Reproducibility in pyrolysis GC/MS of trace solid polymers

- Particle size of polyethylene terephthalate and the reproducibility -

[**Background**] In pyrolysis (Py)-GC/MS, it has been reported that reproducibility varies with sample's form and the higher reproducibility is observed for thin films or fine powders.[1)] In recent years, there has been a growing interest for microplastic analysis. However, due to significant variations in sample size and smaller sample amounts compared to typical Py-GC/MS measurements, it is necessary to investigate how these factors impact the reproducibility of pyrograms. In this report, repeated measurements of small amounts of polyethylene terephthalate (PET) with various particle sizes were conducted to examine the pyrogram reproducibility.

[**Experimental**] For the measurements, in addition to commercial PET powder (35 µm, Group A), PET powders were prepared by cryo-grinding PET pellets using IQ MILL-2070. Then, the ground powders were sieved by particle size through different meshes and classified as Group B (a particle size of 106 µm or less) and Group C (a particle size of 106-280 µm). 10 µg of the powder from each group was put in a sample cup and subjected to Py-GC/MS measurement at 600 ºC. In the pyrogram of PET, three prominent peaks are observed (Fig. 3), and the peak area ratios of **2** to **1** and **3** to **1** were calculated, and the reproducibility was obtained by repeated measurements.

[**Results**] The peak area ratios by particle size and their reproducibility (n=5) are summarized in Table 1. It was observed that the smaller the particle size, the smaller the RSD values. This may be because as the particle size becomes larger, the thermal conductivity becomes less, resulting in the less reproducibility of pyrograms. From the above, even with a trace amount of PET, it is found that the particle size impacts the reproducibility in pyrolysis, and that the smaller the particle size is, the better the reproducibility is.

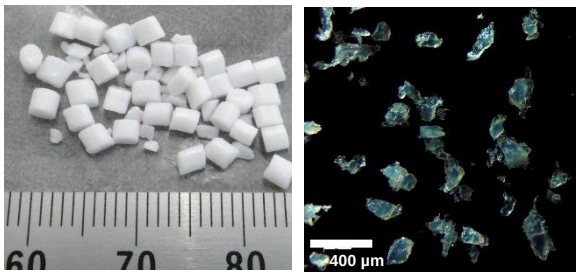

Fig. 1 PET sample before and after grinding.

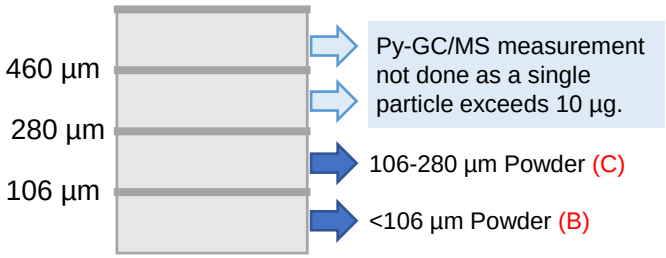

Fig. 2 Classification by sieving.

Rotation speed: 3000 rpm, Grinding duration: 10 s, No. of cycles: 1, Grinding ball: tungsten carbide sphere (12Φ), Grinding temp.: cryogenic, Grinding aid: none, Sample amount: 0.5 g

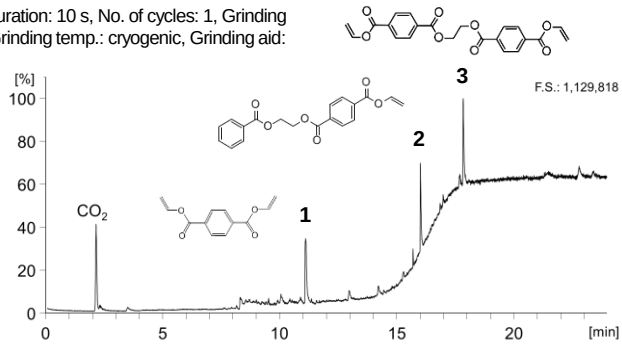

Fig. 3 Pyrogram of PET.

Furnace temp.: 600 ºC, GC injector temp.: 300 ºC, GC oven temp.: 40 ºC (2 min) - 320 ºC (20 ºC/min, 8 min hold), Separation column: UA$^+$-5 (5 % diphenyl-95 % dimethylpolysiloxane, L=30 m, i.d.=0.25 mm, df=0.5 µm), Column flow rate: 1.0 mL/min, Split ratio: 1/50, MS scan range: m/z 29 - 450, Sample amount: 10 µg (weighed by an ultramicrobalance).

Table 1 Peak area ratio and the reproducibility by PET particle size (n=5).

PET particle size	A: 35 µm		B: <106 µm		C: 106~280 µm	
	Peak area ratio	RSD [%]	Peak area ratio	RSD [%]	Peak area ratio	RSD [%]
Peak **2** / Peak **1**	**78.8**	**2.66**	**80.4**	**3.22**	**74.6**	**6.30**
Peak **3** / Peak **1**	**85.0**	**2.91**	**85.9**	**4.93**	**84.3**	**5.35**

Keywords : Powdering, Microanalysis, Pulverization, Cryogenic grinding, Microplastics, MPs

Products used : Cryogenic Mill, Multi-Shot Pyrolyzer, Auto-Shot Sampler, UA+-5, Eco-Cup LF, F-Search, Vent-free GC/MS Adapter

Applications : General polymer analysis, Microplastic analysis

Related technical notes : PYT-039E, PYT-018E[1)]

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
www.frontier-lab.com