在JMS-T2000GC上使用GC-EI/FI法、去活毛细管-FI法和FD法进行多角度原油分析

相关产品：质谱仪(MS)

前言

在JMS-T2000GC上使用EI/FI/FD*组合离子源能够在维持真空状态下切换电离法。本报告将介绍如何发挥这些电离法各自的特长进行原油分析。Figure 1中显示了本实验采用的四种分析方法的示意图，Table 1显示了四种分析方法各自的特征。在Figure 1的① GC-EI法和② GC-FI法中，样品被引入GC进样器，通过气相色谱柱被分离后，使用硬电离EI和软电离FI进行了测量。这两种方法获得的测量数据可以使用msFineAnalysis AI软件进行整合与分析。

在③ Blank tube-FI(去活毛细管-FI)法中，样品被引入GC进样器，通过去活毛细管后，使用软电离FI进行了测量。在④ FD法中，样品被直接涂敷在发射器上，使用软电离FD进行了测量。通过软电离获得的质谱可以使用msRepeatFinder轻松分析。

*EI: Electron Ionization(电子电离)，FI: Field Ionization(场电离)，FD: Field Desorption(场解吸)

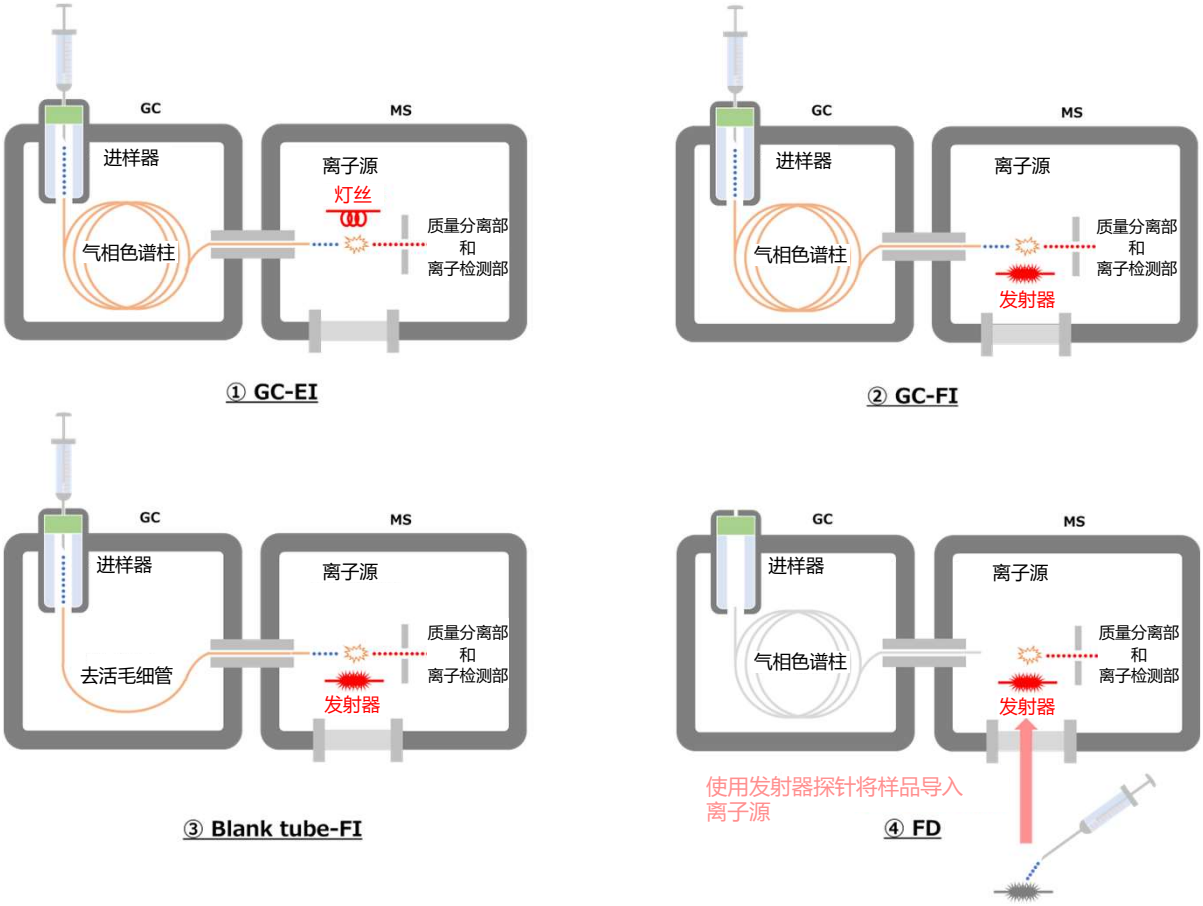

Figure 1 Measurement method for crude oil in JMS-T2000GC

Table 1 Characteristics of each measurement method

电离法	分离	低沸点 (沸点.< 200 °C)	高沸点 (沸点不超过 550 °C)	极高沸点 (沸点 > 550 °C)	测量时间
①GC-EI/②GC-FI	GC + MS	优	普通	不合适	较长 (30 分钟~)
③ 去活毛细管FI	仅MS	优	良	普通	极短 (~1分钟)
④ FD	仅MS	不合适	优	良	极短 (~1分钟)

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实验

实验所采用样品为美国国家标准与技术研究院(NIST)提供的标准参考材料(SRM)2779。GC-EI法和GC-FI法的GC测量条件参考了美国材料与试验协会(ASTM International)提供的标准试验方法D6730。此试验方法，通过串联两根色谱柱可以获得分离效能较高的色谱图。实验所采用气相色谱柱为Restek公司生产的Rtx-5 和Rtx-DHA。Table 2显示了各电离法的测量条件。

Table 2 Measurement conditions

	① GC-EI	② GC-FI	③ 去活毛细管-FI	④ FD
样品				
稀释	不稀释		100 mg/mL	
注射量	1μL			
气相色谱条件				
预GC柱	Rtx-5, 5 m长, 0.25 mm内径, 1μm厚度		不采用	
GC柱	Rtx-DHA, 100 m长, 0.25 mm内径, 0.5μm厚度		去活毛细管, 4m	
分流比	150:1		20:1	不采用
GC入口温度	300°C			不采用
烤箱温度	30°C (保持2分钟) – 2°C/分钟 – 300°C (保持43分钟)		300°C (等温)	不采用
载气	He, 2mL/分钟			不采用
质谱条件				
电离	EI (70eV)	FI		FD
质量范围	*m/z* 35-800		*m/z* 35-1600	

结果和分析

Figure 2 显示了① GC-EI和② GC-FI的TIC色谱图。检测出的大量元素峰，中包含了 C_5~C_{32} 的直链烷烃。

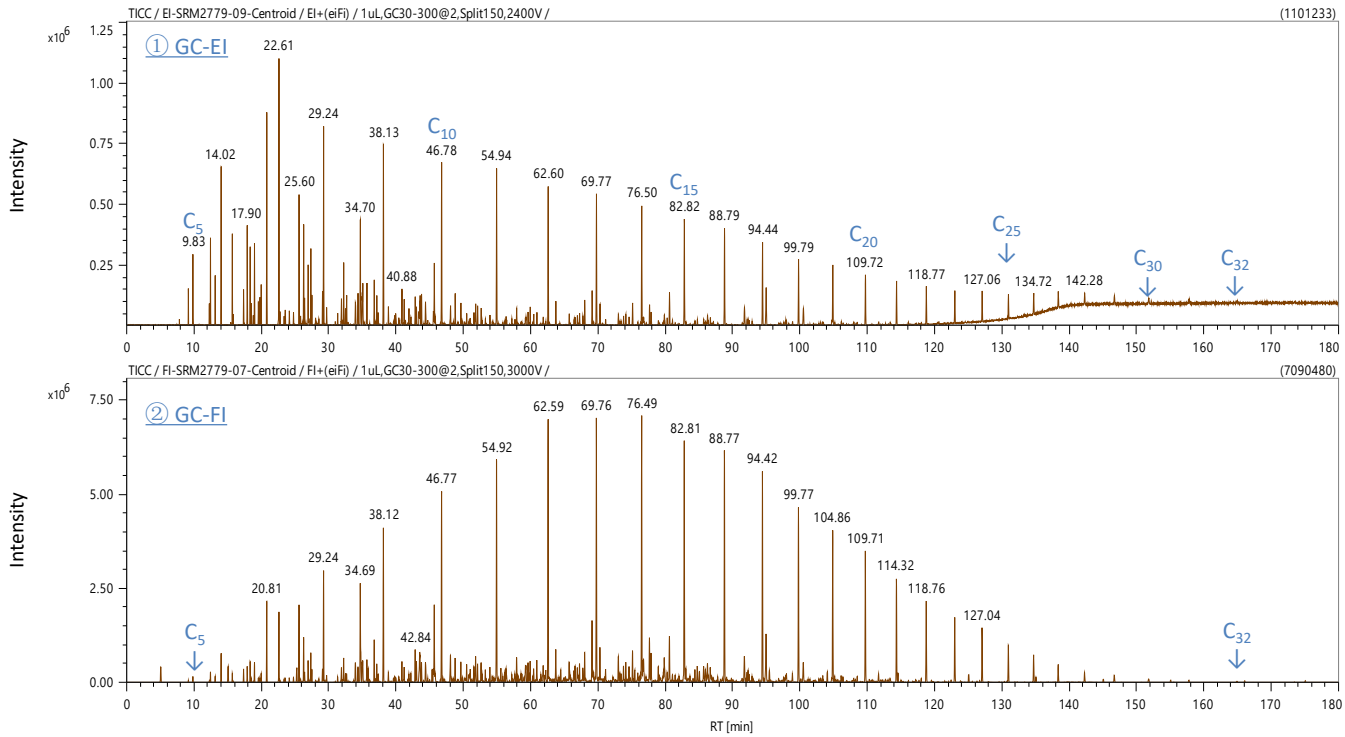

Figure 2 TIC chromatograms of GC-EI and GC-FI

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Figure 3显示了msFineAnalysis AI软件对GC-EI和GC-FI数据的综合分析结果。对色谱图在庚十烷($C_{17}H_{36}$)到二十烷($C_{20}H_{42}$)的保留时间附近进行。扩大分析后发现主要成分虽是由碳和氢组成的简单碳氢化合物，但同时也检测到了微量的含硫化合物烷基二苯并噻吩。虽然NIST数据库不包含此化合物，通过AI结构分析成功获得了其结构式。

Figure 3 Result of integrated analysis using msFineAnalysis AI

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Figure 4显示了③ 去活毛细管-FI法和④ FD法获得的TIC色谱图和质谱图。这两种方法，可在1分钟不到的极短时间内获得分子量分布。去活毛细管-FI法能够测量质量从低到高的大范围组分。FD法虽可以测量更高质量的组分，但发射器探针伸入离子源时，低质量组分会因挥发而无法被检测。因此，选择电离法时需考虑到样品类型和测量目的。

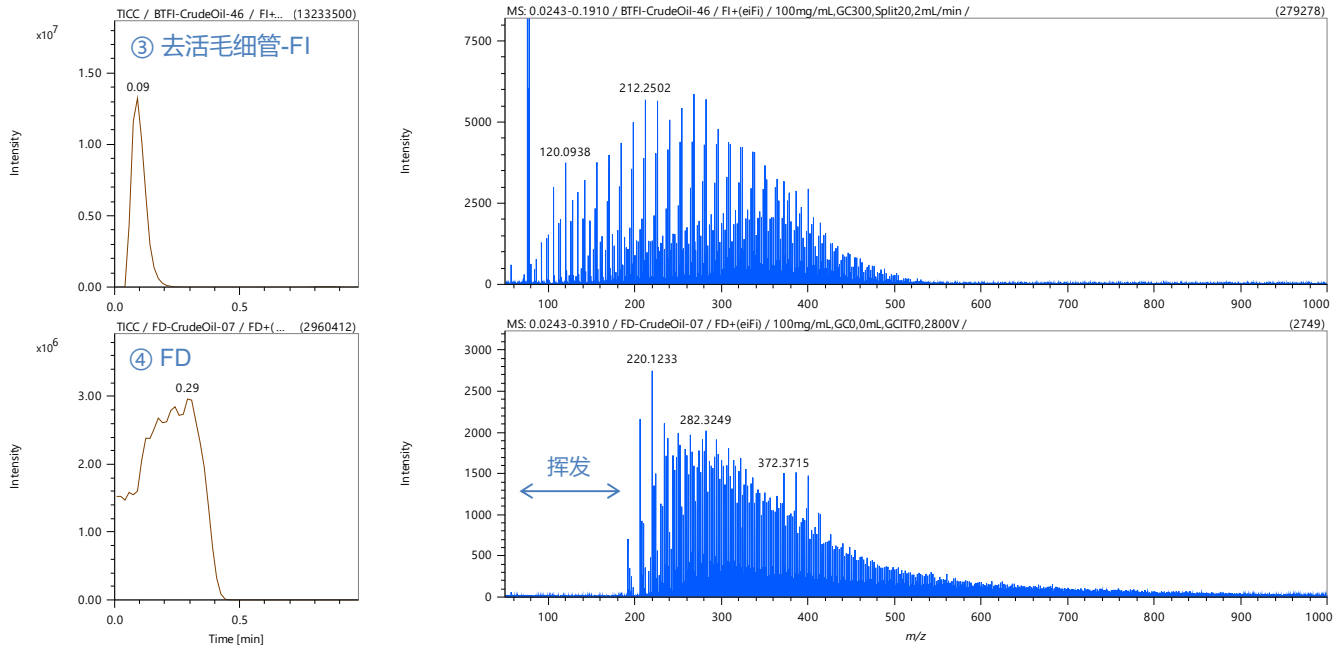
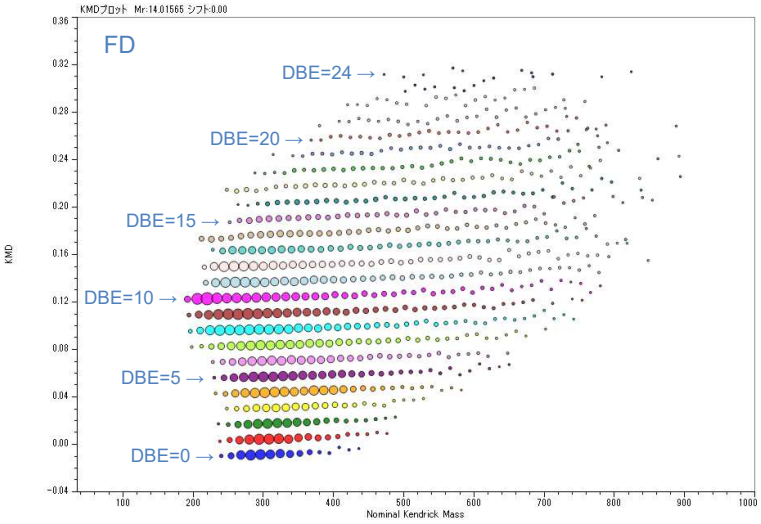


Figure 4 TIC chromatograms and mass spectra of Blank tube-FI and FD

Figure 5显示了由msRepeatFinder创建的FD法的KMD**图和组数据。使用KMD图，可以轻松评估主要组分烃类的特性，例如不饱和度(DBE)和聚合度的分布。类似的分析也可以用于去活毛细管-FI法。

**KMD：Kendrick Mass Defect(Kendrick质量缺陷)



组号	化学式	DBE	强度总和	强度总和(%)	数均分子量(m/z)	重均分子量(m/z)	分散度
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

结语

原油作为一种复杂的混合物，使用单一分析方法很难获取所有信息。JMS-T2000GC则能够通过切换电离法进行多角度原油分析。去活毛细管-FI法和FD法能够轻松评估原油主要组分烃类的特征。GC-EI法和GC-FI法则能轻松分析原油的次要组分。此外，使用msFineAnalysis AI软件还可以对原油中未知化合物进行结构分析。

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