Evaluation of degradation degree of lubricating oil by thermal desorption and pyrolysis combined with DART-MS (TDP/DART-MS)

Chikako Takei, Kenichi Yoshizawa ; BioChromato, Inc.

Introduction

Lubricating oil is composed of base oil and additives.
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). However for R&D, QC and market research, it is important to obtain the information on base oils and additives.

Recently, thermal desorption and pyrolysis/direct analysis in real time (TDP/DART)-MS [1–3] and Kendrick Mass Defect (KMD) analysis [4] is using for polymer analysis, respectively.

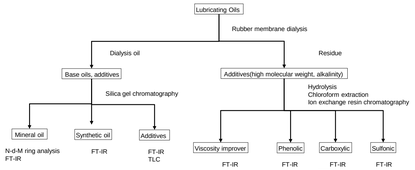
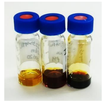


Fig.1 analysis flow chart [5]

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

Materials and Methods

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

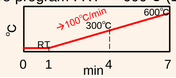


◆ Analytical methods :
TDP/DART-MS (Fig.3)

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

Kendrick Mass Defect(KMD) analysis was used a “Spectra Scope (BioChromato)” software.

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



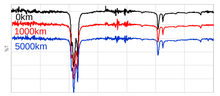


Fig.2 FT-IR spectra

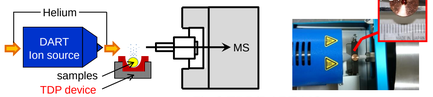


Fig.3 TDP/DART-MS system

Results and discussions

In order to bird's-eye view of the whole mass spectra, heat map (horizontal axis: *m/z*, vertical axis: temperature) of each samples were shown in Fig. 4.

Compounds with locally high strength at thermal desorption region (300 ℃) and with repeating structure which seems to be polymer at pyrolysis region (450 ℃) were detected.

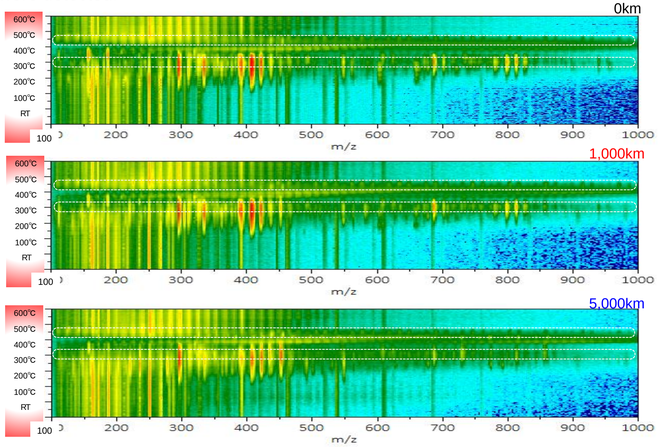


Fig. 4 Heat map of the whole mass spectra of each samples using TDP/DART-MS

Thermal desorption region ~ Additives ~

- A phenol type antioxidant, an amine type antioxidant, a salicylic acid type detergent dispersant were detected and determined from all samples(Fig. 5, 6).
- 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(Fig. 5).
- TDP/DART-MS enables evaluation of degradation degree of lubricating oils using the additive intensity as a marker (Fig. 7).

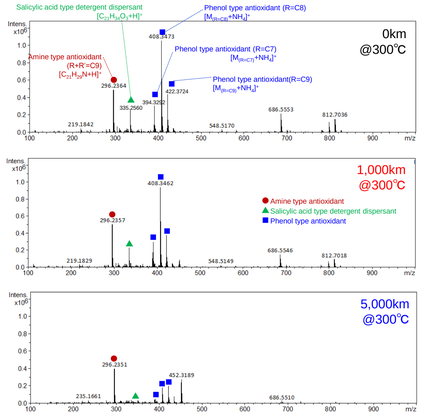


Fig. 5 Mass spectra of each samples using TDP/DART-MS

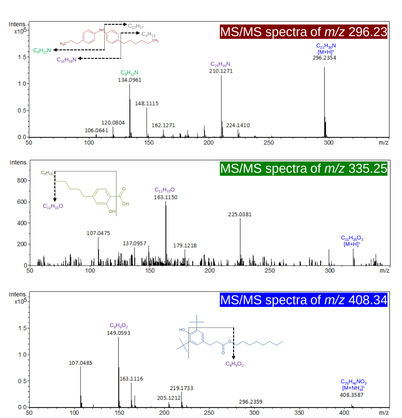


Fig. 6 MS/MS spectra of each precursor ions using TDP/DART-MS

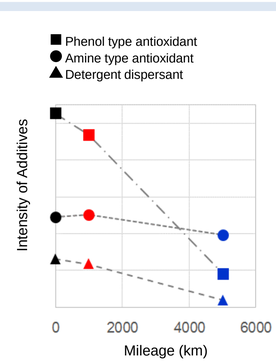


Fig.7 Results of TDP/DART-MS

Pyrolysis region ~ Base oil ~

- Using KMD analysis, the glycol compounds were detected by automobile running, clearly. And it increased with increasing in mileage (Fig. 8~11).
- It was assumed that the glycol compounds were one of degradation compounds of lubricating oils.
- KMD analysis was valuable way to search the differences between complex mass spectra.

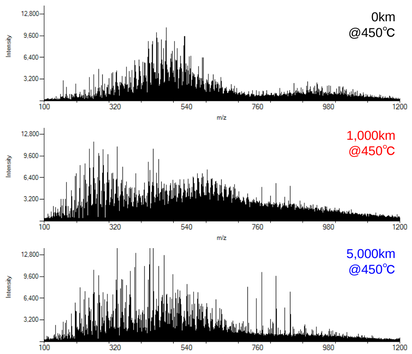


Fig. 8 Mass spectra of each samples using TDP/DART-MS

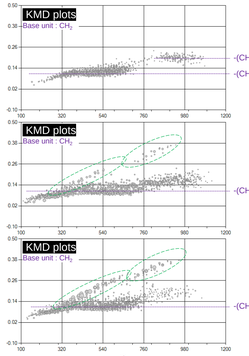


Fig. 9 KMD plots using TDP/DART-MS at pyrolysis region (Fig.8)

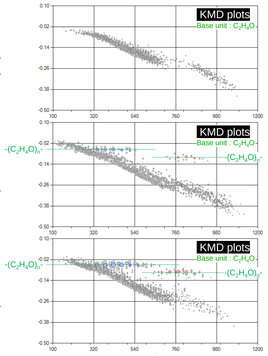


Fig. 10 KMD plots using TDP/DART-MS at pyrolysis region (Fig.8)

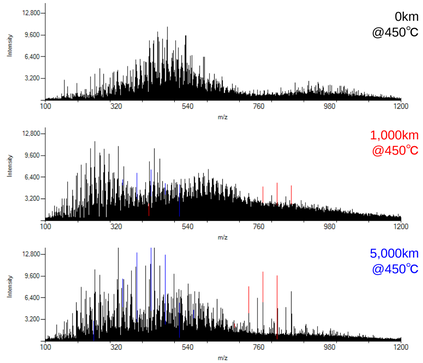


Fig. 11 Mass spectra of each samples using TDP/DART-MS
The color of each peaks correspond to the color of KMD plots

Conclusion

A combination of TDP/DART-MS and KMD analysis enables analysis both additives and base oil without any pretreatment.

Therefore, the combination can contribute to elucidate of the degradation mechanism, failure analysis, R&D, and quality control in the field of automobiles.

References

1. C.Takei, K.Kinoshita, T.Nishiguchi, h.Shimada, K.Maeno, Y.Shida; 63rd ASMS Annual Conference, Poster ThP74 (2015)
2. R.B.Cody, C.Takei, H.Shimada, Y.Shida, A.Kusai; 64th ASMS Annual Conference, Poster MP545(2016)
3. C.Takei, K.Yoshizawa, H.Ohtani; 65th ASMS Annual Conference, Poster WP605(2017)
4. H.Sato, S.Nakamura, K.Teramoto, T.Sato; JASMS, 2014, 25(8), 1346-1355
5. Minoru Fujita “Petroleum analysis”, Petroleum Analysis Chemistry Lab (1992)