

Effect of hydrogen carrier gas on Py-GC/MS analysis of polymers

Part 3 Library search using existing database

[Background] Hydrogenation of unsaturated pyrolyzates can occur during the pyrolysis of the polymer in a hydrogen (H₂) atmosphere and may also occur during the ionization process in the MS ion source. The effects on high density polyethylene (HDPE) are negligible (PYA4-007E, PYA4-008E). On the other hand, there is a concern that pyrograms and mass spectra obtained in a hydrogen atmosphere may differ from helium-based data which is routinely used to compile the MS libraries and the difference may affect the library search results when using the existing databases. This report extends the previous study to other types of polymers. In addition to HDPE, the match quality in library search is examined using pyrograms of polystyrene (PS), polycarbonate (PC), styrene-butadiene rubber (SBR) obtained under H₂ carrier gas.

[Experimental] 100 µg of HDPE, PC and SBR was each placed in a sample cup. In the case of PS, 5 µL of the solution (50 mg in 10 mL of dichloromethane) was used. Samples were analyzed using a Multi-Shot Pyrolyzer (EGA/PY-3030D) which was directly interfaced to the split injector of a GC instrument. A metal capillary column (Ultra ALLOY⁺-5, 5% diphenyl 95% dimethylpolysiloxane, L=30 m, i.d.=0.25 mm, df.=0.25 µm) was used as a separation column. He and H₂ were used as carrier gases and the column flow rate for all tests was fixed at 1 mL/min. The sample was pyrolyzed at 600°C and pyrolyzates were analyzed by GC/MS. Polymers were identified using F-Search. The searchable database was compiled using data generated in a helium atmosphere.

[Results] The pyrograms of HDPE, PS, PC and SBR obtained in a H₂ atmosphere were processed using F-Search. The results are summarized in Table 1. The match quality for all candidates in all four polymers, is ≥ 95%. The library search results indicate that the effect of the hydrogenation of the pyrolyzates is negligible for the polymers investigated. The major pyrolyzates are not altered and therefore the summation mass spectra of the major peaks are not affected.^{1,2)}

Table 1 Library search results (F-Search) of pyrograms using existing polymer library

HDPE					PC				
He carrier gas			H ₂ carrier gas		He carrier gas			H ₂ carrier gas	
No.	Candidate	Match Q. (%)	Candidate	Match Q. (%)	No.	Candidate	Match Q. (%)	Candidate	Match Q. (%)
1	HDPE (C1-C40)	99	HDPE (C1-C40)	99	1	PC (solvent method)	95	PC (solvent method)	98
2	HDPE* (C1-C20)	99	HDPE* (C1-C20)	99	2	PC (melt method)	94	PC (melt method)	91
3	PE, oxidized	98	PE, oxidized	98	3	PC (thermally stabilized)	83	PC (C1-40)	90

PS					SBR				
He carrier gas			H ₂ carrier gas		He carrier gas			H ₂ carrier gas	
No.	Candidate	Match Q. (%)	Candidate	Match Q. (%)	No.	Candidate	Match Q. (%)	Candidate	Match Q. (%)
1	PS(C1-C40)*	99	PS (C1-C20)*	99	1	SBR (C1-C20)*	96	SBR (C1-C20)*	97
2	PS(C1-C20)	99	PS (C1-C10)	99	2	SBR (C1-C40)	96	SBR (C1-C40)	97
3	PS(C1-C40)*	99	PS (C1-C20)*	99	3	SBR (C1-C20)*	93	SBR (C1-C10)	95

* Same polymer obtained from different sources.

¹⁾ Reproduced from A. Watanabe, *et al.*, *Anal. Chem.*, **88** (2016) 5462–5468

²⁾ [F-Search System catalog](#)

Keywords : H₂ carrier gas, Hydrogenation, Py-GC/MS, HDPE, PS, PC, SBR, F-Search, Library search, Match quality

Products used : Multi-functional pyrolyzer, Auto-Shot Sampler, UA⁺-5

Applications : General polymer analysis

Related technical notes : [PYA4-007E](#), [PYA4-008E](#)

Please forward your inquiries via our web page or send us a fax message.

R&D and manufactured by :
Frontier Laboratories Ltd.

Phone: (81)24-935-5100 Fax: (81)24-935-5102
<http://www.frontier-lab.com/>