Applications Note

AccuTOF-GCv Series

Monitoring Rotary Vacuum Pump Oil Degradation by Using Field Desorption (FD)-TOFMS and Group-type Analysis Software

Introduction

Field Desorption (FD) is a technique that ionizes analytes by electron tunneling from the analyte molecules to a solid surface (emitter) in a high electric field. The sample is applied directly onto the emitter and heated by applying an electric current through the emitter for desorption and ionization. FD has been used for the analysis of nonvolatile compounds, synthetic polymers, etc., as a soft ionization method to produce molecular ions with little or no fragmentations. As a result, the average molecular weight of a sample can be calculated directly from the masses (or "*m/z*") and intensities for all of the ions observed in the FD mass spectrum. Furthermore, by applying group-type analysis, the components can be classified into types based on their functional groups and/or unsaturations. Average molecular weight, polydispersity index, or relative abundance of each type can also be obtained.

In this work, new and used rotary vacuum pump (RP hereafter) oils were analyzed by FD. Afterwards, the change in their compositions was determined by performing group-type analysis on the resulting mass spectra.

Method

Samples

RP oil (new and used) as shown in Fig. 1.

MS Conditions

Mass spectrometer: JMS-T100GC AccuTOF-GC
Ionization mode: FD(+)
Cathode potential: -10 kV
Emitter current: 0 mA → 51.2 mA/min → 40 mA
Acquired mass range: *m/z* 35 – 1,600
Spectral recording interval: 0.5 sec

Fig. 1 RP oil (left: used, right: new)

Results and Discussion

The acquired FD mass spectra are shown in Fig. 2.

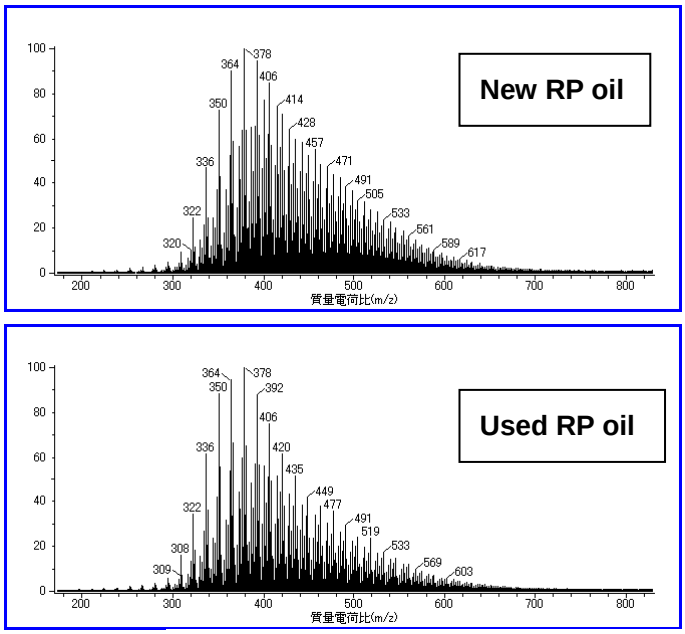
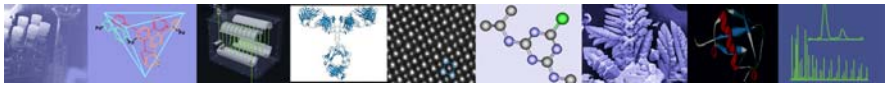


Fig. 2 Acquired FD mass spectra

The FD mass spectral patterns shown in Fig. 2 are typical for hydrocarbon mixtures. Since the difference was rather subtle (more peaks were observed for the new oil at around *m/z* 500), group-type analysis was performed to determine the differences in their composition. Hydrocarbon types with different degrees of unsaturation (C_nH_{2n+2}, C_nH_{2n}, C_nH_{2n-2}, C_nH_{2n-4}, C_nH_{2n-6}, and C_nH_{2n-8}) were used for these calculations. The results are shown in Tables 1 and 2. A comparison between their hydrocarbon compositions is shown in Table 3.

As shown in Table 3, the fraction of highly unsaturated hydrocarbons, i.e., C_nH_{2n-4}, C_nH_{2n-6}, and C_nH_{2n-8}, decreased while the fraction of moderately unsaturated and saturated hydrocarbons, i.e., C_nH_{2n-2}, C_nH_{2n}, and C_nH_{2n+2} increased in the used RP oil. This suggests

MS Tips #98



either opening of ring structures or hydrogenation of double bonds or triple bonds in C_nH_{2n-4}, C_nH_{2n-6}, and C_nH_{2n-8}.

Another possibility is oxidative degradation of unsaturated hydrocarbons. The exact masses of an oxidation product and its hydrocarbon isobar are very close and can not be mass-resolved with the analysis conditions used for this study. Even so, the apparent increase of the saturated and moderately unsaturated hydrocarbons and decrease of the highly unsaturated hydrocarbons could be partly due to the oxidation products. The difference in the compositions of the new and used RP oil was clearly revealed by the group-type analysis.

Table 1. Type analysis result of new RP oil

Series Label	Mn	Mw	Mz	PD	DPn	DPw	DPz	Percent Series
Total/Average	453.82	483.97	531.27	1.07	25.57	27.73	31.10	100.00
C_nH_{2n+2}	447.44	479.98	533.06	1.07	24.78	27.10	30.89	15.47
C_nH_{2n}	435.82	462.47	504.05	1.06	24.10	26.00	28.96	23.19
C_nH_{2n-2}	451.28	482.02	530.39	1.07	25.34	27.54	30.99	16.70
C_nH_{2n-4}	464.22	498.14	551.19	1.07	26.41	28.83	32.61	12.69
C_nH_{2n-6}	459.36	486.90	529.76	1.06	26.21	28.17	31.23	18.90
C_nH_{2n-8}	478.50	511.38	561.52	1.07	27.72	30.06	33.64	13.06

Table 2. Type analysis result of used RP oil

Series Label	Mn	Mw	Mz	PD	DPn	DPw	DPz	Percent Series
Total/Average	446.82	483.77	546.99	1.08	25.05	27.68	32.20	100.00
C_nH_{2n+2}	434.74	473.54	544.08	1.09	23.88	26.64	31.68	16.76
C_nH_{2n}	425.93	455.81	507.39	1.07	23.39	25.52	29.20	26.43
C_nH_{2n-2}	444.90	481.25	543.39	1.08	24.89	27.48	31.91	17.57
C_nH_{2n-4}	461.91	506.41	581.41	1.10	26.24	29.42	34.77	12.03
C_nH_{2n-6}	458.94	494.97	555.72	1.08	26.18	28.75	33.08	16.65
C_nH_{2n-8}	485.15	530.63	603.67	1.09	28.19	31.44	36.65	10.58

Table 3. Difference in hydrocarbon compositions

	New		Used
Series Label	Percent Series		Percent Series
Total/Average	100.00		100.00
C_nH2_{n+2}	15.47	– increase →	16.76
C_nH_{2n}	23.19	– increase →	26.43
C_nH_{2n-2}	16.70	– increase →	17.57
C_nH_{2n-4}	12.69	– decrease →	12.03
C_nH_{2n-6}	18.90	– decrease →	16.65
C_nH_{2n-8}	13.06	– decrease →	10.58

