Quantum Analytics

Frontier Laboratories and Quantum Analytics

Seminar with Lab Sessions
October 19 & 20, 2016
Aspen Research Corporation
Maple Grove, MN

Roger Tank roger@frontier-lab.com 989.941.7717

FRONTIER LABORATORIES LTD.

Quantum Analytics

Special thanks to Roger Pearson, Douglas Doster, Erik Swanson, and Alenea Urbaniak for helping to arrange these seminars here at Aspen Research Corporation.

Agenda

- Frontier Lab Introduction and Overview
- Run actual samples with PY-GC/MS in the lab.
- Pyrolysis Techniques: Pyrolysis (PY), Thermal Desorption (TD), Evolved Gas Analysis (EGA), Heart-cutting (HC-EGA/GC/MS), Reactive Pyrolysis (RxPy)
- Quantitation examples: FAMEs in food & tires; Additives in polymers; e.g., Irganox 1076 and 1010, Eyeliner deformulation; Biomass; Phthalates in PVC (ASTM D-7823);.
- Data review techniques
- F-Search hands-on workshop

Frontier Lab Team USA

Dave Randle, Bob Freeman, Itsuko Iwai, Roger Tank, Terry Ramus
Frontier Lab Technology Center, Antioch, CA

Frontier Lab–a Brief History

- Frontier Laboratories, Ltd. was founded in 1991 by Dr. Chu Watanabe. His experience working at Hewlett Packard's Analytical Division and Dow Chemical made him uniquely qualified to design and market analytical instruments for materials characterization. Dr. Watanabe, with the support of polymer scientists at Nagoya University in Japan, developed a pyrolyzer based on a vertical micro-furnace design. Today the patented fourth generation vertical micro-furnace serves as the cornerstone for the 3000 Series of products developed and marketed worldwide by Frontier Laboratories.
- The 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.
- For Agilent Technologies GC and GC/MS systems, Frontier Lab products are sold and serviced in North America by Quantum Analytics, an Agilent Technologies Premier Solution Partner.
- There are thousands of Frontier Lab systems in use globally, with over 50% used on a daily basis by companies in North America such as Dow Chemical, BASF, 3M, Sherwin Williams, PPG, Covestro, The Getty Conservation Institute, Smithsonian, U. of MN, IA St. U., Dow AgroSciences, Shell, General Motors, Volkswagen, Michelin, Goodyear, ExxonMobil, Chevron, Phillips 66, Boston Scientific, St. Jude Medical, H. B. Fuller, NASA, NREL, St. of MN Crime Lab, and many others.

Application Areas using Multi-functional Pyrolyzer

Polymers	: characterization, quality assurance, deformulation
Additives	: surfactants, plasticizers, residual monomers, solvents, volatile catalysts, impurities
Plastics	: resins, plasticizers, mold release agents, UV-antioxidants, films, foams, gels
Coatings	: pigments, solvents, driers, film formers
Fibers	: blends, natural materials, non-woven
Elastomers	: sulfur-compounds, natural rubbers, synthetics, silicones
Adhesives	: thermoplastics, anaerobics, acrylics, epoxy
Inks	: pigments, resins, solvents, defoamer, waxes, toners
Paper	: coatings, sizing
Product Areas	: textiles, personal care products, packaging
Related Scientific	: forensic evidence, degradation studies, environmental

FRONTIER LAB

Applications by Market

Polymers, additives, adhesives, elastomers

- Wide market use from petrochemical, automotive, biopharmaceutical to medical devices

Coatings

- Ranges from inks, paints, and sealers in forensics, museums, and industrial uses

Energy

- Biomass analysis for producing biofuels in universities and industry. Oil shale.

Consumer products

- Packaging, cloth (fibers), cosmetics, and food

AIChE Webinar archived now

Rapid Characterization of Polymers, Biomass and Feedstocks by Fast Pyrolysis and Catalytic Pyrolysis

This webinar is sponsored by Frontier Laboratories Ltd. and reflects their views, opinions, and recommendations. Attendance to this webinar is free.

https://www.youtube.com/watch?v=0ZcZ2PUq2_Y

Now on YouTube

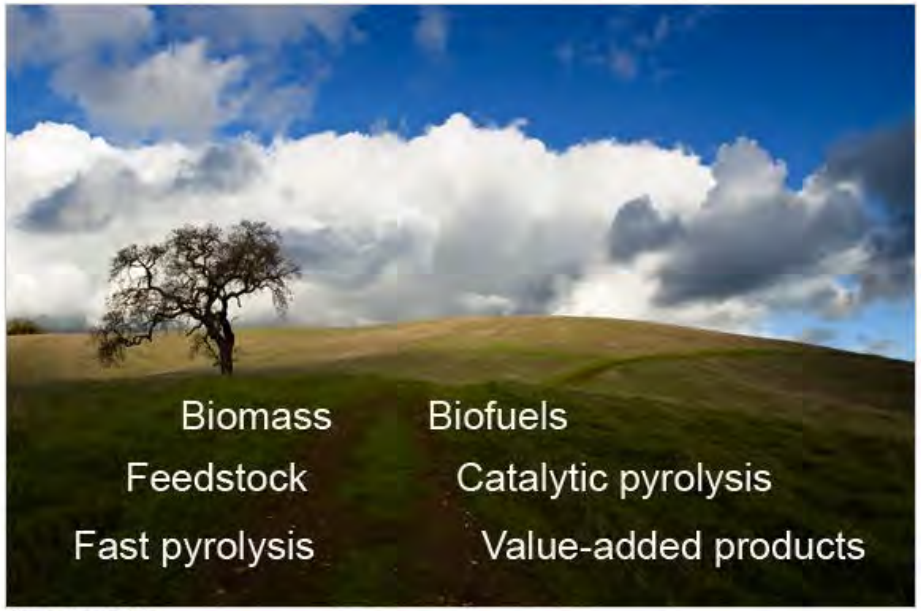

Photo: Scott Hein

Learn how fast pyrolysis, hydropyrolysis and catalytic pyrolysis are used to convert biomass to biofuels or other value-added chemicals. Two types of pyrolysis systems are described: (1) A third generation pyrolyzer which uses a patented micro-furnace to instantaneously heat the sample and (2) a bench-top, tandem micro-reactor - GC/MS system. The tandem micro-reactor is a new tool for researchers working with biomass conversion. It can be used to quickly perform complex studies on virtually any feedstock in concert with any catalyst in various atmospheres (e.g., helium, hydrogen, air) over a range of temperatures and pressures. Multiple modes of operation rapidly generate lots of useful and critical data.

Catalytic pyrolysis utilizes a catalyst to convert pyrolyzates to value-added chemicals. The tandem µ-reactor consists of two reactors in series. Solids, liquids or gases are introduced into the first reactor. Solids are pyrolyzed, liquids are vaporized. The vapors from the first reactor are swept into the second reactor which contains the catalyst bed. Once through the catalyst, the vapors flow directly to a GC/MS where the compounds are separated and identified. The transformation of Jatropha "press cake" to BTEX will be used to demonstrate the functionality of the tandem µ-reactor.

Dr. Robert Brown, founding director of the Bioeconomy Institute (BEI), summarizes the research at Iowa State University with fast pyrolysis, hydropyrolysis and catalytic pyrolysis using these pyrolysis and reactor systems. Learn, first hand, how high through-put pyrolysis and catalytic pyrolysis are used to examine the fundamental phenomena associated with these processes.

Presenter(s):

Dave Randle

David A. Randle is the Technical Director for Frontier Laboratories, Ltd. Supporting Frontier Lab's business partners in North America, Dave brings over 20 years domestic and international management and business development experience with companies such as Hewlett-Packard and Agilent Technologies to lead Frontier's strategic direction and growth. As a former lab manager, Dave also has hands-on experience with many analytical techniques including GC/MS, which is a critical component to the pyrolysis and catalysis products manufactured by Frontier. Dave conducts customer training, develops... **Read more →**

Robert Brown

Dr. Robert Brown is Anson Marston Distinguished Professor in Engineering and Gary and Donna Hoover Chair in Mechanical Engineering at Iowa State University (ISU). Dr. Brown is the founding director of ISU's Bioeconomy Institute (BEI), which coordinates ISU's research, educational, and outreach activities related to biobased products and bioenergy. Dr. Brown is also the director of the Center for Sustainable Environmental Technologies, a center within ISU's Institute for Physical Research and Technology that conducts multi-disciplinary, multi-investigator research into thermochemical... **Read more →**

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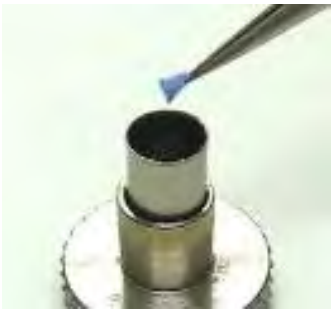
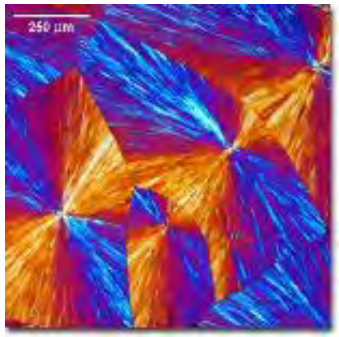
www.frontier-lab.com

Greatly Expand Your GC/MS Capabilities with Frontier Lab Pyrolyzers

Materials Characterization for the 21st Century





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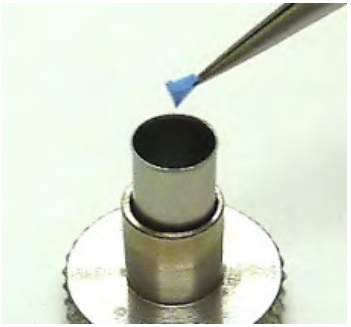
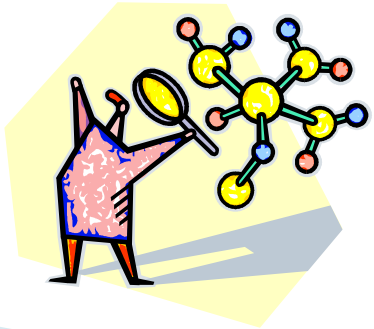
Sample Preparation
Sample Amount: 100–200 µg



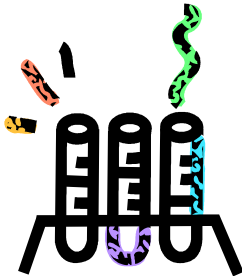
- 100–200 µg (0.1–0.2 mg) total in sample cup is sufficient for most analyses
- Introducing too much sample is the #1 issue we find with customers having analysis problems



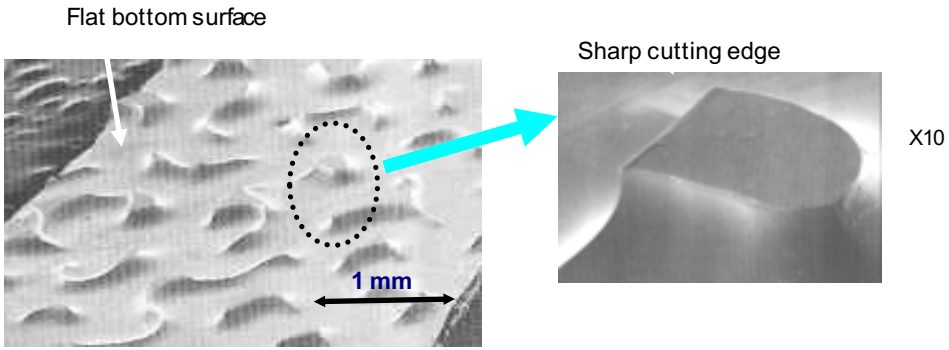
It's a small world

Sample Preparation
Sample form affects reproducibility

- Best is thin film method
  - Dissolve sample in solvent, add to cup, evaporate solvent



- Fine particles are excellent
  - Use Polymer Prepper or Freeze Pulverization
- Finely chopped pieces are good



SEM Image of Cutting Surface of Polymer Prepper (medium)

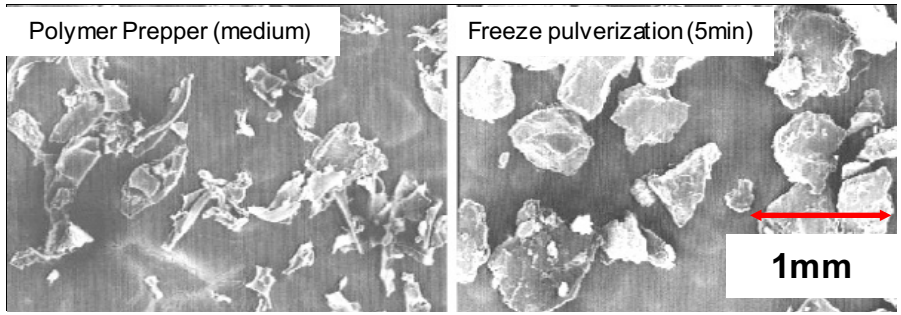


Fig. 1 Particle Shapes of Polystyrene Powdered by Polymer Prepper and Freeze Pulverization

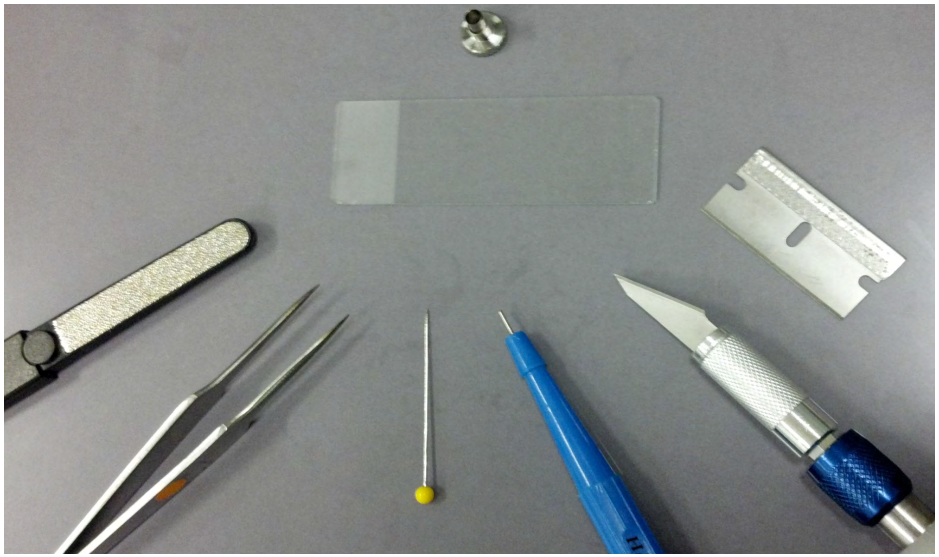
Sample form	Thin film	Fine powder		Small particles (cutting method)	
		Polymer Prepper (medium)	Freeze pulverization	4 pieces (0.4mm square)	1piece (1mm square)
R.S.D.(%) of SSS/S	1.07	1.97	2.11	3.64	8.90

SSS: Styrene trimer
S: Styrene monomer

Pyrolysis temp: 550° C
Sample size: ca. 0.5mg

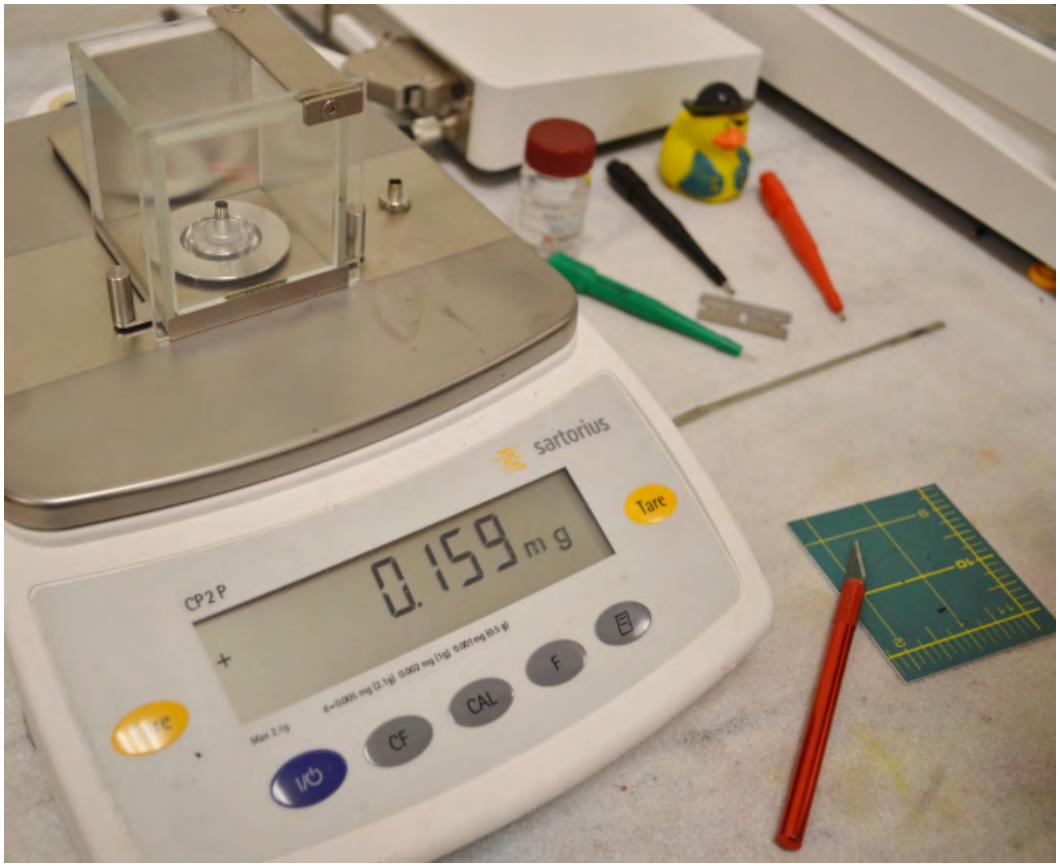
Sample Preparation
Use special tools to handle small samples

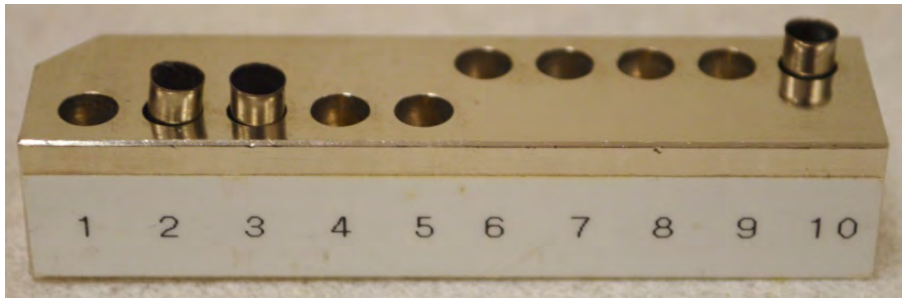
- Polymer Prepper
  - 2 sided nickel file with fine & medium cutting surfaces
- Micro-puncher
  - 7 sizes from 0.5mm to 5.0mm.
  - Good for thin dry films
- Razor blades, X-Acto knives, metal files, tweezers and pins are all handy



- Variations; 0.5, 0.75, 1.25, 2.0, 3.0, 4.0 and 5.0 mm diameter of micro-puncher and cutting mat 65 x 75 mm.

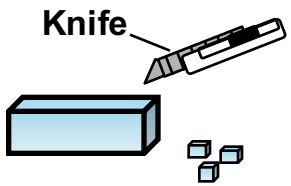
Sample Preparation

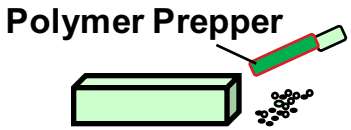




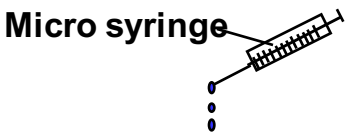
Sample preparation

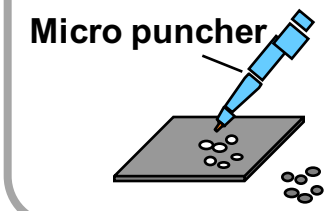
Step 1





Filed; Cryo milled

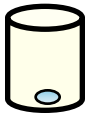




Step 2

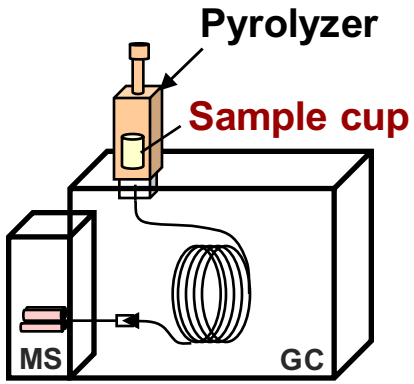
Weigh a sample into the sample cup

50-200µg



No solvent extraction

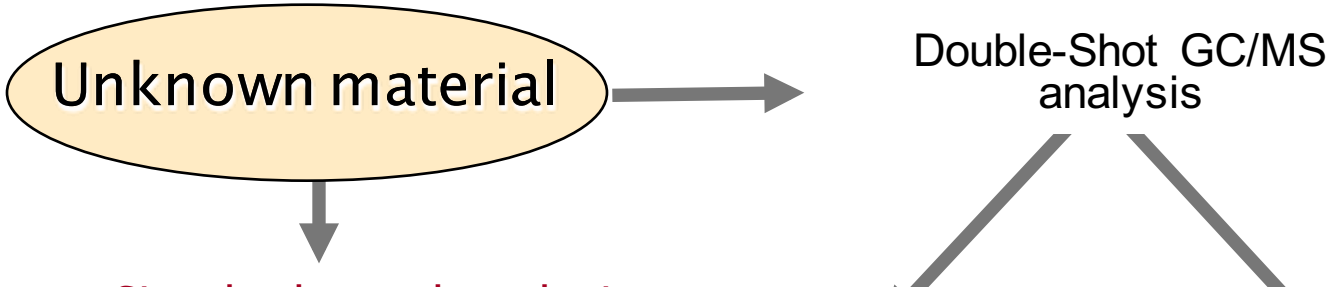
Step 3



Ready for Analysis !!

Sample

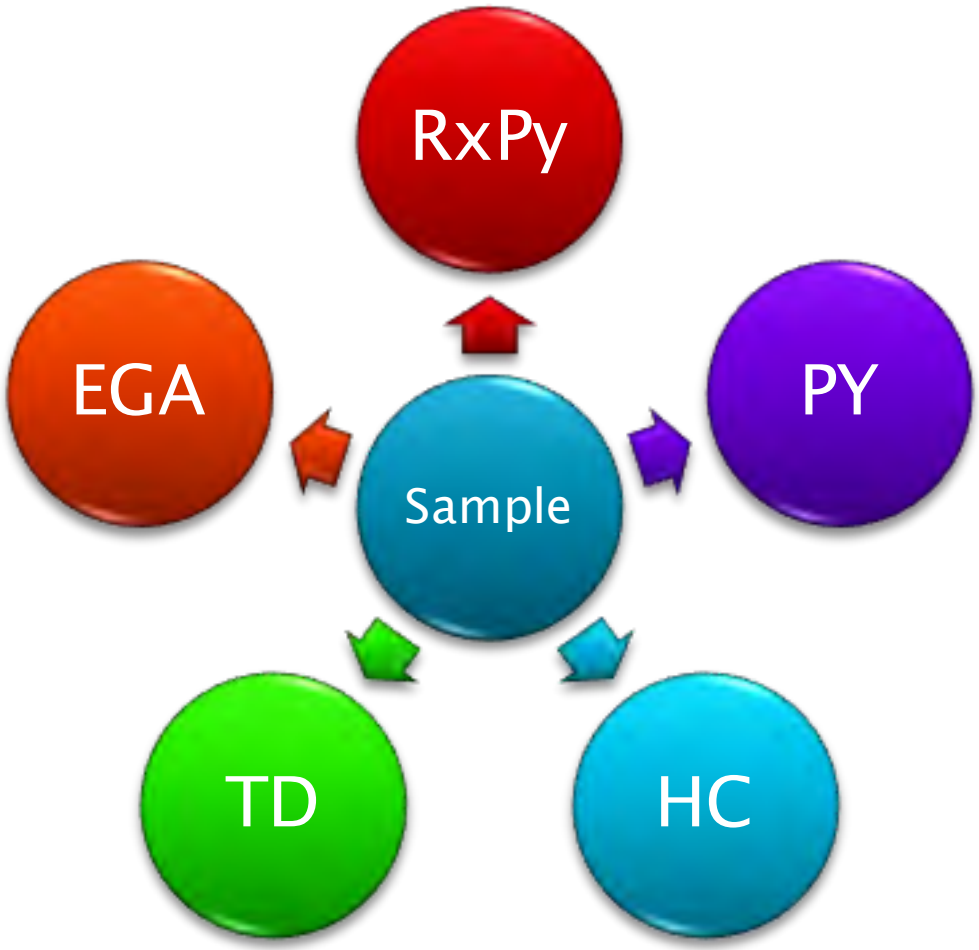
Approach in characterizing unknown materials



< Simple thermal analysis >

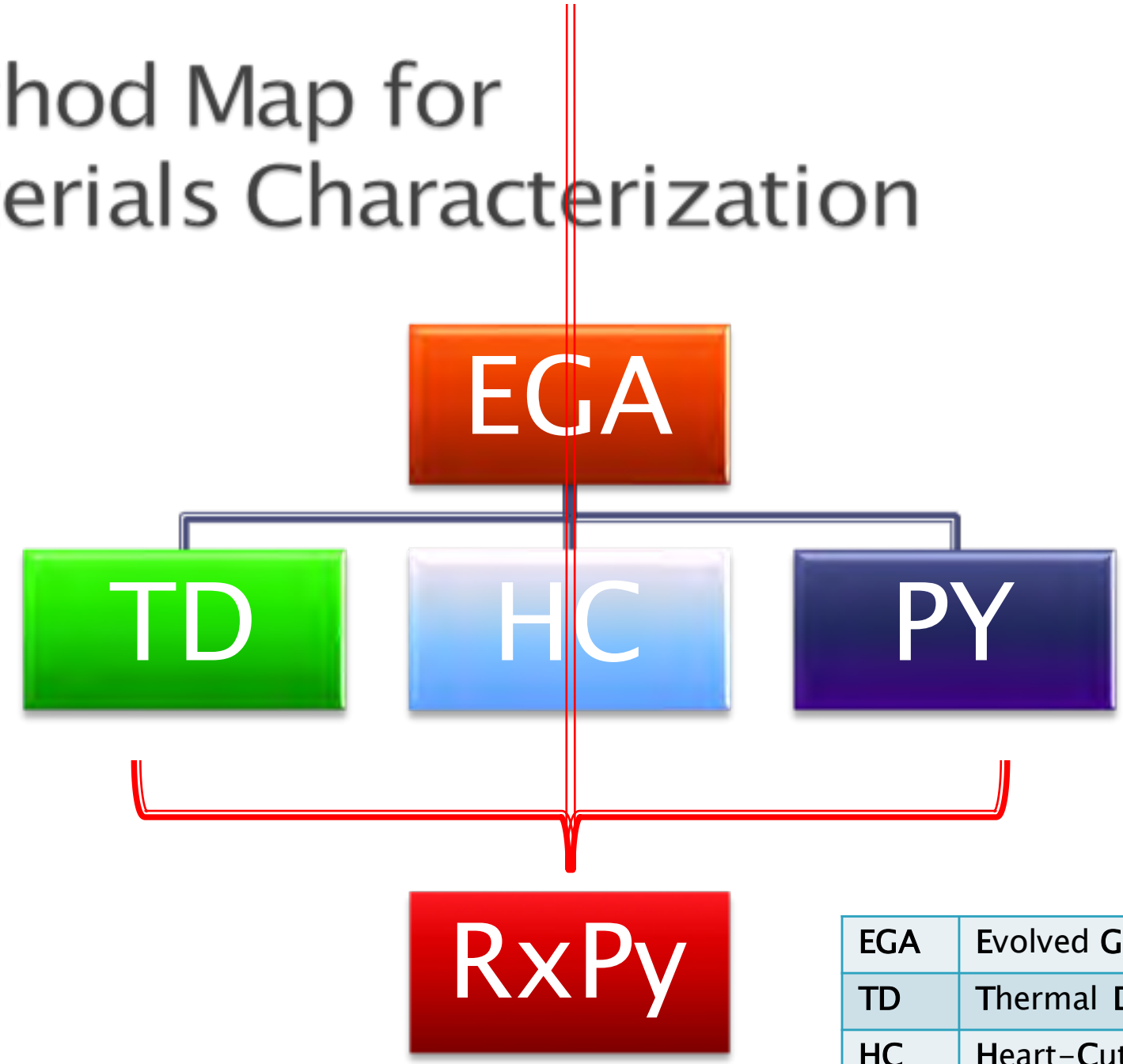
Analytical method	Evolved gas analysis (EGA)	Thermal desorption (TD)	Flash pyrolysis (Py)
Typical Temp Range	40–800°C	40–420°C	420–1050°C
Remarks	Temp Prog. 20°C/min	Temp Prog. or isothermal	Isothermal, typical 600°C
Analytical targets	Volatiles / non-volatiles	Additives (volatile)	Polymer (non-volatile)
	Complexity of the material and thermal distribution of its components	Components that could be released by heat.	Solids that can only be broken down at high temperature
	Thermograms	Chromatograms	Pyrograms

Techniques Used For Samples



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

Method Map for Materials Characterization



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

Temperature Programmed Micro Furnace Techniques

EGA

TD

Isothermal or
Temp. Programmed

HC

100°C @20°C/Min 800°C

Isothermal Temperature Micro Furnace Techniques

PY

Thermolysis

Typically 500–800°C

RxPy

Sample + Reagent (i.e., TMAH)

Thermally assisted chemolysis and derivatization

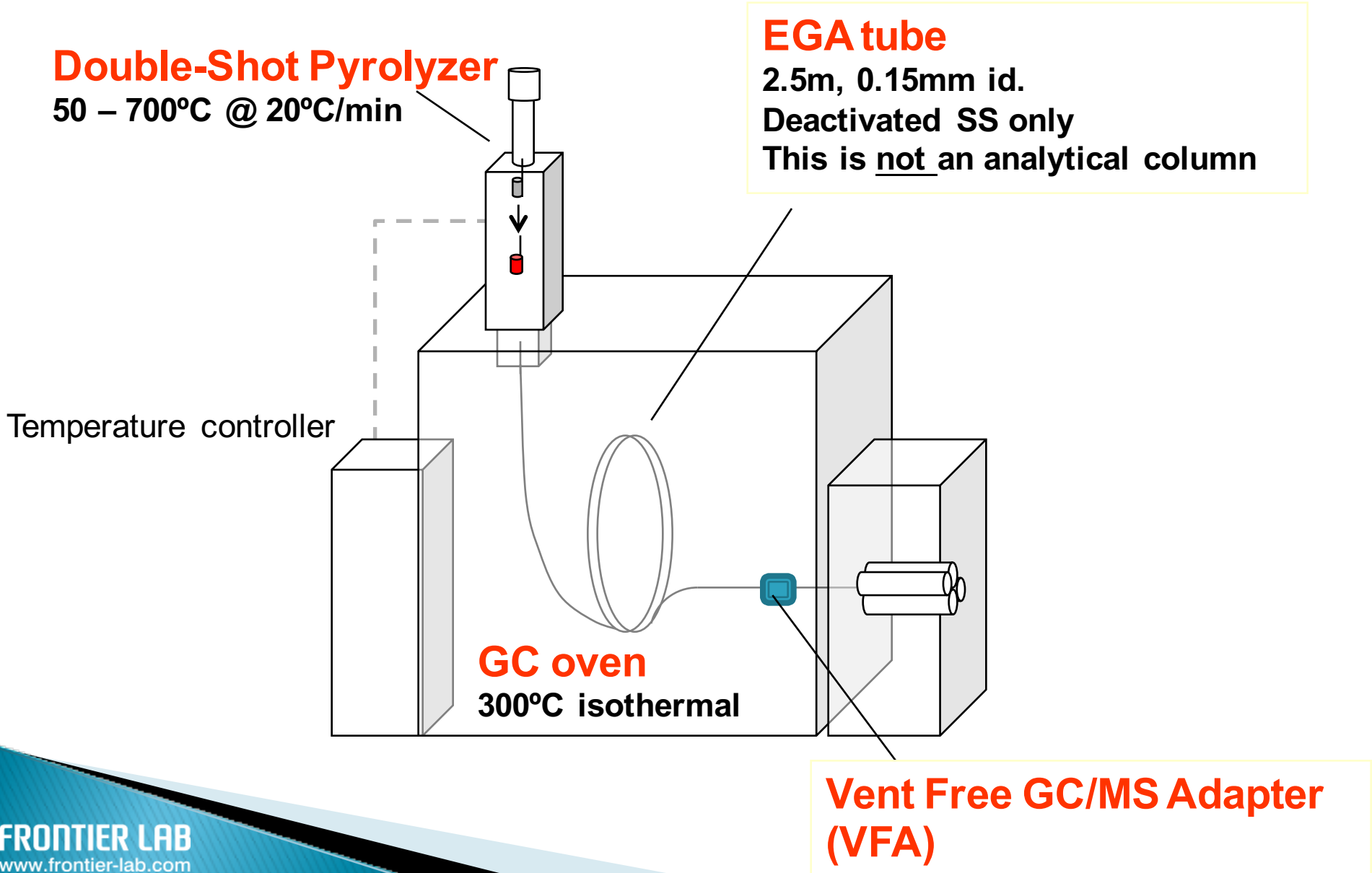
Typically 250–380°C

EGA/PY-3030D and EGA

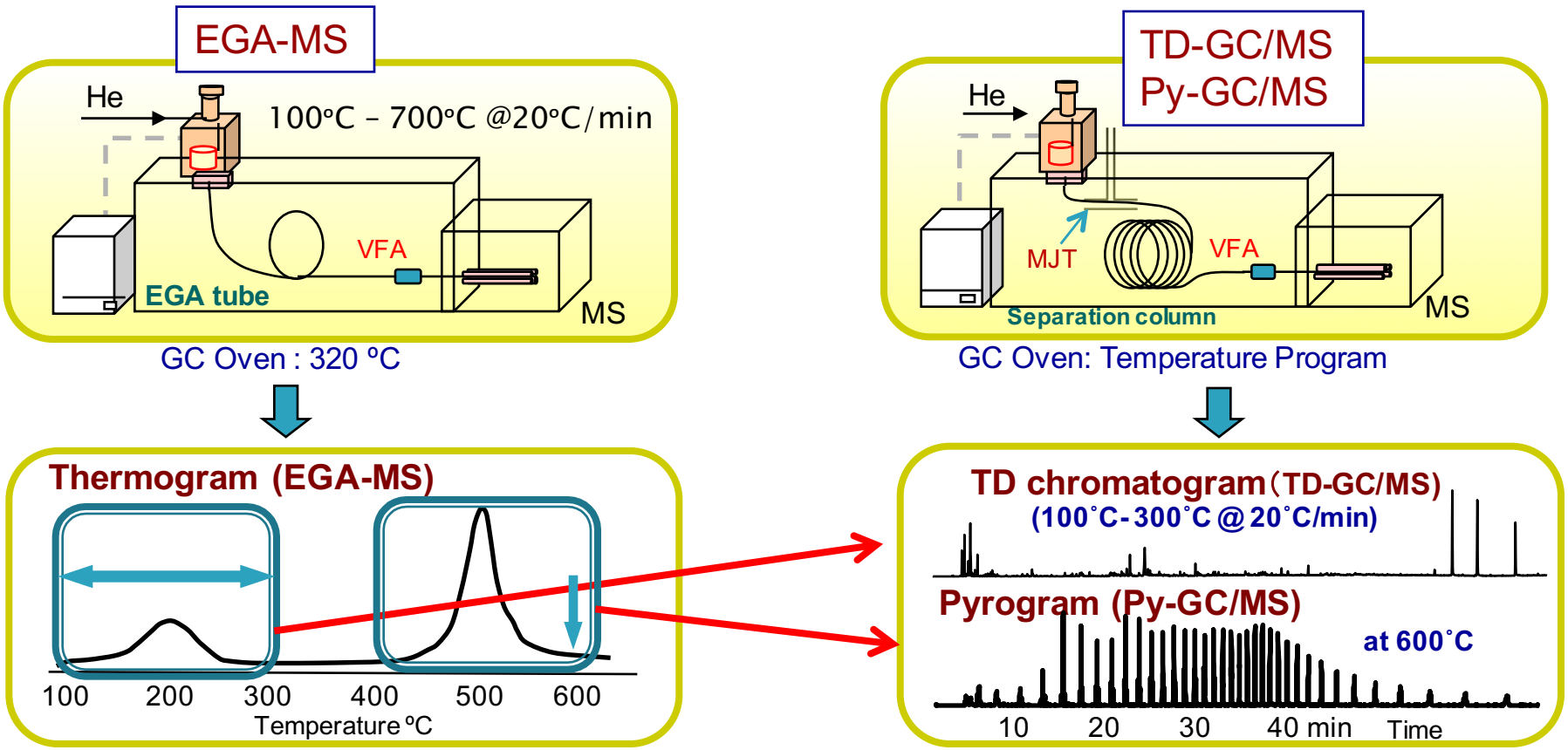
- EGA (Evolved Gas Analysis) is performed with a short inert tube (not an analytical column) and produces a thermogram.
- Frontier has found the information in an EGA thermogram so valuable that we created an entire EGA-MS library with 268 polymers for our customers.
- Once an EGA thermogram is generated for an unknown sample we then install an analytical column into the GC/MS.
  - This change over time is very fast using our Vent-free adapter (VFA).
  - The information gained from the EGA guides the analyst on what "thermal" blades are needed to slice the sample into pieces to simplify the chromatograms and provide better information.
- The next slides shows examples of how to use the EGA information to perform a thermal desorption (TD) of the volatile portion of the sample followed by a pyrolysis (Py) of the polymeric portion of the sample. We call this a Double-shot.

3030D. "D" is for Double-shot

Flow diagram and analytical conditions for EGA Analysis



Diagrams of EGA-MS vs. TD/Py-GC/MS



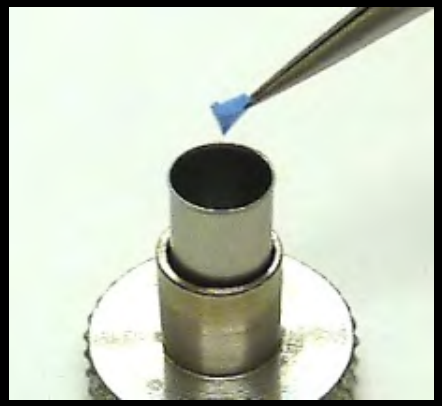
-EGA-MS is the recommended first step to characterize a sample, and uses an uncoated metal tube (2.5m x 0.15mm i.d.) to connect the GC inlet to the MS.
-Subsequent analyses (TD-GC/MS and Py-GC/MS) are performed using an analytical column. (30m x 0.25mm x 0.25μm).
-Switching from the tube to the column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

TD followed by Py on a single sample is called a Double-Shot.

Lab Exercise

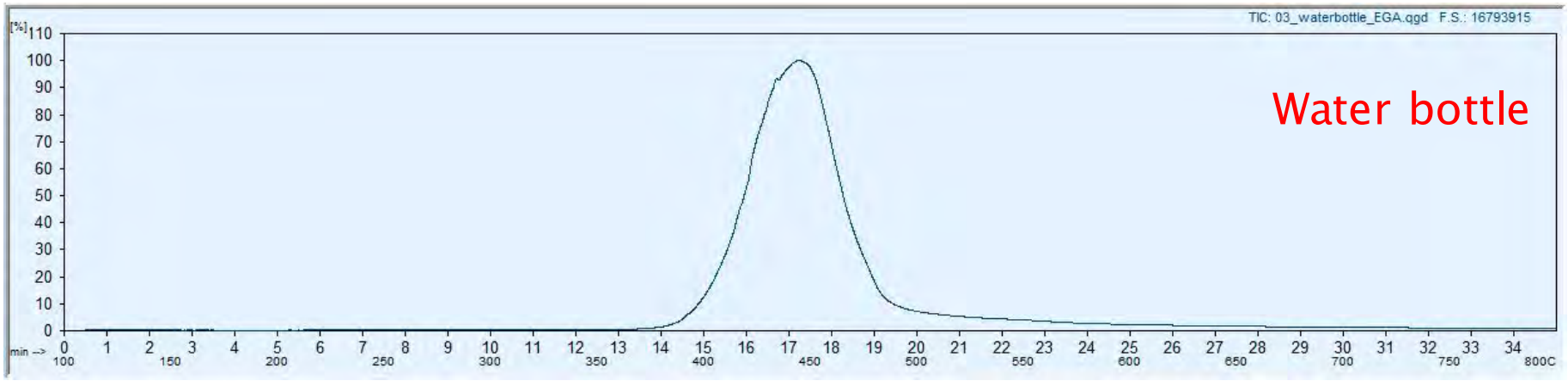
- Plastic bottle samples
- File or cut small amount onto piece of paper
- Tare sample cup
- Weigh 100-200ug
- Record weight, sample name and your name
- Place in sample rack and note position #

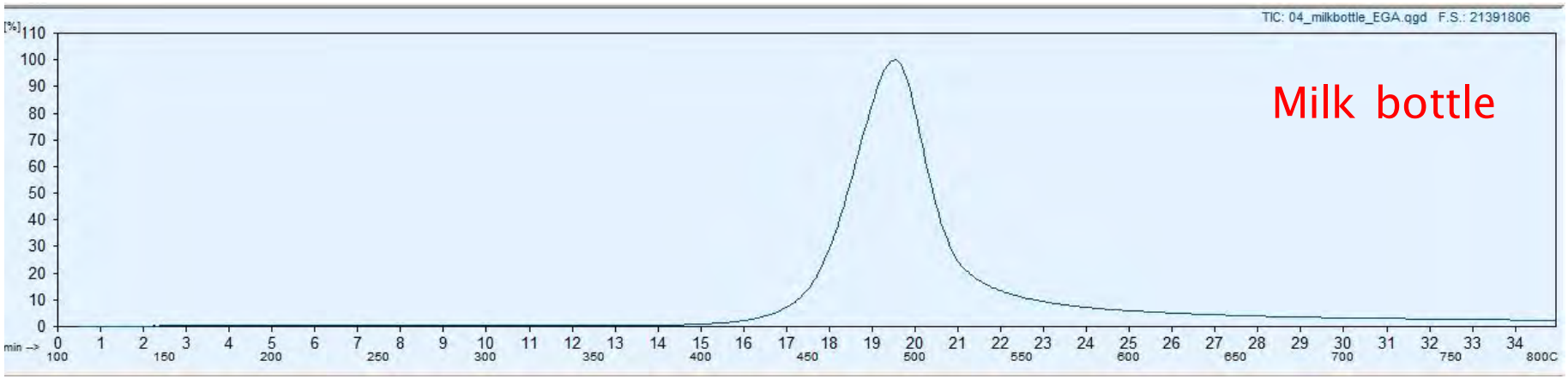
Plain paper



EGA

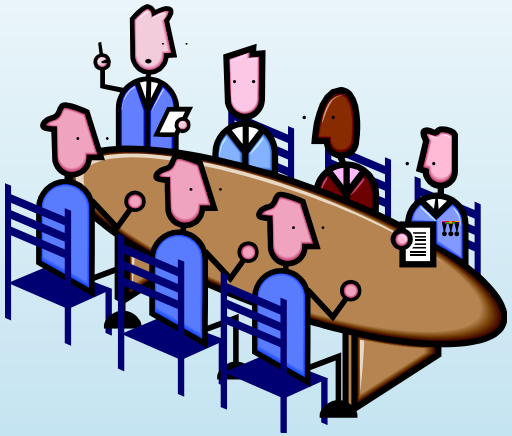
EGA Thermograms of Water bottle & Milk bottle





Itsuko will show you these thermograms and how we choose temp for PY runs.

- Go to Lab



- Finish at 9:45 am then a 15 minute break and back to conference room by: 10:00 am

Fundamentals of Pyrolysis

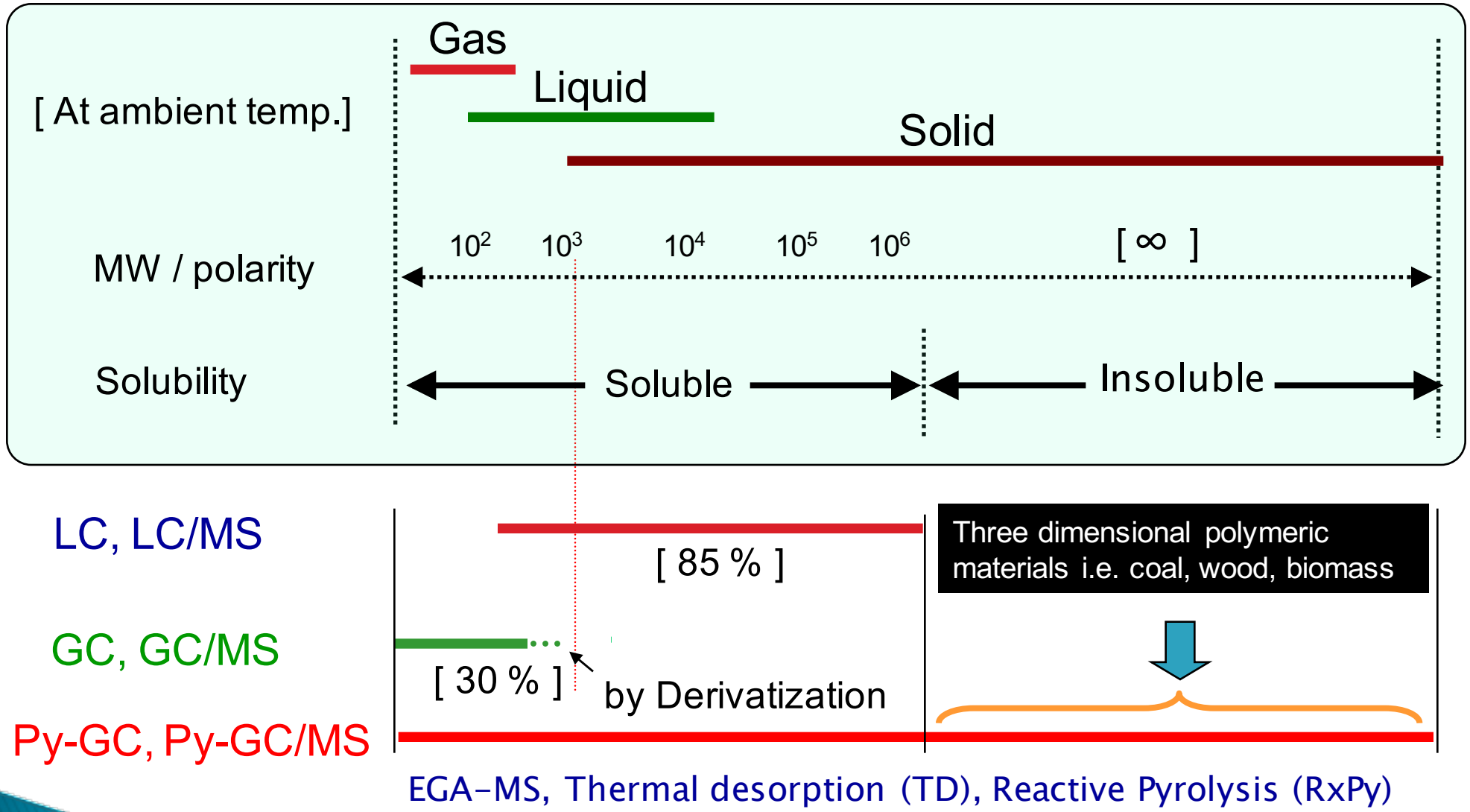
Analytical Pyrolysis

Analytical Pyrolysis Defined

- **Pyrolysis** is a thermochemical decomposition of organic material at elevated temperatures without the participation of oxygen. It involves the simultaneous change of chemical composition and physical phase, and is irreversible. The word is coined from the Greek-derived words *pyr* "fire" and *lysis* "separating"*.
- Think of analytical pyrolysis as breaking apart or manipulating organic molecules in a controlled and predictable manner using the precise use of heat.

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

“Expansion of Application Areas with Py-GC”



Regular GC/MS vs. PY–GC/MS

- Liquid or gas injection only
- GC Inlet temperature max ~320°C
- Limited to organics that vaporize at <320°C
- Single analysis per sample
- MS libraries are based on limited b.p. range

- Gas, liquid or solids analysis
- Pyrolyzer temps up to 1050°C
- ANY ORGANICS can be analyzed
- Multiple analyses on a single sample
- MS libraries range from low b.p. to pyrolyzates

Chronicle of Analytical Pyrolysis

[Analytical Pyrolysis]

1945

Madorsky, *et al.* and Wall, *et al.*, (1948) Py-MS of polymers

1950

Bradt, *et al.*,(1953) On-line Py-MS

Davison, *et al.*, (1954) Off-line Py-GC

Lehrle, *et al.*, Radell, *et al.* and Martin (1959) On-line Py-GC of Polymers

1960

Simon (1964) Curie-point pyrolyzer

Simon (1966) Py-capillary GC-MS

Hummel, *et al.*, (1968) Py-FI/MS

1970

Meuzelaar, *et al.*, (1973) Curie-point PyMS

Tsuge (1977) micro-furnace PY

J.Anal. Appl. Pyrol.<Elsevier>
First issue:1979 (June)

1980

Tsuge and Ohtani (1989)
Py-GC data base for 136 polymers

1990

Takayama and Watanabe (1991)
Ultra ALLOY capillary columns

Tsuge, Ohtani, Watanabe (2006)
Py-GC/MS data base for 165 polymers

2000

Watanabe, Tsuge, Ohtani (2009)
Micro-online UV/Py-GC/MS System

2010

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

[Gordon Conf.]

- 1st (1979)
- 2nd (1981)
- 3rd (1983)
- 4th (1985)
- 5th (1987)
- 6th (1989)
- 7th (1991)
- 8th (1993)
- 9th (1997)

[Intl. Symposium]

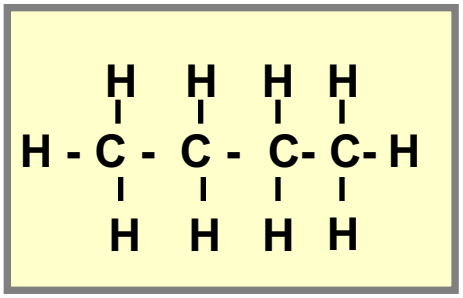
- 1st (1965) Paris
- 2nd (1972) Paris
- 3rd (1976) Amsterdam
- 4th (1979) Budapest
- 5th (1982) Vail, CO
- 6th (1984) Weisbaden
- 7th (1986) Reading
- 8th (1988) Lund
- 9th (1990) Noordwijkerhout
- 10th (1992) Hamburg
- 11th (1994) Nagoya
- 12th (1996) Venice
- 13th (1998) Munich
- 14th (2000) Seville
- 15th (2002) Leoben
- 16th (2004) Alicante
- 17th (2006) Budapest
- 18th (2008) Canary Islands
- 19th (2012) Linz
- 20th (2014) Birmingham UK

[Related Techniques]

- Org. Ms(EI)
- GC (1952)
- Capillary GC
- FID for GC (1959)
- CI-MS (1966)
- GC/MS(1965。~1970)
- FI/FD-MS (1969)
- SIMS(1975)
- Fused-silica capillary for GC
- (1979)
- MALDI-MS (1988)
- AED for GC (1989)
- Deactivated stainless steel capillary GC (1991)
- EGA/PY-3030D; On-line micro reaction & TD sampler (2011)
- Rapid Screening Reactor (catalysts) (2012)

Pyrolysis of polymeric materials and pyrolyzates

Butane
(MW: 58)



ΔH (Heat energy)

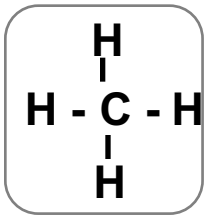
burn in air

$CO_2 + H_2O$

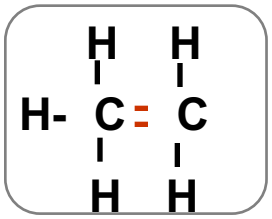
In He

ΔH
(Heat/ Electron)

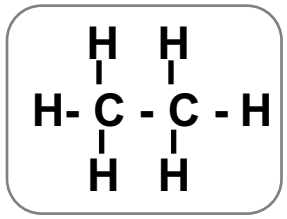
C1



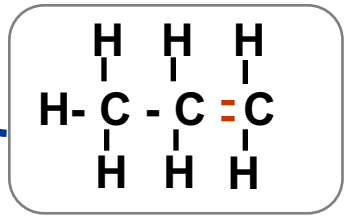
C2'



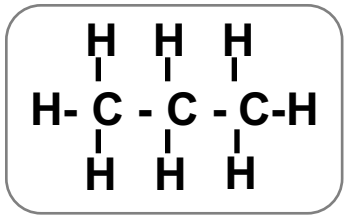
C2



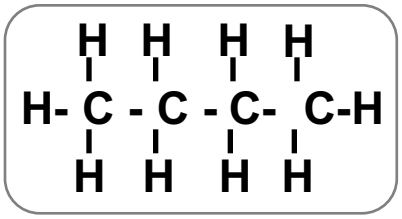
C3'



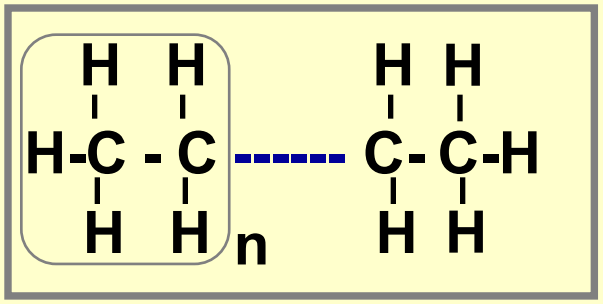
C3



C4"+C4'+C4



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



n = 300 ~ 30,000

ΔH

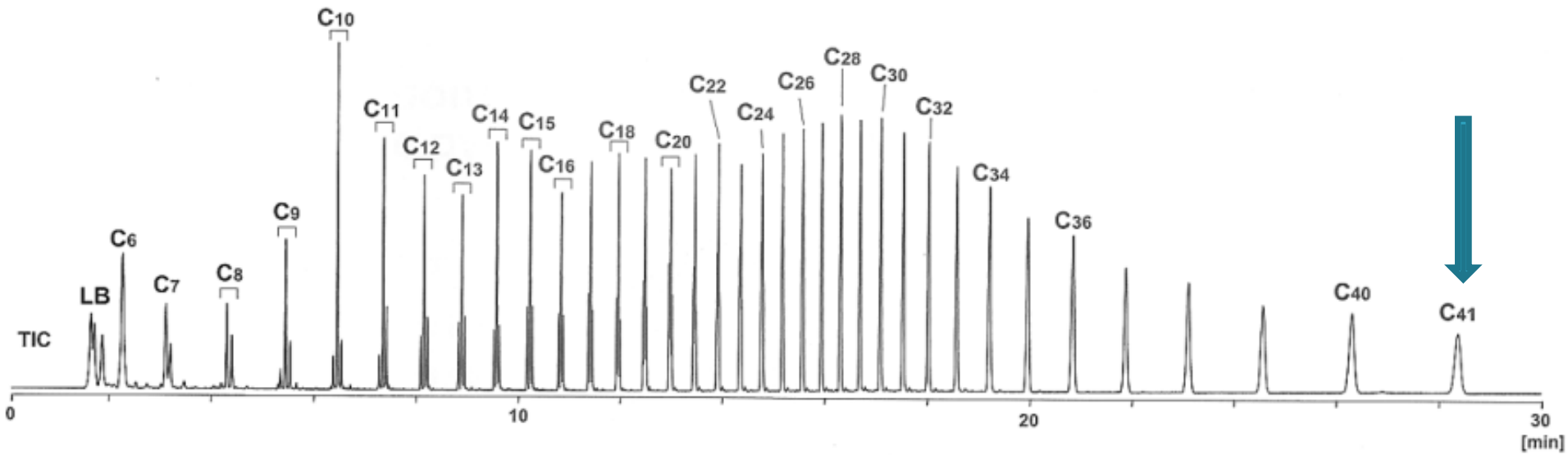
(Heat/ Electron)

C1, C2',C2, C3', C3,C4', C4"… Cx

Py–GC/MS of Polyethylene

001 Polyethylene (high density); PE(HDPE)

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

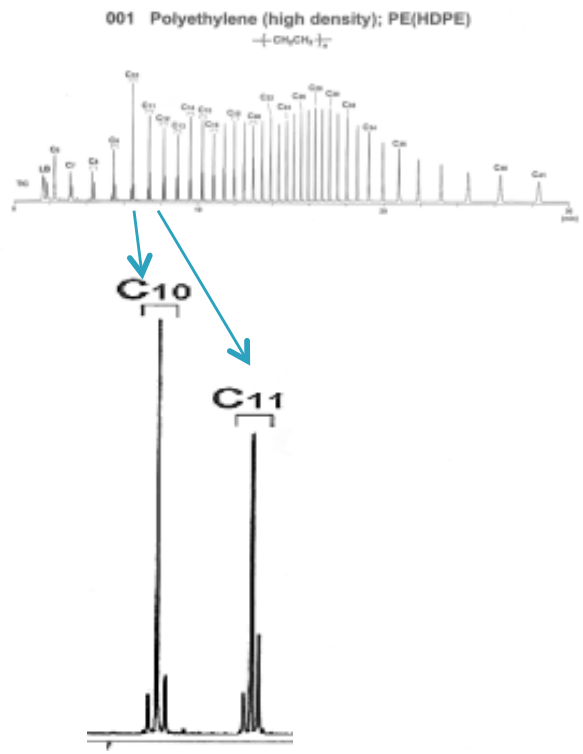


Pyrolysis Temperature: 600°C
Column: Ultra ALLOY-5; 30M x 0.25u x 0.25u
Oven Temp: 40°C (2min) -20°C/min-320°C (13min)

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

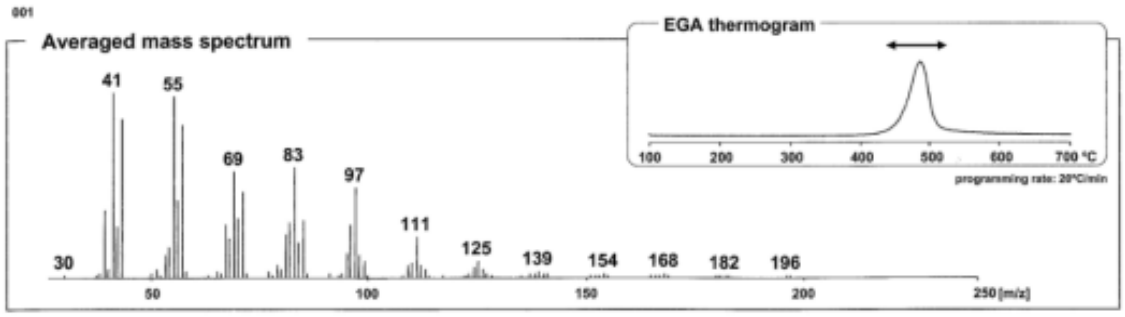
Py–GC/MS of Polyethylene

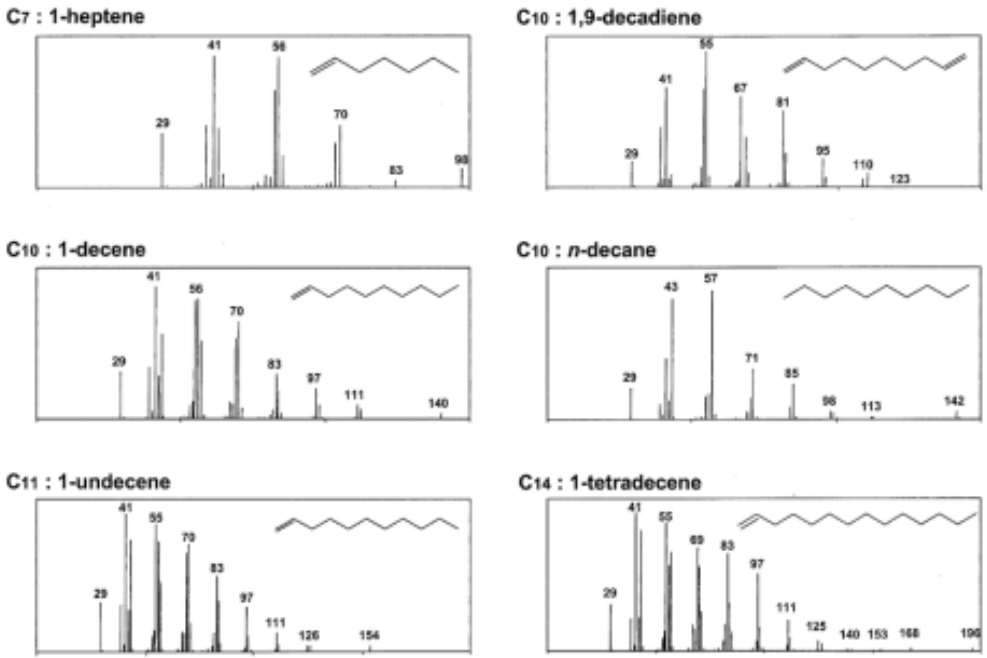
Peak Notation	Assignment of Main Peaks	Molecular Weight	Retention Index	Relative Intensity
LB	propylene + propane	42; 44	300	43.7
C_6	$CH_2=CH(CH_2)_3CH_3$	84	583	91.8
C_7	$CH_2=CH(CH_2)_4CH_3$	98	689	42.4
	$CH_3(CH_2)_5CH_3$	100	700	19.3
C_8	$CH_2=CH(CH_2)_4CH=CH_2$	110	782	2.1
	$CH_2=CH(CH_2)_5CH_3$	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
	$CH_3(CH_2)_{18}CH_7$	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

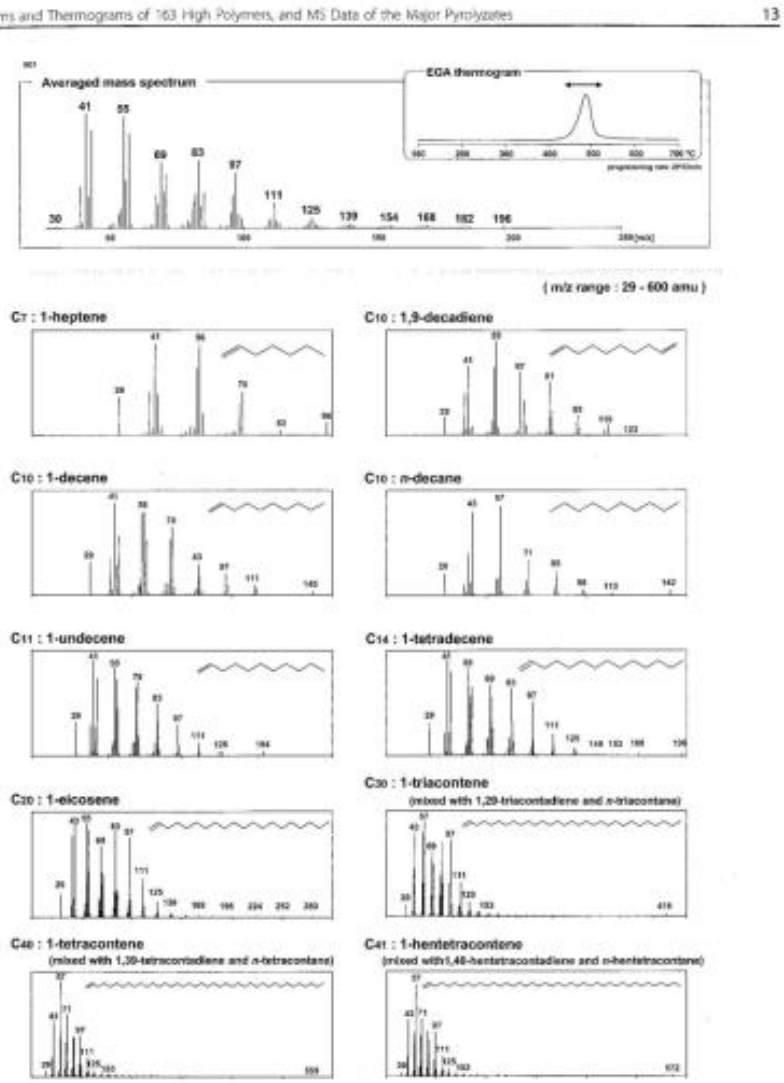


Pyrolysis GC/MS Data Book of Synthetic Polymers, 2011
Tsuge, Ohtani, Watanabe

Py–GC/MS of Polyethylene

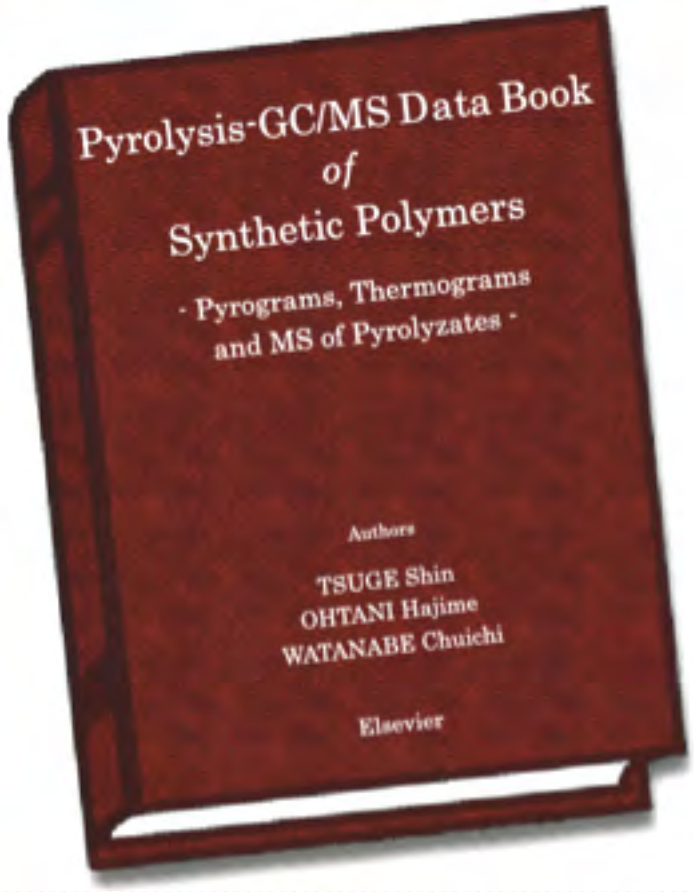






Pyrolysis GC/MS Data Book of Synthetic Polymers, 2011
Tsuge, Ohtani, Watanabe

Pyrolysis GC/MS Data Book of Synthetic Polymers



(Price: $295)

~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~

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

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Features:

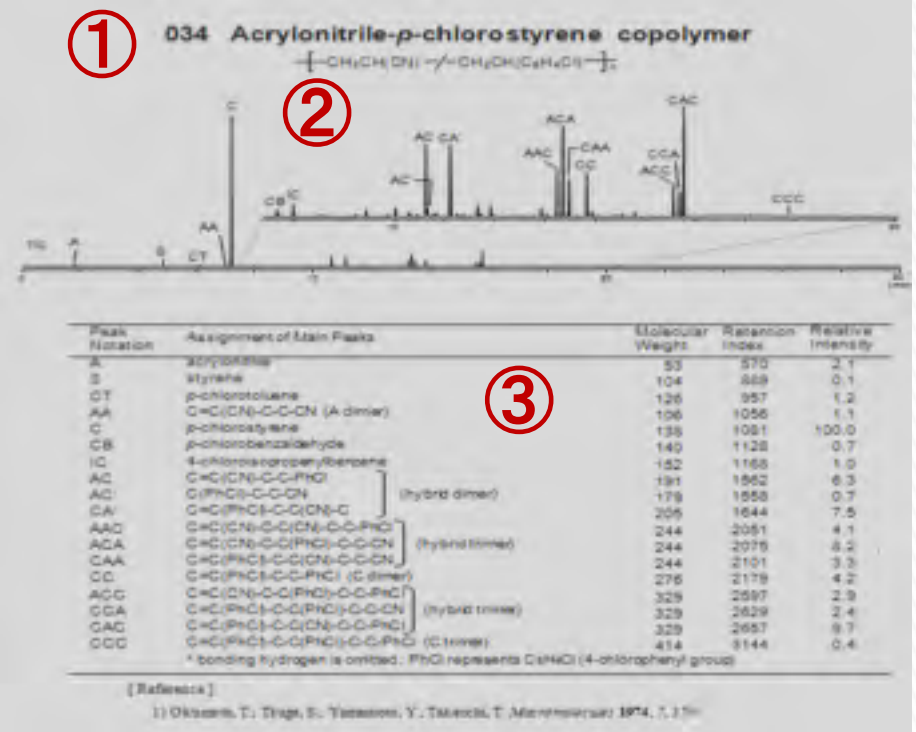
- Data compilation of pyrograms, thermo- grams and MS data of major pyrolyzates for 163 typical polymer samples with detailed peak assignment Tables and Thermograms for each polymer.
- Data compilation of pyrograms of 33 condensation polymers through reactive pyrolysis (RP) in the presence of tetramethyl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

Available Now

From Elsevier & Amazon

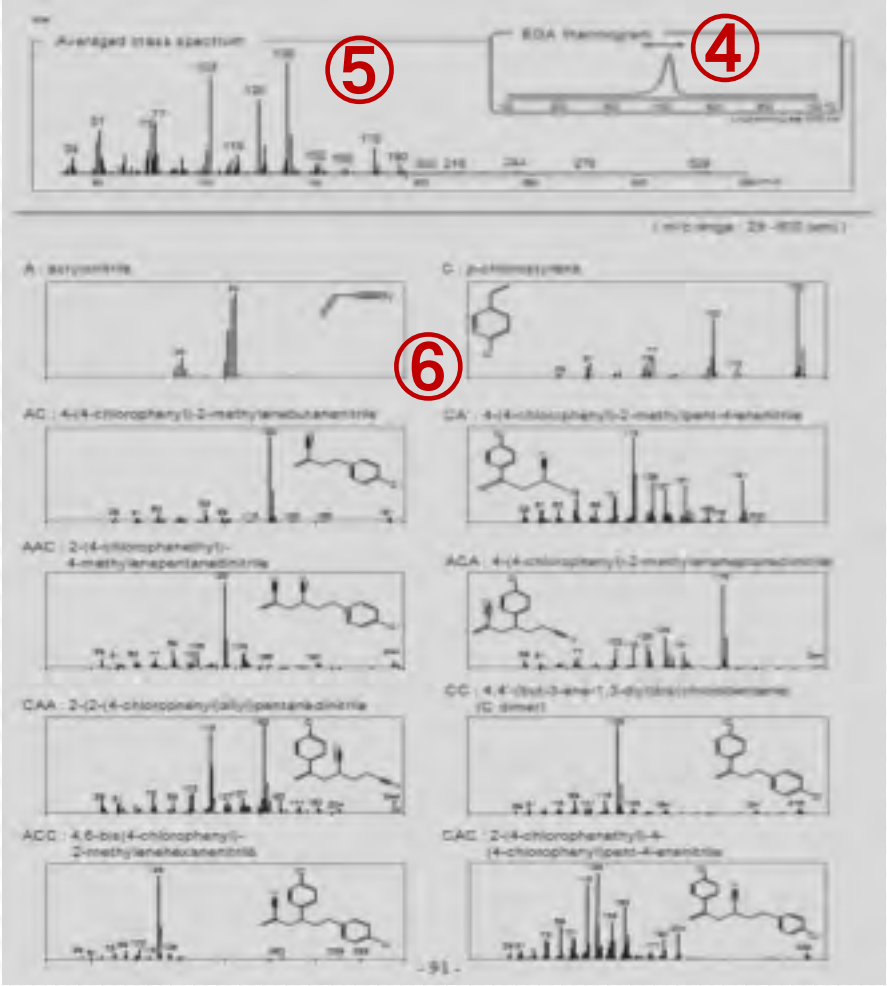
Hint: Search ISBN "9780444538925" in Amazon books

Example pages from Pyrolysis Book



[Acrylonitrile-p-chlorostyrene copolymer]

Note- every two pages are organized this way with left & right layout



① Sample number, polymer name, and chemical structure

② Pyrogram at 600 ˚C separated by a capillary column

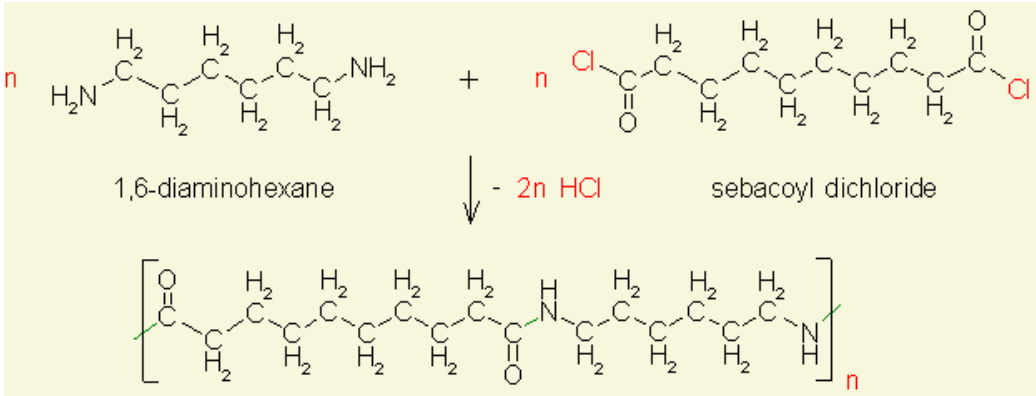
③ Peak assignment table together with molecular weight (MW), relative peak intensity and retention index (RI) data

④ EGA thermogram: 100 to 700 ˚C at a rate of 20 ˚C/min

⑤ Average mass spectrum of the EGA thermogram

⑥ Mass spectrum of the top 10 major peaks

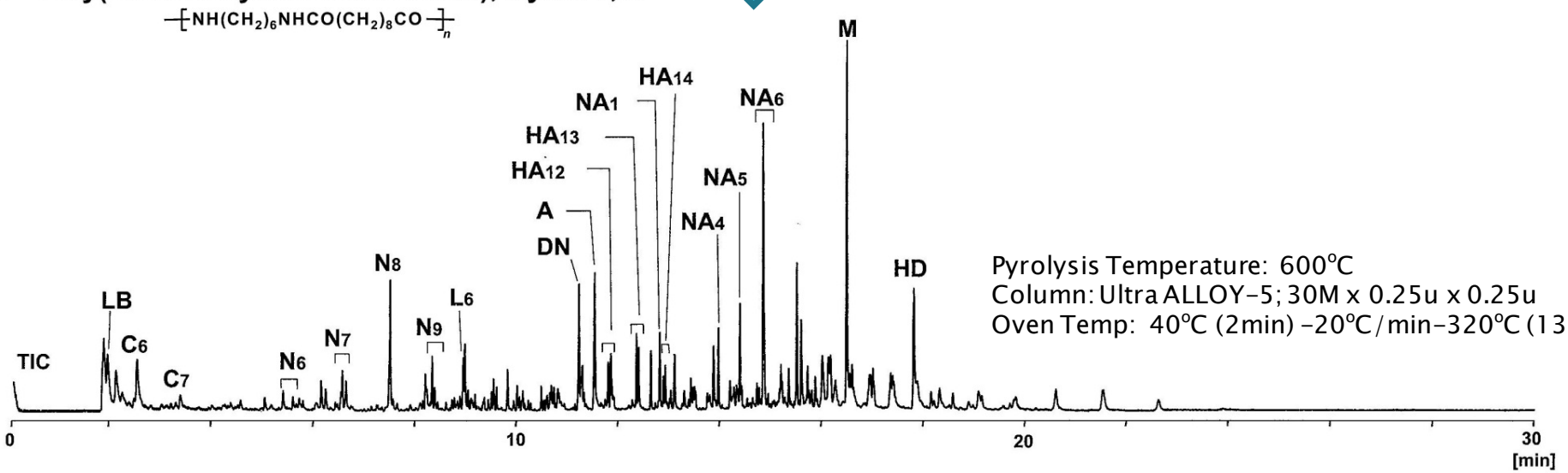
Pyrolyzates of Nylon 6,10 (synthetic polyamide polymer)



Pyrolyze at 600 °C

087 Poly(hexamethylene sebacamide); Nylon-6,10

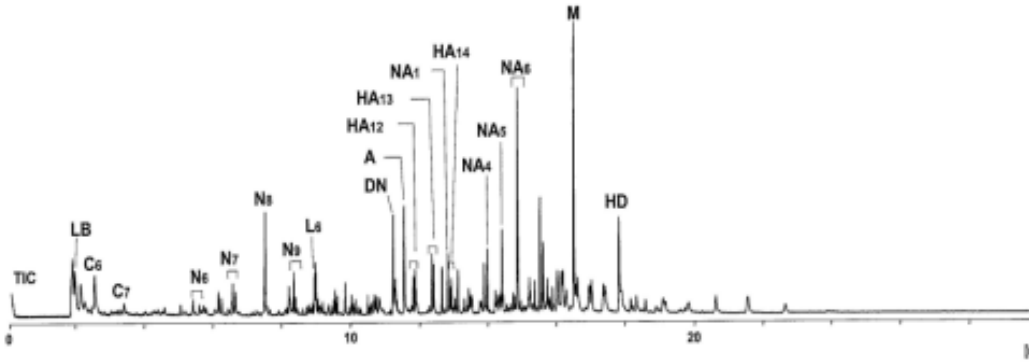
$-[NH(CH_2)_6NHCO(CH_2)_8CO]_n-$



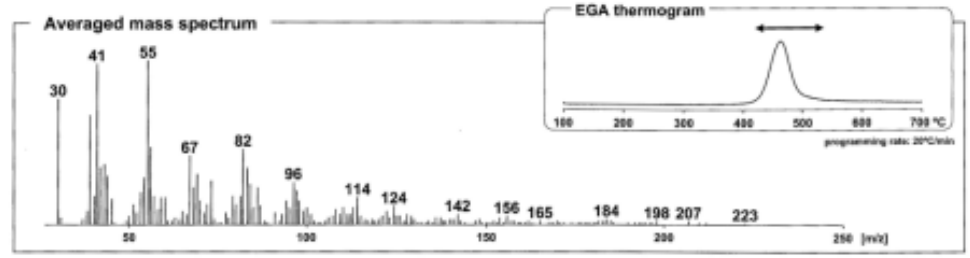
Pyrolysis Temperature: 600°C
Column: Ultra ALLOY-5; 30M x 0.25u x 0.25u
Oven Temp: 40°C (2min) -20°C/min-320°C (13min)

087 Poly(hexamethylene sebacamide); Nylon-6,10

$$-\left[NH(CH_2)_6NHCO(CH_2)_8CO\right]_n-$$

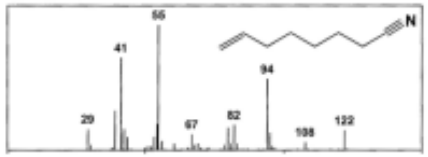


Peak Notation	Assignment of Main Peaks	Molecular Weight	Retention Index	Relative Intensity
LB	1-butene	56	385	31.1
C6	1-hexen	84	595	31.0
C7	1-heptene	98	694	7.7
N6	$CH_2=CH(CH_2)_3CN$	95	863	6.7
	$CH_3(CH_2)_4CN$	97	880	4.1
N7	$CH_2=CH(CH_2)_4CN$	109	975	8.8
	$CH_3(CH_2)_5CN$	111	982	10.4
N8	$CH_2=CH(CH_2)_5CN$	123	1079	37.4
N9	$CH_2=CH(CH_2)_6CN$	137	1079	8.4
	$CH_3(CH_2)_7CN$	139	1187	5.0
L6	$(CH_2)_5CONH$	113	1263	14.9
DN	$NC(CH_2)_8CN$	164	1617	33.5
A	$NC(CH_2)_8COOH$	183	1670	48.6
HA12	$CH_2=CH(CH_2)_{m-2}CONH(CH_2)_{n-2}CH=CH_2$ ($m+n=12$, $m<8$, $n<6$)	209	1717	10.9
	$CH_2=CH(CH_2)_{m-2}CONH(CH_2)_{n-1}CH_3$ ($m+n=12$, $m<8$, $n<6$)	211	1726	17.2
	+ $CH_2(CH_2)_{n-2}CONH(CH_2)_{m-1}CH_3$	211		
HA13	$CH_2=CH(CH_2)_{m-2}CONH(CH_2)_{n-2}CH=CH_2$ ($m+n=13$, $m<8$, $n<7$)	223	1820	15.3
	$CH_2=CH(CH_2)_{m-2}CONH(CH_2)_{n-1}CH_3$ ($m+n=13$, $m<8$, $n<7$)	225	1828	15.5
	+ $CH_2=CH(CH_2)_{n-2}CONH(CH_2)_{m-1}CH_3$	225		
NA1	$CH_3NHCO(CH_2)_8CN$	196	1909	18.6
HA14	$CH_2=CH(CH_2)_6CONH(CH_2)_4CH=CH_2$	237	1923	6.5
	$CH_2=CH(CH_2)_6CONH(CH_2)_5CH_3$	239	1931	9.0
	+ $CH_2=CH(CH_2)_4NHCO(CH_2)_7CH_3$	239		
NA4	$CH_3(CH_2)_3NHCO(CH_2)_8CN$	238	2152	18.6
NA5	$CH_2=CH(CH_2)_3NHCO(CH_2)_8CN$	250	2246	21.3
NA6	$CH_2=CH(CH_2)_4NHCO(CH_2)_8CN$	264	2353	68.3
	$CH_3(CH_2)_5NHCO(CH_2)_8CN$	266	2359	13.4
M	$(CH_2)_6NHCO(CH_2)_8CONH$	282	2776	100.0
HD	$CH_2=CH(CH_2)_4NHCO(CH_2)_8CONH(CH_2)_5CH_3$?	366 ?	3097	47.4

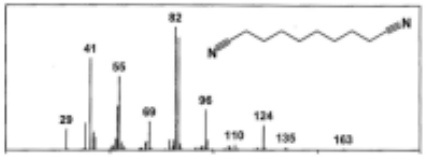


(m/z range : 29 - 600 amu)

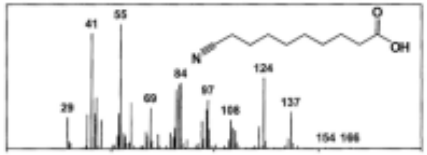
N8 : 7-octenenitrile



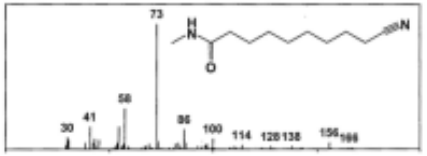
DN : decanedinitrile



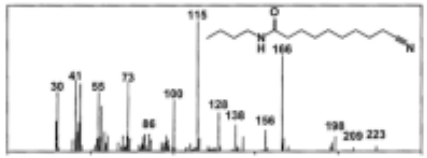
A : 9-cyanononanoic acid



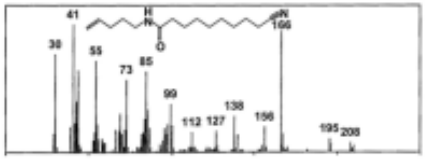
NA1 : 9-cyano-*N*-methylnonanamide



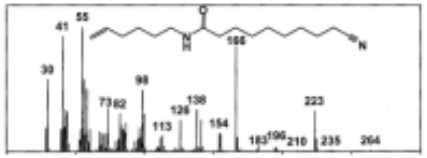
NA4 : *N*-butyl-9-cyanononanamide



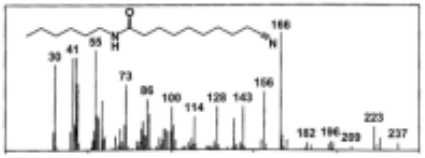
NA5 : 9-cyano-*N*-(pent-4-enyl)nonanamide



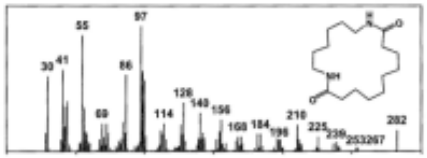
NA6 : 9-cyano-*N*-(hex-5-enyl)nonanamide



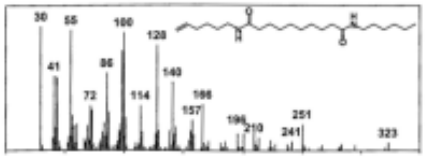
NA6 : 9-cyano-*N*-hexylnonanamide



M : 1,8-diazacyclooctadecane-9,18-dione



HD : N^5-(hex-5-enyl)-N^{10}-hexyldecanediamide



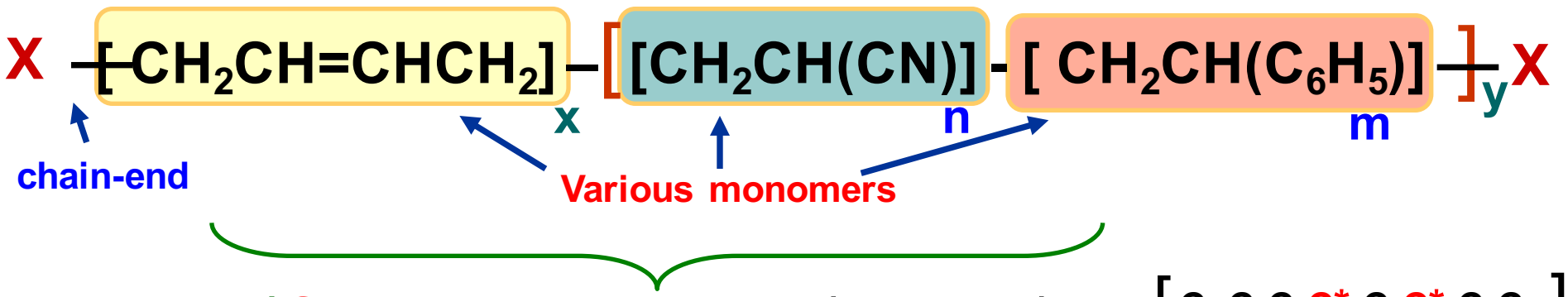
Pyrolysis GC/MS Data Book of Synthetic Polymers, 2011
Tsuge, Ohtani, Watanabe

Characterization of Polymers by Py-GC/MS

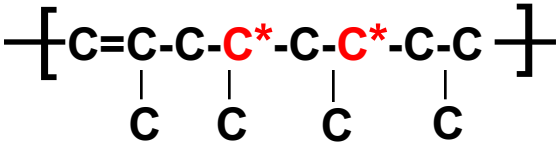
A: Identification of polymeric materials

Unknown materials (PP/ PVC/ SBR?)

B: Structural characterization of polymers



MW / Sequence distributions (x-n-m-n..)
Blend or copolymer (X+Y or X&Y)



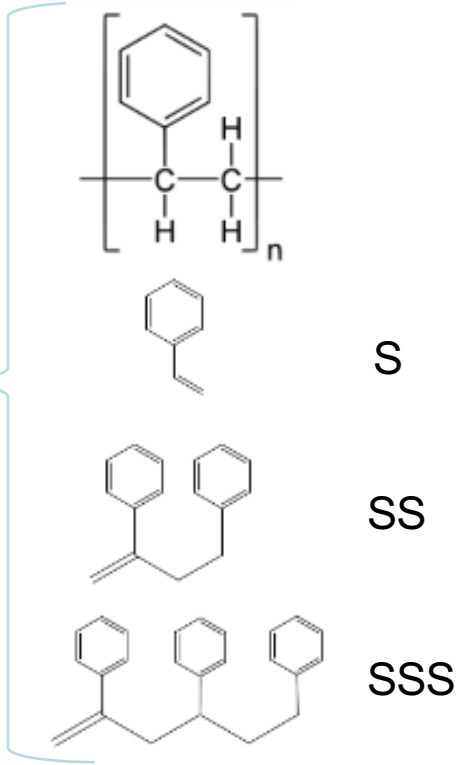
stereo regularity

C: Mechanisms and kinetics of polymer degradation

D: Qualitative and quantitative analysis of additives

Polymer degradation mechanisms

- Random scission
  - Polyolefins (polyethylene, polypropylene, polybutylene, etc.)
  - C-C bonds break to produce fragment patterns of increasing oligomer sizes (see prior PE example)
- 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*)



Most "big" pyrolyzates are not in NIST MS libraries

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

Quick Points on Pyrolysis

- Pyrolyzates are complex
- F-Search and its MS libraries have a majority of polymers, pyrolyzates, and additives
  - Identification is much easier than the old days
  - Many pyrolyzates are NOT found in NIST or Wiley MS libraries
- Pyrolysis has many modes:
  - Thermal desorption (TD)
  - Flash pyrolysis (PY)
  - Temperature programming such as EGA
  - Chemistry such as reactive pyrolysis (RxPy)
  - UV Irradiation
- How do we use these Py techniques for materials identification, and even quantitative analysis?

Acronyms/Abbreviations

Pyrolysis	PY or Py
Evolved Gas Analysis	EGA
Heart-Cutting	HC
Reactive Pyrolysis	RxPy
Thermal Desorption	TD
Interface	ITF
Combined	TD/PY

- Double-shot is TD followed by PY
- Heart-cutting based on EGA thermograms: HC-EGA

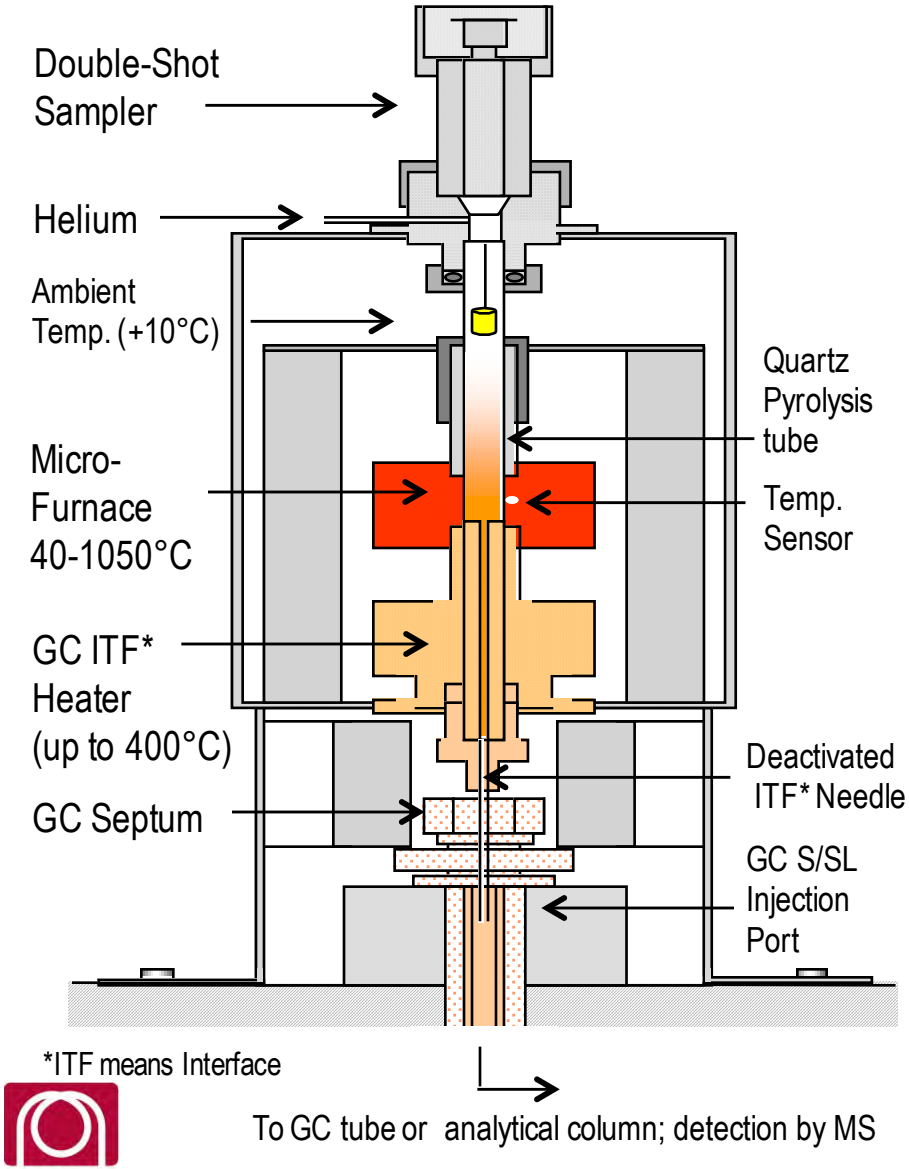
Essential Elements for Successful Applications of Analytical Pyrolysis

- Precise and reproducible temperature control
  - Fast Pyrolysis temperatures (<100 msec)
  - Programmable temperatures (Ambient +10°C–1050°C)
  - Precise temperature control (+/- 0.1°C) and calibration
- Apply "just enough" heat to obtain desired results
- Pyrolyzer engineered with inert, minimal and correctly heated sample path from start to finish
  - Deactivated surfaces throughout
  - Low dead volume
  - No cold spots
- Sample amount* and state (i.e. thin film, particle size, homogeneity)
- Data interpretation tools

*100 micrograms

Wish List
- Ease of Use
- Reliability
- Automation
- Flexibility
- Solves my problems

Sample Introduction and Schematic of Frontier EGA/PY-3030D Multi-Shot Pyrolyzer



Sample Introduction Modes

- Manual (Double-Shot Sampler)
- Automated (Auto-Shot Sampler)

Temperature Modes

- Isothermal
- Temperature Programmed

Multiple micro-Furnace Modes

- Evolved Gas Analysis (EGA)
- Thermal Desorption (TD)
- Flash Pyrolysis (PY or Single-Shot)
- TD/PY (Double-Shot)

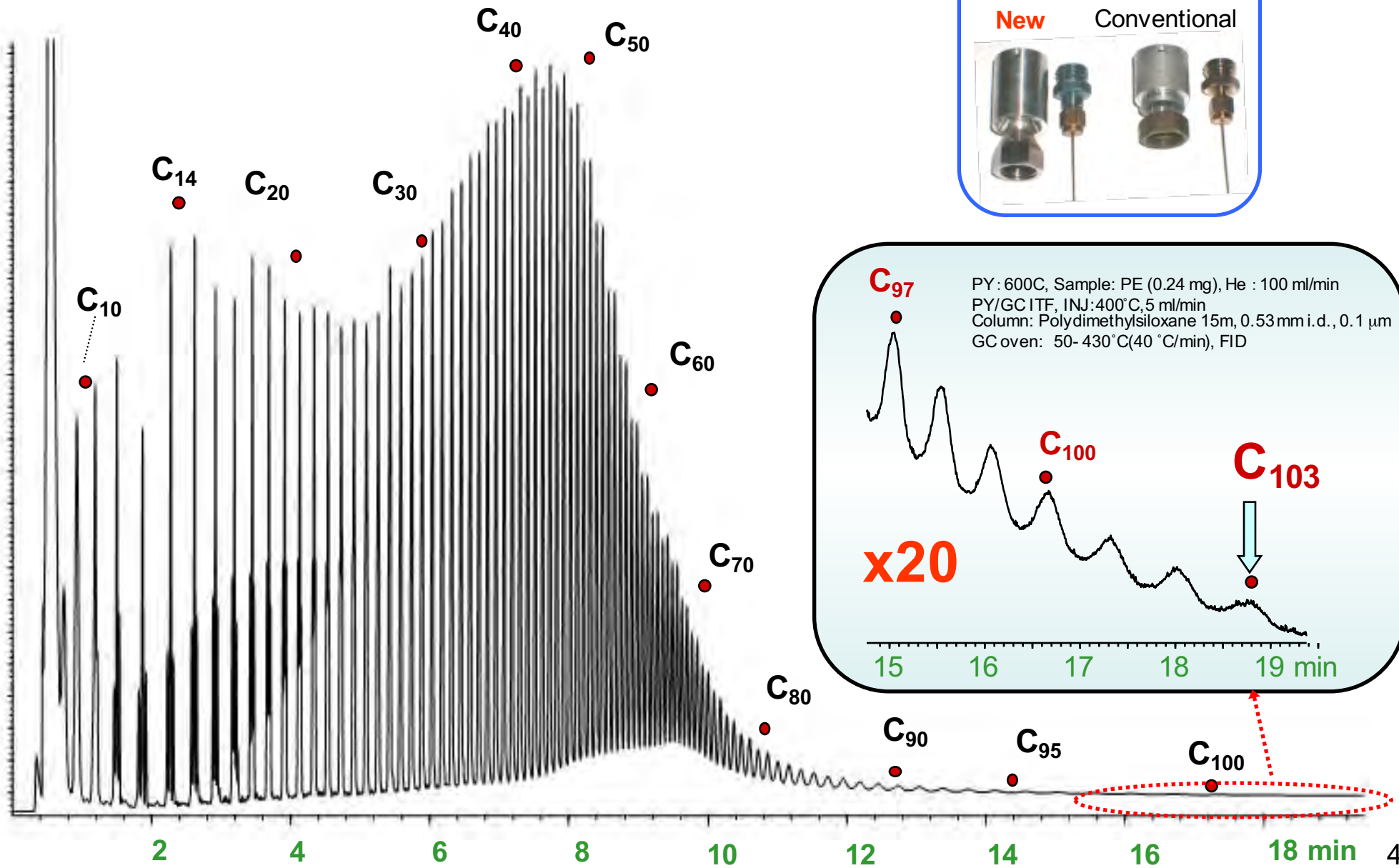
RxPy Method uses:

- Isothermal TD + Reagent (i.e. TMAH)

FRONTIER LAB

Frontier 3030D design = thermal integrity

FID pyrogram of Polyethylene at 600℃



PY/GC ITF Union

New Conventional

Important Factors for Materials Characterization by Pyrolysis

A. Pyrolyzer Types:

(a) Curie-point pyrolyzer
(b) Flash-filament pyrolyzer
(c) Vertical Micro-furnace pyrolyzer

B. High-resolution capillary columns for GC:

(a) Fused-silica capillary columns
(b) Deactivated stainless steel capillary columns

C. Highly sensitive and/or selective detectors for GC:

(a) Universal detector for C-containing compounds (FID)
(b) Specific detectors: FPD (for S and P), NPD (for N and P) ECD (for halides), etc.

D. Specific peak identification methods on pyrograms:

(a) Py-GC/MS
(b) Py-GC/FTIR (IRD)

E. Thermally assisted chemolysis:

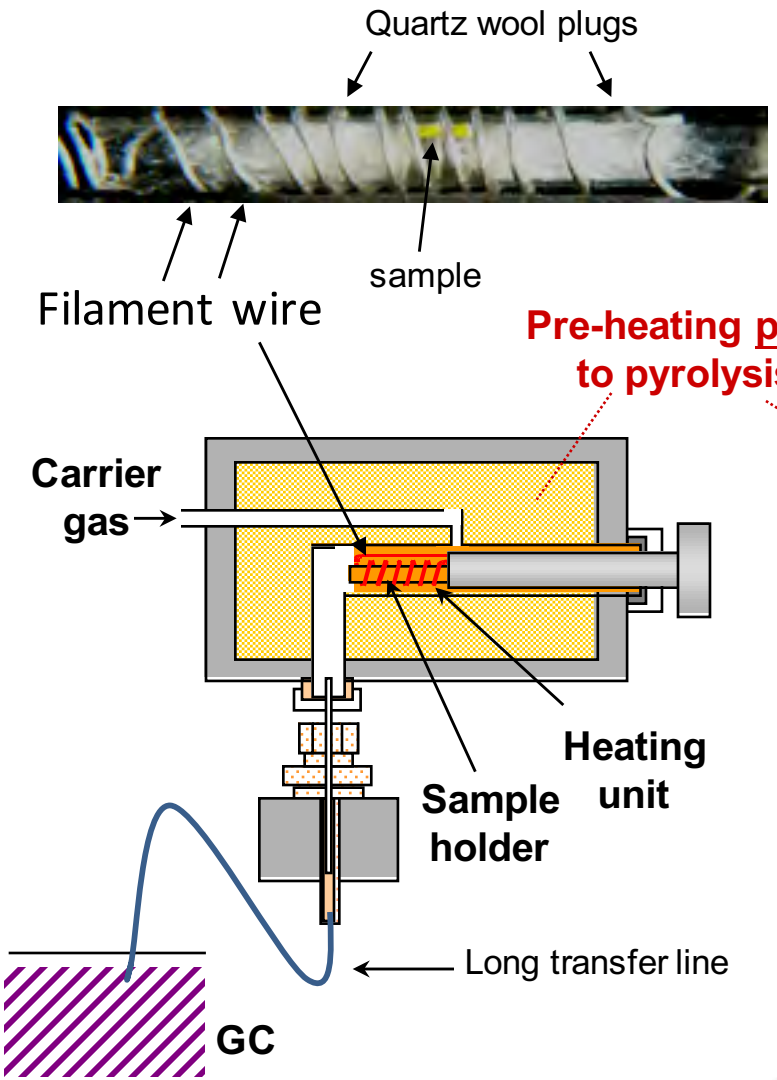
(a) On-line hydrogenation
(b) On-line methylation (RxPy)
(c) Catalysis-assisted thermolysis, etc.

F. Computer-assisted data processing and chemometrics

F-Search

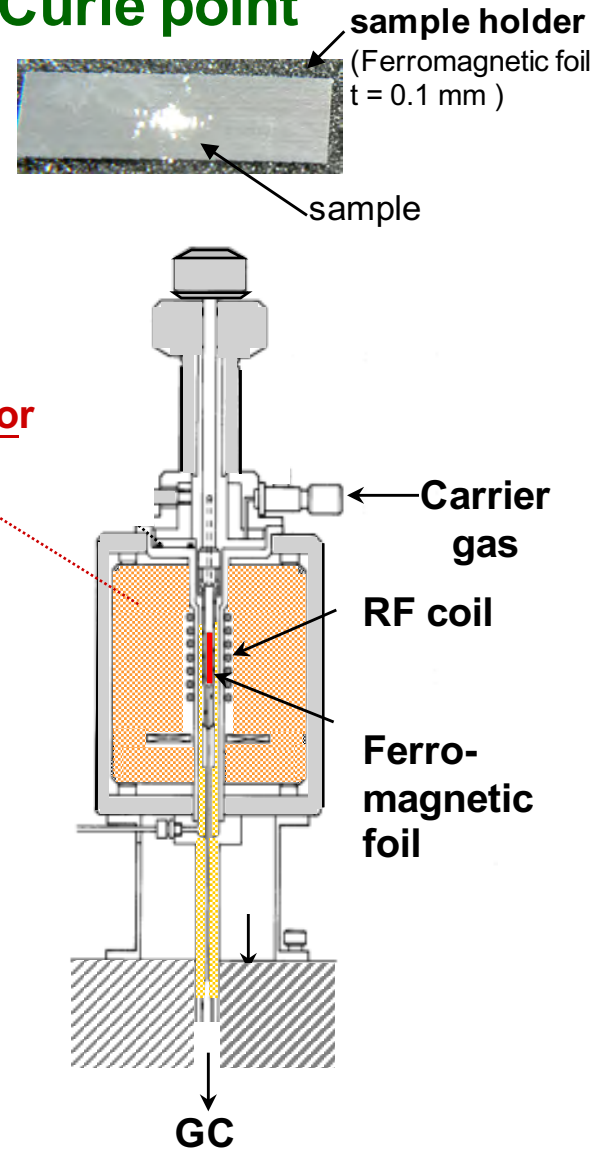
Schematic Diagrams of Various Pyrolyzers

Filament



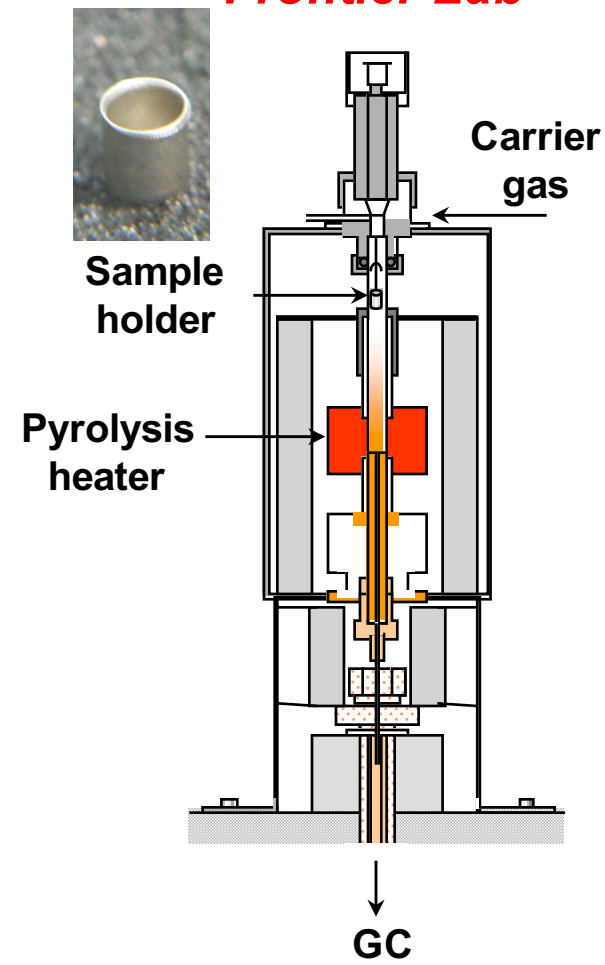
Pulse-mode pyrolyzer

Curie point



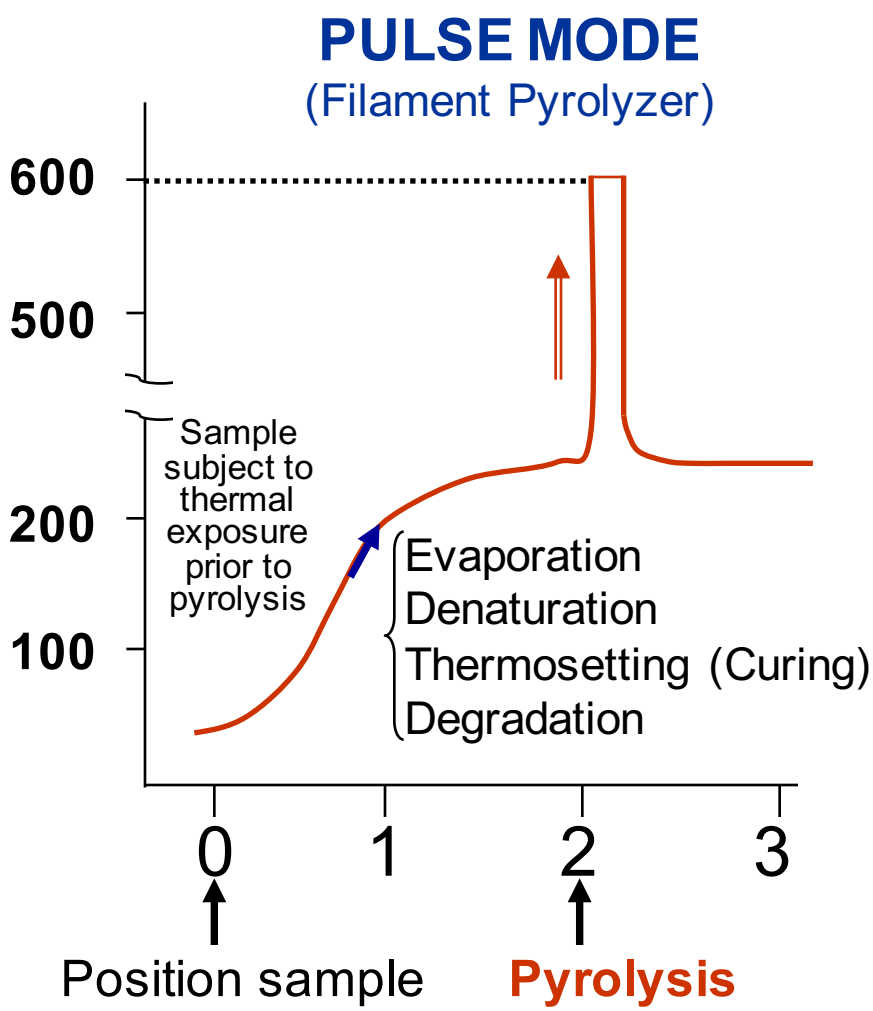
Micro-furnace

Frontier Lab

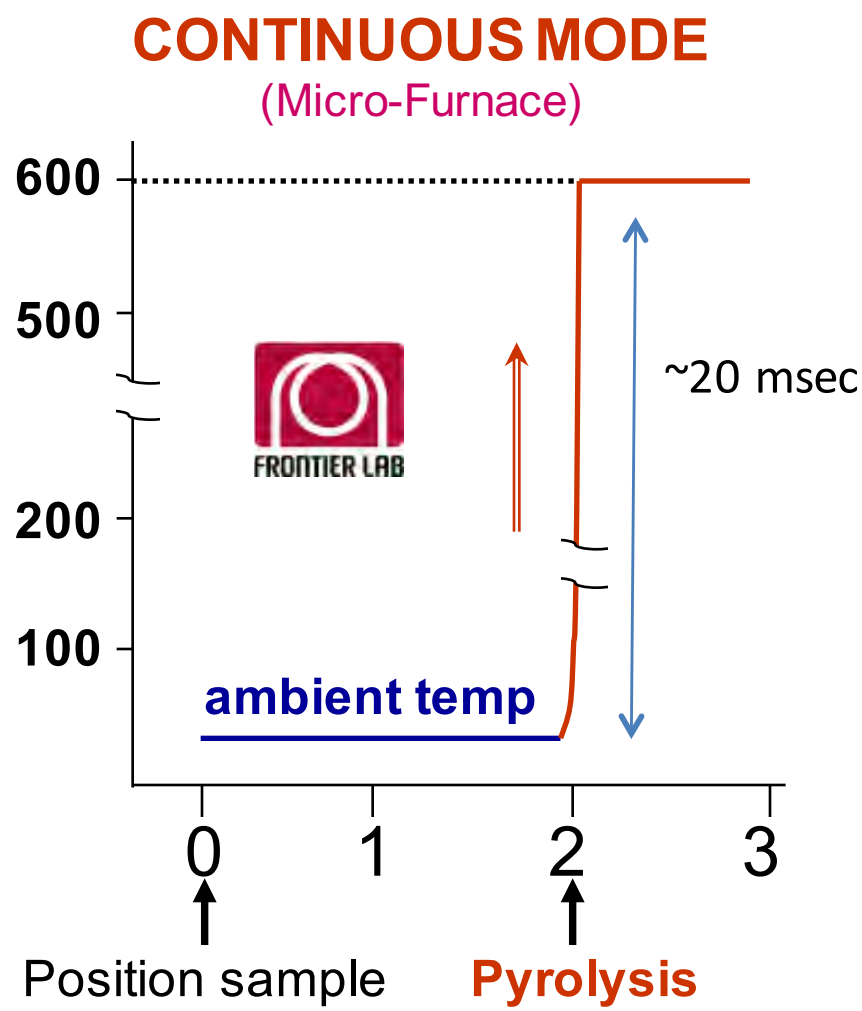


Continuous-mode pyrolyzer

Time and delay differences: filament vs. Micro-Furnace



Sample is inserted into the heated manifold. Time is needed to stabilize the sample temperature and purge the "air' with carrier gas before pyrolysis.



Sample held at near ambient; purged with helium, then dropped into furnace at the actual pyrolysis temperature.

Frontier EGA/PY-3030D

This is not your grandfather's pyrolyzer

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EGA/PY-3030D Multi-Shot Pyrolyzer -most common configuration

- Frontier Instrument Hardware
  - EGA/PY-3030D Multi-shot Pyrolyzer
  - Auto-shot Sampler (AS-1020E)
  - *MicroJet Cryo-trap (MJT-1035E)
    - 30 Liter Liquid Nitrogen Dewar
  - Vent-free Adapter (VFA) (MS402180)
  - *Selective Sampler (SS-1010E)
  - EGA tube: (UADTM-2.5N)
    - **Deactivated stainless steel 2.5m x 0.15m
  - Ultra ALLOY® Column: (UA5-30M-0.25F)
    - **Stainless steel 30m x.0.25mm i.d. x 0.25 µm 5% diphenyl PDMS film
  - Sample cup: Eco-cup LF (PY1-EC80F)
    - **Deactivated stainless steel 80 µl disposable cup
- Frontier Software
  - *F-Search and four MS Libraries (PY-1110E-141)

*Patented **Proprietary

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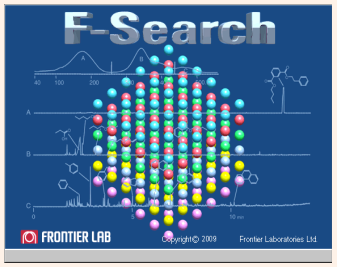
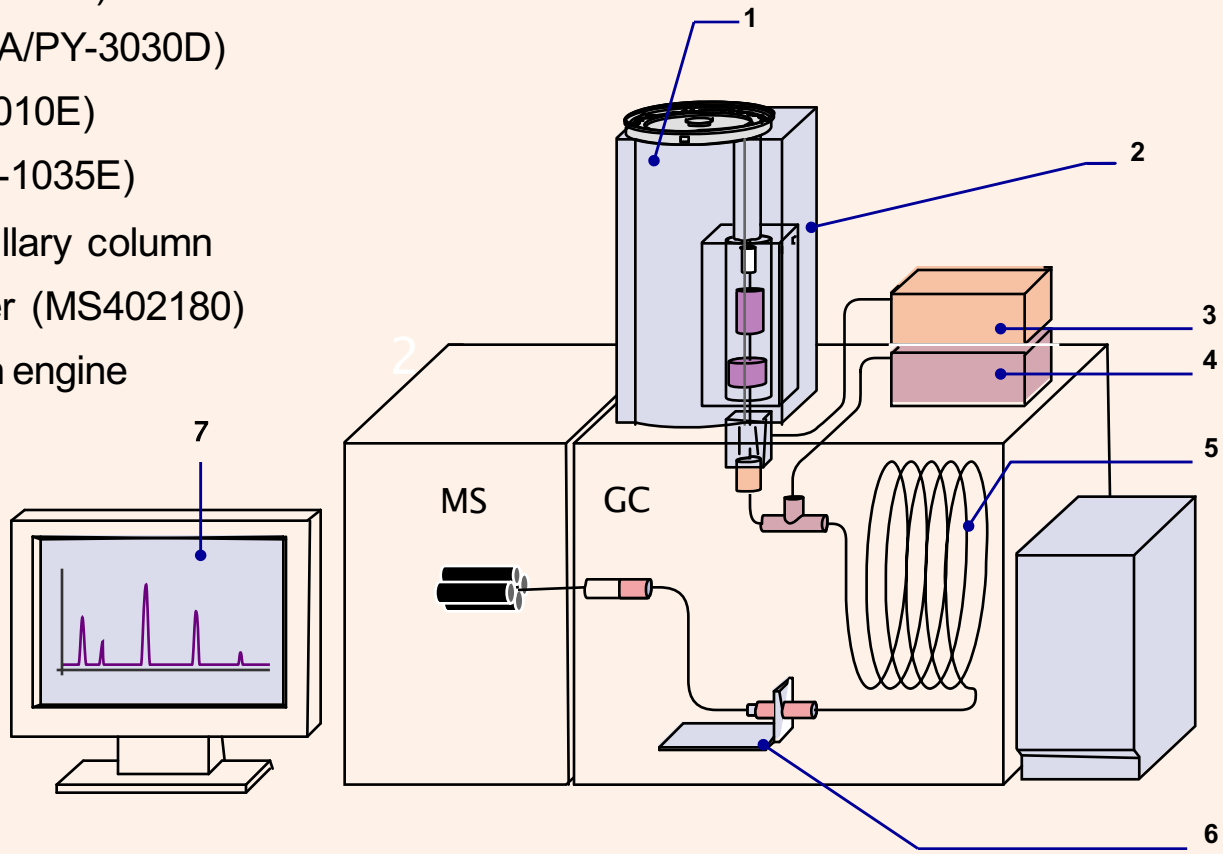
EGA/PY-3030D Multi-Shot Pyrolyzer -most common configuration

1. Auto-Shot Sampler (AS-1020E)
2. Multi-Shot Pyrolyzer (EGA/PY-3030D)
3. Selective Sampler (SS-1010E)
4. MicroJet Cryo-Trap (MJT-1035E)
5. Ultra ALLOY® metal capillary column
6. Vent-Free GC/MS adapter (MS402180)
7. F-Search system (search engine and MS libraries)





GC/MSD: 7890/5975
EGA/PY-3030D/MJT/SS/CGS/AS

Diablo Analytical, Inc.
A Technology and Development Company

Agilent 7890 GC Option SP-1 and Frontier Pyrolyzers

August 2012

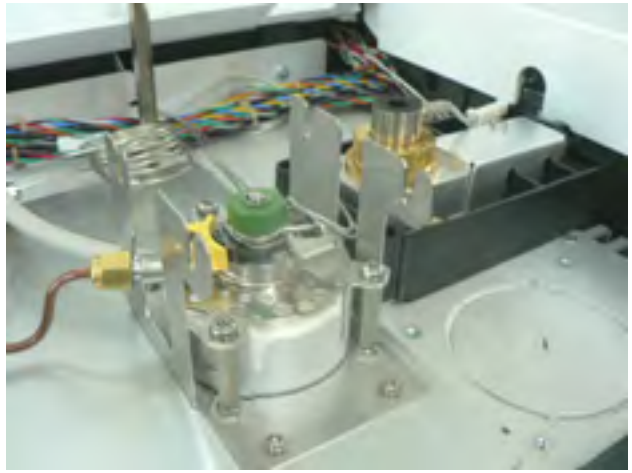
FRONTIER LABORATORIES LTD.

IW120809E_v1.3

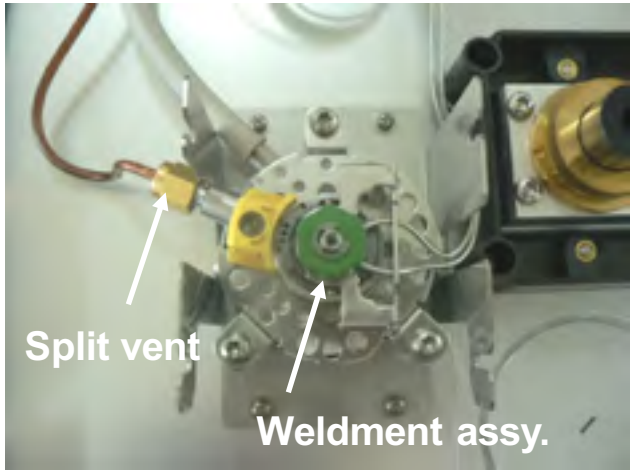
7890 GC Option SP-1

Front view with the detector cover

Rear left view



Front left view

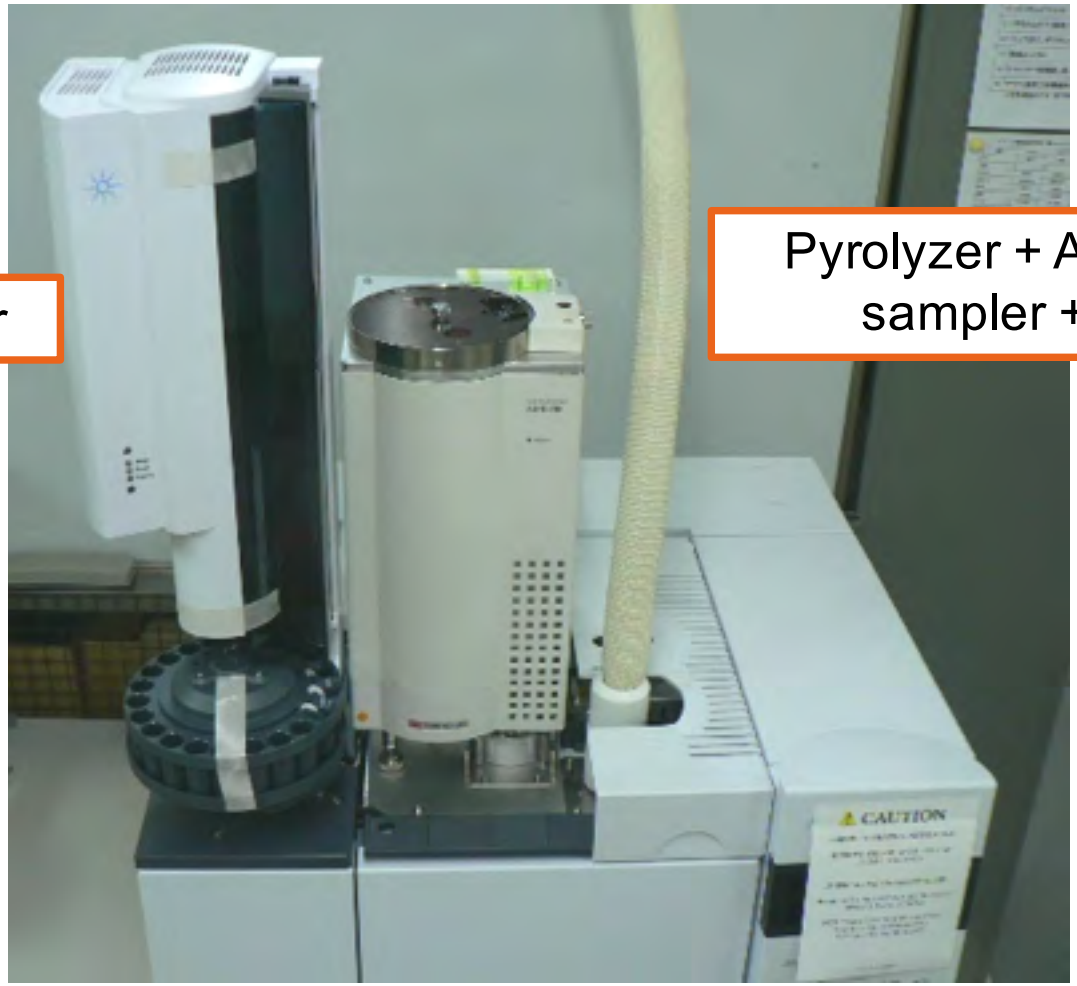


Top view

Agilent SP-1 is only available on new GC's

7890 GC Option SP-1
<Pyrolyzer system and Auto Injector>

Agilent autoinjector



Pyrolyzer + Auto-Shot sampler + MJT

7890 GC

EGA/PY-3030D Multi-Shot Pyrolyzer

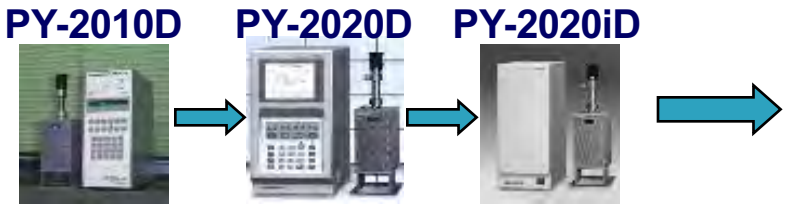
Complete Materials Characterization System

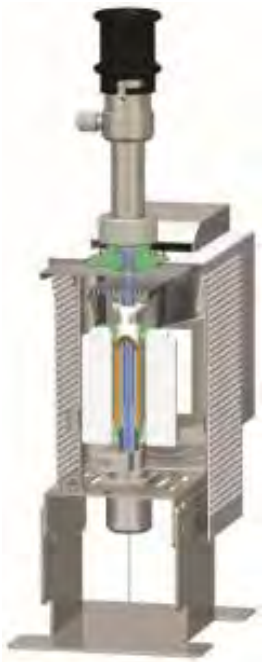
- Analytical Techniques
  - Evolved Gas Analysis (EGA-MS)
  - Heart-cut EGA (EGA-GC/MS)
  - Thermal Desorption (TD-GC/MS)
  - Pyrolysis (PY-GC/MS)
  - Reactive Pyrolysis (RxPy-GC/MS)
- Accessories
  - UV Irradiation
  - Sorbent-based TD
  - High pressure, high temperature reaction chemistry

- Highly Versatile System
  - Analyze C2 gases to C100 solids
  - Guaranteed reproducibility and accuracy.
    - Perform routine quantitative analyses
    - Temperature reproducibility $\pm$ 0.1°C
  - Fast, easy and green sample preparation
    - Saves time, money and minimizes or eliminates solvent use
  - Highly automated
    - Fast cycle times means higher sampler throughput
    - Auto-shot sampler has 48 sample capacity for unattended operation
    - Single-shot, double-shot and multi-shot on a single sample is automated
- Extremely reliable
  - 2 year warranty

EGA/PY-3030D Multi-Shot Pyrolyzer What's New vs. 2020D?

- Improved precision, accuracy, range
  - New ceramic heater
  - Expanded temperature range: Ambient +10 to1050°C ± 0.1°C precision (vs. 40-800°C ± 0.5°C)
    - Higher Interface temperature maximum: 450°C (vs. 400°C)
- Productivity enhancements
  - Faster cycle times: 3X
    - Faster cooling: 800-50°C <10 min (vs. 30 min)
    - Faster ramp rates: TD-PY 40-800°C <4min (vs. 14min)
- Redesigned for even easier maintenance, performance and ruggedness
  - New & improved parts; easier Py tube replacement
  - Guaranteed reliability and reproducibility
- 2 Year Warranty!





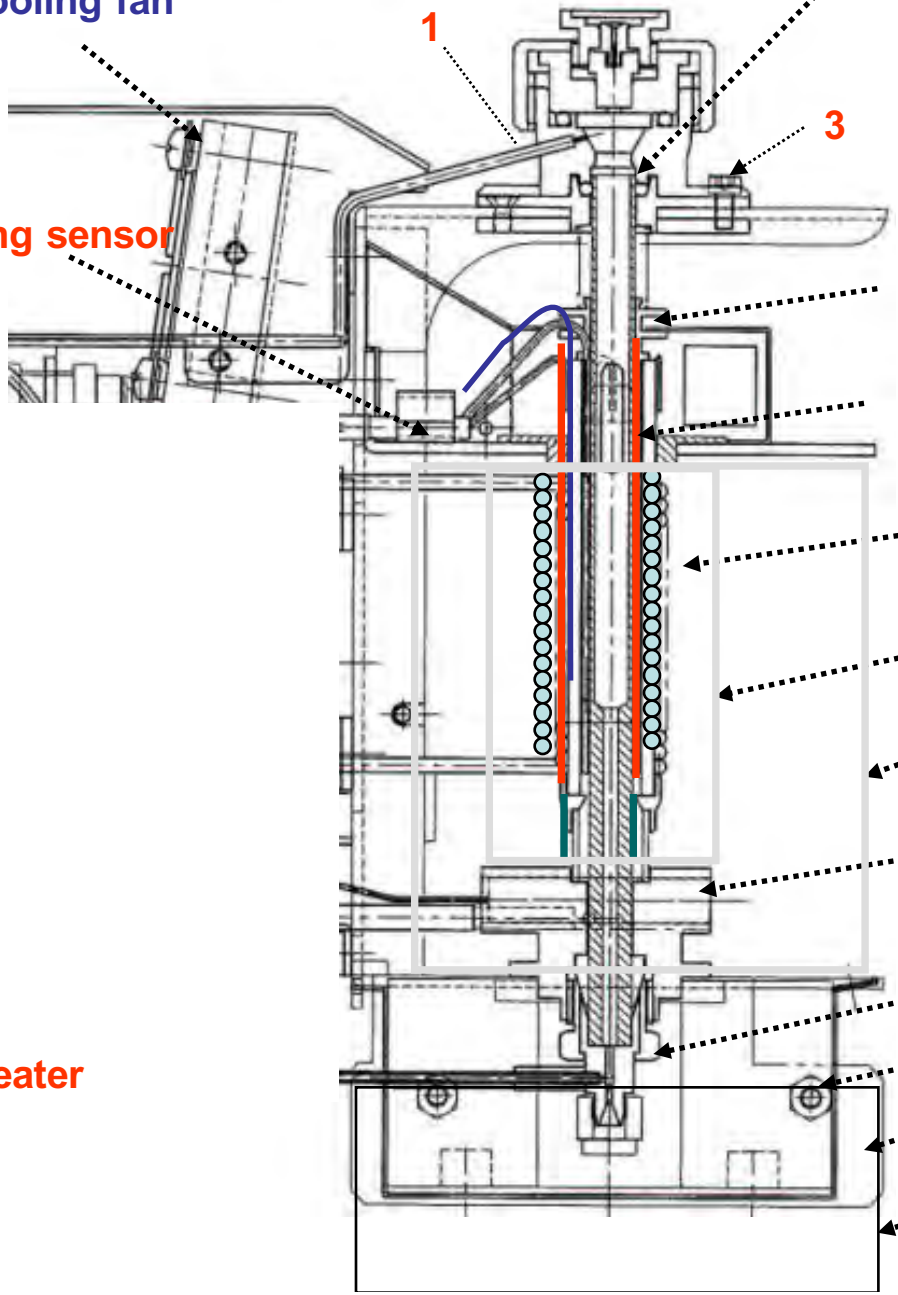
EGA/PY-3030D

Newly developed parts in EGA/PY-3030D

14: Powerful cooling fan

15: Over heating sensor

5 Ceramic heater

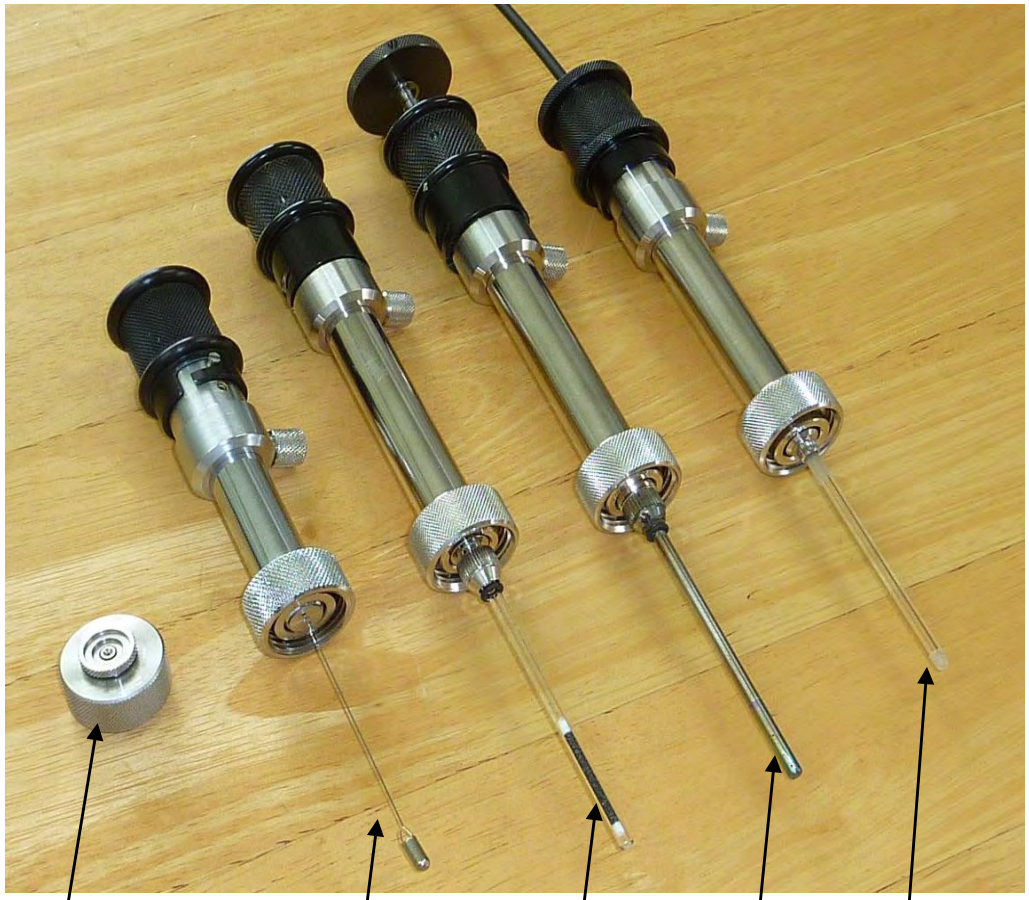


Multi-Functional Pyrolysis Systems

- EGA/PY-3030D
  - Multi-shot pyrolyzer
- PY-3030S
  - Single-shot pyrolyzer
- Auto-Shot Sampler
- Micro TD Sampler
- Micro Reaction Sampler
- UV Irradiator
- Liquid Sampler
- Accessories
  - MicroJet Cryo-trap
  - Vent-free adapter
  - Selective sampler
  - Carrier gas selector
  - Magic Chemisorber
- Ultra ALLOY Columns
- F-Search software v3.3
  - 4 MS libraries

More capability: 5 samplers

EGA/PY-3030D with Double-Shot sampler



① Liquid sampler

② Double-Shot sampler

③ TD sampler

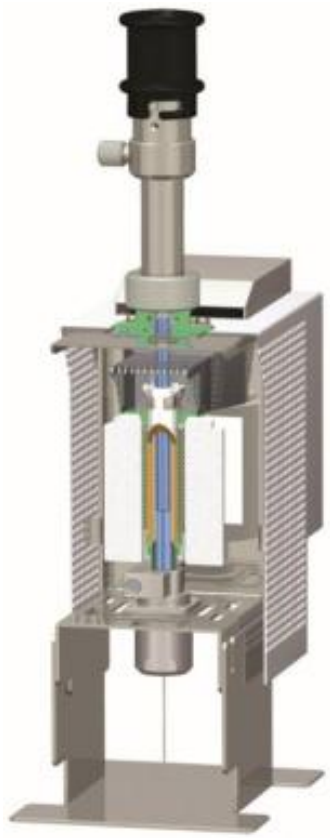
④ On-line micro reaction sampler

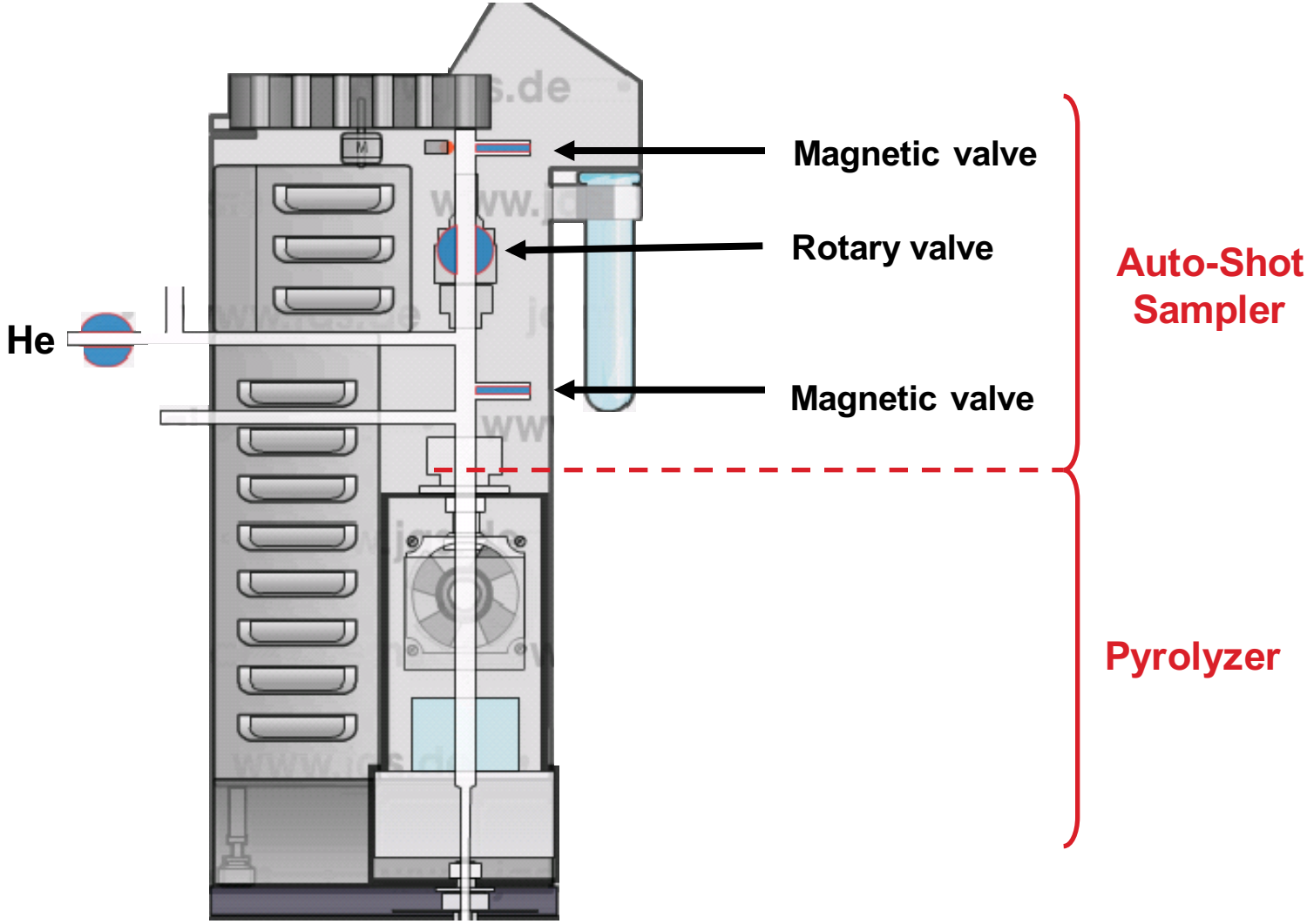
⑤ UV sampler

Auto-Shot autosampler

- 48 samples
  - Eco-cup (80µl)
  - Works with 3030S and 3030D
- Extremely Reliable
- Combined with the new faster cycle times of the 3030D (vs. 2020), sample throughput is increased by up to **80%**

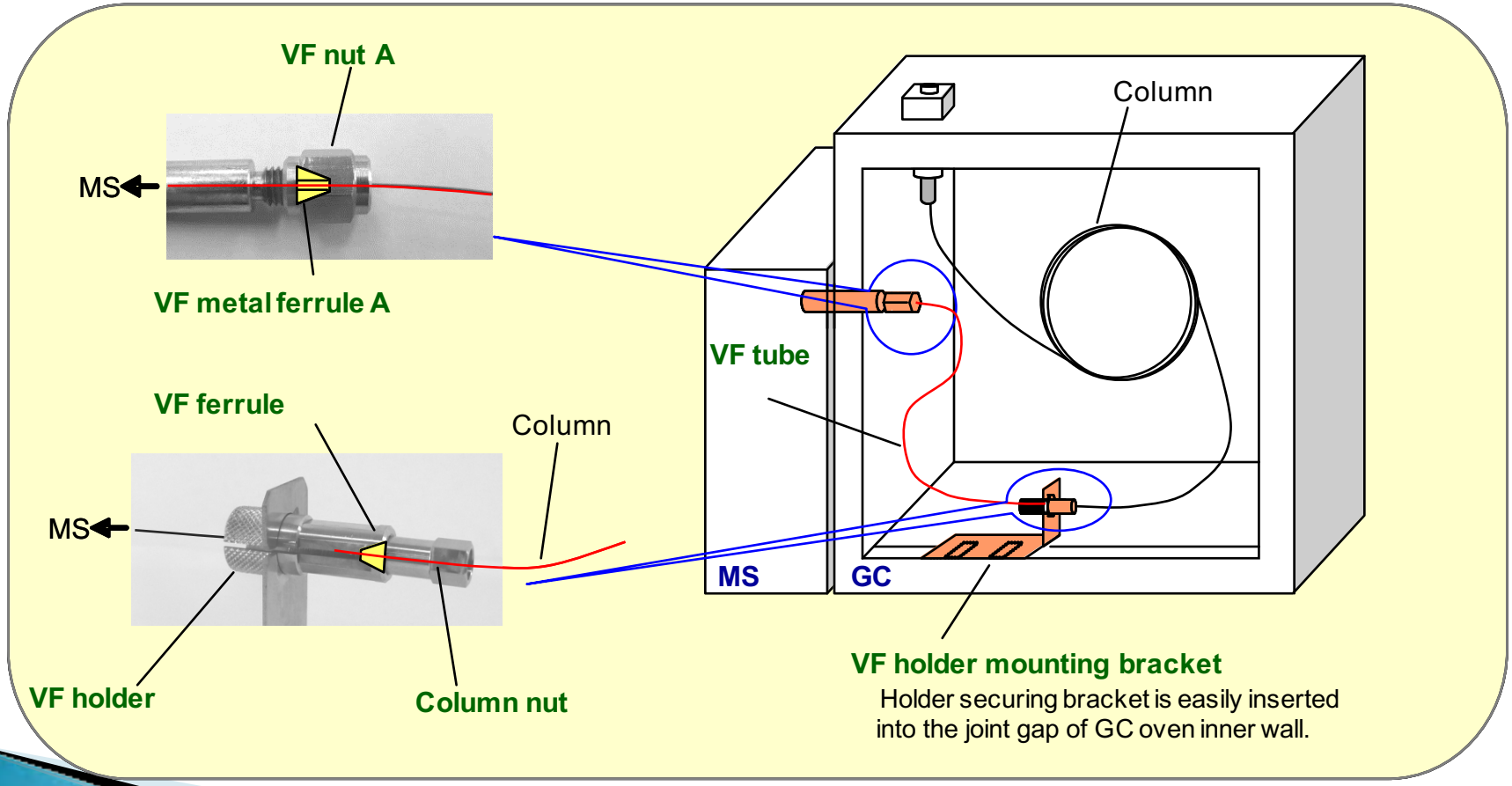
Double-shot with or without Auto-shot sampler





Vent-free GC/MS adapter (VFA) (MS402180)

Vent-free GC/MS Adaptor is a simple and useful interface used for GC/MS analysis, and allows switching of GC separation columns while the MS detector is in operation by connecting a highly deactivated capillary tube (id 0.15mm, length 2.5M) between the separation column and the MS detector to protect the MS detector



Display on PC of “Direct EGA Analysis”

EGA/PY-3030D Control

File View Tools Help

Direct EGA Analysis

START STOP

Pyrolyzer

Furnace

Step	Initial (°C)	Initial (min)	Rate (°C/min)	Final (°C)	Final (min)	Total (min)
1st	100	0.00	20	600	0.00	25.00
2nd			10	700	5.00	40.00
3rd			5	800	5.00	65.00
4th			1	900	5.00	170.00

Interface Upper Temp. 320 °C Auto Manual

Accessories

SS MJT AS CGS UV Settings

Monitor

Not Ready

Run

	Actual		Set	
Furnace	100.0	°C	100	°C
Interface	200.1	°C	200	°C
Sampling	-	Zone		
Cryo-Trap	21	°C		

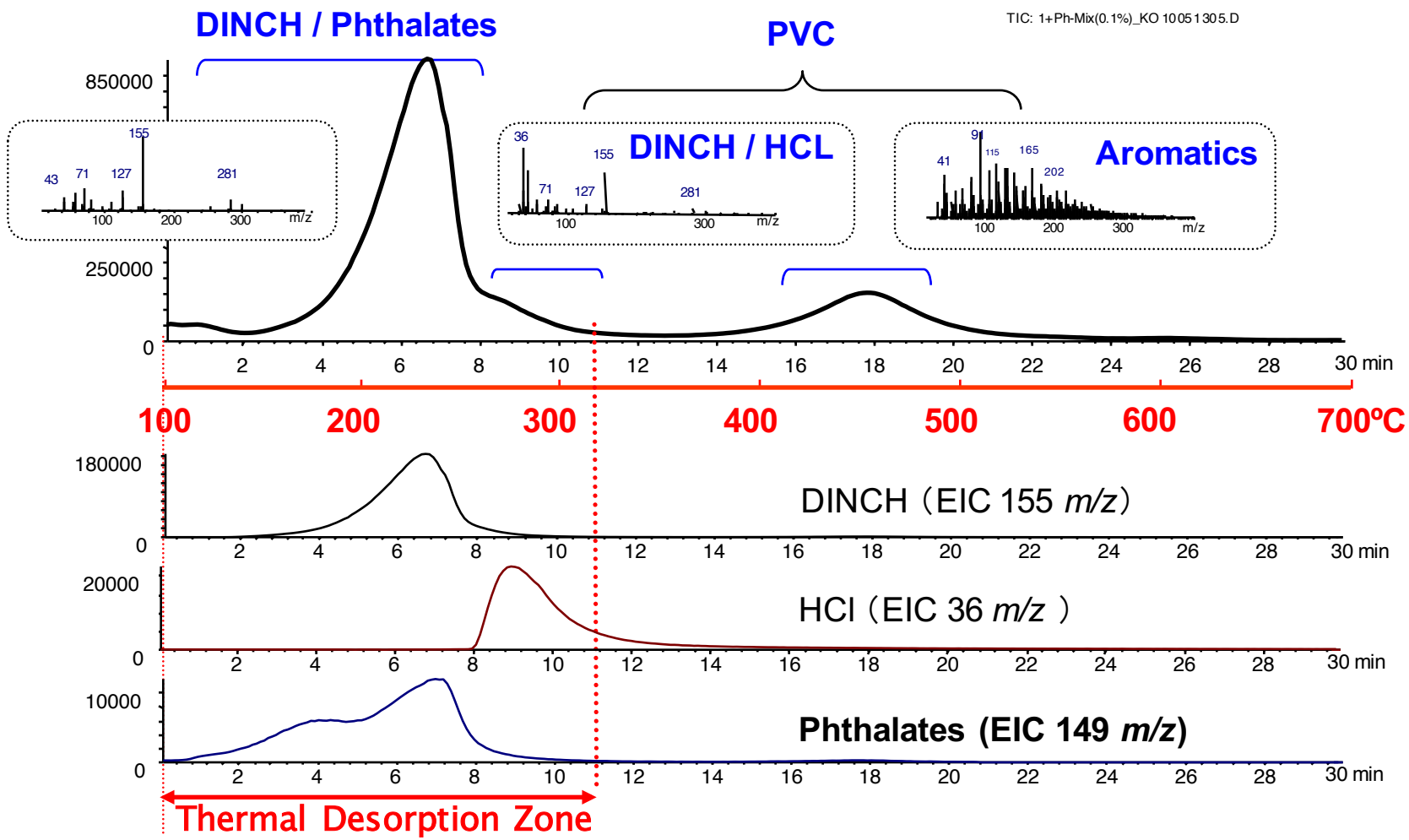
	Elapsed		Set	
Time	0.00	min	170.00	min

Elapsed Time

Review of techniques so far

- Pyrolysis — PY or Py
- Evolved Gas Analysis — EGA
- Heart-Cutting — HC
- Reactive Pyrolysis — RxPy
- Thermal Desorption — TD
- Combined — TD/PY
  - Double shot is TD followed by PY: **Next Lab**
  - Heart-cutting based on EGA thermograms: HC-EGA

Thermogram of PVC containing six regulated phthalates



100 – 320˚C (20˚C/min, 5 min hold)

Lab: Double-Shot (TD & PY)

- File or cut rubber duck sample
- Tare sample cup
- Weigh 100-200ug
- Record weight, sample name and your name
- Place in sample rack and note position #

- EGA data previously shows TD is:
  - (100-320°C @20°C/min
- EGA shows PY temp is 600°C
-
- Itsuko will show set up screens for TD and PY and demonstrate the Double-Shot technique.

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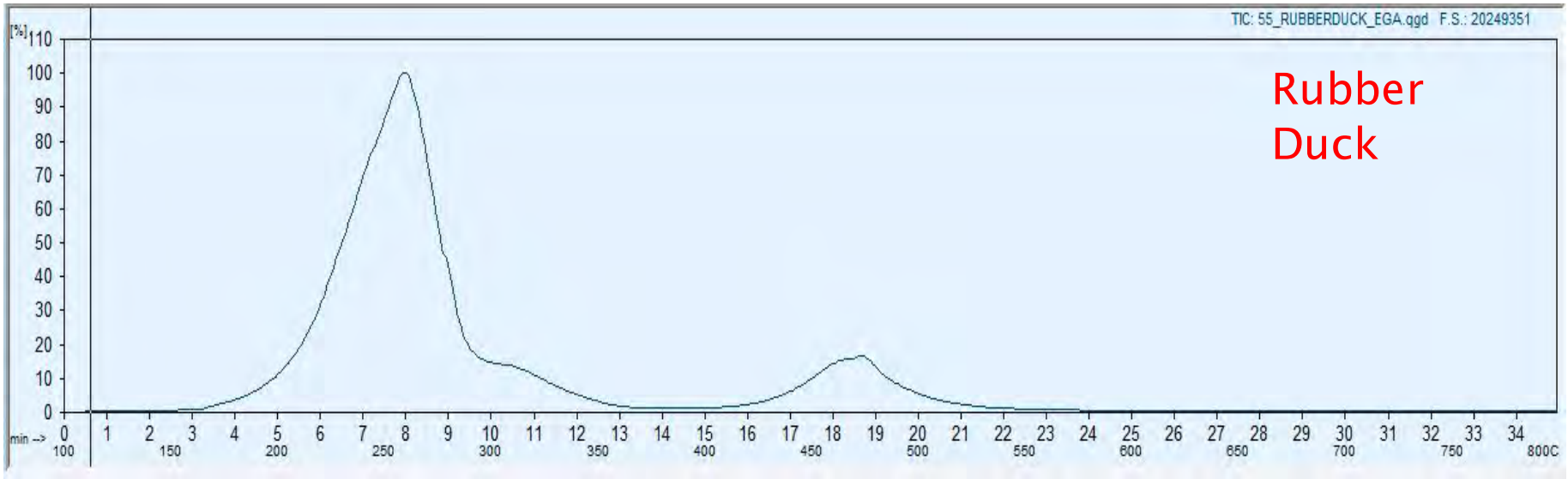
EGA Thermogram of Rubber Duck

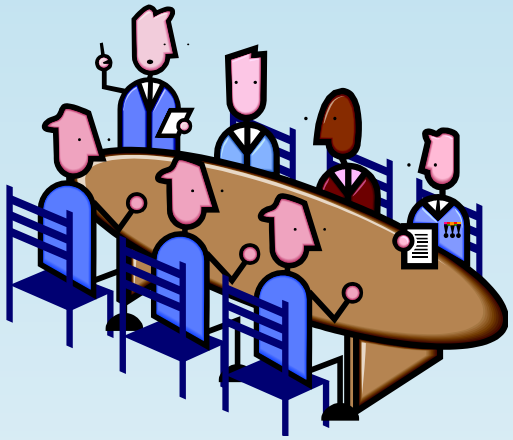


This is actual rubber duck thermogram
Phthalates come out before 320°C.
Polymer is out by 600°C.

This single sample can be easily run using
The Double-Shot Technique.

- Go to Lab

- Back to conference room for lunch at: 11:30 am



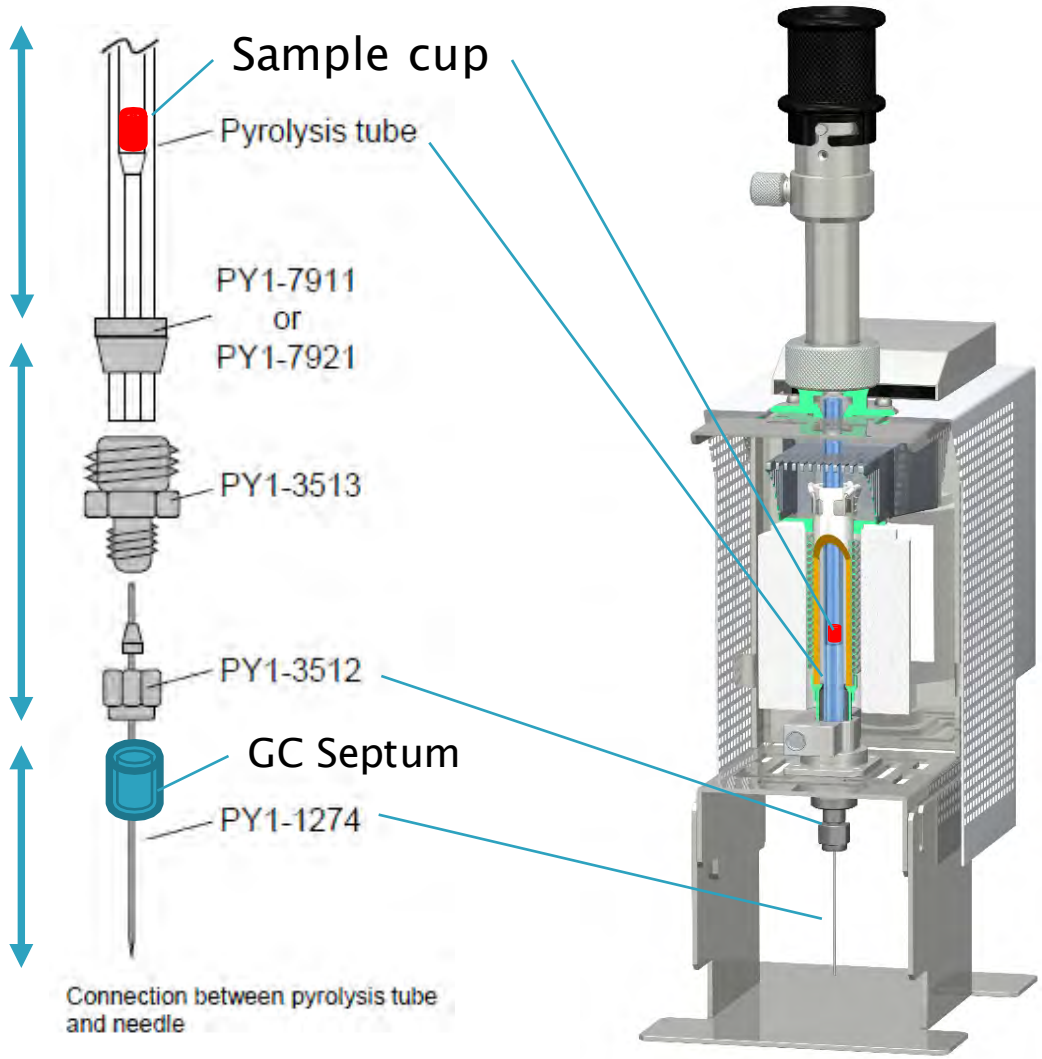
Frontier Simple Flow Path

Inert, heated, low dead volume, easy to clean flow path

Micro Furnace Zone

Heated Interface Zone

SPL Inlet Zone



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Next: Quantitation using

- Pyrolysis — PY or Py
- Evolved Gas Analysis — EGA
- Heart-Cutting — HC
- Reactive Pyrolysis — RxPy
- Thermal Desorption — TD
- Combined — TD/PY
  - Double shot is TD followed by PY
  - Heart-cutting based on EGA thermograms: HC-EGA

Show GCI Video on TMAH

The Getty Conservation Institute

- Intro to ~1min Video>Lacquer Videos>PyGCMS Schilling
- 4.51 min Py Peaks
- 5:02-8:41 manual TMAH
- 8:42-11:02 autosampler TMAH
- Acknowledgment Mike Schilling, Senior Scientist, GCI

PITTCON CONFERENCE & EXPO 2012

Determination of Stearic Acid in SBR Using Reactive Pyrolysis GC/MS

Atsushi Watanabe *and Chu Watanabe* : Frontier Laboratories Ltd., Japan

Robert Freeman : Frontier Laboratories USA, CA, USA

FRONTIER LABORATORIES LTD.

Background of research

Composition of rubber products

Rubber raw materials

Additives

- Vulcanizing agent
- Vulcanization accelerator
- Accelerator activator
- Antioxidant, etc.

Analysis of free fatty acid (stearic acid) in vulcanized rubber products

Solvent extraction

- Large amount of solvent required
- Time consuming process
- Cumbersome procedures

Thermal desorption-GC/MS

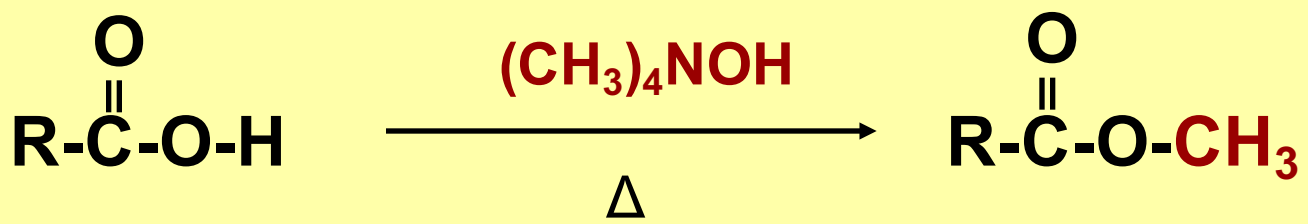
- Small amount of sample
- No pretreatment required

Both methods suffer from peak tailings in chromatogram due to the polar nature of fatty acids, leading to the deterioration of results.

Objective

Simple and rapid derivatization and determination of free fatty acids in vulcanized rubber products

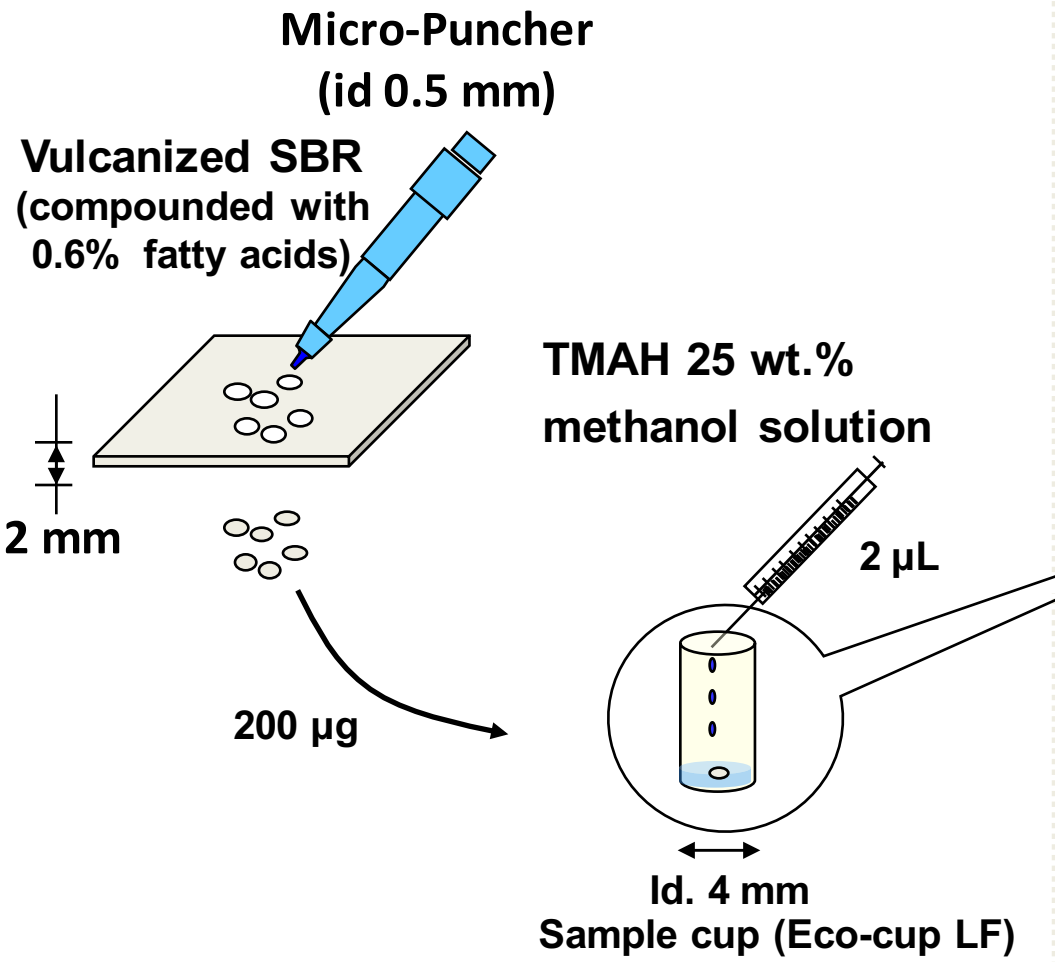
Investigate the viability of reactive pyrolysis GC/MS of vulcanized styrene-butadiene rubber (SBR) sample using tetramethylammonium hydroxide (TMAH) for simple and rapid determination of free fatty acids.



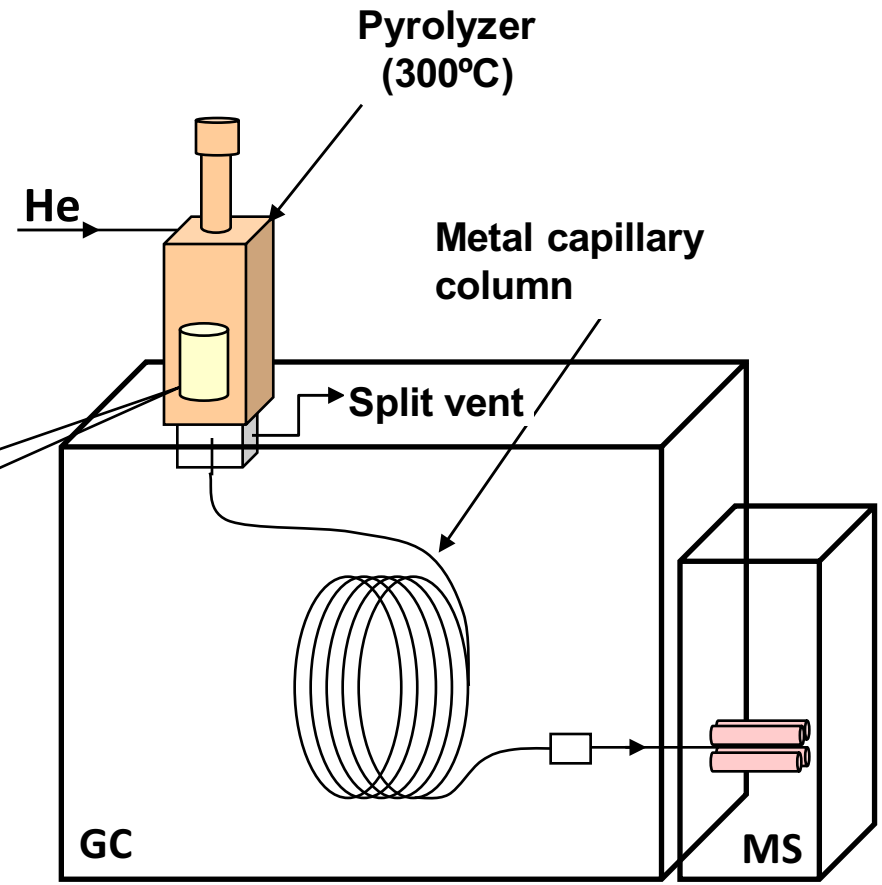
*** The sum of palmitic acid and stearic acid is regarded as free fatty acids in this study.**

Analytical procedures and instrumentation

Sample preparation



Reactive pyrolysis-GC/MS



Using a Harris micro puncher, a 2 mm thick SBR rubber sheet was punched out to obtain small discs. To a 200 µg of powdered sample in a sample cup was added 2 µL of 25% methanol solution of TMAH. Then it was subjected to reactive pyrolysis-GC/MS at 300ºC.

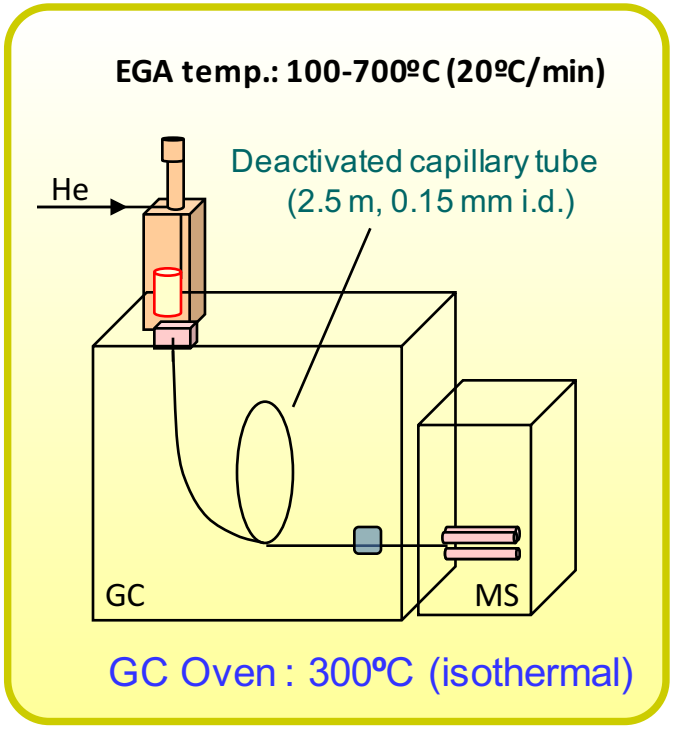
Analytical conditions

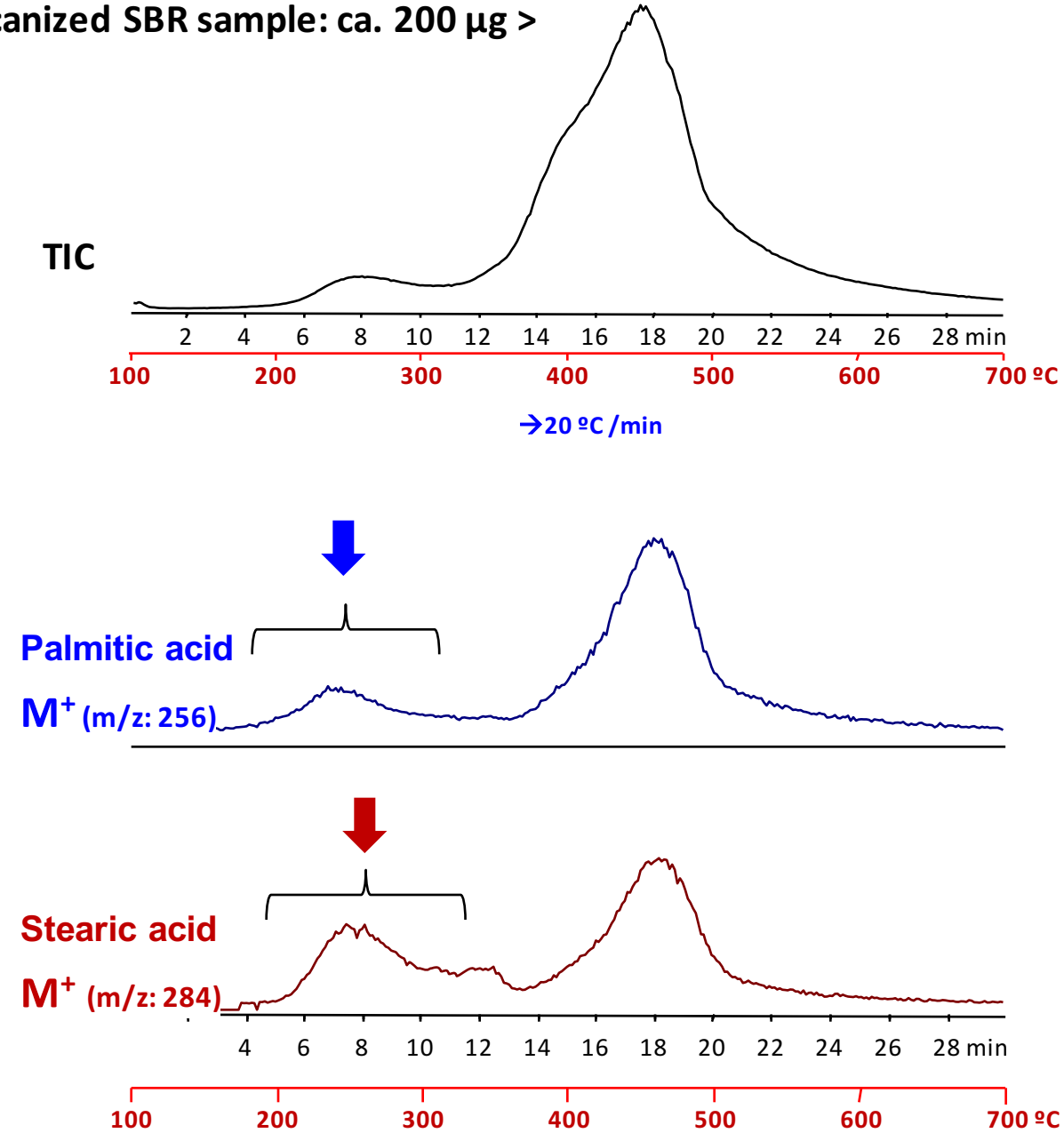
Pyrolyzer	:	Multi-Shot pyrolyzer (EGA/PY-3030D), Frontier Lab Ltd.)
Separation column	:	Ultra ALLOY-5 (5 % phenyl 95 % dimethylpolysiloxane, Frontier Lab Ltd.), L= 30 m, id.= 0.25 mm, df= 0.25 µm
GC oven temp.	:	70 - 280ºC (20ºC/min, 3 min hold)
Py-GC ITF temp.	:	320ºC
GC injector temp.	:	300ºC
Column flow rate (He)	:	1 ml/min
Split ratio	:	1/100
Detector	:	MS
Scan range	:	29 - 550 (m/z)
Scan rate	:	Approx. 5 scans/sec

Thermogram of vulcanized SBR sample obtained by evolved gas analysis (EGA)

< Vulcanized SBR sample: ca. 200 µg >

Evolved gas analysis (EGA)-MS



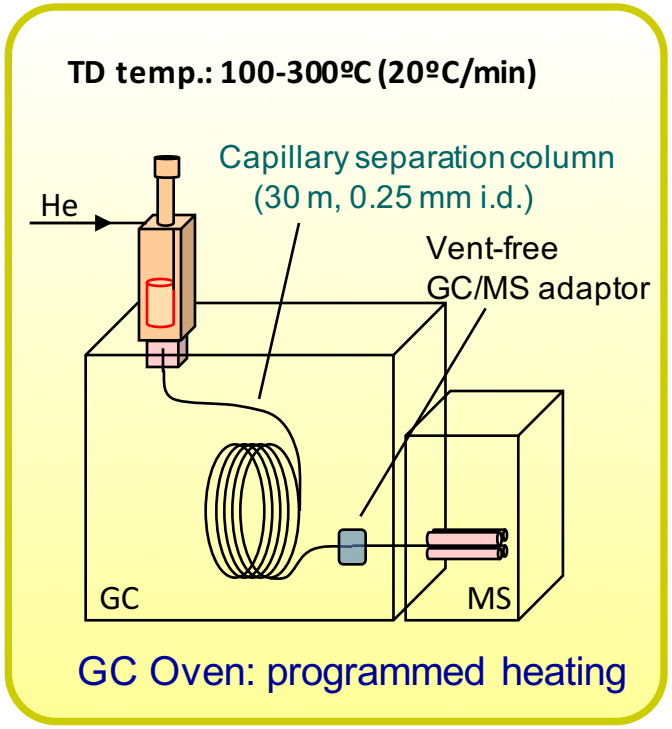


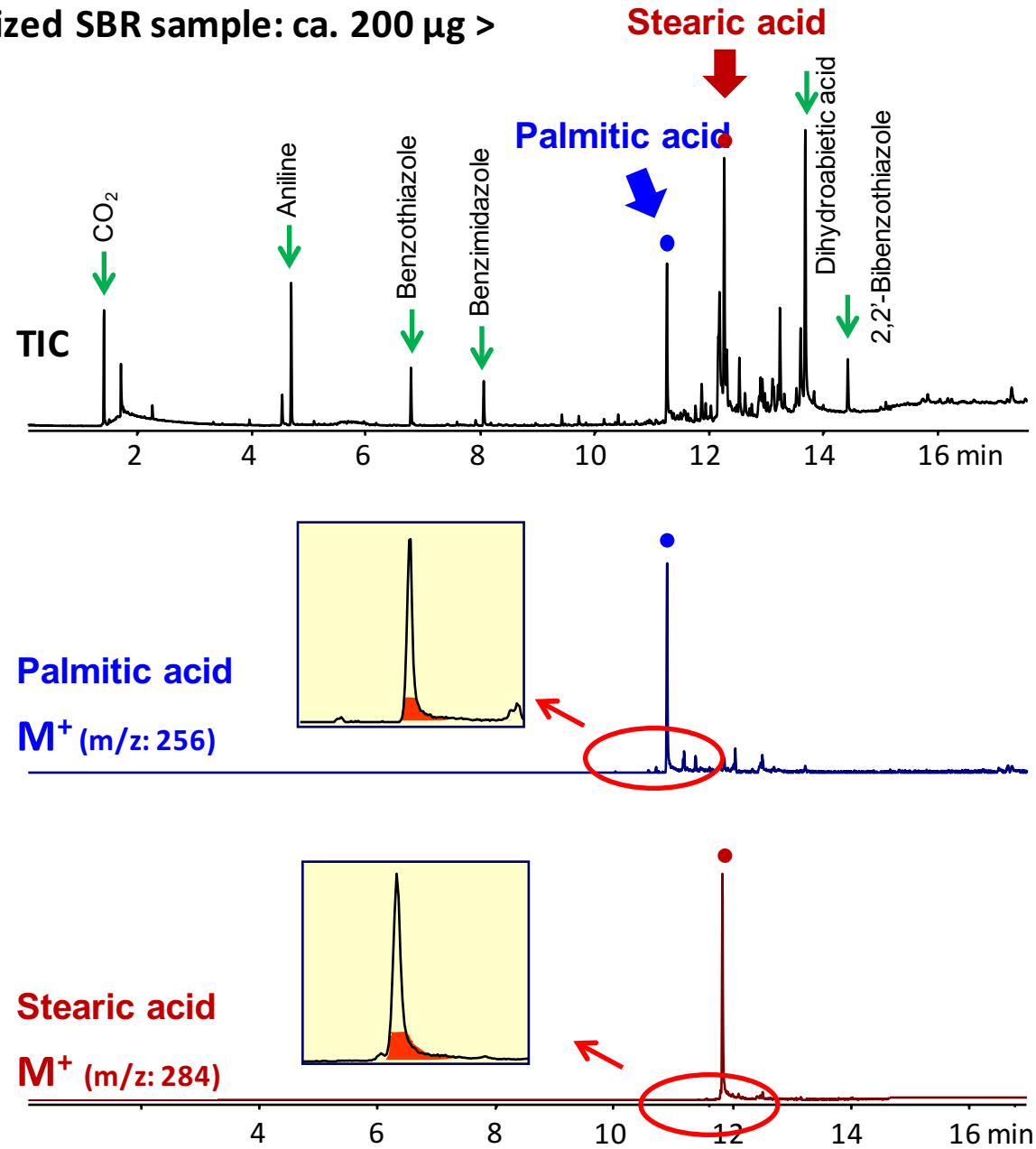
Elution peaks for free fatty acids (stearic acic and palmitic acid) were observed in the 150ºC to 300ºC range. Based on this observation, the optimal thermal desorption range was determined then thermal desorption-GC/MS analysis was performed.

Chromatogram of vulcanized SBR sample obtained by thermal desorption TD GC/MS (No reagent)

< Vulcanized SBR sample: ca. 200 µg >

Thermal desorption (TD)-GC/MS



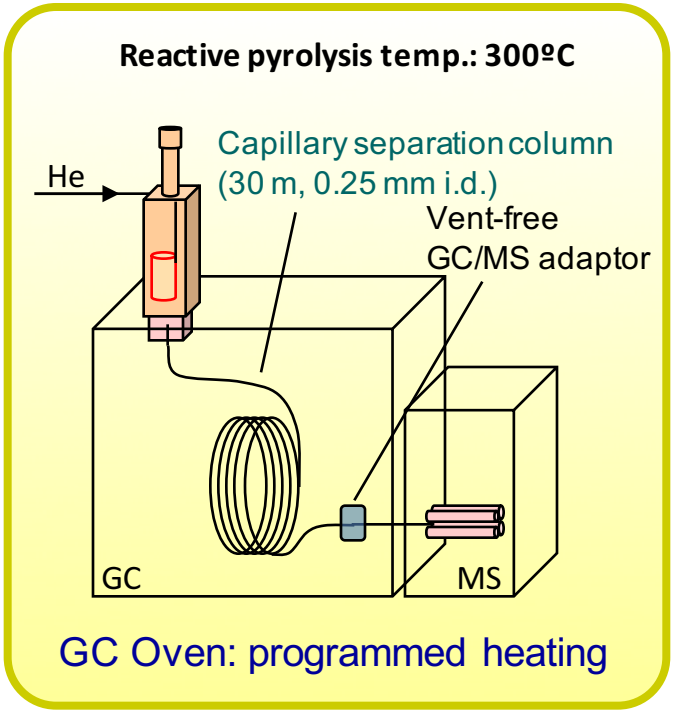


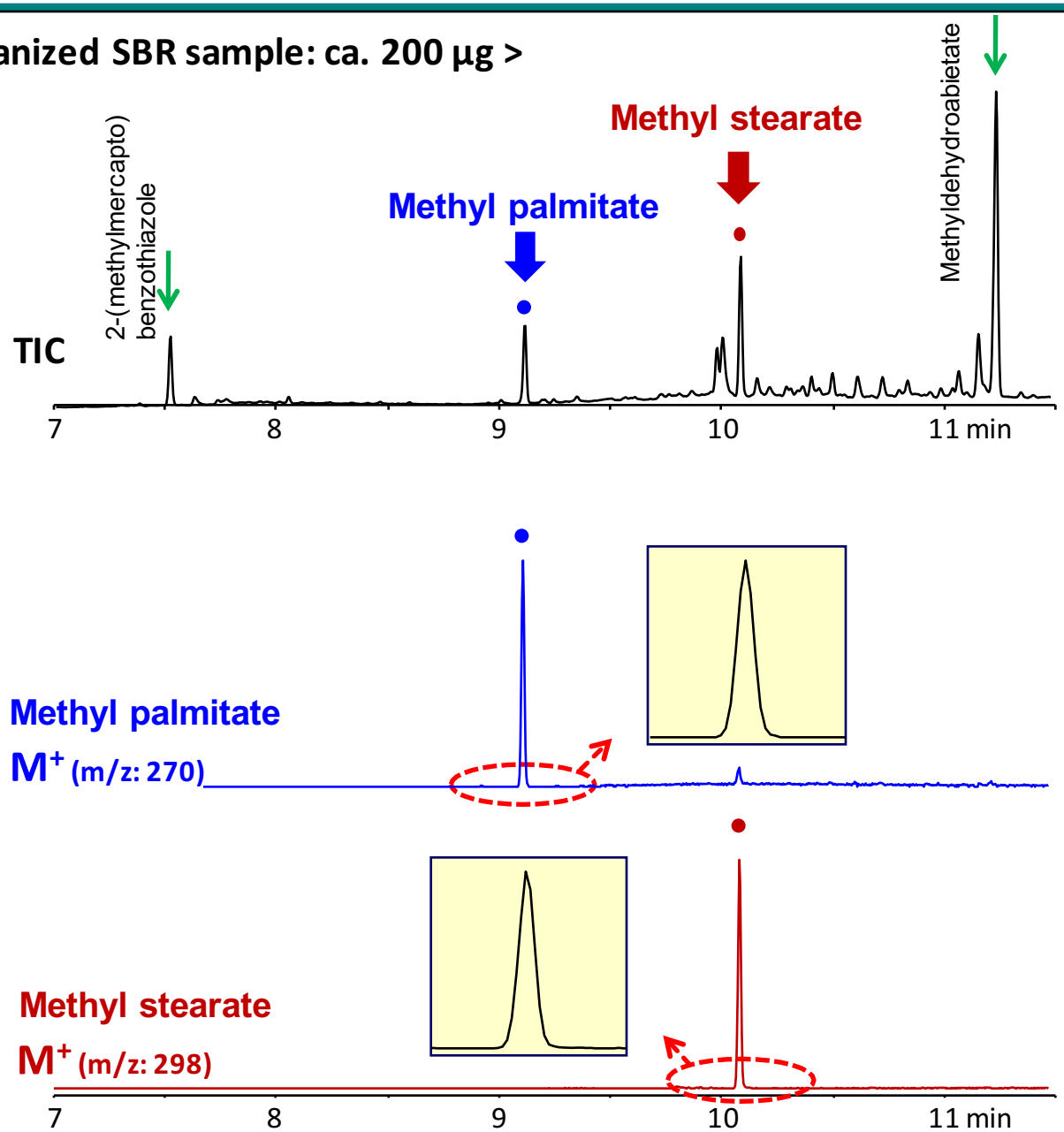
TD-GC/MS analysis showed that both of free fatty acids (palmitic acid and stearic acid) eluted as tailing peaks.

Chromatogram of vulcanized SBR sample obtained by reactive pyrolysis- RxPy GC/MS with TMAH

< Vulcanized SBR sample: ca. 200 µg >

Reactive pyrolysis-GC/MS





Free fatty acids which were methyl-derivatized by the reactive pyrolysis-GC/MS showed up as symmetrical peaks without tailing.

Total amount of fatty acids found in vulcanized SBR sample and reproducibility (n=5)

	Fatty acid contents (%) in vulcanized SBR < Compounded concentration: 0.6 % >		
Amount of sample (µg)	Methyl palmitate	Methyl stearate	Total fatty acids
197	0.160	0.456	0.616
194	0.155	0.441	0.596
203	0.152	0.449	0.601
202	0.156	0.479	0.635
204	0.159	0.479	0.638
Avg	0.156	0.461	0.617
Relative std. deviation (%RSD)	2.12	3.84	3.16*

The reactive pyrolysis-GC/MS of the SBR samples was performed repeatedly five times. The peak areas for methyl palmitate and methyl stearate in the mass chromatograms drawn by m/z: 298 ion were summed as the total of fatty acids. The total fatty acid content in the SBR sample was found to be 0.6%. The reproducibility was excellent with a relative standard deviation (RSD) of 3.16%.

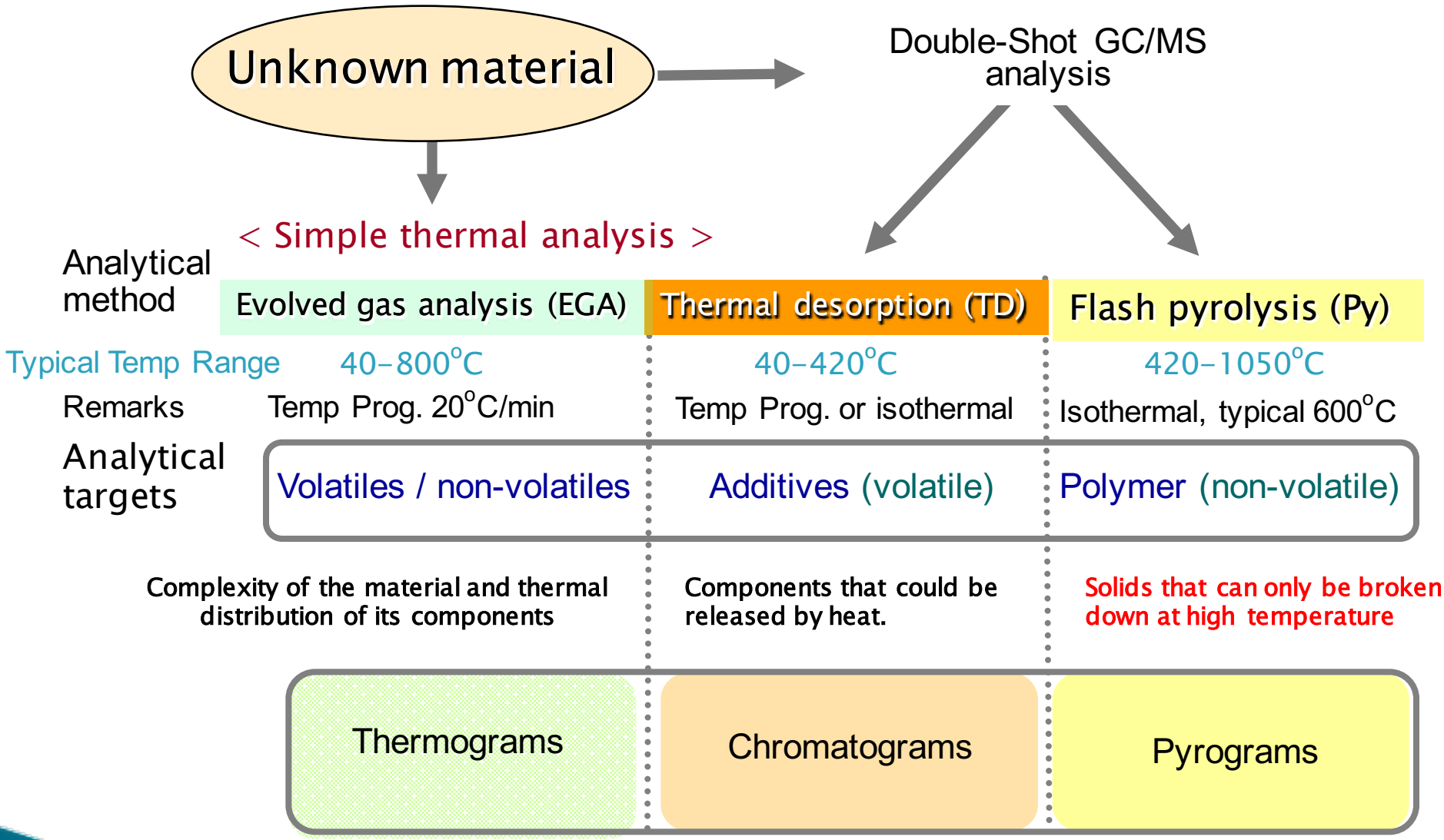
Summary

1. Free fatty acids contained in vulcanized rubber products were determined as methyl derivatives by reactive pyrolysis-GC/MS.

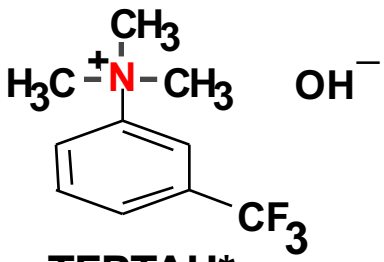
2. The fatty acids content was determined to be 0.6 %, and was in a good agreement with the actual total acid concentration (0.6 %). The reproducibility was 3.2 %RSD (n=5).

As summarized above, we have developed a simple and highly reliable analytical method, which requires no pretreatment, for a quantitative analysis of free fatty acids (stearic acid) in vulcanized rubber products.

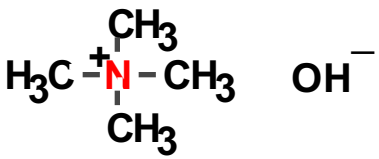
Approach in characterizing unknown materials



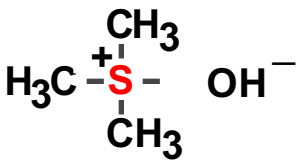
Preparing the Sample for Reactive Pyrolysis (RxPy)



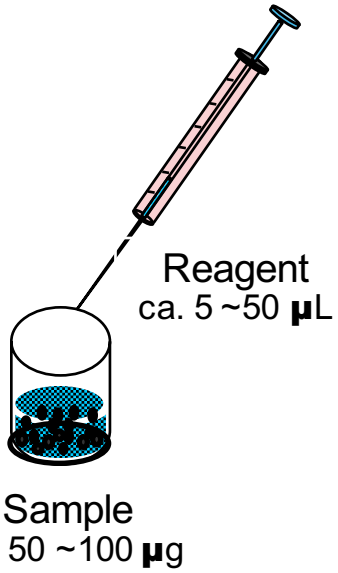
m-TFPTAH*



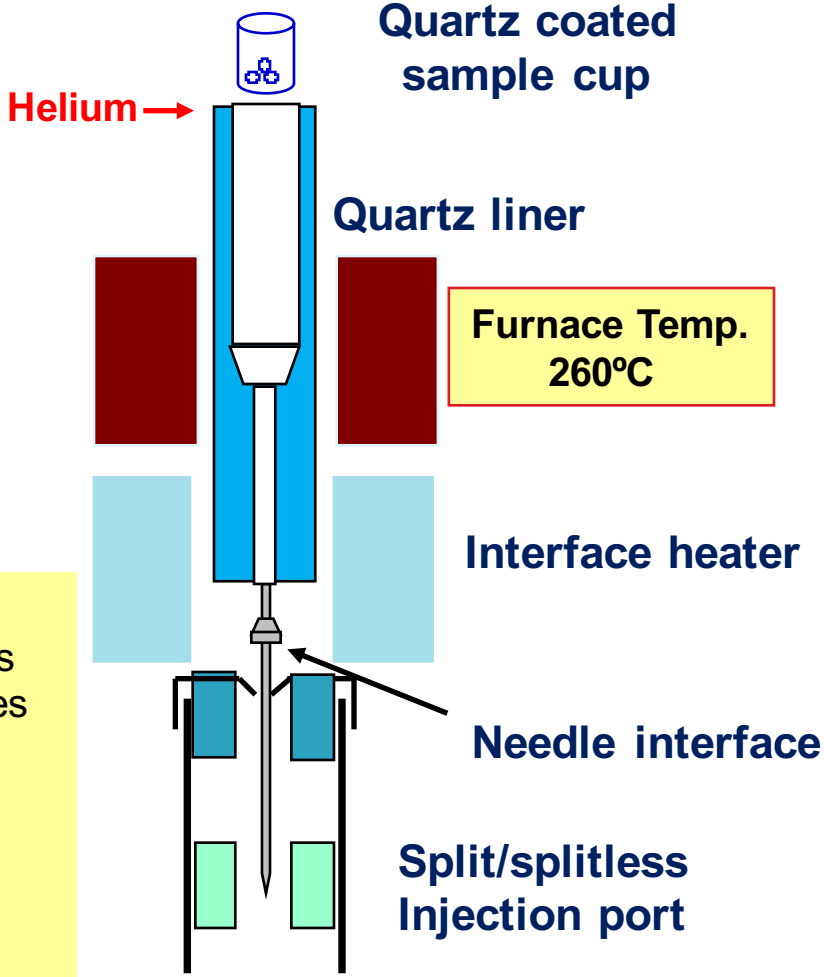
TMAH



TMSH



Once the furnace is "at temperature," the sample free falls into the hot zone. The sample goes from near ambient to the furnace temperature in less than 20msec. The combination of heat and the organic alkali results in the hydrolysis and derivatization.



*m-trifluoromethylphenyltrimethylammonium hydroxide (m-TFPTAH)

Reactive Pyrolysis (RxPy) Technique

--Used for Vapor Phase Methylation of Ester Functional Groups--

Eco-Cup G

o.d. 4mm

8mm

- Thickness : 0.5 mm
- Volume : 50 µL
- Glass surface

Eco-Cup GQ

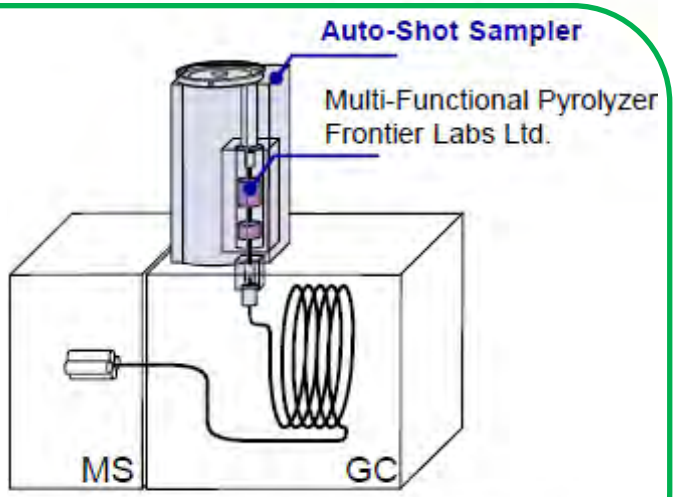
o.d. 4mm

8mm

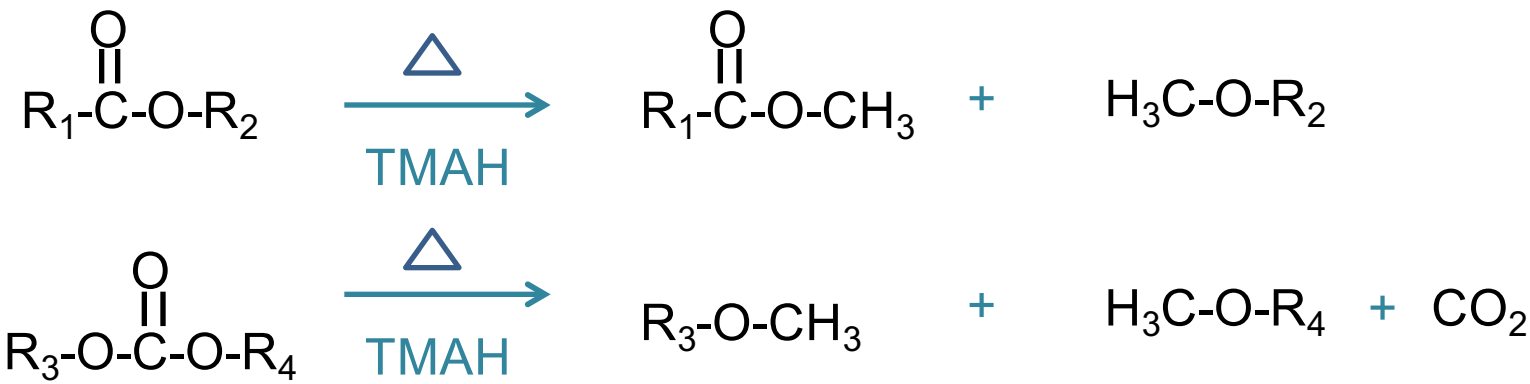
- Thickness : 0.5 mm
- Volume : 50 µL
- Quartz surface

Sample Cup Choices

Eco-Cup SS: 1050°C
-Quartz coated SS
Eco-Cup G: 450°C
-Glass*
Eco-Cup GQ: 600°C
-Quartz coated glass



MS system equipped with Multi-Functional Pyrolyzer and Auto-Shot Sampler



*Glass Eco-Cups are good for RxPy; add AS Teflon to Auto-Shot.

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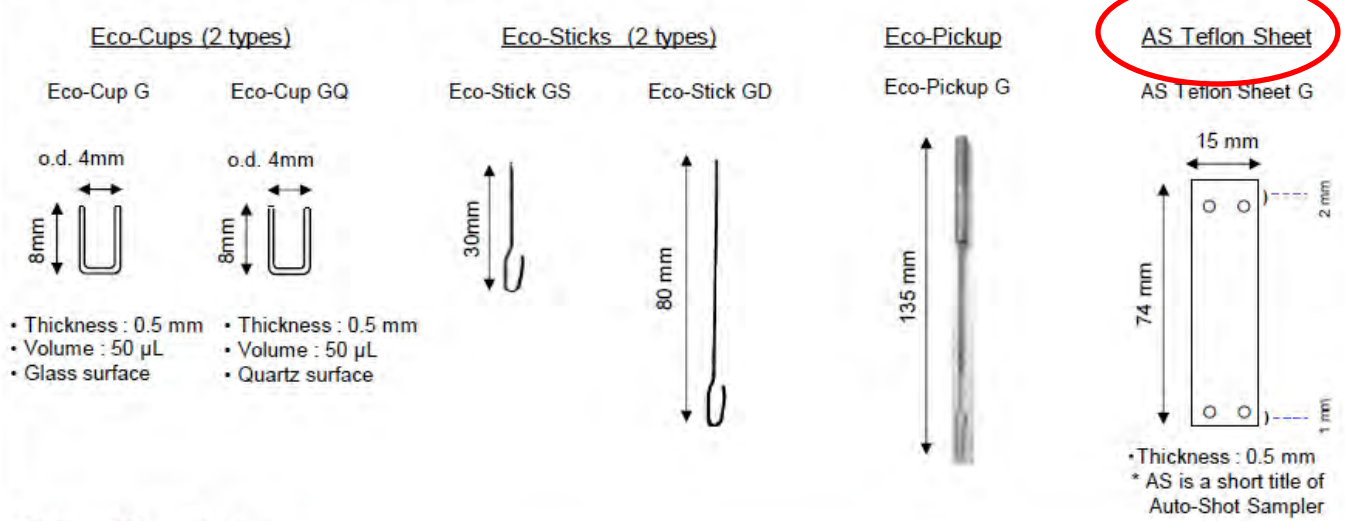
New Eco-Cup G and GQ –Great for RxPy

Eco-Cup G and GQ and related parts



Specifications

Max 450°C

Max 600°C

Product name	Part number	Description
Eco-Cup G	PY1-EC50G	Glass, 50 µL, a package of 100 pcs, for thermal desorption and reactive pyrolysis (max use temp.: 450ºC)
Eco-Cup GQ	PY1-EC50GQ	Glass coated with a bonded quartz layer, 50 µL, a package of 30 pcs, for thermal desorption, reactive pyrolysis and pyrolysis (max use temp.: 600ºC)
Eco-Stick GS *1	PY1-ES10G	Deactivated stainless steel tool to pick up Eco-Cup G or GQ used for single-shot analysis, L= 30 mm, a package of 50 pcs
Eco-Stick GD *1	PY1-ES20G	Deactivated stainless steel tool to pick up Eco-Cup G or GQ used for single-shot analysis, L= 80 mm, a package of 50 pcs
Eco-Pickup G *1	PY1-EP50G	Glass sample cup retrieving tool, 1 pc
AS Teflon Sheet G *2	AS1-7814	Teflon sheet for Auto-Shot (AS) cup chute, 3 pcs, with 4 spare screws

*1 Eco-Cup G and Eco-Cup GQ have smaller inner diameters than stainless steel cups. Use only the Eco-Stick and Eco-Pickup shown above.

*2 When using Eco-Cup G or Eco-Cup GQ with the Auto-Shot Sampler, the Teflon sheet is attached to the cup chute which prevents the glass cups from breaking. The cup chute with the Teflon sheet attached can also be used with stainless steel Eco-Cups.

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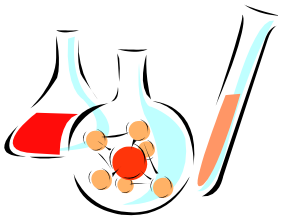
Developing the Analytical Method Using Reactive Pyrolysis (RxPy)



- Selecting the organic alkali
- Concentration of the organic alkali
- Reaction temperature
- Sample state (liquid, solid, particle size)
- Sample homogeneity
- Stability of the pre-reaction mixture
- Choose calibration method (standard addition is most common)

Characterization and Determination of Irganox 1076 and 1010 in Polyethylene using Thermal Desorption and Reactive Pyrolysis – GC/MS

Dave Randle, Itsuko Iwai, Terry Ramus, Aki Hosaka & Ichi Watanabe - Frontier Laboratories Ltd.

GCC
"Serving The World of Chemical Analysis"

Gulf Coast Conference
October 16, 2013

FRONTIER LABORATORIES LTD.

Characterization and Determination of Irganox 1076 and 1010 in Polyethylene using Thermal Desorption and Reactive Pyrolysis – GC/MS

Itsuko Iwai, R.R. Freeman and Dave Randle, Frontier Laboratories
Terry Ramus, Diablo Analytical

Introduction

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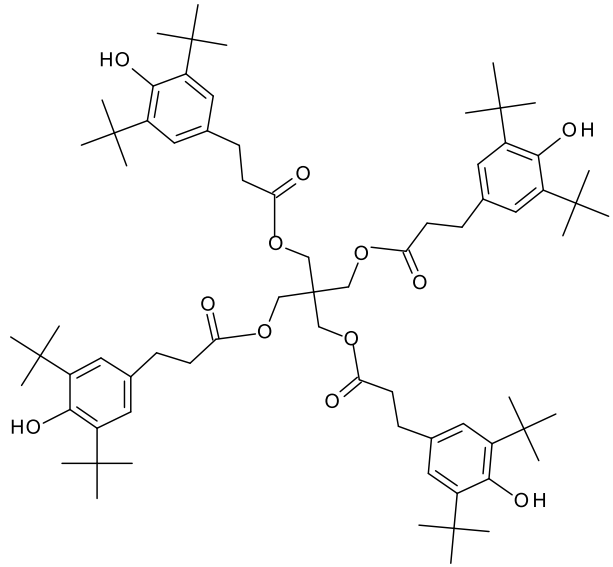
Two of the more commonly used antioxidants, Irganox 1076 and 1010, are phenolic primary antioxidants used to provide long-term thermal stability to the end product. They are widely used in polyolefins such as polyethylene, polypropylene, polybutene and copolymers such as polyurethane. Analysis of 1076 and 1010 is difficult because each is highly resistant to conventional extraction and has a very low vapor pressure. The structural similarities can be seen in figure 1.

This report details a GC/MS-based analytical method for the qualitative and quantitative determination of Irganox 1076 and 1010 in polyethylene.

Irganox 1010



Irganox 1076

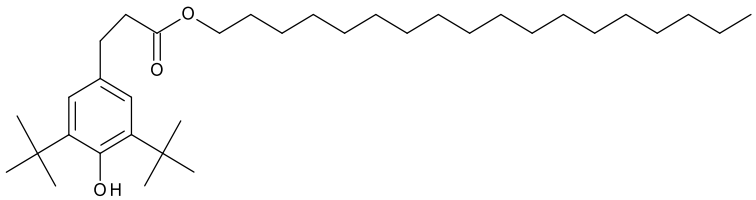


Figure 1. Structures of Irganox 1010 and 1076. Note that both additives have the exact same phenolic group in the ratio of 4:1

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Overview of the thermal desorption and reactive pyrolysis – GC/MS methods

Analytical methods

Thermal Desorption (TD) [1] - Irganox 1076:

Several very small (mesh ≤ 45 µm) particles of the sample are placed in an 80µL sample cup (Eco-cup) and weighed. The cup is then placed in the autosampler (Auto-Shot) carousel interfaced to an EGA/PY-3030D Multi-functional pyrolyzer. The sample is subsequently dropped into the furnace which is at 320°C. The Irganox 1076 thermally desorbs from the polyethylene matrix and is flushed onto the analytical separation column. Thermal desorption is conceptually and operationally very simple. Sufficient heat must be available to vaporize the target compounds. Generally speaking the smaller the sample particle size (high surface area to weight ratio), the better the precision. Small particles are easy to obtain from solid polymer samples by simply filing with a metal file.

Reactive Pyrolysis (RxPy)[2,3] – Irganox 1076 and 1010:

Several very small (mesh ≤ 45 µm) sample particles are placed in an 80µL sample cup (Eco-cup) and weighed; several microliters of an organic alkali (TMAH in methanol) are added to the cup and the solvent is allowed to evaporate. When the sample + reagent are dropped into the furnace which is at 260°C, the ether bond isothermally hydrolyzes and the resulting radicals are methylated.

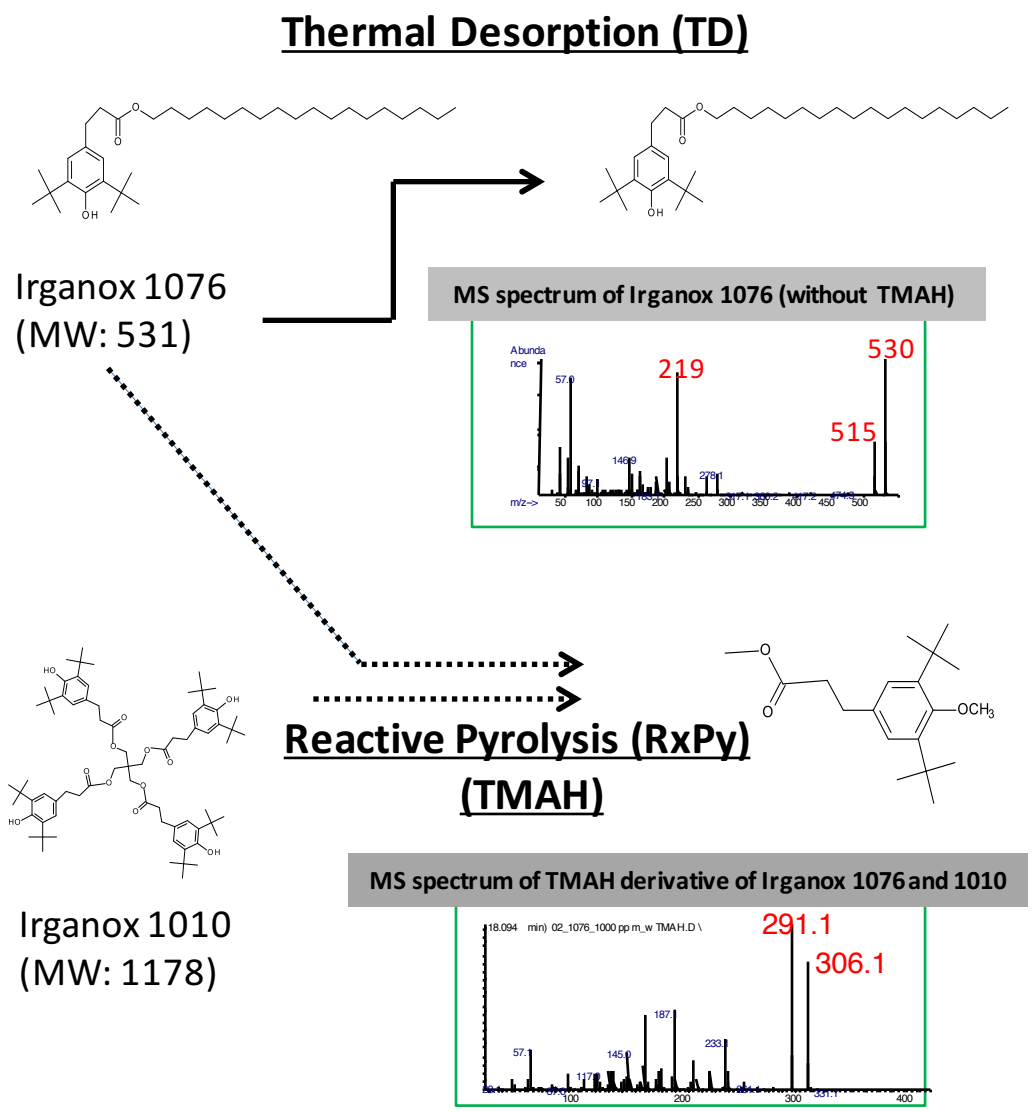


Figure 2. Irganox 1076 can be thermally desorbed from polyethylene at 320°C. The mass spectrum has a base peak of *m/z* 530 – representing the molecular ion. Both 1076 and 1010 have an ether linkage which can be thermally hydrolyzed and methylated using tetramethylammonium hydroxide (TMAH). The derivatized product is the same for both 1010 and 1076; the mass spectra of the derivatized additives are also identical and exhibit large peaks at *m/z* 291 & 306. The stoichiometric ratio of the derivatized product compound for Irganox 1010 is 4:1 compared to Irganox 1076. Reactive pyrolysis alone cannot be used to differentiate Irganox 1076 and 1010.

Reactive pyrolysis (RxPy) optimization

Selecting the furnace temperature

Two series of experiments were run to ascertain the effect of the reaction temperature on the signal-to-noise ratio of *m/z* 306, which is the quant ion chosen from the reaction product spectrum for Irganox 1010 and 1076. Figure 3 clearly shows that the best signal-to-noise is obtained when the RxPy is done at 260°C. Keep in mind that this temperature is dependent on the organic alkali being used and, to a lesser extend, the polymer matrices, and the sample particle size (or surface area to weight ratio).

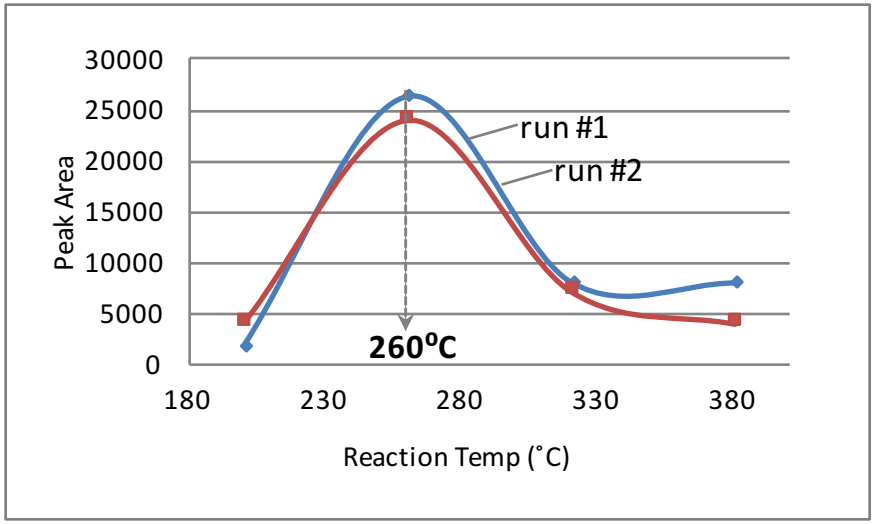


Figure 3. Reaction temperature vs. peak area

Selecting the reagent amount

A set of experiments were performed to determine the effect of increasing the amount of reagent to a fixed amount of Irganox 1010 in polyethylene. The test sample was 100 µg of polyethylene spiked with 1 µg of Irganox 1010. The results are shown in Figure 4. As the amount of TMAH increases, the peak area of the quant ion (*m/z* 306) increases.

These two studies clearly indicate that reactive pyrolysis should be done at 260°C and that a minimum of 20-30 µL of tetramethylammonium hydroxide (TMAH) reagent should be combined with 100 µg of polyethylene sample for optimal results.

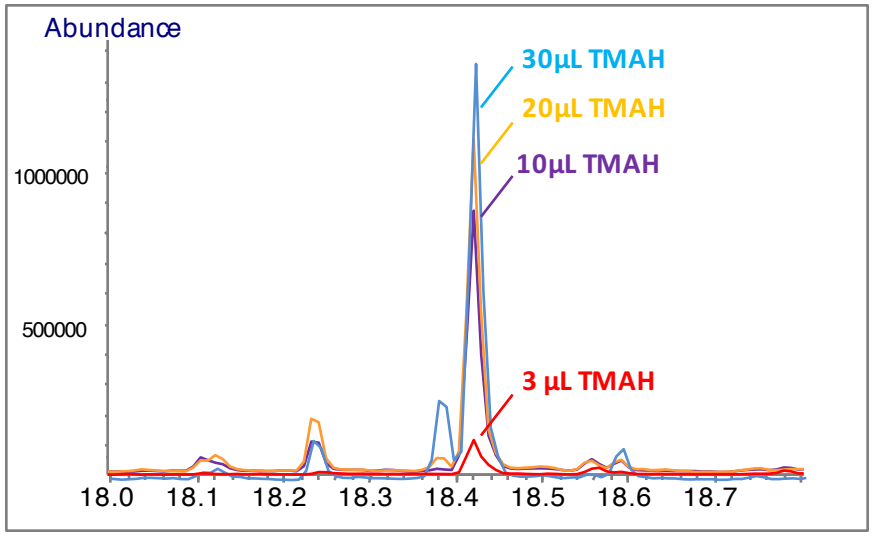


Figure 4. The effect of increasing the amount of organic alkali on peak area. Sample is 100 µg of polyethylene + 1 µg Irganox 1010

Reactive pyrolysis (RxPy): Irganox 1010 in polyethylene

A polyethylene sample was analyzed using reactive pyrolysis (RxPy). A portion of the EIC (*m/z*=306) chromatogram is shown in Figure 5. Included in Figure 5 are the three spike levels used in the standard addition calibration.

Analytical Instruments and Conditions:

- Frontier Lab EGA/PY-3030 Multi-shot Pyrolyzer
- Agilent 7890, 5975 Performance Turbo GC/MS
- Reaction Temp: 260°; Interface = 300°C
- Column: UA-5; 30m X 0,25mm i.d., film = 0.25µm
  Flow 1 mL/min; split ratio – 30:1
  40°C (2min) → 150°C @10°C/min → 320°C (7 min) @20°C/min
- Sample: 100µg polyethylene particles,
  Reagent: TMAH 5% in methanol (12µL)
- SIM or EIC ions *m/z* 291 & 306

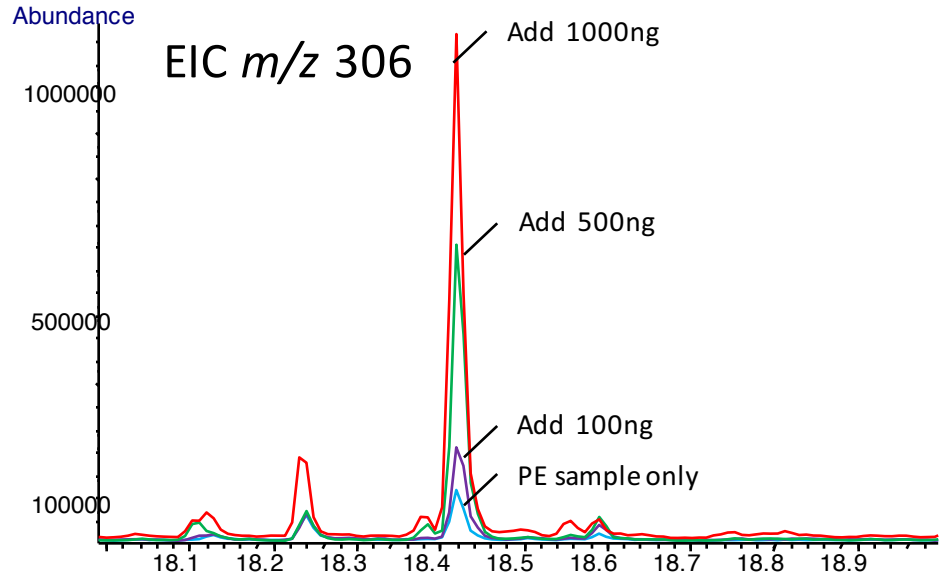
Quantitation of Irganox 1010:

The four point Irganox 1010 calibration is shown in Figure 5. Standard addition is used because it provides the best way to eliminate non-target interference in the sample. The coefficient of determination (R^2)* for Irganox is 0.9995. The analysis of the polyethylene using reactive pyrolysis indicated that the concentration of Irganox 1010 in sample PE #1 is 1053 ppm which compares favorably with the known concentration (1000 ppm) of Irganox 1010.

Analysis (ppm)	Actual (ppm)	% Error
1053	1000	5.3

Table 1. Analysis amount vs. actual amount (ppm) and accuracy (% error) of Irganox 1010 in PE #1 by RxPy.

*R^2 is a statistical measure of how well a regression line approximates real data points; an r-squared (R^2) of 1.0 (100%) indicates a perfect fit.



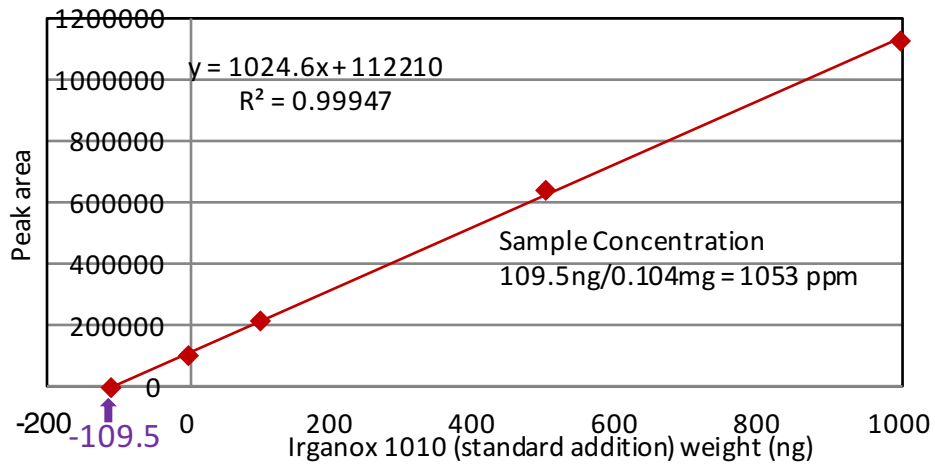


Figure 5. Top trace is the EIC (*m/z*-306) plot of Irganox 1010 after reactive pyrolysis. Bottom trace is the standard addition calibration used for Irganox 1010.

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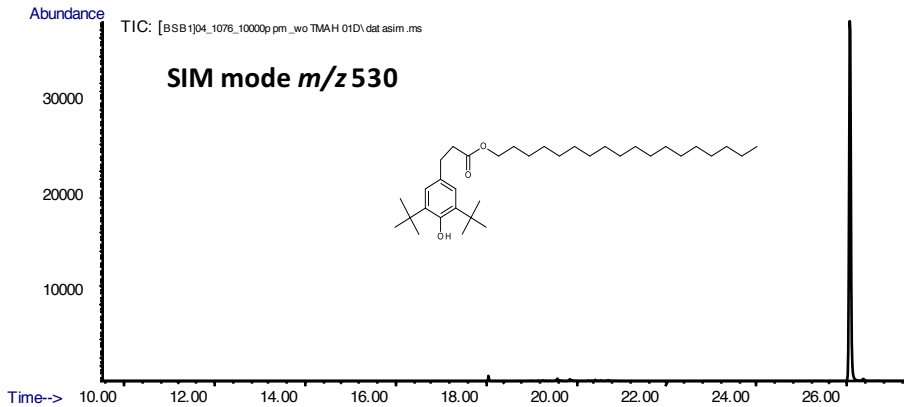
Irganox 1076 - Reactive pyrolysis and thermal desorption

Previously, it was shown that Irganox 1076 could be determined in a polymeric matrix using either thermal desorption or reactive pyrolysis. If thermal desorption is used, the quant ion is *m/z* 530, which is the base peak in the mass spectrum (see Fig. 2, upper spectrum). If reactive pyrolysis is used, the quant ion is *m/z* 306 which is the base peak of the derivatized product following hydrolysis and methylation (see Fig. 2, lower spectrum). Figure 6 shows that the SIM chromatograms in either mode are free of interference from other peaks.

<u>Analytical Conditions for Thermal Desorption (TD):</u>

- Frontier Lab EGA/PY-3030 Multi-shot Pyrolyzer
- Bench top Single Quadrupole GCMS
- Desorption Temp: 320°; Interface = 300°C
- Column: UA-5; 30m X 0,25mm i.d., film = 0.25µm
  Flow 1 mL/min; split ratio – 30:1
- Oven Temp. Program:
  40°C (2min) → 150°C at 10°C/min
  150°C → 320°C (7 min) at 20°C/min
- Sample: 100µg polyethylene particles
- SIM ion = *m/z* 530 and 219.

Thermal desorption (TD)



Reactive pyrolysis (RxPy)

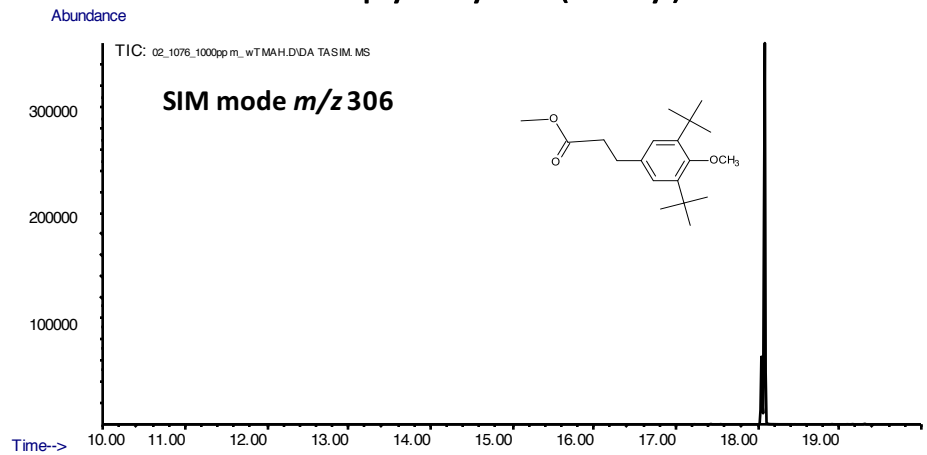


Figure 6. Top SIM chromatogram is the plot of *m/z* 530 when Irganox 1076 is thermally desorbed (furnace temp: 320°C). The bottom SIM trace (*m/z* 306) is obtained when Irganox 1076 is analyzed using reactive pyrolysis (using TMAH @ 260 ^{o}C).

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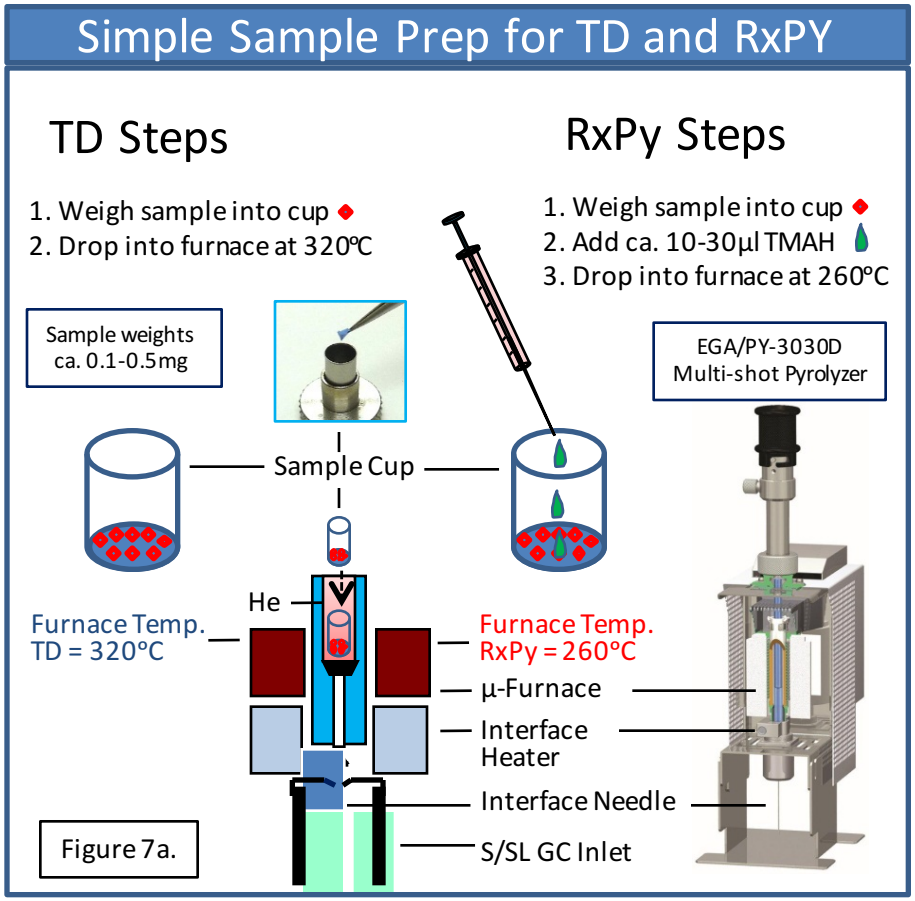
Analysis of Irganox 1076 in polyethylene using thermal desorption and reactive pyrolysis

A polyethylene sample was analyzed using thermal desorption (TD) and reactive pyrolysis (RxPy). The SIM mode chromatograms are shown in Figure 7b. The sample was also analyzed in duplicate (n=2) using reactive pyrolysis. (RxPy). Sample prep steps are shown in Fig. 7a.



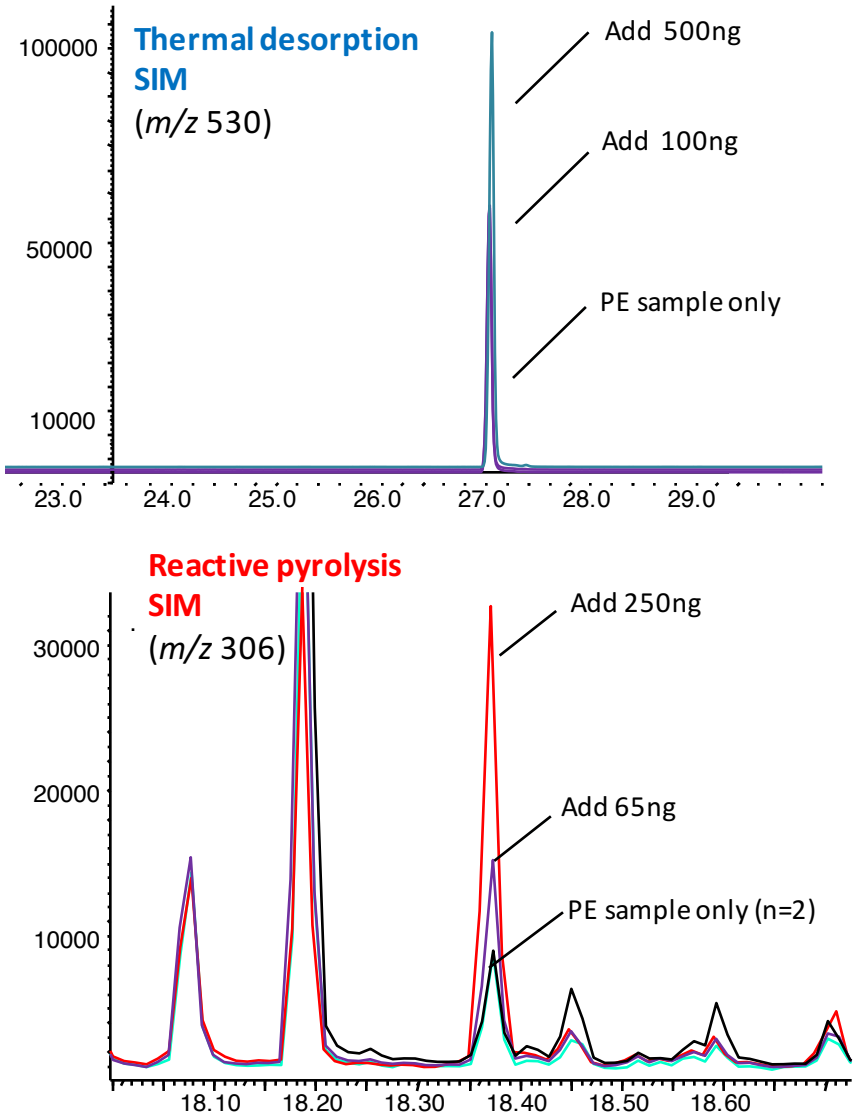


Figure 7b. Top chromatogram is the SIM trace (*m/z* 530) of Irganox 1076 in polyethylene at different spike levels. Bottom trace is SIM trace (*m/z* 306) analysis of Irganox 1076 in PE after reactive pyrolysis at different spike levels.

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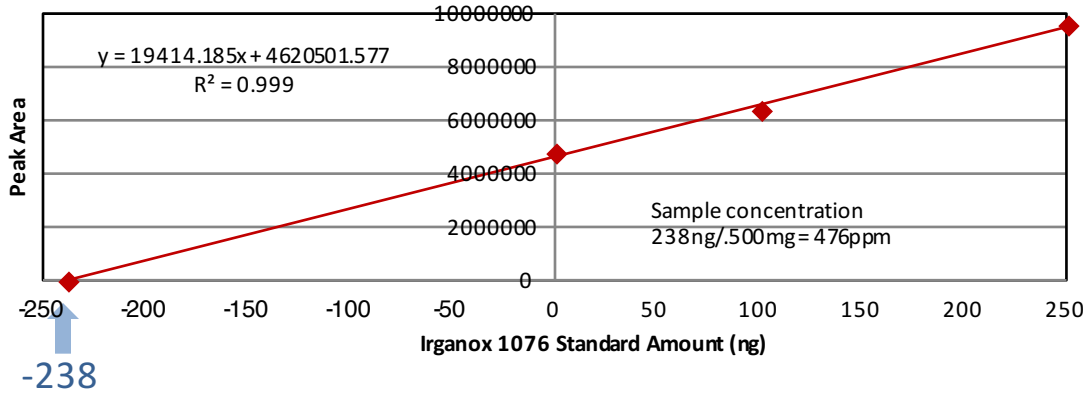
Thermal Desorption of Irganox 1076 in polyethylene

Figure 9 shows overlays from 4 runs of the full scan (29 – 600 amu) total ion chromatogram (TIC) of a polyethylene sample containing a number of additives. The peak around 26.4 minutes is Irganox 1076. The sample was analyzed four times; see inset for the amounts of Irganox spiked in the sample prior to analysis. The concentration of 1076 in the PE unknown sample was determined using the standard addition calibration and found to be 476 ppm.



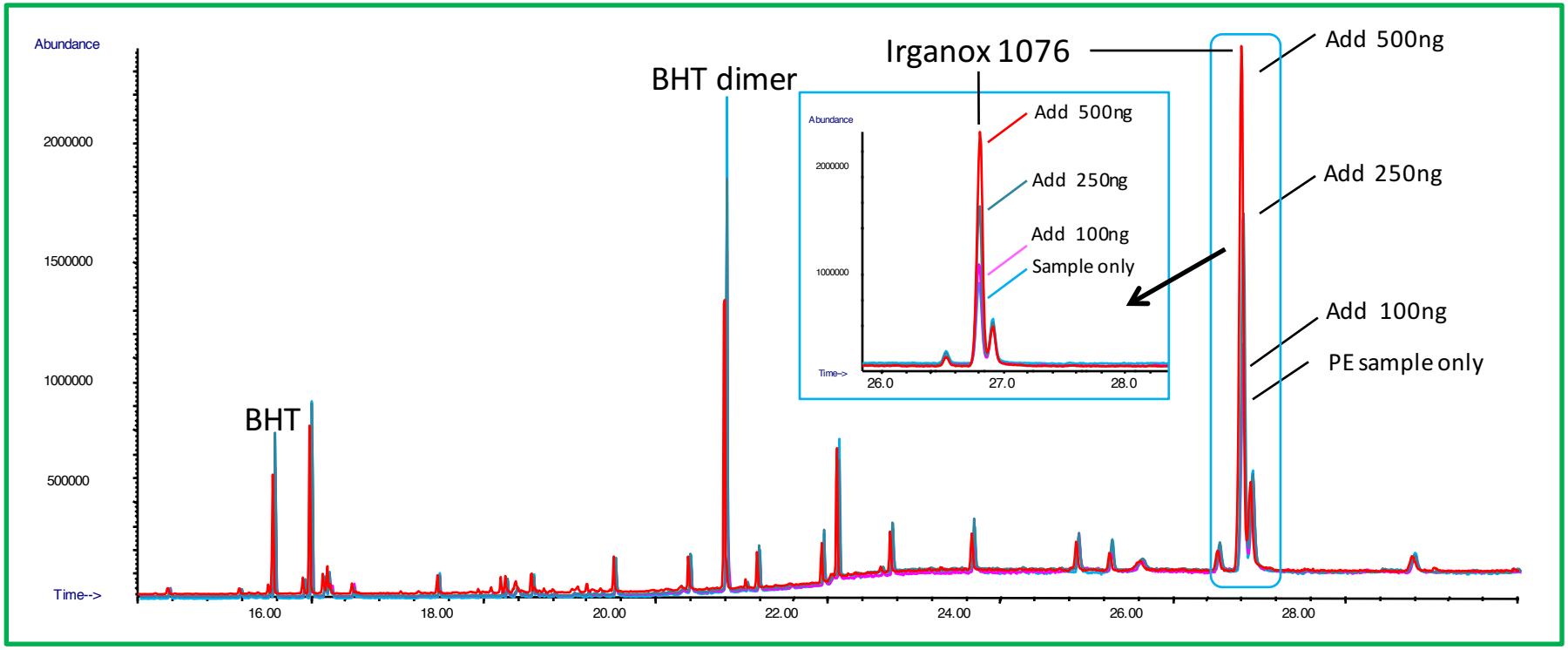


Figure 9. Total ion chromatogram (TIC) of polyethylene (PE). Thermal desorption temperature is 320°C. Standard addition calibration of Irganox 1076 in PE is shown at top of page

Precision and accuracy for Irganox 1010 & 1076 in PE

It is a relatively simple process to identify and quantitate both Irganox 1010 and 1076 in polyethylene. Analysis of the sample using reactive pyrolysis (RxPy) yields the total ppm of the two additives. A second analysis of the sample using thermal desorption quantitates the Irganox 1076.

Simply subtracting the two numbers is all that is necessary to find the amount of Irganox 1010:

1010 &1076 (RxPy) total – 1076 (TD) = 1010 amount.

Example shown in Table 5 for the PE Unknown Sample where the calculated amount of 1010 is 1406 ppm.

Compound	Technique	RSD (%)
Irganox 1010 (in PE #2)	Reactive pyrolysis (RxPy) (260°C)	7.9 (n=5)
Irganox 1076 (in PE #3)	Thermal desorption (TD) (320°C)	3.6 (n=5)

Table 4. Reproducibility (RSD%) of the RxPy technique for 1010 and the TD technique for 1076 for five runs (n=5).

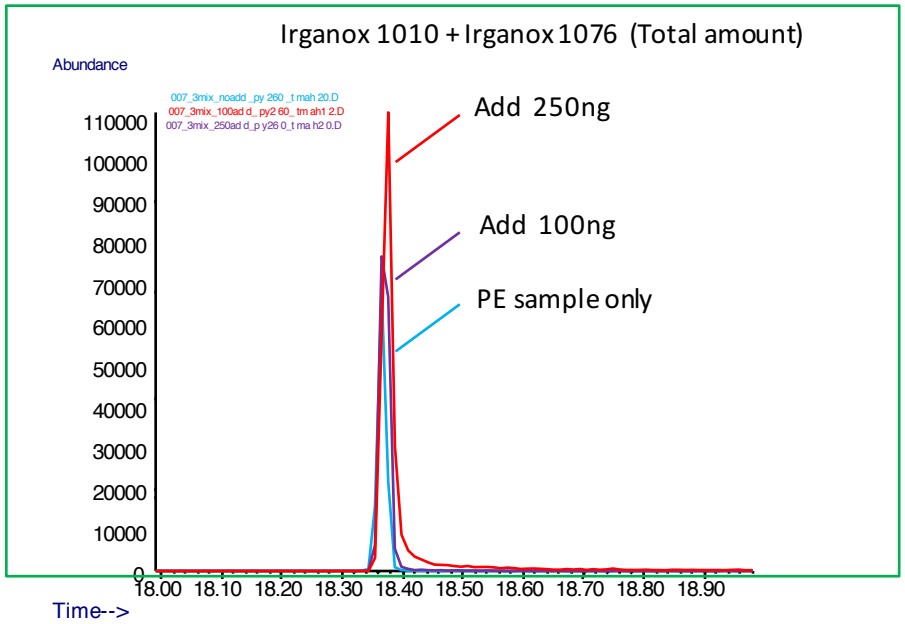


Figure 10. SIM (*m/z*=306) chromatogram of polyethylene sample containing both Irganox 1076 and 1010 using reactive pyrolysis (RxPy).

PE Sample #	Irganox 1010			Irganox 1076				
	Actual Amt. (ppm)	Calculated Amt. (ppm) by RxPy	% Error	Actual Amt. (ppm)	Calculated Amt. (ppm) by TD	Calculated Amt. (ppm) by RxPy	Ave. Amt. (ppm)	% Error
PE #1	1000	1053	5.3%	-	-	-	-	-
PE #2	470	429	8.7%	-	-	-	-	-
PE #3	-	-	-	340	374	393	384	12.9%
PE unknown	-	1406		-	476	-	-	-

Table 5. Results summary of the analysis of four polyethylene (PE) samples for Irganox 1010 and 1076. For samples with a known amount of additives the accuracy of the quantitative technique is indicated by the % error comparing the actual amount vs. calculated amount.

Summary

Complex samples can rarely be fully characterized using a single analytical technique; consequently, the analyst must analyze the simple a number of times using different analytical tools. This work clearly illustrates the value of having a chromatographic system that can be configured to perform multiple analytical techniques. The EGA/PY-3030 Multi-shot Pyrolyzer from Frontier Laboratories can be used to characterize a sample using evolved gas analysis, pyrolysis, multi-zone thermal desorption, and reactive pyrolysis. Both liquid and solid samples can be analyzed directly; conventional sample prep regimes are unnecessary.

The analysis of Irganox 1076 and 1010 is difficult because of their low volatility. It is not unusual for a laboratory to use HPLC or LC/MS for these two additives. Using a Frontier EGA/PY-3030D interfaced to a GC/MS will immediately increase laboratory productivity.

- **A single EGA/PY-3030D & GC/MS can be used to qualitatively and quantitatively determine the additives of interest, in a variety of polymeric materials. This simplifies the operation of the laboratory and gives the quantitative data internal consistency.**
- **The entire process can be automated.**
- **Both liquid and solid samples can be analyzed directly, thus eliminating the need for complicated, time consuming sample preparation.**
- **Data quality (precision and accuracy) compares favorability with that obtained using other analytical techniques.**

Additional materials by TD

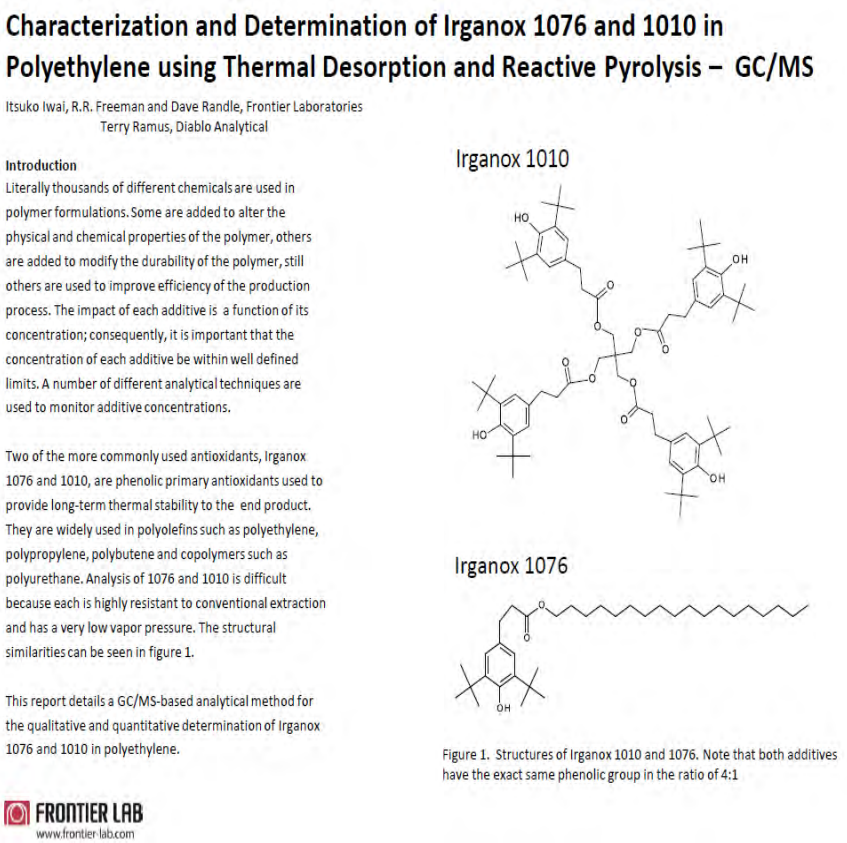
- Brominated flame retardants
- Residual BPA in polycarbonate
- Phthalates in consumer products
- ASTM D-7823
- Antidegradants in rubber

References:

1. *Rapid and Simple Determination of phthalates in plastic toys by a thermal desorption-GC/MS method*, T. Yuzawa, C. Watanabe, R. Freeman and S. Tsuge, Anal.Sci., Vol. 25, pages 1-2.
2. *Review: the development and applications of thermally assisted hydrolysis and methylation reactions*, J.M. Challinor, J. Anal. and Appl Pyrolysis, 61(2001), 3-34.
3. *Characterization of Condensation Polymers by pyrolysis-GC in the presence of organic alkali*, H. Ohtani and S. Tsuge, Applied Pyrolysis Handbook, Second Edition, pages 249-269.

Technical Brief

- This 10 page technical brief is available.
- Ask Dave for a copy
- roger@frontier-lab.com
- www.frontier-lab.com
  - There are about 150 Technical Notes available on our website.



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Irganox 1010

Irganox 1076

Figure 1. Structures of Irganox 1010 and 1076. Note that both additives have the exact same phenolic group in the ratio of 4:1

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TB also available: Phthalates using ASTM D7823; Additives in Polyethylene

Free Technical Brief

Additional RxPy References

Reactive Pyrolysis

literature title	author	*journal*	issue	page	year
Effects of Solvents and Inorganic Salts on the Reactive Pyrolysis of Aromatic Polyester in the Presence of Tetramethylammonium Hydroxide Studied by Pyrolysis-Gas Chromatography/Mass Spectrometry	Y.Ishida, H.Ohtani, S.Tsuge	*J. Anal. Appl. Pyrolysis*	33	167-180	1995
Sequence Distributions of Polyacetals Studied by Reactive Pyrolysis-Gas Chromatography in the Presence of Cobalt Sulfate	Y.Ishida, H.Ohtani, K.Abe, S.Tsuge, K.Yamamoto, K.Katoh	*Macromolecules*	28	6528-6532	1995
Compositional Analysis of Cationic Polyacrylamide Resins by Reactive Pyrolysis-Gas Chromatography in the Presence of Organic Alkali	Y.Ishida, S.Tsuge, H.Ohtani, F.Inokuchi, Y.Fujii, S.Suetomo	*Anal. Sci.*	12	831-840	1996
Characterization of Copolymer Type Polycarbonates by Reactive Pyrolysis-Gas Chromatography in the Presence of Organic Alkali	Y.Ishida, S.Kawaguchi, Y.Ito, S.Tsuge, H.Ohtani	*J. Anal. Appl. Pyrolysis.*	40.41	321-329	1997
Mechanisms of Thermal Degradation of a Polyester frame-retarded with Antimony Oxide/Brominated Polycarbonate Studied by Temperature-programmed Analytical Pyrolysis	H.Sato, K.Kondo, S.Tsuge, H.Ohtani, N.Sato	*Polym. Degradation and Stabilitiy*	62	41-48	1998
Quantitative and Discriminative Analysis of Carnauba Waxes by Reactive Pyrolysis-GC in the Presence of Organic Alkali Using a Vertical Microfurnace Pyrolyer	L. Wang, S. Ando, Y. Ishida, H. Ohtani, S. Tsuge, T. Nakayama	*J. Anal. Appl. Pyrolysis*	58-59	525-537	2001
Thermally Assisted Hydrolysis and Methylation Gas Chromatography of Poly(Aryl Ether Sulfone)s in the presence of tetramethylammonium hydroxide	H. Ohtani, Y. Ishida, M. Ushiba, S. Tsuge	*J. Anal. Appl. Pyrolysis*	61	35-44	2001

Utility of a system consisting of EGA/PY-3030D and QP-2010 GC/MS

- Analysis of cosmetic eyeliner

Akihiko Hosaka, Koichi Ito, Ichi Watanabe, Chuichi Watanabe

ABSTRACT

The analysis of eyeliner is used to demonstrate the capabilities of a system consisting of an EGA/PY-3030D pyrolyzer and a QP-2010 GCMS. The eyeliner was first analyzed using evolved gas analysis (EGA-MS). The EGA thermogram shows that the eyeliner contains compounds with a wide range of properties - from volatile organic solvents to nonvolatile polymers. The compositional analysis of each temperature zone on the EGA thermogram was determined using a high-resolution capillary column interfaced to the GC/MS.

Instrument Configuration

The analytical system consisted of a micro-furnace based Multi-Shot pyrolyzer (EGA/PY-3030D, Frontier Laboratories Ltd.) The pyrolyzer is directly interfaced to the split/splitless injector of the GC. When doing an EGA analysis, the injector is directly connected to the MS through a deactivated EGA tube (no stationary liquid phase, L=2.5 m, id=0.15 mm). The GC oven temperature is isothermal at 250°C, and gases evolved from the sample (as it is heated from 40°C to 600°C (or up to 1050°C) at 20°C/min) were immediately introduced into the MS without separation. Therefore, the evolved gases can be monitored in real time.

If the EGA tube is connected to the MS using a Vent-Free GC/MS adaptor[11)] (Frontier Laboratories Ltd.), switching from an EGA tube to a separation column takes just a few minutes. This is done without venting the MS.

Heart-cut EGA-GC/MS analysis uses the Selective Sampler (SS-1010E, Frontier Laboratories Ltd.) to either selectively "vent" compounds that are not of interest or introduce gases of interest to a separation column. During the heart-cutting, the sample vapors must be "held" at the head of the column. This can often be accomplished by using a low Initial temperature. If the evolving vapors can not be held using column temperature, a MicroJet Cryo-Trap (MJT-1035Ex) can be used to cryo-trap low boiling gases at the head of the separation column. The trapped gases are later thermally desorbed prior to GC/MS analysis.

EGA/PY-3030D

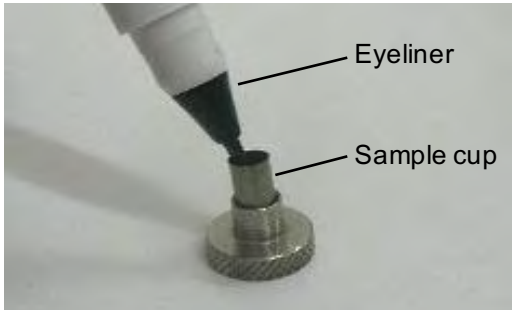
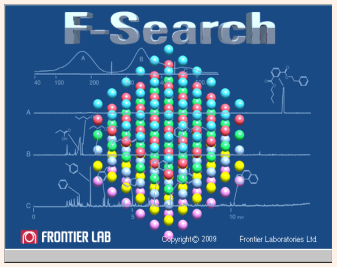
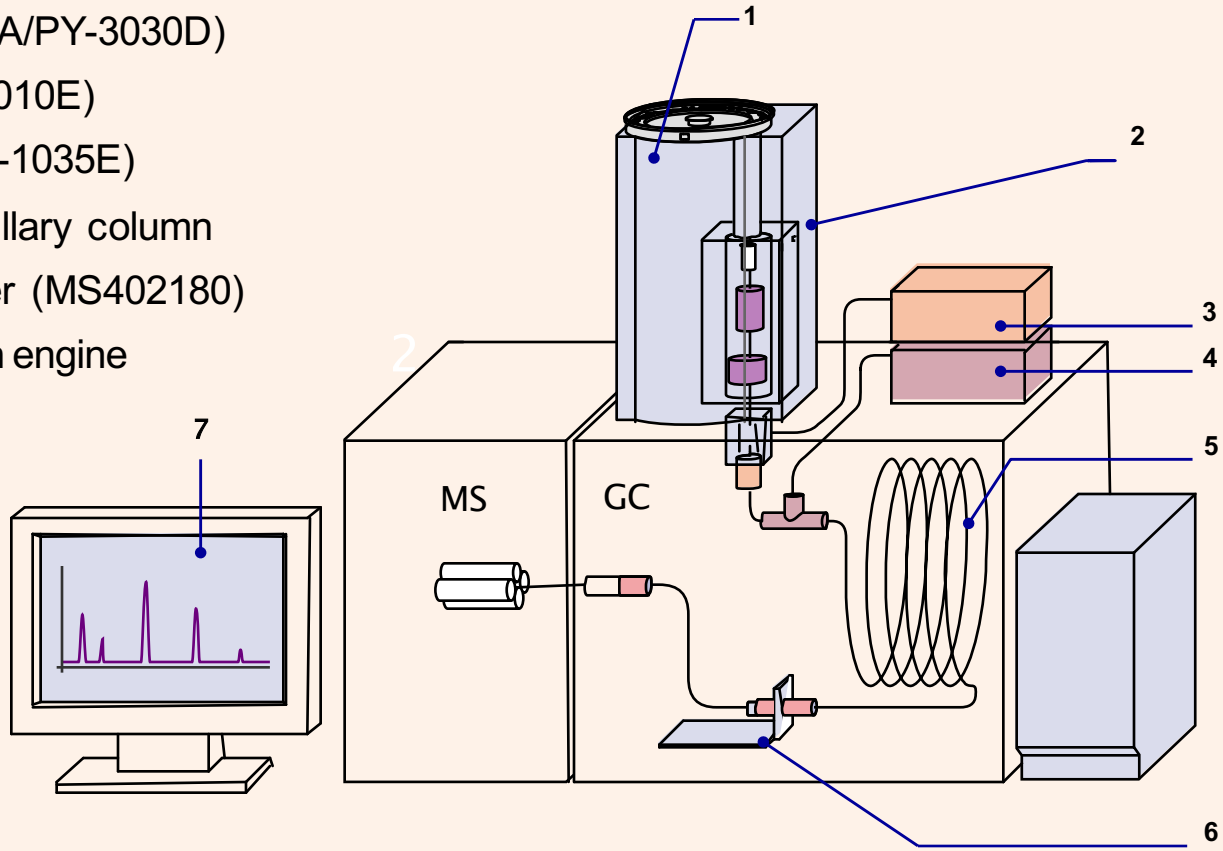


Figure.1: Collecting eyeliner sample in an Eco cup.

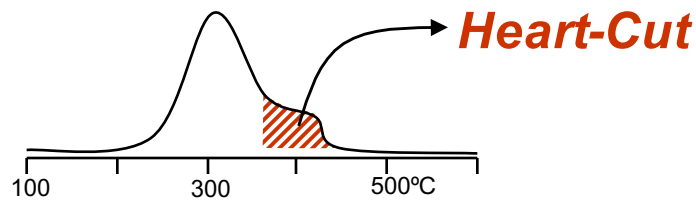
1. Auto-Shot Sampler (AS-1020E)
2. Multi-Shot Pyrolyzer (EGA/PY-3030D)
3. Selective Sampler (SS-1010E)
4. MicroJet Cryo-Trap (MJT-1035E)
5. Ultra ALLOY® metal capillary column
6. Vent-Free GC/MS adapter (MS402180)
7. F-Search system (search engine and MS libraries)



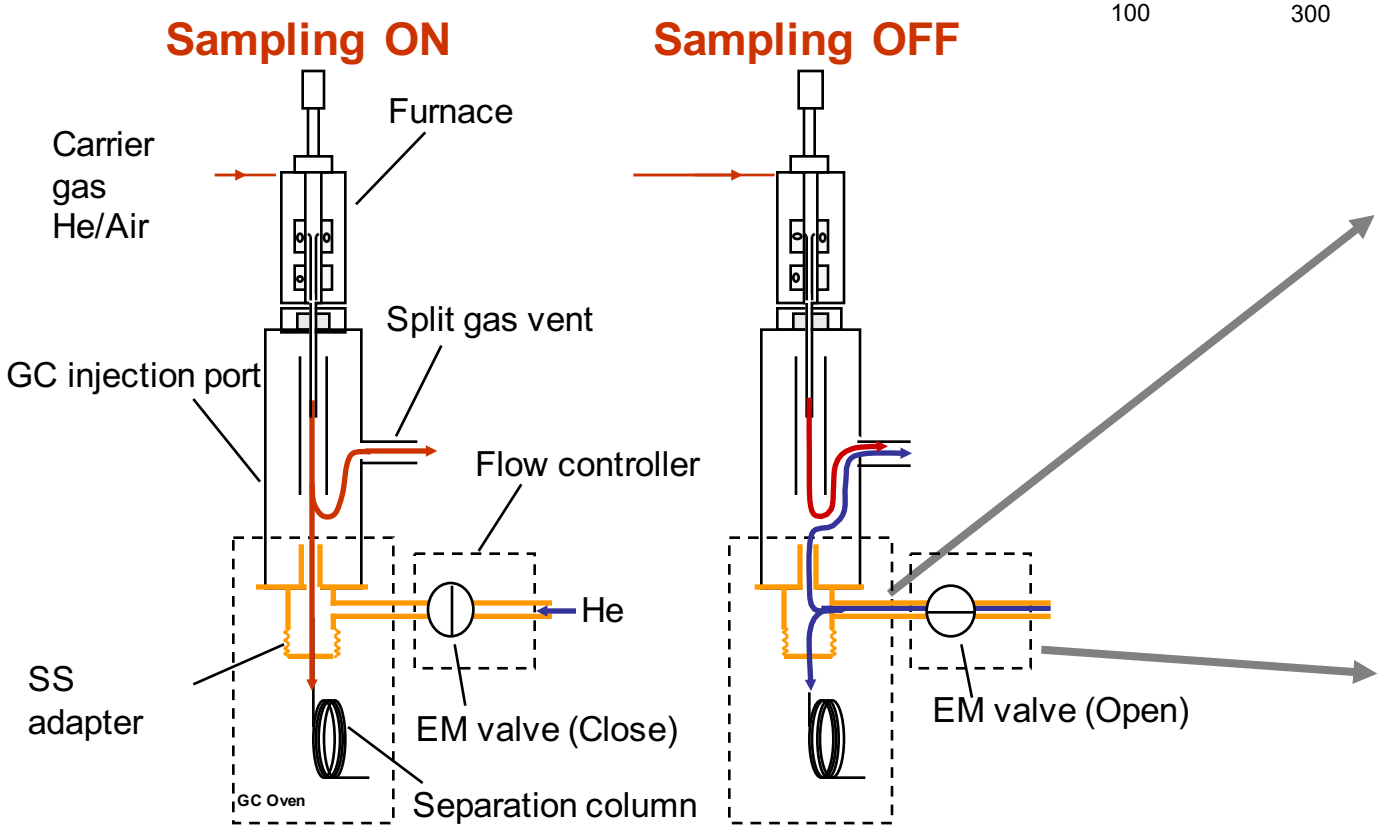


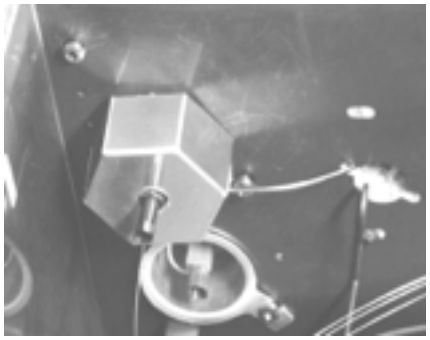
Accessories : Selective Sampler (SS-1010E)

SS-1010E achieves flow switching. With this function, any set of peaks in the Evolved Gas Analysis curve from Double-Shot Pyrolyzer or Thermogravimetry (TG) can be Heart-Cut. The technique also eliminates flow path contaminations with polar species, and tars on the metal surfaces which are the problems with conventional rotary valve systems.



Flow Switching





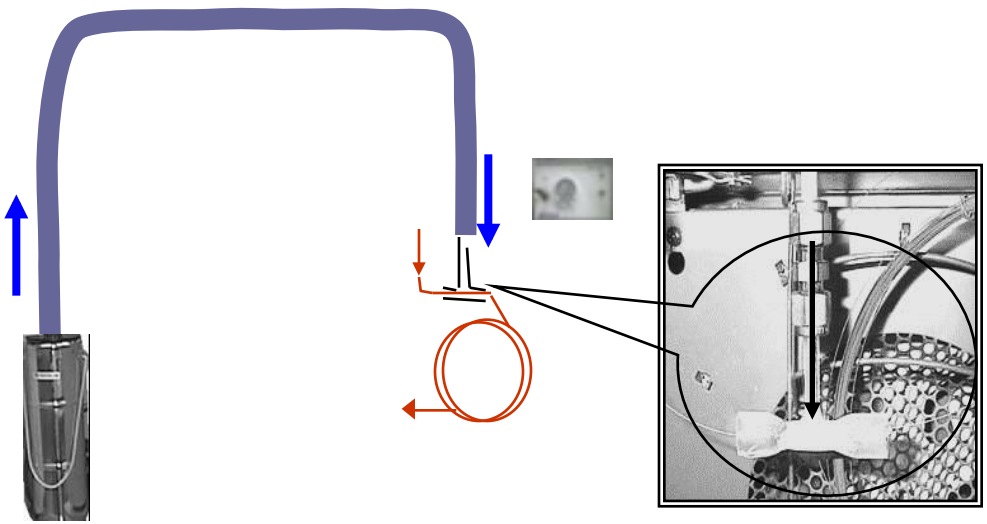
Install the adapter at the outlet of the GC injection port

Flow controller

(* Japan patent No.3290893)

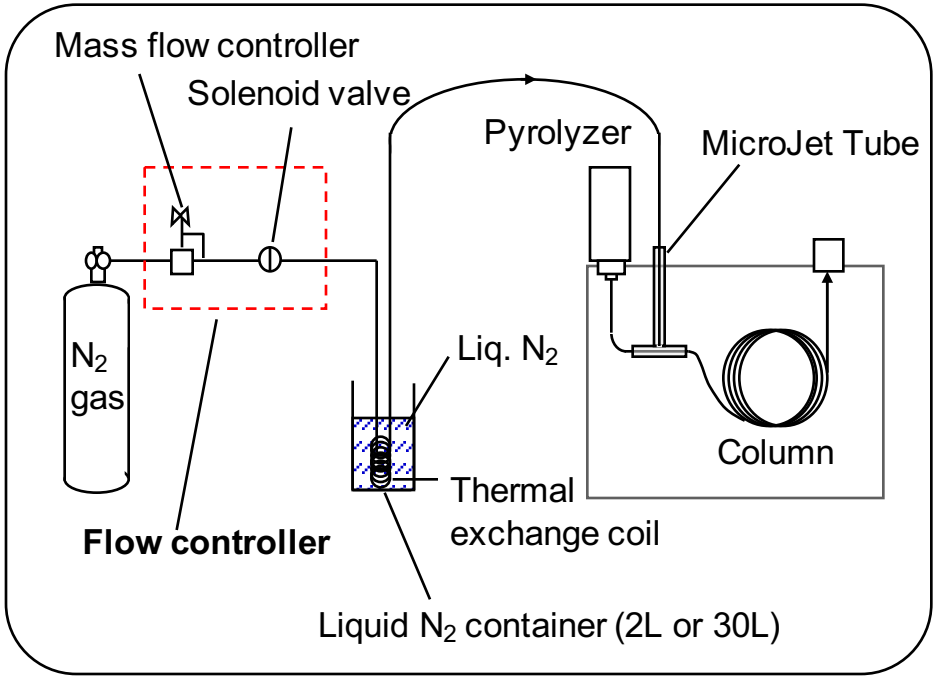
Accessories : MicroJet cryo-trap (MJT-1035E)

To analyze the volatile compounds from the heated sample over minutes using Double-Shot Pyrolyzer, trapping them at the front of the separation column and rapid desorption is required to achieve good separation. MJT-1035E achieve this tasks with low cost, easy operation and high efficiency by employing an innovative technique not found in the past.



Inner view of the GC Oven equipped MicroJet Cryo-Trap

Flow Diagram



(* Japan patent No.3290968, US patent No. 6190613B1)

Analytical Conditions
EGA–MS and Heart–cut EGA–GC/MS

	EGA-MS	Heart-cut EGA-GC/MS
Instruments		
Pyrolyzer	: Multi-Shot Pyrolyzer 3030D (Frontier-Lab)	Multi-Shot Pyrolyzer 3030D (Frontier-Lab)
GC/MS	: 7890 GC; 5975 MS (Agilent Technologies)	7890 GC; 5975 MS (Agilent Technologies)
Tube/Column	: EGA Tube 2.5 m x 0.15 mm I.D. (Frontier-Lab)	Ultra ALLOY-5 (MS/HT) (L: 30 m, ID: 0.25 mm, df: 0.25 µm Frontier-Lab)
Analytical Conditions		
Pyrolyzer		
Furnace Temp.	: 40ºC (0 min) - (20ºC/min) - 600ºC	40ºC (0 min) - (20ºC/min) - 600ºC (0 min)
Py-GC ITF Temp.	: Max 320ºC (Auto Mode)	Max 320ºC (Auto Mode)
GC		
Injection Temp.	: 300ºC	300ºC
Column Temp.	: 250ºC (isothermal)	40ºC (0 min) - (20ºC/min) - 320ºC (0 min)
Injection Mode	: Split	Split
Carrier Gas	: He (1ml/min)	He (1ml/min)
Split Ratio	: 1/50	1/50
Sample amount	: ca. 0.5 mg	ca. 0.5 mg
MS		
Ion Source Temp.	250ºC	250ºC
Interface Temp.	: 280ºC	280ºC
Scan Range	: m/z 29 - 600	m/z 29 - 600
Event Time	: 5 sec	0.3 sec
Scan Speed	: 116 amu/sec	2,000 amu/sec

Results of EGA Thermogram

Results obtained by EGA-MS

The EGA-MS thermogram of the eyeliner is shown in Figure.3a. Zones A through C contain solvents and additives, while zones D and E contain polymers. These results show that the eyeliner contains a wide variety of compounds ranging from low boiling to high boiling compounds.

Identification of volatiles by GCMSsolution

In EGA-MS, a normal separation capillary column is not used; therefore, a peak often represents multiple compounds This is clearly shown in the two-dimensional multi-ion chromatogram using the two dimensional display feature of F-Search (Figure.3b). For example, peaks observed in zone A seem to be essentially the same in peak shape and apex temperature. In this case, as illustrated in Figure.4, the main component in zone A is identified as 1,3-butanediol by the NIST library search from F-Search.

On the other hand, in zone B, multiple volatile compounds are easily observed. In a case like this, identification cannot be done using the EGA alone, Each zone must be analyzed independently using heart-cut EGA-GC/MS.

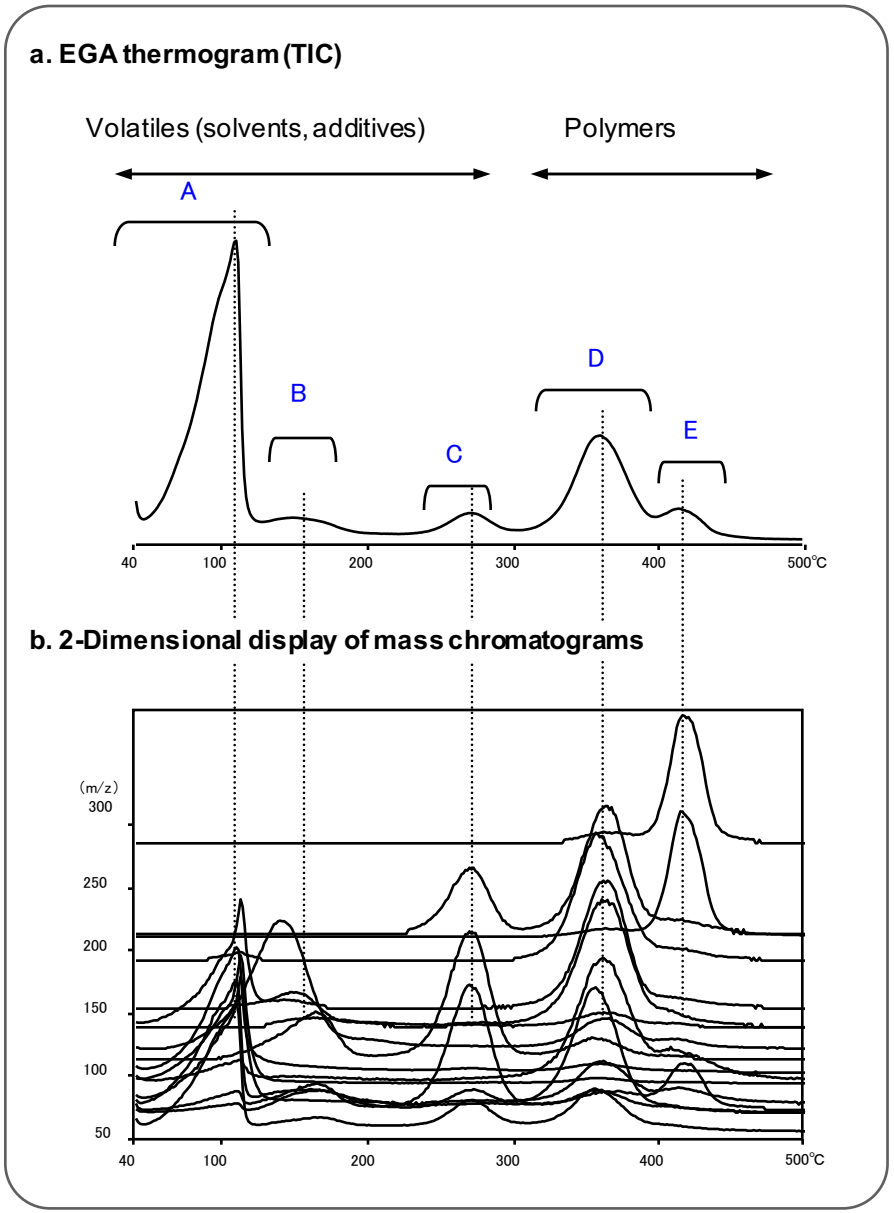


Figure.3: EGA thermogram of eyeliner and analysis using mass chromatograms

HC-EGA is "Thermal Slicing"

Results of Heart-cut EGA-GC/MS

The heart-cut GC/MS results of the zones A through E observed on the EGA thermogram (Figure.3) are shown in Figure 5. Zone A contains 1,3-butanediol as well as a number of other volatiles, while in zones B and C, relatively high boiling compounds derived from additives are observed. On the other hand, methyl methacrylate (MMA) as a pyrolyzate of the polymer observed in zone D. This is the monomer of poly-methylmethacrylate (PMMA), which is a polymer commonly used for paints, and is formed by the pyrolysis of PMMA. In zone E, a series of cyclic dimethylsiloxanes derived from pyrolysis of poly-dimethylsiloxane are observed.

As described above, detailed analysis can be accomplished by sequentially heart-cutting each of temperature zones in the EGA thermogram (Figure.3) and introducing them into a separation column for GC/MS analysis.

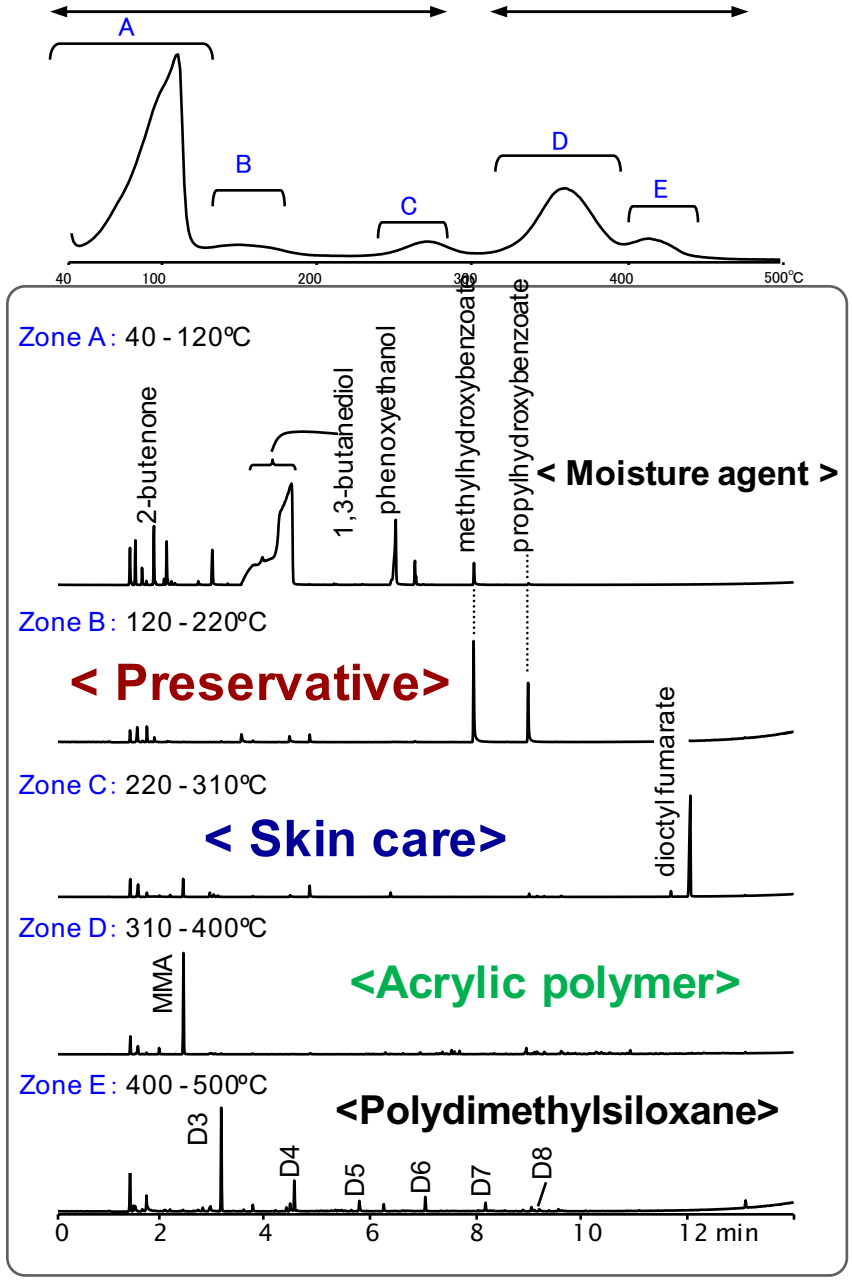


Figure.5: Heart-cut EGA-GC/MS analysis of zones A to E of EGA thermogram of an eyeliner.

EGA and EGA Heart-cutting are powerful tools for materials characterization

Samples of cosmetic eyeliner were analyzed using a EGA/PY-3030D pyrolyzer interfaced to a GC/MS. EGA-MS and heart-cut EGA-GC/MS methods, used in this study, provided a nearly complete characterization of the demonstration sample. The study indicates that the multi-shot pyrolyzer EGA/PY-3030D can be used to characterize a wide variety of complex materials ranging from volatile organics to polymers. These techniques can be applied to many application needs in the cosmetics, paints, coatings, dyes, pigments and museum conservatory market sectors.

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Review of Pyrolysis Techniques

- Pyrolysis — PY or Py
- Evolved Gas Analysis — EGA
- Heart-Cutting — HC
  - MicroJet Cryo-trap
  - Selective Sampler
- Reactive Pyrolysis — RxPy
- Thermal Desorption — TD
- Combined — TD/PY
  - Double-shot is TD followed by PY
  - Heart-cutting based on EGA thermograms: HC-EGA

Biomass pyrolysis papers

Dr. Robert C. Brown,
Office of Biorenewables Programs

Iowa State University

Authors/Title
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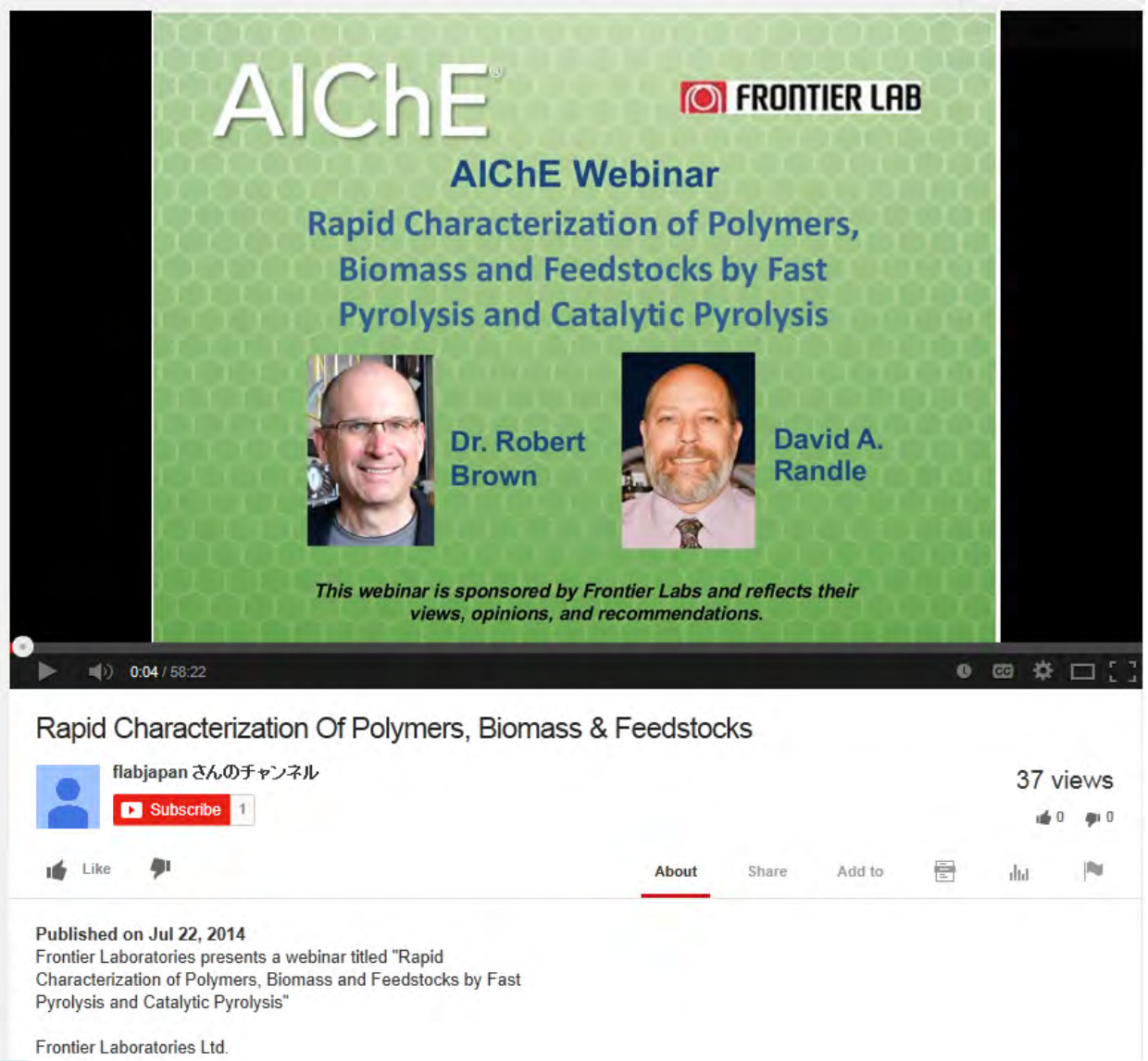

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Frontier Lab Tandem micro-Reactor

Tandem μ-Reactor
Rx-3050TR

Rapid Screening of Catalysts by GC/MS

Tandem micro-Reactor

Customers

- Process engineers
- R&D of catalysts, chemical processes, and biomass conversion to fuels or high value chemicals

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Tandem micro-Reactor for GC/MS

1. What is a Tandem micro-Reactor?

- It consists of two independently controlled heated zones called micro-Reactors stacked vertically in tandem and mounted on a bench-top GC/MS. Reaction gases, temperatures, flows and any sample type (gas, liquid and solid) can be controlled. A quick-change catalyst bed is located in the lower or 2nd micro-Reactor. The system is based on the proven "micro-Furnace pyrolysis platform". The Tandem micro-Reactor is one model in a series of products referred to as "Rapid Screening Reactors".

2. What does a Tandem micro-Reactor do?

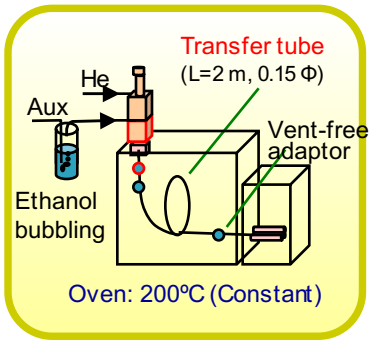
- The 1st micro-Reactor heats the sample to a user defined temperature between 40 and 900°C. Depending on whether sample is a gas, liquid or solid the 1st micro-Reactor can preheat a sample, or heat a sample to a temperature at which compounds of interest evolve intact (vaporization), or pyrolyze a solid or liquid sample prior to introduction to the 2nd micro-Reactor.
- The 2nd micro-Reactor contains the catalytic bed. Vapors from the 1st micro-Reactor are swept through the catalyst using any reaction gases at any temperature.
- Reaction products are carried to the GC/MS for detailed compositional analysis.

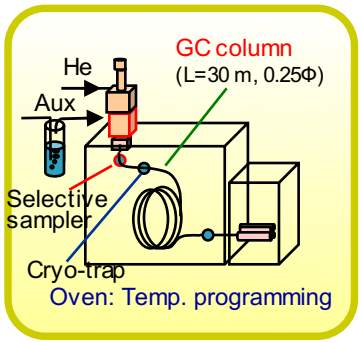
Tandem micro-Reactor for GC/MS

3. What are the available analytical methods for the Tandem system?

A: Stepwise temp. program. /Real Time Monitoring (RTM) and zone analysis

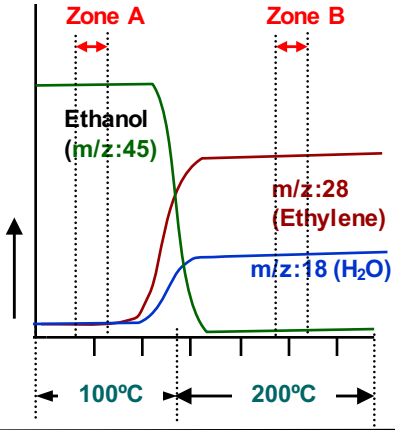
(Continuous sample flow and zone analysis)

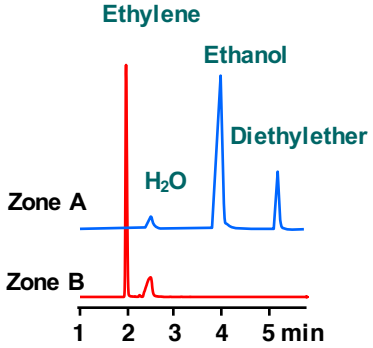




On-line monitoring of products by step temp. of catalyst

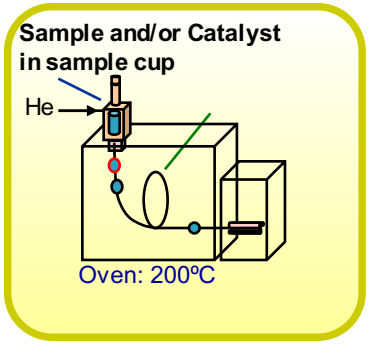
Analyses of "Zone A & B"

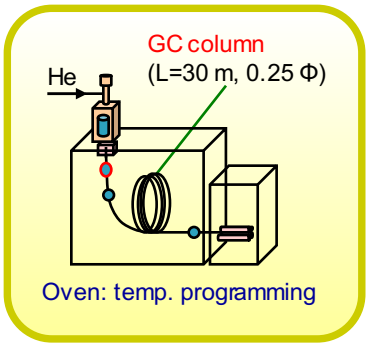




B: Linear temp. program. / Real Time Monitoring (RTM) and zone analysis

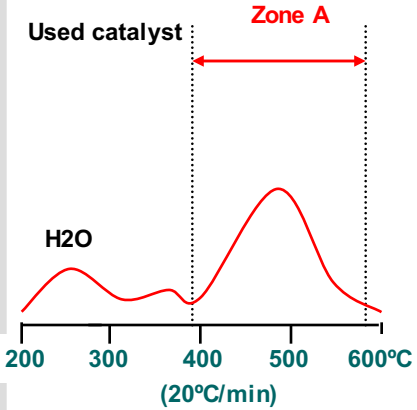
(Sample cup/ EGA and zone analysis)

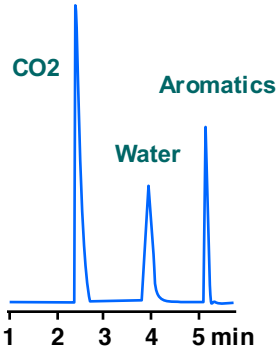




On-line monitoring of products by linear temp. heating of sample/catalysts

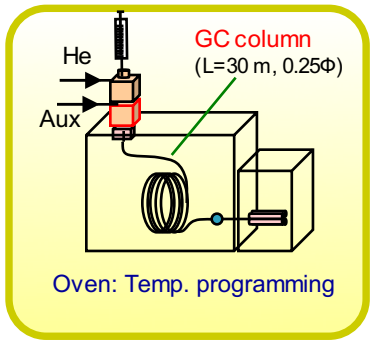
Analysis of "Zone A"



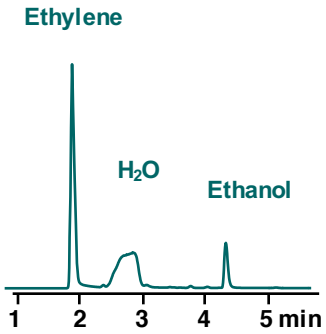


C: Single-shot GC/MS analysis

(Gas, liquid or solid)

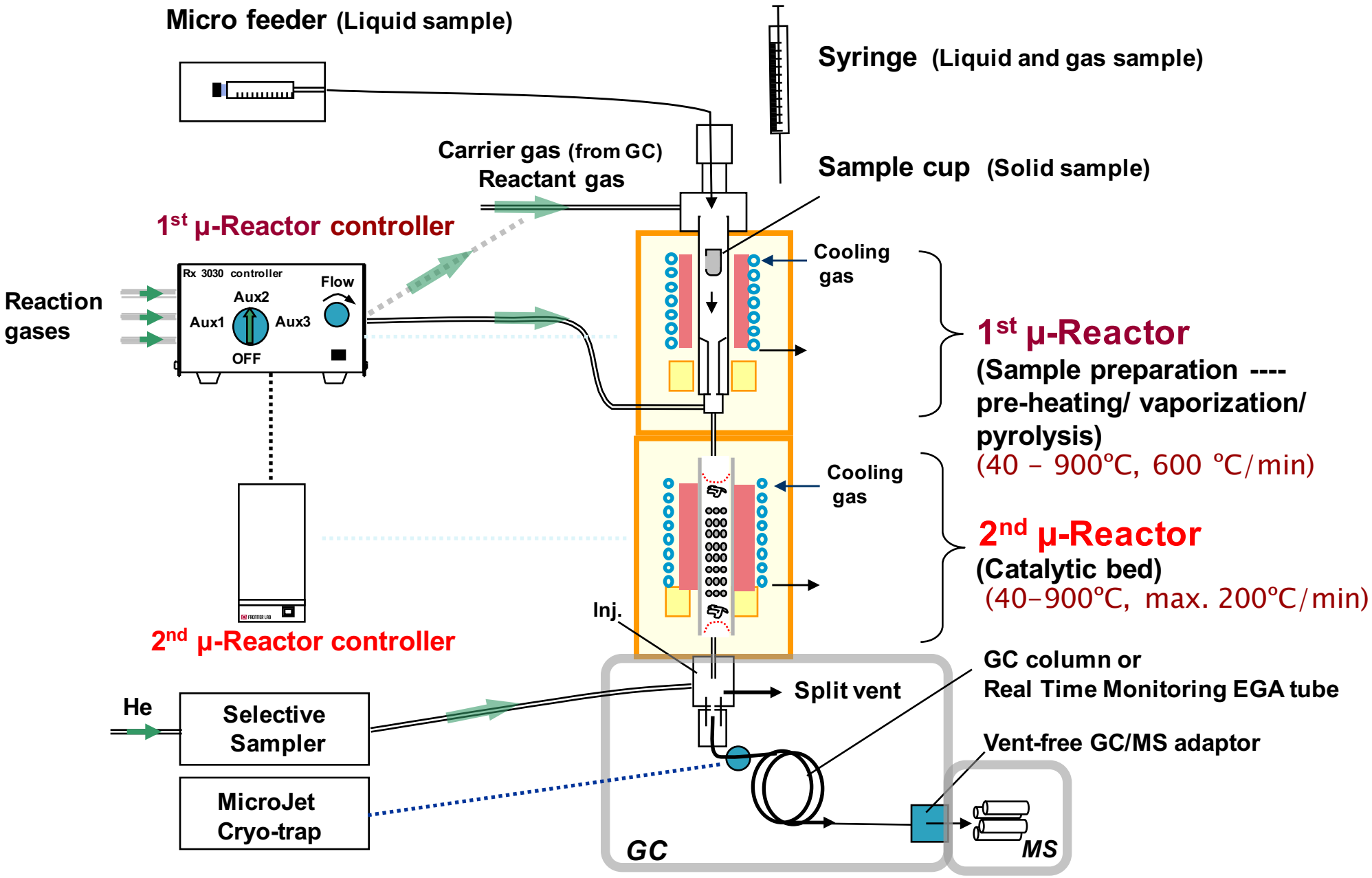


Analysis of injected sample by micro-syringe / cup



This illustrates the three methods available for the system. The figure on the left shows MS monitoring of the variation in reactive products as the reactive temperature increases stepwise from 100 to 300°C. Ethanol is introduced continuously, and it reacts to produce ethylene and water via dehydration of diethylether followed by zone A&B GC/MS analysis by partial sampling with a Selective Sampler and MicroJet Cryo-trapping. The center figure shows evolved gas analysis (EGA) with sample and catalyst together, and its subsequent zone analysis. The figure on the right shows a detailed GC-MS analysis of reactive products from a batch injection of ethanol.

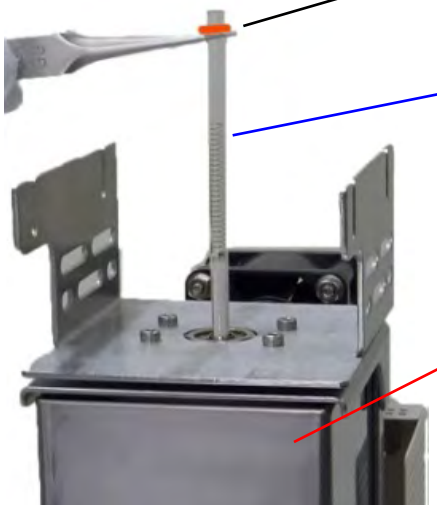
Configuration of the Tandem micro-Reactor System

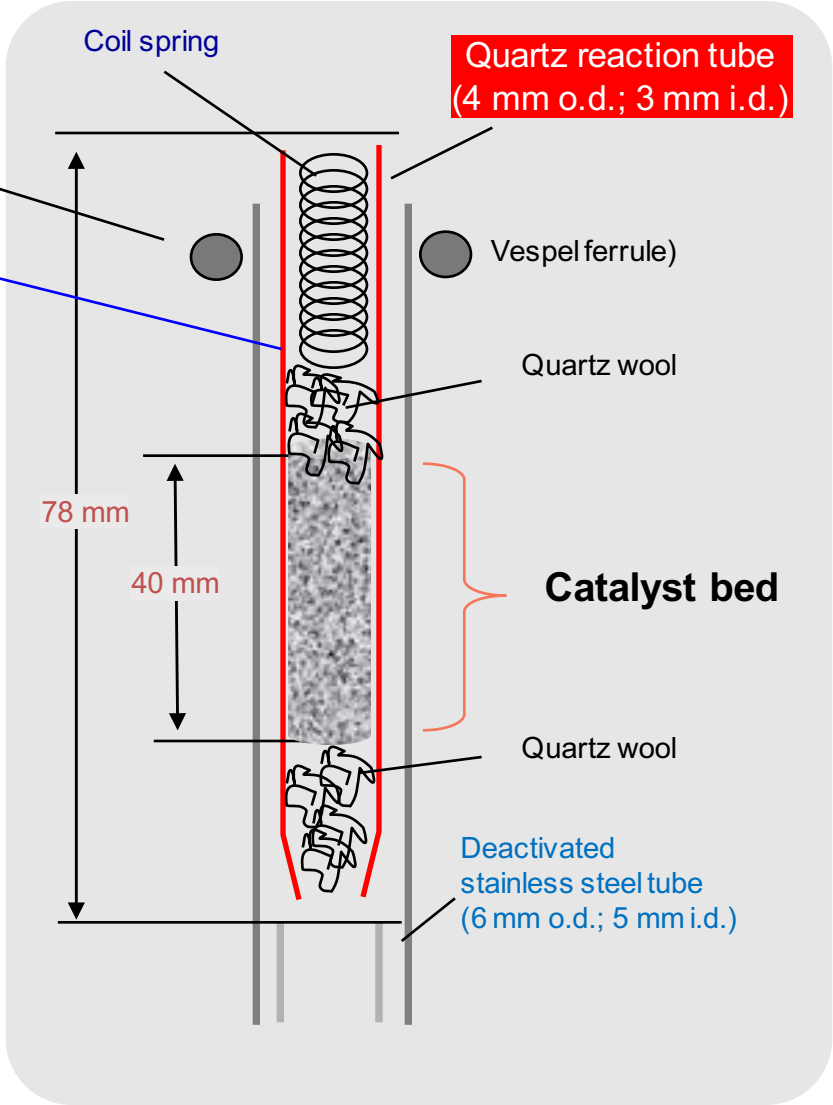


This shows the Tandem system configuration. Gas, liquid and solid samples can be introduced into the 1st micro-Reactor. Product liquids and gases from the 2nd micro-Reactor can be monitored as reactions vary during continuous injection of sample. Furthermore, the Selective Sampler and MicroJet Cryo-trap can be effectively used for automatic sampling and cryo-focusing the reactive products at the head of the separation column in this system.

Packing the Catalytic Bed

Tandem µ-Reactor





Reaction Tubes (quartz)

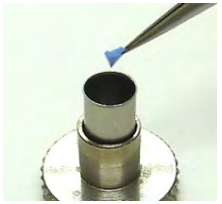
- Quick-change
- Two sizes
  - 4 mm o.d.; 2 mm or 3 mm i.d
  - Allows visual observation of catalyst
- Simple packing
  - Quartz wool and spring
  - Pack catalyst directly or on inert support

This illustrates the design of the catalytic tube assembly. It is quick and easy to replace and maintain the catalyst. The reaction tubes are made from quartz. The quartz tube is inserted into a deactivated SS tube. The packing length of catalyst bed is 40 mm, sufficient for complete reaction. The coil spring and quartz wool in both end of the tube retain the catalytic bed in place during pressure and flow changes.

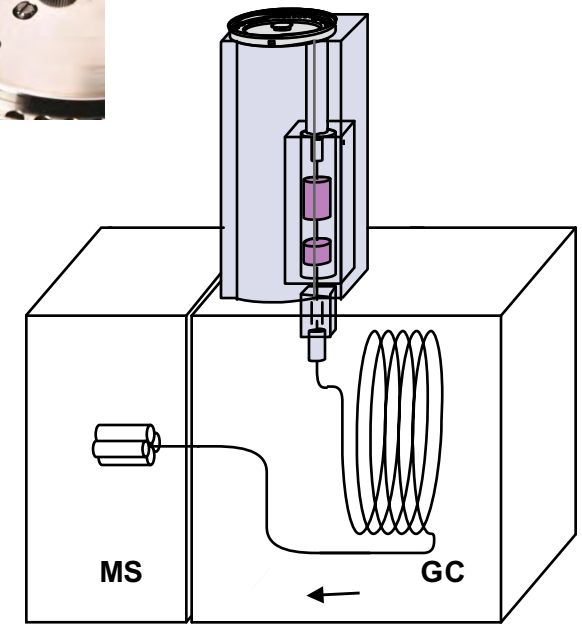
Auto-Shot Sampler (AS-1020E) for Tandem micro-Reactor (Rx-3050TR)

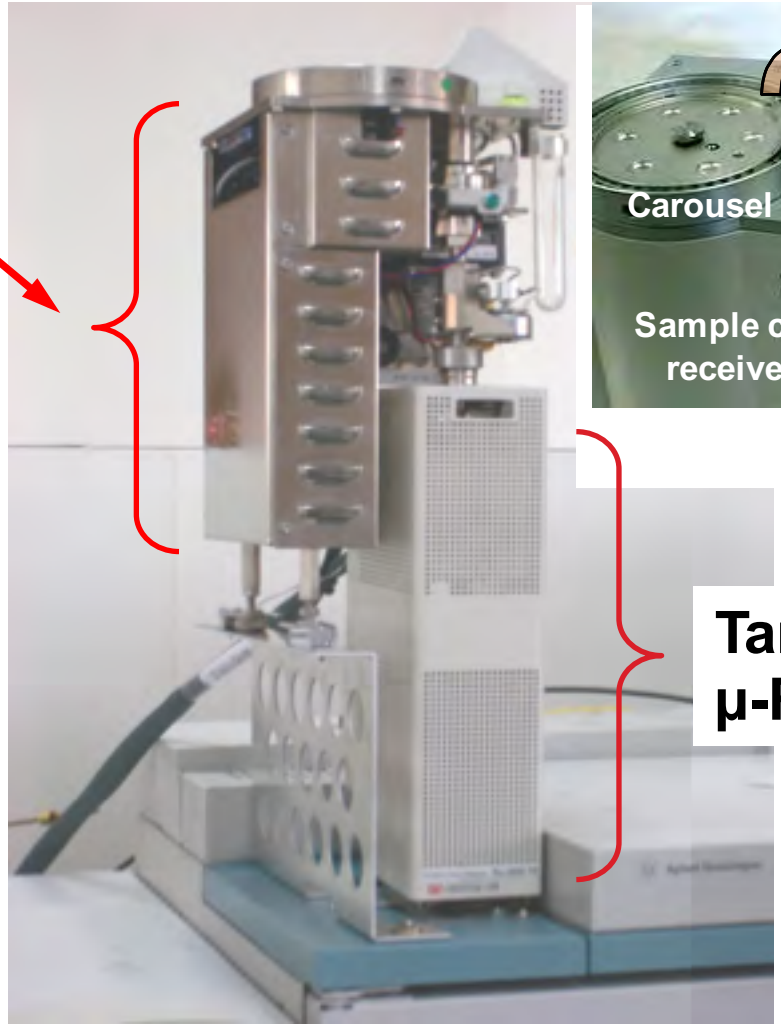
The Auto-Shot Sampler has a 48 sample carousel for use with solid samples

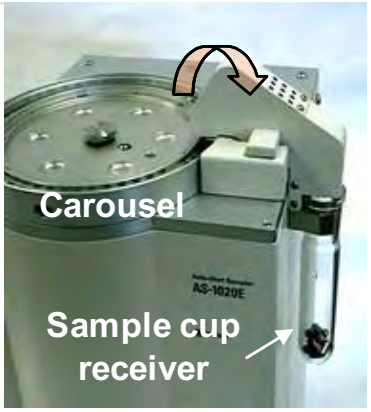
Auto-Shot sampler



Sample Cup
(Eco-cup)





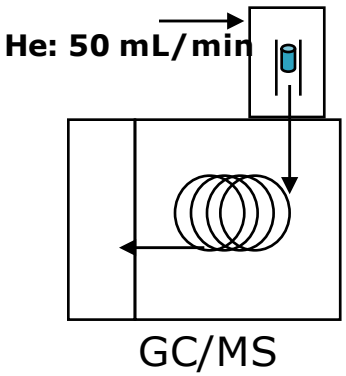


Tandem μ-Reactor

Transformation of "Jatropha press cake" to "BTEX"

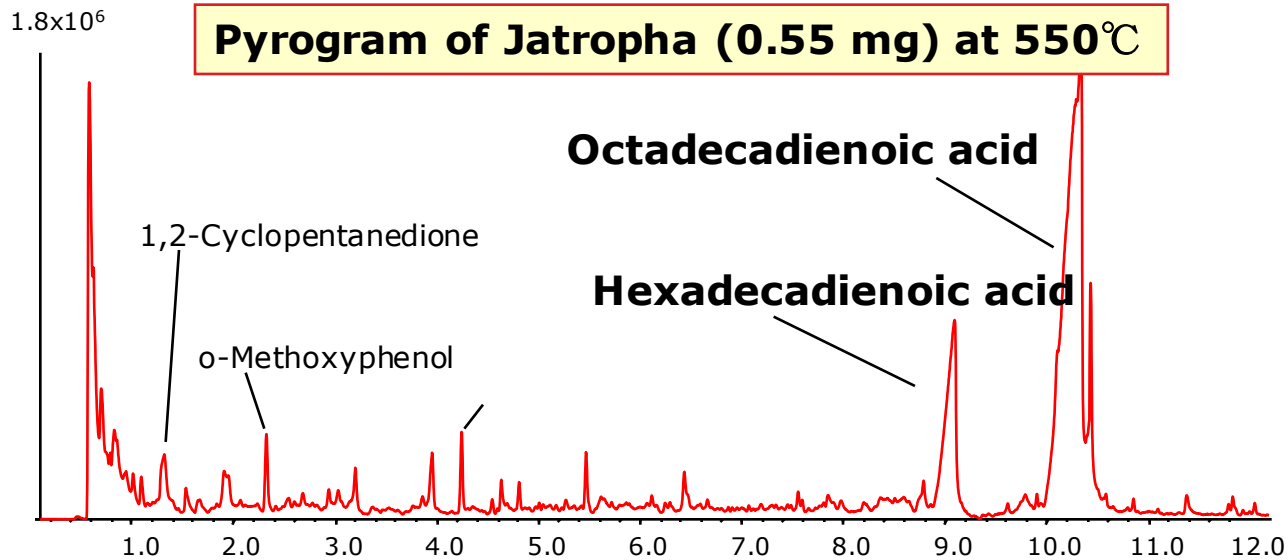
Jatropha sample and Zeolite catalyst was provided by Dr. Murata of energy group of AIST, Japan

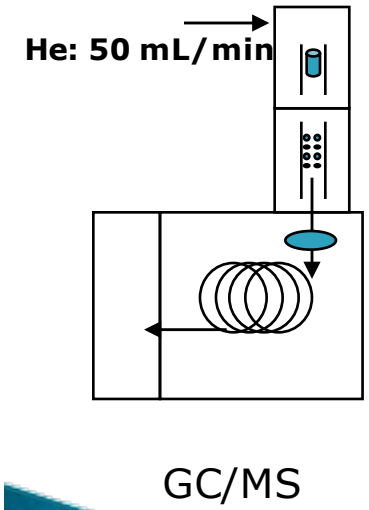
Column: DX30-15M-0.15F, He: 1 ml/min, 1/50, GC: 70(0)-@15-320ºC(10 min), PY: 550ºC (ITF: 320ºC)



550ºC (Flash Py)

Pyrogram of Jatropha (0.55 mg) at 550℃



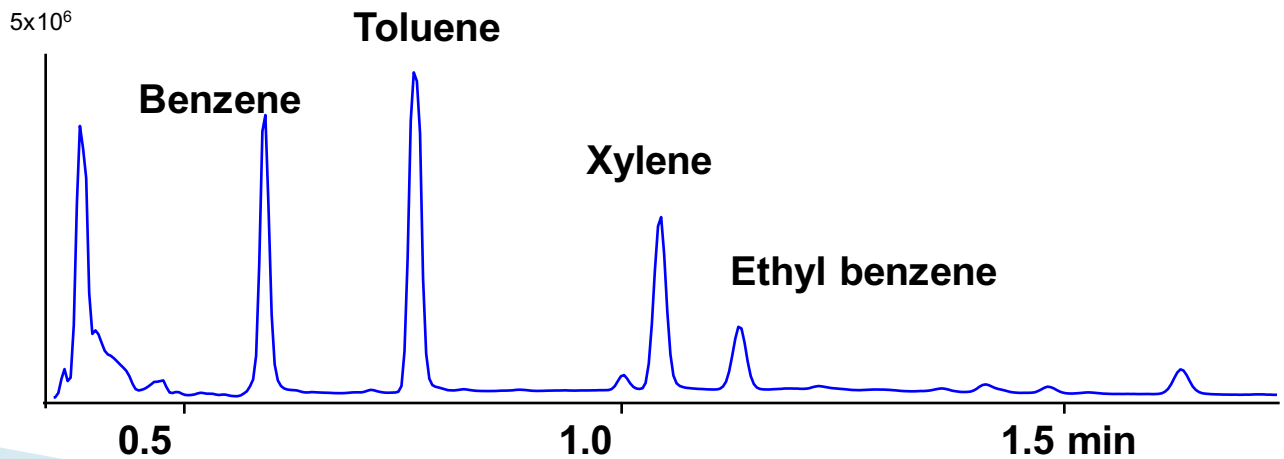


550ºC (Flash Py)

550ºC (Transformation)

Zeolite Catalyst

Jatropha (0.55 mg) pyrolyzates from 1st Reactor flow into 2nd Reactor and transformed by catalyst



Summary

The Tandem micro-Reactor* is a Rapid Screening Reactor useful for characterizing catalysts using GC/MS.

1) **Flexible and easy to use analytical instrument**
   - Multi-modes of operation
   - Quick-change catalyst reaction tubes
   - Low maintenance
2) **High precision temperature control & fast heating and cooling**
   - Quality reproducible results
   - High sample throughput
     - 48 sample autosampler for solids
3) **GC/MS analysis and identification of transformed compounds**
   - Gases, liquids or solids can be analyzed

Acknowledgements

Some material in this document is based on a presentation given at the 19th International Symposium on Analytical and Applied Pyrolysis, Linz, Austria, May 2012. Chu Watanabe [1]*, Koichi Ito [1], Terry. L. Ramus [2]. This version was edited by Dave Randle [2] [1]. Frontier Laboratories, Ltd. Koriyama, Japan. [2]. Frontier Laboratories USA. Antioch, CA USA

*Model RX-3050TR

ASTM D7823-13: A Rapid And Simple Thermal Desorption-GC/MS Method For Determination Of Phthalates In Consumer Products

Dave Randle, Itsuko Iwai, Terry Ramus, Aki Hosaka & Ichi Watanabe
- Frontier Laboratories Ltd.

GCC
"Serving The World of Chemical Analysis"

Gulf Coast Conference
October 16, 2013

FRONTIER LABORATORIES LTD.

Booth #515

ASTM D7823-13 Method

Designation: D7823 – 13

Standard Test Method for Determination of Low Level, Regulated Phthalates in Poly (Vinyl Chloride) Plastics by Thermal Desorption—Gas Chromatography/Mass Chromatography[1]

This standard is issued under the fixed designation D7823; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

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Active Standard ASTM D7823 | Developed by Subcommittee: D20.70

Book of Standards Volume: 08.03

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Regulation of phthalates goes beyond “children’s toys”

Stakeholders:

Polymer formulators

Recyclers

Product manufacturing

Retailers

Consumers

Many "global" corporations have quality control guidelines for phthalates in place

Company	Substance	Business Dept.	Requirement

P&G removing DEP, triclosan from its products

U.S. consumer-products manufacturer Procter & Gamble is in the process of eliminating diethyl phthalate from its products… The company has cut its DEP use by 70% and aims to completely remove it by 2014. Phthalates have raised concerns among some consumer health advocates…

TheDailyGreen.com (9/9/13)

Smart Phone
DEHP 1.5 %

Game controller
Exceeds the regulatory limit of DINP

Phthalates are restricted on a global scale

Regulation	Reference	Substances	Requirement
RoHS	Candidates for regulation	DBP, BBP, DEHP, DiBP	0.1 % (1000 mg/kg)
REACH	SVHC Candidate	DBP, BBP, DEHP, DiBP	0.1 % (1000 mg/kg)
CPSIA 1)	Section 108	DBP, BBP, DEHP, DNOP, DINP, DIDP	0.1 % (1000 mg/kg)
REACH	(EC) No. 1907/2006 Annex XVII, #51 & 52	DBP, BBP, DEHP, DNOP, DINP, DIDP	0.1 % (1000 mg/kg)
CA Prop 65	AB Package 21	DBP, BBP, DEHP, DnHP, DIDP	0.1 % (1000 mg/kg)
CCPSA 2)	SOR/2010-298	DBP, BBP, DEHP, DNOP, DINP, DIDP	0.1 % (1000 mg/kg)
KC 3)	Annex 35	DBP, BBP, DEHP, DNOP, DINP, DIDP	0.1 % (1000 mg/kg)

1) CPSIA : Consumer Products Safety Improvement Act
2) 2) CCPSA : Canada Consumer Products Safety Act
3) 3) KC : Korea Certification

Thermal Desorption Defined

- Thermal Desorption (TD) in this context is defined as the use of heat to thermally vaporize a solid sample in the absence of oxygen.
- The vaporized sample is swept (using helium carrier gas) directly onto a GC column, the components separated and detected by GC/MS.
- TD may be isothermal or temp. programmed.
  - For phthalates, it is a temp. programmed method.
  - Many other material characterization methods use TD.
  - TD is often used as a quantitative method.
- TD can isolate additives from polymers

Thermal desorption – a "green" alternative to solvent based extraction regimes

- Common TD analytical examples
  - BHT, Irganox 1010, Irgafos 168 in polymers
  - Brominated flame retardants
  - Residual bisphenol A (BPA) in polycarbonate
  - Anti-degradants in rubber
  - Phthalates in polymers (D7823 for PVC)
- Ideally suited for solid samples
- Significantly improves data quality
- Very easy, productive and efficient method
- Often requires little or no solvents

ASTM D7823 Sample Prep Quick & Simple

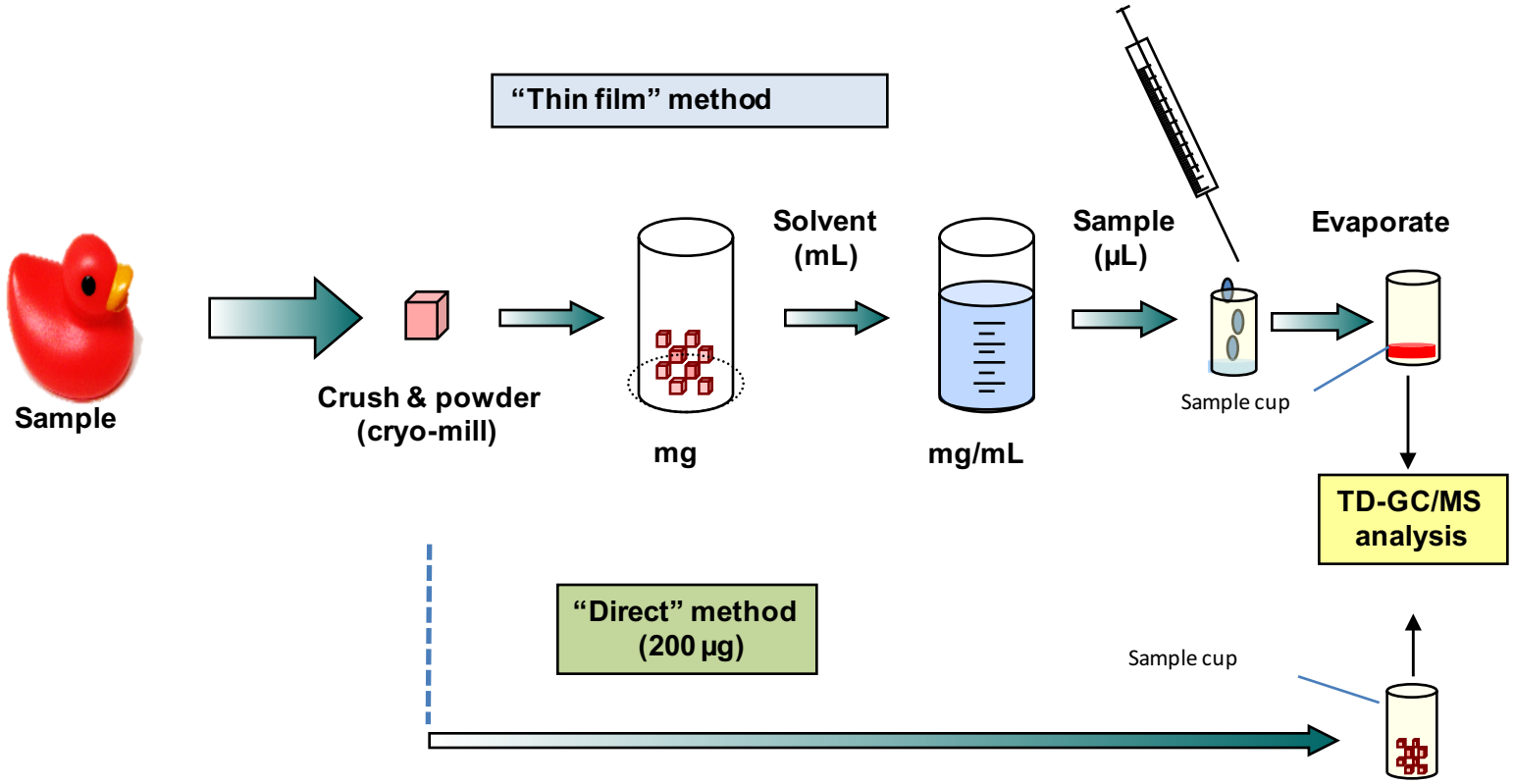


Figure 1. Quick, simple and "green" sample preparation. The "thin film" method requires that a quantitative solution of the sample be prepared. An aliquot of the THF solution is placed in the sample cup.

Thin Film vs. Direct Method

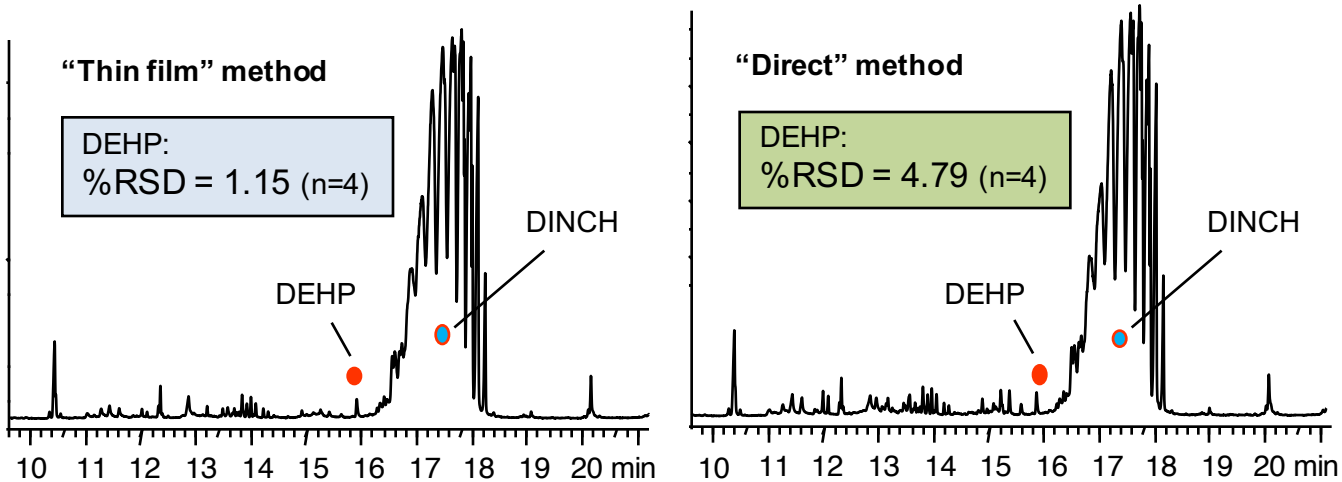
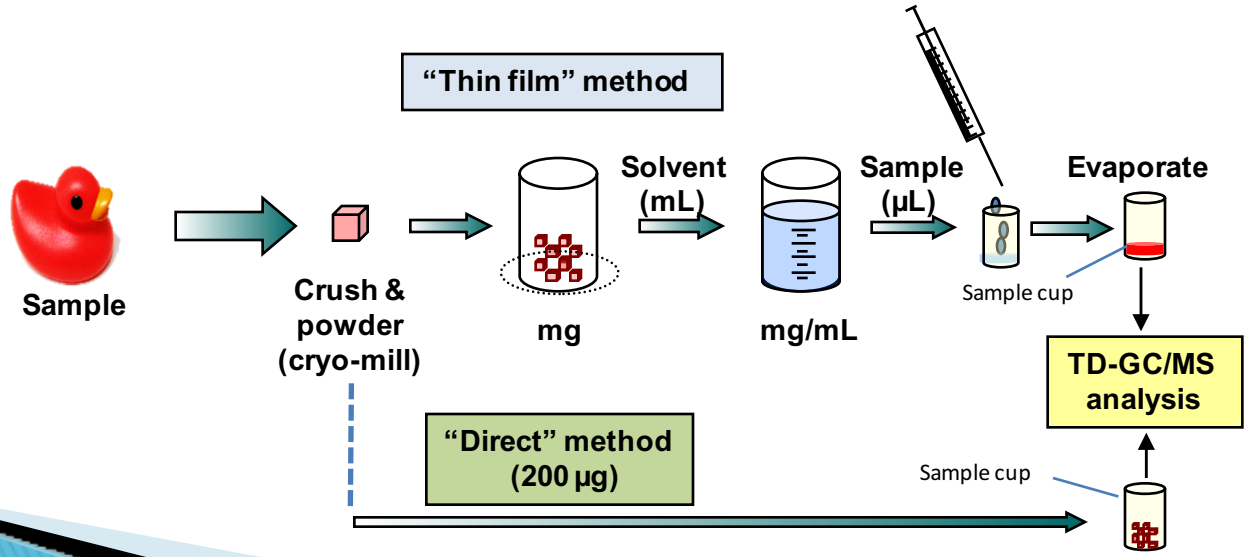
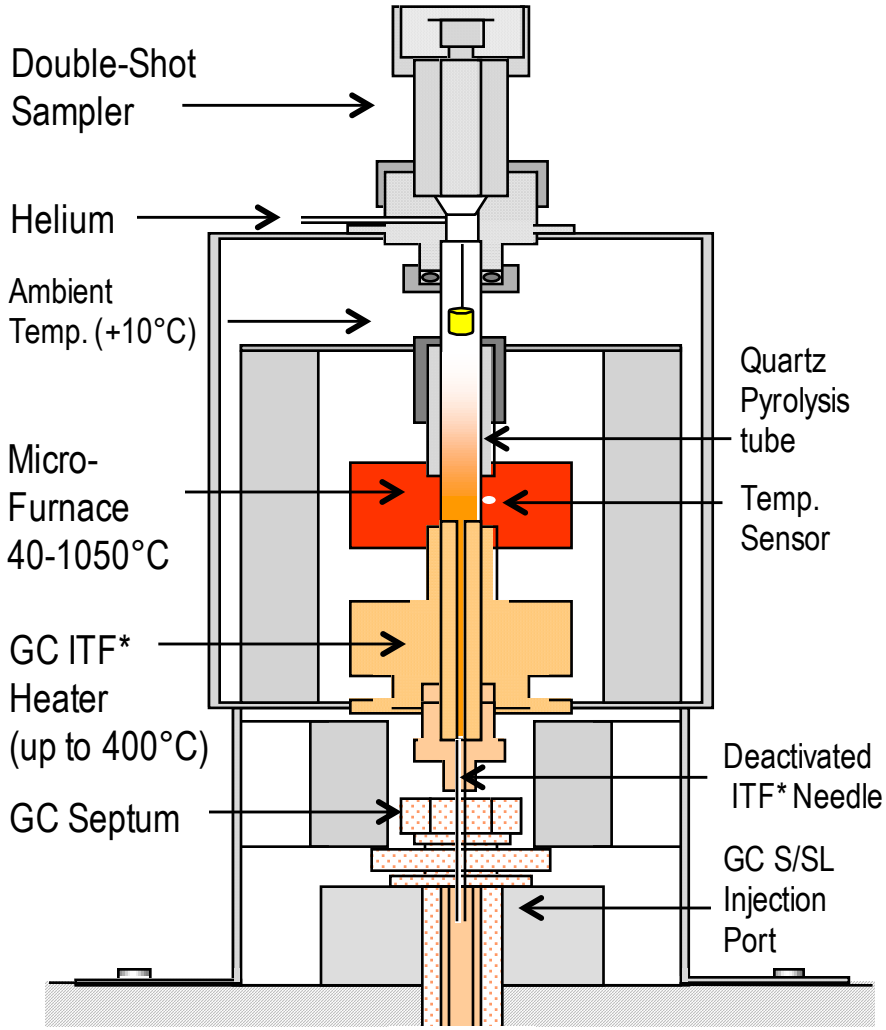


Figure 2. Influence of the sample preparation method on analytical precision. Sample: 0.5 mg plastic toy (PVC & DINCH); Thin film: 20 µL THF solution. Direct sampling: powder < 45 mesh.



Sample Introduction and Schematic of Frontier EGA/PY-3030D Multi-Shot Pyrolyzer



*ITF means Interface

To GC tube or analytical column; detection by MS

Sample Introduction Modes

- Manual (Double-Shot Sampler)
- Automated (Auto-Shot Sampler)

Temperature Modes

- Isothermal
- Temperature Programmed

Multiple micro-Furnace Modes

- Evolved Gas Analysis (EGA)
- Thermal Desorption (TD)
- Flash Pyrolysis (PY or Single-Shot)
- TD/PY (Double-Shot)

ASTM D7823 Phthalate Method uses:

- Temperature Programmed TD Mode

Thermal Desorption (TD)-GC/MS Analysis

TD temperature:	100 - 20°C/min - 320°C (5 min hold)
Py interface:	320°C (Auto mode),
GC injector :	300°C

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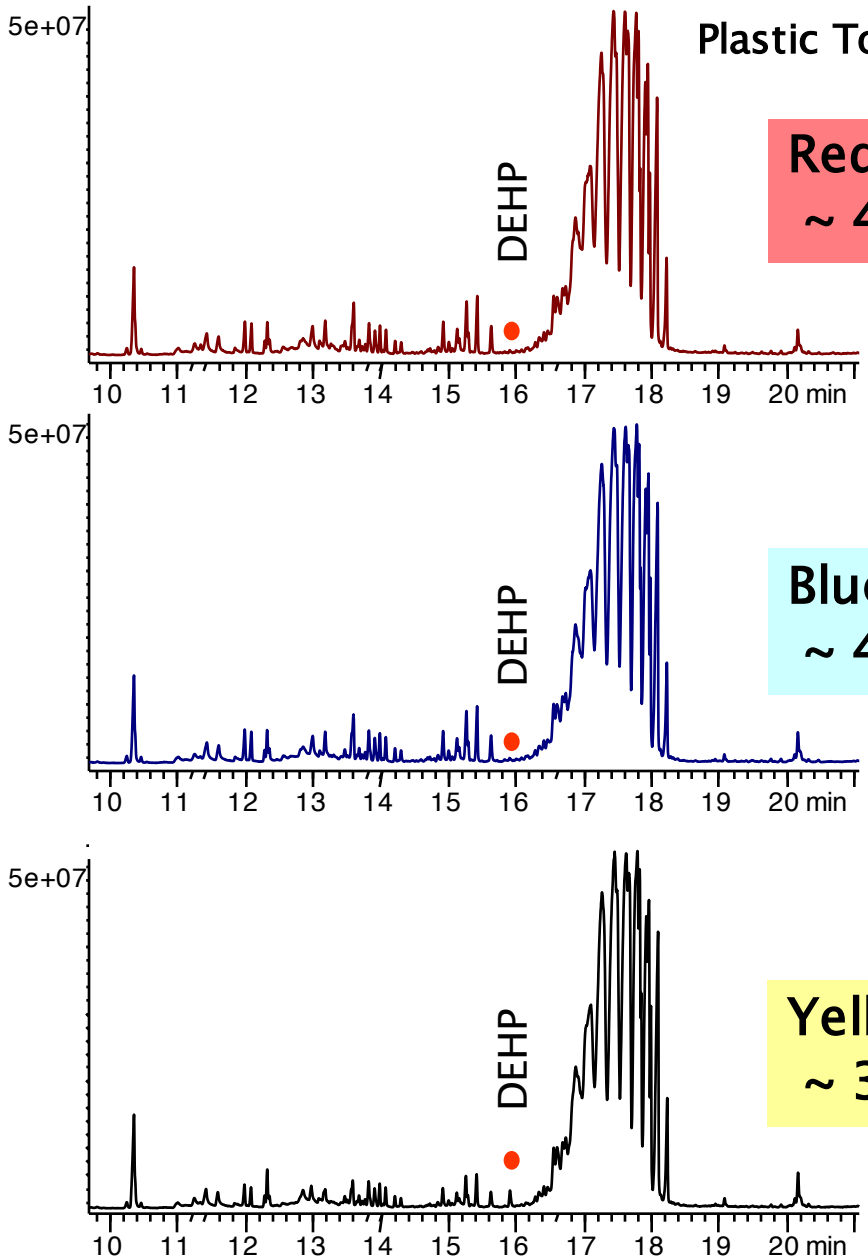
Determination of DEHP on different parts of toy A

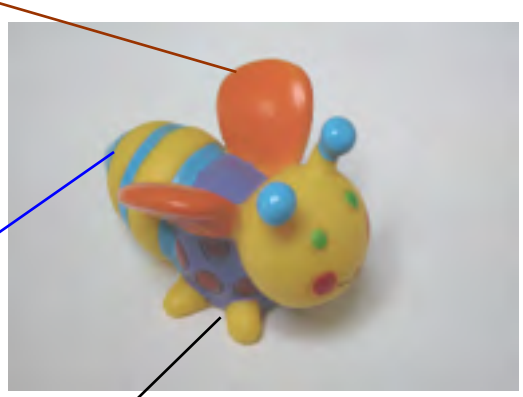
Plastic Toy-A, powder, TD: 100- 20ºC/min-320ºC (5 min)



Red part ~ 40ppm

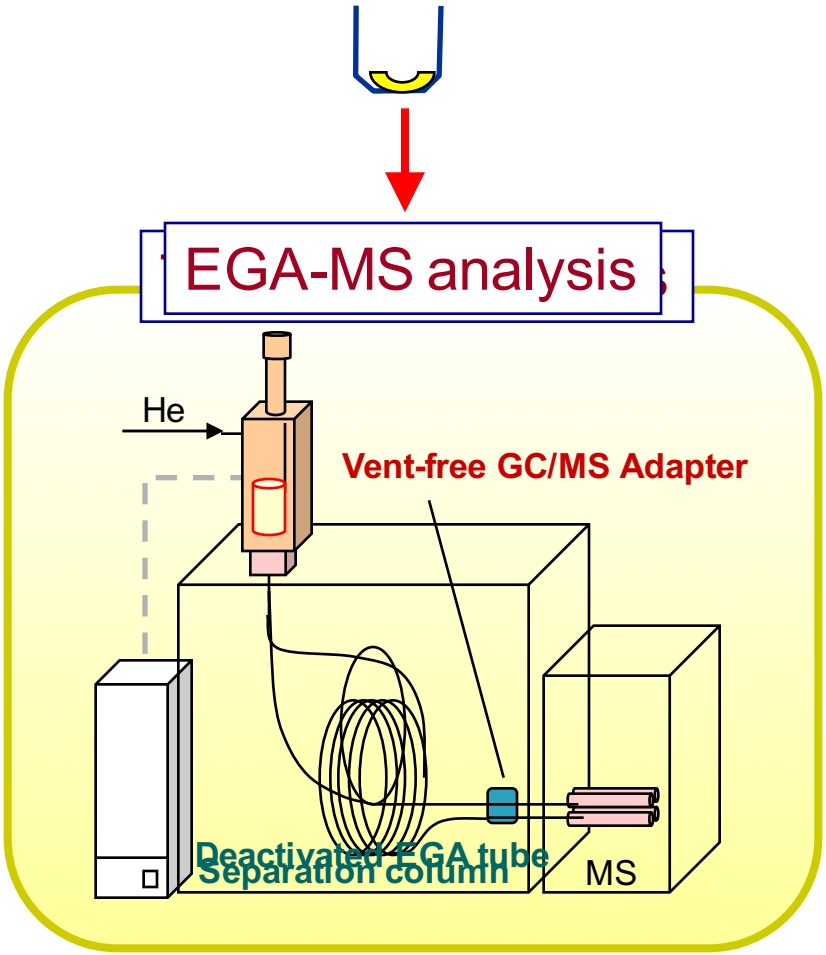
Blue part ~ 40ppm

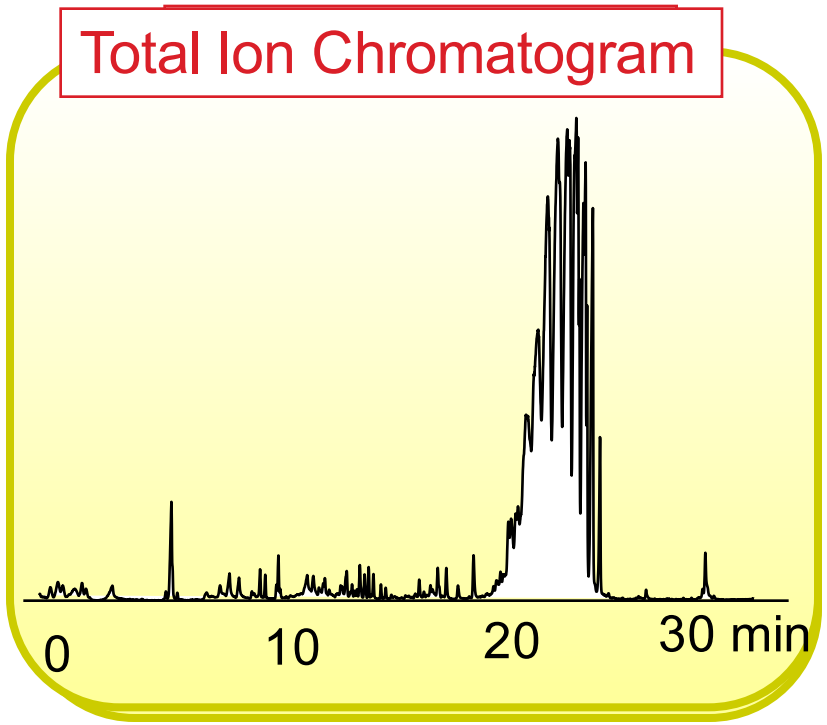
Yellow part ~ 300ppm



Sample Homogeneity Must Be Considered

Method development using the multi-functional pyrolyzer

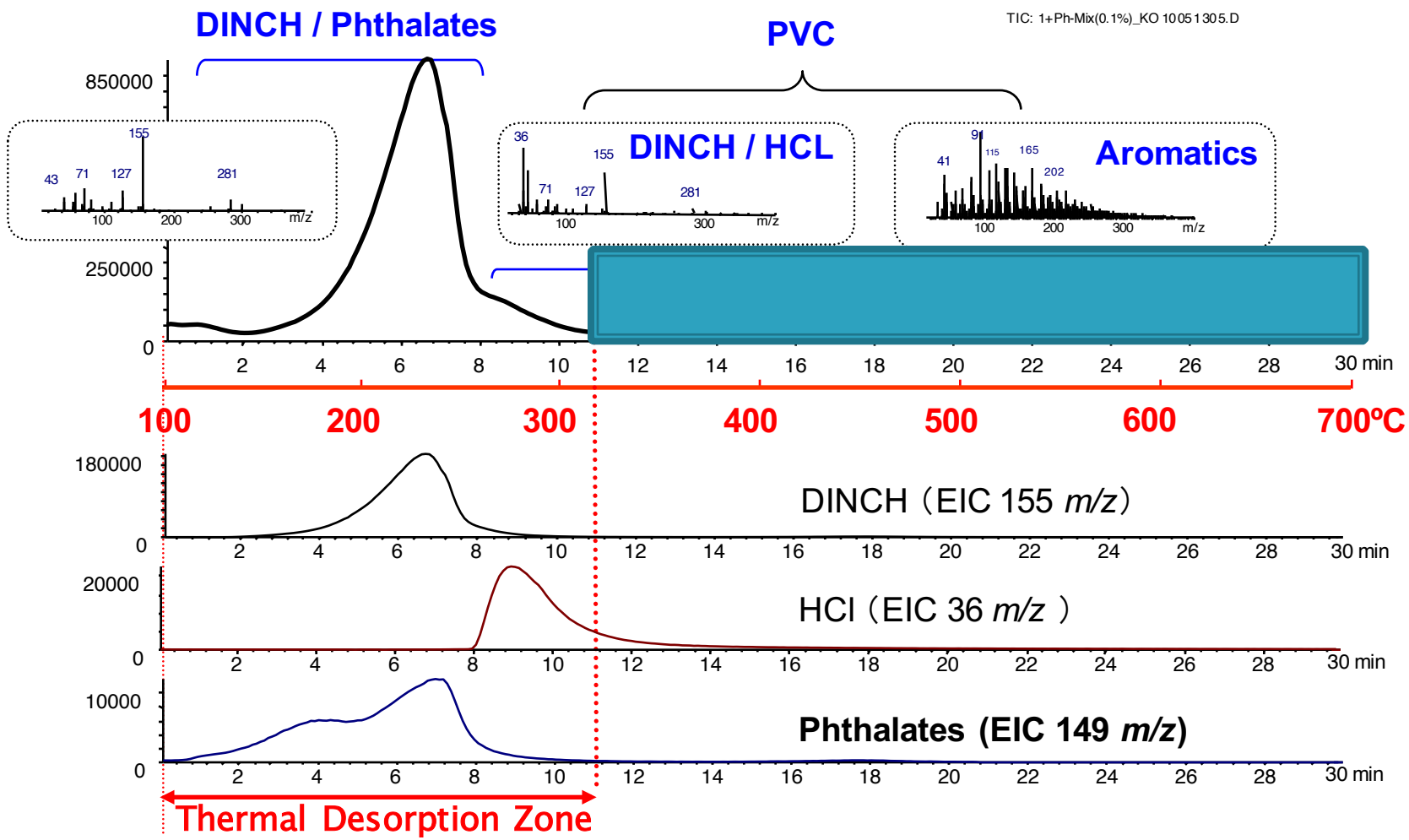




PY and GC oven temperature programmed

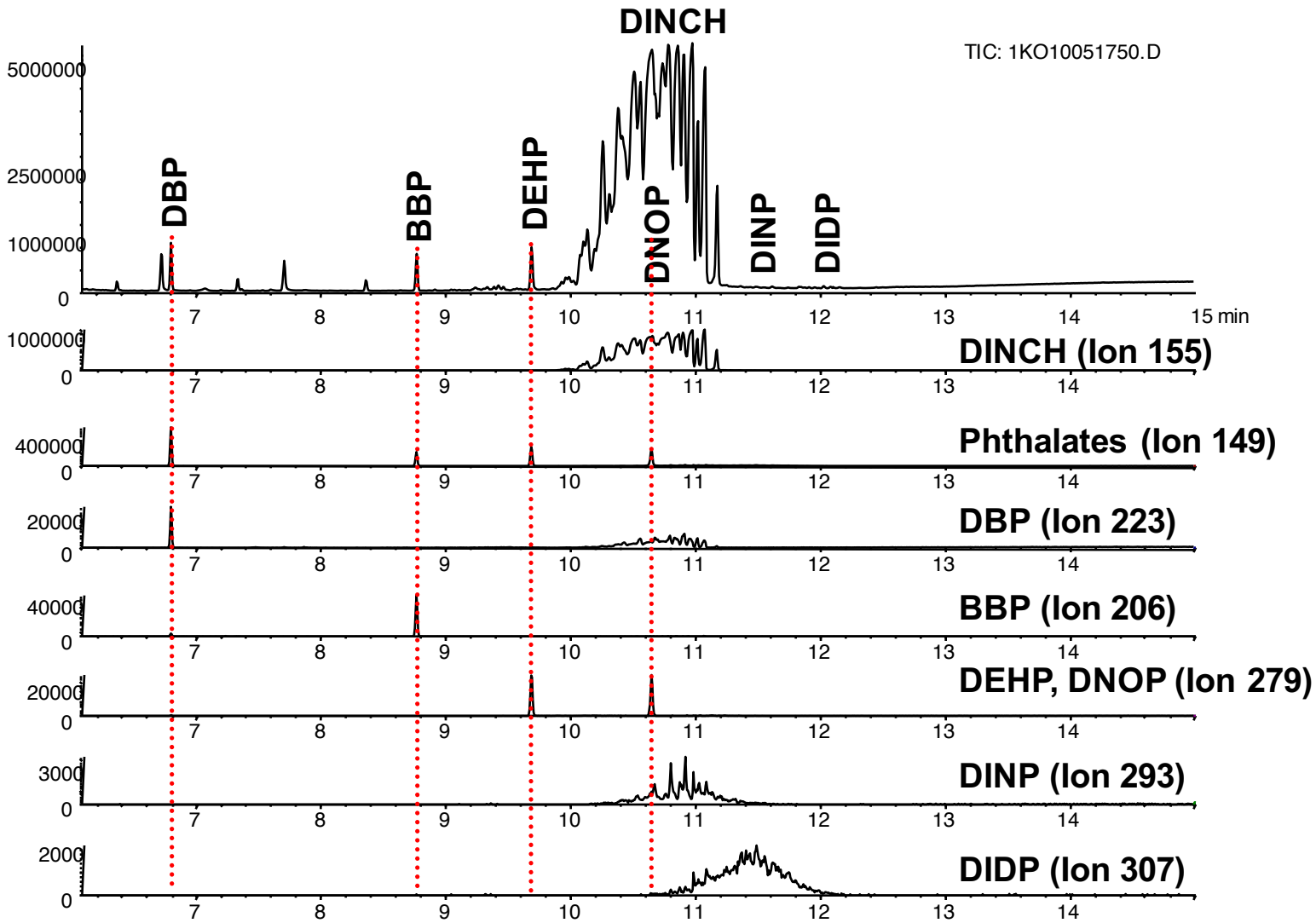
PY temperature programmed
GC oven isothermal

Thermogram of PVC containing six regulated phthalates



100 – 320˚C (20˚C/min, 5 min hold)

Total ion chromatogram of the desorbed portion of a PVC DINCH Phthalate standard

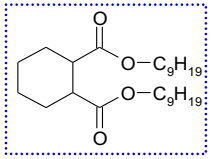


Analytical precision: ASTM D-7823

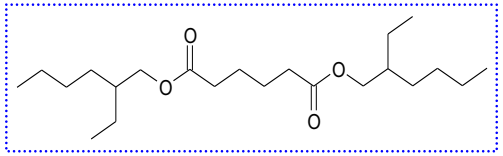
Each phthalate at 1000 ppm, thin film method

Compound Quant ion	DBP m/z=223	BBP m/z=206	DEHP m/z=279	DNOP m/z=279	DINP m/z=293	DIDP m/z=307
	%RSD (n=6)	%RSD (n=6)	%RSD (n=6)	%RSD (n=6)	%RSD (n=6)	%RSD (n=6)
PVC DINCH	1.35	1.46	2.54	1.60	1.33	2.52
PVC DOA	2.08	0.76	1.42	0.85	2.03	2.07
PVC Mesamoll II	2.58	1.20	1.47	1.67	0.99	1.90

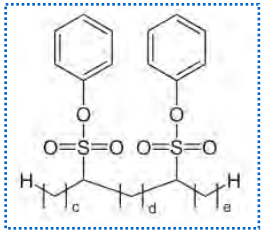
DINCH

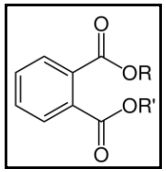


DOA



Mesamoll ii



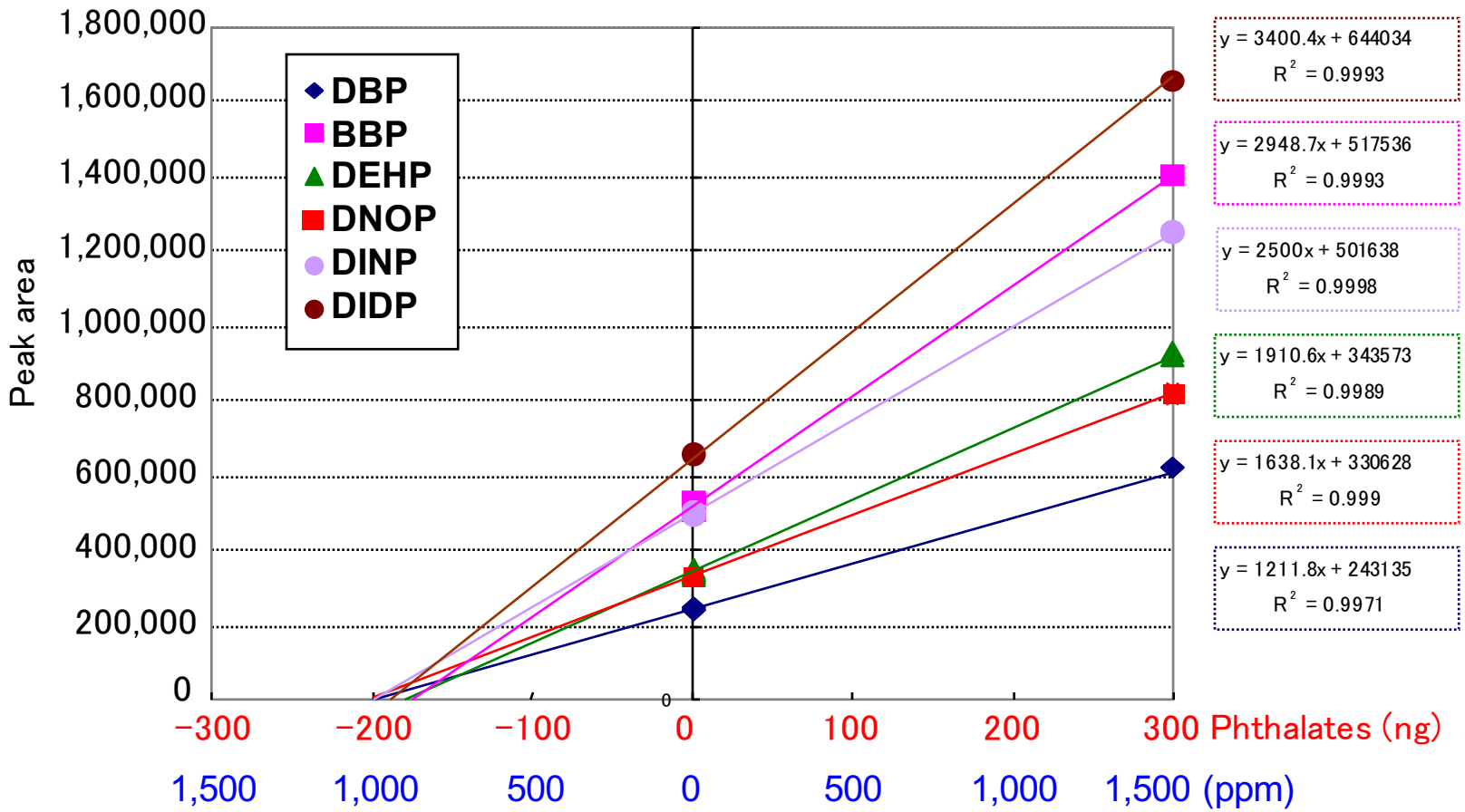


Phthalates

Restricted phthalates

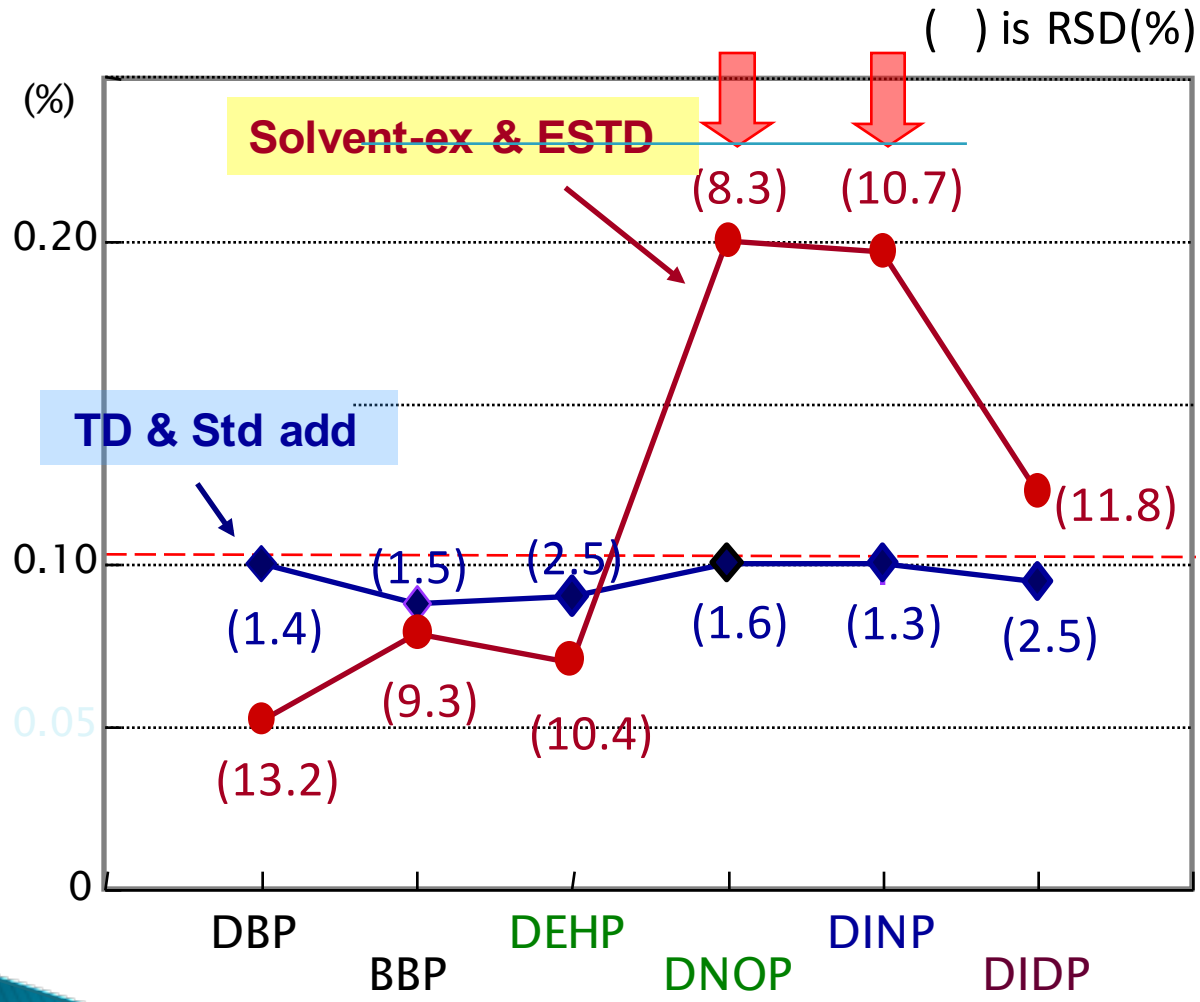
DBP: Dibutylphthalate
BBP: Butylbenzylphthalate
DEHP: di-2-ethylhexyl phthalate
DNOP: di-n-octylphthalate
DINP: di-isononylphthalate
DIDP: di-isodecylphthalate

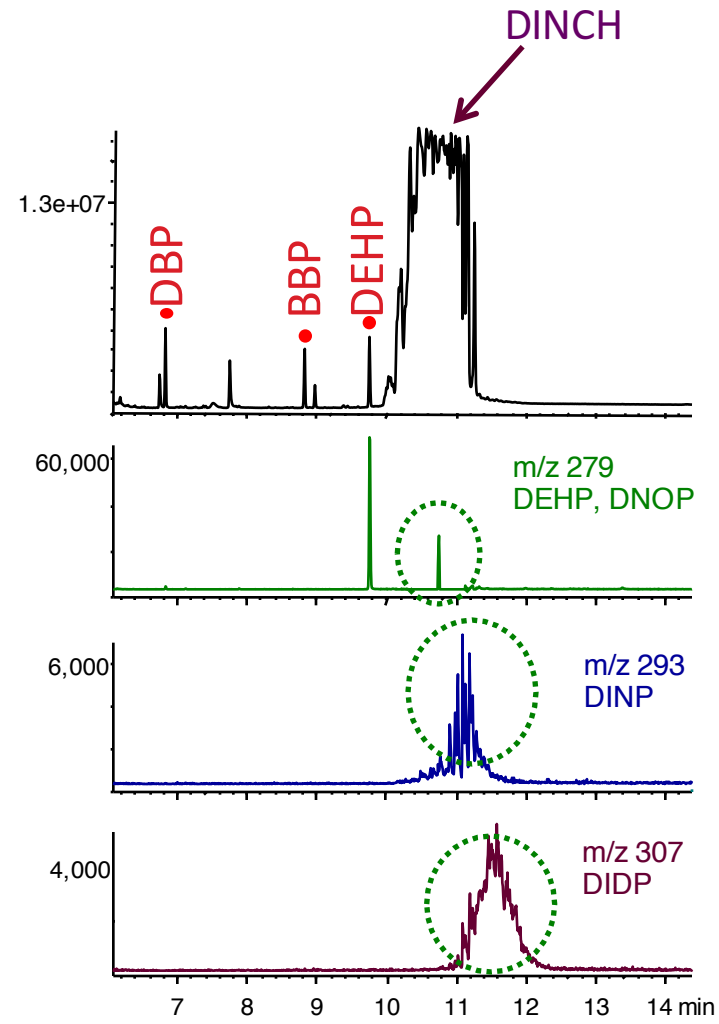
Standard addition calibration for the phthalates



Quantitative analysis of PVC-DINCH: accuracy & precision

Blind sample containing 0.1025 % each phthalate





Analytical precision for ASTM D-7823: phthalates

PVC DINCH (thin film)

	DBP	BBP	DEHP	DNOP	DINP	DIDP
Quant ion	223	206	279	279	293	307
ng	200.8	175.5	179.8	201.8	200.2	189.4
ppm	1003	878	899	1009	1003	947
%RSD	1.35	1.46	2.54	1.80	1.33	2.52
%ERROR	2.1	14	12	1.5	2.1	7.5

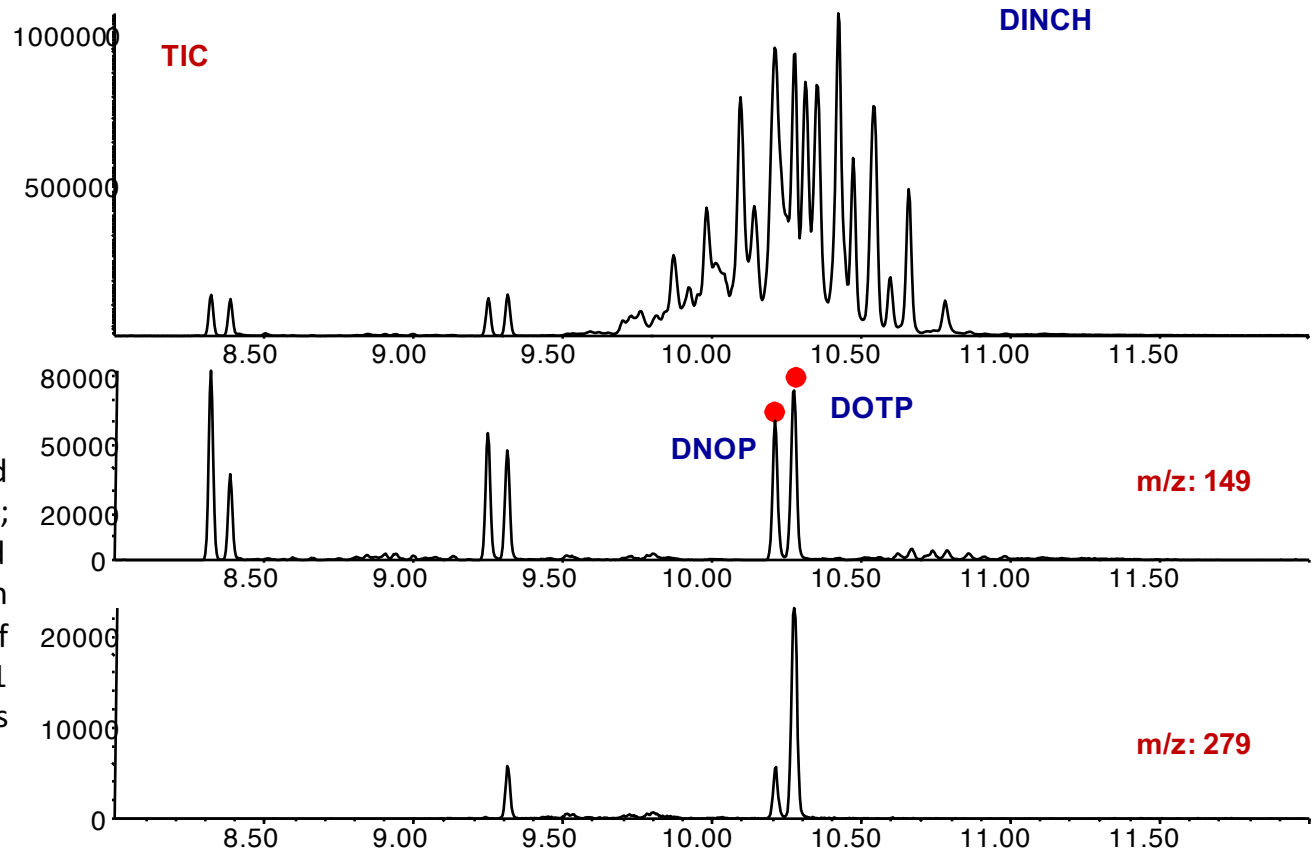
$$\frac{|\text{Approximate Value} - \text{Exact Value}|}{|\text{Exact Value}|} \times 100\%$$

DNOP vs. DOTP

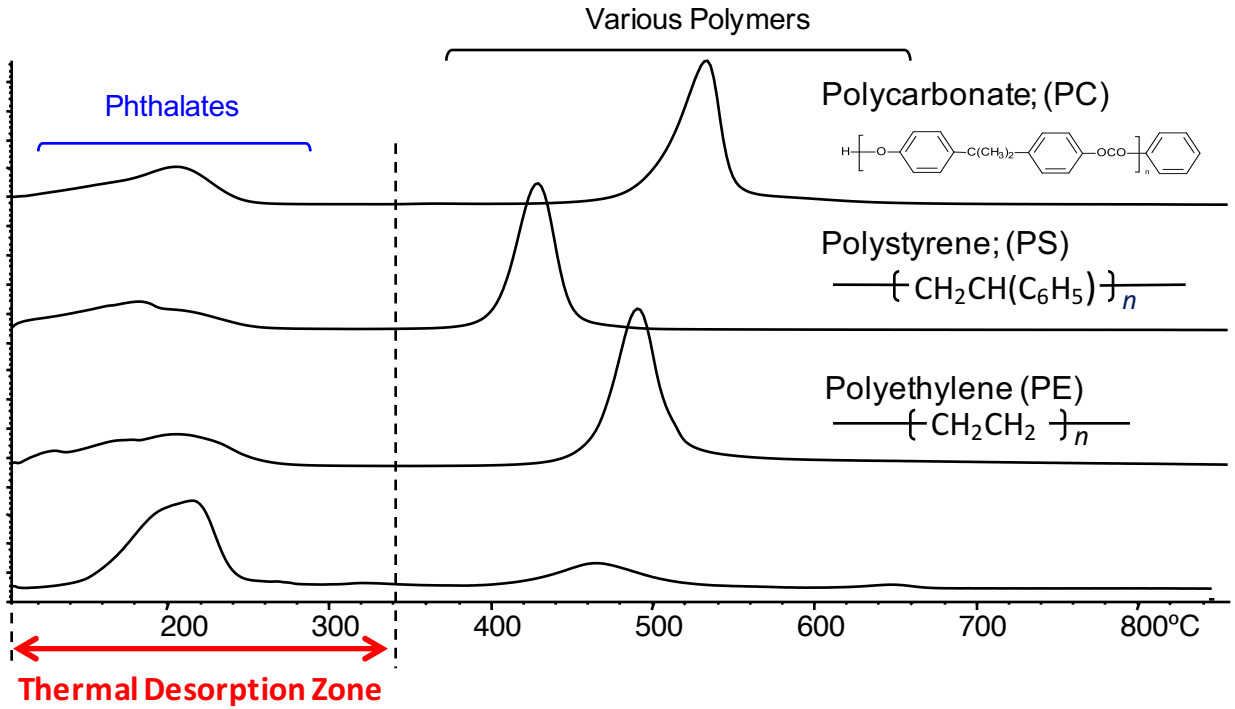
Section 11.8 (ASTM method) cautions about the possible co-elution of DNOP and DOTP

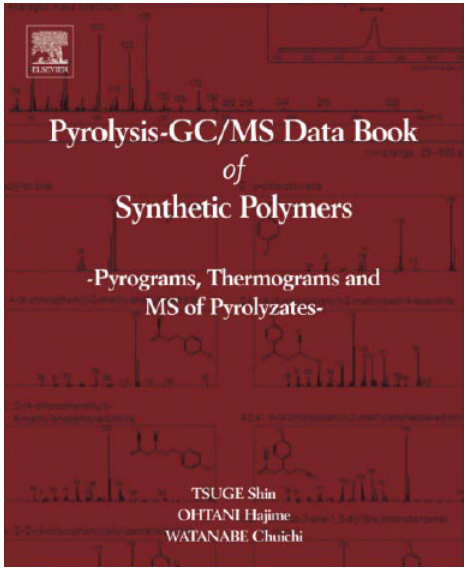
Attention must be given to the possibility that there are similar compounds which co-elute and have similar mass spectra to the phthalate of interest. One such compound is dioctyl – terephthalate (DOTP) (CAS# 6422-86-2) which is very similar to DNOP (117-84-0).

DNOP and DOTP are based lined resolved using the GC method described in D7823-13; the areas are easily and accurately integrated even though both compounds co-elute with various DINCH isomers, m/z 279 is free of interference. In addition, DOTP has an 261 ion; DNOP and DINCH do not, which provides a confirming ion for DOTP.



Phthalates in other polymers





Tip: This book has 163 polymers with EGA Thermograms

ASTM D7823-13 is written specifically for phthalates in polyvinyl chloride. However, the solubility and diffusivity of phthalates in most non-crystalline polymers is the same; consequently, the thermal desorption temperature range is independent of the polymer substrate. When using TD to isolate additives that are beyond the scope of ASTM D7823-13 or are incorporated into a polymeric base that has not been evaluated, it is wise to verify the thermal desorption zone using EGA-MS.

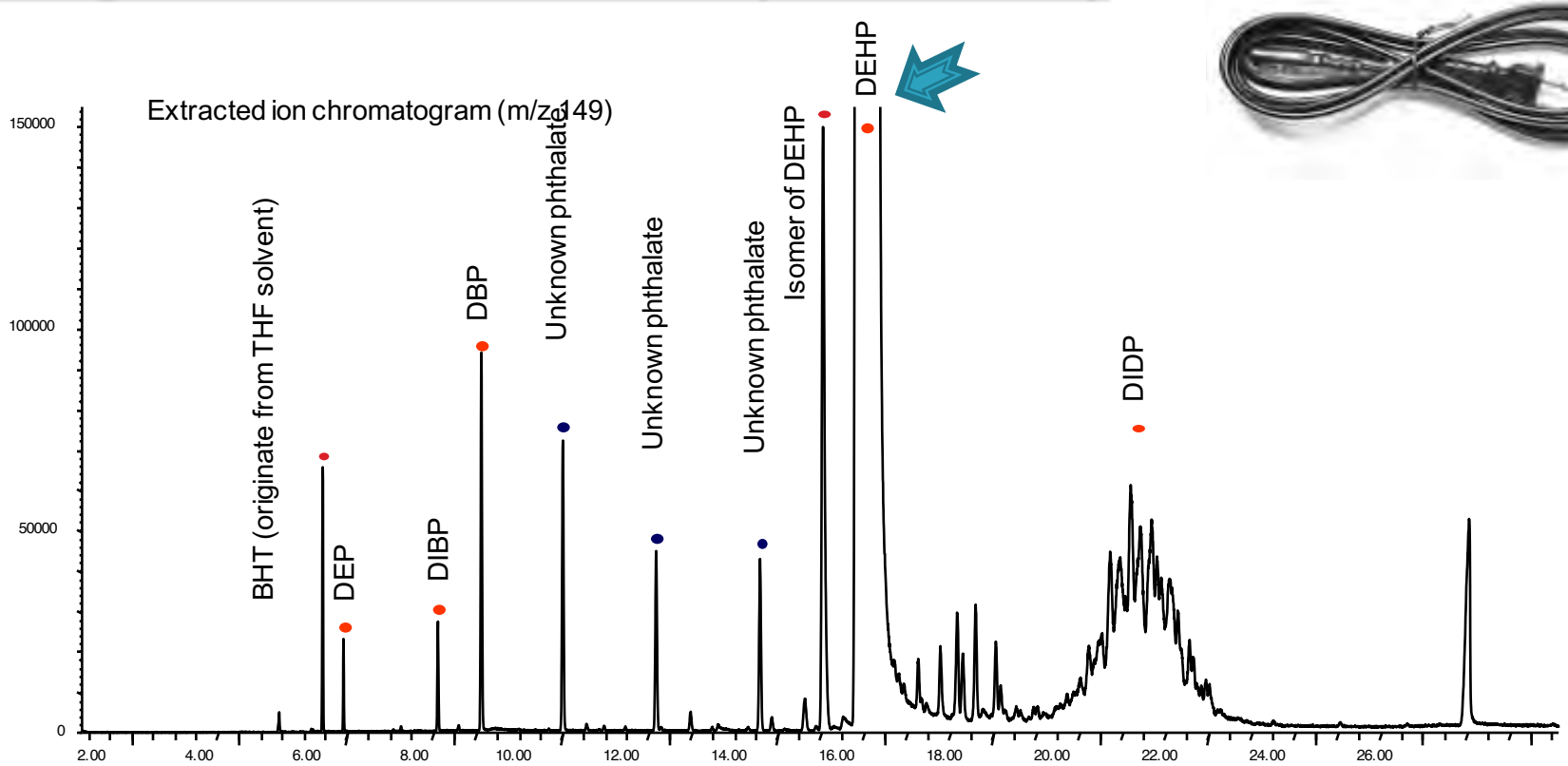
Expanded phthalate target list

These 15 phthalates have been determined using ASTM D7823-13. The six regulated phthalates are highlighted in red. (*DIHP, DIOP, DIDP and DINP are technical mixtures. Care should be taken to ensure that the correct standards are used). Also note that these mixtures will have multiple peaks that need to be integrated and summed together. The column temperature program specified in D7823-13 is modified to ensure resolution of the extended list. GC oven: 40 – 200°C (at 40 °C/min), 200 – 300°C (at 5 °C/min, 1 min hold), 300 – 320°C (at 20 °C/min, 2.5 min hold). Retention times are provided to give the reader a sense of the relative retention of each phthalate using a 5% phenyl/methyl stationary phase column.

RT	Name	Acronym	CAS No.
7.805	Dimethyl phthalate	DMP	131-11-3
8.7	Diethyl phthalate	DEP	84-66-2
9.915	Di-n-propyl phthalate	DRPR	131-16-8
10.6	Diisobutyl phthalate	DIBP	84-69-5
11.34	Dibutyl phthalate	DBP	84-74-2
12.957	Di-n-pentyl phthalate	DPP	131-18-0
14.686	di-n-Hexyl phthalate	DHP	84-75-3
14.778	Benzyl butyl phthalate	BBP	85-68-7
15+	Diisoheptyl phthalate	DIHP	71888-89-6*
16.328	Dicyclohexyl phthalate	DCHP	84-61-7
16.509	Bis(2-ethylhexyl) phthalate	DEHP	117-81-7
17+	Diisooctyl phthalate	DIOP	27554-26-3 *
18.056	Di-n-octyl phthalate	DNOP	117-84-0
18 +	Diisononyl phthalate	DINP	68515-48-0 *
19 +	Diisodecyl phthalate	DIDP	26761-49-1*

Extended target compound list

Phthalates identified in a "power cord" sheath using ASTM D7823-13 (modified)



Thermal desorption temperature: 100 - 320°C @ 20°C/min

GC Injection port: 300°C

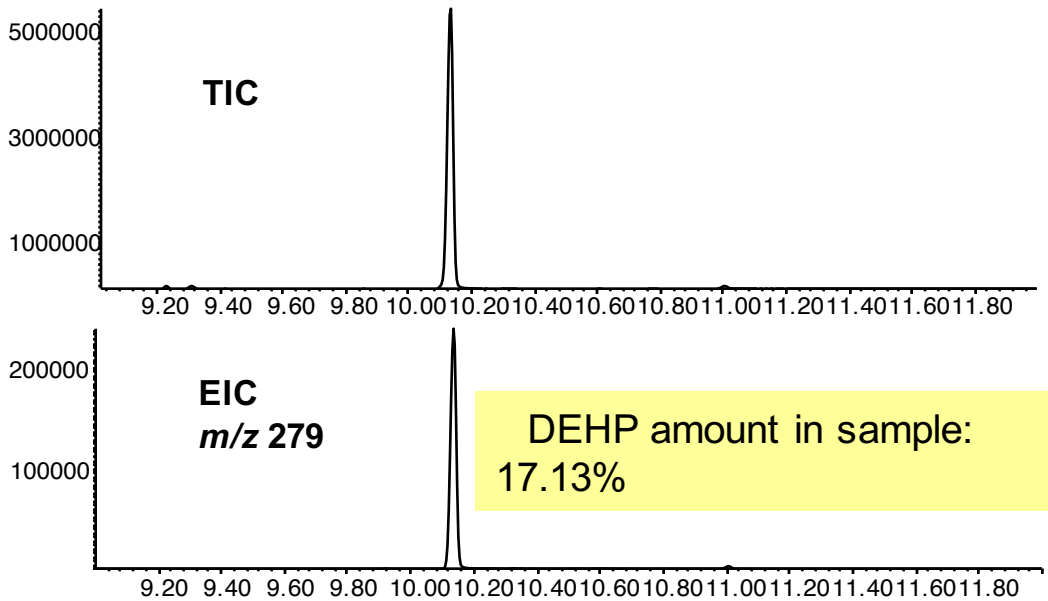
GC Oven: 40 – 200°C (@20°C/min) – 300°C (@20°C/min, 1 min hold) – 320°C (@20°C/min, 2.5 min hold)

Column: Ultra ALLOY-5 (MS/HT) 30m X 0.25mm i.d., 0.5µm film

Column Flow: 1.2 mL/min; Split ratio: 1/20; Scan speed: 4 scans/sec

Sample weight: 2.1 & 200 mg dissolved in 10 mL THF ; 2.1- 200 µg in sample cup

DEHP sample reduced 100X and reanalyzed.



DEHP amount in sample: 17.13%

Sample Name	Sample amount (µg)	Standard addition (ng)	Area
PVC Sample	2.15	0	3059903
PVC Sample + spike	2.15	900	10535796
Quant value (%)			**17.13 %**

Comment: Samples, such as this power cord sheath, can have an immediate and potentially disastrous effect on the instrumentation. High level system contamination is common and will requires time and effort to eliminate.

If possible, "unknown" samples should be screened using Infrared (IR) Spectroscopy [8]. At a minimum, this will flag the sample and it can be initially analyzed at a very high dilution like was done with the power cord sheath.

New Eco-Cup G and GQ

FEATURES

Eco-Cup G

- It is economical, at about half the cost of deactivated stainless steel cups.
- Because of its inertness, it can be used for the analysis of reactive compounds like brominated flame retardants.
- Maximum temperature is 450°C which is ideal for both thermal desorption and reactive pyrolysis applications.

Eco-Cup GQ

- Its quartz surface is the ultimate inert surface.
- Maximum temperature is 600°C.

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SUMMARY

- Thermal desorption (TD) uses heat rather than solvents to isolate target compounds from the polymeric matrix

  → Samples can be analyzed 'as is' (sample homogeneity: Direct *vs* thin film)
  → Eliminates need for special glassware (purchase and certification)
  → Eliminates need for bulk solvents (purchase and disposal)
  → Minimizes worker exposure

- TD-GC/MS facilitates the automation of the entire analytical sequence

- Data quality (precision and accuracy) is, as a rule, better than that obtained when the samples are prepared using conventional solvent-based techniques.

  → Minimal sample processing and hold time
  → Minimizes sample carry-over

Technical Brief

- This 13 page technical brief is available with many additional tips for performing the ASTM D7823 method, including the expanded list of target phthalates.
- roger@frontier-lab.com
- www.frontier-lab.com

A fast, easy and "green" thermal desorption-GC/MS method for the analysis of phthalate esters in PVC

A discussion of the central factors that influence data quality when using ASTM D7823-13[1] for the determination of phthalates in polymeric substrates

R. Freeman, A. Hosaka, I. Watanabe, D. Randle, and C. Watanabe,
Frontier Laboratories

Introduction

Phthalates, which are esters of phthalic acid, have been used in the manufacture of a wide range of consumer products. They are added to plastics to make them more flexible and harder to break. Although the wide-spread use of phthalates in the manufacturing of polymeric products has been largely discontinued, they continue to pose a risk to human health. Phthalates are easily released into the environment because they are not covalently bonded to the polymer; consequently, exposure can be through direct contact, food, water and the atmosphere.

Several phthalates are tightly regulated on a global scale. The United States[2], Canada, the European Union, Japan and many other nations have banned the use of and passed regulations designed to monitor for the concentration of phthalates in consumer products. In the US, Congress has permanently banned three phthalates (DEHP, DBP, BBP) in any amount greater than 0.1 percent (per plasticized component part of a children's toy or child care article). There is also an interim ban on DINP, DIDP and DNOP, which only applies to children's toys that can be placed in a child's mouth[3,4].

Although a number of different analytical techniques can be used to determine the presence of phthalates, most laboratories use solvent based techniques to extract the phthalates from the polymer matrix. The extract is then analyzed using GC or HPLC to separate and quantitate the individual phthalates. "Traditional" sample preparation is, at best, cumbersome, time consuming, costly and does not always completely isolate the phthalates from the polymer matrix. Thermal desorption (TD) is a viable alternative to traditional solvent-based sample preparation.

Thermal desorption is based on the fact that there is free volume within the polymer structure through which small molecules (e.g., phthalates) are free to "move". The motion is due to intermolecular collisions (i.e., Brownian motion). Random motion from regions of high concentration to regions of lower concentration is called diffusion. Factors affecting the rate of diffusion are the solubility and diffusivity of the small molecules in the polymer. Increasing the temperature of a polymer causes the small molecules on the surface to vaporize and the concentration gradient across the polymer to increase. In addition, the permeability of the polymer increases with temperature. These two factors result an even greater flux of small molecules to the surface.

The phthalate vapors are analyzed using GC/MS. Phthalates are identified using both retention data and compound specific ions. The entire process can be automated.

Ask Dave for a copy

Free Technical Brief

Questions?

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Pyrolysis User's Training Course

Lecture and Lab Training on Frontier Lab Pyrolysis Products

- Pyrolysis Demystified
- Hardware Overview
- Pyrolysis GC/MS Use
- Run real samples
- Data review tools
- F-Search Workshop
- Sample Preparation
- Method Development
- Materials Characterization & Unknowns Method Map
- Routine Maintenance
- Common Questions
- Universal Applications
- Advanced Techniques

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Dates	December 6, 7, 8, 2016
Time	9:00 a.m. to 5:00 p.m.
Location	Diablo Analytical
Address	5141 Lone Tree Way, Antioch CA 94531

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Special guest instructor-see next page for details

Register Today!

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Join Terry Ramus, Ph.D., Roger Tank, Business Development Manager, and Itsuko Iwai, Senior Analyst, for 3 full days of lectures and labs. You'll learn how to quickly characterize materials, optimize parameters, perform precise quantitation, and maintain your Frontier pyrolyzer for quality results in your lab. Register early on-line at:
www.diabloanalytical.com **Click on Events, then Frontier Lab Events.**

Airport choices are Oakland (OAK), San Francisco (SFO) or Sacramento (SMF).
*We require a minimum of 3 attendees or we reserve the right to reschedule the class. 10 is the maximum enrollment.

For more information Contact:

Roger Tank
roger@frontier-lab.com
(989) 941–7717

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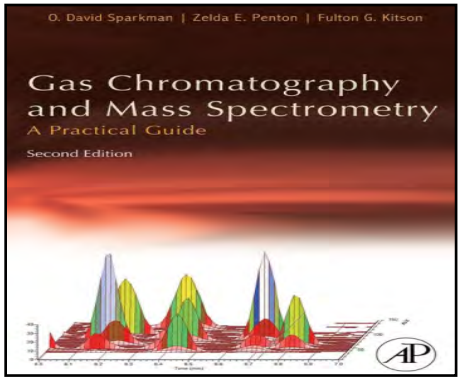
GC/MS Basics

Optional Training on Monday December 7, 2015

- Definition of GC/MS techniques
- Types and components of GC/MS
- Data acquisition requirements
- Columns and injectors
- MS ionization types
- Data Analysis Introduction:

- interpretation
- nitrogen rule
- fragmentation mechanisms
- Introduction to MS databases for identification of unknowns
- Introduction to AMDIS



Provided:

- Lite Breakfast
- Book:

Gas Chromatography and Mass Spectrometry: A Practical Guide, 2nd Edition. O. David Sparkman, et al.

- Lunch
- Refreshments
- Course Materials

Special Guest Instructor:

Dr. O. David Sparkman: Adjunct Professor of Chemistry at University of the Pacific; Contractor to NIST Mass Spectrometry Data Center; Consultant; MS instructor (www.mass-spec-training.com). See LinkedIn for more information.

Dates	December 5, 2016
Time	9:00 a.m. to 5:00 p.m.
Location	Diablo Analytical
Address	5141 Lone Tree Way, Antioch CA 94531

GC/MS Basics

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- 1 Full Day

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Class Size*: 3-10

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Roger Tank
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Join world renowned professor, author, and mass spectrometry expert, Dr. O. David Sparkman, for an information packed day all about GC/MS. The course is optional to the Pyrolysis User's Training Course. Register early on-line at:

www.diabloanalytical.com **Click on Events, then Frontier Lab Events. You can select the optional GC/MS Basics training when you register for the Pyrolysis User's Training Course.**

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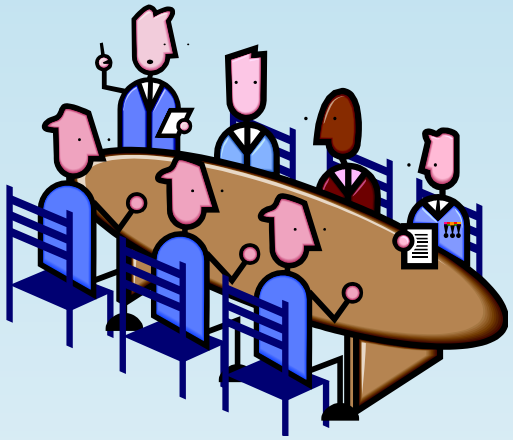
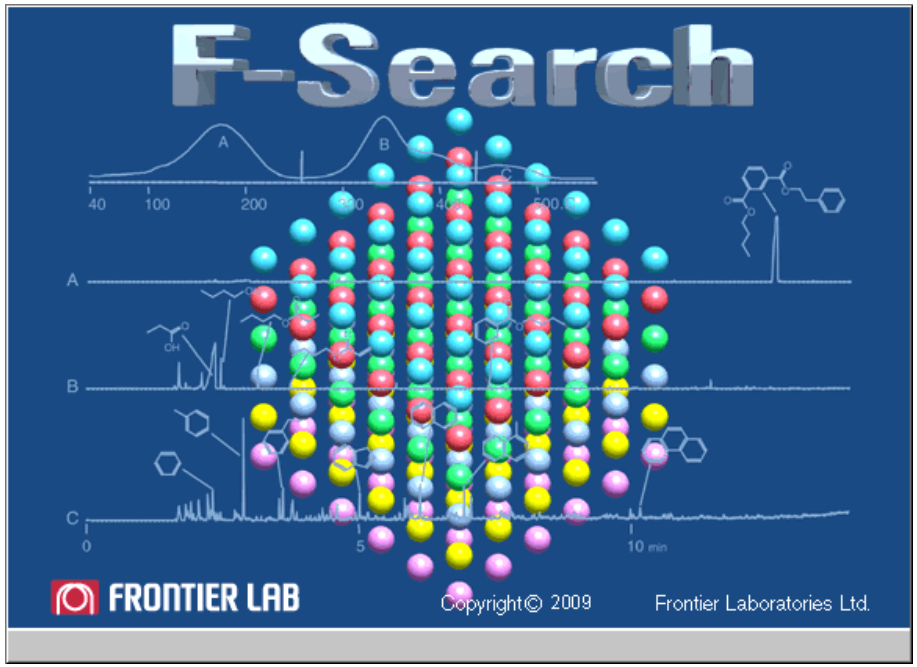
- Break

- Back to conference room at: 1:45 pm



F–Search Overview



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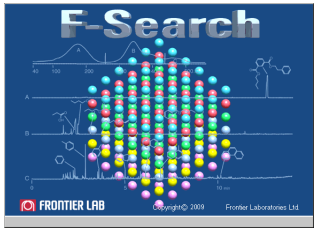
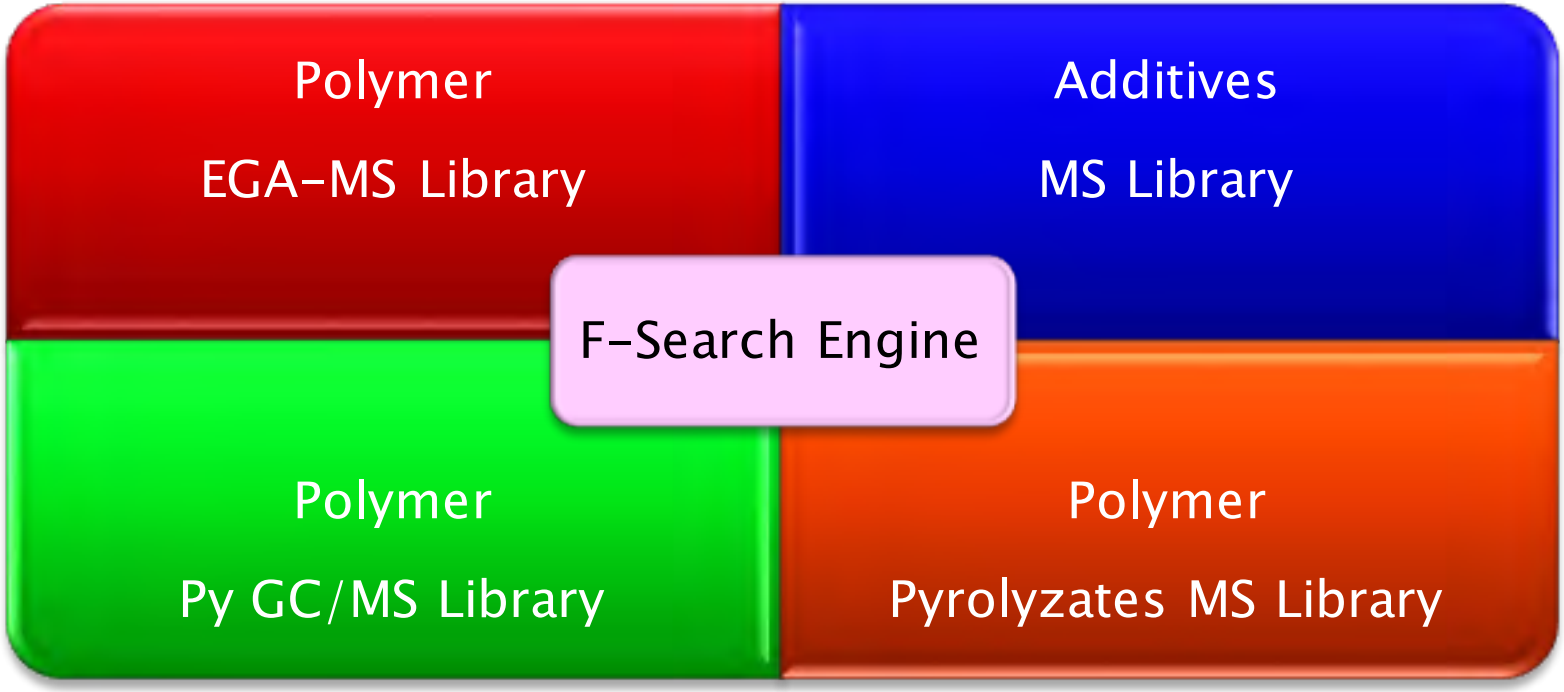
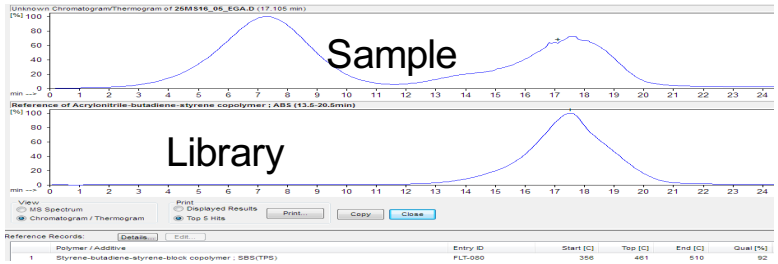
F-Search System

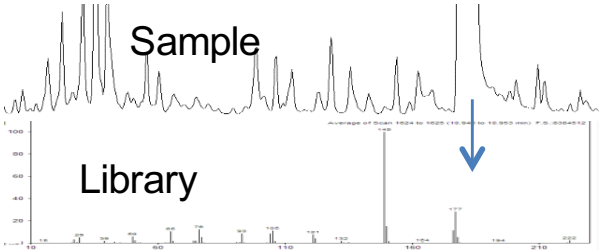


- F-Search is a data interpretation system that consists of a patented search engine software and four unique mass spectral libraries.



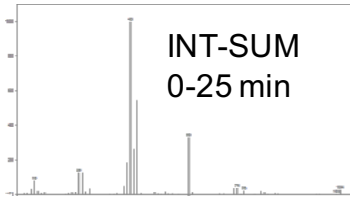
F-Search Libraries are Unique

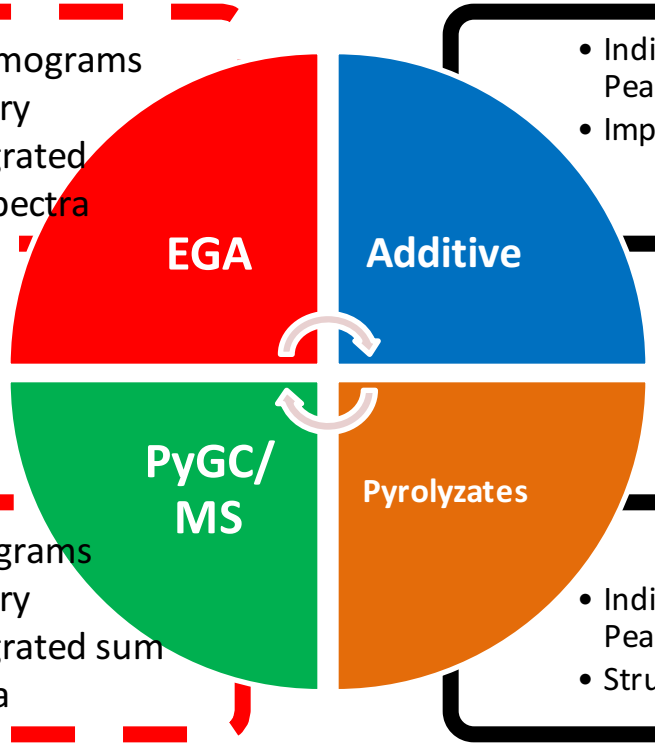


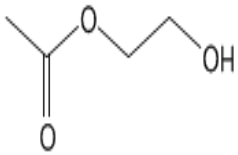


> Thermograms
In library
> Integrated
Sum Spectra

- Individual Peak Spectra
- Impurities

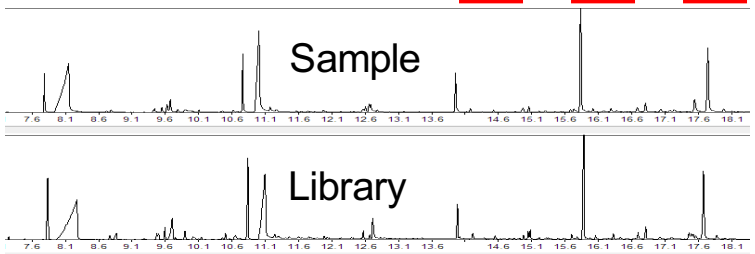


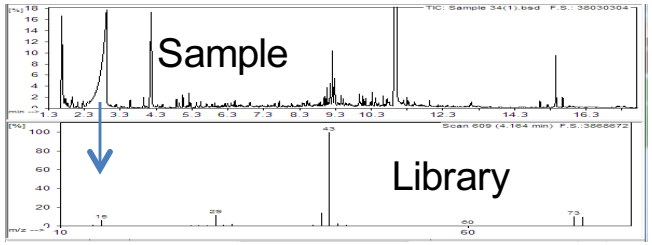




> Pyrograms
In library
> Integrated sum
Spectra

- Individual Peak Spectra
- Structures





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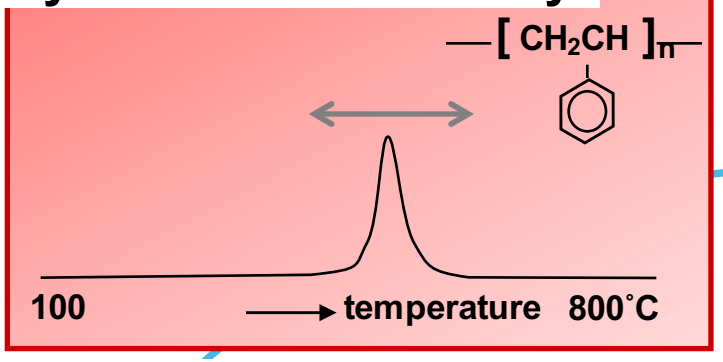
Overview of F-Search system

700 polymers

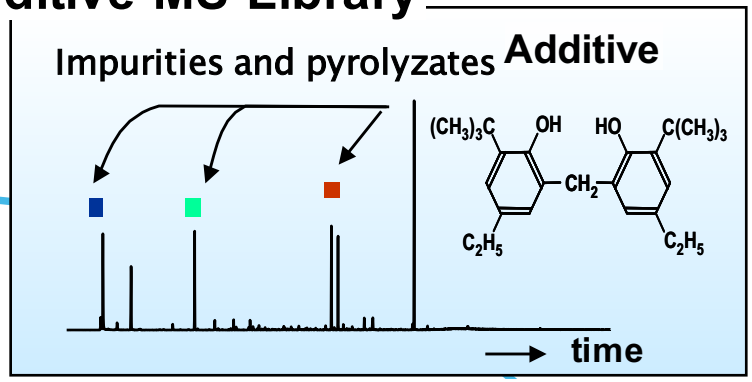
Polymer EGA-MS Library



Thermogram (Entire information)

Additive-MS Library

494 Additives

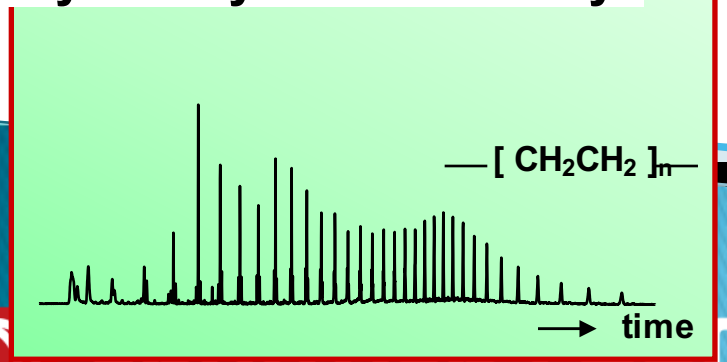


TD / Py chromatogram
(Individual information)

F-Search ver 3.5

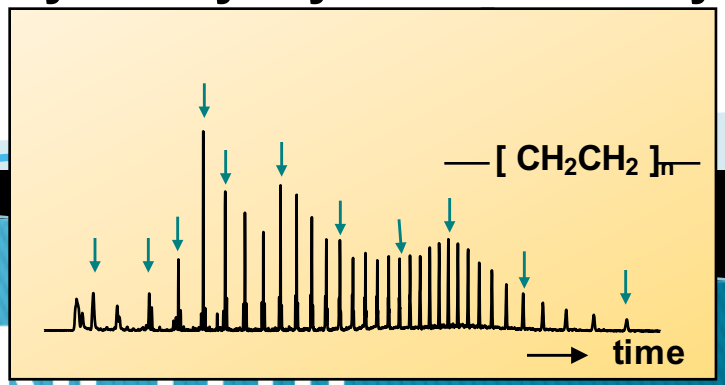
700 polymers

Polymer-PyGC-MS Library



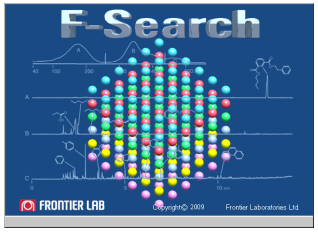
Pyrogram (Entire information)

Polymer Pyrolyzate-MS Library



Pyrogram (Individual information)

F–Search Features

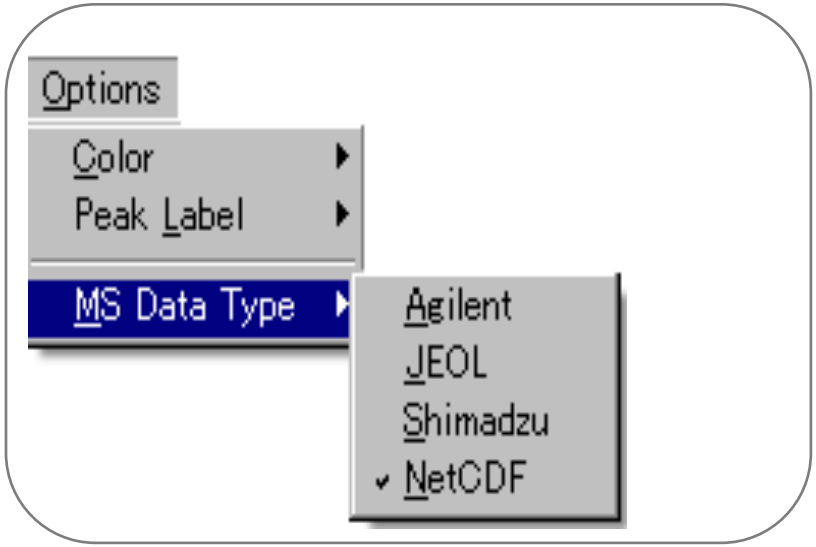


- **The search software F-Search allows you to quickly search different types of data such as pyrograms and EGA data.**
- **It can also accommodate various GC/MS data formats for your convenience.**

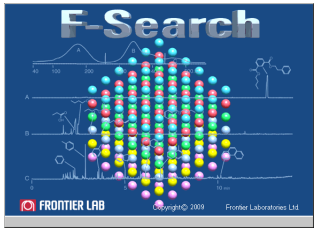
Because the unique search algorithm is used to compare mass spectra, candidate compounds are instantly displayed. Also, the search can be simultaneously performed across multiple libraries.

GC/MS data formats of Agilent, Shimadzu, and JEOL can be directly read without any translation or conversion, while other data formats can also be read upon converting to AIA format (NetCDF) files.

Compatible with major GC/MS systems



F–Search Features



The unique search algorithm employed in F-Search is not greatly influenced by the factors such as changes in analytical conditions and separation columns.

How can F-Search engine accomplish this?

- This is because the mass spectral database of pyrograms are grouped: C1 through C10 , C1 through C20 and C1 through C44.
  - This grouping provides reliable search results independent of the analytical conditions.
- The spectra of pyrograms in the PyGC/MS library are an integrated sum of all pyrolyzate peaks.
  - Therefore the resulting integrated sum spectra is independent of the peak elution order or retention times.

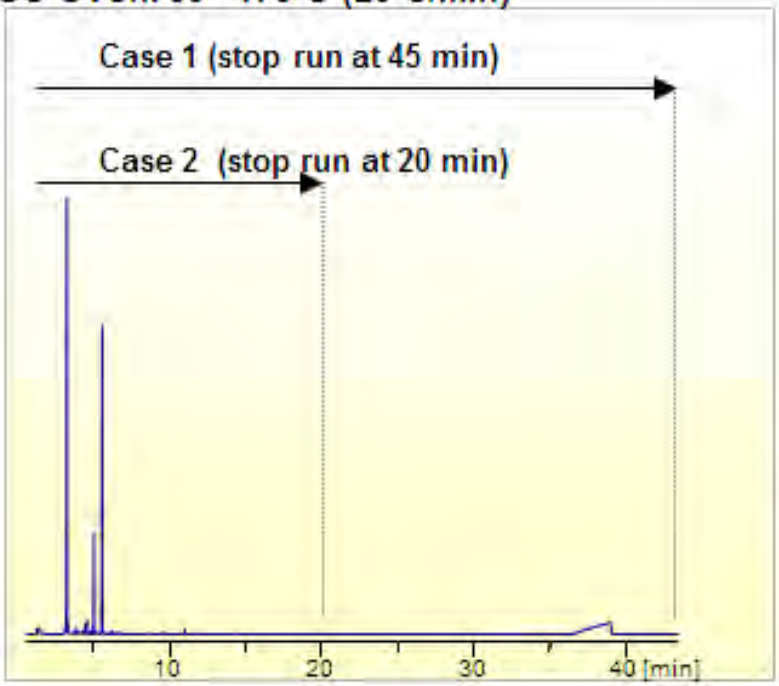
F–Search example 1

Two runs (different run times)—same library result

Data 1

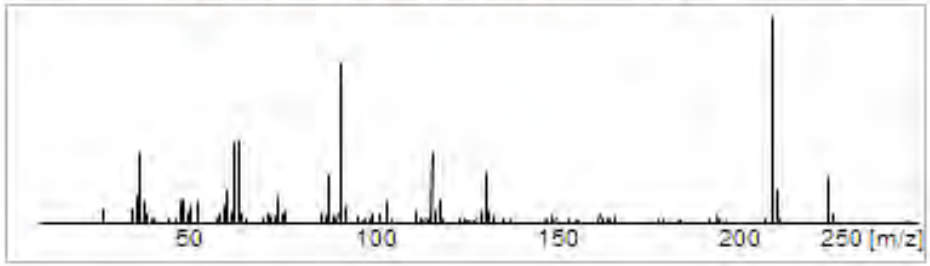
Py Temp.: 600°C, Col: UA-5 (MS/HT) (30 m, 0.25 mm i.d., 0.25 µm)

GC Oven: 60 - 170°C (20°C/min)



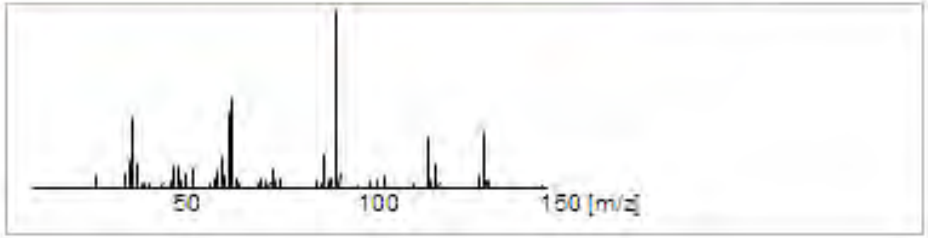
Case 1 (mass spectrum of the peaks detected from 0 to 45 min)

	Polymer/Additive	EntryID	Qual[%]
1	Bismaleimide triazine resin ; BT resin (C1-C40)	P(FL)-107	84
2	Polycarbonate (thermally stabilized) (C1-C40)	P(FL)-130	63
3	Polycarbonate(melt method) ; MM-PC (C1-C40)	P(FL)-127	61



Case 2 (mass spectrum of the peaks detected from 0 to 20 min)

	Polymer/Additive	EntryID	Qual[%]
1	Polycarbonate (solvent method) ; SM-PC (C1-C10)	P(FL)-128	80
2	Polyetherimide ; PEI (C1-C10)	P(FL)-108	79
3	Polyarylate ; PAR (C1-C10)	P(FL)-120	79
⋮			
14	Bismaleimide triazine resin ; BT resin (C1-C20)	P(FL)-107	76

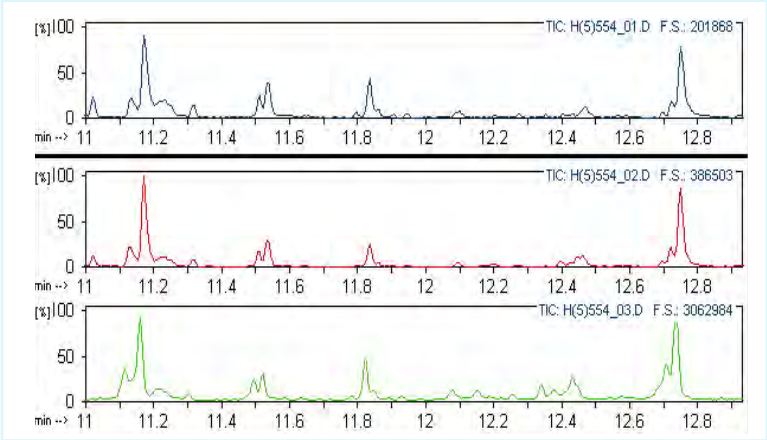


Case 1 result C1-C40. 84% match

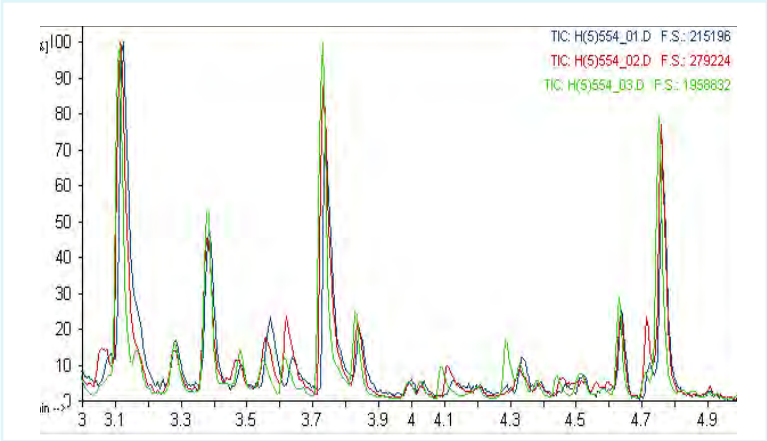
Case 2 result C1-C20. 76% match

New Functions of F-Search 3.2 (Search Engine)

1. Overlay of Multiple TICs

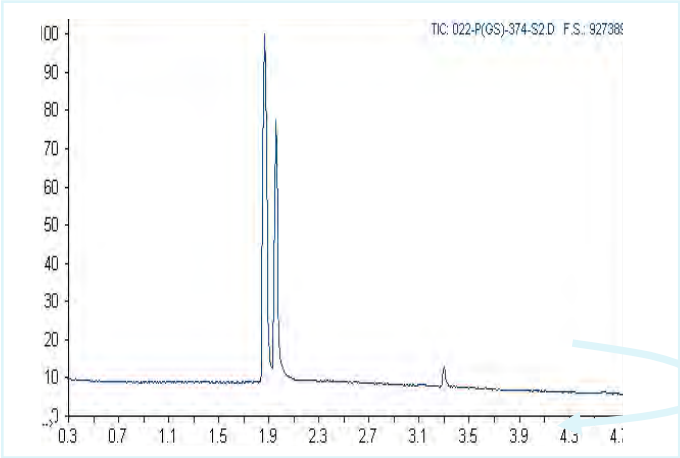


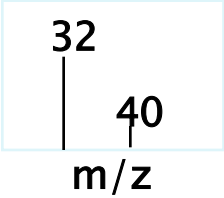
Separate display of TICs

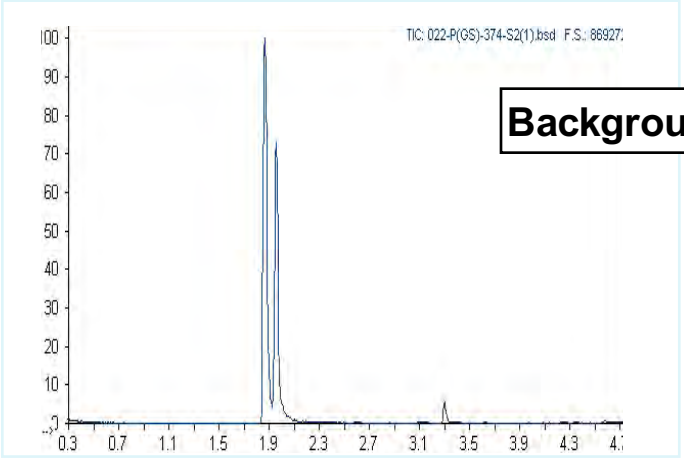


Overlay display of TICs

2. Subtracting a mass spectrum from a TIC





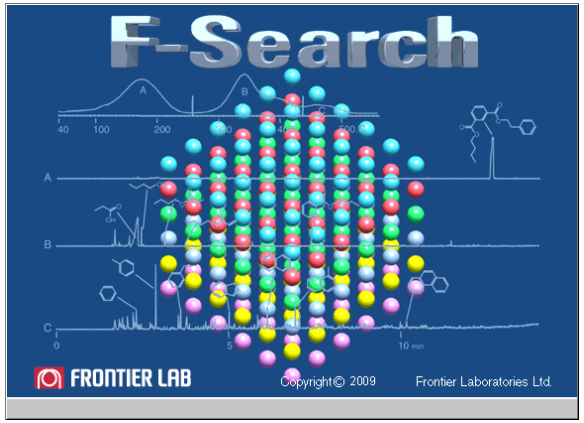


Background Subtraction

F-Search Demo Videos

www.frontier-lab.com

Support>Video>Demo



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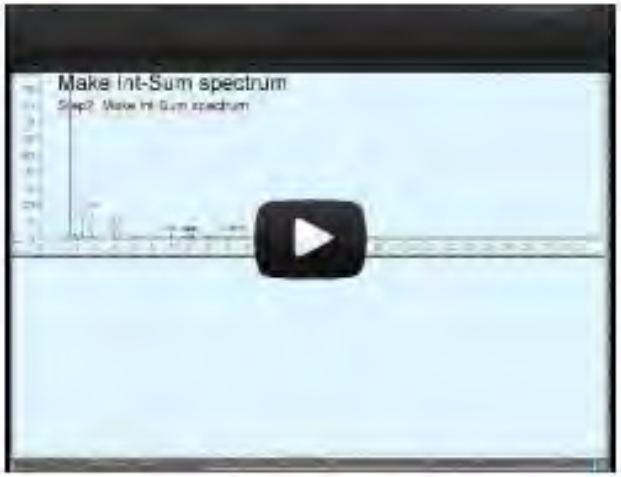
Demo Video

1	F-Search system - EGA library	Jan. 25, 2012
2	F-Search system - Polymer library	Jan. 25, 2012
3	F-Search system - Pyrolyzate library	Jan. 25, 2012
4	F-Search system - Additive library	Jan. 25, 2012
5	F-Search system - 2D Mass Chromatogram Display	Jan. 25, 2012

F-Search system - EGA library

F-Search system - Polymer library



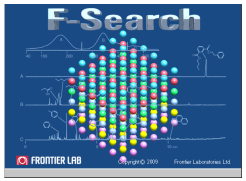
Acknowledgments

- Getty Conservation Institute, Michael R. Schilling, for supplying the MS data files for this demonstration.
  - POPART Py-GC/MS research team: Henk van Keulen (RCE); Nathalie Balcar (C2RMF).
  - GCI: Giacomo Chiari – Chief Scientist; Tom Learner, Emma Richardson, Rachel Rivenc, Herant Khanjian, Joy Mazurek, Alan Phenix.
  - Frontier Laboratories Ltd:, Dr. Chu Watanabe – President, Stephanie Matsui, Miho Sugawara, Bob Freeman, Dave Randle.

F-Search Hands On (answer)

Data name	Purpose	Polymer, additives	Match (%)	Tsuge book page
sample14.d	Find Polymer			
Sample8.d	Find Polymer			
Sample5.d	Find Polymer			
S1	• Find Polymer • Find additives (at least 2 additives) If needed, See EGA data too.			
Sample34.d	• Find Polymer • Find additives (at least 2 additives) If needed, See EGA data too.			
S2	Find Polymers (mix?)			
S3, S4	What is different between 2 data set?			

Instructions and Tips



Instructions for F-Search Workshop v1.0

All data files are preloaded on the PC.
Open F-Search
Load the data file from the list.
Examine pyrogram for major peaks, possible additives, background, etc.
- Use zoom feature: left mouse click and drag.
- To zoom out, double click with left mouse button.
- To get a spectrum double click with right mouse button.

To do a global background subtraction, find a portion of pyrogram (usually near the end of the run) and right click and drag for 2-4 minutes range.
- Select File, Subtract Background. Pyrogram will change and show .bsd on file name to remind you this was background subtracted.

Select PyGC-MS and Detect Peaks. You will see the peaks are integrated and baselines are drawn.
- You can zoom in to see if the integrator worked well or not. If okay go to next step, otherwise go back and change integrator parameters such as min. intensity or peak width, then integrate again.

Select PyGC-MS and Make Mass Spectrum.
- Start with the complete time range (default) and click OK. You will see the INT-SUM or integrated-sum spectrum in the lower window.
- Select Library, Select Libraries for Search, and check Pyrogram (Polymer Search)

Right double click on the spectra window. You will get a library match with a spectra and list of candidates.
- Click on the candidate list to compare spectra. These are integrated sum spectra.
- You can also switch views from MS Spectrum to Chromatogram/Thermogram by checking the radio buttons. This is very handy.
  - When in the Chromatogram/Thermogram view you are seeing pyrograms in the F-Search library!
    - You can use the zoom feature and compare you sample pyrogram to the library pyrogram in great detail.

F–Search Workshop

- Roger will demo one file (Sample 14.D) and you can follow along.
- All the data files are loaded on the PC; start with Sample 8.D.
- Focus on pyrograms today.
- Itsuko and Roger are here to help you, but you all have to run the mouse and do the work.
- Write down your best answers and move to next sample data file.
- Complete as many as you can

Complete F-Search Workshop

- Groups of 1-2 per PC
  Write down answers/notes
  Final Review at 2:40 p.m.

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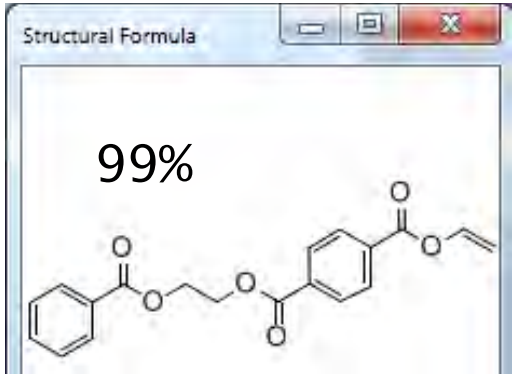
F–Search answers

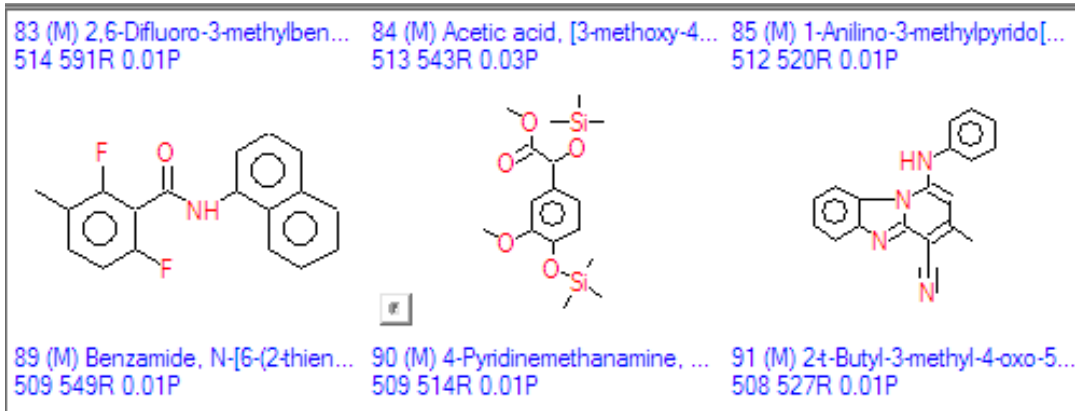
F-Search Hands On (answer)

Data name	Purpose	Polymer, additives	Match (%)	Tsuge book page
sample14.d	Find Polymer	PS	99	42
Sample8.d	Find Polymer	PET	98	238
Sample5.d	Find Polymer	PBT	93	240
S1	• Find Polymer • Find additives (at least 2 additives) If needed, See EGA data too.	Natural Rubber (Nonflex QS, Ozonoc 6C)	96 96 99	154
Sample34.d	• Find Polymer • Find additives (at least 2 additives) If needed, See EGA data too.	Cellulose Acetate Phthalates (DEP, DEHP)	97 91 99	310
S2	Find Polymers (mix?)	PBMA,PMMA	94, 97	82,84
S3, S4	What is different between 2 data set?	S3,S4 are both FEP and PTFE	94 96 97	130,131

F-Search Hands On

Data name	Polymer	Reason/Comments	Tsuge book page
sample14.d	PS	Monomer, dimer and trimer	42
Sample8.d	PET	Easy — Note Biggest peaks are not in NIST (F. G)	238
Sample5.d	PBT	Easy2 — Structure is similar, but pyrograms are different	240
Sample34.d	CA	Subtract DEP, the search result improves very much. Run EGA first and phthalates are obvious.	310





NIST all wrong hits for PET peak F

NIST Generates Poor Search Match Candidates for many PET Pyrolyzates

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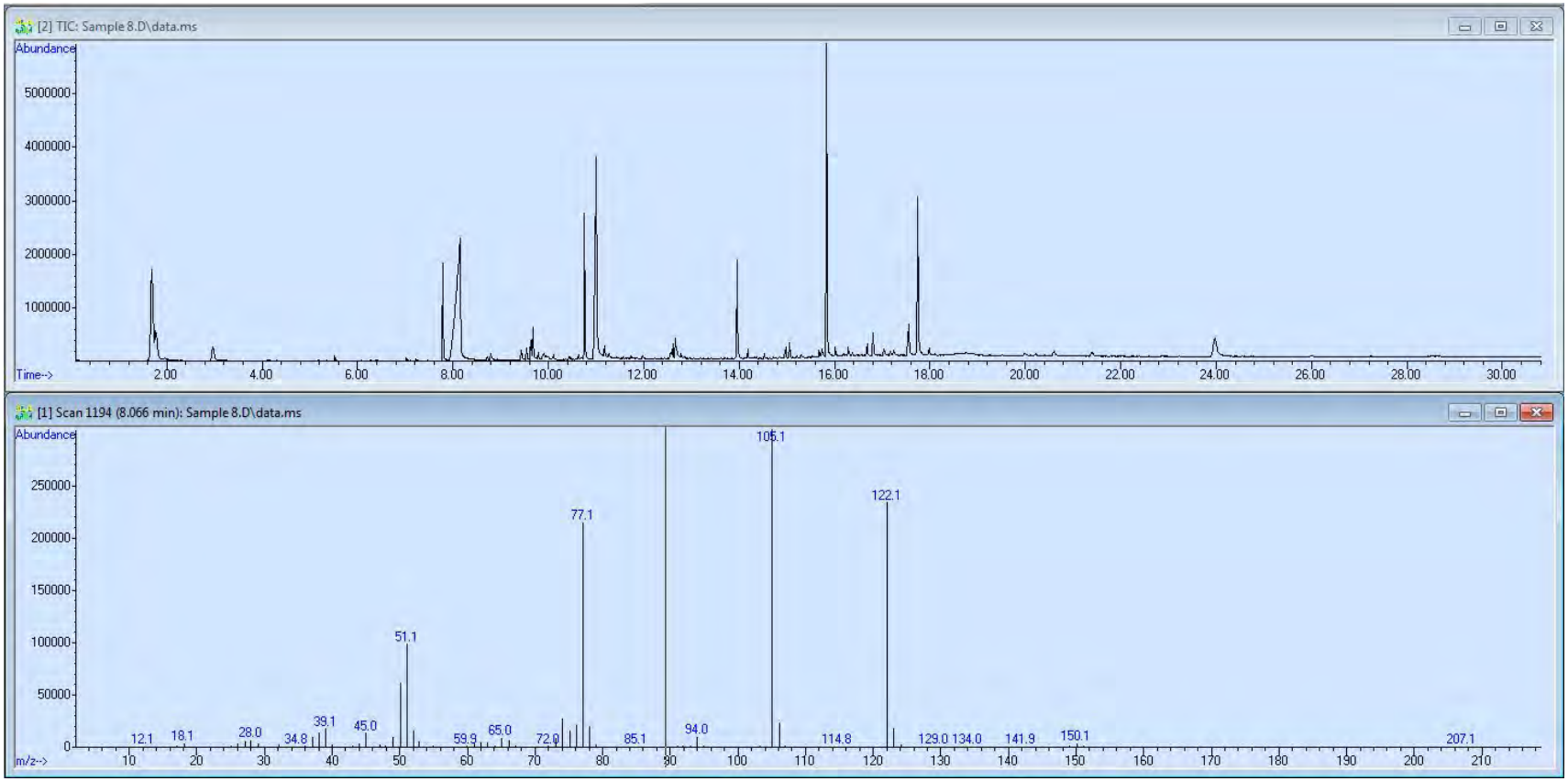
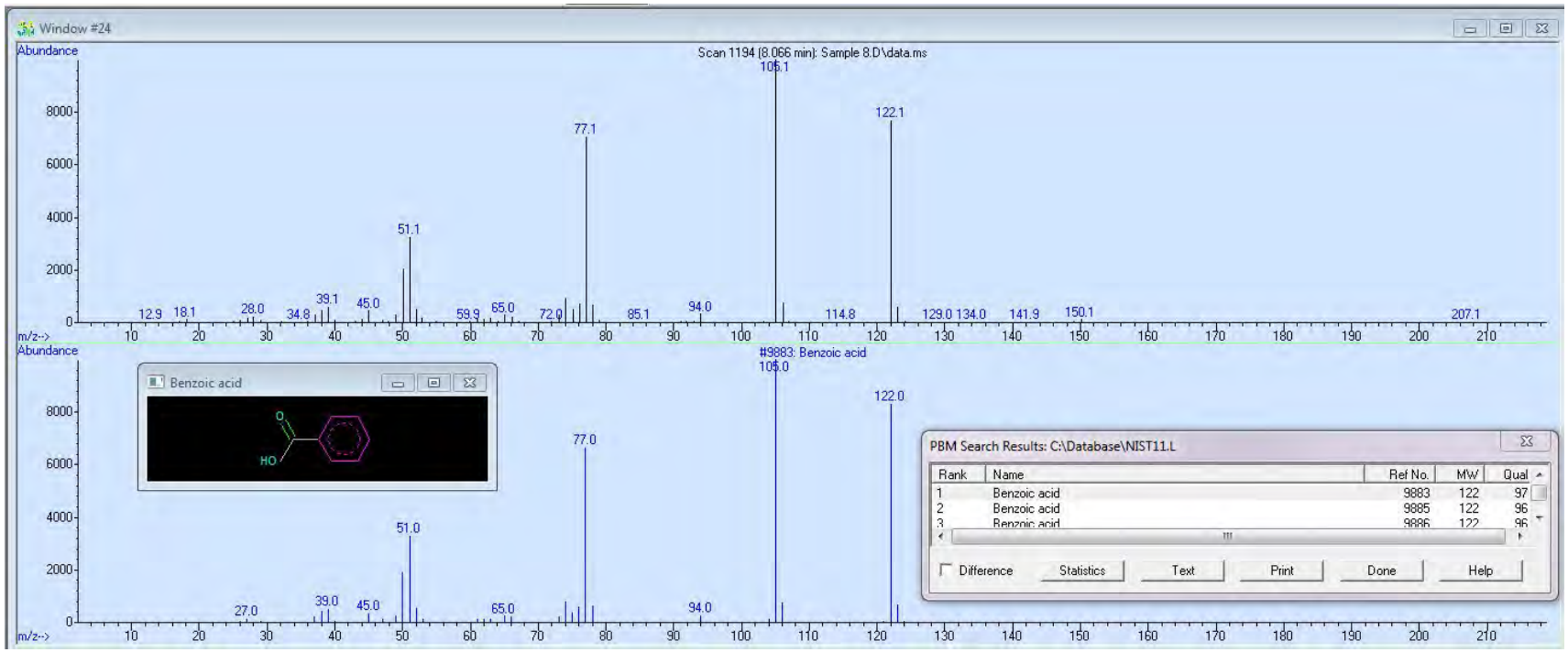
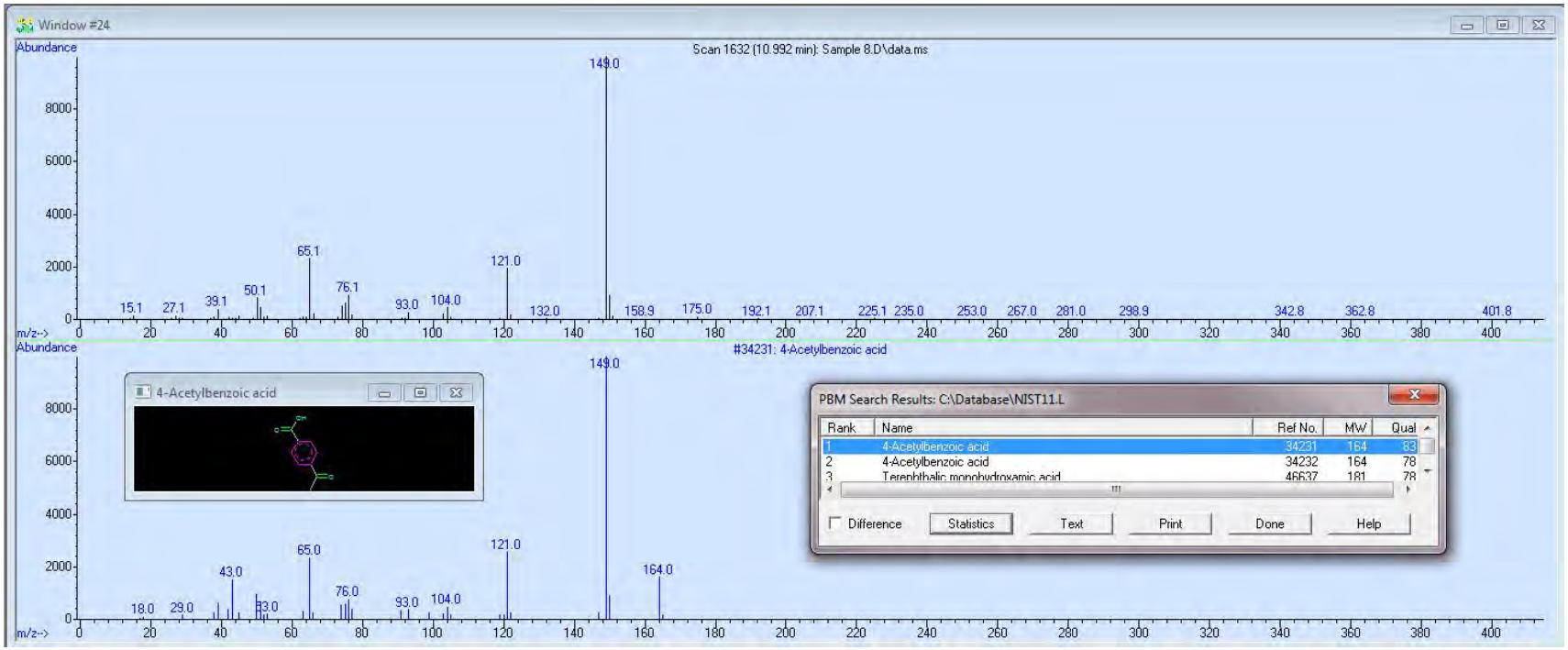
Pyrogram for PET – What are the Pyrolyzates?



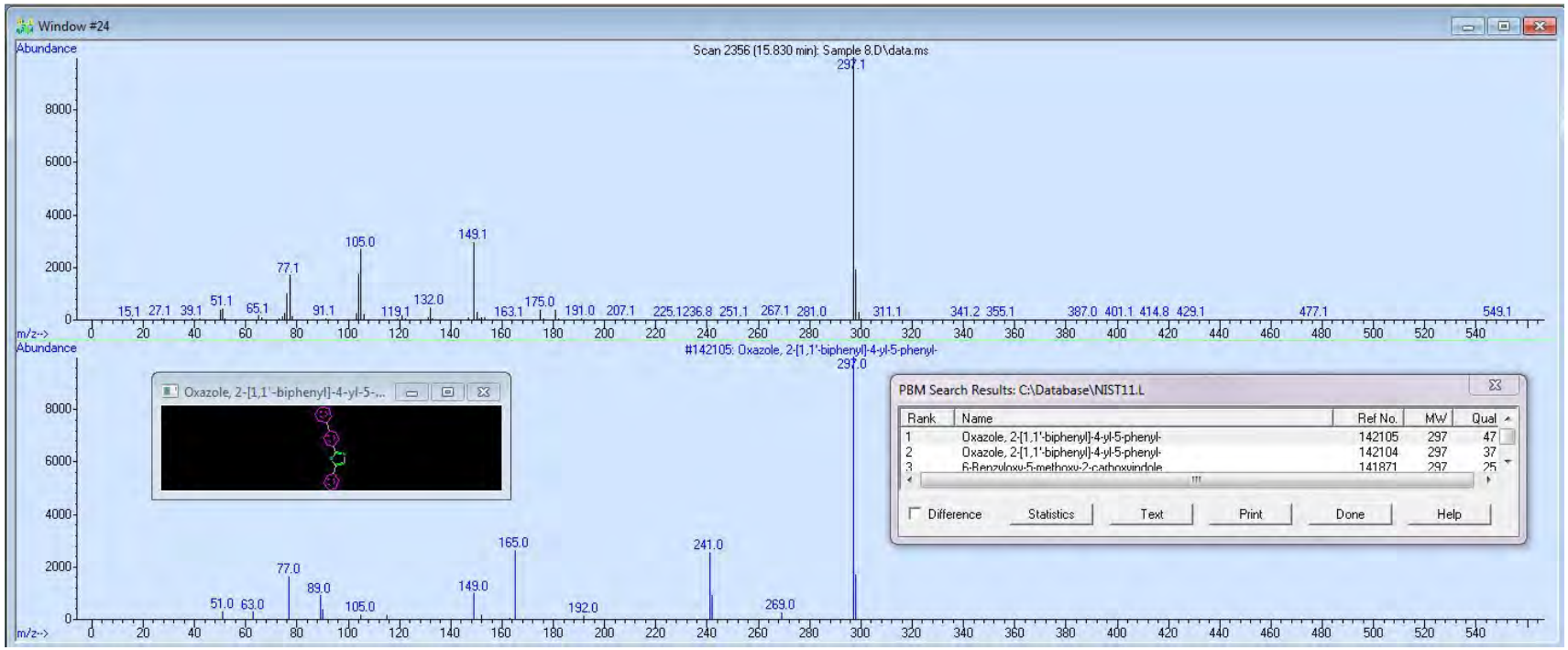
PET Pyrolyzate at 8.07 min. – Benzoic Acid – Good Match with NIST Library (97)



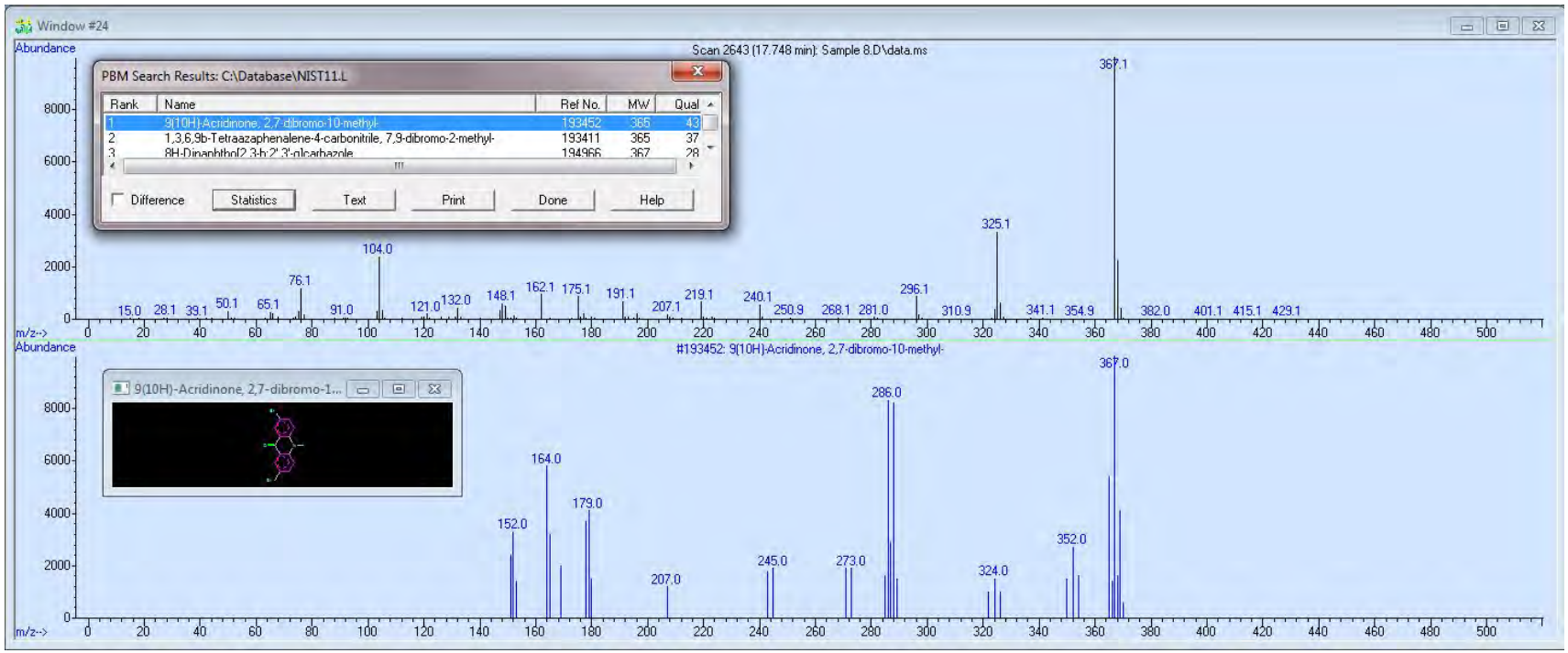
PET Pyrolyzate at 11.03 min. – Poor Match with NIST Library (83)



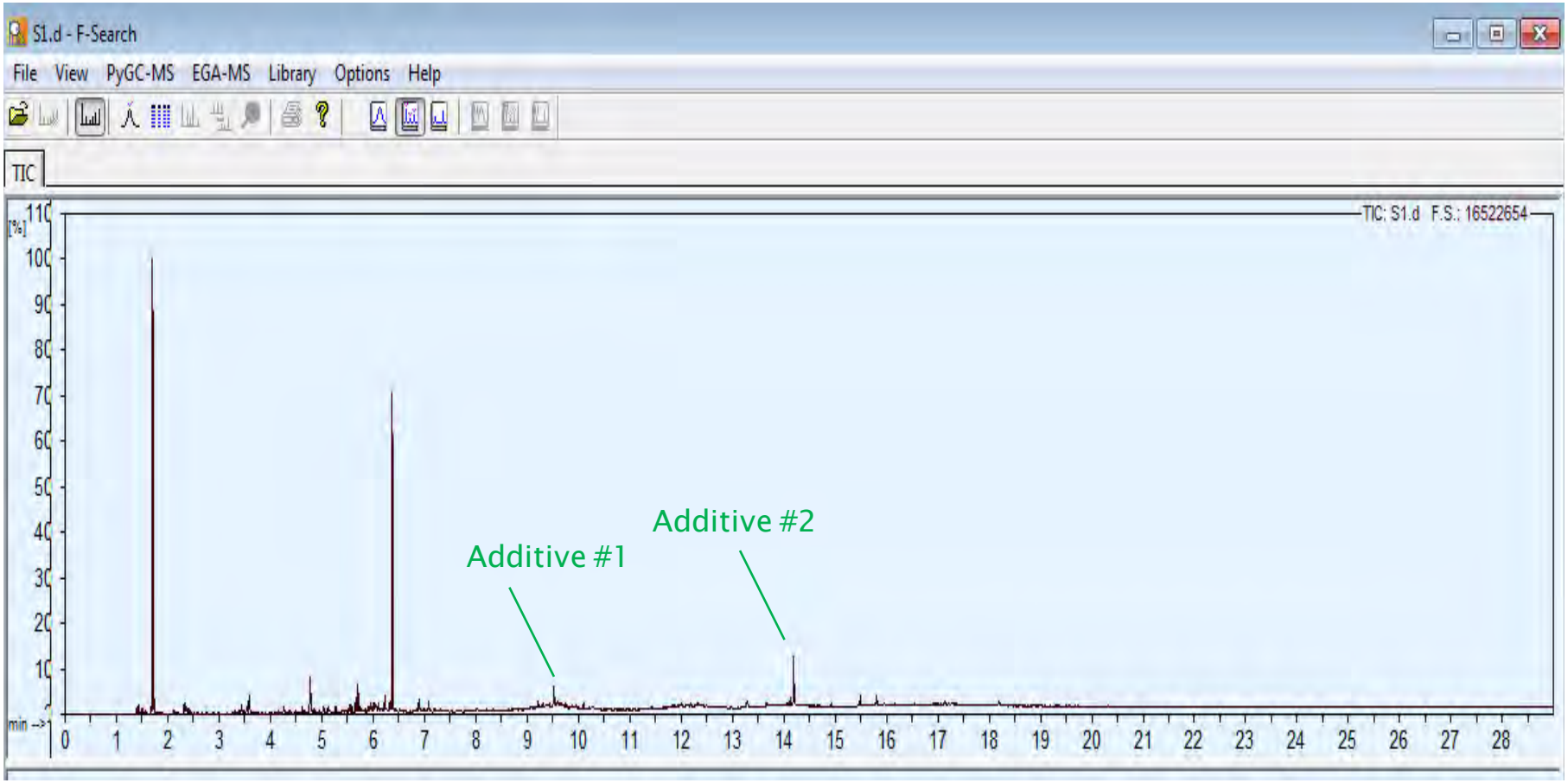
PET Pyrolyzate at 15.83 min. – Poor Match with NIST Library (47)



PET Pyrolyzate at 17.75 min. – Poor Match with NIST Library (43)



S1



Hint 1 polymer 2 additives (at least)

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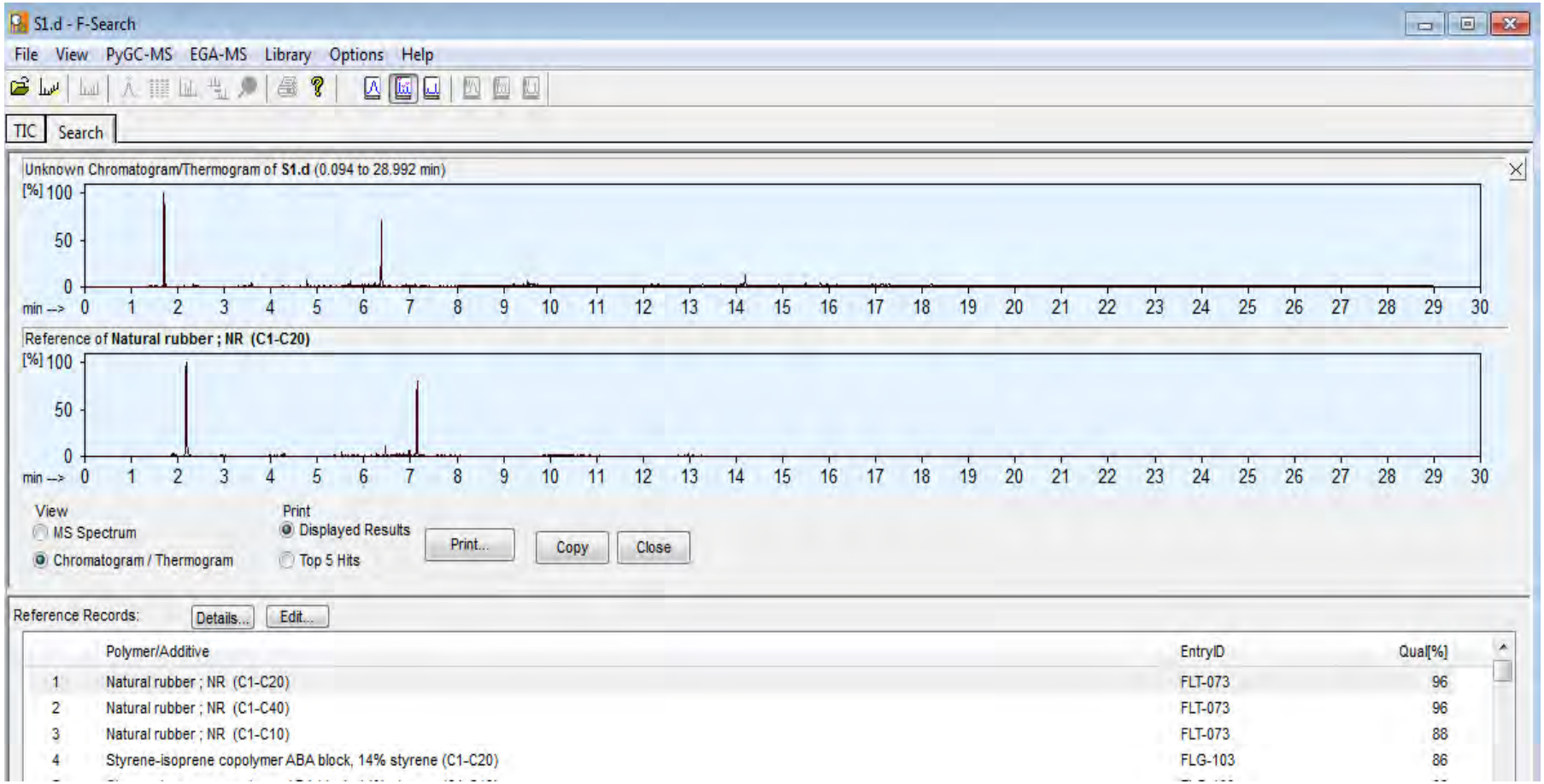
S1



Natural Rubber Match Qual.
96%

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Additive #1

File View PyGC-MS EGA-MS Library Options Help

TIC Search

Unknown Mass Spectrum of **S1.d** (9.521 min)

Reference of 2,2,4-Trimethyl-1,2-dihydroquinoline: Polymerized 2,2,4-trimethyl-1,2-dihydroquinoline

View: MS Spectrum / Chromatogram / Thermogram

Print: Displayed Results / Top 5 Hits

Print... Copy Close

Entry Information : ADD-MS13B.fl

Polymer / Additive	Polymerized 2,2,4-trimethyl-1,2-dihydroquinoline
Compound	2,2,4-Trimethyl-1,2-dihydroquinoline
Mol.Formula	C12H15N
Mol.Weight	173.12
Entry ID	W(1)-001
Ref.No	#12949
Peak ID	
Retention Index	1464
Ret. Time	9.863 [min]
Miscellaneous Information	Additive; Synonyms: Nocrac 224(Ouchishinko Chemical Industrial), Nonflex QS(Seiko Chemical), Antage RD(Kawag

Include in search

Advanced >> Print... Close

Reference Records: Details... Edit...

	Peak	Assignment	Polymer / Additive	Entry ID	Rt Idx	Rt Time
1		2,2,4-Trimethyl-1,2-dihydroquinoline	Polymerized 2,2,4-trimethyl-1,2-dihydroquinoline	W(1)-001	1464	9.86
2		2,2,4-Trimethyl-1,2-dihydroquinoline	Reaction production of amine and acetone	W(1)-005	1462	9.85
3		2,2,4-Trimethyl-1,2-dihydroquinoline	Reaction product of diphenylamine,aniline and acetone	W(1)-004	1464	9.86
4		Dimer of 2,2,4-Trimethyl-1,2-dihydroqui...	Reaction production of amine and acetone	W(1)-005	2755	16.04
5	BB	Bromobenzene	Brominated Polycarbonate ; Br-PC	FLT-131	937	5.94
6	c	Unidentified	Cellulose acetate butyrate ; CAB	FLTR-149	1225	8.57
7		Dimer of Reaction product of diphenyla	Reaction product of diphenylamine aniline and acetone	W(1)-004	2806	16.23

Structural Form...

Ready VIEW LIB

2,2,4-Trimethyl-1,2-dihydroquinoline (Nonflex QS) Match Qual 96%

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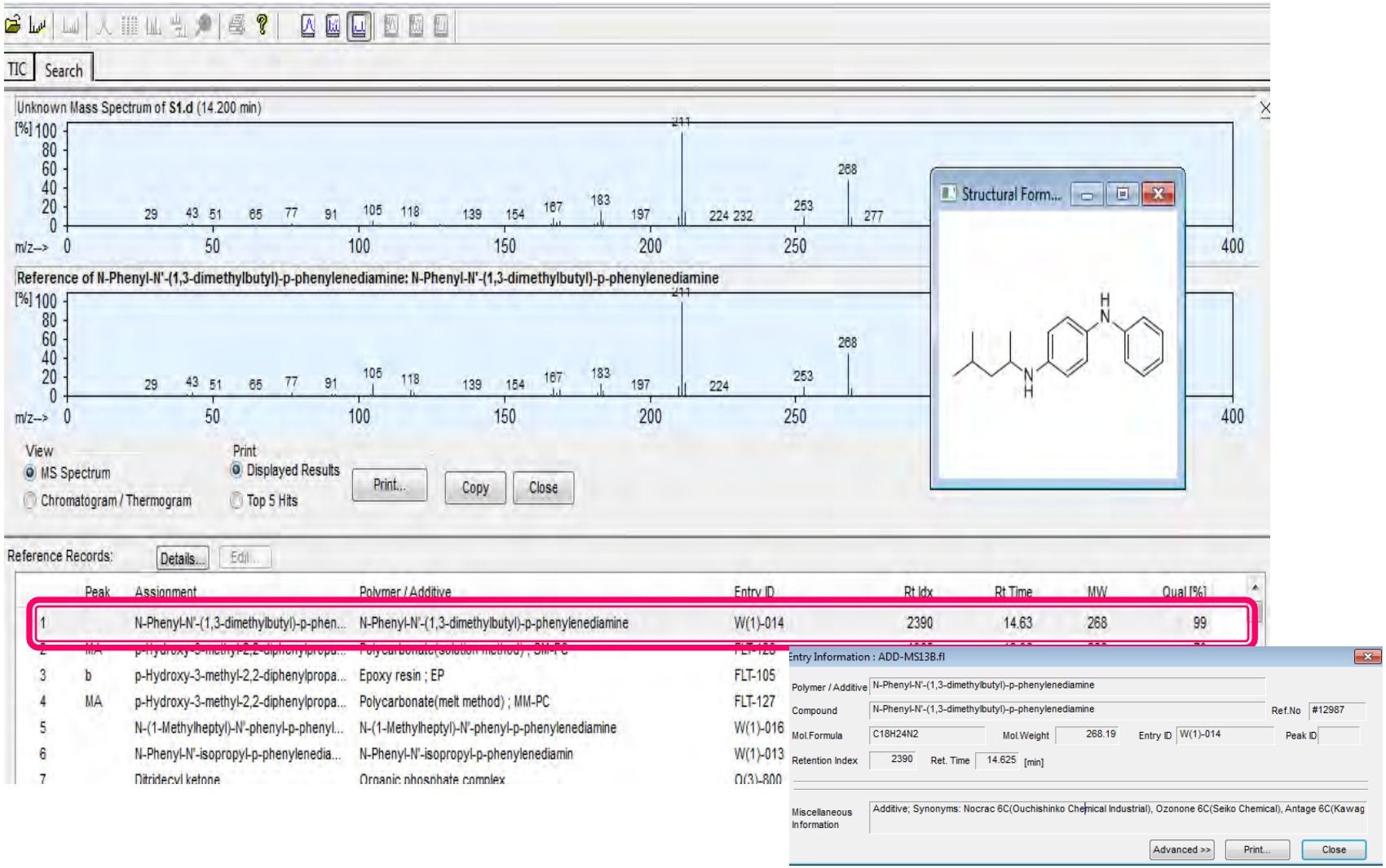
Additive #2



N-Phenyl-N'-(1,3-dimethylbutyl)-p-phenylenediamine (Ozonoc 6C) Match Qual 99%

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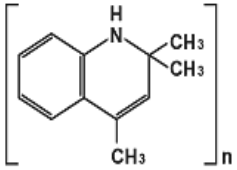
NONFLEX QS

Polymerized 2,2,4-trimethyl-1,2-dihydroquinoline



Properties	Applications
Appearance : Light brown pellets Melting Point : 55°C min. Ash : 0.3% max. Heating Loss : 0.5% max.	An efficient antioxidant for general purpose use in natural and synthetic rubber products. The polymerized protective agent tends to low bleed, low bloom and less volatile, effects against heat and flexcracking.Good dispersibility and less contamination despite amine-type. No effect on scorch and physical properties of peroxide vulcanized rubber, however, it tends to accelerate vulcanization in CR application. (Recommended dosage : 0.5 ~5.0 phr)

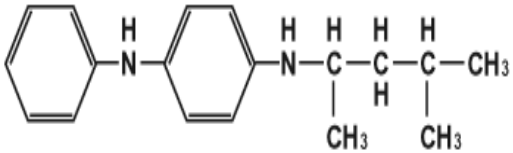
Packing : 20kg Paper bag

CAS RN 26780-96-1

CLOSE

OZONONE 6C

N-(1,3-Dimethylbutyl)-N'-phenyl-*p*-phenylenediamine



Properties	Applications
Appearance : Dark purple beads Melting Point : 47°C min. Ash : 0.1% max. Heating Loss : 0.3% max.	An excellent antiozonant providing good protection against heat, oxygen, ozone and flexcracking. In addition, OZONONE 6C features good compatibility with rubbers, low volatility and moisture resistance which permit the long-lasting potency, and causes no significant skin irritation. (Recommended dosage: 1~3 phr)

Packing : 20kg paper bag

CAS RN 793-24-8

Two of Antioxidants in the sample

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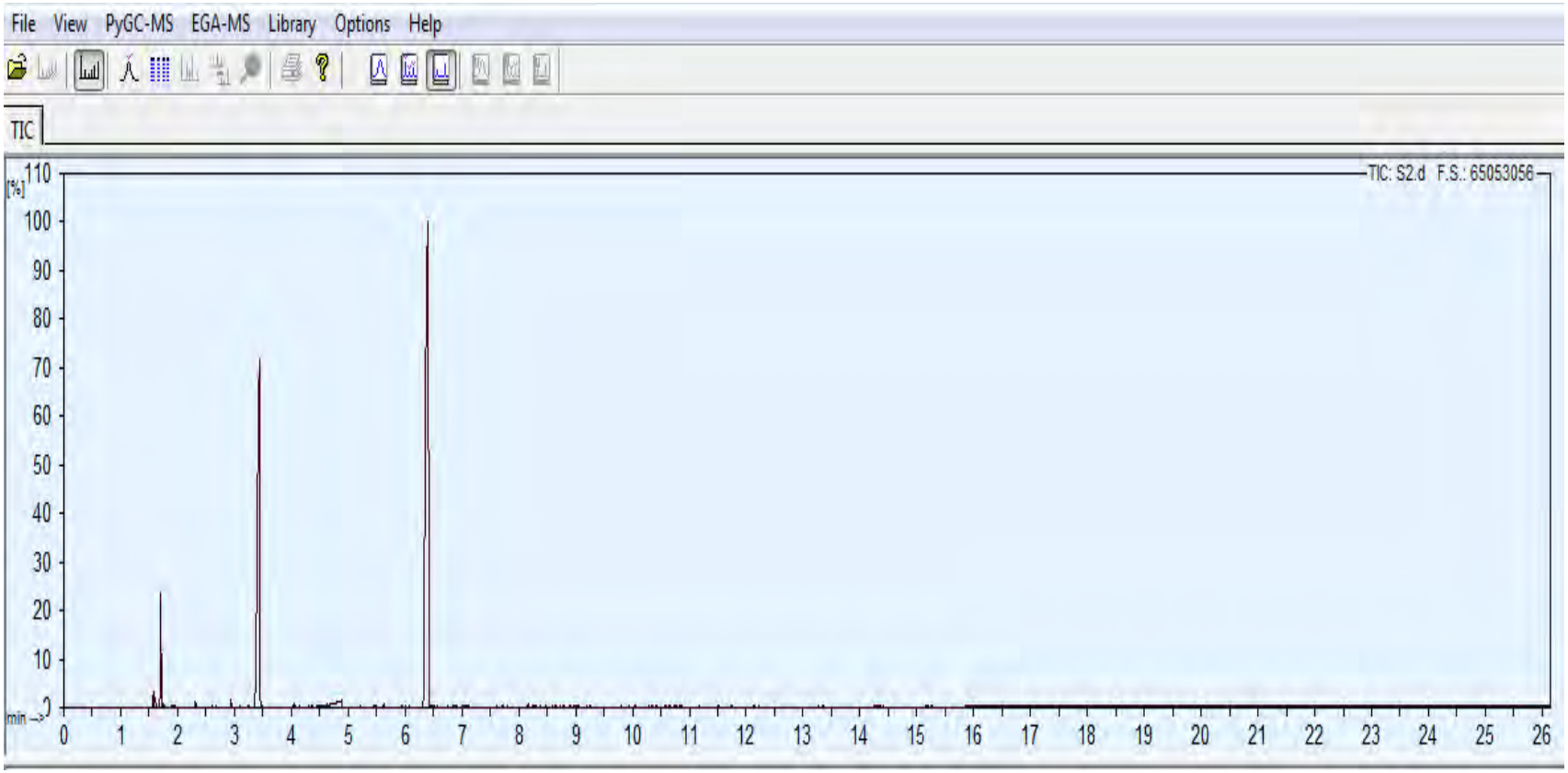
S2



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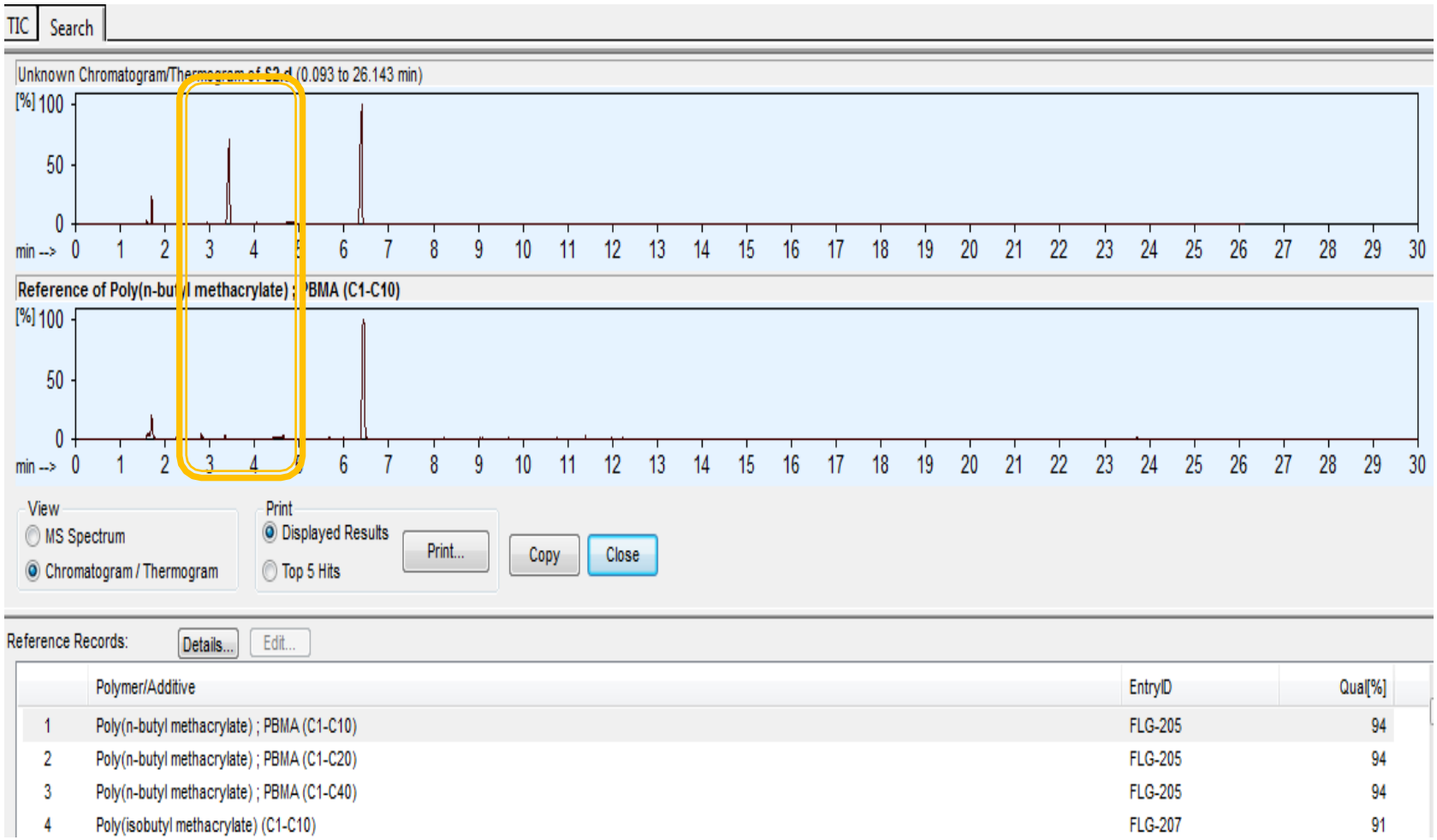
S2



	Polymer/Additive	EntryID	Qual[%]
1	Poly(n-butyl methacrylate) ; PBMA (C1-C10)	FLG-205	94
2	Poly(n-butyl methacrylate) ; PBMA (C1-C20)	FLG-205	94
3	Poly(n-butyl methacrylate) ; PBMA (C1-C40)	FLG-205	94
4	Poly(isobutyl methacrylate) (C1-C10)	FLG-207	91

One polymer is PBMA. But something is missing…

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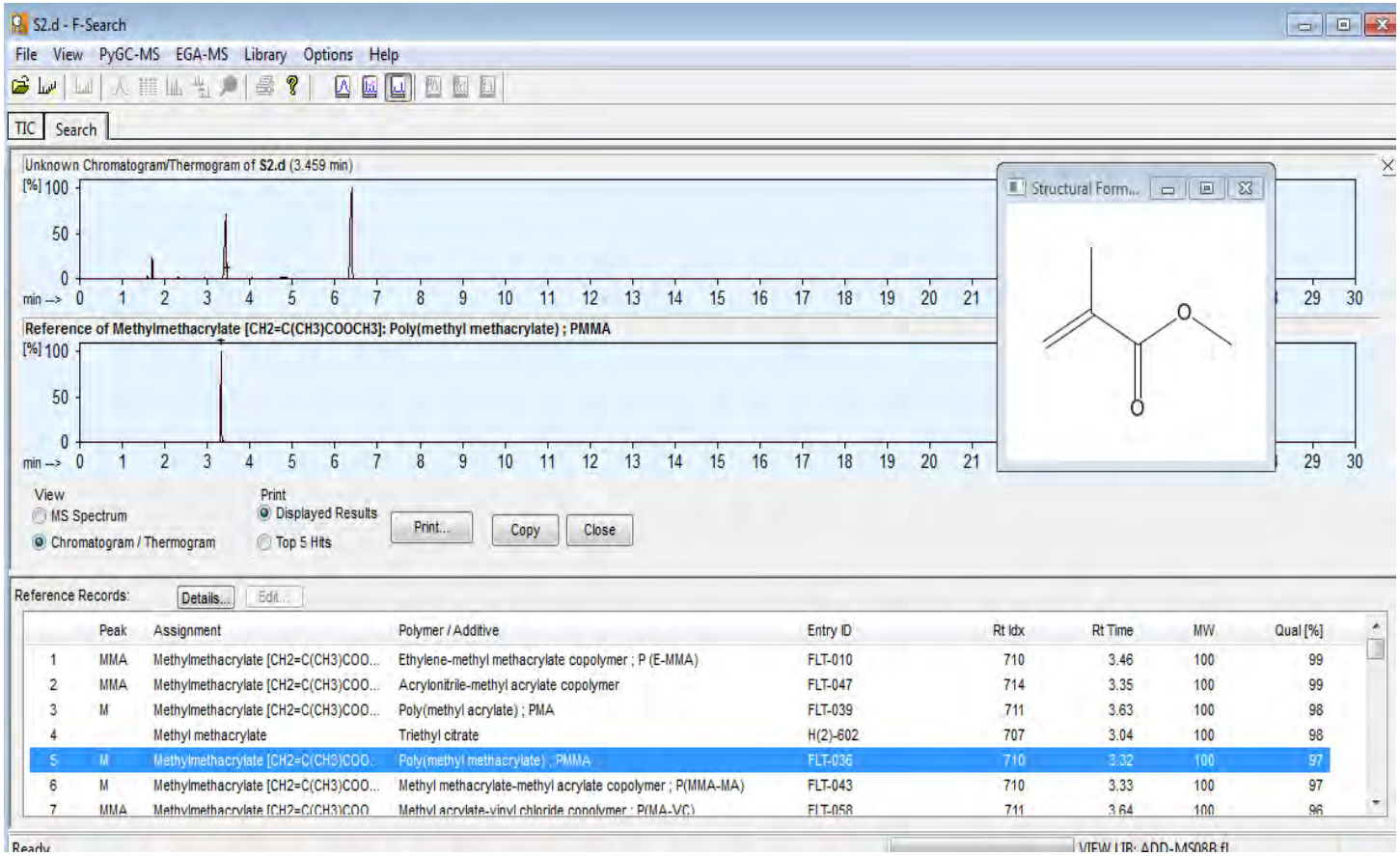
S2



Another polymer is PMMA

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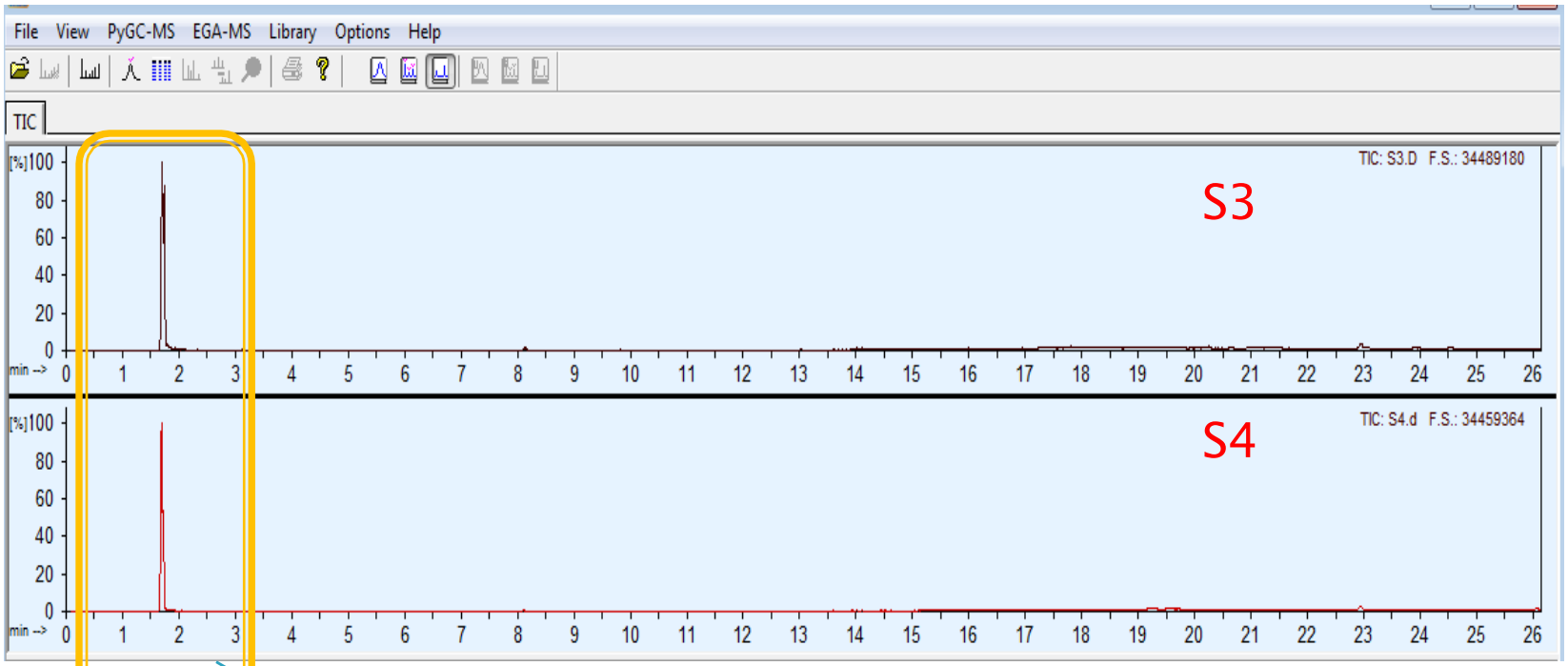
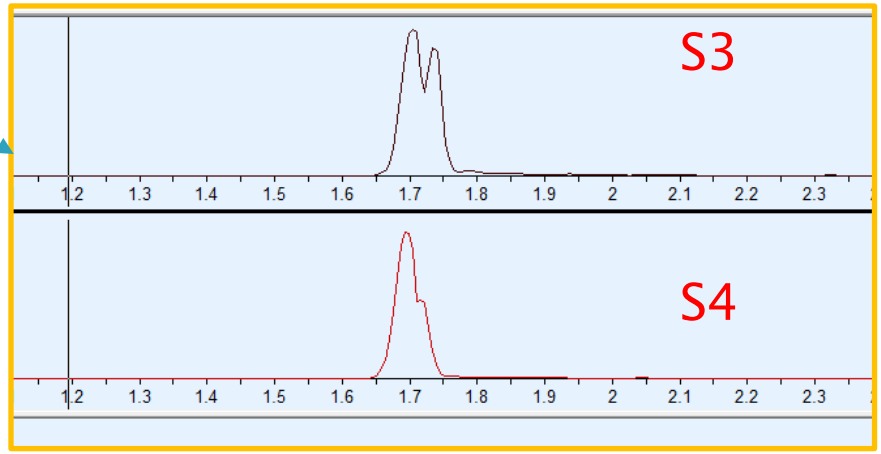
S3, S4

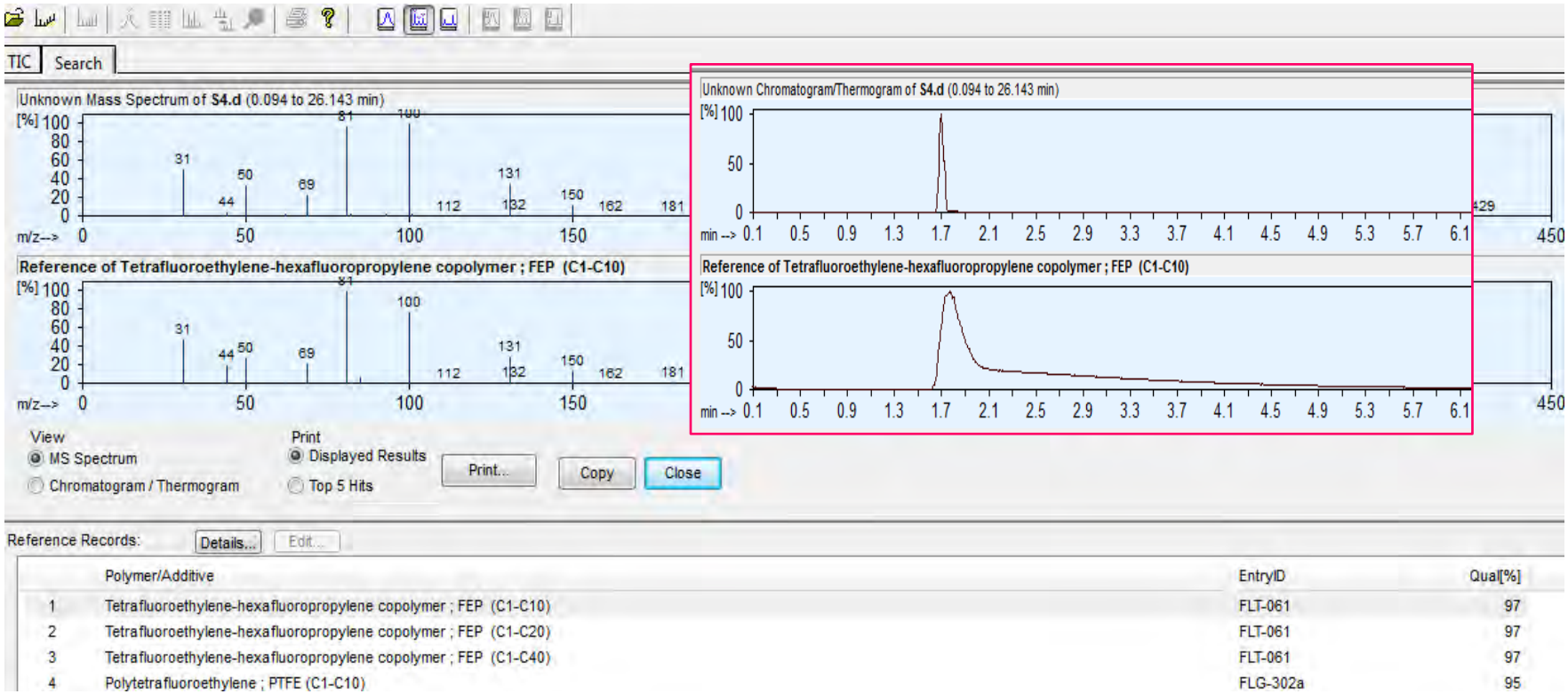
S3, S4



Enlarge



S4 Polymer Search



Tetrafluoroethylene-hexafluoropropylene copolymer ; FEP
Match qual. 97%

$$-\left(CF_2CF_2- \;/\; -CF_2CF(CF_3)\right)_n-$$

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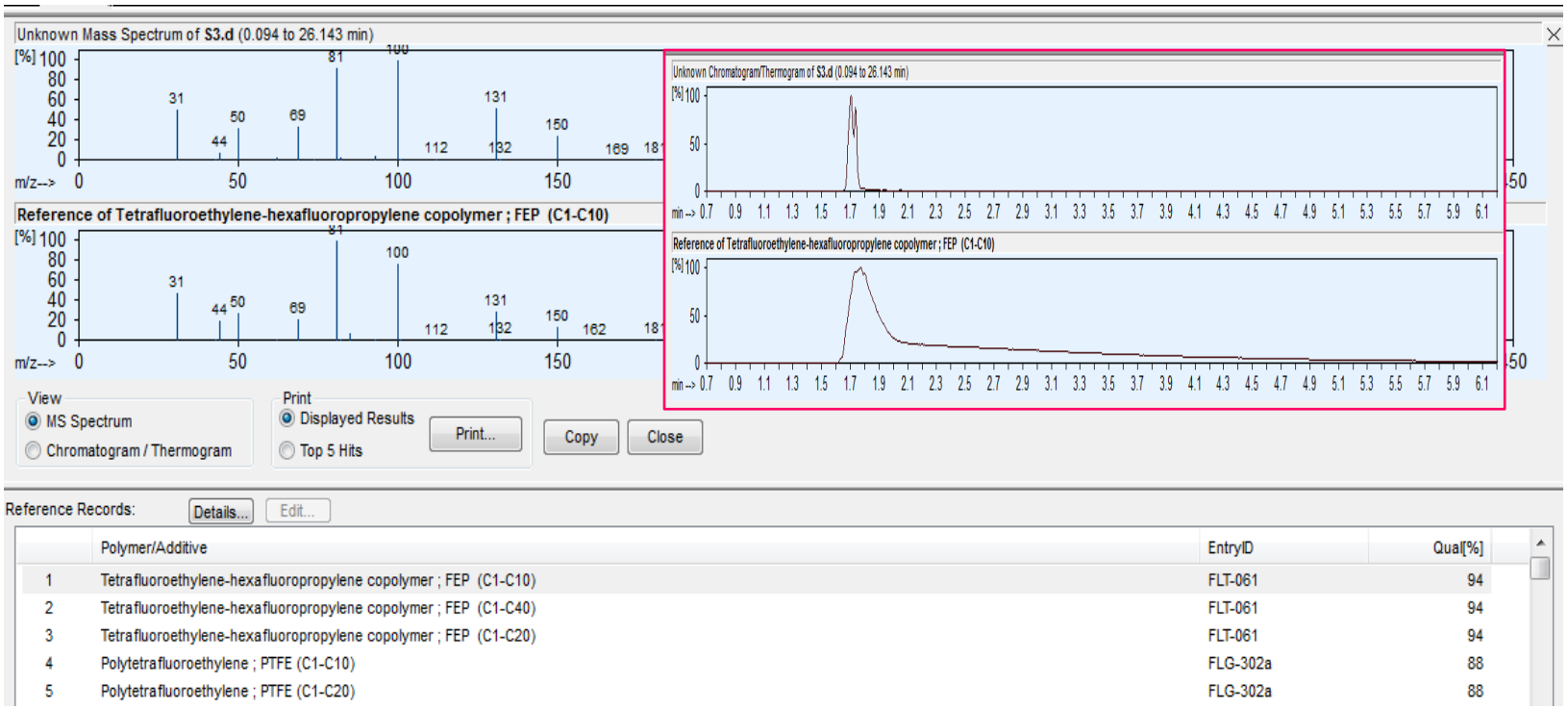
S3 Polymer Search



Tetrafluoroethylene-hexafluoropropylene copolymer ; FEP
Match qual. 94%

$$-\left[CF_2CF_2- \ / \ -CF_2CF(CF_3) \right]_n-$$

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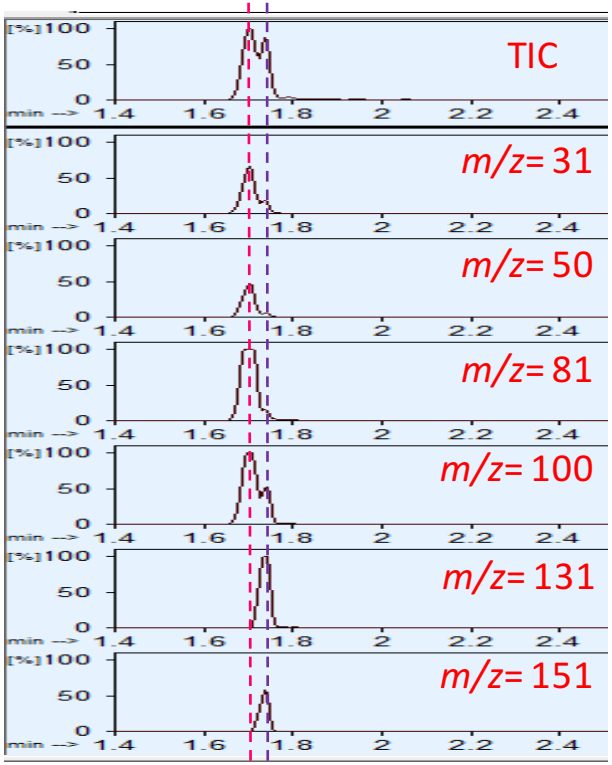
S3, S4

S3, S4 TIC & EIC

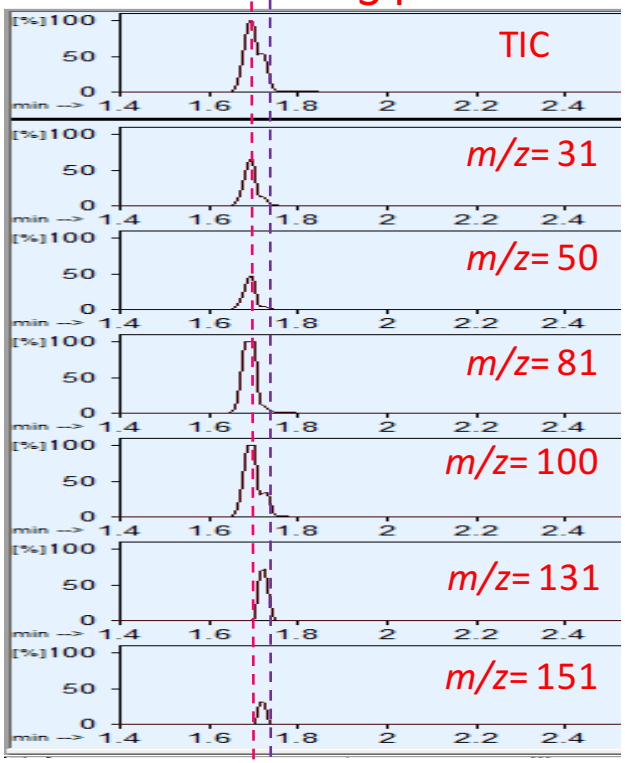
Peak #1 Peak #2

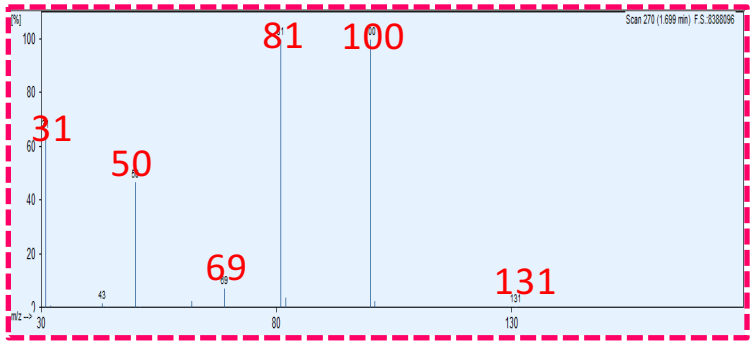
S3



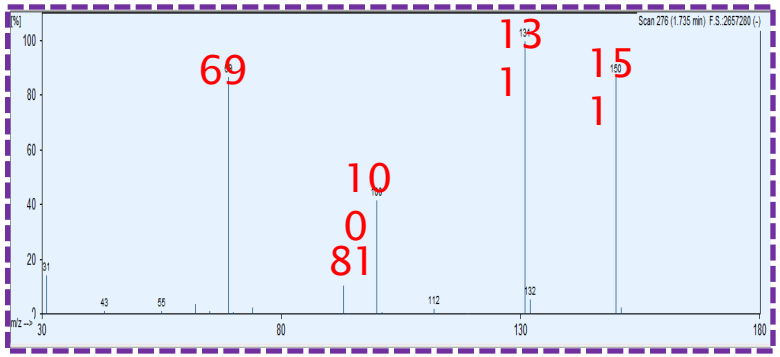
Peak #1 Peak #2

S4





Peak #1 MS spectrum



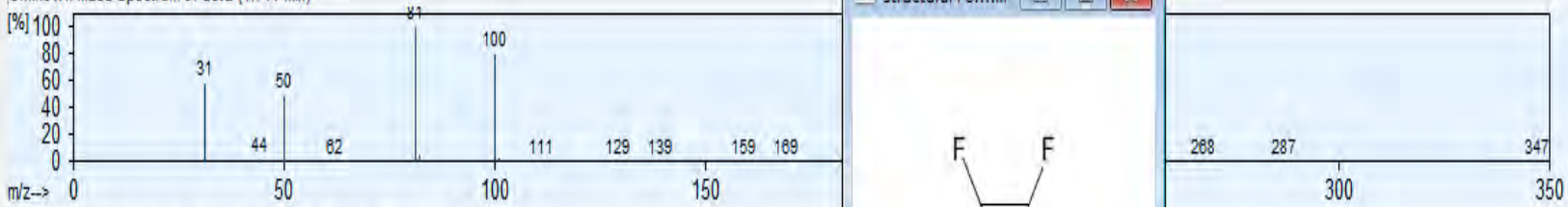
Peak #2 MS spectrum

S3, S4

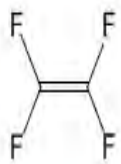
Peak #1 Pyrolyzate library Search Result

TIC | Search

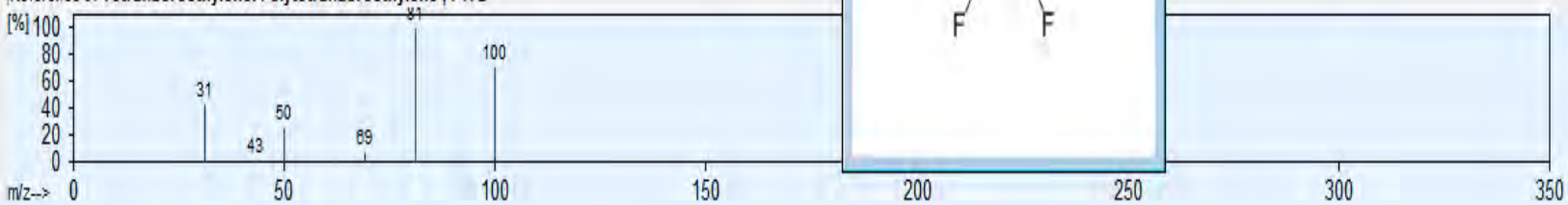
Unknown Mass Spectrum of S3.d (1.711 min)



Structural Form...



Reference of Tetrafluoroethylene: Polytetrafluoroethylene ; PTFE



View
- MS Spectrum
- Chromatogram / Thermogram

Print
- Displayed Results
- Top 5 Hits

Print... | Copy | Close

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

	Peak	Assignment	Polymer / Additive	Entry ID	Rt Idx	Rt Time	MW	Qual [%]
1	M	Tetrafluoroethylene	Polytetrafluoroethylene ; PTFE	FLT-060	-	1.93	100	96
2	M	Tetrafluoroethylene (mixed with hexafl...	Tetrafluoroethylene-hexafluoropropylene copolymer ; FEP	FLT-061	-	1.77	100	42
3	H	2,4-Hexadienal	Poly(vinyl alcohol) ; PVA	FLT-067	901	5.57	96	36

Tetrafluoroethylene Polymer PTFE Match
Qual 96%

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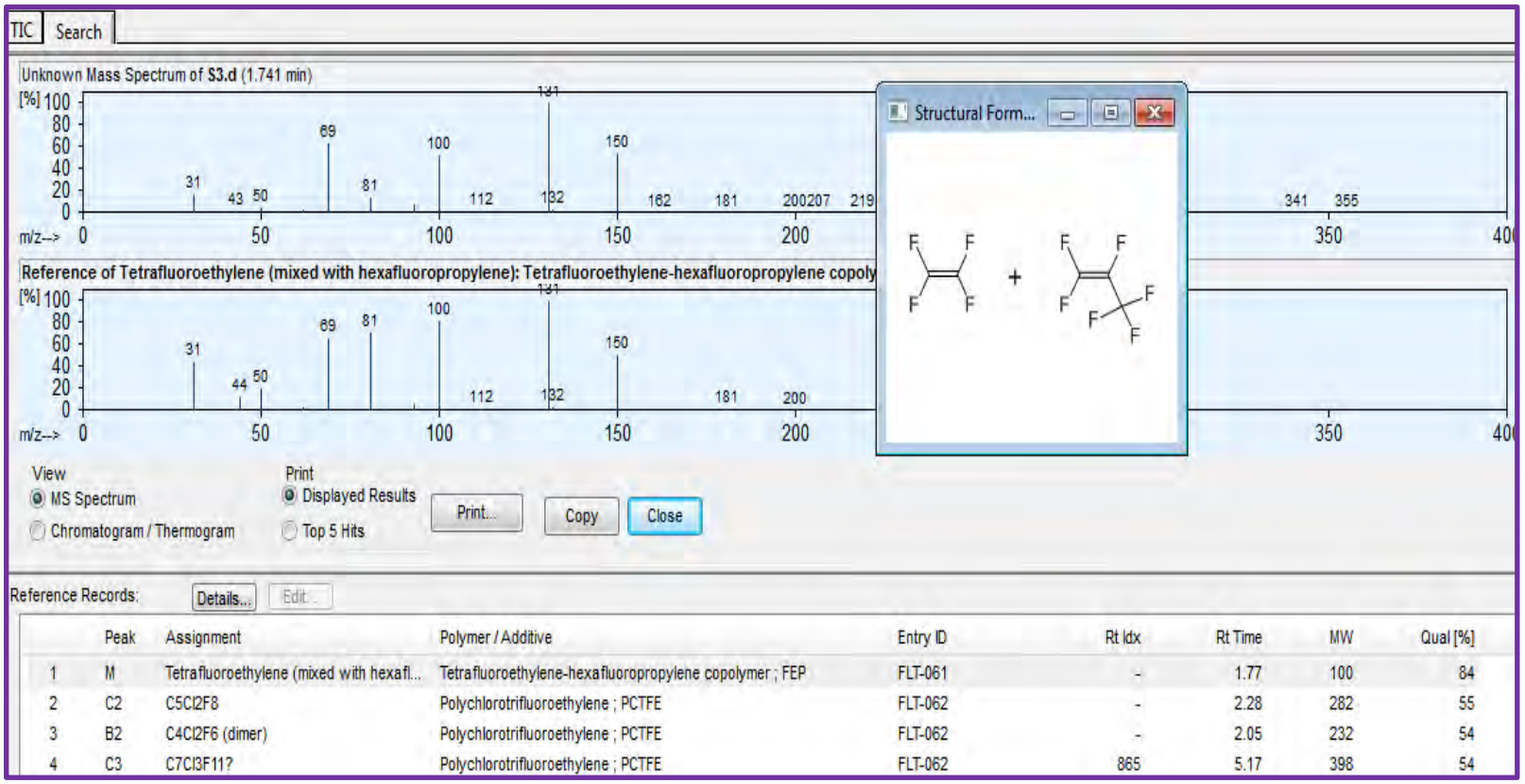
S3, S4

Peak #2 Pyrolyzate library Search Result



	Peak	Assignment	Polymer / Additive	Entry ID	Rt Idx	Rt Time	MW	Qual [%]
1	M	Tetrafluoroethylene (mixed with hexafl...	Tetrafluoroethylene-hexafluoropropylene copolymer ; FEP	FLT-061	-	1.77	100	84
2	C2	C5Cl2F8	Polychlorotrifluoroethylene ; PCTFE	FLT-062	-	2.28	282	55
3	B2	C4Cl2F6 (dimer)	Polychlorotrifluoroethylene ; PCTFE	FLT-062	-	2.05	232	54
4	C3	C7Cl3F11?	Polychlorotrifluoroethylene ; PCTFE	FLT-062	865	5.17	398	54

Tetrafluoroethylene (mixed with hexafluoropropylene) Polymer FEP
Match Qual 84%

Conclusion : both S3,S4 are "FEP" but, S3 include PTFE too.

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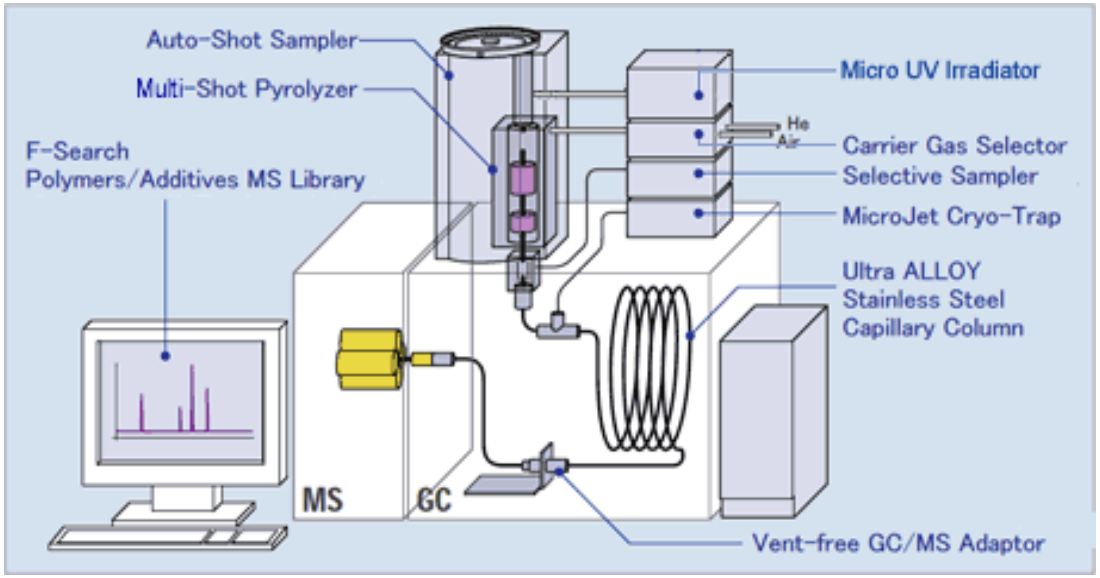
Frontier EGA/PY-3030D Multi-functional System



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Frontier Lab Contact: Dave Randle

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Frontier Laboratories USA
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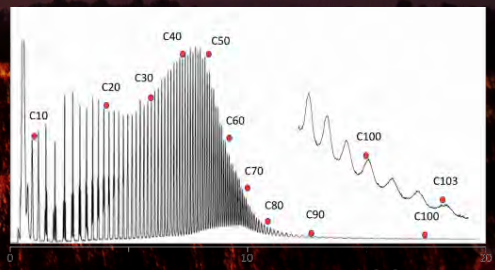

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