

**Rapid analysis using inactivated fused silica tube
(a.k.a. “guard column”) as a sample inlet (2)****Introduction**

Average molecular weight is an important reference for evaluating samples with molecular weight distributions, such as crude oils, which are complex mixtures, or synthetic polymers. Almost all the ions observed in field desorption (FD) and field ionization (FI) mass spectra are molecular ions since these are soft ionization methods. Average molecular weight of the sample can be calculated directly from the masses (or “ m/z ”) and intensities of all ions observed by FD or FI. 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 be obtained.

In MS Tips No. 111, the details of the “blank tube inlet / FI” method was discussed. In this application note, crude oil, diesel fuel, and kerosene were analyzed by blank tube inlet / FI, capillary GC/FI, and FD and the results were compared and discussed.

Methods

The samples were commercially available kerosene, commercially available diesel fuel, and crude oil from Middle East. The parameters used in the analyses are summarized in Table 1.

Table 1 Operating conditions for blank tube inlet/FI, capillary GC/FI and FD.

	Blank tube inlet/FI	Capillary GC/FI	FD
GC parameter			
Injection mode	Split(100:1)	Split(500:1)	—
Inlet temp. / °C	280	280	—
Column	—	ZB-5ms, 30 m × 0.25 mm, 0.25 μm	—
Fused silica tube	3 m × 0.1mm	—	—
Oven temp. / °C [hold time / min]	280 [1]	40[1]-300[1]	—
Oven temp. ramp rate/ °C min ⁻¹	—	10	—
Sample Volume / μL	1	1	—
He Carrier gas flow rate / mL min ⁻¹	0.1	1	—
TOFMS parameter			
Ionization mode	FI(+)	FI(+)	FD(+)
Emitter wire diameter / μm	5	5	10
Emitter current / mA	5	5	0-50
Emitter current ramp rate / mA min ⁻¹	—	—	51.2
Flush time after recording spectrum / ms	50	50	—
Cathode voltage / V	-10000	-10000	-10000
Transfer line temp. / °C	280	280	—
Acquired m/z range / $m z^{-1}$	35-800	35-800	35-800
Spectrum redording time / s	0.5	0.5	1

Results and discussion

The reconstructed total ion current chromatograms (RTICCs,) the mass spectra, and the summary of the type-group analysis results are shown in Fig. 1, Fig. 2, and Table 2 respectively.

With GC/FI, the analyses took 20 min, 25 min, and 30 min for kerosene, diesel fuel, and crude oil respectively, although each component can be examined in detail due to the separation. FD and blank tube inlet / FI do not provide separation but the analysis times were very short; within 1 minute in both methods and for all 3 samples.

As was discussed in MS Tips No. 111, the blank tube inlet / FI has a number of advantages. Unlike FD, it did not miss low boiling point components or over-emphasize high boiling point components. The analysis time was very short and high boiling point components of up to m/z 600 and trace components were detected. For group-type analysis in which parameters such as relative abundance and average molecular weight for each type are obtained, m/z 's and summed intensities of all the detected ions are used; no separation is required. The blank tube inlet / FI method is well suited for the group-type analysis of petrochemicals because of short analysis time, better detectability of low boiling point components than FD, better detectability of high boiling point and trace components than GC/FI. It can handle larger amount of sample injection than GC; well suited with FI whose ionization efficiency is lower than EI.

References

M. Ubukata et al., *J. Mass Spectrom. Soc. Jpn.*, **56**, 13-19 (2008).

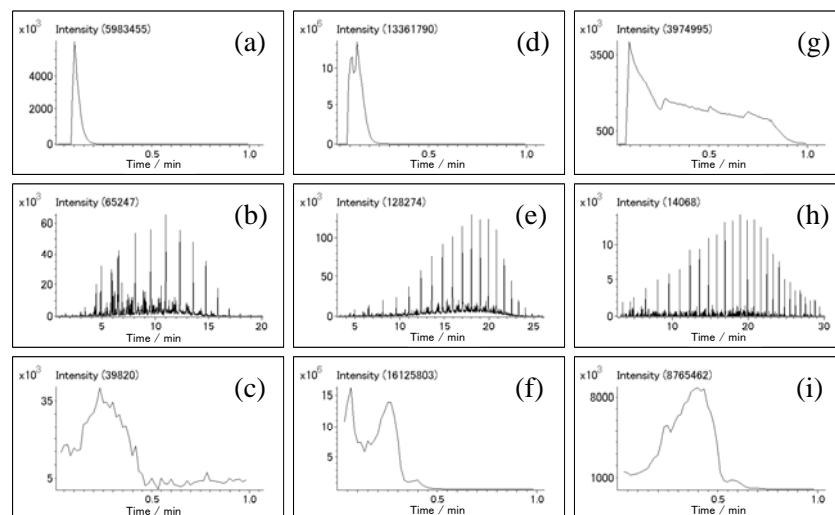


Fig. 1 Comparison of TICs of kerosene, diesel oil and crude oil by using differ methods; (a) kerosene by blank tube inlet/FI. (b) kerosene by capillary GC/FI. (c) kerosene by FD. (d) diesel oil by blank tube inlet/FI. (e) diesel oil by capillary GC/FI. (f) diesel oil by FD. (g) crude oil by blank tube inlet/FI. (h) crude oil by capillary GC/FI. (i) crude oil by FD.

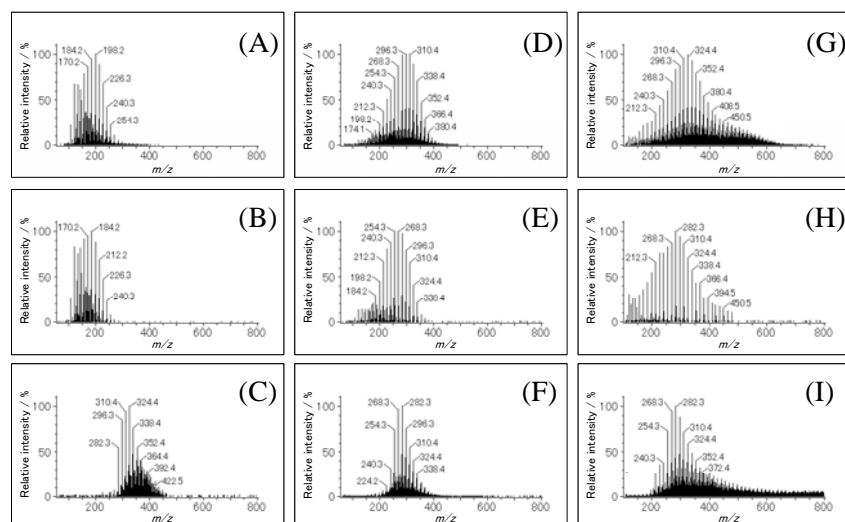


Fig. 2 Comparison of averaged mass spectra of kerosene, diesel oil and crude oil by using differ methods; (A) kerosene by blank tube inlet/FI. (B) kerosene by capillary GC/FI. (C) kerosene by FD. (D) diesel oil by blank tube inlet/FI. (E) diesel oil by capillary GC/FI. (F) diesel oil by FD. (G) crude oil by blank tube inlet/FI. (H) crude oil by capillary GC/FI. (I) crude oil by FD.

Table 2 Summary of type analysis results.

	Blank tube inlet/FI	Capillary GC/FI	FD
Kerocene			
Measuring time / min	0.2	18	0.5
M_n	179.2	165.3	348.9
PD	1.04	1.03	1.02
Base peak	$C_{14}H_{30}$	$C_{13}H_{28}$	$C_{23}H_{48}$
Diesel oil			
Measuring time / min	0.3	25	0.5
M_n	282.6	247.6	299.4
PD	1.04	1.04	1.02
Base peak	$C_{22}H_{46}$	$C_{20}H_{42}$	$C_{20}H_{42}$
Crude oil			
Measuring time / min	1.0	>30	0.7
M_n	365.7	264.6	403.0
PD	1.09	1.10	1.12
Base peak	$C_{23}H_{48}$	$C_{20}H_{42}$	$C_{20}H_{42}$

$n = 3$; M_n : number-average molecular weight; PD: polydispersity