Lubricating Oils Analysis
Using Thermal Desorption and Pyrolysis / Direct Analysis in Real Time-Mass Spectrometry (TDP/DART®-MS)

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Introduction

Lubricating oil is composed of base oil and additives. In order to satisfy the high demand level accompanying the development of machinery and automobiles, synthetic base oils and various functional additives are used. So, it is important to obtain the information on base oils and additives, for market research, research and development and quality control.

In order to analyze the base oils and additives of lubricating oils, complicated pretreatment which takes a lot of time and effort were required, generally. (Fig. 1).

Recently, we have reported some polymer analysis results using Thermal Desorption and Pyrolysis combined with Direct Analysis in Real Time- Mass Spectrometry (TDP/DART-MS), and it is a useful method for qualitative and quantitative analysis of plastic products composed of additives and polymer matrix .

The purpose of this work :
analysis directly and evaluate the degradation degree of lubricating oils.

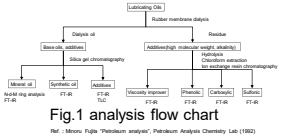


Fig.1 analysis flow chart

Ref. : Minoru Fujita "Petroleum analysis", Petroleum Analysis Chemistry Lab (1992)

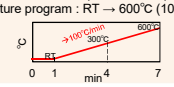
Materials and Methods

◆ Samples :
Automotive engine oil
*Mileage : 0km, 1000km, 5000km

◆ Analytical methods :
TDP/DART-MS (Fig.3)

1μL of sample were put into the POT. Mass spectra were measured as the samples were heated

Mass Spec. : micrOTOF QIII (Bruker)
Mass range : *m/z* = 100-2000
Ion Source : DART-SVP (IonSense)
Ionization gas : Helium
Helium gas temperature : 400℃
TDP device : ionRocket (BioChromato)
Temperature program : RT → 600℃ (100℃/min)



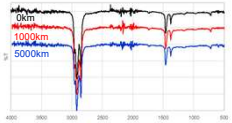
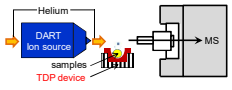


Fig.2 FT-IR spectra



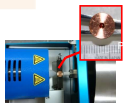


Fig.3 TDP/DART-MS system

Results and discussions

◆ As a results of FT-IR, no significant difference was detected among samples (Fig. 2).

◆ Heat map (horizontal axis: m / z, vertical axis: temperature) of each samples were shown in Fig. 4. From all the samples, compounds with locally high strength at 300 ℃ and compounds with repeating unit structure which seems to be polymer at 450 ℃ were detected.

◆ MS spectra and MS/MS spectra at 300 ℃ were shown in Fig. 5, 5a, 5b, and 5c. By analyzing these spectra, additives such as a phenol type antioxidant, an amine type antioxidant, a salicylic acid type detergent dispersant were detected and determined from all the samples. There was no significant difference in the amount ratio of additive components at 0 km and 1000 km running, but at 5000 km, salicylic acid type detergent and phenolic antioxidant was remarkably decreased.

◆ MS spectra at 450 ℃ were shown in Fig. 6. In the mass spectra of at 0 km, the base oil was mainly detected, but at 1000 km, the glycol compounds were also detected, and at 5000 km, the glycol compounds were remarkably increased. In addition, as it was recognized that the spectral pattern of the base oil compounds changed with the increase in mileage. So, these spectra were would involved the degradation state of the base oil.

◆ By using this analysis method, it became clear that structural information on additives and base oil in automotive engine oils can be detected without any pretreatment. In addition, since it is possible to analyze structural information of additives and base oils even for degraded automotive engine oils, it is expected to be applied to evaluate the degradation degree of automotive engine oils and maintenance of machinery equipment.

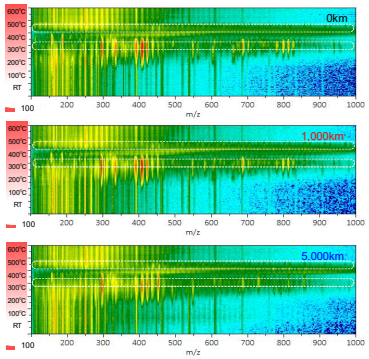


Fig.4 Heat map

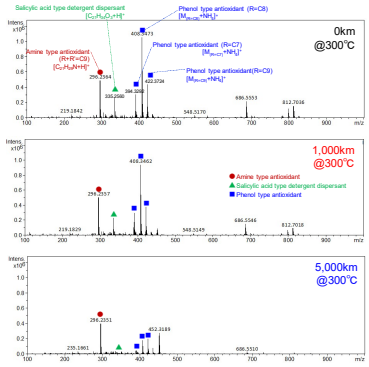


Fig.5 Mass spectra at 300℃

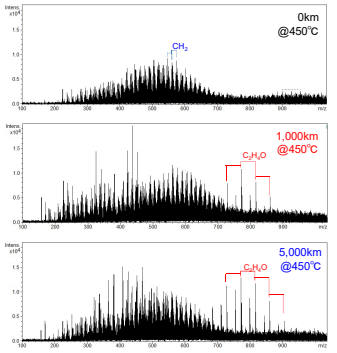


Fig.6 Mass spectra at 450℃

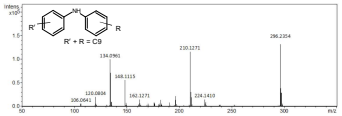


Fig.5a MS/MS spectra of *m/z* 296.23

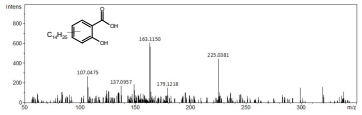


Fig.5b MS/MS spectra of *m/z* 335.25

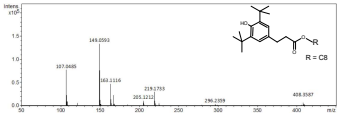


Fig.5c MS/MS spectra of *m/z* 408.34

Conclusion

◆ We adopted TDP/DART-MS to direct analysis and evaluate the degradation degree of lubrication oils.

◆ This analysis method enables detection additives and base oil in the lubricating oils respectively by gradient heating, without any pre-treatment. Moreover, this analysis method enables detection the difference between new and degraded automotive engine oils, which has not been detected by FT-IR analysis. (Fig. 7 and Fig. 8)

◆ In the additives of automotive engine oils, this analysis method enables detection the difference between the new and degraded. Therefore, it would be useful method for evaluation of degradation degree by using the additives amount as a degradation marker.

◆ In the base oils of automotive engine oils, since this analysis method enables detection the difference between the new and degraded, it would be useful method to analyze the change in chemical structure (e.g. oxidation state, molecular weight, etc.).

◆ Therefore, this analysis method is expected to contribute to elucidate of the degradation mechanism, failure analysis, R&D, and quality control.

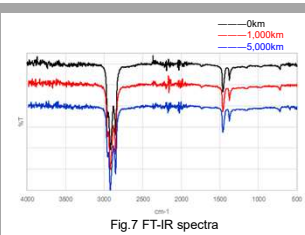


Fig.7 FT-IR spectra

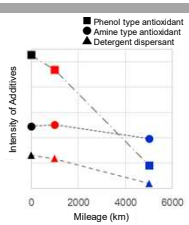


Fig.8 Results of TDP/DART-MS

Thermal Desorption & Pyrolysis device for DART®-MS

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