

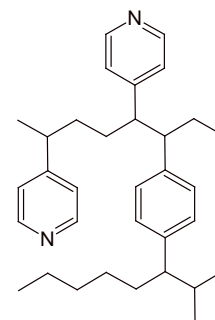
## Ion Exchange Resin Analysis by using Pyrolysis-GCxGC-MS

Product used : Mass Spectrometer (MS)

### 【Introduction】

Recently, we developed a new gas chromatography/high resolution time-of-flight mass spectrometer (GC/HR-TOFMS) system which allows using multiple ionization techniques not only electron ionization (EI) but also field ionization (FI) and photo ionization (PI). PI is a soft ionization technique that provides high sensitivity and molecular ion information for compounds with ionization energies below the maximum practical photon energy (10.8 eV) of the deuterium lamp used in our current design.

In this study, pyrolysis(Py)/GCxGC/HR-TOFMS system was applied to investigate the pyrolysis products of Vinylpyridine and Divinylbenzene copolymer as the ion exchange resin sample.



Vinylpyridine and Divinylbenzene copolymer structure

### 【Result and discussion】

To evaluate the potential of Py/GCxGC technique, we compared the chromatographic peak separation between regular 1DGC and 2DGC. In the 1DGC data, a lot of co-elute components were observed and they were difficult to identify clearly. In 2DGC data, these compounds were separated with 2nd GC dimensions and we observed approximately 600 compounds. Chromatographic peaks of the pyrolysis products were distributed on the TIC chromatogram according to monomer, dimer and trimer regionally.

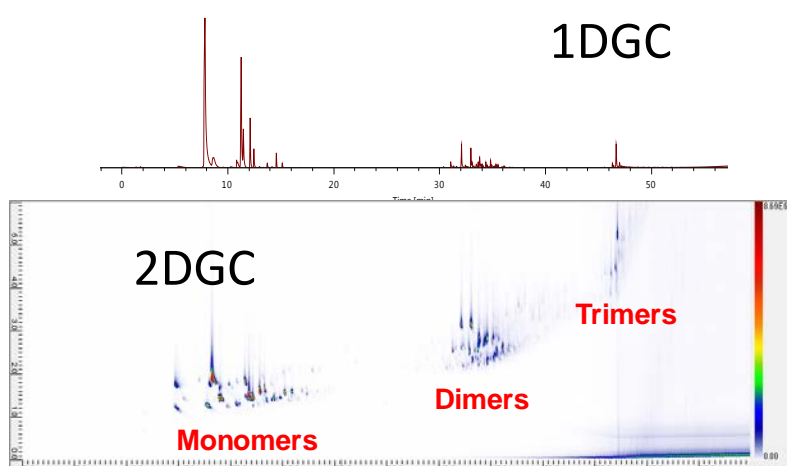


Fig.1 Comparison of the 1DGC and 2DGC TICs

Table 1 Measurement condition

#### 【Pyrolysis condition】

Pyrolysis Temp.: 450 °C

#### 【GCxGC condition】

1st column: Trajan SGE BPX5,  
30m x 0.25mm, 0.25um

2nd column: Trajan SGE BPX50,  
2m x 0.1mm, 0.1um

Oven temp.:  
50 °C (3 min) -> [5 °C/min]  
-> 320 °C (13 min)

Inj. Temp.: 300 °C  
Inj. Mode: Split mode (200:1)  
Column flow: 1.2 mL/min  
Modulation period: 6 sec

#### 【MS condition】

MS: JEOL, JMS-T200GC  
Ion source: EI/PI combination ion source  
Ionization: EI+, 70 eV, 300 uA  
PI+, D2 lamp: 115-400 nm  
(10.8 eV@115 nm)  
Mass range: *m/z* 40-600

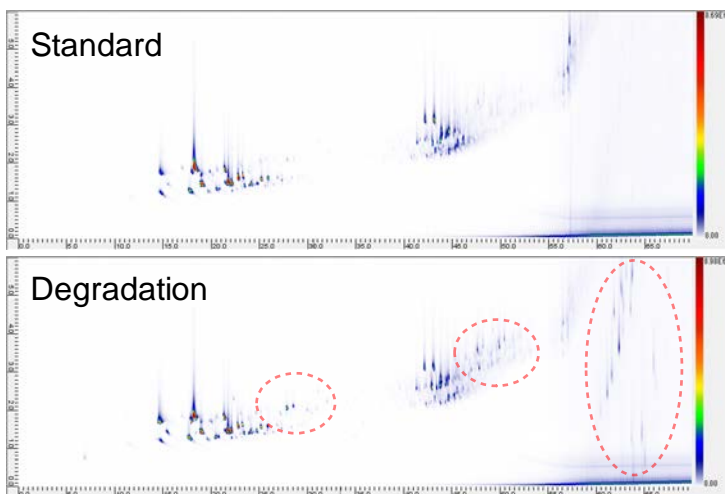


Fig. 2 Comparison of the 2DGC TICCs

In the after degradation sample, many compound were detected higher relative intensity in the longer 1st column retention time. We suspect that un-stable end group copolymers were generated by the thermal degradation under non oxidative condition at 200 °C , and then these compounds were generated from these un-stable end group copolymers.

In the monomer region, we found the Di-alkyl benzene series, Vinyl benzene series and Pyridine series were separated clearly. In the dimer and trimer regions, so many compounds were detected, but they were very difficult to identify by using NIST EI database search only. In this case, we estimated these chemical formulas for the molecular ion detected in PI mass spectra which give molecular ion information mainly as a result of soft ionization technique.

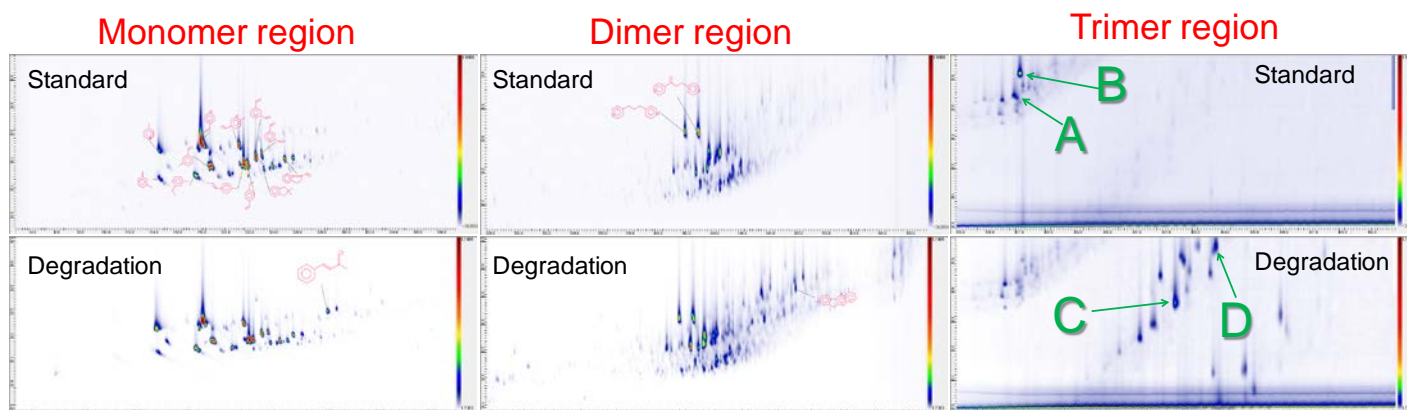


Fig. 3 GCxGC/EI qualitative analysis result

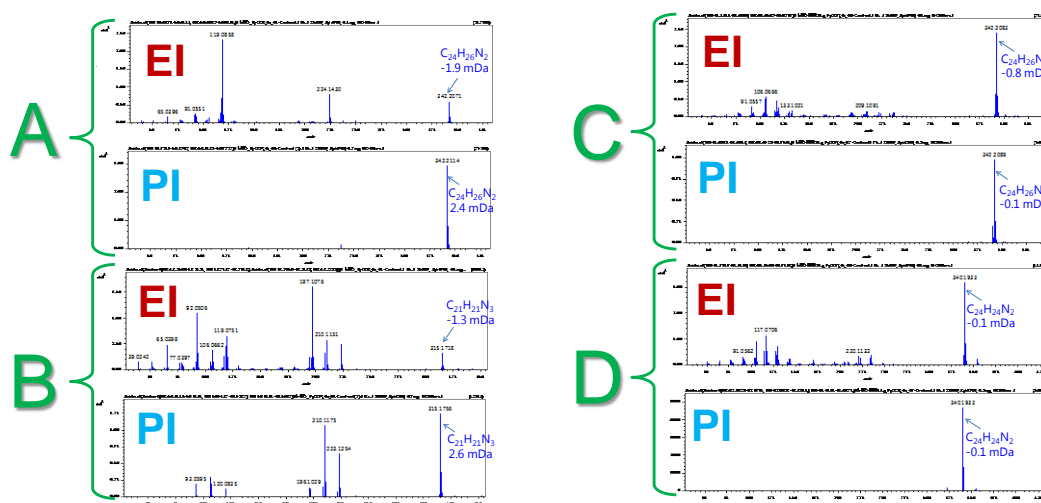


Fig.4 Mass spectra and accurate mass analysis for the compound A , B. C and D on the 2DGC TICC.

### 【Conclusion】

- ❑ GCxGC TIC give an easy interpretation for the differences between standard and degradation sample.
- ❑ EI database search is still first step for the GC/MS qualitative analysis.
- ❑ Soft ionizations and accurate mass analysis is useful for the compound identification.

The combination of PY/GCxGC/HRTOFMS and multiple ionization technique is a quite useful for qualitative analysis of the pyrolysis products of resins.

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