

Group-type analysis of Crude Oil using GC/FI-TOFMS 2**~Reproducibility of group-type analysis results~****Introduction**

Field Desorption (FD) and Field Ionization (FI) are ionizing analytes by electron tunneling from analyte molecules to the solid surface (emitter) in a high electric field. In case of FD, the sample is applied on the emitter and heated by applying an electric current through the emitter for desorption and ionization. In the case of FI, vaporized analyte molecules are introduced to the proximity of the emitter.

FI is a soft ionization method that yields intact molecular ions and in most cases, with very few fragment ions. It was used to ionize analytes that are easy to fragment and where molecular ions are difficult to be detected, such as hydrocarbons in crude oil.

For complex mixtures such as crude oil or synthetic polymers, molar mass distributions and average molecular weights are important chemical properties. By analyzing a FI mass spectrum, mostly consisting of molecular ions of complex hydrocarbon mixture, and using a group-type analysis software, one can obtain molar mass distributions and average molecular weights of the various hydrocarbon types (e.g., paraffin, naphthene, olefin, aromatics) in the mixture.

We have analyzed a crude oil sample by GC/FI method using JMS-T100GC "AccuTOF GC" and processed the obtained data using a group-type analysis software.

Methods**Sample** Crude Oil

(Refer Fig. 1 for preparation)

Analysis conditions**GC conditions**

GC:	Agilent 6890N
Column:	DB-5ms 30 m x 0.25 mm I.D., 0.25 μ m
Oven:	50°C → 15°C/min → 280°C (5 min)
Injection port:	280 °C, Split (1:200)
Injection volume:	1.0 μ l
Carrier gas:	He (1 mL/min, constant flow mode)

MS conditions

MS:	JMS-T100GC "AccuTOF GC"
Ionization:	FI+ (Cathode voltage: -10 kV, Emitter current: 0 mA)
Mass range:	m/z 35 - 500
Acquisition rate:	0.3 s/spectrum

Software Polymerix™ (Sierra Analytics, Inc.)

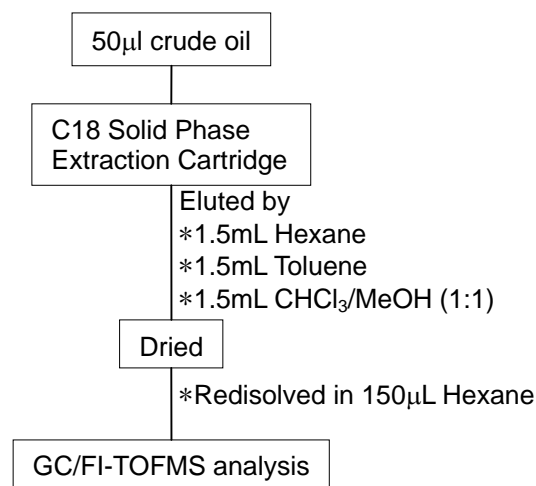


Fig. 1 Sample preparation flow

Results and Discussion

Group-type analysis for 5 hydrocarbon types with an unsaturation degree from 0 to 4 and for the total/average of the 5 types was performed. (Refer MS Tips No. 71 for details.)

The table below shows the properties calculated for the total/average of the 5 hydrocarbon types for 10 repeated analyses and their statistics.

Table 1 Results of the group-type analysis of the crude oil (Total/Average)

Total/Average	M_n	M_w	M_z	PD	DP_n	DP_w	DP_z
1	206.188	217.016	229.273	1.053	8.699	9.471	10.346
2	204.957	214.545	225.075	1.047	8.854	9.297	10.048
3	200.606	211.629	225.105	1.055	8.298	9.085	10.046
4	205.978	215.44	225.597	1.046	8.685	9.36	10.085
5	200.029	208.101	216.649	1.041	8.261	8.837	9.447
6	205.491	215.402	226.173	1.049	8.654	9.361	10.13
7	206.532	217.31	229.255	1.052	8.723	9.492	10.344
8	205.573	215.814	227.008	1.05	8.656	9.387	10.185
9	209.459	220.152	231.519	1.051	8.937	9.7	10.511
10	209.18	220.678	233.522	1.055	8.907	9.728	10.644
Average	205.399	215.609	226.918	1.050	8.667	9.372	10.179
Std. Dev.	3.074	3.722	4.598	0.004	0.229	0.265	0.327
C.V. (%)	1.50	1.73	2.03	0.42	2.64	2.83	3.21

M_n : number average molecular weight

DP_n : M_n/R

M_w : weight average molecular weight

DP_w : M_w/R

M_z : z average molecular weight

DP_z : M_z/R

PD: polydispersity

(R: mass of repeating unit)

(DP: degree of polymerization)

The coefficients of variation are very good and around or below 3% for all properties calculated. Especially, the coefficient of variation for PD is excellent at 0.42%.

Group-type analysis of a crude oil using GC/FI method on the AccuTOF GC and Polymerix™ group-type analysis software is confirmed to have excellent reproducibility.