Multifaceted crude oil analysis using GC-EI/FI, blank tube-FI, and FD on JMS-T2000GC

Product used: Mass Spectrometer (MS)

Introduction

JMS-T2000GC can switch ionization methods without breaking the vacuum by using a EI/FI/FD* combination ion source. In this MSTips, we will introduce crude oil analysis that takes advantage of these ionization methods. Figure 1 shows a schematic diagram of the four analytical methods used in this experiment, and Table 1 shows their characteristics. In ①GC-EI and ②GC-FI, the sample is introduced into the GC injection port, separated by the GC column, and measured using hard ionization EI and soft ionization FI. These two measured data can be integrated and analyzed using msFineAnalysis AI. In ③Blank tube-FI, the sample is introduced into the GC injection port, passed through the blank tube, and measured using soft ionization FI. In ④FD, the sample is applied directly to the emitter and measured using a soft ionization FD. These mass spectra obtained by soft ionization can be easily analyzed using msRepeatFinder.

*EI: Electron Ionization, FI: Field Ionization, FD: Field Desorption, **KMD : Kendrick Mass Defect

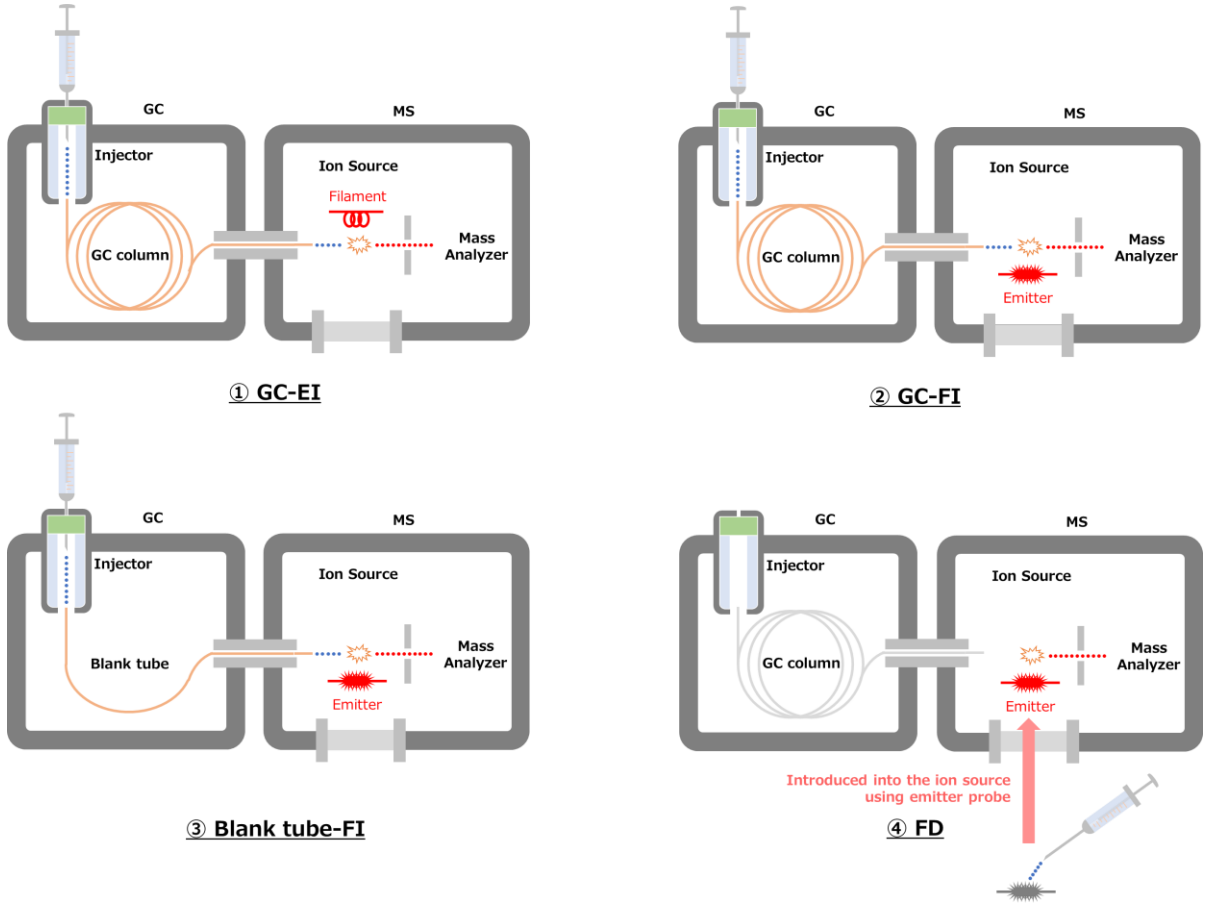


Figure 1 Measurement method for crude oil in JMS-T2000GC

Table 1 Characteristics of each measurement method

Method	Separation	Low-boiling (b.p.< 200 Da)	High-boiling (b.p. up to 550 Da)	Very high-boiling (b.p.> 550 Da)	Meas. Time
GC-EI/GC-FI	GC + MS	Excellent	Fair	Not suitable	Long (30 min. ~)
Blank tube FI	MS only	Excellent	Good	Fair	Very quick (~1 min.)
FD	MS only	Not suitable	Excellent	Good	Very quick (~1 min.)

Experiments

Standard reference material (SRM) 2779 provided by NIST was used as the sample. The GC conditions of GC-EI and GC-FI were based on standard test method D6730 provided by ASTM International. In this method, it is possible to obtain a highly separated chromatogram by connecting two columns in series. Rtx-5 and Rtx-DHA manufactured by Restek corporation were used as columns. Table 2 shows the measurement conditions for each method.

Table 2 Measurement conditions

	GC-EI	GC-FI	Blank tube-FI	FD
Sample				
Dilution	Not dilution		100 mg/mL	
Injection volume	1µL			
GC conditions				
Pre column	Rtx-5, 5 m length , 0.25 mm i.d., 1µm thickness		None	
Column	Rtx-DHA, 100 m length, 0.25 mm i.d., 0.5µm thickness		Blank tube, 4m	
Split	150:1		20:1	None
Inlet temperature	300°C			None
Oven temperature	30°C (2 min hold) – 2°C/min – 300°C (43 min hold)		300°C (isothermal)	None
Carrier gas	He, 2mL/min			None
MS conditions				
Ionization	EI (70eV)	FI		FD
Mass range	*m/z* 35-800		*m/z* 35-1600	

Results

Figure 2 shows the TIC chromatograms of GC-EI and GC-FI. A large number of peaks were detected, including linear alkanes with carbon numbers from C_5 to C_{32}.

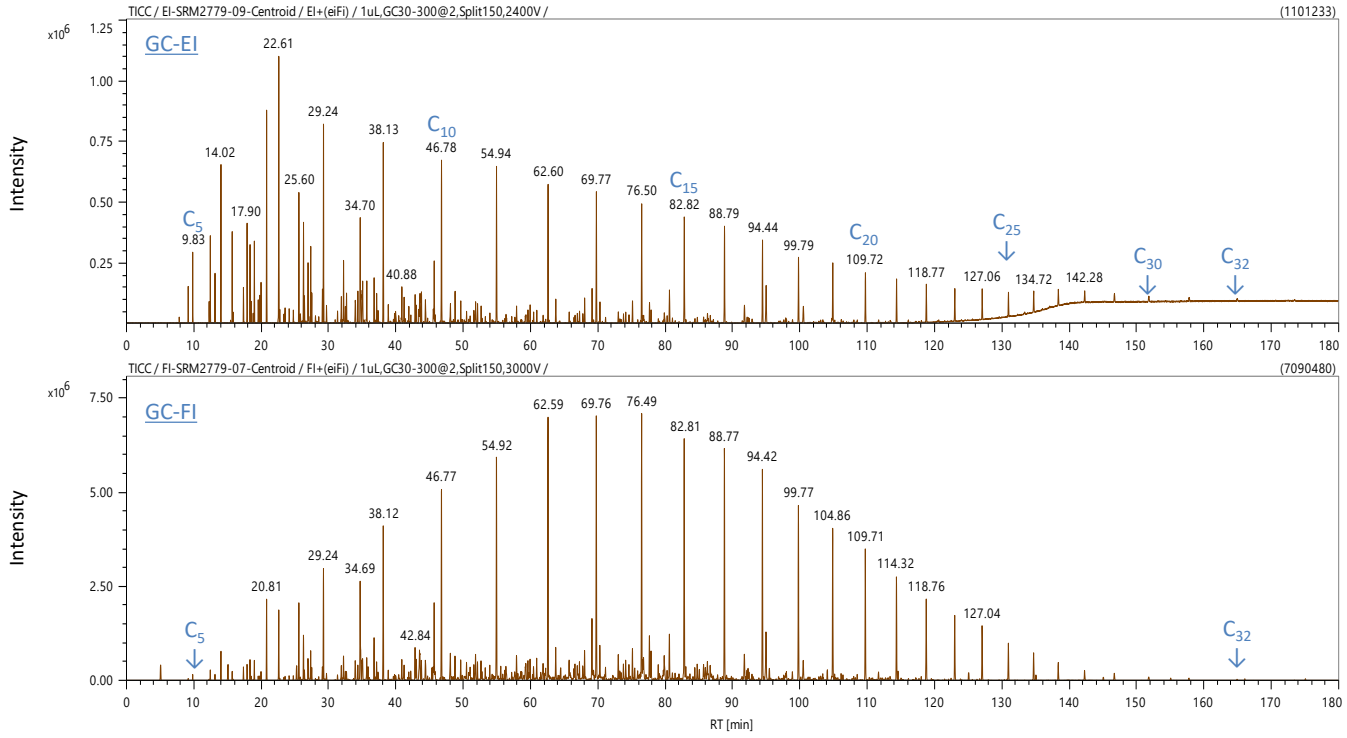


Figure 2 TIC chromatograms of GC-EI and GC-FI

Figure 3 shows the integrated analysis results of GC-EI and GC-FI using msFineAnalysis AI. The chromatograms were expanded around the retention time of Heptadecane (C17H36) to Eicosane (C20H42). The main components were simple hydrocarbons consisting of only C and H, but the minor component which is sulfur compound alkylated dibenzothiophenes were detected. Although this compound was not registered in the NIST library, its structural formula could be obtained using AI structural analysis.

Figure 3 Result of integrated analysis using msFineAnalysis AI

Figure 4 shows the TIC chromatograms and mass spectra of Blank tube-FI and FD. In both method, the molecular weight distribution could be confirmed with a short measurement time of less than 1 minute. Blank tube-FI can measure a wide range of components from low to high mass components. Although FD can measure higher mass components, lower mass components are lost due to volatilization when the emitter probe is introduced into the ion source. Therefore, it is necessary to select the method according to the sample type and purpose.

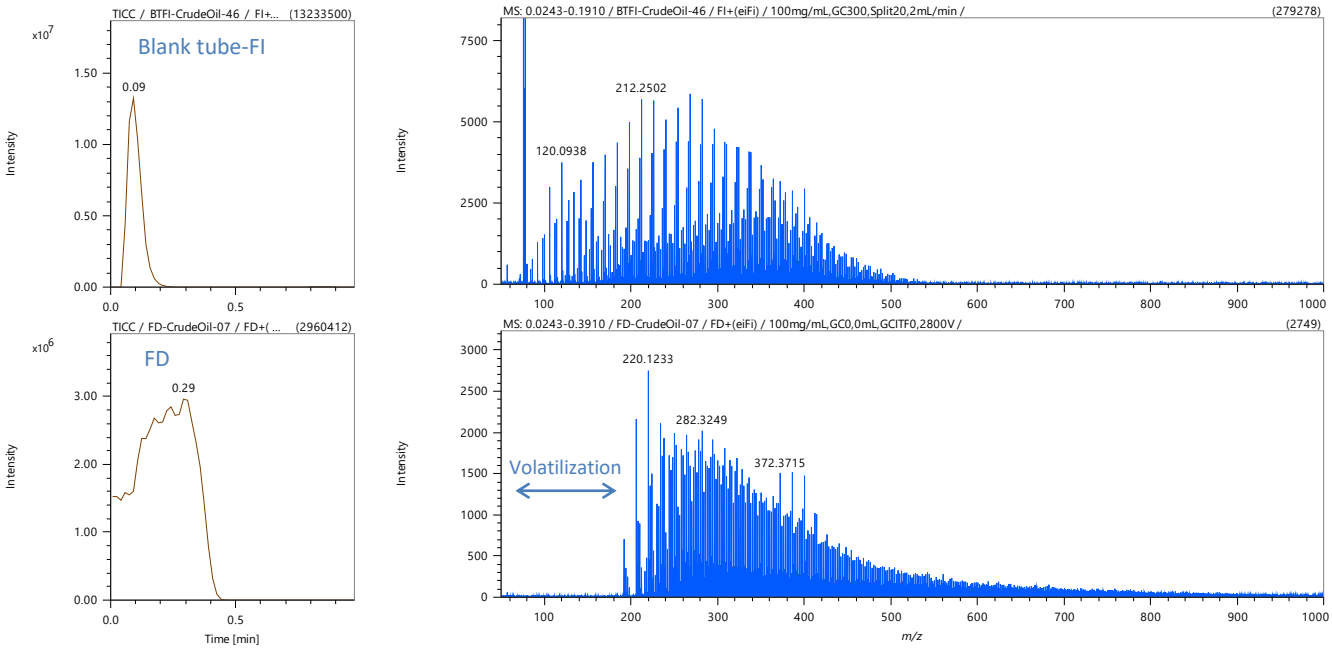
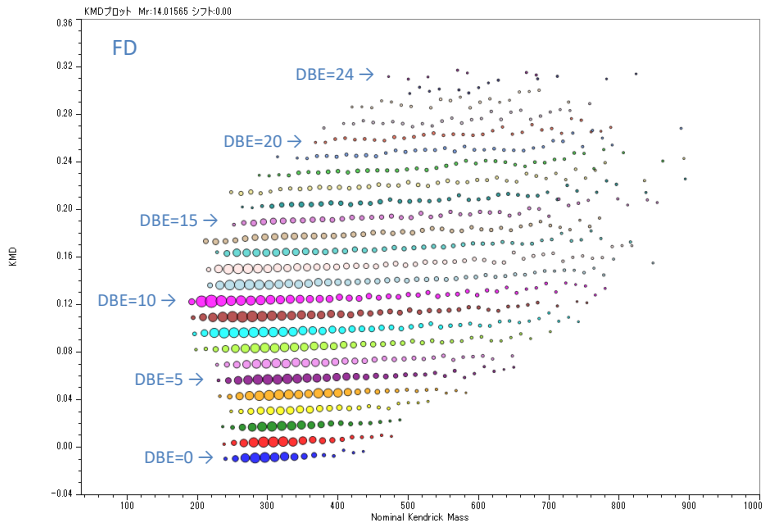


Figure 4 TIC chromatograms and mass spectra of Blank tube-FI and FD

Figure 5 shows the KMD plot and group data of FD created by msRepeatFinder. Using KMD plot, it is easily to evaluate the characteristics of main components hydrocarbons such as the distribution of the degree of unsaturation and degree of polymerization. Similar analysis is also possible with blank tube-FI.



Group No	Formula	DBE	Sum of Intensities	Sum of Intensities (%)	Number average of molecular weight(m/z)	Weight average of molecular weight(m/z)	Dispersity
1	CnH2n+2	0	49895.21	3.2	308.872	313.964	1.016
2	CnH2n	1	63053.11	4.05	325.154	332.335	1.022
3	CnH2n-2	2	58579.68	3.76	333.236	341.267	1.024
4	CnH2n-4	3	47973.88	3.08	351.483	361.948	1.03
5	CnH2n-6	4	88825.9	5.7	353.896	367.534	1.039
6	CnH2n-8	5	93683.89	6.02	362.091	382.682	1.057
7	CnH2n-10	6	83758.31	5.38	368.199	390.325	1.06
8	CnH2n-12	7	95520.16	6.13	363.512	392.136	1.079
9	CnH2n-14	8	121215.6	7.78	351.742	389.505	1.107
10	CnH2n-16	9	126618.8	8.13	352.161	391.016	1.11
11	CnH2n-18	10	131303.2	8.43	345.344	395.685	1.146
12	CnH2n-20	11	111168.2	7.14	379.367	426.848	1.125
13	CnH2n-22	12	102184.5	6.56	386.843	439.888	1.137
14	CnH2n-24	13	76593.43	4.92	410.575	458.512	1.117
15	CnH2n-26	14	68110.21	4.37	413.433	462.744	1.119
16	CnH2n-28	15	53807.96	3.45	454.961	503.944	1.108
17	CnH2n-30	16	41703.31	2.68	496.435	539.076	1.086
18	CnH2n-32	17	38560.32	2.48	483.339	531.838	1.1
19	CnH2n-34	18	30633.16	1.97	524.287	561.88	1.072
20	CnH2n-36	19	23713.93	1.52	548.411	580.581	1.059
21	CnH2n-38	20	18733.59	1.2	563.554	588.241	1.044
22	CnH2n-40	21	14032.14	0.9	566.201	584.476	1.032
23	CnH2n-42	22	9657.344	0.62	566.157	578.661	1.022
24	CnH2n-44	23	5351.587	0.34	614.837	627.88	1.021
25	CnH2n-46	24	2802.556	0.18	577.314	587.023	1.017

Figure 5 KMD plot and group data of FD

Conclusions

Crude oil is a complex mixture, and it is difficult to obtain all the information using a single analytical method. JMS-T2000GC allows multifaceted analysis by switching the ionization method. In blank tube - FI and FD, It is easy to evaluate the main component hydrocarbons. In GC-EI and GC-FI, it is easily to analyze minor component. Furthermore, structural analysis of unknown compound is also possible using msFineAnalysis AI.

JEOL Ltd.
3-1-2 Musashino Akishima Tokyo 196-8558 Japan Sales Division Tel. +81-3-6262-3560 Fax. +81-3-6262-3577
www.jeol.com ISO 9001 • ISO 14001 Certified
▼ Local office
• AUSTRALIA & NEW ZEALAND • BELGIUM • BRAZIL • CANADA • CHINA • EGYPT • FRANCE • GERMANY • GREAT BRITAIN & IRELAND • ITALY • KOREA • MALAYSIA • MEXICO • RUSSIA • SCANDINAVIA • SINGAPORE • TAIWAN • THE NETHERLANDS • USA