

AccuTOF-GCv Series

Rapid Analysis Using Deactivated Fused Silica Tubing (a.k.a. “Guard Column”) as the Sample Inlet (1)

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 of the ions observed in field desorption (FD) and field ionization (FI) mass spectra are molecular ions because they are both soft ionization methods. As a result, the average molecular weight of a sample can be calculated directly from the masses (or “ m/z ”) and intensities for all of the ions observed in the FD or FI mass spectra. 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.

A diesel fuel was analyzed on JMS-T100GC “AccuTOF-GC” with 3 sample introduction methods and the results were compared:

- Capillary GC / FI
- Rapid FD in which the analysis time was shortened by ramping the emitter current much faster than for conventional analyses on double-focusing mass spectrometers
- Blank tube inlet / FI in which a fused silica tube was used to connect the GC injector and the ion source

Method

Blank tube inlet / FI

The schematics of the GC-related sample inlets are shown in Fig. 1. The specifications of the GC column and the fused silica tube used in the experiments are also shown in Fig. 1.

In ordinary GC/MS analysis, a mixture is separated by a GC column and then detected by MS. When performing group-type analysis from GC/MS data, however, all acquired spectra are summed into a single mass spectrum. Component separation or individual spectra in the data are not really necessary.

In blank tube inlet / FI, a sample is introduced from the GC injection port through a short fused silica tube (“guard column”), held in the isothermal GC oven, to the ion source. The advantages are:

- Short analysis time
- Loss of the low boiling point components are minimized compared with probe based methods, such as FD, DEI, and DCI, in which the sample is put on the probe at ambient pressure. However, low boiling point components are evaporated as the probe is introduced into the vacuum.
- Loss of high boiling point and trace components is minimized compared to the GC/MS method since there are no interactions with a GC stationary phase.
- GC conditions are not critical; no need to worry about separation.
- Larger amounts of sample can be injected than in the GC/MS method; no GC column overloading.

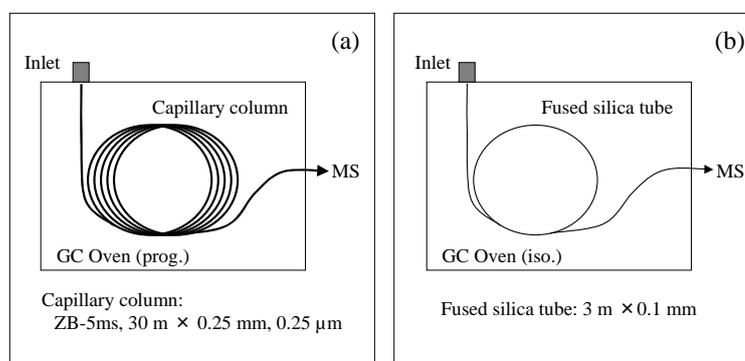
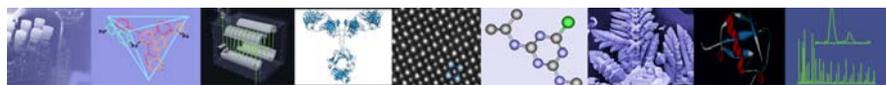


Fig.1 Schematic diagrams of sample introduction system by using GC, (a) capillary GC/FI (b) blank tube inlet/FI.



Results and Discussion

The results are shown in Fig. 2 and 3. The mass spectra in Fig. 3 were generated by summing the spectra in the time ranges shown by the arrows in Fig. 2.

With GC/FI, the analysis took 25 minutes although each component can be examined in detail due to the separation. FD and the blank tube inlet / FI do not provide separation but the analysis times were very short---both within 1 minute.

By comparing the spectra from the 3 methods, blank tube inlet / FI detected:

- 1) Low boiling point components ($n\text{-C}_{18}\text{H}_{38}$ (m/z 254) and smaller) that were missing in FD
- 2) High boiling point and trace components that were missing in GC/FI.

For group-type analysis in which parameters such as relative abundance and average molecular weight for each type are obtained, the m/z 's and the 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 the short analysis time, better detectability of low boiling point components than FD, and better detectability of high boiling point and trace components than GC/FI. Additionally, this technique can handle larger sample injections than GC which is well suited for FI whose ionization efficiency is lower than EI.

Reference

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

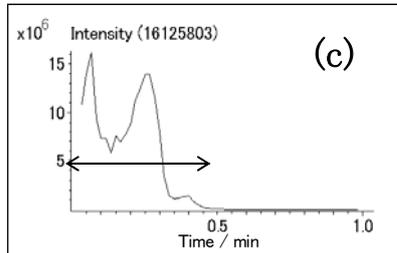
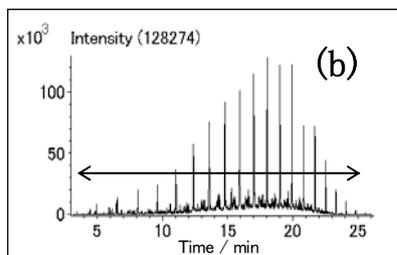
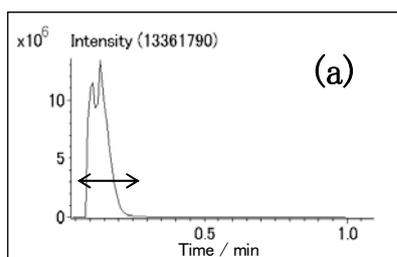


Fig.2 TICs of diesel oil
(a) blank tube inlet/FI,
(b) capillary GC/FI, (c) FD

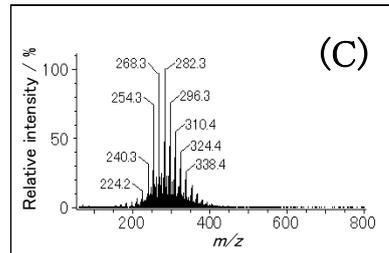
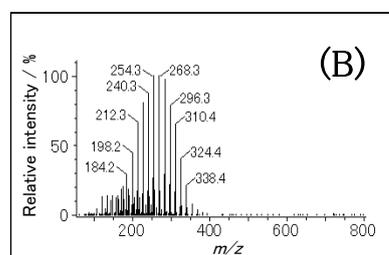
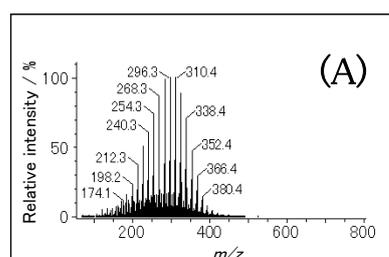


Fig.3 Mass spectra of diesel oil
(A) blank tube inlet/FI,
(B) capillary GC/FI, (C) FD