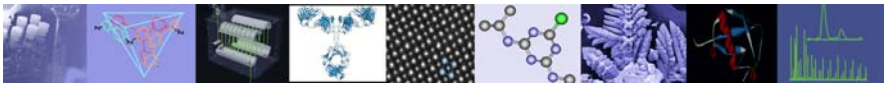

AccuTOF-GCv Series

Group-type Analysis of Crude Oil by Using GC/FI-TOFMS 2

Reproducibility of group-type analysis results

Introduction

Field Desorption (FD) and Field Ionization (FI) are both techniques that ionize analytes by electron tunneling from the analyte molecules to a solid surface (emitter) in a high electric field. In the case of FD, the sample is applied directly onto 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 into the proximity of the emitter.

Both FI and FD are soft ionization methods that generally yield intact molecular ions and, in most cases, produce very few fragment ions. Generally, these two techniques are used to ionize analytes that are easy to fragment and do not generally produce molecular ions during electron ionization (EI), such as hydrocarbons in crude oil.

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

In this work, we analyzed a crude oil sample 10 times by using the JMS-T100GC "AccuTOF-GC" GC/FI method and then processed the resulting data using a group-type analysis software package. Afterwards, these results were then compared to each other to confirm the reproducibility of the analyses.

Method

Sample: Crude Oil
(Refer to Fig. 1 for Sample Preparation)

GC Conditions

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

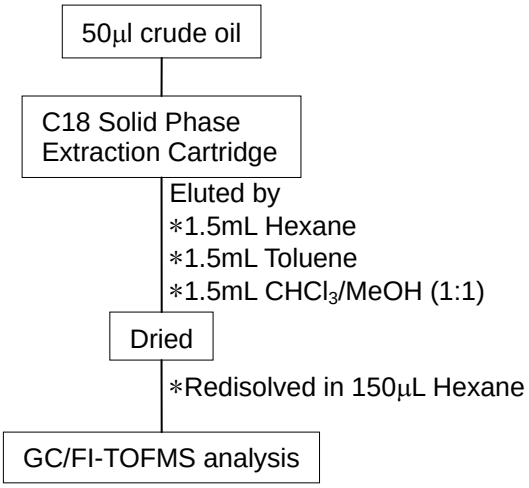

Fig. 1 Sample preparation flow

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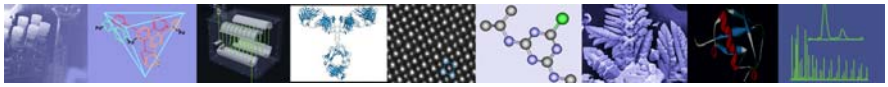

Total/Average	M_n	M_w	M_z	PD	DP_n	DP_w	DP_z
1	206.188	217.016	229.273	1.053	8.699	9.471	10.346
2	204.957	214.545	225.075	1.047	8.854	9.297	10.048
3	200.606	211.629	225.105	1.055	8.298	9.085	10.046
4	205.978	215.44	225.597	1.046	8.685	9.36	10.085
5	200.029	208.101	216.649	1.041	8.261	8.837	9.447
6	205.491	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
M_w: weight average molecular weight
M_z: z average molecular weight
PD: polydispersity

DP_n: M_n/R
DP_w: M_w/R
DP_z: M_z/R
(R: mass of repeating unit)
(DP: degree of polymerization)

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

Results and Discussion

All of the mass spectra acquired by the AccuTOF-GC during the retention time range of the sample were summed to form a single mass spectrum. Afterwards, this mass spectrum was directly read into the Polymerix™ software for processing. A group-type analysis was then performed for 5 hydrocarbon types with degrees of unsaturation from 0 to 4 for the total/average of the 5 types. Please refer to MS Tips No. 71 (Group-type Analysis Part 1) for the details of this analysis. Table 1 shows the properties calculated for the total/average of the 5 hydrocarbon types for 10 repeated analyses and their statistics.

The coefficients of variation were very good in this experiment and showed calculated values below 3.3% for all properties. In particular, it is worth noting that the coefficient of variation for PD is excellent at 0.42%.

Conclusions

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

