Analyse des Kalzinierungs-Stabilisierungsmechanismus von Polyacrylnitril-Kohlenstofffaser-Precursor unter Verwendung von EGA-MS, Pyrolyse GC/MS und Heart Cut-GC/MS

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Agenda

1. Vorstellung Frontier Lab
2. Grundlagen der analytischen Pyrolyse
3. Instrumentierung und analytische Verfahren (Methoden-Karte)
4. PAN Anwendung: Analysen und Resultate
5. Zusammenfassung

Fraunhofer LBF

1. Frontier Lab-a Brief History

- Frontier Laboratories, Ltd. was founded in 1991 by Dr. Chu Watanabe (Chu-san). Dr. Watanabe, with the support of polymer scientists at Nagoya University in Japan, developed a pyrolyzer based on a *vertical micro-furnace design.*
- We are a global corporation and our main products, supported by a number of accessories and software, include the EGA/PY-3030D Multi-Functional Pyrolysis System, the PY-3030S Single-Shot Pyrolyzer, the 3050 series of Rapid Screening Reactors for catalyst screening, and a line of Ultra ALLOY® stainless steel capillary columns.

Office Locations:

- **Japan (Headquarters)**
- **North America**
- **Germany (Europe)**
- **Singapore (Asia/Oceania)**
- **China**
- **Russia**

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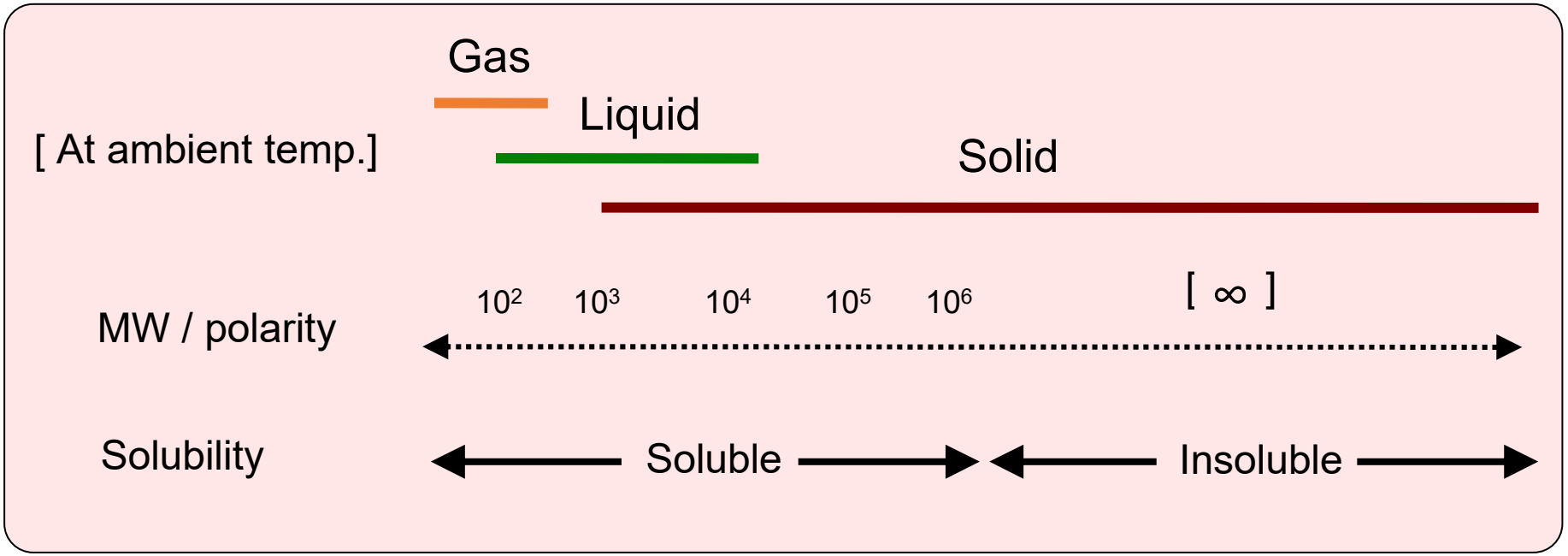
Frontier Laboratories, Ltd. Company's profile

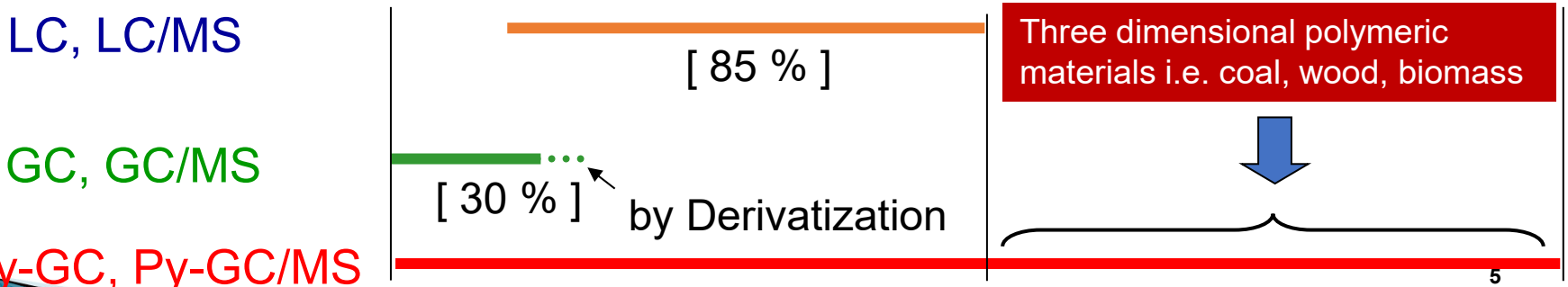
- Founded August 12, 1991
- Located in Koriyama, Fukushima, Japan
- 59 employees (incl. 11 in overseas)
- Office: Japan (HQ and Tokyo Bay R&D), China,

Frontier Laboratories, Ltd. Company's profile

New R&D building opened Jan 2020

Expansion of Application Areas with Py-GC/MS

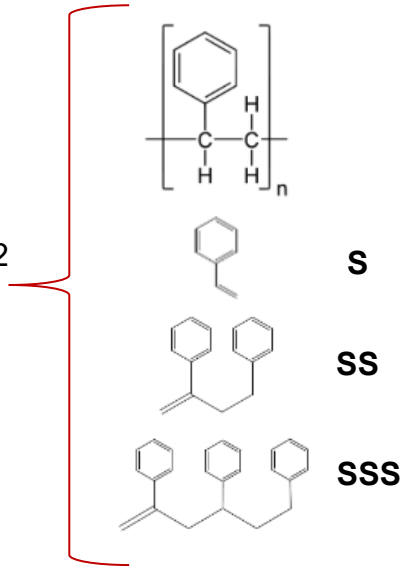




EGA-MS, Thermal Desorption (TD), Reactive Pyrolysis (RxPy)

Polymer Degradation Mechanisms

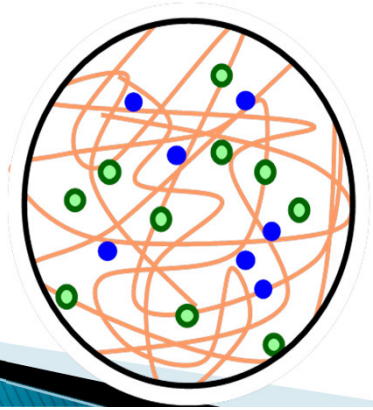
- **Random Scission**
  - Polyolefins (polyethylene, polypropylene, polybutlyene, etc.)
  - C-C bonds break to produce fragment patterns of increasing oligomer sizes
- **Depolymerization**
  - Polymer thermally degrades into monomeric units
  - Polystyrene shows monomer (S), dimer (SS) and trimer (SSS) (see page 42 in Py-GC/MS Data Book*)
- **Side Group Elimination**
  - Side groups (i.e. Cl) attached to the side of a polymer chain break before C bonds.
  - Cl removes H from polymer chain = unsaturated polyenes + HCl. These polyenes form aromatic compounds.
  - Polyvinyl chloride (PVC) is an example.
    - PVC pyrolyzates contain single aromatic rings (BTEX), double rings (i.e. naphthalene) and even triple rings (i.e. anthracene).
    - Big peak of HCl. (see page 110 in Py-GC/MS Data Book*)



*Pyrolysis GC/MS Data Book of Synthetic Polymers, 2011, Tsuge, Ohtani, Watanabe

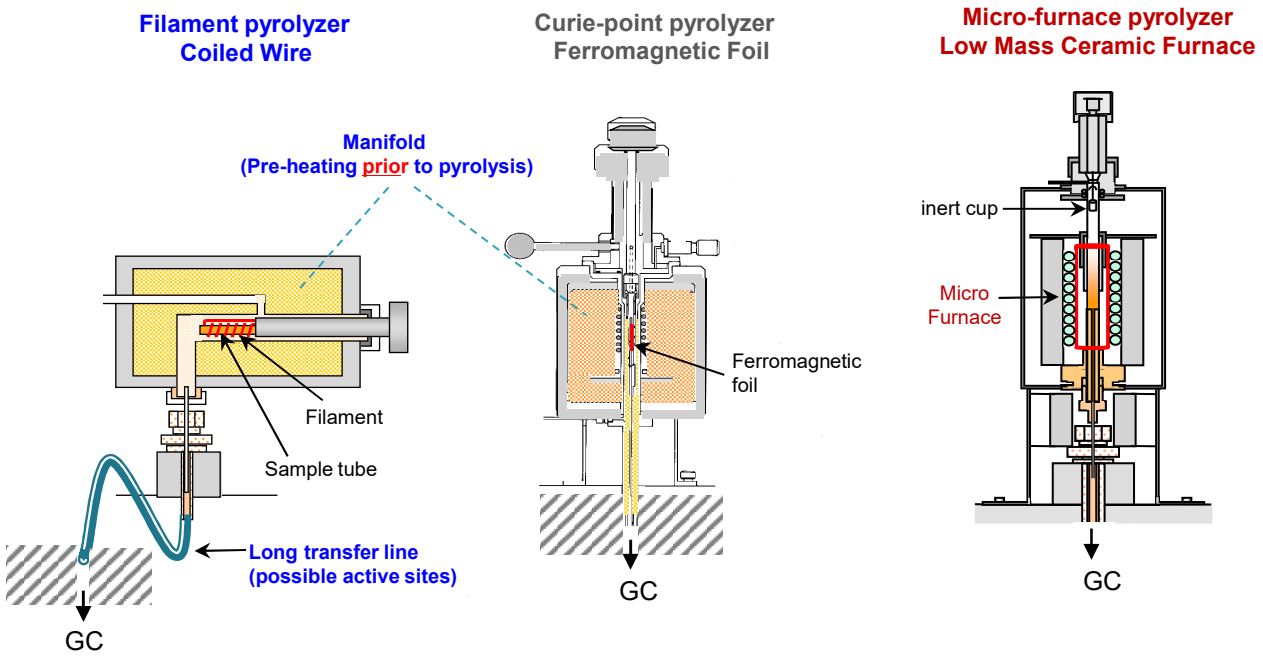
Materials and Analytes for PY-GC/MS

- 1. Synthetic Polymers (plastics, textiles, micro-/nano-plastic, Recyclates)
- 2. paints, inks und lacquers
- 3. natural polymers (lignin, paper, polysaccharide, silk)
- 4. coal, tobacco
- 5. Additives (Antioxidants, Stabilizers, phthalates, flame retardants)
- 6. Soil (organic matter)

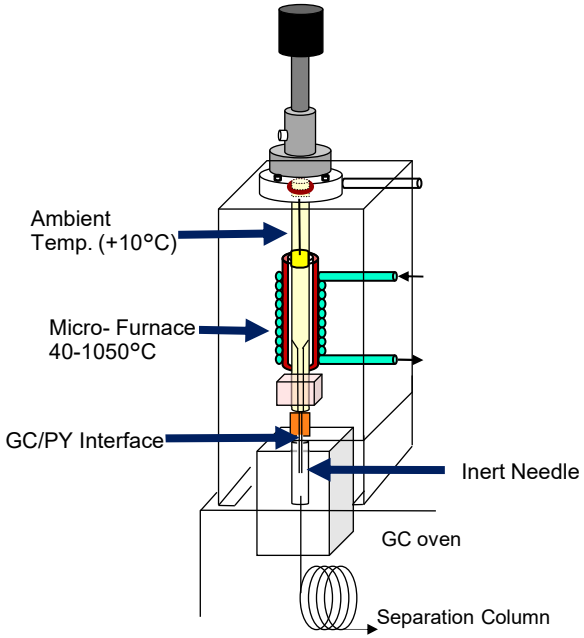


: Additives
: Polymer
: Inorganics

Different Pyrolyzer Technologies

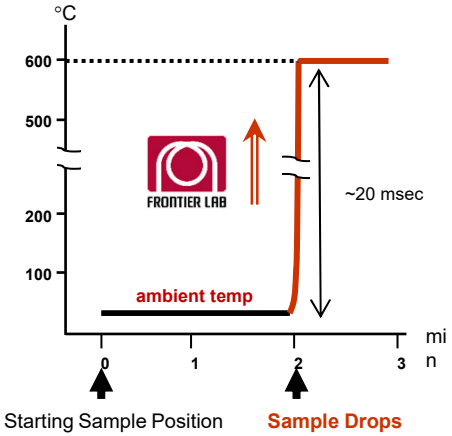


Micro-Furnace Technology



Sample introduction is nearly instantaneous. The sample is placed in the inert sample cup (Eco-cup) and is held at near ambient temperature in helium. The micro-furnace is then preheated to the desired temperature (e.g., 650°C) that is precisely measured with a thermal couple sensor. The sample cup then drops into the quartz pyrolysis tube where the sample is rapidly and reproducibly pyrolyzed. The pyrolyzates are directly swept onto the GC analytical column for separation and detection by MS or any other detector.

This single-step pyrolysis of the micro-furnace technology allows low and high molecular-weight as well as polar compounds to be detected and analyzed. The absence of any transfer line is also critical for the ability to detect heavy and polar pyrolyzates as well as additives.

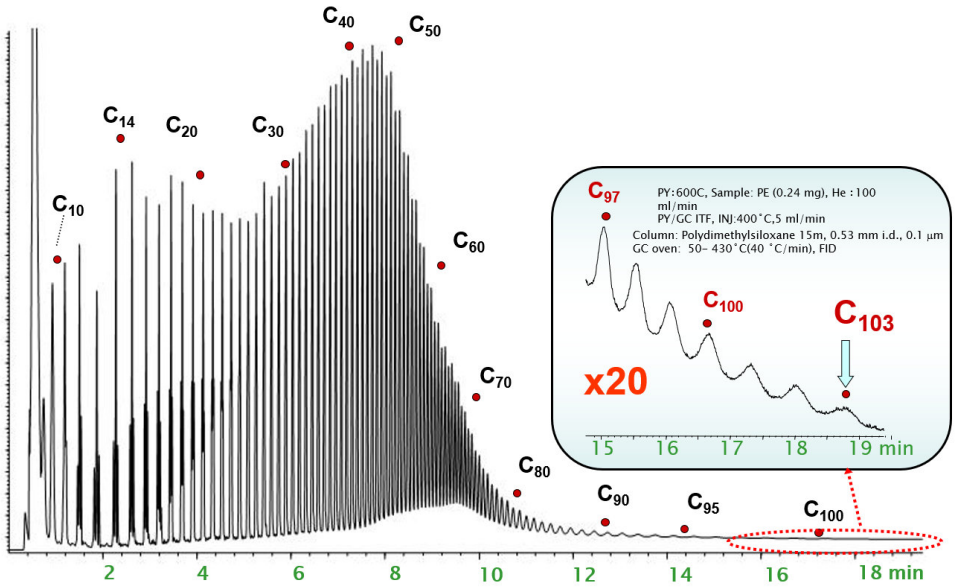


- **No transfer line**
- **No evaporation, degradation, or thermosetting before the analysis**
- **Continuous (1 step) analysis**
- **Full range thermal profiling**
- **Reproducibility and accuracy of the temperature with ±0.1°C**

Micro-Furnace Technology

Full Range Analysis (low MW, high MW, and Polar Compounds)

FID pyrogram of Polyethylene at 600℃



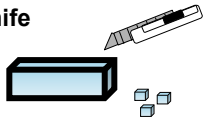
Micro-Furnace Technology:

- Directly deposits all pyrolyzates on-column in a single step process
- No switching valves
- No trap
- No transfer line
- No Pre-heating Prior to Pyrolysis
- Heavy and polar compounds are directly placed on-column and light compounds are never lost.

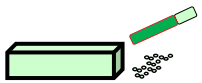
Easy Sample Preparation

Step 1

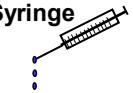
Knife



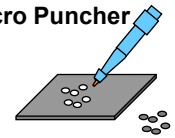
Filed; Cryo milled



Micro Syringe



Micro Puncher



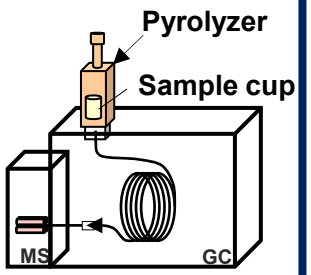
Step 2

Weigh the sample into the sample cup

No Solvent Extraction

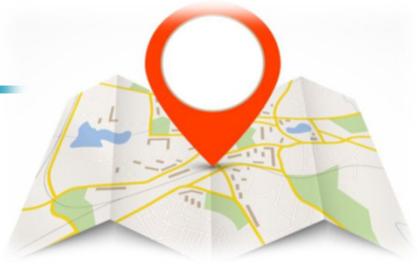
Sample

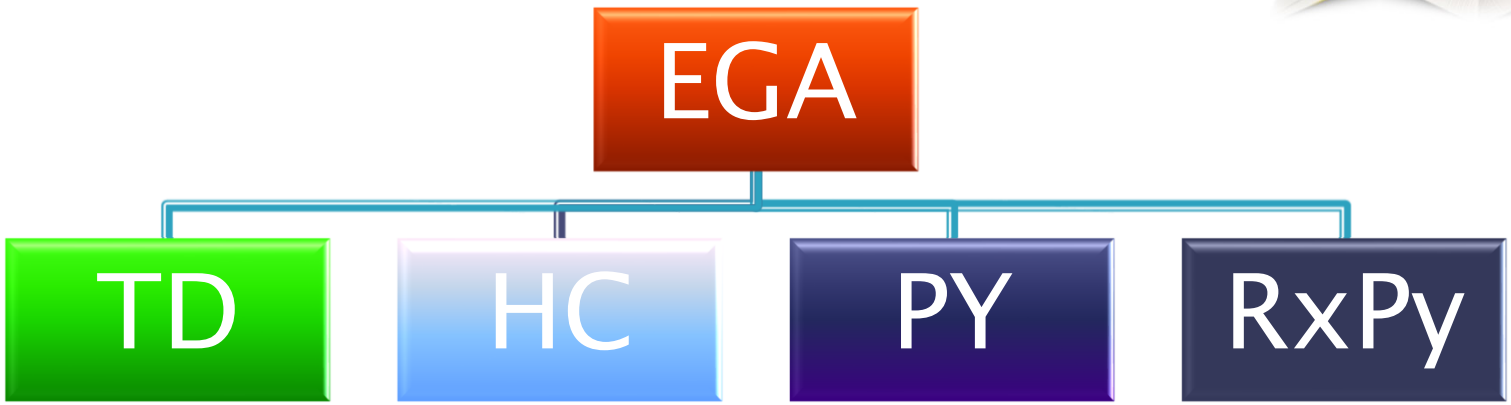
Step 3



Ready for Analysis !!

“Method Map” for Materials Characterization



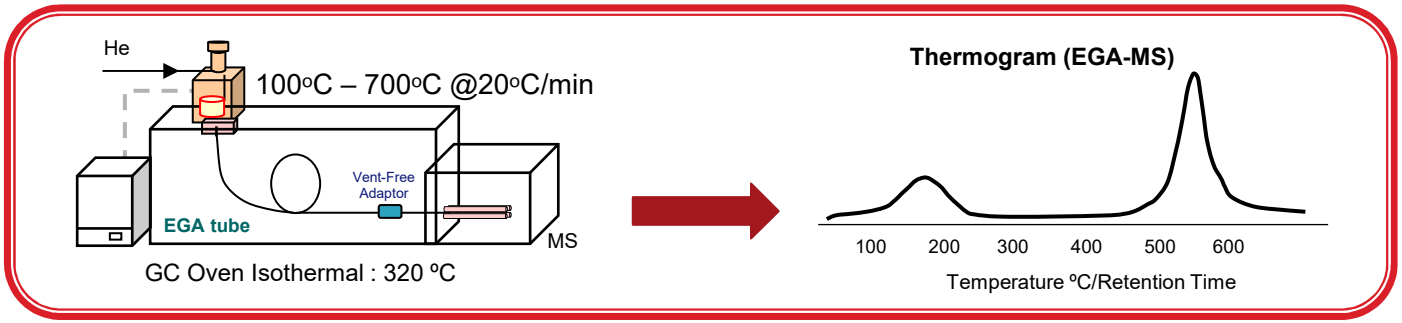


EGA	Evolved Gas Analysis
TD	Thermal Desorption
HC	Heart-Cutting
PY	Pyrolysis
RxPy	Reactive Pyrolysis

Evolved Gas Analysis: Rapid Screening

1st step in the "Method Map"

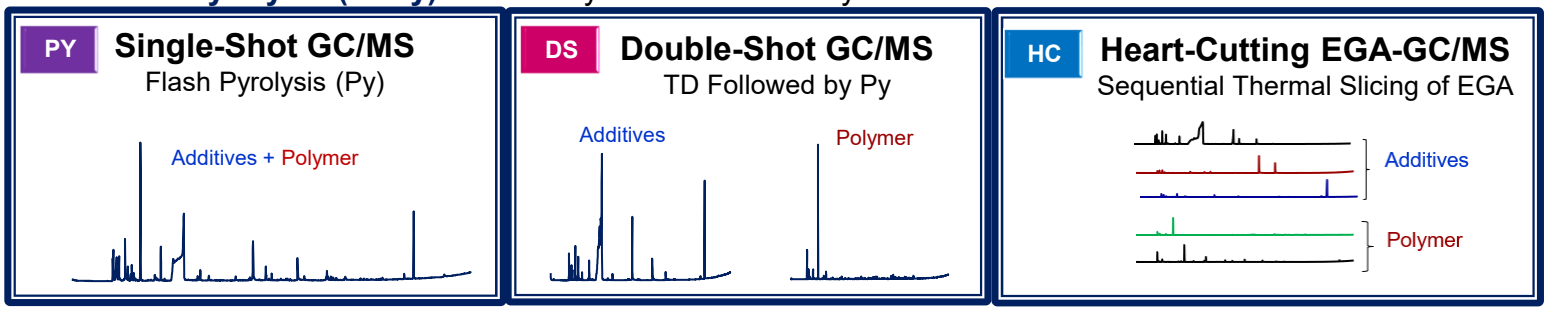
- No column is used; a short, small diameter (2.5m, 0.15 mm id.) deactivated tube connects the injection port to the detector
- The sample is dropped into the furnace which is at a relatively low temperature (*ca.* 40-100˚C). The furnace is then programmed to a much higher temperature (*ca.* 600-800˚C)
- Compounds "evolve" continuously from the sample as the temperature increases. A plot of detector response versus furnace temperature is obtained



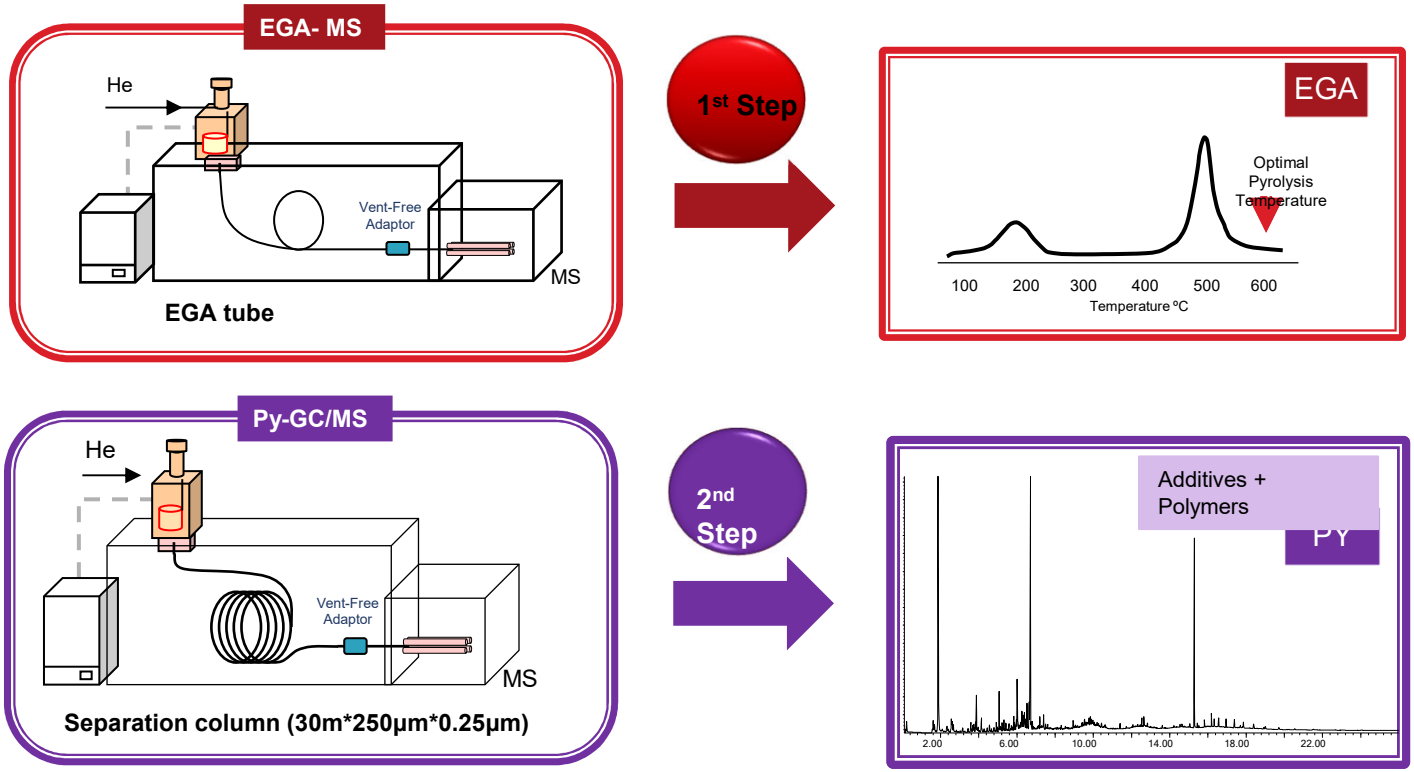
Isothermal &Temperature Programmed Micro Furnace Techniques

2nd step: Use the EGA thermogram and selected ion chromatograms (EIC) to define the thermal zones of interest and then perform one or combination of the following techniques:

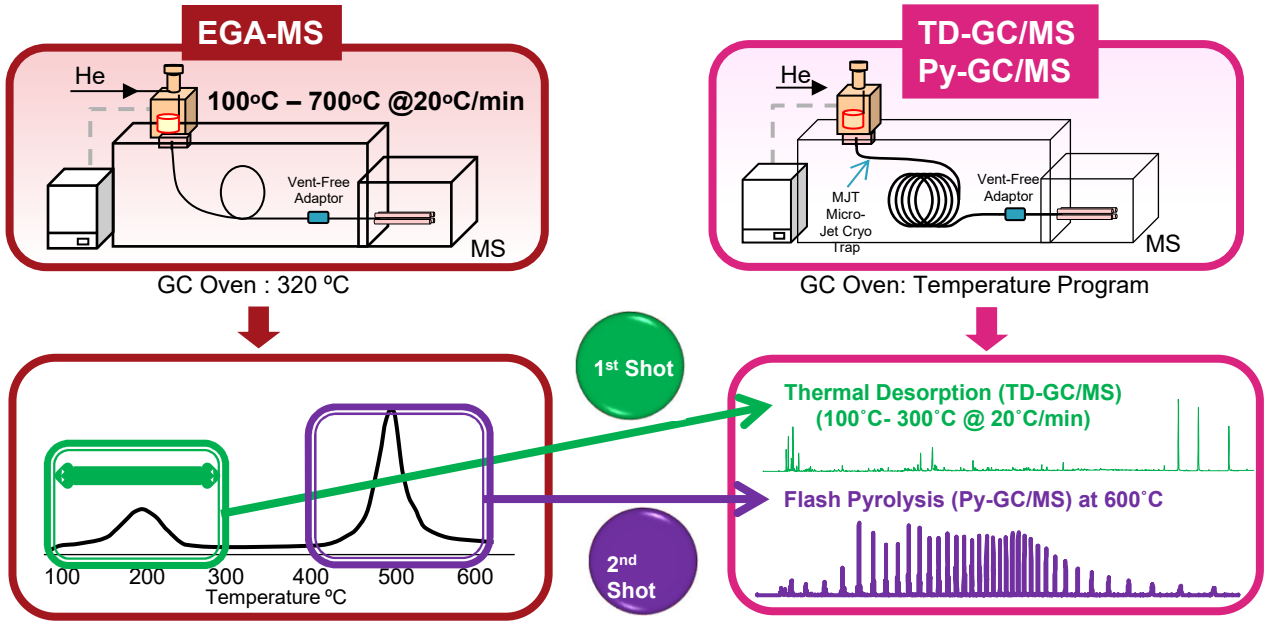
- **Thermal Desorption (TD):** Thermal Extraction of additives & volatiles (No solvent extraction or sample pretreatment)
- **True Flash Pyrolysis (Py):** Single-Shot GC/MS; polymer analysis
- **Double-Shot GC/MS:** Thermal Desorption followed by Flash Pyrolysis on one sample
- **Heart Cutting (HC):** Thermally slicing EGA thermogram (up to 8 programmable temperature zones); deformulation/reverse engineering, failure, “Good vs. “Bad”, and contamination analysis
- **Reactive Pyrolysis (RxPy):** Thermally assisted thermolysis & derivatization



Flash Pyrolysis (Single-Shot GC/MS)



Double-Shot: Thermal Desorption + Pyrolysis



- EGA-MS is the recommended first step to characterize a sample and uses an uncoated metal tube **(2.5m x 0.15mm i.d.)** to connect the GC inlet to the MS. **TD followed by PY on a single sample is called a Double-Shot.**
- Subsequent analyses (TD-GC/MS and Py-GC/MS) are performed using an analytical column **(30m x 0.25mm x 0.25µm).** Switching from the tube to the column takes only minutes using the Vent-free Adapter (VFA).

Heart-Cutting-GC/MS: Sequential Thermal Slicing of EGA-MS

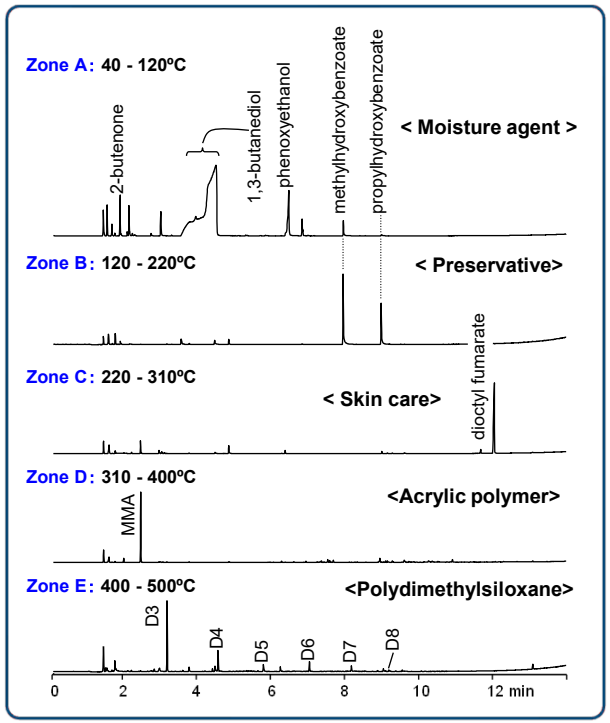
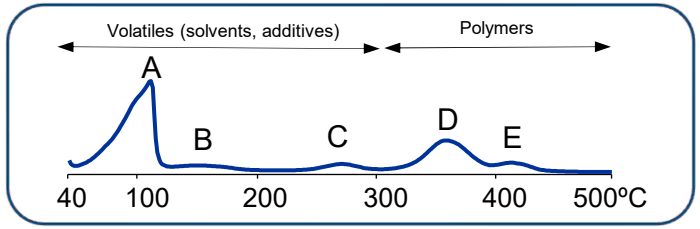
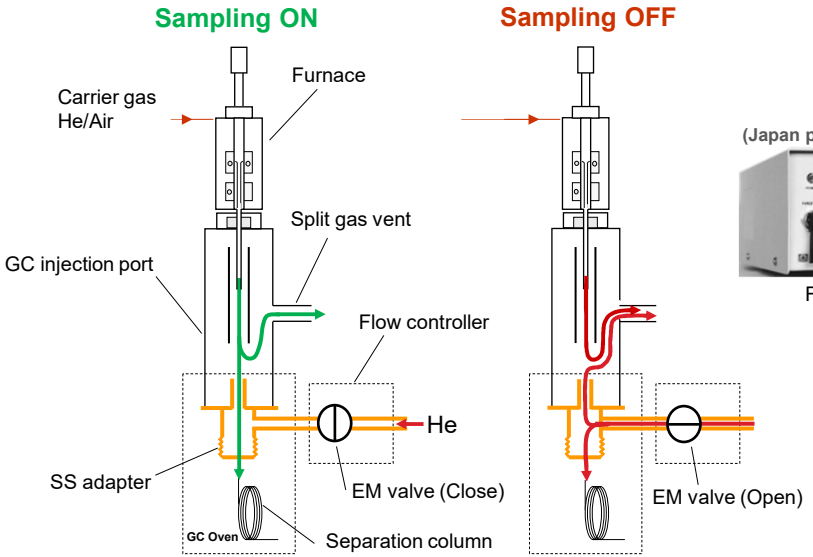


Figure.1: Heart-cut EGA-GC/MS analysis of zones A to E of EGA thermogram of an eyeliner.



Selective Sampler



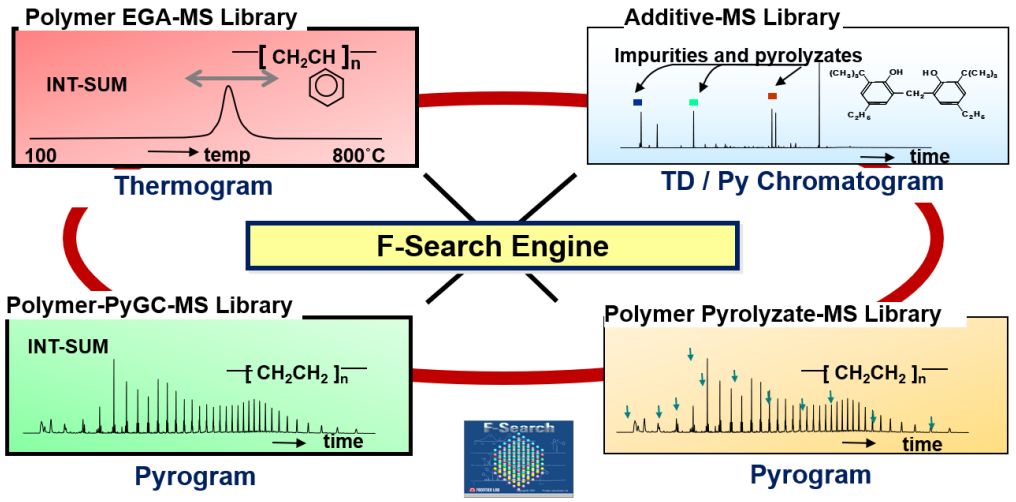
(Japan patent No.3290893)

Flow controller

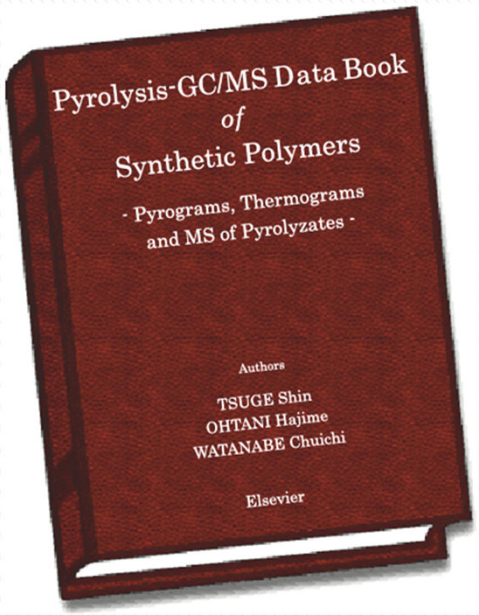
Simplify and Improve Data Interpretation Using F-Search

Identification of polymers and additives from data obtained by evolved gas analysis, thermal desorption, or pyrolysis GC/MS analysis. User library can also be created.

1) EGA-MS polymer library : 1000 polymers stored (300 newly added)
2) PyGC-MS polymer library : 1000 polymers stored (300 newly added)
3) Pyrolyzate-MS library : 268 polymers stored (103 newly added)
4) ADD-MS library : 494 additives stored



Pyrolysis GC/MS Data Book of Synthetic Polymers



- ***TSUGE Shin, Nagoya University***
- ***OHTANI Hajime, Nagoya Institute of Technology***
- ***WATANABE Chuichi, Frontier Laboratories Ltd.***

Features:

- **Data compilation of pyrograms, thermo- grams and MS data of major pyrolyzates for 163 typical polymer samples with detailed peak assignment Tables and Thermograms for each polymer.**
- **Data compilation of pyrograms of 33 condensation polymers through reactive pyrolysis (RP) in the presence of tetramethyl ammonium hydroxide (TMAH) with the detail detailed peak assignment.**

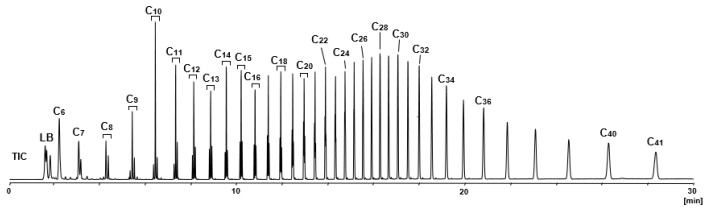
Search ISBN “9780444538925” in Amazon books

Py-GC/MS of Polyethylene from the Book

1 001 Polyethylene (high density) ; PE(HDPE)

$-(CH_2CH_2)_n-$

2



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Peak Notation	Assignment of Main Peaks	Molecular Weight	Retention Index	Relative Intensity
LB	propylene, propane	42, 44	297	43.7
C6	$CH_2=CH(CH_2)_3CH_3$	84	583	91.8
C7	$CH_2=CH(CH_2)_4CH_3$	98	689	42.4
	$CH_3(CH_2)_5CH_3$	100	700	19.3
C8	$CH_2=CH(CH_2)_4CH=CH_2$	110	782	2.1
	$CH_2=CH(CH_2)_5CH_3$	112	791	25.1
	$CH_3(CH_2)_6CH_3$	114	800	14.3
C9	$CH_2=CH(CH_2)_5CH=CH_2$	124	883	5.8
	$CH_2=CH(CH_2)_6CH_3$	126	892	30.4
	$CH_3(CH_2)_7CH_3$	128	900	10.3
C10	$CH_2=CH(CH_2)_6CH=CH_2$	138	983	6.6
	$CH_2=CH(CH_2)_7CH_3$	140	991	64.2
	$CH_3(CH_2)_8CH_3$	142	1000	10.4
C11	$CH_2=CH(CH_2)_7CH=CH_2$	152	1083	7.1
	$CH_2=CH(CH_2)_8CH_3$	154	1092	49.8
	$CH_3(CH_2)_9CH_3$	156	1100	16.1
C14	$CH_2=CH(CH_2)_{10}CH=CH_2$	194	1385	12.3
	$CH_2=CH(CH_2)_{11}CH_3$	196	1392	49.2
	$CH_3(CH_2)_{12}CH_3$	198	1400	13.5
C20	$CH_2=CH(CH_2)_{16}CH=CH_2$	278	1985	25.3
	$CH_2=CH(CH_2)_{17}CH_3$	280	1993	38.0
	$CH_3(CH_2)_{18}CH_7$	282	2000	16.2
C30	$CH_2=CH(CH_2)_{27}CH_3$	420	2993	100.0
C40	$CH_2=CH(CH_2)_{37}CH_3$	560	3997	94.1
C41	$CH_2=CH(CH_2)_{38}CH_3$	574	4096	82.8

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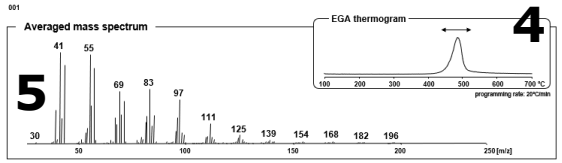

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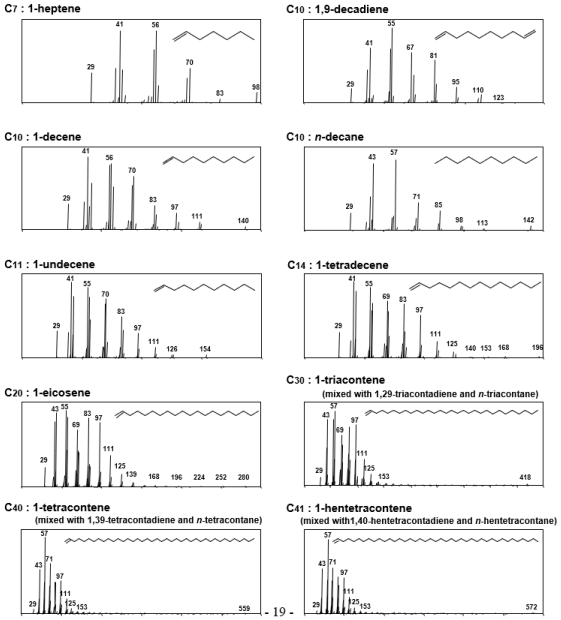
(m/z range : 29 - 600 amu)



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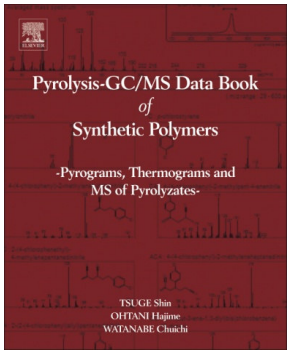
Pyrolysis Temperature: 600°C, Column: Ultra ALLOY-5; 30M x 0.25u x 0.25id, Oven Temp: 40°C (2min) -20°C/min-320°C (13min)

Pyrolysis GC/MS Data Book of Synthetic Polymers, 2011, Tsuge, Ohtani, Watanabe

Multi-Shot Pyrolyzer EGA/PY-3030D with peripherals



PY Data book