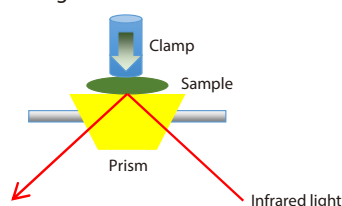

Fig. 3 Principle of ATR Method

■ Soot Measurement Method

A calibration curve showing the relationship between the soot content [mass%] and absorbance values was prepared using samples with known soot concentrations, as shown in Table 1. Table 2 shows the measurement conditions, Fig. 4 shows the infrared spectrum, and Fig. 5 shows the prepared calibration curve. Because soot (carbon) has absorbance over the entire infrared range, its existence is not shown by a designated peak in the infrared spectrum, but rather by a rise in the baseline.

Here, the soot content was calculated by using the absorbance value of 1,850 cm^{-1}. Although ASTM E2412-10 describes measurement of soot content from absorbance at 2,000 cm^{-1}, this would affect the quantitation value of soot, as it overlaps the absorption band of the diamond prism of the ATR. The above-mentioned 1,850 cm^{-1} wavelength was used to avoid this problem.

Table 1 List of Samples of Known Concentration Used in Preparation of Calibration Curve

Sample	Soot content [mass%]
a	7.96
b	1.03
c	0.97
d	0.50
e	0.48
f	0.43
g	0.30
h	0.22
i	0.12
j	0.06
k	0.02

Table 2 Measurement Conditions

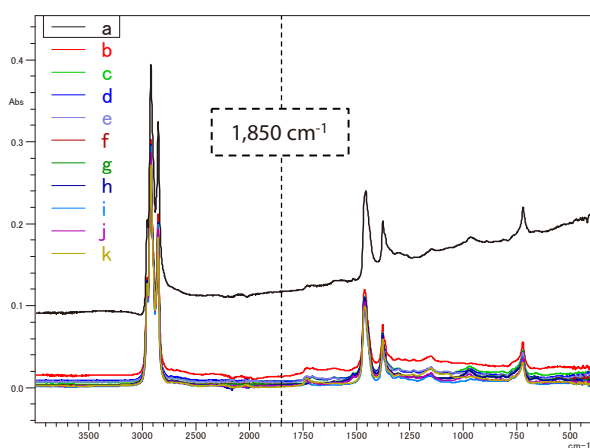|	
Instruments	: IRSpirit-T (KBr window plate) QATR-S (wide-band diamond disc)
Resolution	: 4 cm^{-1}
Accumulation	: 20 times
Apodization function	: Sqr-Triangle
Detector	: DLATGS

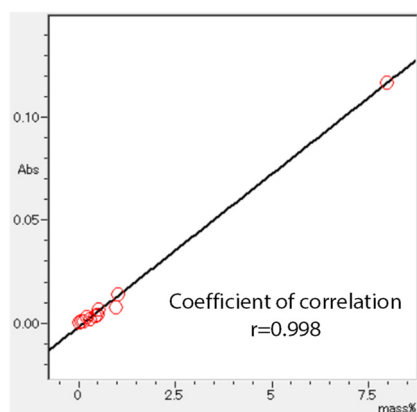**Fig. 4 Infrared Spectrum of Samples of Known Concentration**

Fig. 5 Calibration Curve

The horizontal and vertical axes in Fig. 5 show the soot content and absorbance value at 1,850 cm^{-1}, respectively. This calibration curve shows a high correlation, as the coefficient of correlation r = 0.998.

Next, three samples with unknown soot contents were measured and quantified by using the calibration curve shown in Fig. 5. Table 3 shows the results of the quantitative analysis by FTIR. The reference values obtained by a different technique are also shown to confirm the appropriateness of the soot contents calculated by FTIR.

Values close to the reference values were obtained for samples X and Y. However, the value of sample Z, which had the smallest soot content, was different from the reference value. It is thought that error tends to occur in samples with small soot contents, like sample Z, because even a small amount of baseline noise has a large influence on the quantitation value.

Table 3 Results of Quantitative Analysis by FTIR

Sample	Absorbance	Quantitation value [mass%]	Reference value [mass%]
X	0.008	0.65	0.60
Y	0.004	0.43	0.45
Z	0.001	0.18	0.02

■ Repeatability

To confirm repeatability, samples with soot contents of 0.20 mass% and 3.93 mass% were measured continuously 10 times, and the variation of the baseline (deviation of absorbance value) at 1,850 cm^{-1} was calculated. Here, 10 continuous measurements does not mean the samples were replaced for each measurement, but rather, the sample dripped on the prism plate was measured 10 times in that condition. Fig. 6(a) and (b) show the infrared spectra for the soot contents of 0.20 mass% and 3.93 mass%, respectively.
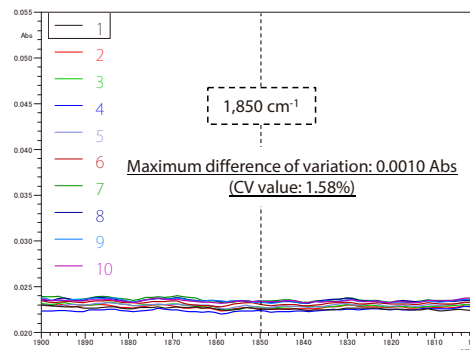

Fig.6(a) Infrared Spectrum for 0.20 Mass% Soot Content
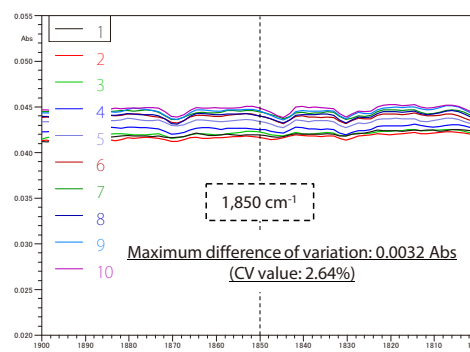

Fig.6(b) Infrared Spectrum for 3.93 Mass% Soot Content

A comparison of the baselines of the samples with soot contents of 0.20 mass% and 3.93 mass% showed larger variation in the high soot content sample. As the reason for this difference, it is thought that soot was gradually deposited around the ATR prism during the continuous measurements, and its effect was more pronounced in the high soot content sample. Moreover, absorbance was higher in the 10th measurement than in the 1st measurement with both samples. From this, it can be inferred that repeatability will be improved by conducting a smaller cumulative number of measurements (to shorten the measurement time).

■ Conclusion

A calibration curve with a high coefficient of correlation was obtained by measuring the soot content in engine oil by the ATR method of FTIR. Quantitation values close to the reference values could also be obtained. However, with a high soot content sample, the change over time in absorbance was comparatively large, and with a low soot content sample, the influence of even minute noise on the quantitation value was clear. It is thought that repeatability can be improved by measuring all samples under the same conditions and studying the optimum samples for preparation of the calibration curve.

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