

# Sample preparation with TMAH using Eco-cup (Sandwich method) in reactive pyrolysis

**[Background]** Sample preparation techniques used when performing reactive pyrolysis GC have been reported by Otani et al.<sup>1)</sup> Researchers have reported that when more than a few  $\mu\text{L}$  of a methanolic solution of TMAH reagent is added to a sample cup (Eco-cup), some of the sample and reagent wicks up and out of the cup. This not only has an adverse effect on the analytical accuracy but it also leaves a sticky film on the outer surface of the cup. A sticky cup does not 'free fall' properly nor does it eject smoothly when an Auto-Shot Sampler is being used. The wicking can be eliminated by adsorbing the TMAH on a piece of glass fiber filter<sup>2)</sup>. The so-called "sandwich" method uses disc-shaped quartz filters coated with carbon powder (average particle diameter  $15\ \mu\text{m}$ ) and a TMAH solution mixed with carbon power as shown in Figure 1. This report demonstrates that the "sandwich" technique is suitable for use when doing reactive pyrolysis. Sticking problems encountered with the Auto shot sampler are eliminated and data quality is, in no way, compromised.

**[Experimental]** The carbon-coated filter paper was made by dipping disc-shaped quartz filters (diameter 4 mm, thickness 0.1 mm) into methanol containing 5 wt% carbon powder. The filters are then dried. The TMAH/carbon mixture in methanol was prepared by adding 30 wt% of carbon powder to 25 wt% TMAH. The sample (Fig. 2) was 50  $\mu\text{g}$  (60 mesh powder) of the three-dimensional copolymer liquid crystal polyester (LCP) prepared from p-hydroxy benzoic acid (PHB), terephthalic acid (TA), and biphenol (BP) in a 2/1/1 ratio. Fig. 1 shows that the one sample was prepared by sandwiching the LCP sample between two carbon-coated filter papers. 4  $\mu\text{L}$  of TMAH solution was added to the sample and to the upper filter paper. For comparison, a second sample was prepared by adding 1  $\mu\text{L}$  of the TMAH reagent to an Eco-cup containing 50  $\mu\text{g}$  of the LCP sample. Both samples were analyzed using reactive pyrolysis GC at 400°C. All analysis were done using the Auto-Shot Sampler.

**[Results]** Fig. 3 shows that methyl p-methoxybenzoate (MMB), dimethyl phthalate, and 4,4-dimethoxybiphenyl (DMB) are present when the sample is prepared using either the "sandwich" or conventional method. The composition ratios, recovery and relative standard deviation (RSD) are summarized in Table 1. The composition ratio (2/0.99/0.93) was close to the original ratio and the recovery was almost the same as that obtained using the conventional method. The %RSD in both sets of data was less than 4% in most cases, the "sandwich" data is more precise than the data obtained using the conventional methodology. The "sandwich" method not only provides high quality data but also appears to be more practical. Up to 5  $\mu\text{L}$  of TMAH reagent can be used without the reagent wicking up and out of the sample cup.; common problem when using the with Auto-Shot Sampler.

- 1) H. Ohtani et al., *J. High. Res. Chromatogr.*, **14**,388(1991)
- 2) Honda et al., *Polymer Anal. Char*, **14**, Nov. 2009

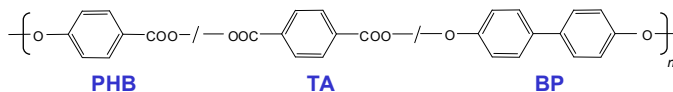


Fig. 2. Structure of LCP

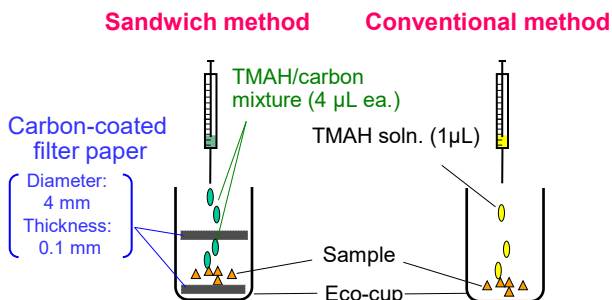


Fig. 1. Sample preparation methods

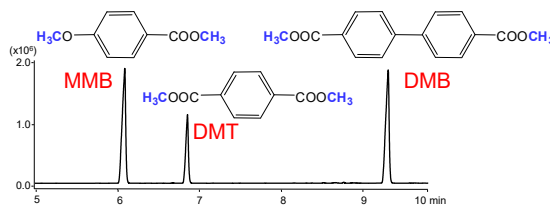


Fig. 3. Pyrogram

Pyrolysis temp.: 400 °C, GC oven: 100 – 280 °C ( 20 °C/min ), separation column: Ultra ALLOY-5 ( 5 % diphenyl 95 % dimethylpolysiloxane, L = 30 m, i.d. = 0.25 mm, df = 0.25  $\mu\text{m}$  ), column flow rate: 1 mL/min, He, split ratio: 1/50, sample: 50  $\mu\text{g}$

Table 1. Results by sandwich and conventional methods (starting LCP ratio=2/1/1)

|                                      | Composition ratio |      |      | Recovery(%)<br>(this method = 100) |     |     | RSD(%) |     |     |
|--------------------------------------|-------------------|------|------|------------------------------------|-----|-----|--------|-----|-----|
|                                      | MMB               | DMT  | DMB  | MMB                                | DMT | DMB | MMB    | DMT | DMB |
| Sandwich method                      | 2                 | 0.99 | 0.93 | 100                                | 100 | 100 | 1.1    | 3.8 | 1.9 |
| Conventional (TMAH 1 $\mu\text{L}$ ) | 2                 | 0.89 | 1.03 | 95                                 | 81  | 109 | 1.0    | 4.8 | 2.8 |

**Keywords :** Quartz filter paper, Reactive pyrolysis, TMAH, Sample preparation, Carbon-coated filter paper, sandwich method, Auto-shot sampler

**Products used :** Multi-functional pyrolyzer, Auto-Shot Sampler, Vent-free GC/MS adapter, UA-5, Auto-Rx Disc

**Applications :** Sample preparation, Polymer analysis, Reactive pyrolysis

**Related technical notes :** PYA2-026E

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