

High-sensitivity detection of polystyrene by F-Splitless Py-GC/MS using Multi-Functional Splitless Sampler

Part 4 LOD, LOQ, and S/N of polystyrene pyrolyzates

[Background] In the previous note (PYA1-156E), the F-Splitless method was found to exhibit a fairly good linearity in the calibration curves. In this note, the detection limit ($LOD=3\sigma/a$), quantification limit ($LOQ=10\sigma/a$), and signal-to-noise ratio (S/N) were explored using the peak areas obtained from the extracted ion chromatograms (EICs) of styrene monomer (S; m/z 104) and trimer (SSS; m/z 91) found in the pyrolyzates of PS. LOD and LOQ were calculated from the slope (a) of the straight line of the calibration curve and the standard deviation (σ) at the lowest concentration.

[Experimental] Employing the previously described methods (PYA1-154E), PS was measured by Py-GC/MS using split and F-Splitless injection methods. Also, blank measurements were made by introducing an empty Eco-Cup into the furnace.

[Results] EICs for S obtained by F-Splitless injection method in a scan mode are shown in Fig. 1. A trace peak of S was also detected in the blank run. In addition, peaks of hexamethyl-cyclotrisiloxane (D3) and octamethylcyclotetrasiloxane (D4) were observed. Both D3 and D4 may originate from the septum, since the septum purge is turned off to prevent pyrolyzates from venting during the cryo-trapping of pyrolyzates in the F-Splitless injection method. The LOD and LOQ obtained from the slope and standard deviation of each calibration curve (PYA1-156E) are summarized in Table 1. The F-Splitless injection method (scan mode) afforded an LOQ for SSS 32 times higher than that of the split method (split ratio: 1/50). In the case of the F-Splitless injection method (SIM mode), the LOD and LOQ of PS determined from the peak area of S were 17 pg and 56 pg, respectively, comparable to those obtained in the scan mode. The S/N values of S and SSS peaks in EICs are shown in Fig. 2. In the F-Splitless method, the S/N values of the S and SSS peaks were 570 and 22, respectively, in SIM mode with 100 pg of sample, which are 7 times larger than the S/N values in the scan mode. Based on the LOQ criterion of $S/N=10$, the F-Splitless injection method (SIM mode) allows the quantification of 1.8 pg of PS using the S peak. In contrast, pyrolysis of styrene-containing polymers such as ABS and SBR also forms S. To distinguish PS from other styrene-containing polymers, SSS can be an indicator compound. In Fig. 2, the S/N of the SSS peak generated by the pyrolysis of 100 pg of PS is 22, corresponding to a LOQ of 45 pg of PS. These results indicate that the F-Splitless injection method is capable of detecting pyrolyzates with high sensitivity.

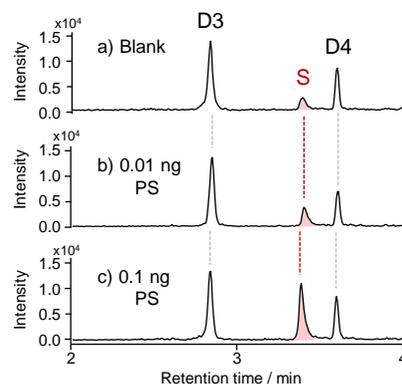


Fig. 1 EICs (m/z 104) for S obtained by F-Splitless injection method (scan mode).

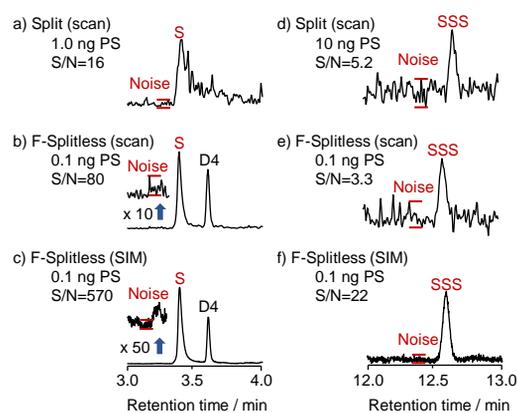


Fig. 2 EICs (S; m/z 104, SSS; m/z 91) of pyrograms obtained by Split and F-Splitless injection methods.

Table 1 LOD ($LOD=3\sigma/a$) and LOQ ($LOQ=10\sigma/a$) of PS based on Split and F-Splitless injection methods.

Injection method		LOD (ng)		LOQ (ng)	
		S	SSS	S	SSS
Split (Split ratio 1/50)	Scan (EIC)	1.75×10^{-1}	2.10	5.82×10^{-1}	6.99
	F-Splitless	1.76×10^{-2}	6.54×10^{-2}	5.88×10^{-2}	2.18×10^{-1}
	SIM	1.67×10^{-2}	3.36×10^{-2}	5.55×10^{-2}	1.12×10^{-1}

* Numerical values represent the peak areas of S and SSS and the data represents the averages of five repetitive measurements.

Reference: K. Tei et al., *J. Anal. Appl. Pyrolysis* 168 (2022) 105707.

Keywords : F-Splitless, Split injection, Secondary reaction, High-sensitivity detection, Microplastics

Products used : Multi-Shot Pyrolyzer, Multi-Functional Splitless Sampler, Auto-Shot Sampler, Eco-Cup LF, Packed GC glass insert, UAMP column kit, Vent-free GC/MS adapter, F-Search MPs 2.1

Applications : Environmental analysis, Trace analysis, General polymer analysis

Related technical notes : PYA1-154E (Part 1), PYA1-155E (Part 2), PYA1-156E (Part 3), PYT-037E, PYT-038E

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