Rubber and Plastic Materials Characterization Using Pyrolysis-GC/MS

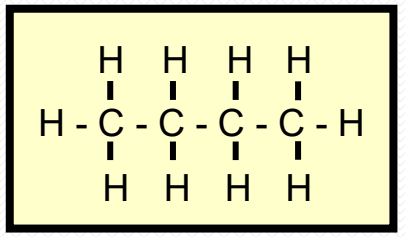
PRESENTED BY

Ratimarth Bunlorm

Pyrolysis?

Pyrolysis and pyrolyzates of polymeric materials

Butane
(MW: 58)



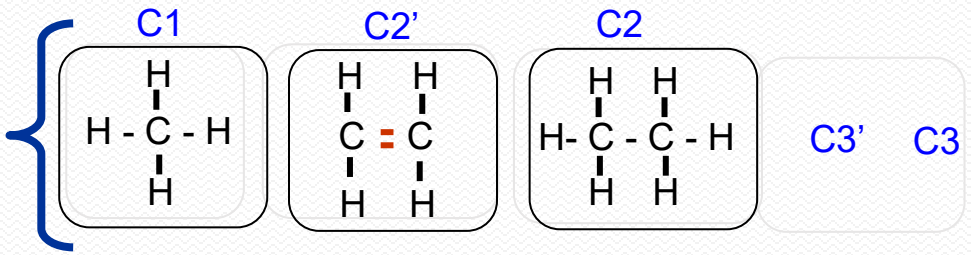
ΔH (Heat energy)

Burn in Air

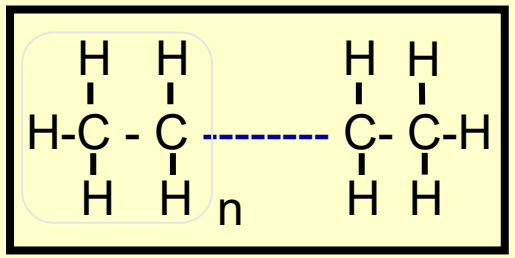
$CO_2 + H_2O$

In He

ΔH
(Heat/Electron)



Polyethylene
(MW: 10,000 ~1,000,000)

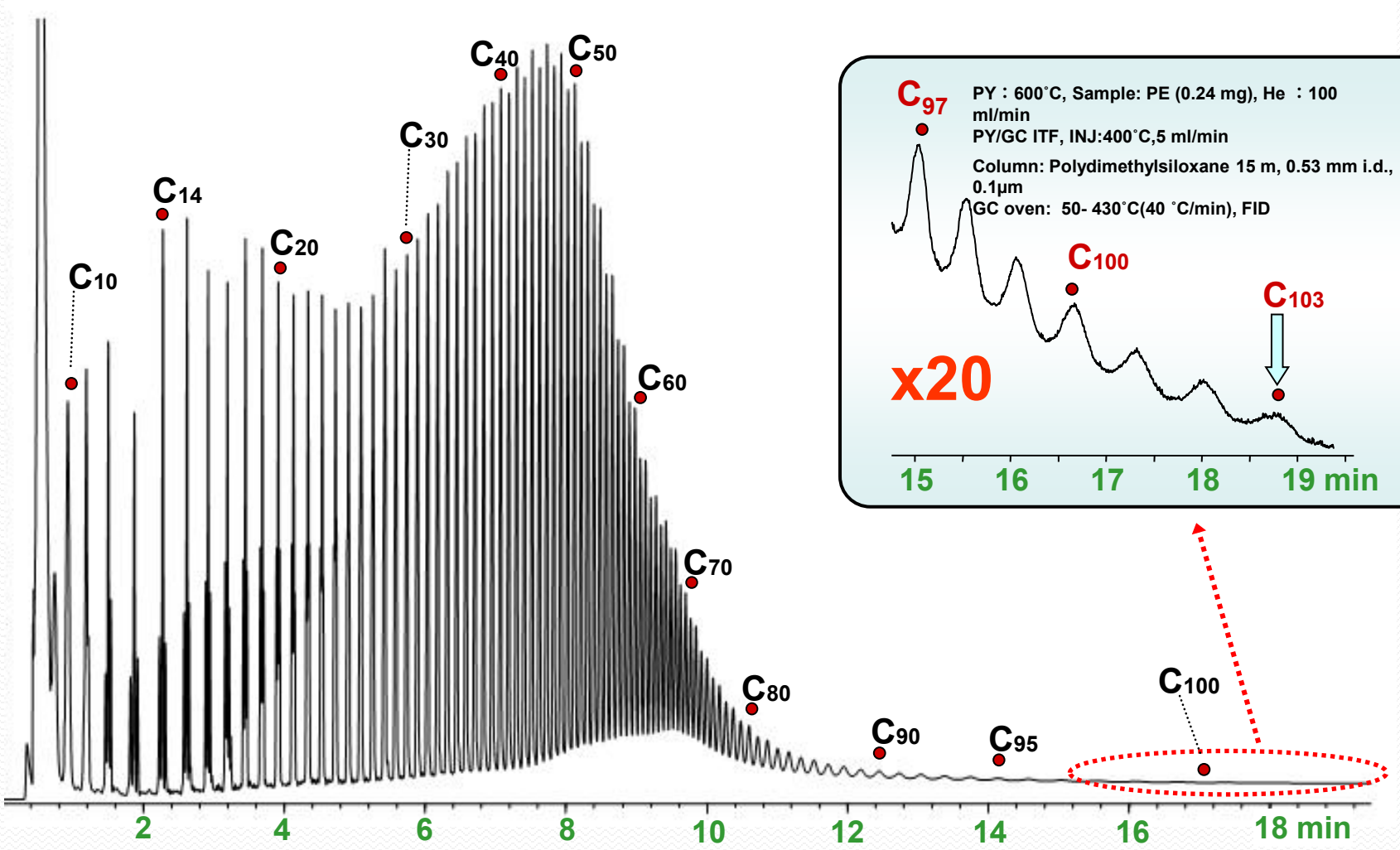


n = 300 ~ 30,000

ΔH
(Heat/Energy)

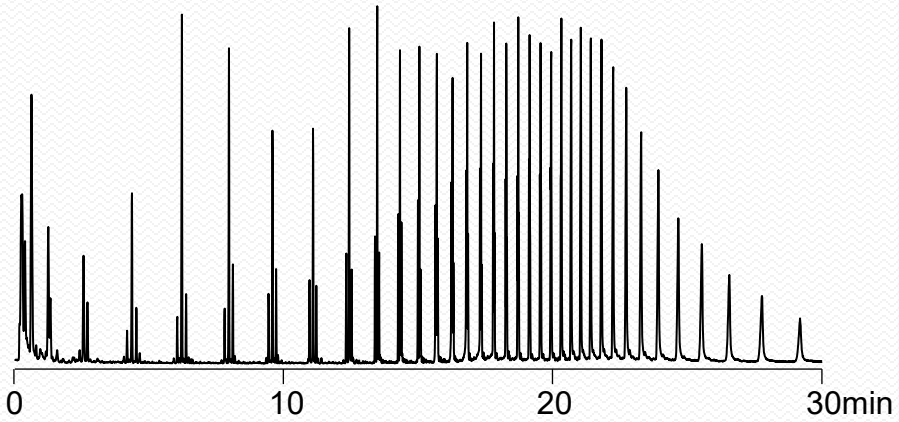
C1, C2',C2, C3',C3
C4', C4" … Cx

Typical pyrogram of polyethylene at 600ºC

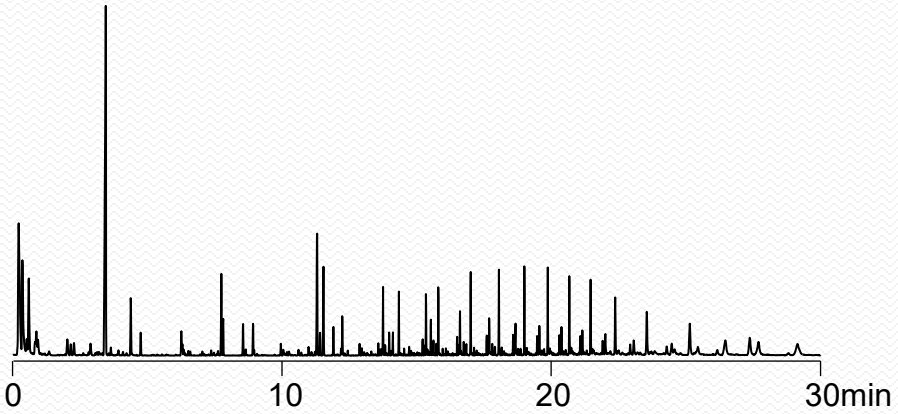


Pyrograms of typical polymers

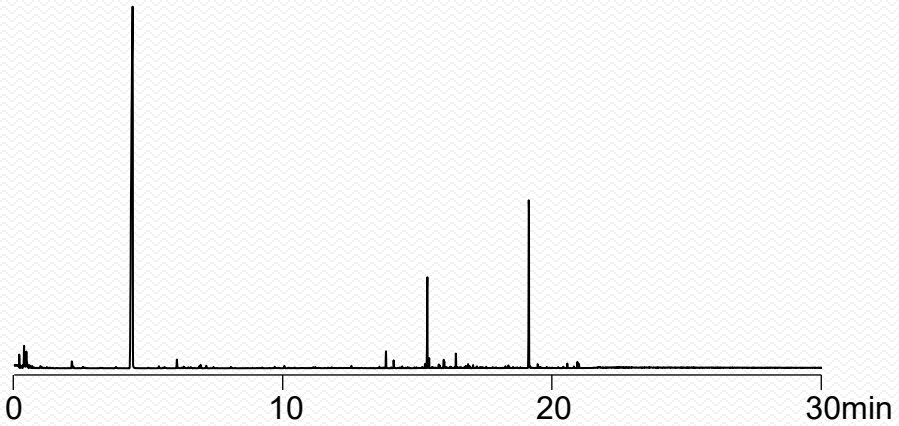
Polyethylene



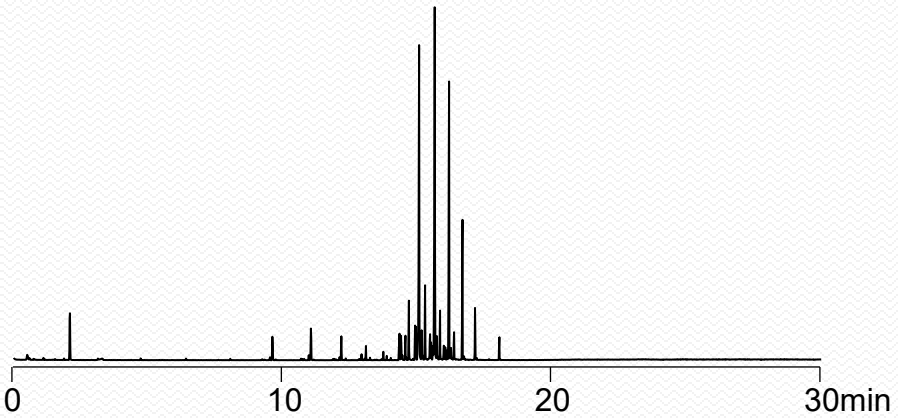
Polypropylene



Polystyrene



Higher methacrylate copolymer

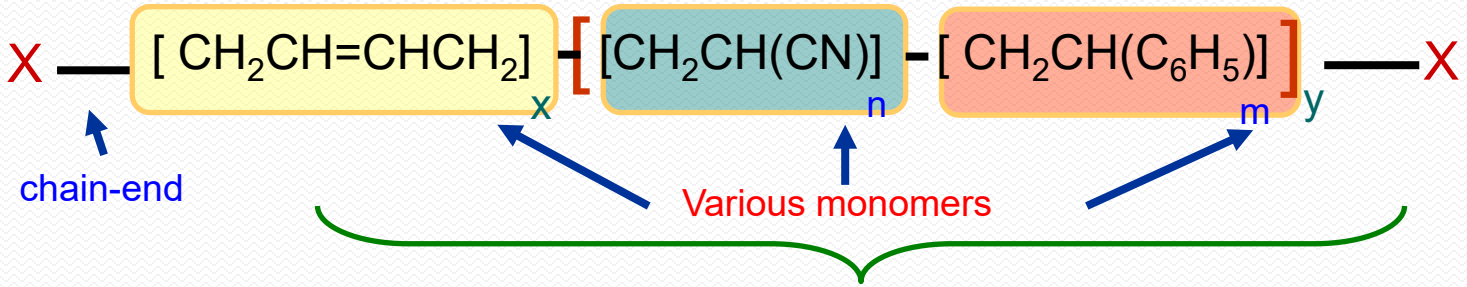


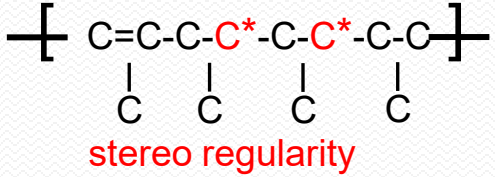
Characterization of Polymers by PY-GC/MS

A: Identification of polymeric materials

Unknown materials (PP/ PVC/ SBR?)

B: Structural characterization of polymers



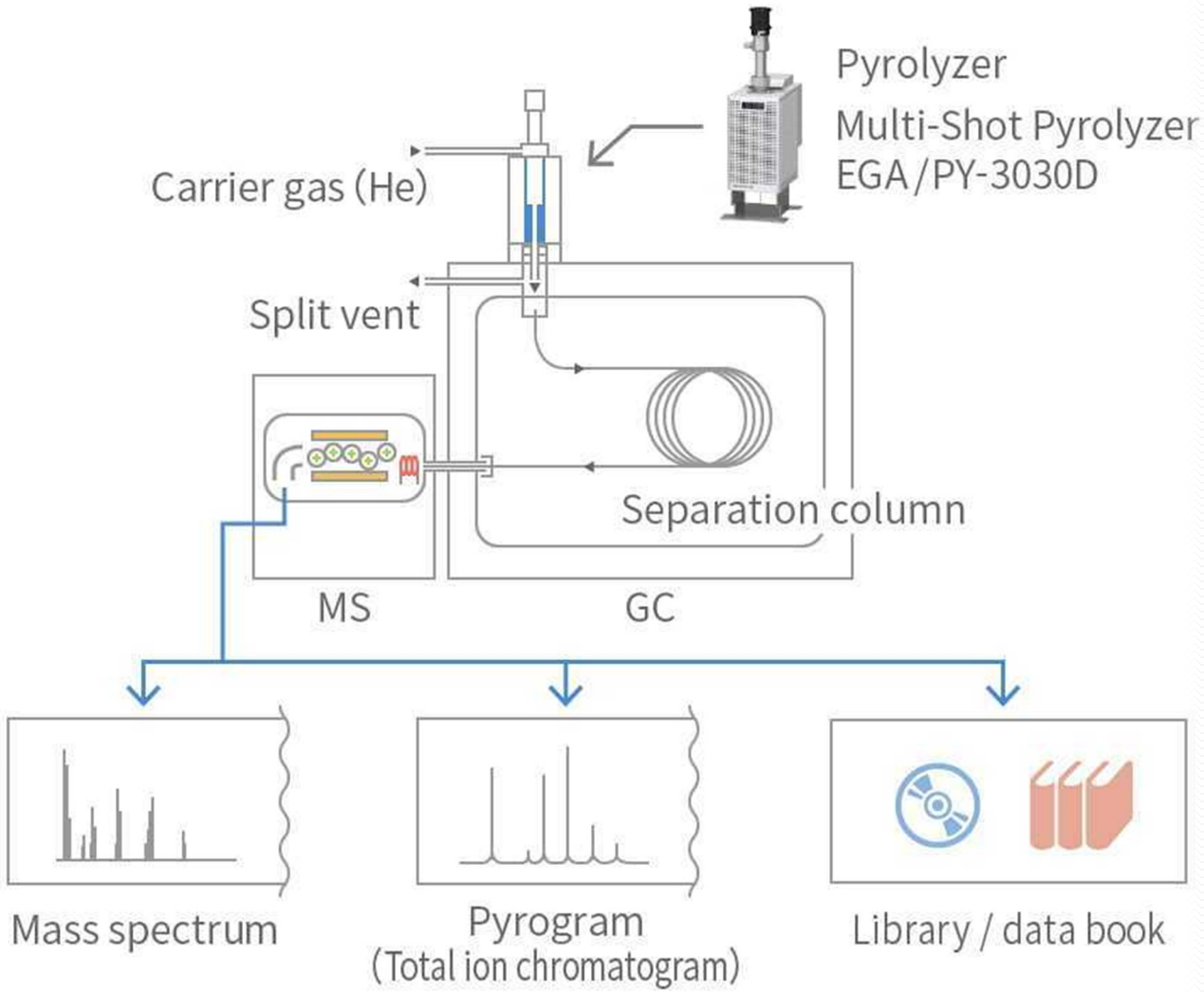


C: Mechanisms and kinetics of polymer degradation

D: Qualitative and quantitative analysis of additives

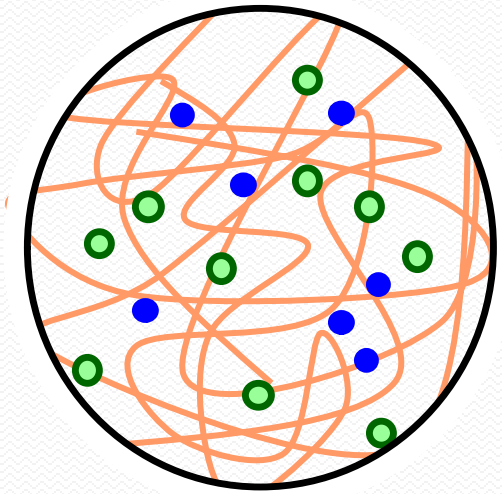
Pyrolysis-GC/MS system and analytical techniques

Configuration of pyrolysis-GC/MS system



Polymeric material and pyrolysis

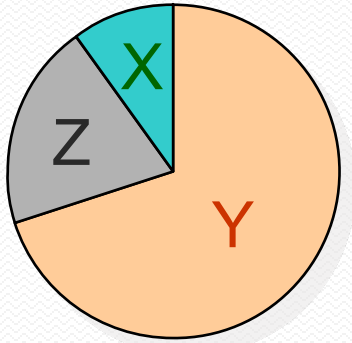
Pattern diagram of
typical polymeric material



: Additives

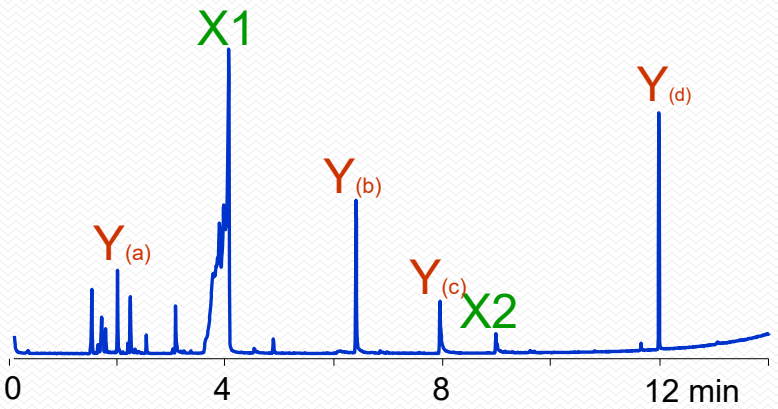
: Polymer

: Inorganics



X: Additives
Y: Polymer
Z: Inorganic

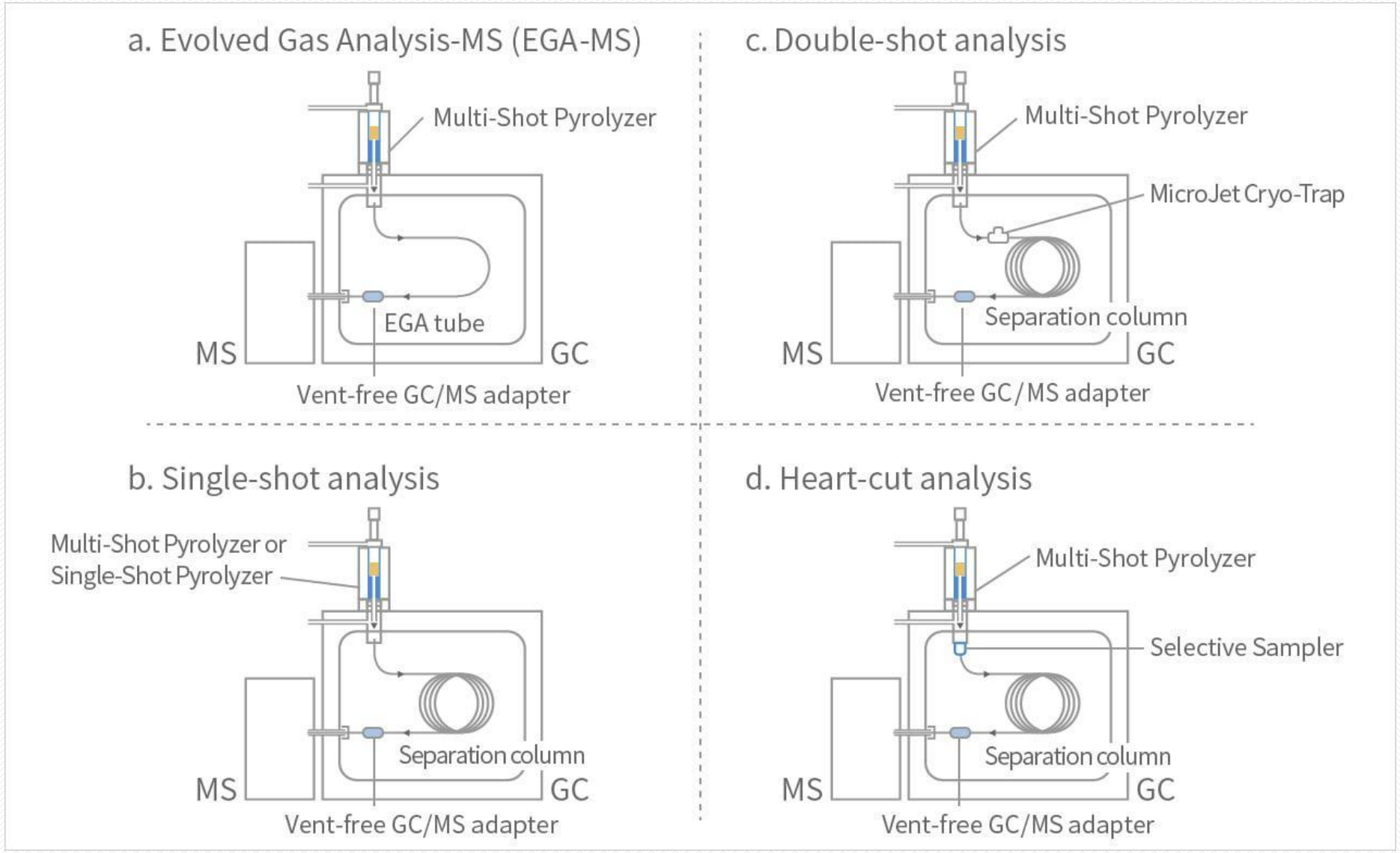
Pyrolysis (Single-Shot)



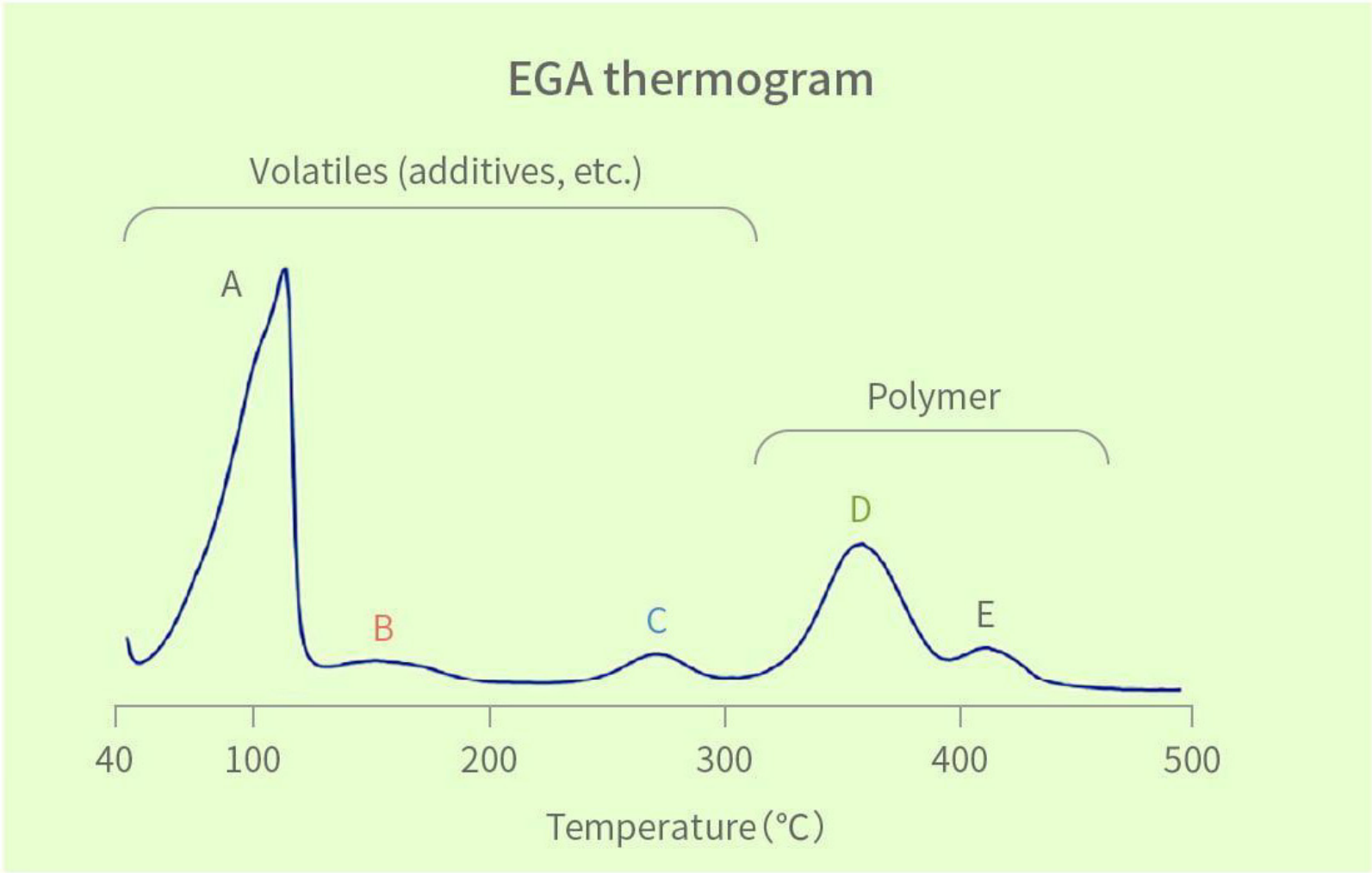
Mixed Information of polymer and volatiles

Sometimes difficult to interpret results !!

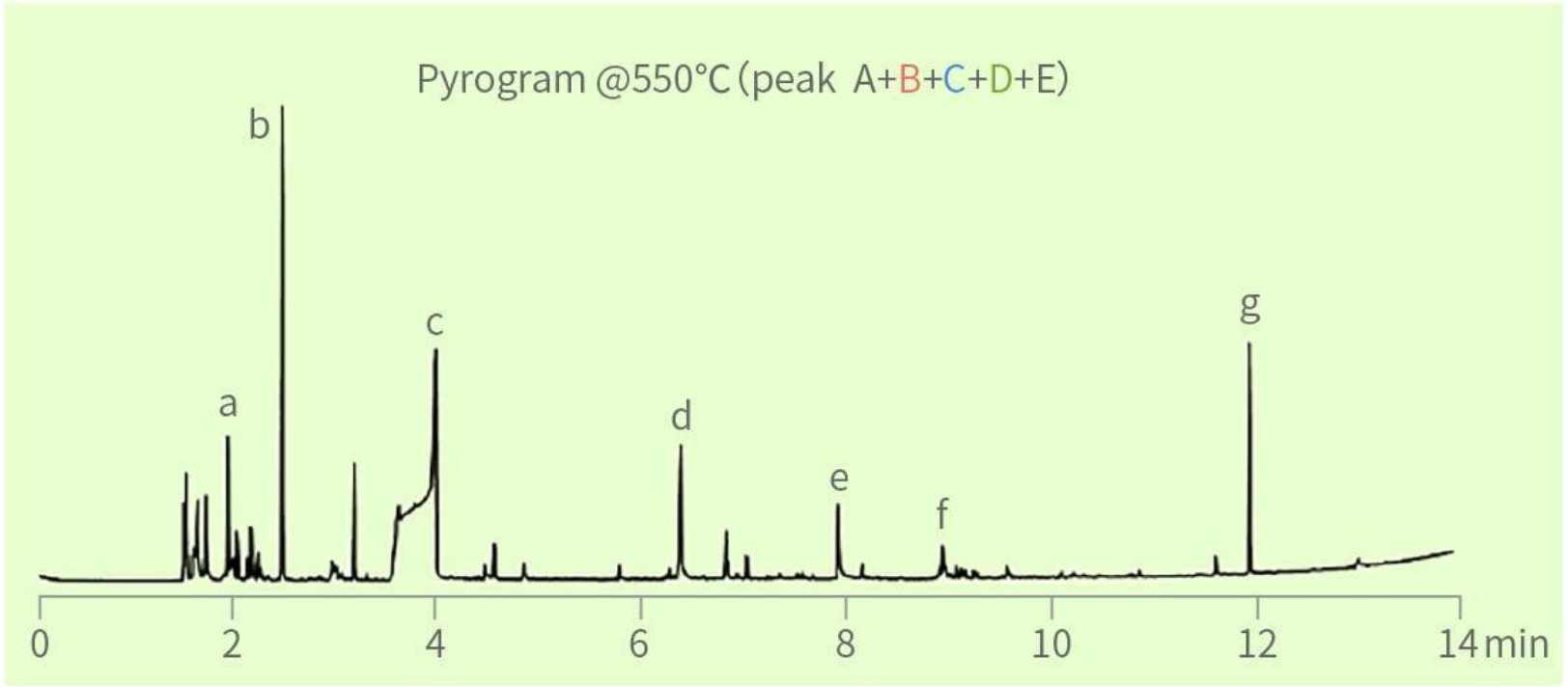
Four analytical techniques



Evolved Gas Analysis (EGA-MS)



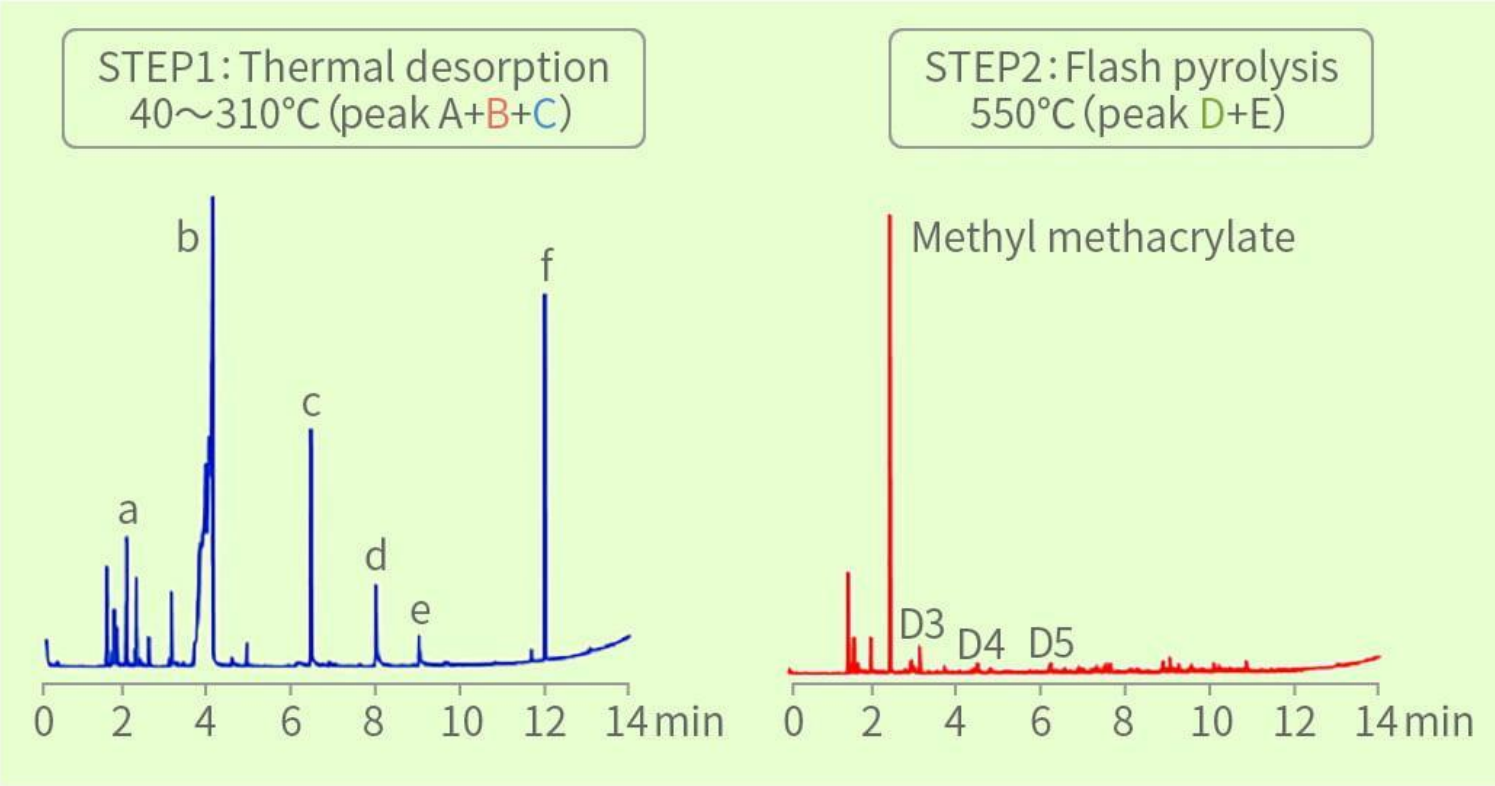
Single-shot analysis



Compound

a. Methyl vinyl ketone
b. Methyl methacrylate
c. 1,3-Butanediol
d. Phenoxyethanol
e. Methyl hydroxybenzoate
f. Propyl hydroxybenzoate
g. 2-Ethylhexyl fumarate

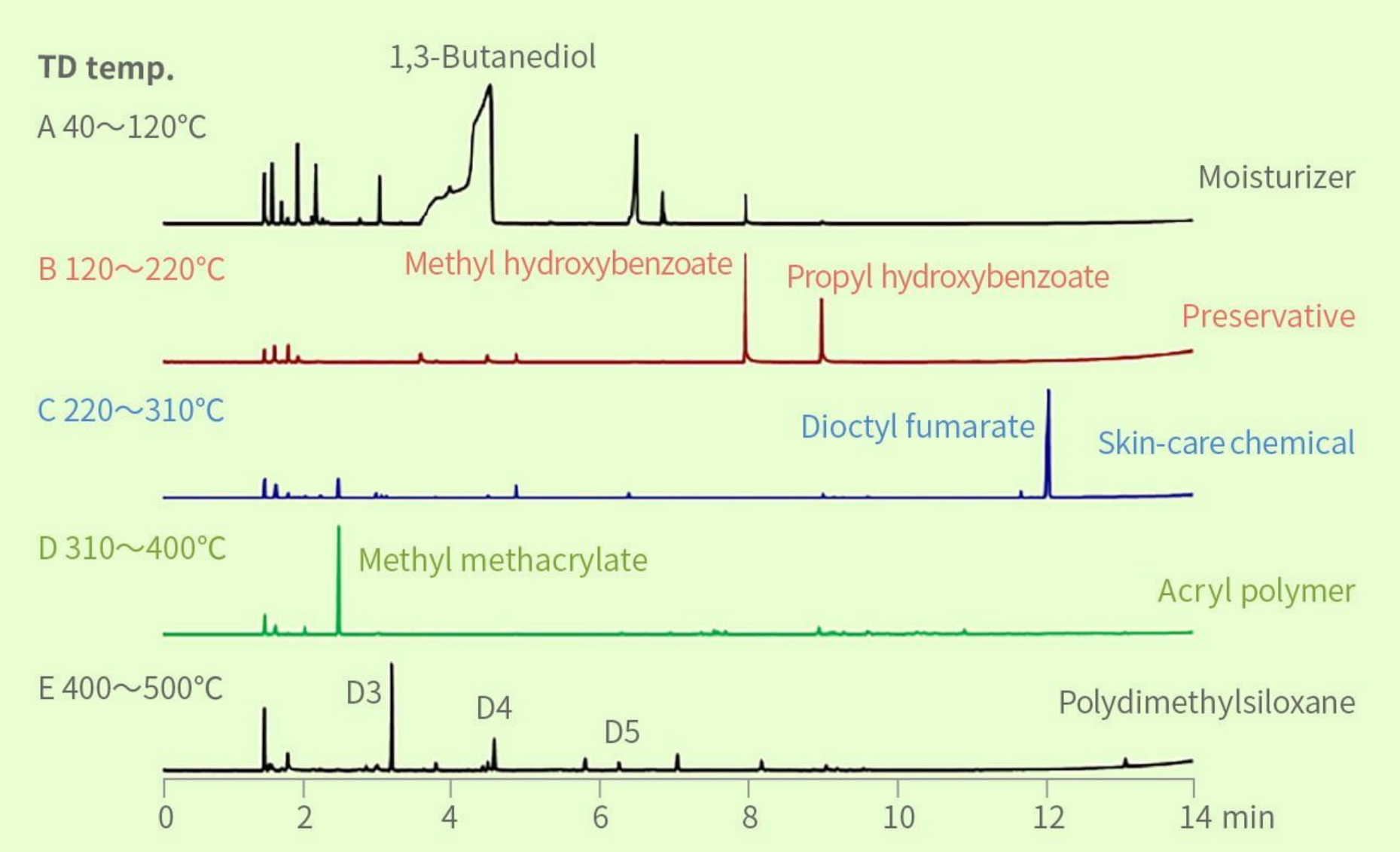
Double-shot analysis



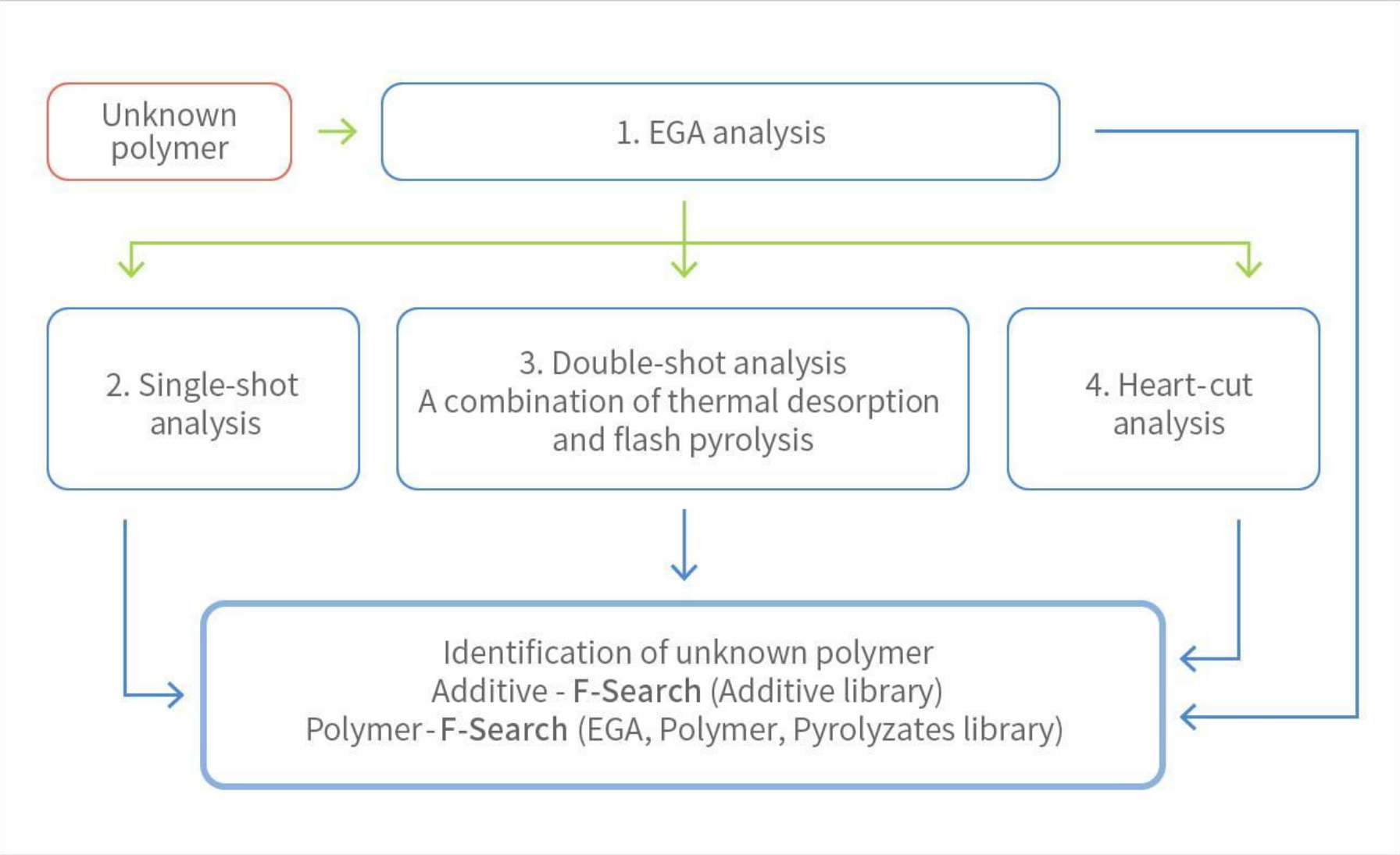
Compound

a. Methyl vinyl ketone
b. 1,3-Butanediol
c. Phenoxyethanol
d. Methyl hydroxybenzoate
e. 2-Ethylhexyl fumarate
f. Propyl hydroxybenzoate

Heart-cut EGA-GC/MS (HC/EGA-GC/MS)



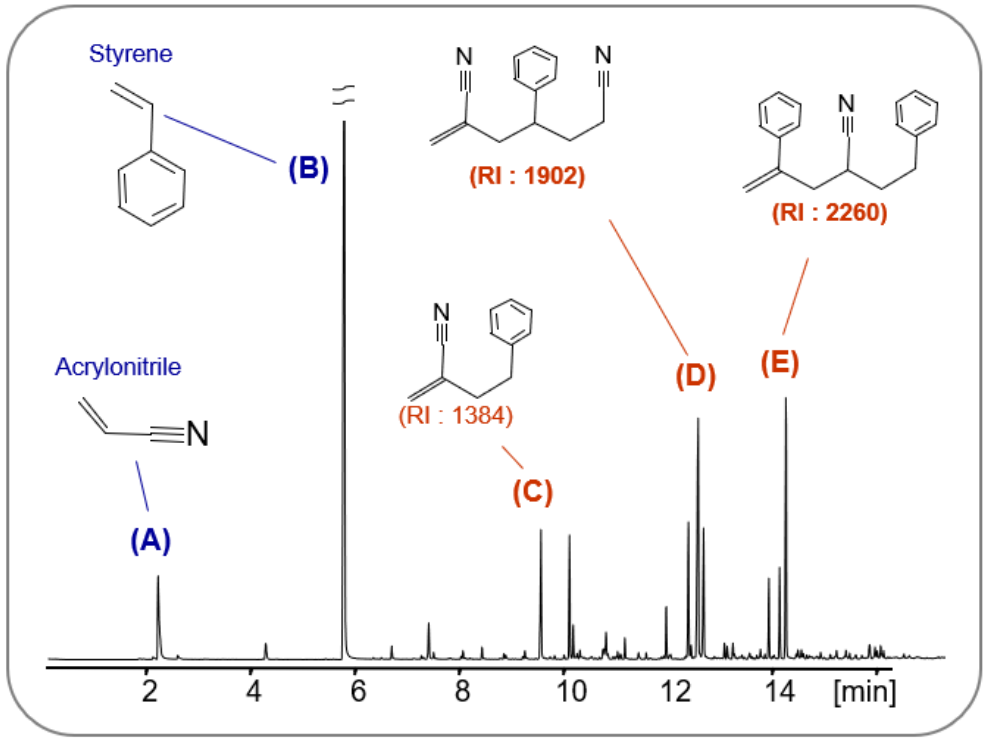
Analysis flow for unknown polymer



F-Search Software

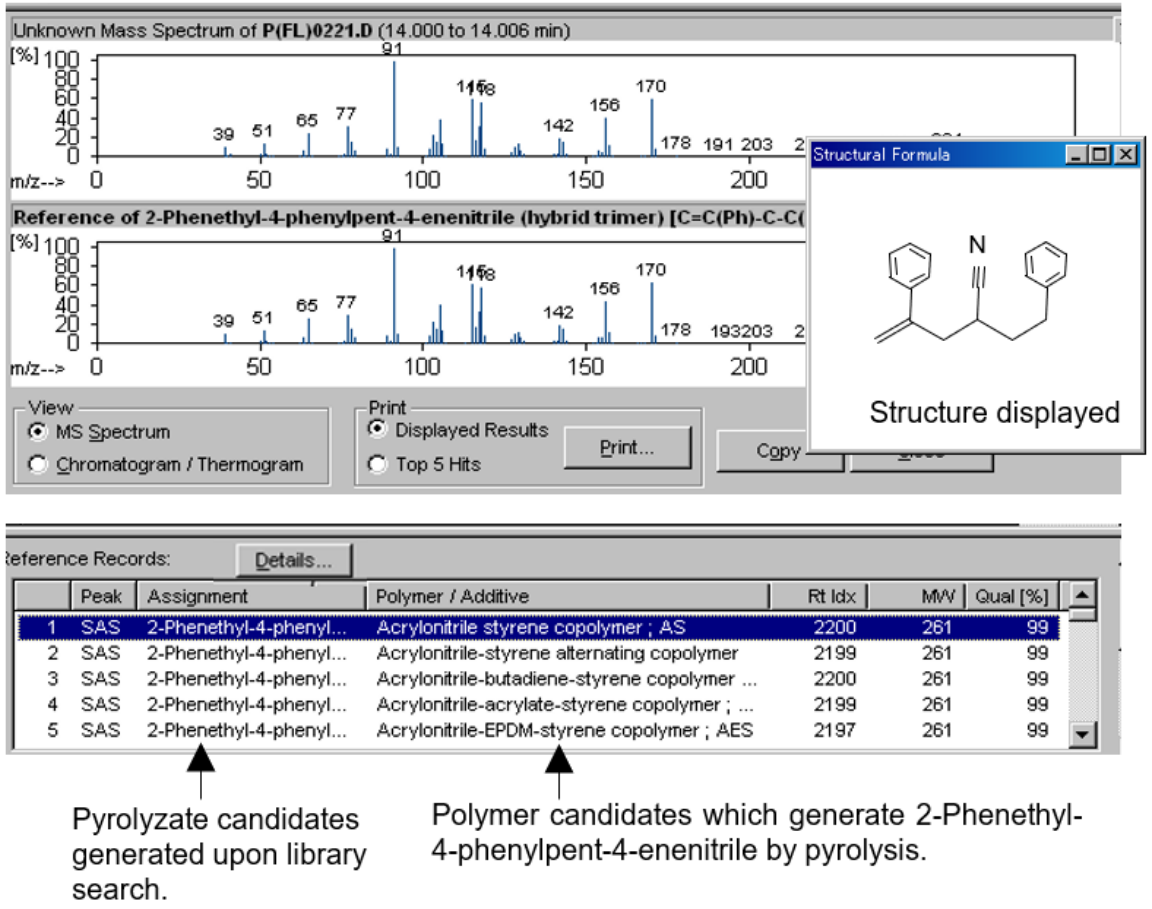
F-Search Software

Polymer search using pyrolyzates of pyrogram



Pyrogram of unknown polymer
(A) and (B) below were identified by library search on NIST library; however, (C) and (E) could not be identified.

Search result for peak (E)

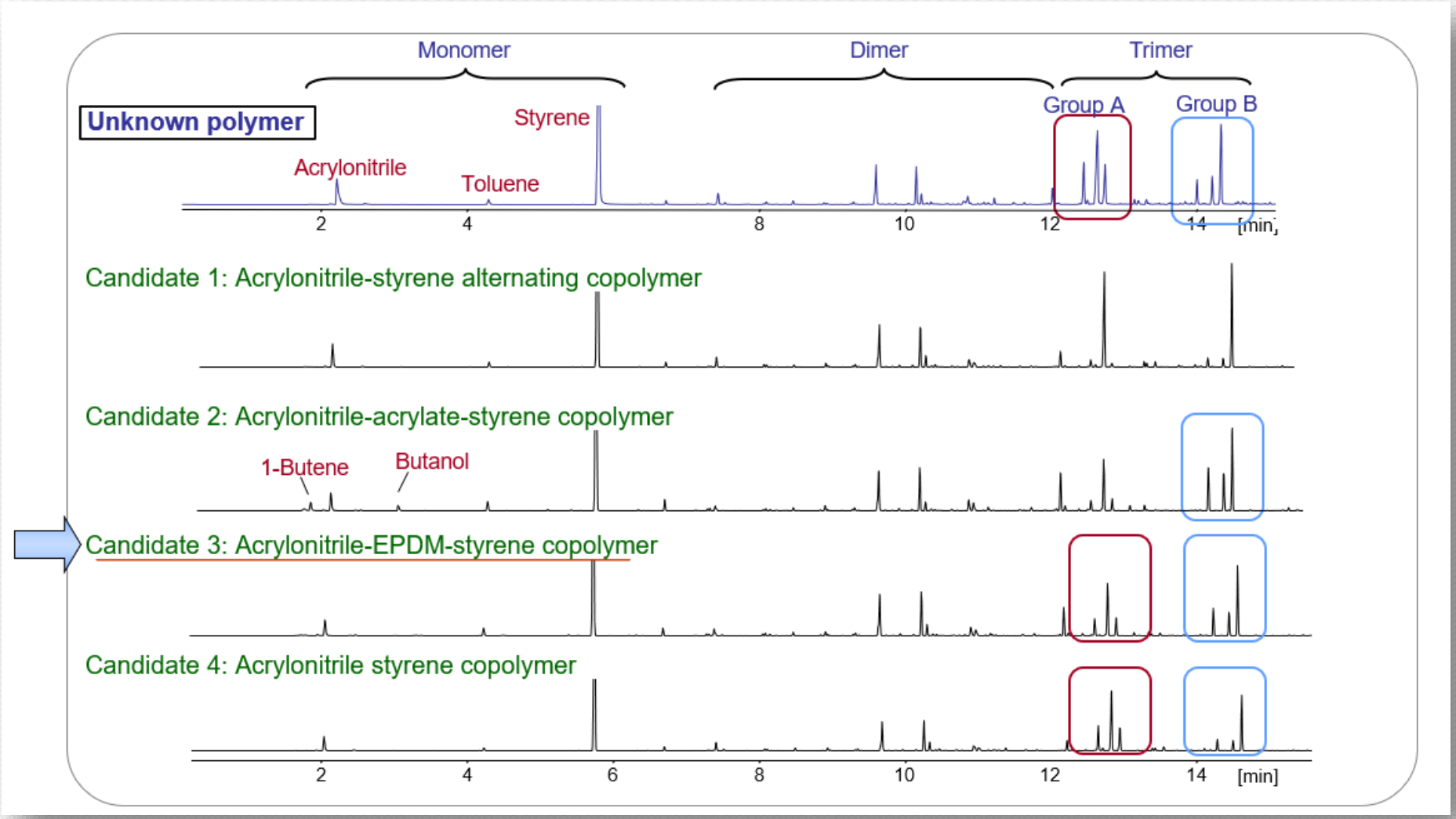


Pyrolyzate candidates generated upon library search.

Polymer candidates which generate 2-Phenethyl-4-phenylpent-4-enenitrile by pyrolysis.

F-Search Software

Visual comparison of pyrograms of polymers stored in the library



F-Search Software

Specifications for F-Search System (Japanese patent 3801355, US patent 6444979)

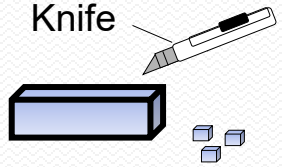
Product name (P/N)	F-Search "All-In-One" (PY-1110E-181)	Optional libraries (search software F-Search (Ver. 3.6) (PY-1111E-181) required)			
		EGA-MS18B (PY-1112E-181)	PyGC-MS18B (PY-1113E-181)	Pyrolyzate-MS18B (PY-1115E-181)	ADD-MS16B (PY-1114E-161)
Analytical technique	Package contains F-Search (Ver. 3.6) and all four libraries	Evolved gas analysis (EGA-MS)	Pyrolysis-GC/MS (Py-GC/MS) and Thermally assisted hydrolysis and methylation-GC/MS (THM-GC/MS)	Pyrolysis-GC/MS (Py-GC/MS) and Thermally assisted hydrolysis and methylation-GC/MS (THM-GC/MS)	Pyrolysis-GC/MS (Py-GC/MS) and Thermal desorption-GC/MS (TD-GC/MS)
Number of polymers/additives		1,000 polymers	1,000 polymers (THM data in 33 polymers)	268 polymers (THM data in 33 polymers)	494 additives (Py and TD data in 110 additives)
Stored chromatogram		Thermogram	Pyrogram/chromatogram		
Number of mass spectra		c.a. 1,900	c.a. 2,800	c.a. 5,500	c.a. 4,800
Other		Contains all polymers listed in "**Pyrolysis - GC/MS Data Book of Synthetic Polymers -Pyrograms, Thermograms and MS of Pyrolyzates-**" S. Tsuge , H.Ohtani and C. Watanabe, 2011, Elsevier Inc.			Contains 321 additives recorded in "Standard Spectral Database for Polymer Additives '94/95", S. Tsuge, S. Takayama, 1994, Nihon Kagaku Johosha, in addition to 37 major additives for rubbers.

Sample preparation

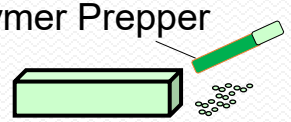
Sample preparation

Step 1

Knife

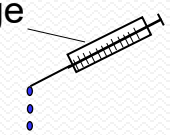


Polymer Prepper

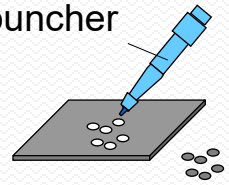


Filed, Cry milled

Micro syringe



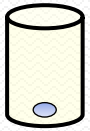
Micro puncher



Step 2

Place a sample
in the sample cup

0.1- 0.5mg

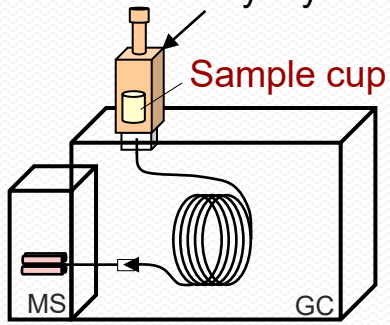


No solvent extraction

Step 3

Pyrolyzer

Sample cup



Ready for Analysis !!

Example application

Analysis of Compounded Rubber

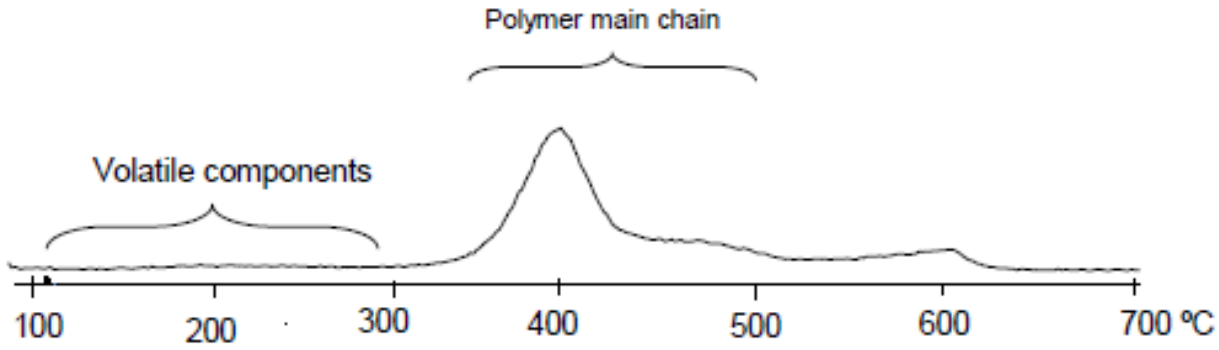


Fig. 1 Evolved Gas Curve of a Compounded Rubber
Pyrolysis temp.: 100 - 700 ºC (20 ºC/min),
Carrier gas : He 50 kPa, Split ratio : ca. 1/20
EGA capillary tube : 0.15 mm id, 2.5 m (UADTM-2.5N), GC oven temp.: 300 ºC
Injection temp.: 320 ºC,
Sample : ca. 5 µg,
Detector : MS (m/z 29 - 400)

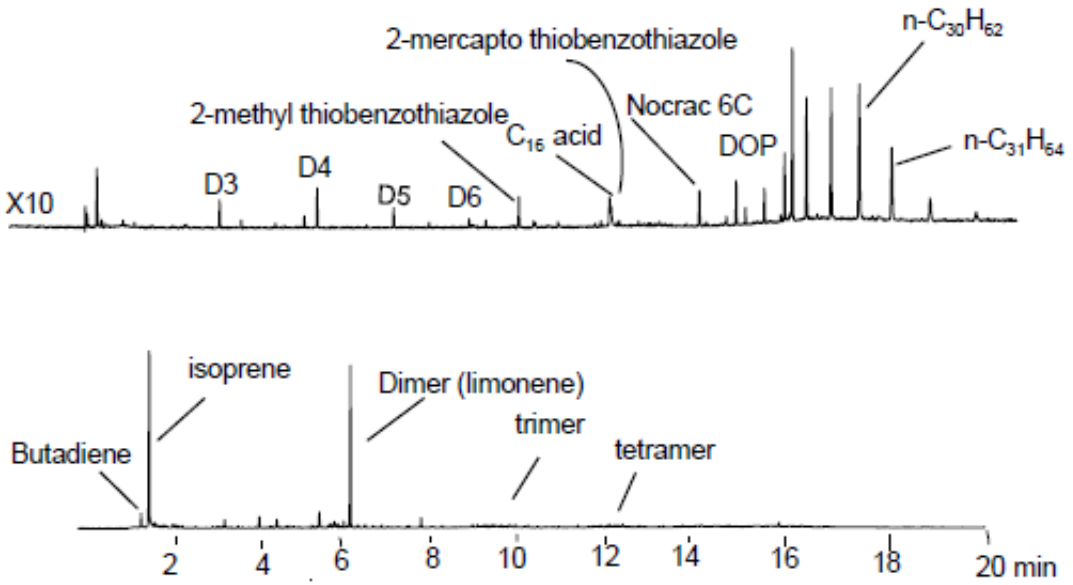


Fig. 2 GC/MS Analysis of Compounded Rubber by Double-Shot Technique
Column flow rate : 1 ml/min (fixed flow rate), Split ratio : 1/20, Separation column: Ultra ALLOY+-5 (5% diphenyl polysiloxane), 30 m, 0.25 mm id, Film thickness : 0.25 µm;
GC oven temp.: 40 - 300 ºC (20 ºC/min),
Sample : 5 µg,
Detector: MS (m/z 29 - 400, 2 scans/sec)

Analysis of Acrylonitrile Butadiene Rubber (NBR) by Double-Shot Technique

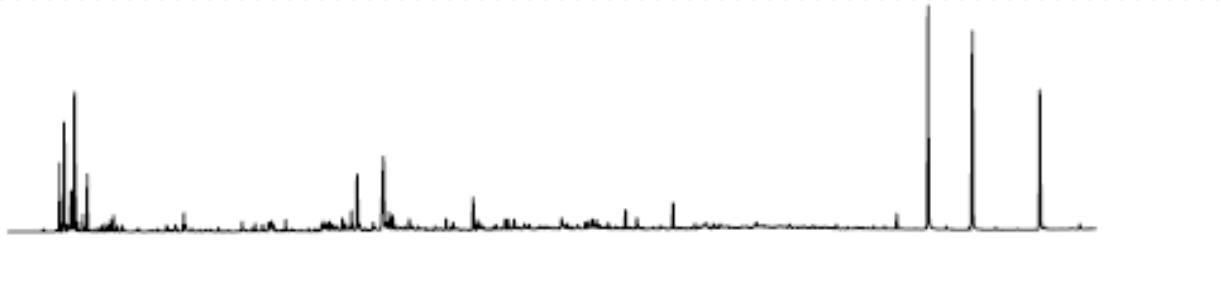


Fig. 1. Pyrogram of NBR by Single-Shot Technique (Total ion chromatogram)
Pyrolysis temp.: 550 ºC, Carrier gas : He, Column flow rate : 1.0 ml/min,
Separation column : Ultra ALLOY-5 (5% phenyldimethylpolysiloxane), 30 m, 0.25 mm id, Film thickness : 0.25 µm
GC oven temp.: 40 ºC (3 min) → 10 ºC/min → 300 ºC (3 min), GC injection port temp.: 320 ºC, Sample : 0.31 mg,
Detector : MS, Scan range : m/z 29 - 400

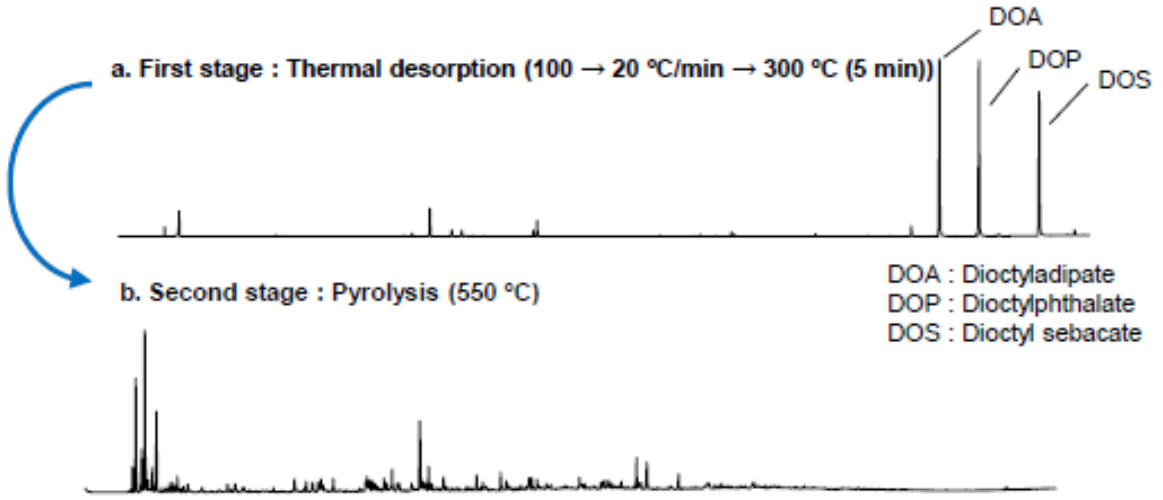


Fig. 2. Pyrogram of NBR by Double-Shot Technique
Analytical conditions are the same as above (Fig. 1.)

Analysis of a Food Wrap Film (Polypropylene and Nylon) using EGA-GC/MS

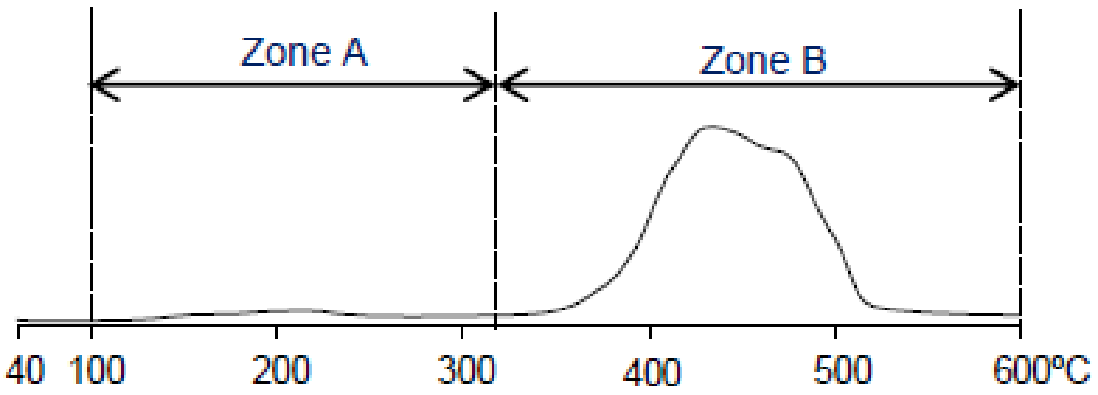


Fig. 1 EGA Profile of Polypropylene + Nylon

Pyrolysis temp: 40 – 600 ºC (30 ºC/min), carrier gas: He
Interface: deactivated metal capillary column (length: 2.5 m, id: 0.15 mm)
Injection port pressure: 50 kPa

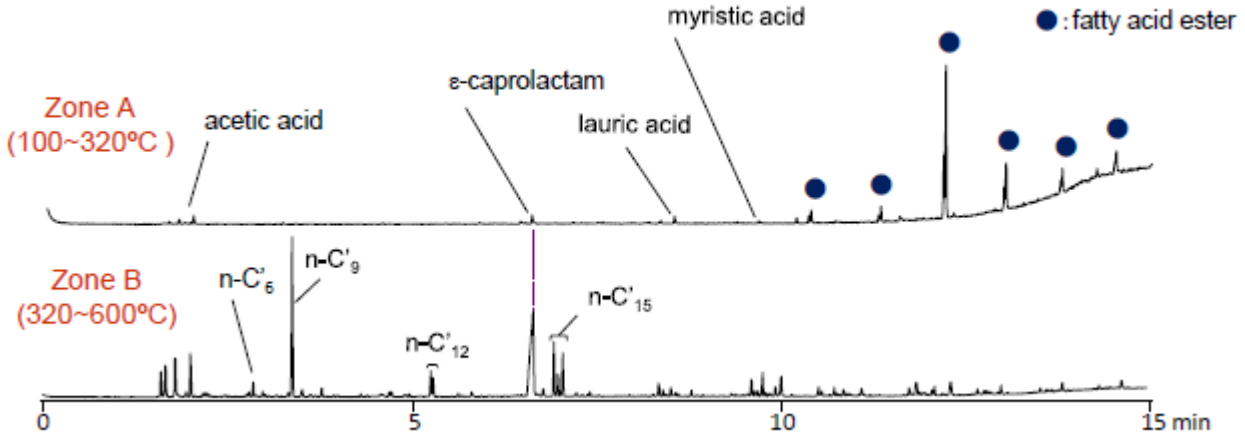
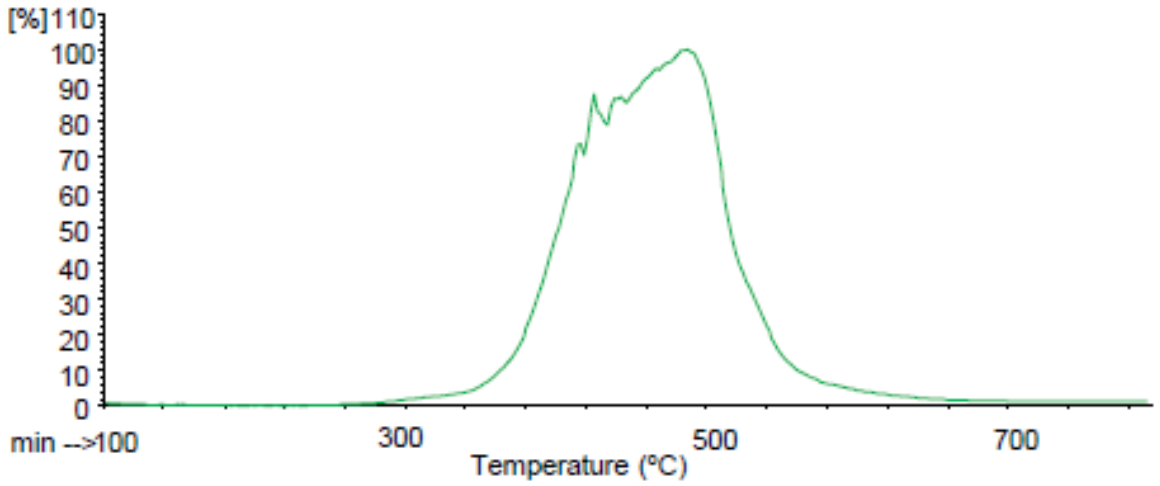
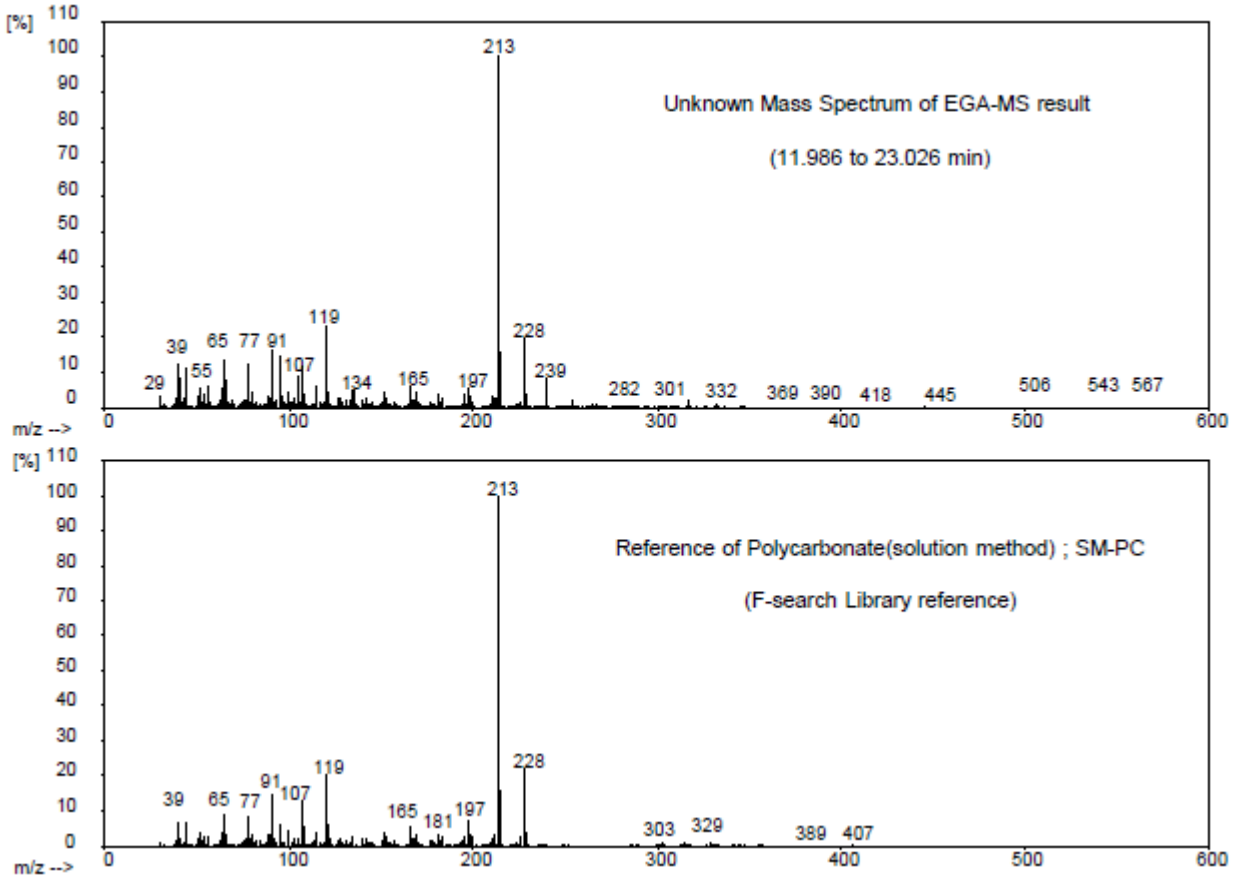


Fig. 2 Analysis Results of Zones A, B, and C of Polypropylene + Nylon

Carrier gas: He, column flow rate: 1 mL/min, total carrier gas flow rate: 40 mL/min, separation column: Ultra ALLOY-5 (5% diphenyl dimethyl polysiloxane), length: 30 m, id: 0.25 mm, film thickness: 0.25 µm,
GC oven temp: 40 ºC (1 min hold) - 320 ºC (20 ºC/min), injection port temp: 320 ºC, Cryo trap temp: -196 ºC,
sample: 0.25 cm2

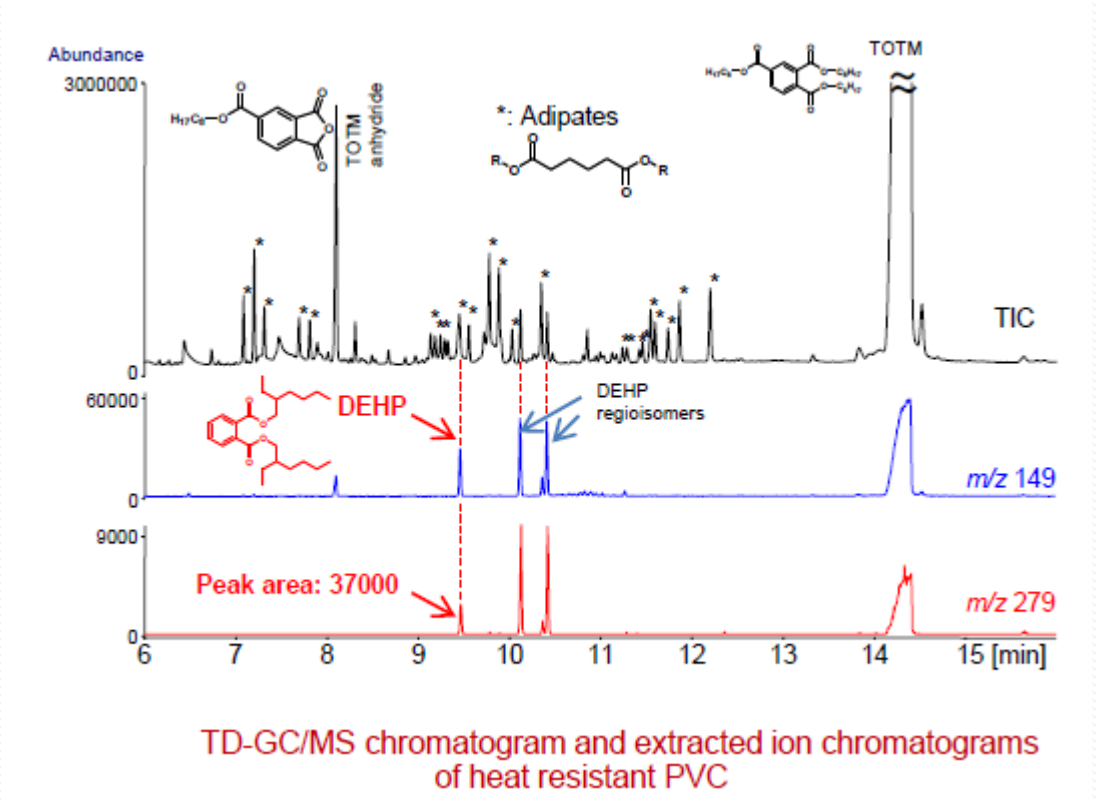
Polycarbonate (PC) Plastic Resins



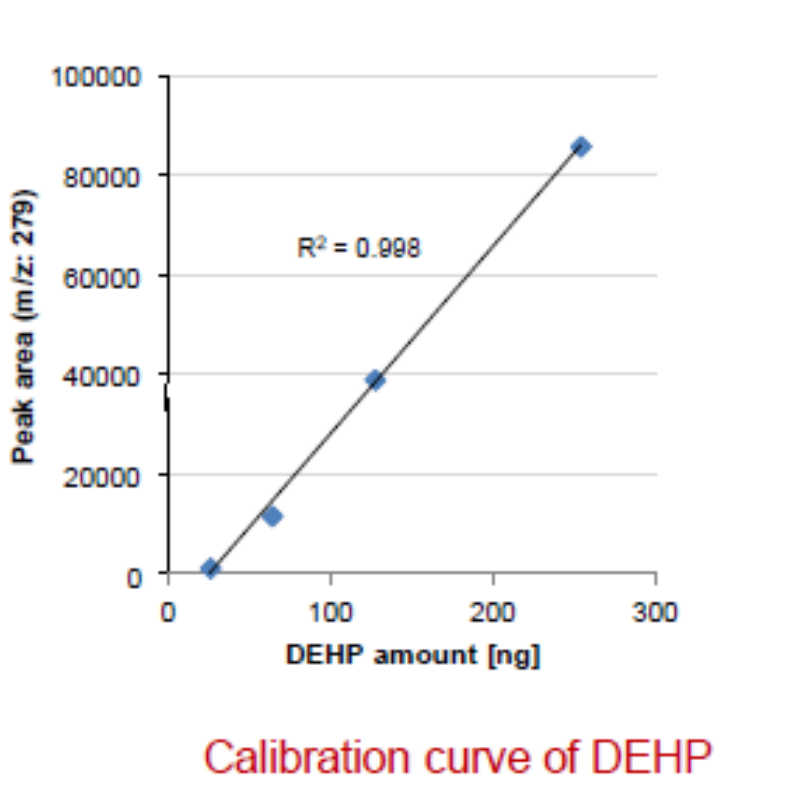


The EGA thermogram demonstrated that the PC filament start to degrade at 320 ºC and will be totally degraded at 600 ºC. Library search is done by F-search, which fits well with the EGA-MS of sample, giving a result of good fitting with PC reference.

Determination of Phthalate Bis(2 - Ethylhexyl) Phthalate (DEHP) in Heat Resistant PVC Sheath



TD-GC/MS chromatogram and extracted ion chromatograms of heat resistant PVC



Calibration curve of DEHP

TD temp.: 100 - 320 ºC (20 ºC/min, 1 min hold), GC oven temp.: 80 (2 min) - 200 ºC (40 ºC/min) - 320 ºC (15 ºC/min, 3 min hold)
Separation column: Ultra ALLOY+-5 (5 % diphenyl 95 % dimethylpolysiloxane, L=30 m, i.d.=0.25 mm, df=0.25 µm)
Column flow rate: 1.2 mL/min He, Split ratio: 1/50, Sample wt: ca. 500 µg

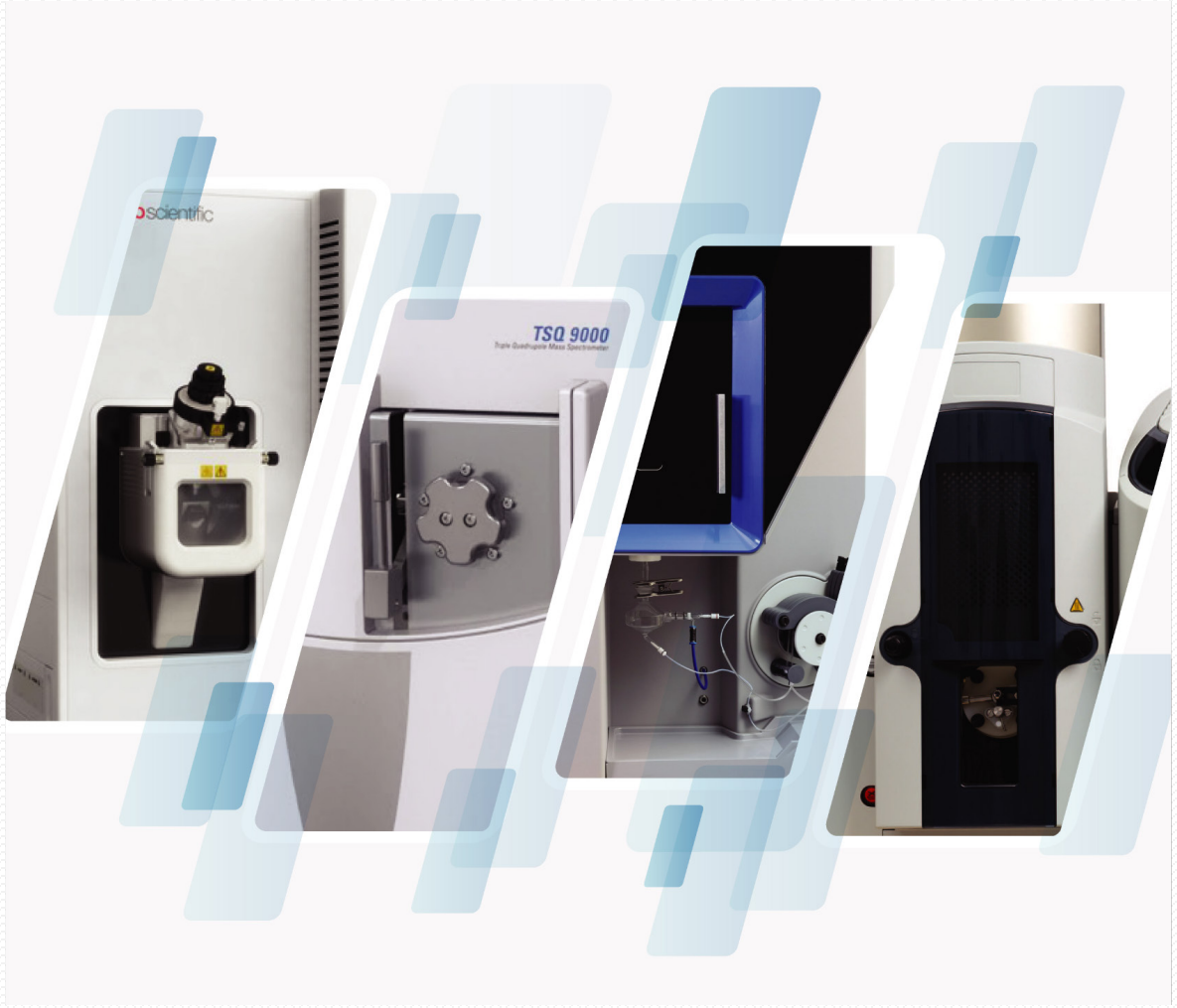
ติดตามกิจกรรมของทางบริษัทได้ที่

www.scispec.co.th

/scispec

@scispec

crm@scispec.co.th



ThermoFisher SCIENTIFIC

MARKES international

FRONTIER LAB

GAS

CTC Analytics

LC Tech
SAMPLE PREPARATION & ANALYSIS

908devices

YOUR SCIENTIFIC SPECIALIST