Usefulness of backflush combined with Smart Pre-Column in pyrolysis-GC/MS measurements

[Background] Pyrolysis (Py-) GC/MS has a challenge: high-boiling-point compounds produced by pyrolysis tend to remain in the separation column, requiring column cleanup by bakeout. To minimize such contamination, it is best to prevent high-boiling-point compounds from entering the separation column. Effective strategies would be the use of a pre-column and backflush (BF) using a Multi-Functional Splitless Sampler (MFS-2015E). BF can significantly reduce measurement time while preventing the compounds with higher-boiling-points than the target analytes from entering the separation column. The use of Smart Pre-Column (SMC) without a coated stationary phase allows to retain high-boiling-point compounds in the pre-column. The absence of a stationary phase in SMC is expected to facilitate rapid removal of retained compounds by BF. In this note, the usefulness of BF combined with SMC was evaluated for the high-density polyethylene (HDPE) pyrolysis, where high-boiling-point compounds were first trapped in the SMC, followed by BF, and the reproducibility of peak areas of the target compounds was examined.

[Experimental] For measurements, a Multi-Shot Pyrolyzer (EGA/PY-3030D) was used, directly interfaced to the GC inlet of a GC/MS system . One end of the SMC was connected to the GC inlet, and the other end was connected to the splitter of MFS-2015E, which was then connected to a separation column (UA5-30M-0.25F) and a mass detector (Fig.1). The insert tube packed with α-alumina with particle diameter of 0.5 mm was used for the injector. About 0.3 mg of HDPE was put in an Eco-Cup LF and was pyrolyzed at 600 ºC. Pyrograms were obtained under two conditions: without BF and with BF at 8, 10, and 12 min after the start of the measurement.

[Results] Pyrograms obtained by BF are shown in Figs. 2 (a)-(c). Without BF, high-boiling compounds up to C44 were detected. However, when BF was started 8 min after the start of the measurement, up to C25 was detected, at 10 min up to C30, and at 12 min up to C36. When analyzing polymers (polyethylene, polypropylene, polystyrene, polyvinyl chloride, polycarbonate, polymethyl methacrylate, polyethylene terephthalate, nylon 6, nylon 66, acrylonitrile-butadiene-styrene resin, styrene-butadiene rubber, and polyurethane) that are produced in large quantities and are primarily targeted in microplastics analysis, the optimal BF time was determined to be 10 min, in which styrene trimer, the pyrolyzate with the longest retention time, is reliably detected, while analysis duration is minimized. To assess the effect of BF on reproducibility, methyl stearate was added as an internal standard (ISTD) for HDPE pyrolysis (Fig. 3), and the ratio of the total peak area of the diene and monoene peaks in the hydrocarbon EIC (*m/z* 82) to the peak area of the ISTD EIC (*m/z* 298) was evaluated. The reproducibility (*n*=4) in the range of C14 to C29 was less than 2 % RSD, confirming that quantitative analysis can be performed with high accuracy.

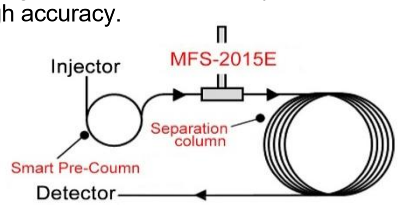

Fig. 1 Connection diagram of Smart Pre-Column, MFS-2015E Splitter, and separation column.

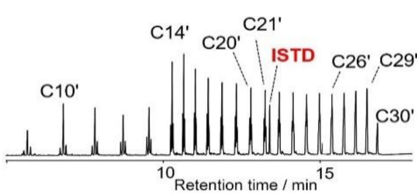

Fig. 3 Typical pyrogram of ISTD added HDPE obtained in reproducibility measurement.

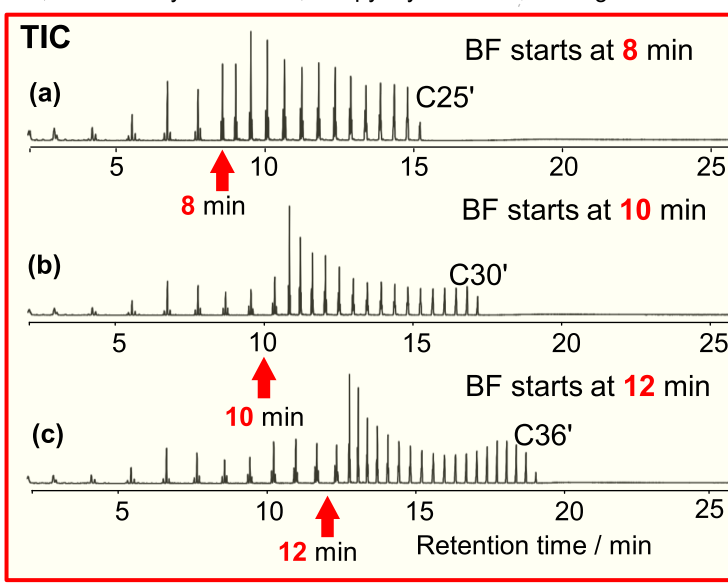

Fig. 2 Pyrograms of HDPE - (a) BF start time: 8 min, (b) BF start time: 10 min, and (c) BF start time: 12 min.

Furnace temp.: 600 ºC, GC injector temp.: 300 ºC, Split ratio: 1/50,
Injector pressure: Constant pressure (75 kPa) for Fig. 2, Constant flow rate for Fig. 3,
GC oven temp.: 40 (2 min hold) - 350 ºC (20 ºC/min, 12.5 min hold),
Pre-column: UADTM-2M (*L*=2.0 m, i.d.=0.25 mm),
Separation column: UA+-5 (5 % diphenyl 95 % dimethylpolysiloxane ; *L*=30 m, i.d.=0.25 mm, df=0.5 μm),
MS scan range: *m/z* 29 - 600, Sample amount: ca. 0.3 mg.

Keywords : Smart pre-column, Backflush, High boiling compounds

Products used : Multi-Functional Pyrolyzer, Auto-Shot Sampler, Multi-Functional Splitless Sampler, Vent-free GC/MS Adapter, Smart Pre-Column, Eco-Cup LF

Applications : Polymeric materials analysis

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