Pyrolyse GC/MS in Reversed Engineering und Schadensanalytik: 2 Fallbeispiele in der Analytik von komplexen Werkstoffen

14. Tagung des Arbeitskreises Polymeranalytik, 22.03.2019, Darmstadt

Fraunhofer LBF

Michael Soll, Frontier Laboratories, EU Business Development Manager

FRONTIER LABORATORIES LTD.

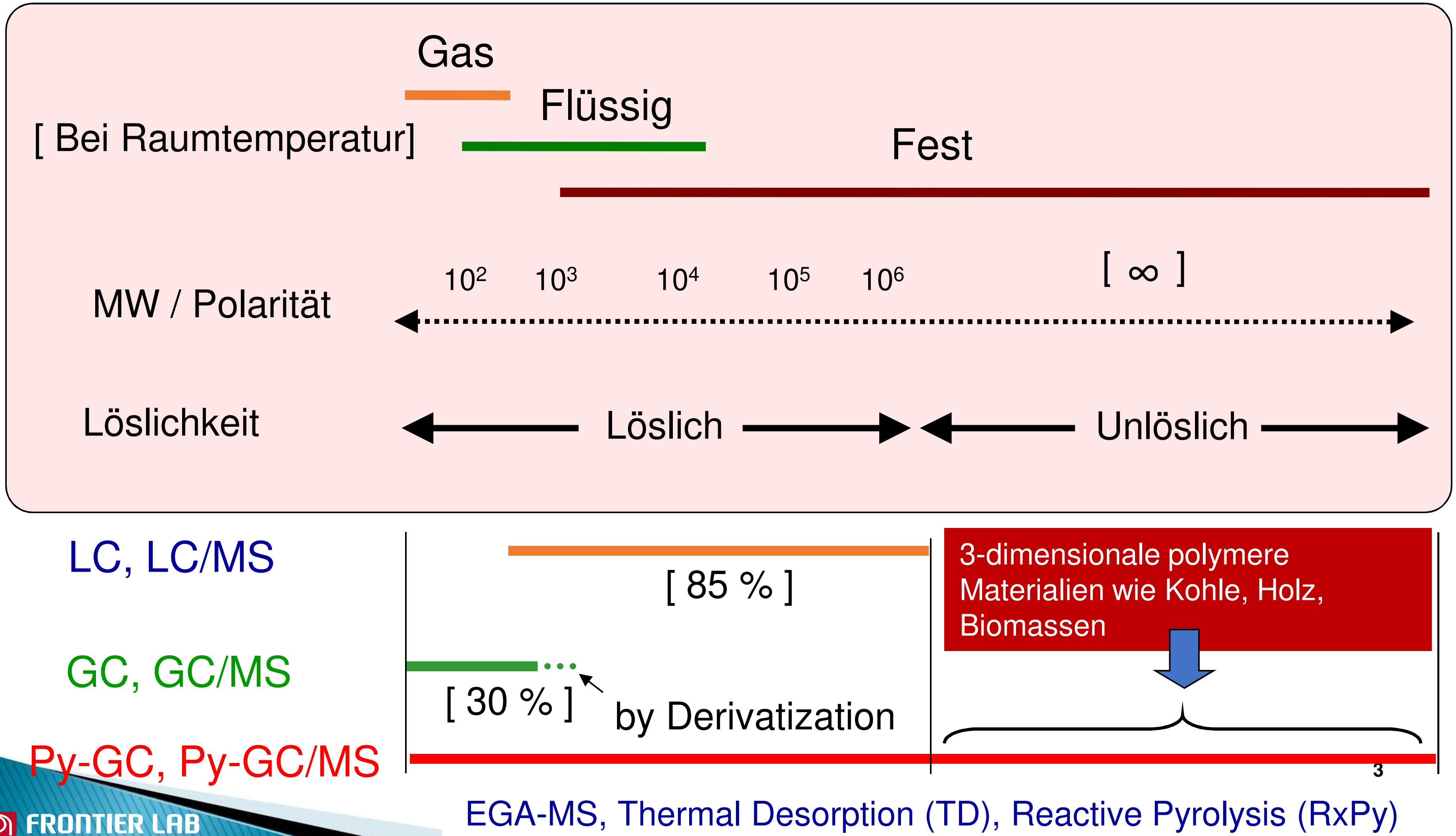
Frontier Lab- Kurzvorstellung

- Frontier Laboratories, Ltd. wurde 1991 von Dr. Chuichi Watanabe (Chu-san) gegründet. Dr. Watanabe entwickelte mit Unterstützung von Polymerwissenschaftlern der Nagoya University in Japan einen Pyrolyser, der auf einem vertikalen Mikro-Ofen-Design basiert.
- Wir sind ein weltweit tätiges Unternehmen und Marktführer auf dem Gebiet der analytischen Pyrolyse. Unsere Hauptprodukte sind: Multifunktionales Pyrolyse-System EGA/PY-3030D, Single-Shot-Pyrolyser PY-3030S, die µ-Screening Reaktoren der Serie 3050 für die Katalysator-Charakterisierung, F-SEARCH Polymer- und Additiv-Datenbank und eine Reihe von Ultra ALLOY® Edelstahl-Kapillarsäulen..

Frontier Lab Standorte:

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

Dein GC/MS wird vielseitiger mit Pyrolyse



Definition der Analytischen Pyrolyse

- Die Pyrolyse ist eine thermochemische Zersetzung von organischem Material bei erhöhten Temperaturen ohne Beteiligung von Sauerstoff. Das Wort ist geprägt von den griechisch abgeleiteten Wörtern pyr "Feuer" und „Lysis“ "Trennen "*.
- Bei der analytische Pyrolyse werden die organische Moleküle kontrolliert und reproduzierbar durch den präzise Eintrag von Hitze zerlegt.

*http://en.wikipedia.org/wiki/Pyrolysis

Polymer-Zersetzungsmechanismen

Random Scission

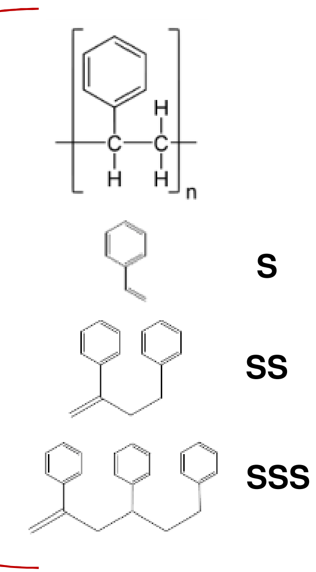
- Polyolefins (polyethylene, polypropylene, polybutlyene, etc.)
- C-C bonds break to produce fragment patterns of increasing oligomer sizes

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

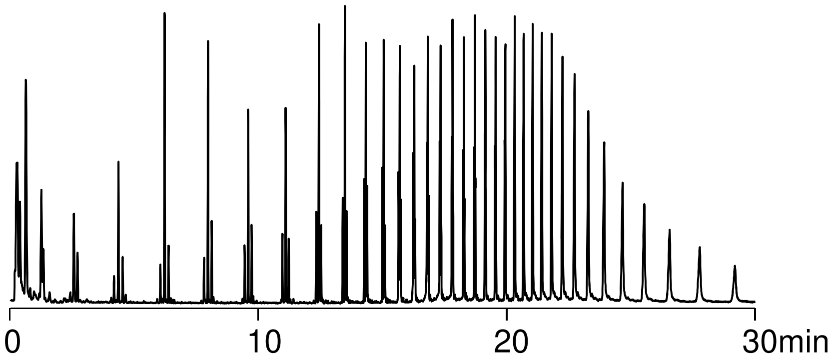
- Side groups (i.e. Cl) attached to the side of a polymer chain break before C bonds.
- Cl removes H from polymer chain = unsaturated polyenes + HCl. These polyenes form aromatic compounds.
- Polyvinyl chloride (PVC) is an example.
  - PVC pyrolyzates contain single aromatic rings (BTEX), double rings (i.e. naphthalene) and even triple rings (i.e. anthracene).
  - Big peak of HCl. (see page 110 in Py-GC/MS Data Book*)



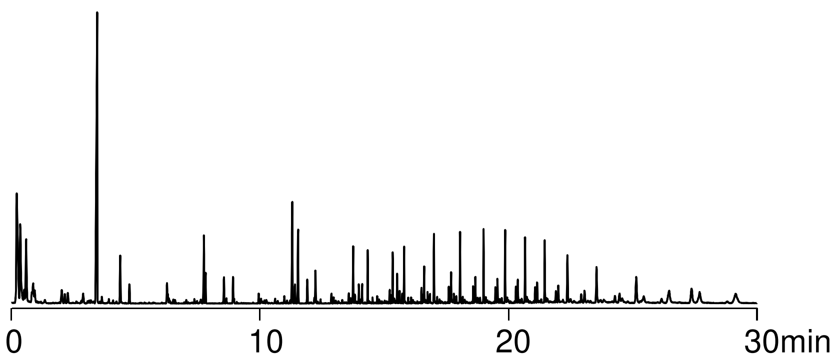
*Pyrolysis GC/MS Data Book of Synthetic Polymers, 2011, Tsuge, Ohtani, Watanabe

Typische Pyrogramme

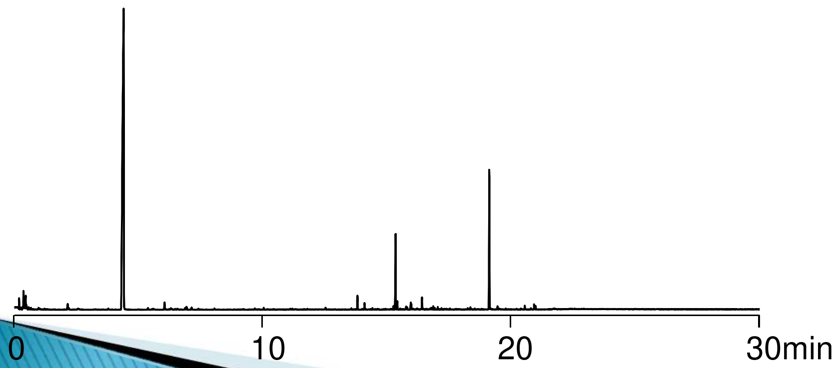
Polyethylen



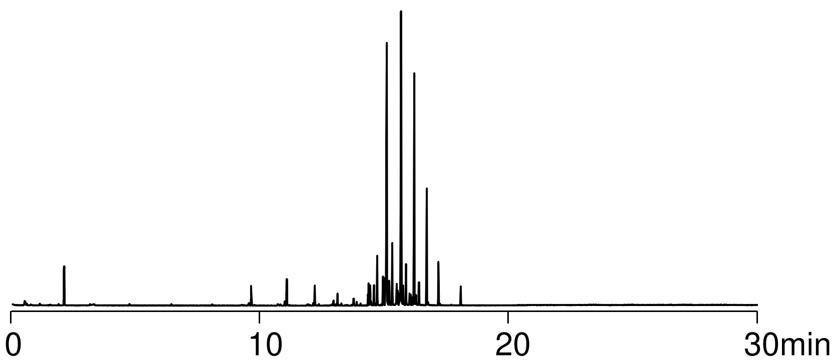
Polypropylen



Polystyrol

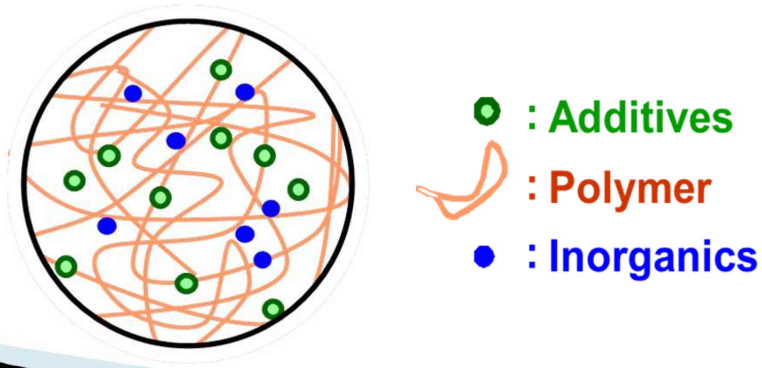


Methacrylat-Copolymer

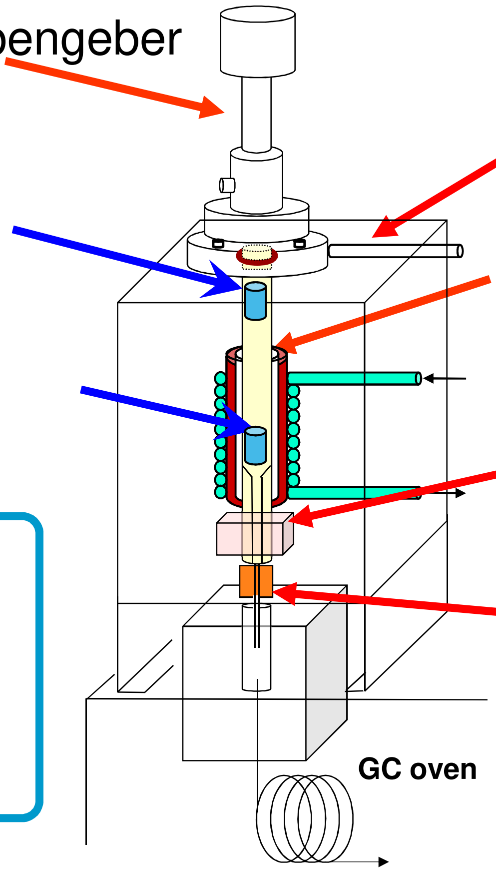


Materialien für PY-GC/MS

- 1. Synthetische Polymere (Plastik, Textilien, “Mikro-Plastik”)
- 2. Farben, Tinten, Lacke
- 3. Natürliche Polymere (Lignin, Papier, Polysaccharide, Seide)
- 4. Kohle, Tabak
- 5. Additive (Antioxidantien, Stabilisatoren, Phthalate, Flammschutzmittel)
- 6. Bodenproben (Organik)



Schematisches Diagramm des Multi-Shot pyrolyzer EGA/PY-3030D



Sample cup

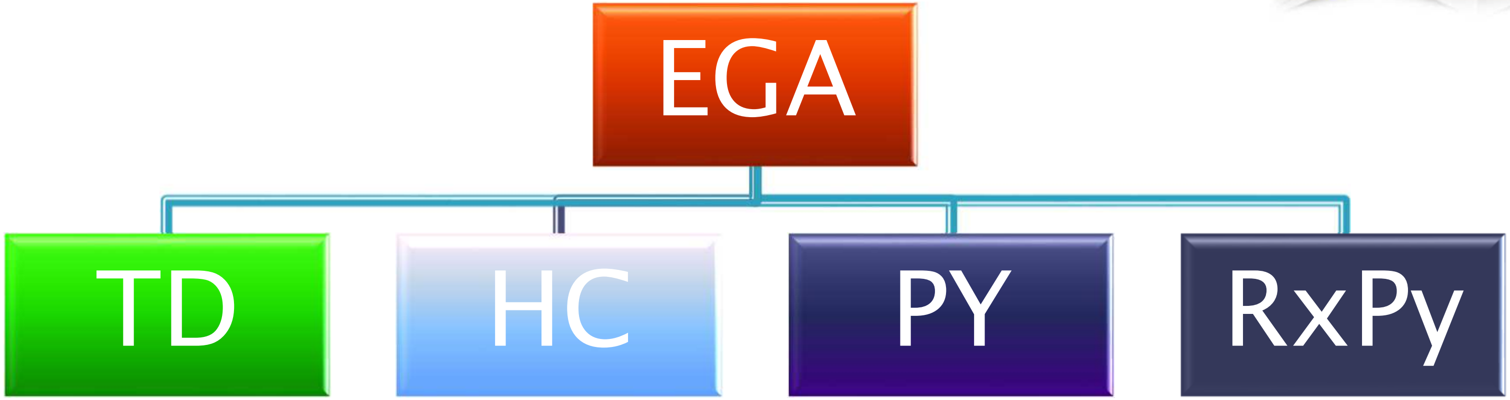
- **Stainless steel deaktiviert (Quarz)**
- **Flüssige oder feste Proben**

Volume: 50μL 80μL

FLAB Multi-Shot Pyrolyse gekoppelt mit GC/MS

- Multi-Shot pyrolyzer
  EGA/PY-3030D
- Single-Shot pyrolyzer
  PY-3030S
- Pyrolyzer accessories

"Method Map" zur Material-Charakterisierung

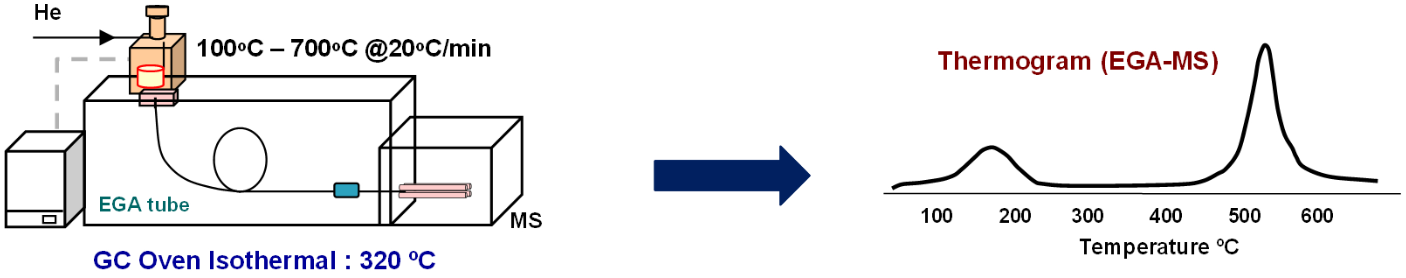


EGA	**Evolved Gas Analysis**
TD	**Thermal Desorption**
HC	**Heart-Cutting**
PY	**Pyrolysis**
RxPy	**Reactive Pyrolysis**

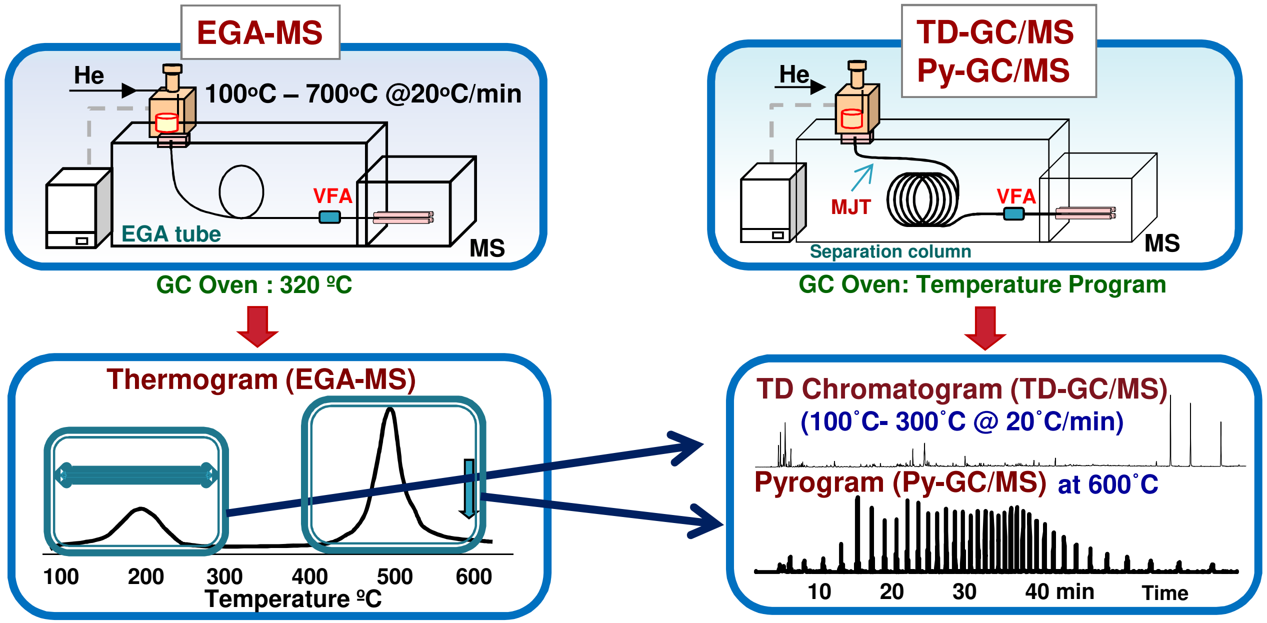
Evolved Gas Analyse: Schnelles Screening der evolvierenden Gase

1st Schritt auf der "Method Map"

- Es wird keine Säule verwendet; ein kurze, unbelegte, deaktivierte Kapillare mit kleinem Durchmesser (2,5m, 0,15 mm id.) deaktivierter Schlauch verbindet den Injektor mit dem Detektor.
- Die Probe wird bei relativ niedriger Temperatur in den Ofen fallen gelassen (ca. 40-100˚C). Der Ofen wird dann auf eine wesentlich höhere Temperatur hochgefahren (ca. 600-800˚C).
- Die Verbindungen „verdampfen" aus der Probe bei ansteigenden Temperatur gemäß ihren jeweiligen Siedepunkten und wir erhalten ein „Thermogramm"



Thermische Extraktion von Additiven aus Polymeren



- **EGA-MS ist der empfohlene erste Schritt zur Charakterisierung einer Probe und verwendet eine unbeschichtete Kapillare (2,5m x 0,15mm i.d.), um den GC-Einlass mit dem MS zu verbinden.**

  TD gefolgt von PY mit der identischen Probe nennen wir "Double-Shot".

- **Nachfolgende Analysen (TD-GC/MS und Py-GC/MS) werden mit einer Trennsäule (30m x 0,25mm x 0,25µm) durchgeführt. Der Wechsel vom Rohr zur Säule dauert mit dem Vent-free Adapter (VFA) nur wenige Minuten.**

Heart-Cutting: Thermisches “Ausschneiden” von EGA-MS Zonen

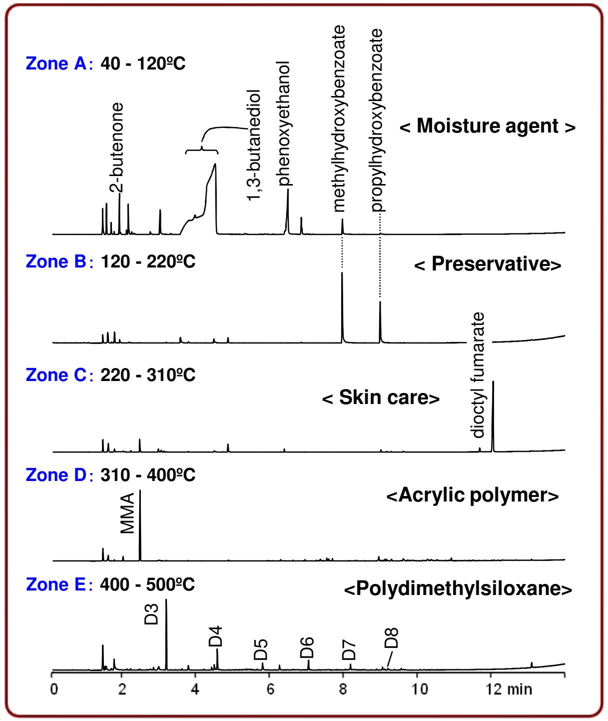
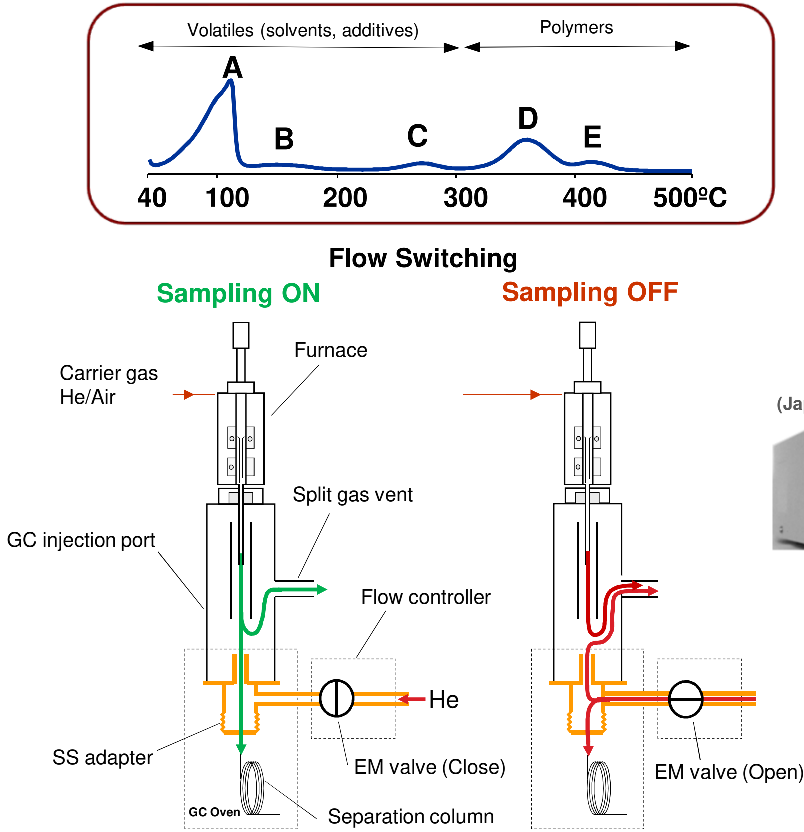


Figure.1: Heart-cut EGA-GC/MS analysis of zones A to E of EGA thermogram of an eyeliner.



(Japan patent No.3290893)

Flow controller

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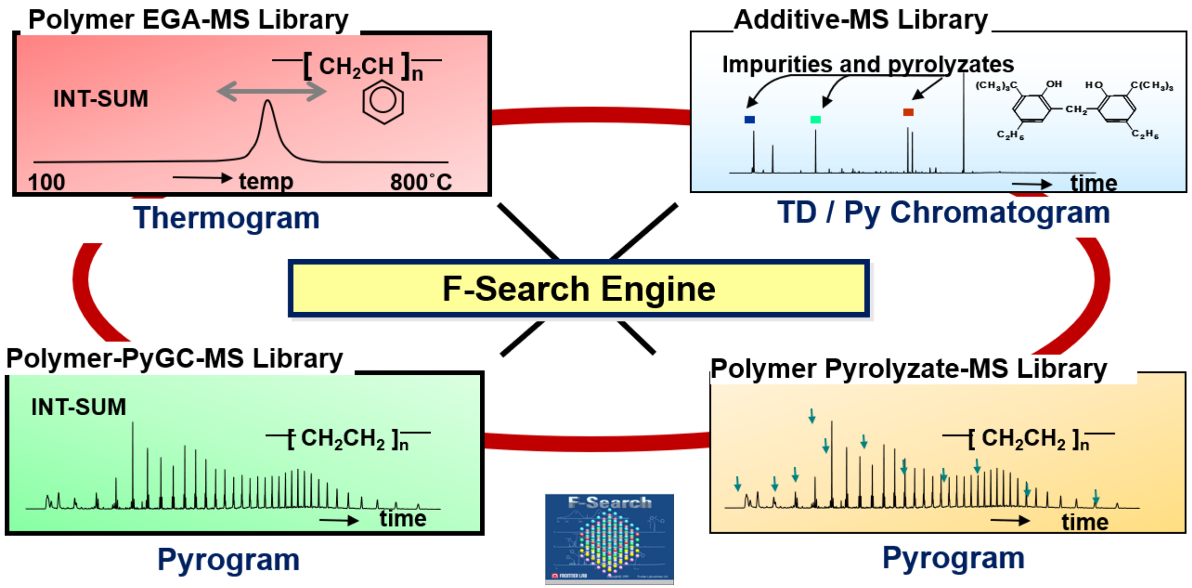
Einfache und zuverlässige Dateninterpretation mit F-Search

Identifizierung von Polymeren und Additiven aus Daten, die durch Gasanalyse, thermische Desorption oder Pyrolyse
GC/MS-Analyse gewonnen wurden. Es kann auch eine Benutzerbibliothek erstellt werden.

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



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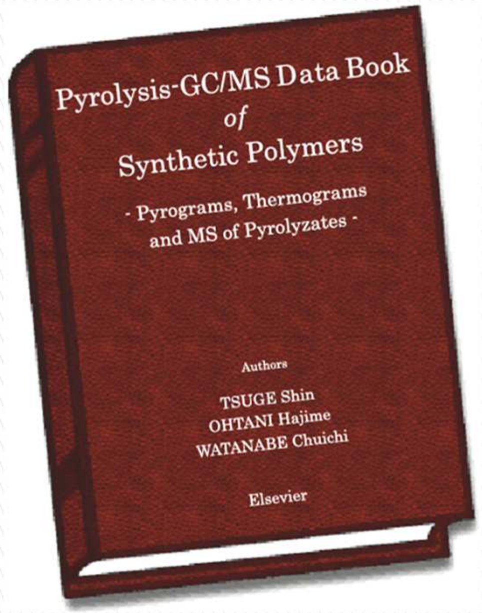
Pyrolysis GC/MS Data Book of Synthetic Polymers



- ***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.**

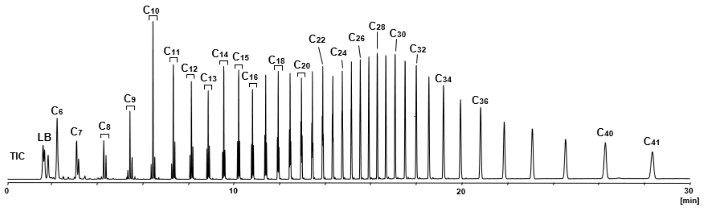
● **Data compilation of pyrograms of 33 condensation polymers through reactive pyrolysis (RP) in the presence of tetramethyl ammonium hydroxide (TMAH) with the detail detailed peak assignment.**

Search ISBN “9780444538925” in Amazon books

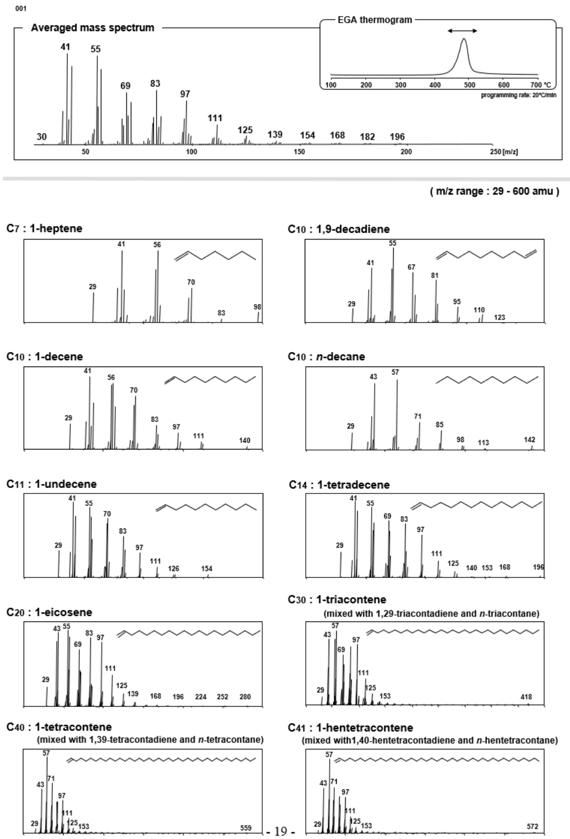
Polyethylene Buchauszug

001 Polyethylene (high density) ; PE(HDPE)

$-\!\!(CH_2CH_2)\!\!-_n$



Peak Notation	Assignment of Main Peaks	Molecular Weight	Retention Index	Relative Intensity
LB	propylene, propane	42, 44	297	43.7
C_6	$CH_2{=}CH(CH_2)_3CH_3$	84	583	91.8
C_7	$CH_2{=}CH(CH_2)_4CH_3$	98	689	42.4
	$CH_3(CH_2)_5CH_3$	100	700	19.3
C_8	$CH_2{=}CH(CH_2)_4CH{=}CH_2$	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
C_9	$CH_2{=}CH(CH_2)_5CH{=}CH_2$	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
C_{10}	$CH_2{=}CH(CH_2)_6CH{=}CH_2$	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
C_{11}	$CH_2{=}CH(CH_2)_7CH{=}CH_2$	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
C_{14}	$CH_2{=}CH(CH_2)_{10}CH{=}CH_2$	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
C_{20}	$CH_2{=}CH(CH_2)_{16}CH{=}CH_2$	278	1985	25.3
	$CH_2{=}CH(CH_2)_{17}CH_3$	280	1993	38.0
	$CH_3(CH2)_{18}CH_7$	282	2000	16.2
C_{30}	$CH_2{=}CH(CH_2)_{27}CH_3$	420	2993	100.0
C_{40}	$CH_2{=}CH(CH_2)_{37}CH_3$	560	3997	94.1
C_{41}	$CH_2{=}CH(CH_2)_{38}CH_3$	574	4096	82.8



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

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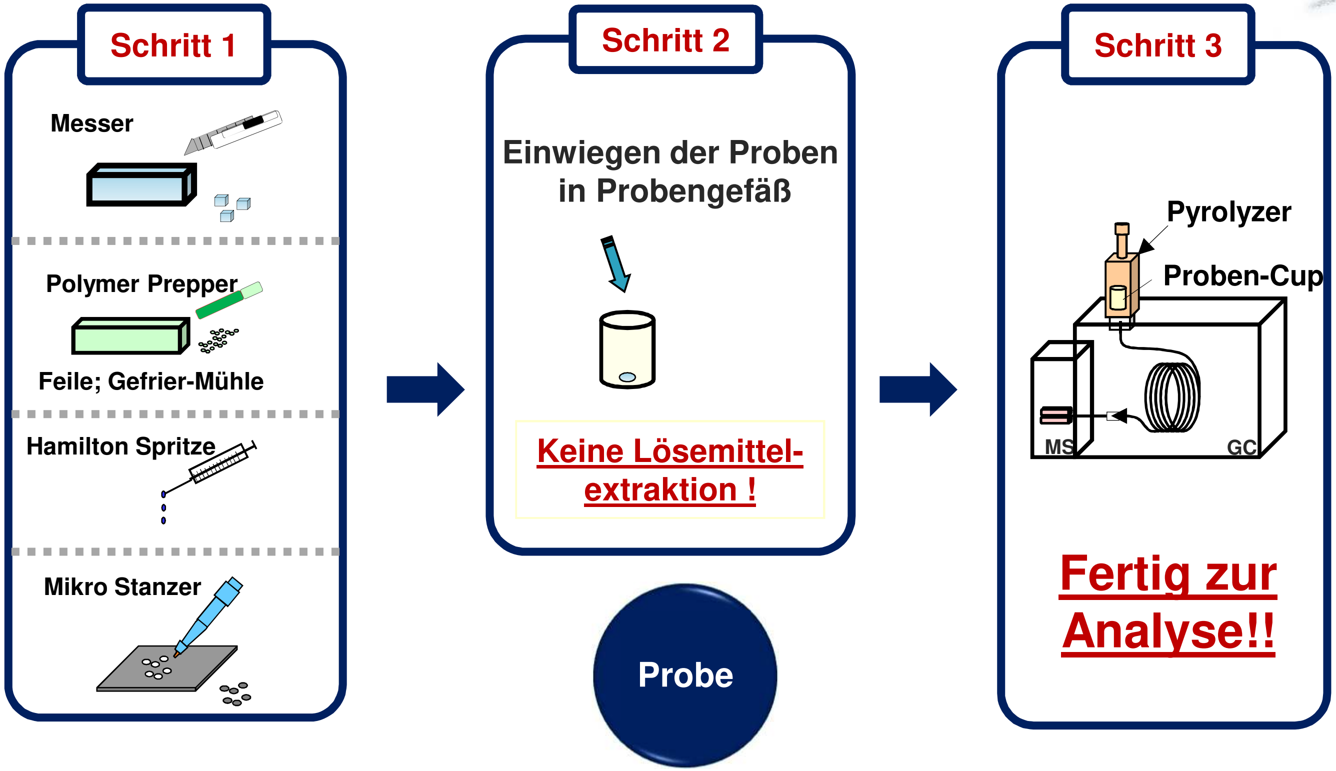
Sehr einfache Probenvorbereitung



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Analyse eines unbekannten Biopolymers

Versuch einer De-Formulierung

EGA-MS, Single Shot PY (SS) and Heart Cut (HC-EGA-GC/MS)

Source:
http://www.legalproductivity.com/

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Material characteristics and facts (data sheet)

- **Thin foil**

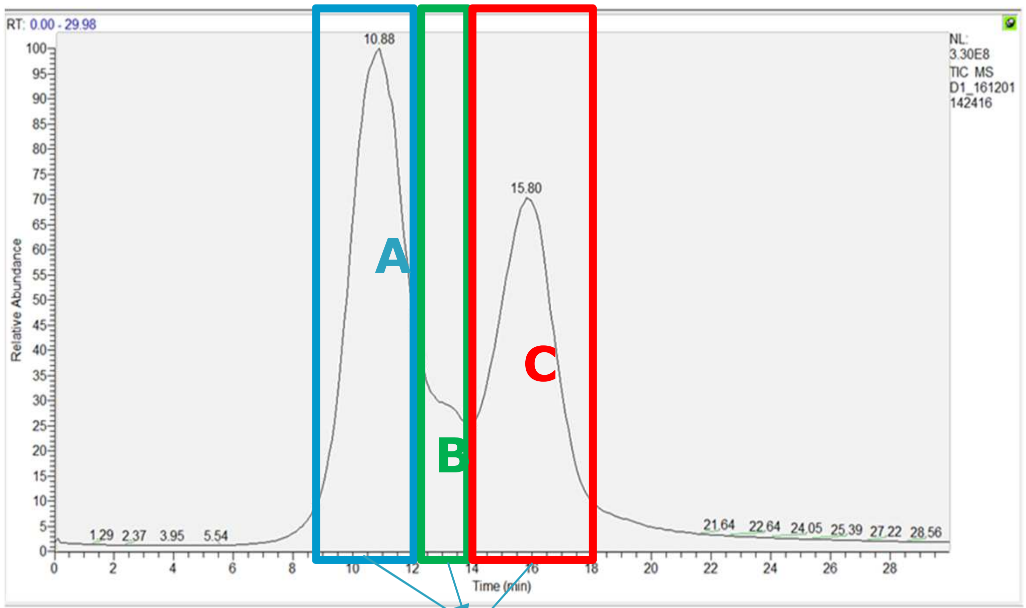
- **The bio-based carbon share of the entire formulation exceeds 50%.**

- **plasticizer-free, thermoplastic material that contains natural potato starch and other biologically sourced polymers**

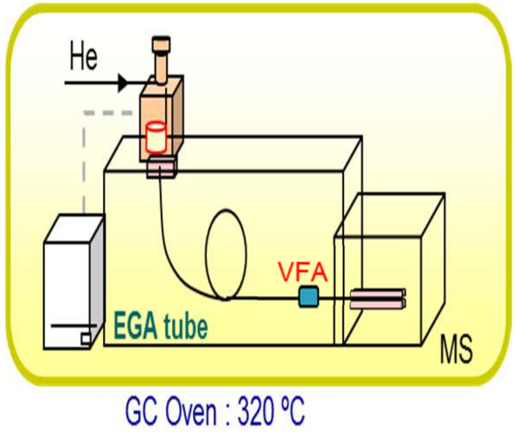
- **fully biodegradable and compostable**

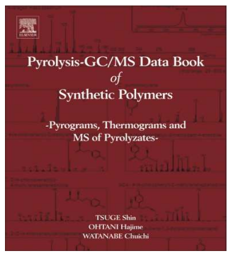
Unknown bio-polymer

1. EGA-MS



100°C – 700°C @20°C/min

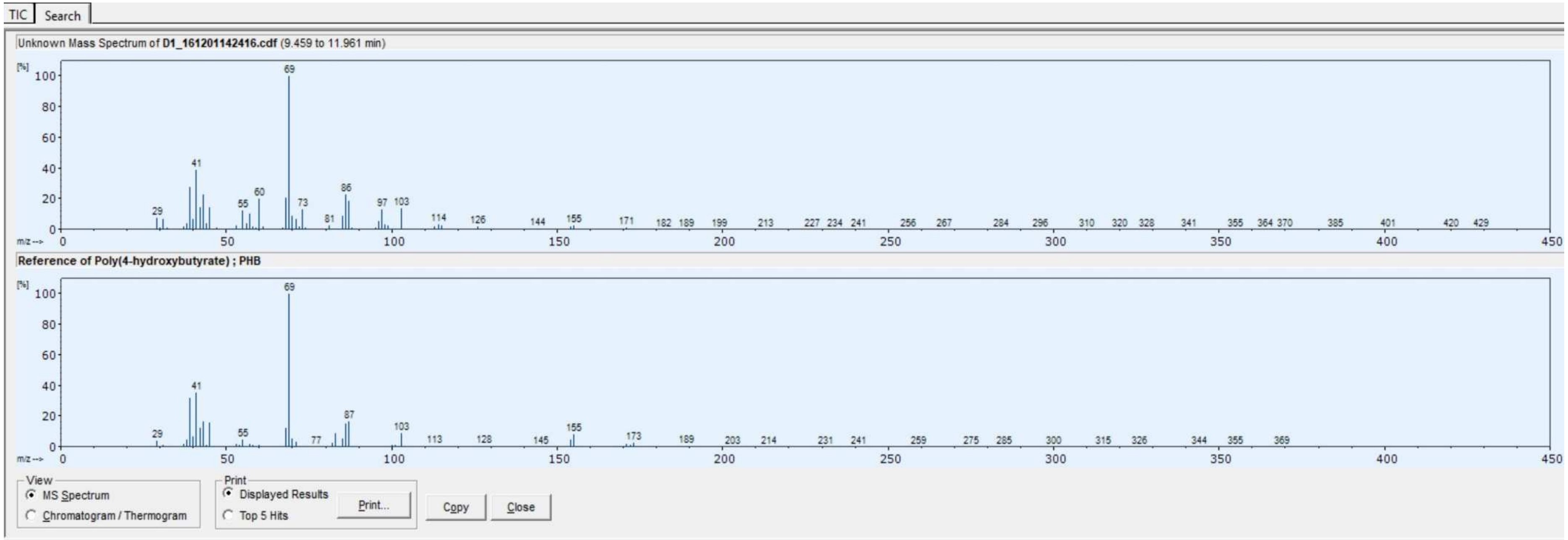




Unknown bio-polymer

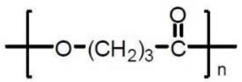
F-Search: EGA Library

Zone A



Reference Records: Details... Edit...

	Polymer / Additive	Qual [%]	Start [C]	Top [C]
1	Poly(4-hydroxybutyrate) ; PHB	89	253	286
2	Polyhydroxybutyrate	88	268	297
3	Poly(3-hydroxy butyrate-co-3-hydroxy valerate)	83	179	289
4	Poly(ethyl methacrylate) (5.5-13.0 min)	78	214	295
5	Poly(ethyl methacrylate) (1.5-18.5 min)	78	129	295



PHB (Polyhydroxybutyrat)

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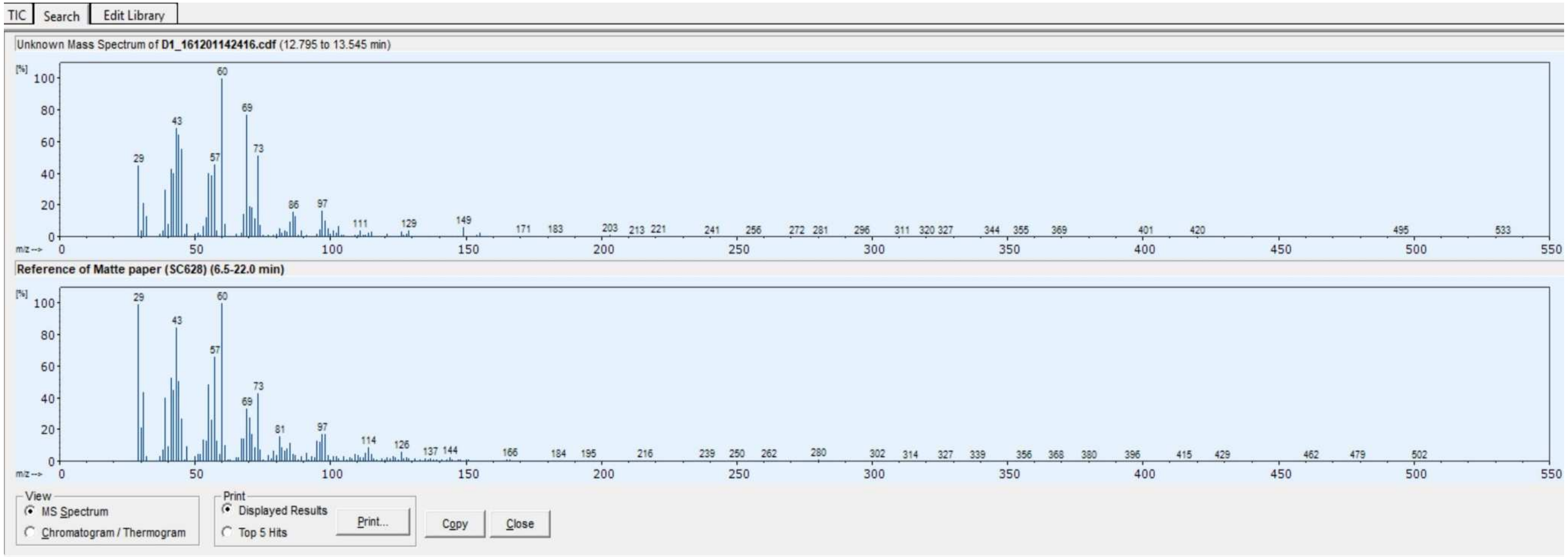
Unknown bio-polymer

F-Search: EGA Library

Zone B



Reference Records: Details... Edit...

	Polymer / Additive	Qual [%]	Start [C]	Top [C]	End [C]	Entry ID
1	Matte paper (SC628) (6.5-22.0 min)	82	180	330	490	FLE-1306
2	Paper (Non-buffer paper, Pure guard 120 white)	81	290	375	450	FLE-0403
3	Paper (Acid-free, Pure guard 120)	81	310	364	410	FLE-0205
4	Cloth YD401-1 (12.0-17.5 min)	81	290	330	400	FLE-1301
5	Cloth YD405-1	81	295	337	374	FLE-1302

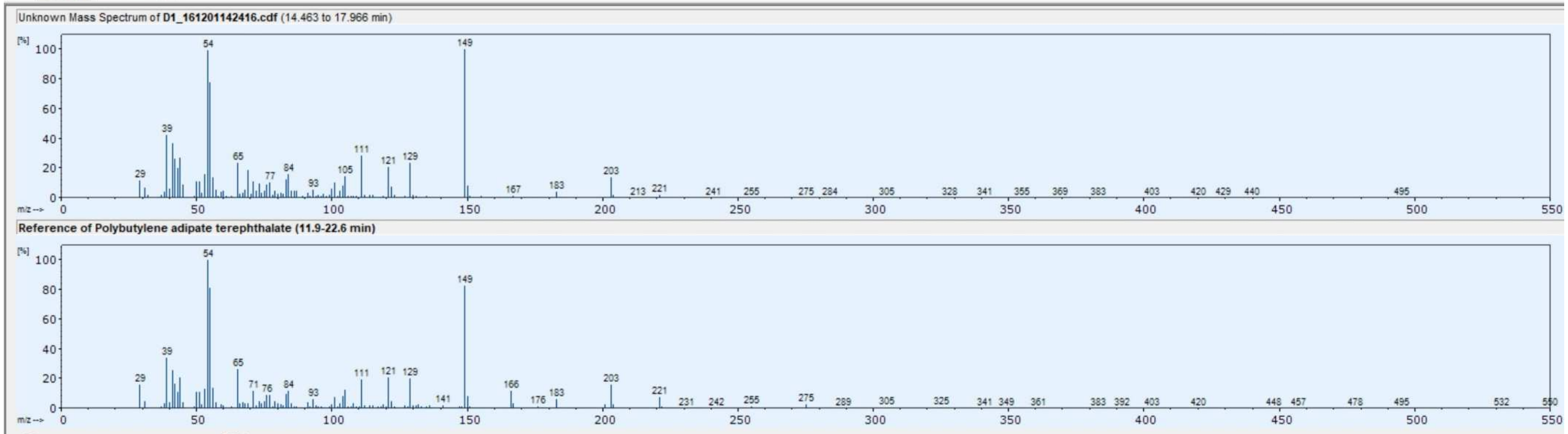
Cellulose

Unknown bio-polymer

F-Search: EGA Library

Zone C

TIC | Search | Edit Library

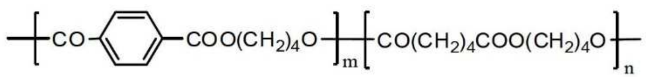


View: MS Spectrum / Chromatogram / Thermogram
Print: Displayed Results / Top 5 Hits — Print... Copy Close

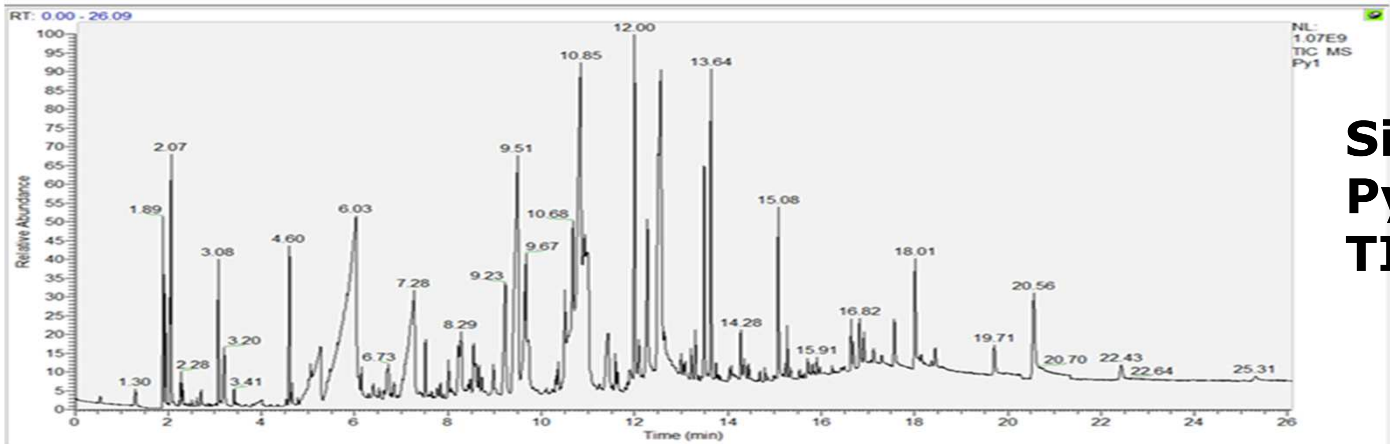
Reference Records: Details... Edit...

	Polymer / Additive	Qual [%]	Start [C]	Top [C]	End [C]	Entry ID
1	Polybutylene adipate terephthalate (11.9-22.6 min)	96	337	405	552	FLK-023
2	Polybutylene adipate terephthalate (5.4-22.6 min)	96	209	405	552	FLK-023
3	Polyester [(Butanediol,ethylene glycol,poly(tetramethylene glycol)):(a...	87	159	423	570	FLK-295
4	Polyester [(Butanediol,ethylene glycol,poly(tetramethylene glycol)):(a...	84	358	423	570	FLK-295
5	Polyester [Butanediol:(adipic acid,terephthalic acid) ; BD:(AA,TPA)]	82	367	415	520	FLK-303

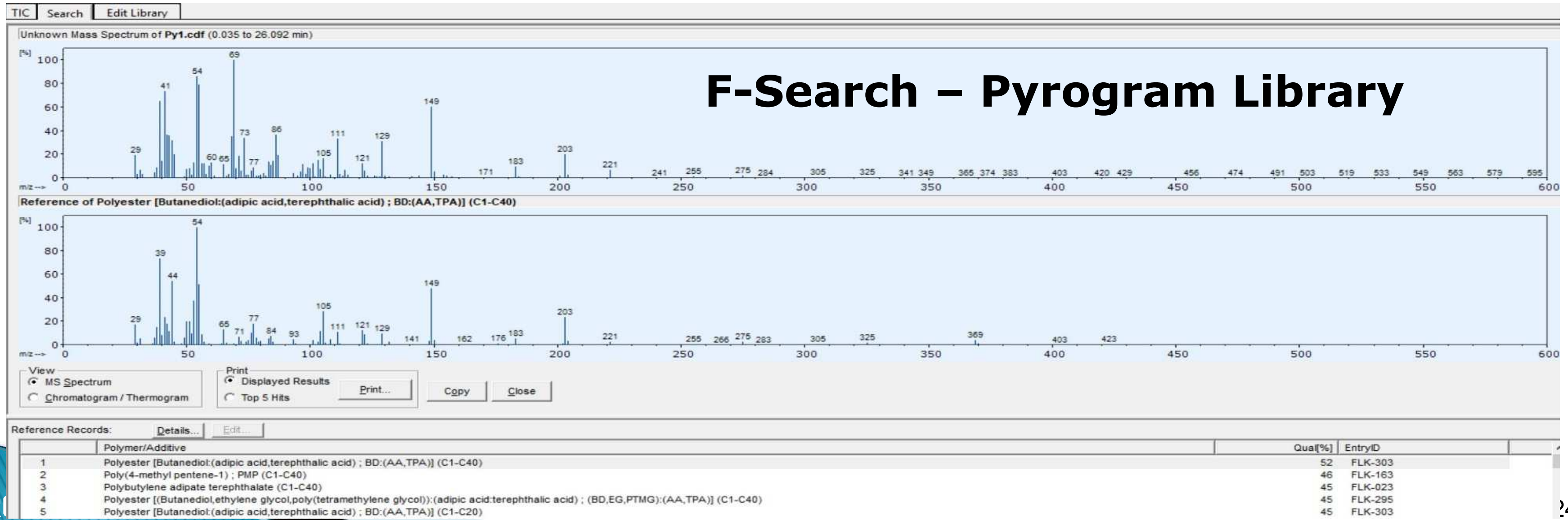
Polybutylene adipate terephthalate



Unknown bio-polymer



Single-Shot Pyrolyse TIC

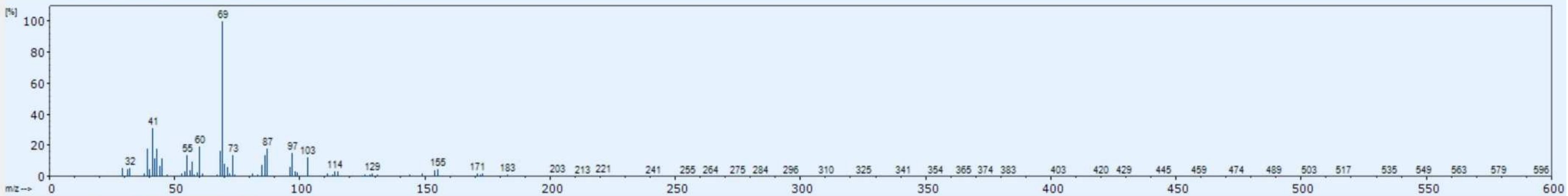


Unknown bio-polymer

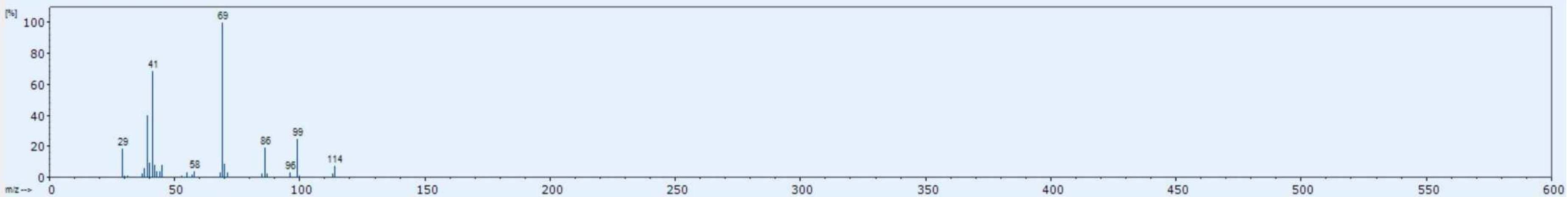
Heart Cut-GC/MS: Zone A

TIC | Search | Edit Library

Unknown Mass Spectrum of **HC1_161202110818.cdf** (0.039 to 26.108 min)



Reference of Poly(ethyl methacrylate) (C1-C10)



View
- MS Spectrum
- Chromatogram / Thermogram

Print
- Displayed Results
- Top 5 Hits

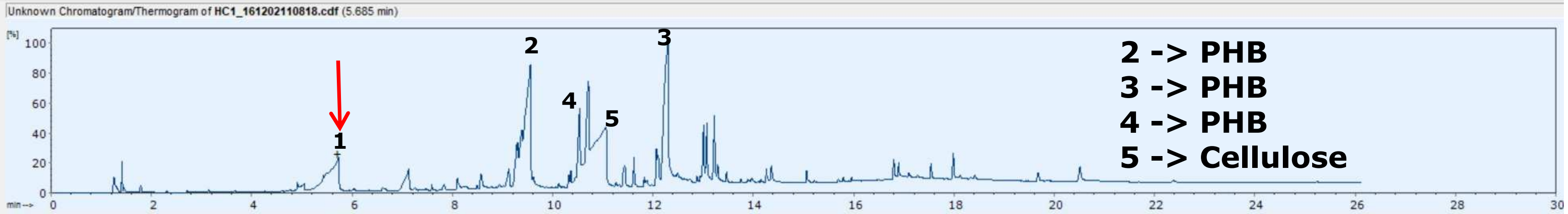
Print... | Copy | Close

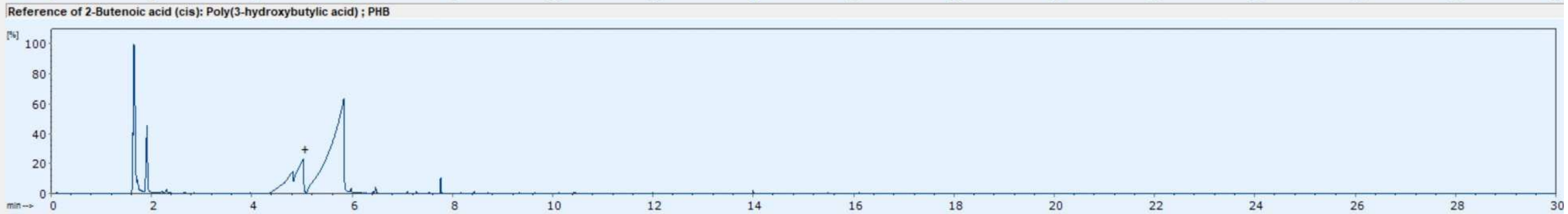
Reference Records: Details... | Edit...

	Polymer/Additive	Qual[%]	EntryID
1	Poly(ethyl methacrylate) (C1-C10)	73	FLG-206
2	Poly(ethyl methacrylate) (C1-C20)	73	FLG-206
3	Poly(ethyl methacrylate) (C1-C40)	73	FLG-206
4	Poly(isobutyl methacrylate) (C1-C10)	71	FLG-207
5	Poly(isobutyl methacrylate) (C1-C20)	71	FLG-207
6	Poly(isobutyl methacrylate) (C1-C40)	71	FLG-207
7	Poly(2-hydroxyethyl methacrylate) ; PHEMA (C1-C40)	70	FLT-038
8	Poly(2-hydroxyethyl methacrylate) ; PHEMA (C1-C20)	70	FLT-038
9	Poly(3-hydroxy butylic acid) ; PHB (C1-C10)	66	FLTR-125
10	Poly(3-hydroxy butylic acid) ; PHB (C1-C20)	65	FLTR-125

Unknown bio-polymer

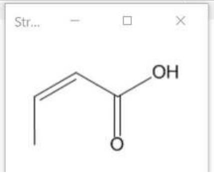
Pyrolyzate-LIB   Heart Cut: Zone A





Reference Records:

	Assignment	Polymer / Additive	Qual [%]	Rt Idx	Rt Time	MW	Entry ID	Peak
1	2-Butenoic acid (cis)	Poly(3-hydroxybutylic acid) ; PHB	99	853	5.03	86	FLT-125	C
2	2-Butenoic acid (trans)	Poly(3-hydroxybutylic acid) ; PHB	99	927	5.84	86	FLT-125	D
3	Methacrylic acid	Butyl methacrylate/isobutyl methacrylate copolymer	90	801	4.51	86	FLG-211	MA
4	Methacrylic acid	Poly(2-hydroxyethyl methacrylate) ; PHEMA	88	798	4.89	86	FLT-038	MA
5	Methacrylic acid	Poly(n-butyl methacrylate) ; PBMA	88	819	4.65	86	FLG-205	MA
6	Methacrylic acid	Poly(ethyl methacrylate)	87	819	4.66	86	FLG-206	
7	Methacrylic acid	Poly(acrylic acid) ; PAA	85	790	4.30	86	FLT-042	MA
8	Methacrylic acid	Poly(sec-butyl methacrylate)	83	859	5.14	86	FLG-210	MA
9	Methacrylic acid	Poly(n-butyl methacrylate) ; PBMA	82	788	4.27	86	FLT-037	MA
10	Isosorbide	Sorbitan monopalmitate	73	1281	8.67	146	I(3)-033P	



Unknown bio-polymer

<u>Main peaks of Heart Cut/Zone B lead to:</u>

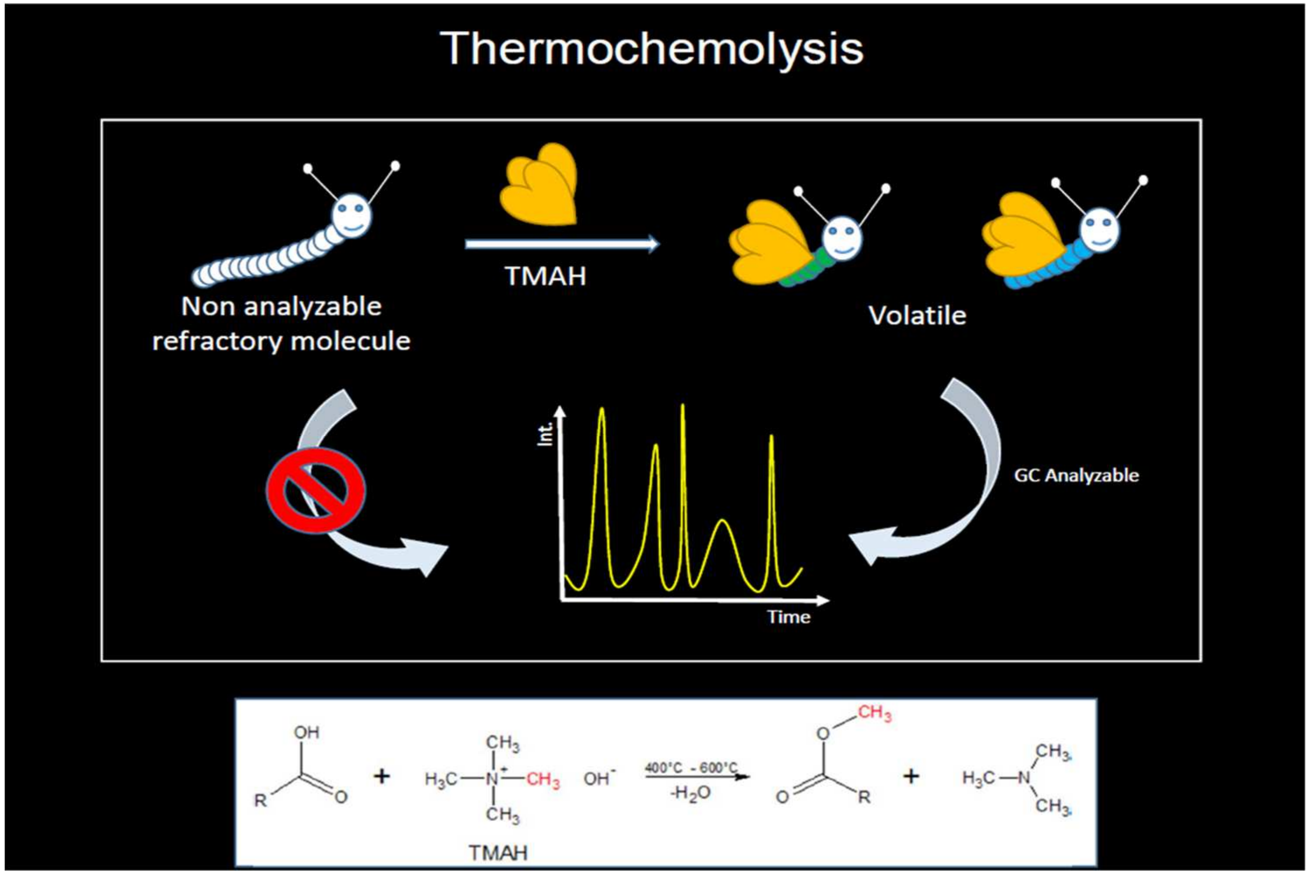
-Cellulose (Levoglucosan peak)
-Polylactic Acid
-PBSA

<u>Main peaks of Heart Cut/Zone C lead to:</u>

-PBT
-PBSA

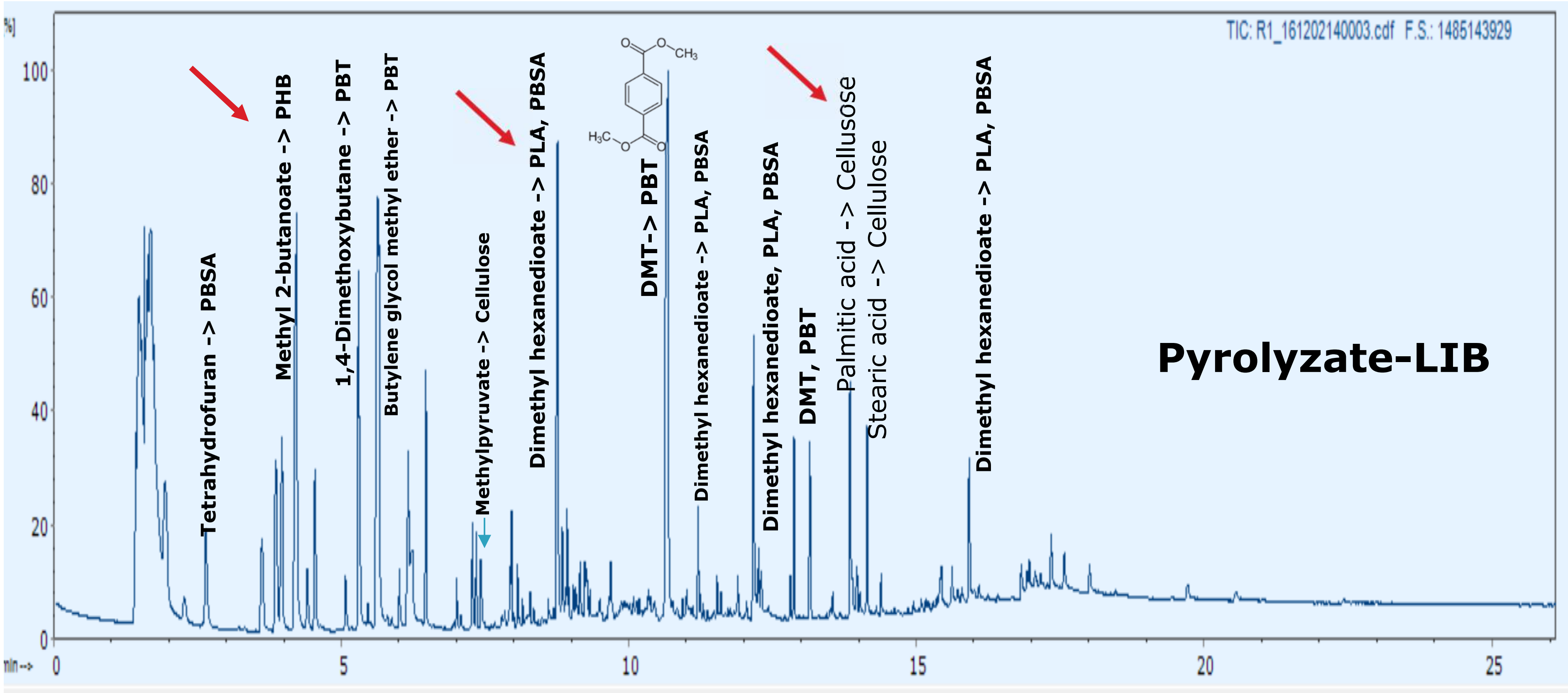
Unknown bio-polymer

TMAH RxPY @ 300 ⁰C: methylation of polar compounds



Unknown bio-polymer

TMAH RxPY @ 300 ^{0}C: methylation of polar compounds



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Unknown bio-polymer

Summery

- **EGA-MS as 1st step always recommended: complexity ?**
- **Single Shot Pyrolyse not sufficient for complex materials**
- **Heart Cut for deformulation of complex samples**
- **Optional reactive pyrolysis with TMAH for polar compounds**
- **F-Search for identification of polymers and additives**
- **<u>Results were in line with expectations of the manufacturer</u>**

Example 2: failure analysis (F-LAB USA)

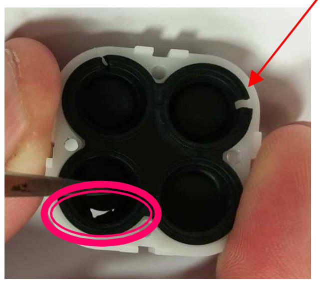
Problem: Early failure of Rubber Pump Diaphragm?

Question: What differences do we seen between the polymers?

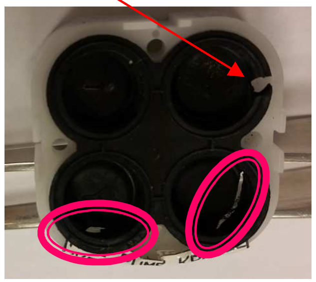
Sample Name	Description
Good (>1200 hrs)	Black rubber
Bad (<800 hrs)	Black rubber

Sampling

Good sample also has a crack.



Good sample



Bad sample

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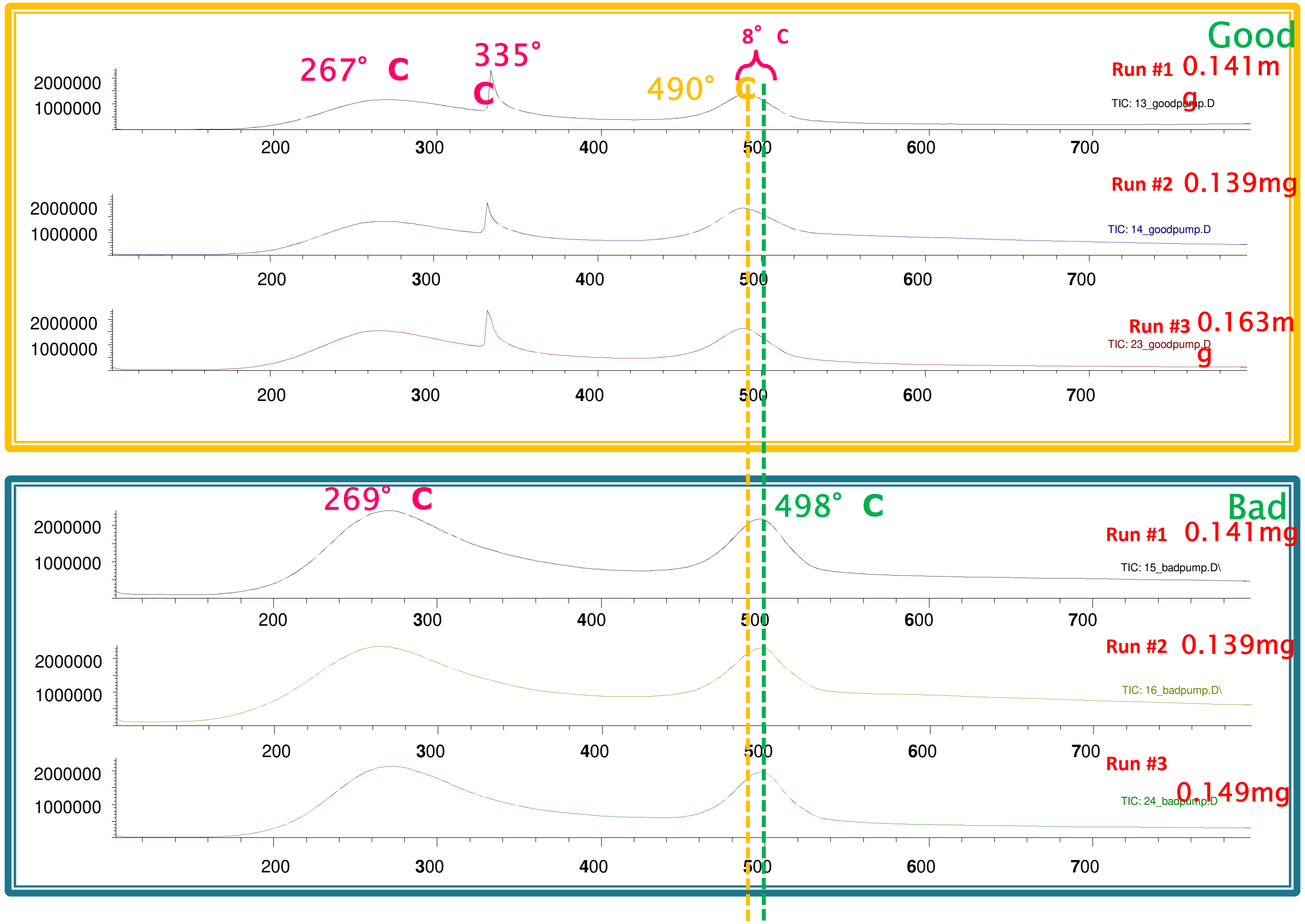
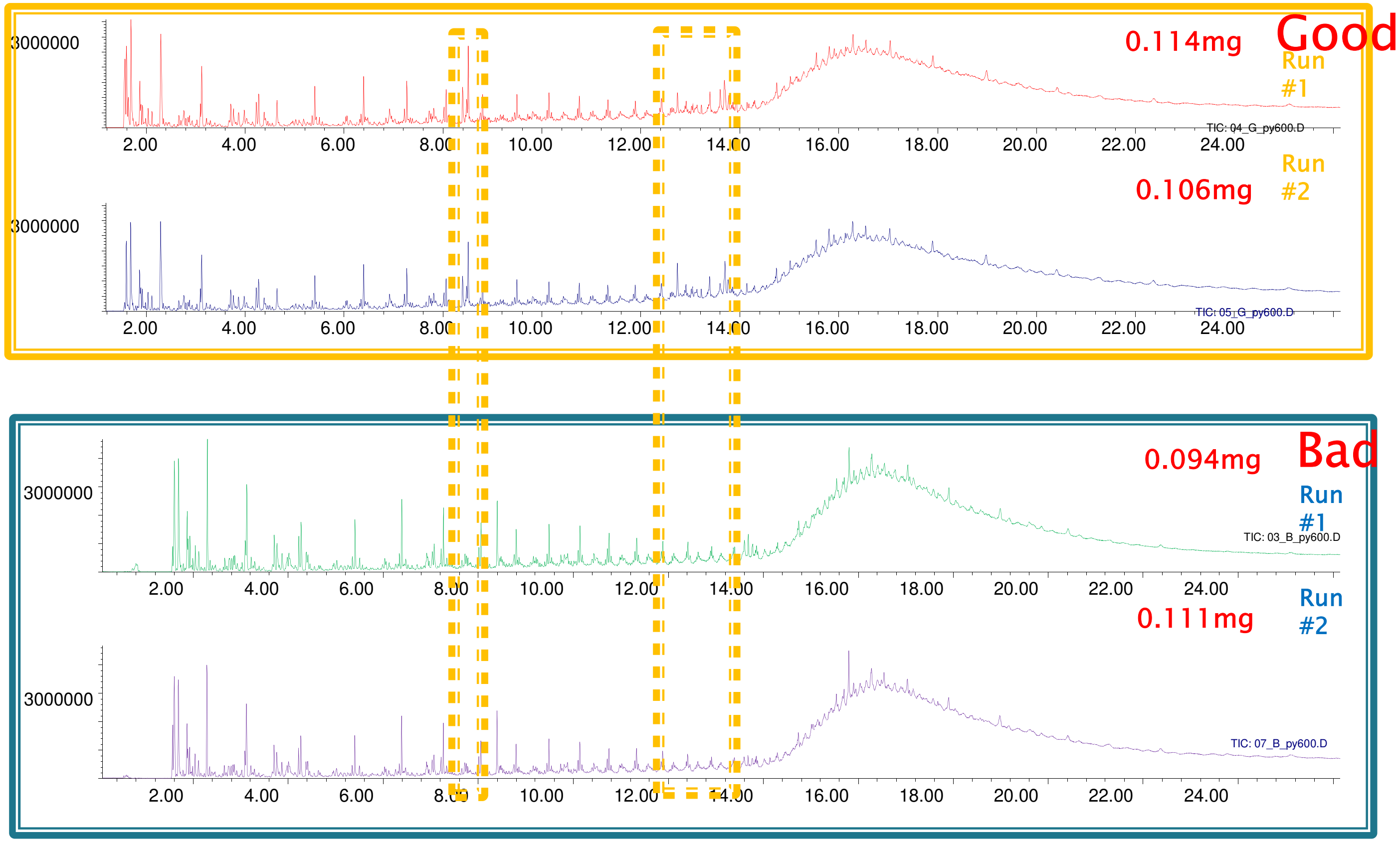
EGA (TIC) Thermogram of Rubber Samples (Triplicate)



Single-Shot Pyrogram (Py 600° C) of Good & Bad Rubber (duplicate)



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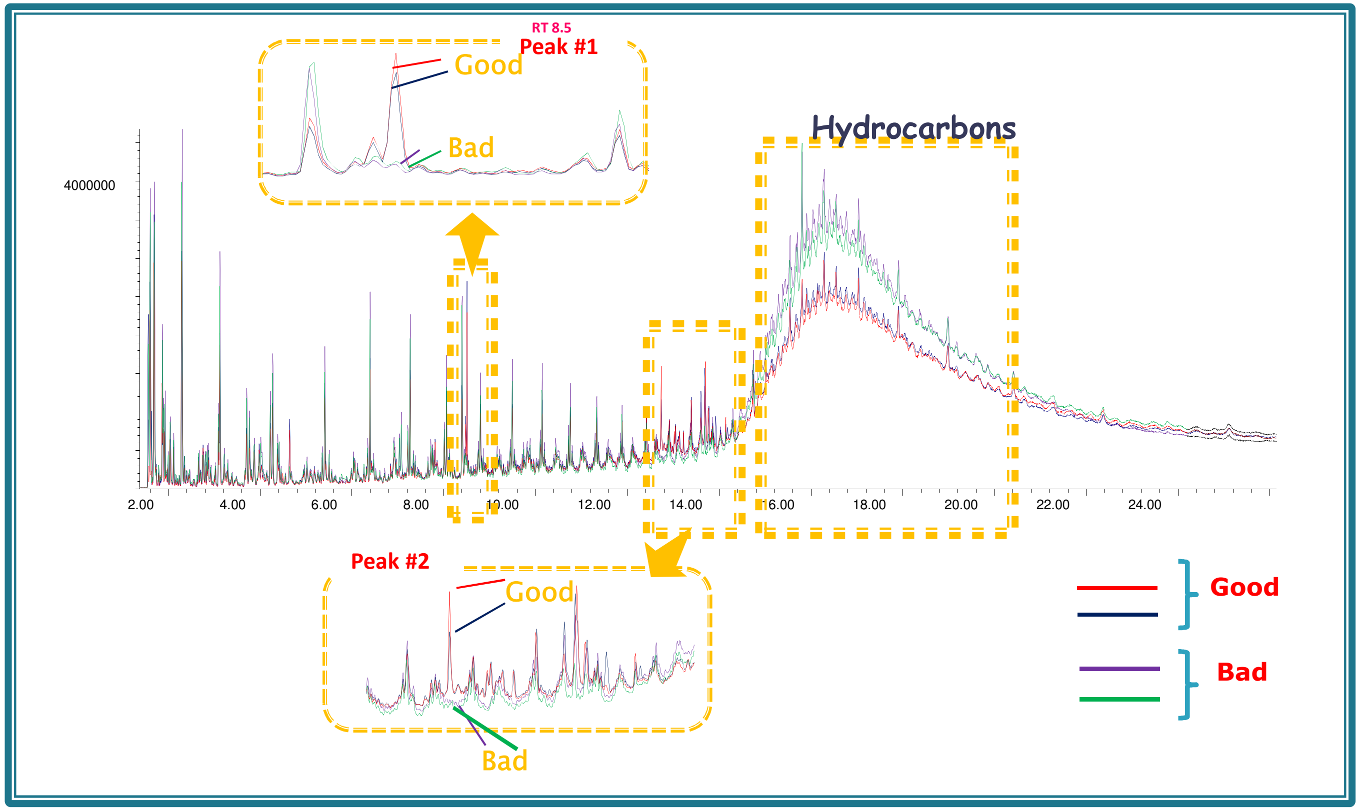
Single-Shot Pyrogram (Py 600° C) Overlay (duplicate) of Good & Bad Rubber



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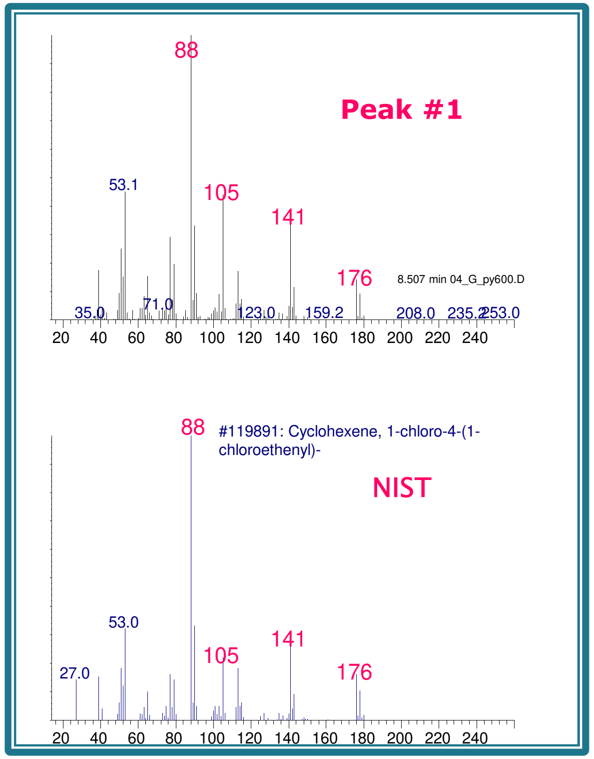
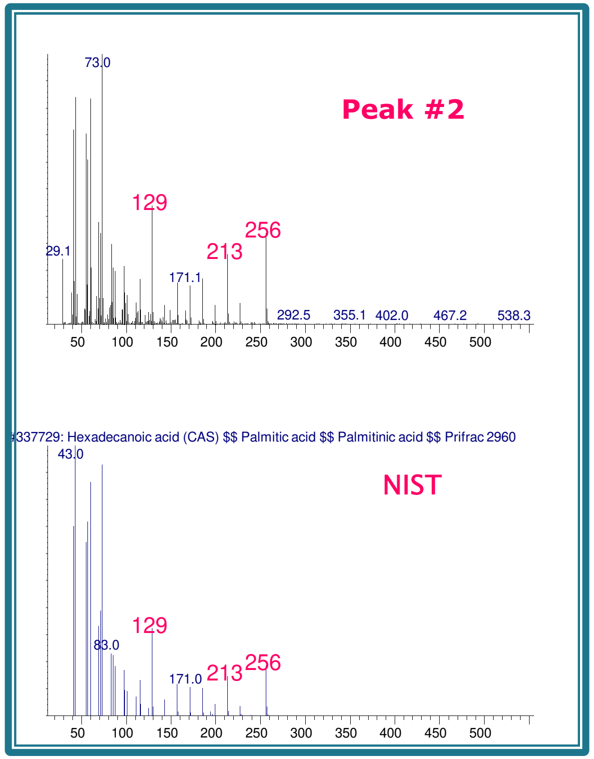
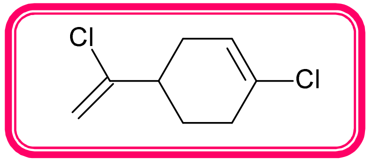
The MS spectra of Peak #1 & Peak #2

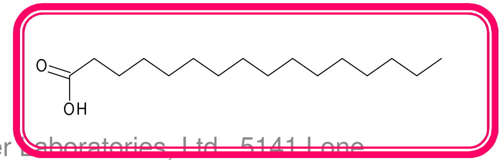




Cyclohexene, 1-chloro-4-(1-chloroethenyl)-
Match Qual. 96%



Palmitic acid Match Qual. 99%



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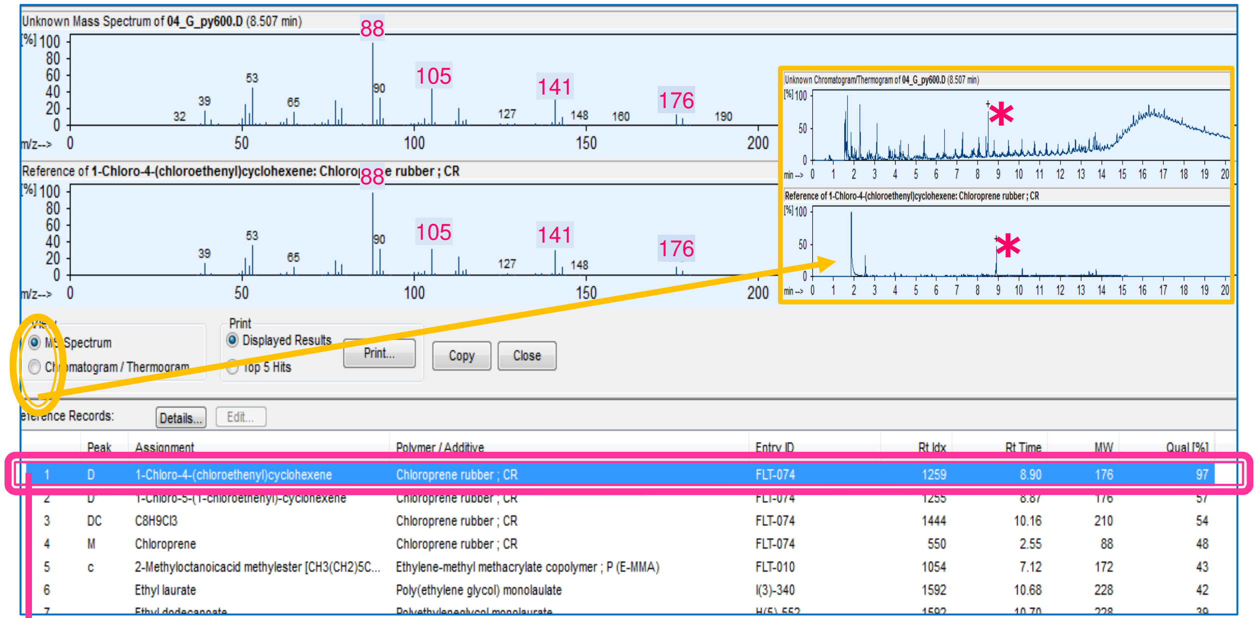
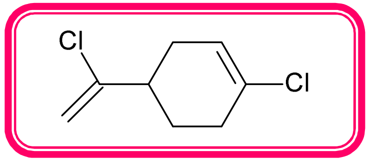
F-Search (Polymer Pyrolyzate, Additive-MS Library)
Search result from peak #1



D 1-chloro-4-(1-chloroethenyl) cyclohexene Chloroprene rubber Match Qual. 97%

"D" means "dimer"



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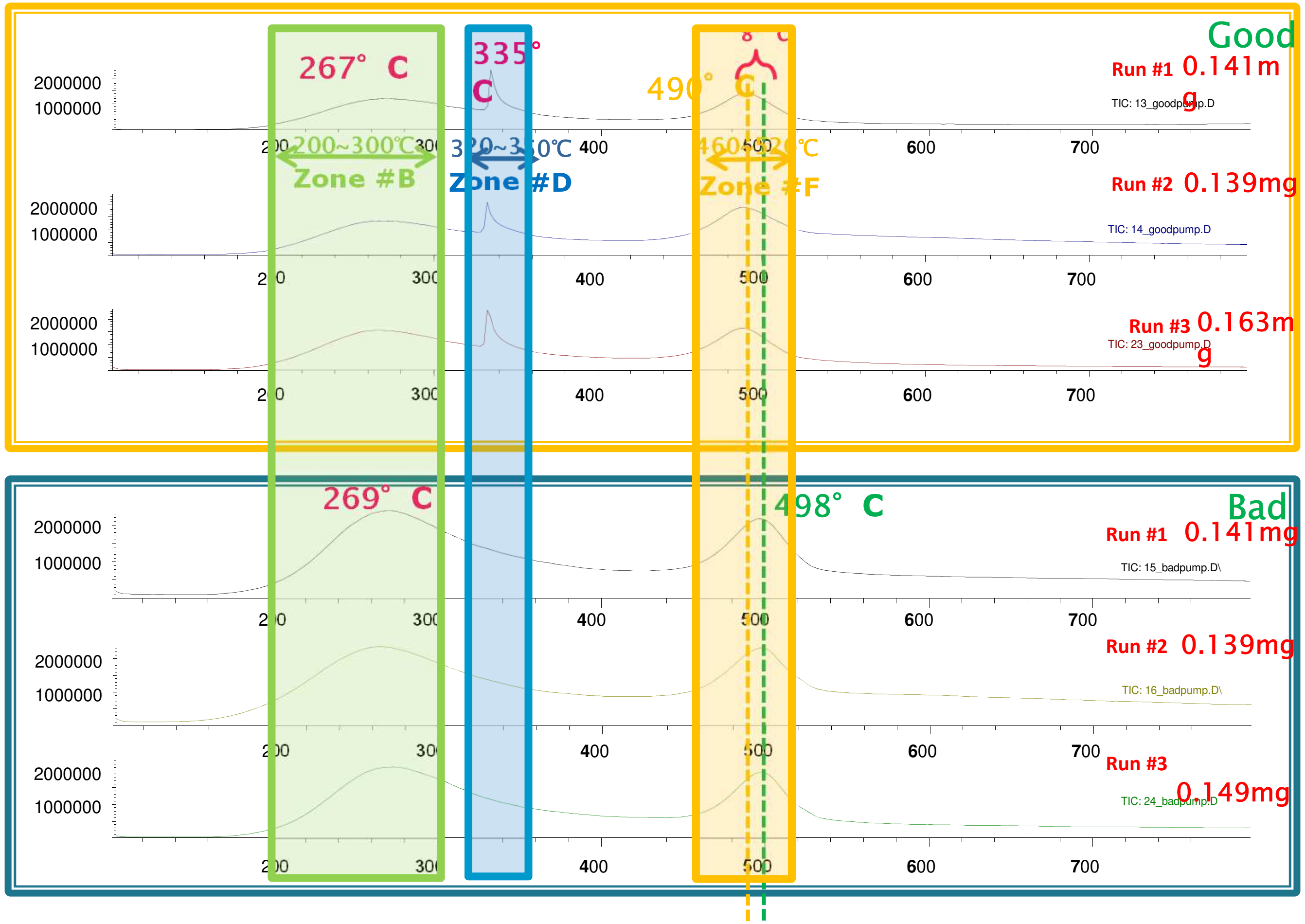
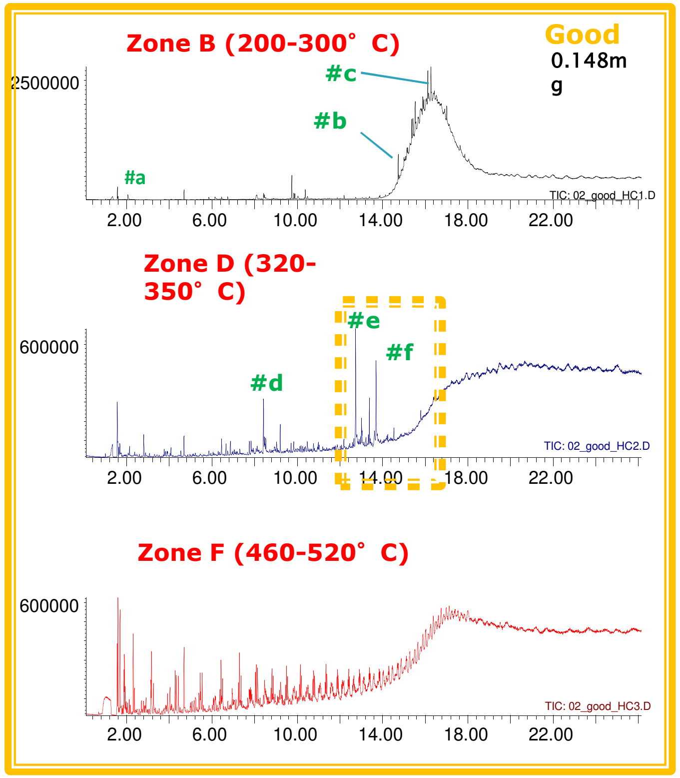
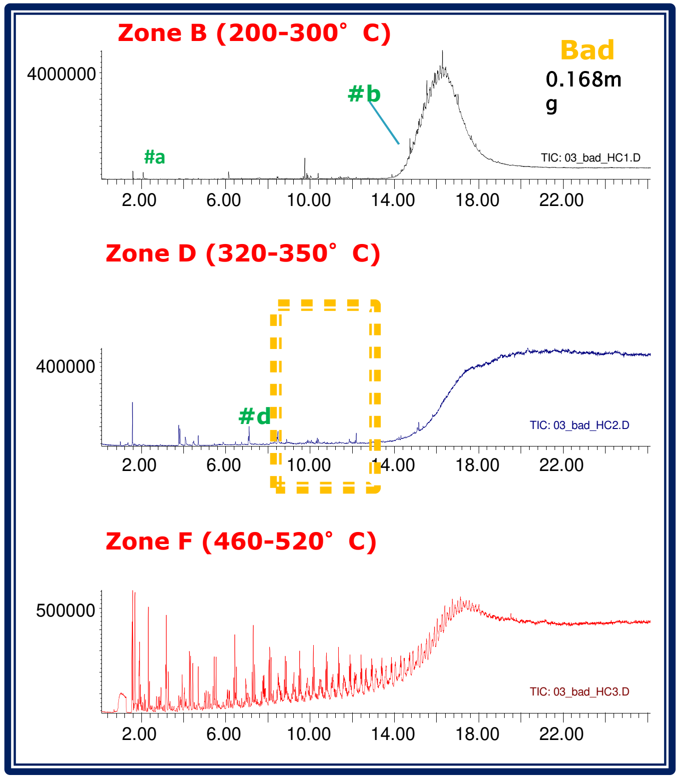
Heart-Cut EGA-GC/MS of Rubber Samples – defining the temp.- zones



The Heart-Cut Chromatograms of Good & Bad Rubber





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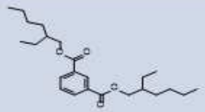
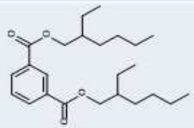
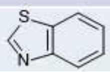
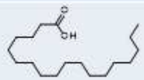
F-Search (Polymer-PyGC-MS Library) Search Results
Peaks a-f

Peak	RT	Compound	Structure	Source/Purpose
Zone B (200-300 °C)				
# a	2.1	CS2		Residual solvent
# b	15.4	DEHP (Di(ethylhexyl) phthalate)		Plasticizer
# c	16.1	DOIP (Dioctyl isophthalate)		Plasticizer
Zone D (320-350 °C)				
# d	8.4	Benzothiazole		Accelerator
# e	12.7	Palmitic acid		
# f	13.7	Stearic acid		

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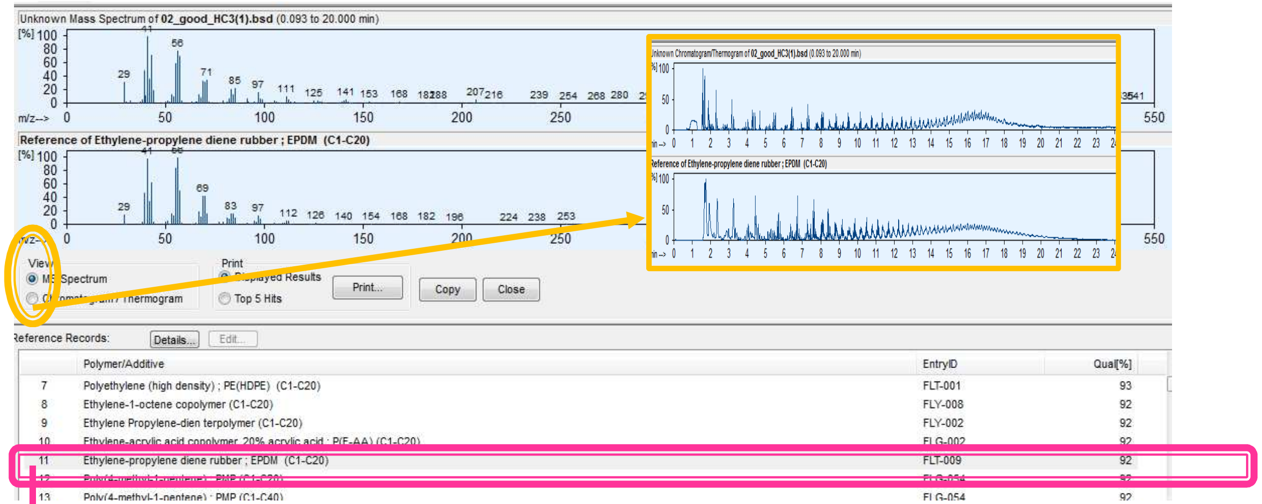
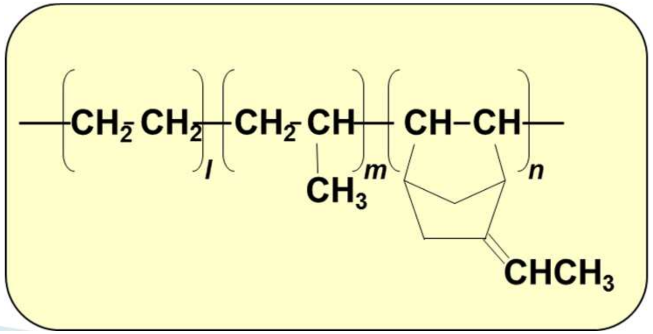
F-search (Polymer-PyGC-MS Library) Search result from HC Zone F



Ethylene Propylene-diene rubber : EPDM Match Qual. 92%



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Summery of differences of “good” and “bad” sample

sample	Polymer	Additive	Other feature
Good	EPDM CR (Chloroprene rubber)	Palmitic acid, Stearic acid Benzothiazole DEHP, DOIP	Less Hydrocarbons
Bad	EPDM	Benzothiazole DEHP	More Hydrocarbons

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Zusammenfassung

Pyrolyse-GC/MS:

- **Erweitert die Anwendungen eines GC/MS Systems: feste, nicht-volatile, unlösliche Proben**

- **Keine Proben-Vorbereitung nötig (z.B. keine Lösemittelextraktion), TMAH Derivatisierung (Rx-PY) als Option z.B. für polare, langkettigen Verbindungen**

- **4 Analytische Methoden: EGA, TD, Single-Shot-Pyrolysis, Heart Cut**

- **Einzigartige F-Search SW/Bibliotheken zur Polymer- und Additive Identifikation**

- **Leistungsstarkes Tool zur Identifikation und Charakterisierung von unbekannten Polymers & Additiven**

- **Weites Anwendungsfeld, z.B. Schadensanalytik, Reversed Eng., QC, R&D, Forensik…..**

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Thank you for your attention

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