

“Sustainability”: Challenges in Polymer characterization and applications of Pyrolysis-GC/MS

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Frontier Laboratories, Ltd. Company profile



- founded August 12, 1991
- Located in Koriyama, Fukushima, Japan
- 55 Employees (incl. 11 outside Japan)
- Office: Japan (HQ and Tokyo R&D), China, Germany, ~~(Russia)~~, India, Singapore and USA
- President/CEO: Dr. Atsushi (Ichi) WATANABE



- Global leading company in Analytical pyrolysis
 - Manufacturer of Pyrolyzer, peripheral devices and Ultra ALLOY[®] capillary column
 - Actively participate in scientific conferences in the world
- Area of expertise
 - Polymer characterization using “Pyrolyzer : EGA / TD /PY/ RxPY” with own brand “Ultra ALLOY[®] metal capillary column”
 - Rapid catalyst evaluation using Tandem and Single micro-Reactors



Multi-Shot pyrolyzer EGA/PY-3030D



Tandem μ -Reactor
Rx-3050TR



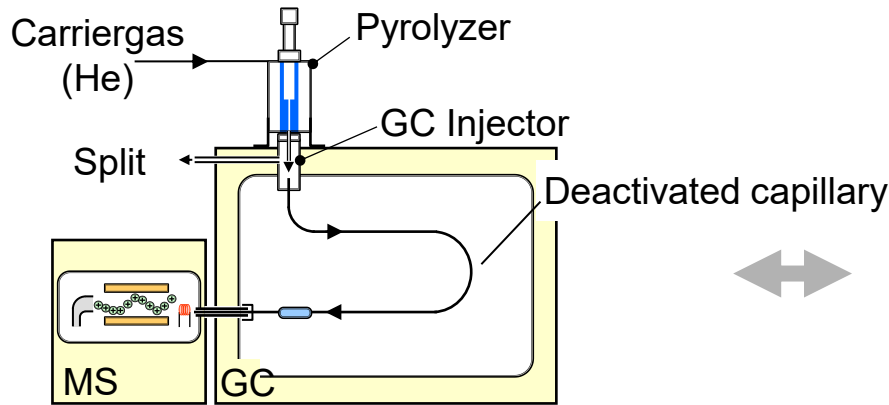
Cryogenic Mill
IQ MILL-2070



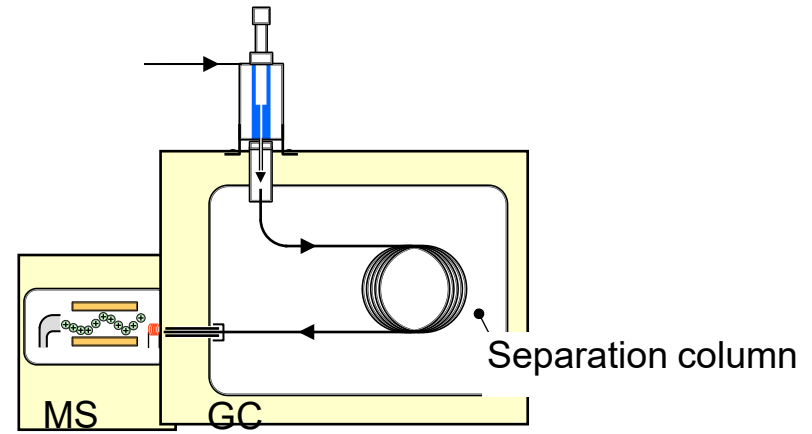
Ultra ALLOY
capillary column

Py-GC/MS System & anal. methods

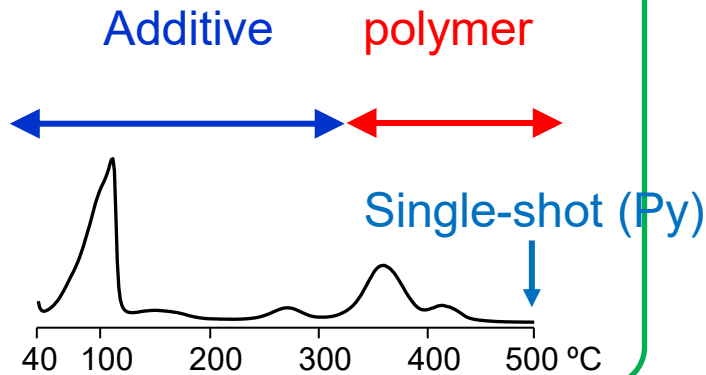
EGA-MS
(Thermal Profil)



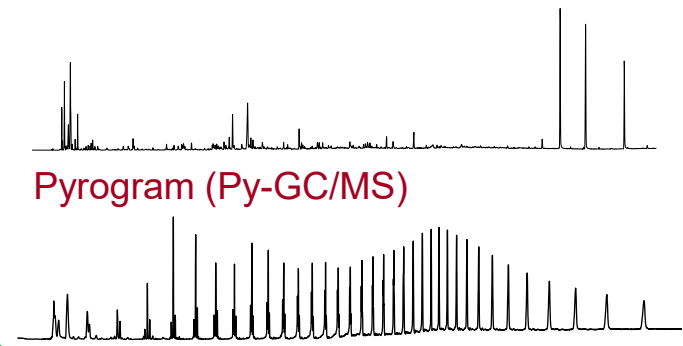
Single-Shot (Py)-GC/MS
(Additive + Polymer Information)
TD-GC/MS (Additive Information)
Double-Shot (TD & Py)-GC/MS



EGA Thermogram



Thermal desorption (TD-GC/MS)



Heart-Cutting: “thermal slicing” of EGA-MS zones

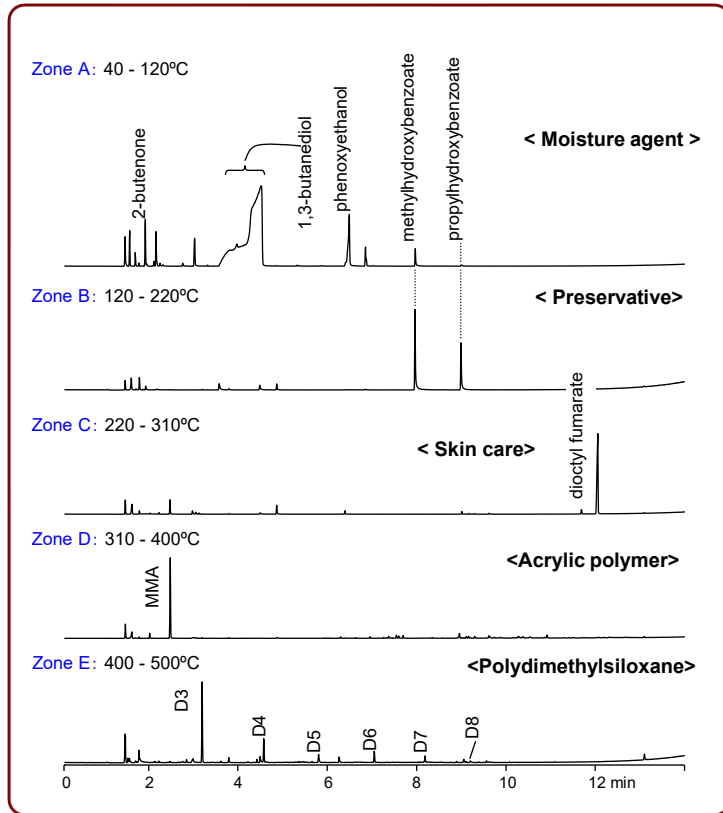
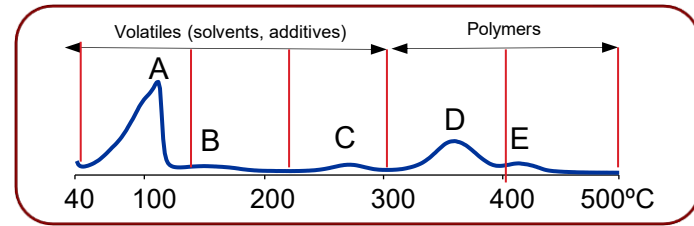


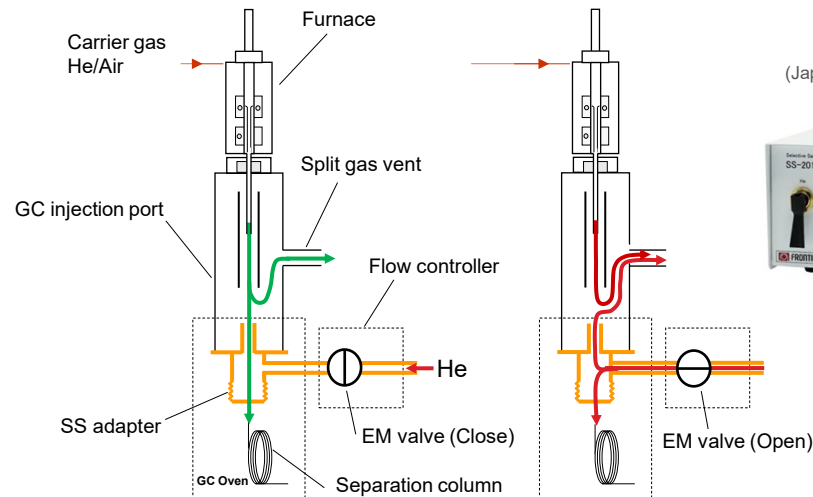
Figure.1: Heart-cut EGA-GC/MS analysis of zones A to E of EGA thermogram of an eyeliner.



Flow Switching

Sampling ON

Sampling OFF



(Japan patent No.3290893)



Flow controller

Tools to meet the analytical challenges of our time:

FOR OUR ENVIRONMENT AND SUSTAINABILITY



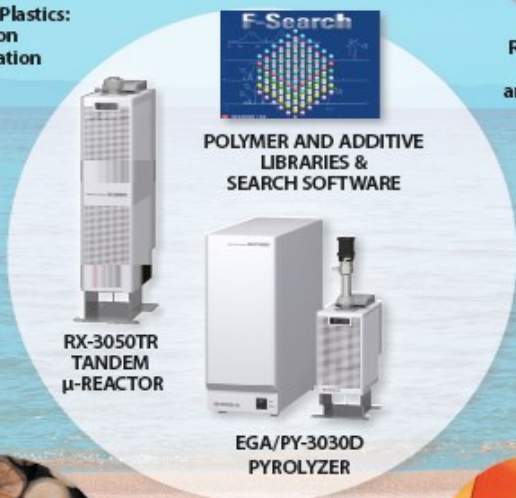
Micro- and Nano Plastics:
Identification
and Quantification



Biopolymer
Characterization



Recycled Materials:
Characterization
and Contaminations



POLYMER AND ADDITIVE
LIBRARIES &
SEARCH SOFTWARE

RX-3050TR
TANDEM
μ-REACTOR

EGA/PY-3030D
PYROLYZER



Renewable Energy:
Biomass and Catalysts



Aging and Stability:
Degradation and Deterioration

Complex Samples:

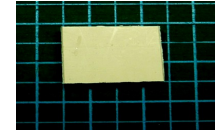
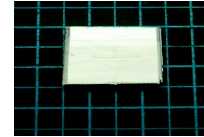
**Polymers, Additives, Environmental matrix
Inorganik**

- Recycled Materials: „whole Aldrich catalogue“, „exploded Pharmacy“, Native/Recycled
- Microplastic: Polymermixtures, Env. matrices, (Additives / Nanoplastics)
- Aging / Stability- : Additives
- Bio-Based & Biodegradable : Additive, natural Polymers + synth. Polymers
- Biomasses/ catalytic reactions

Applications

1 cm

1. Yellowing of PVC foils



2. Analysis of Bio-based and Bio-degradable plastic bags

Biomass A BP-A



30 % biomass

3. Failure analysis of recycled ABS material



4. Microplastics in sediments



Study on the cause of yellowing of PVC materials with the Py-GC/MS system

Objective and analytical methods

PVC sheet material with
white and yellow surfaces



Analysis of yellowing of material by
multi-functional pyrolyzer using various
analytical methods

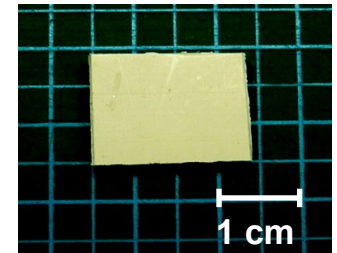
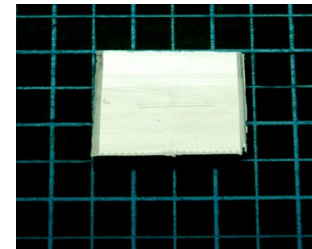
PVC sheet under sunshine

Front

(Good for White)

Back

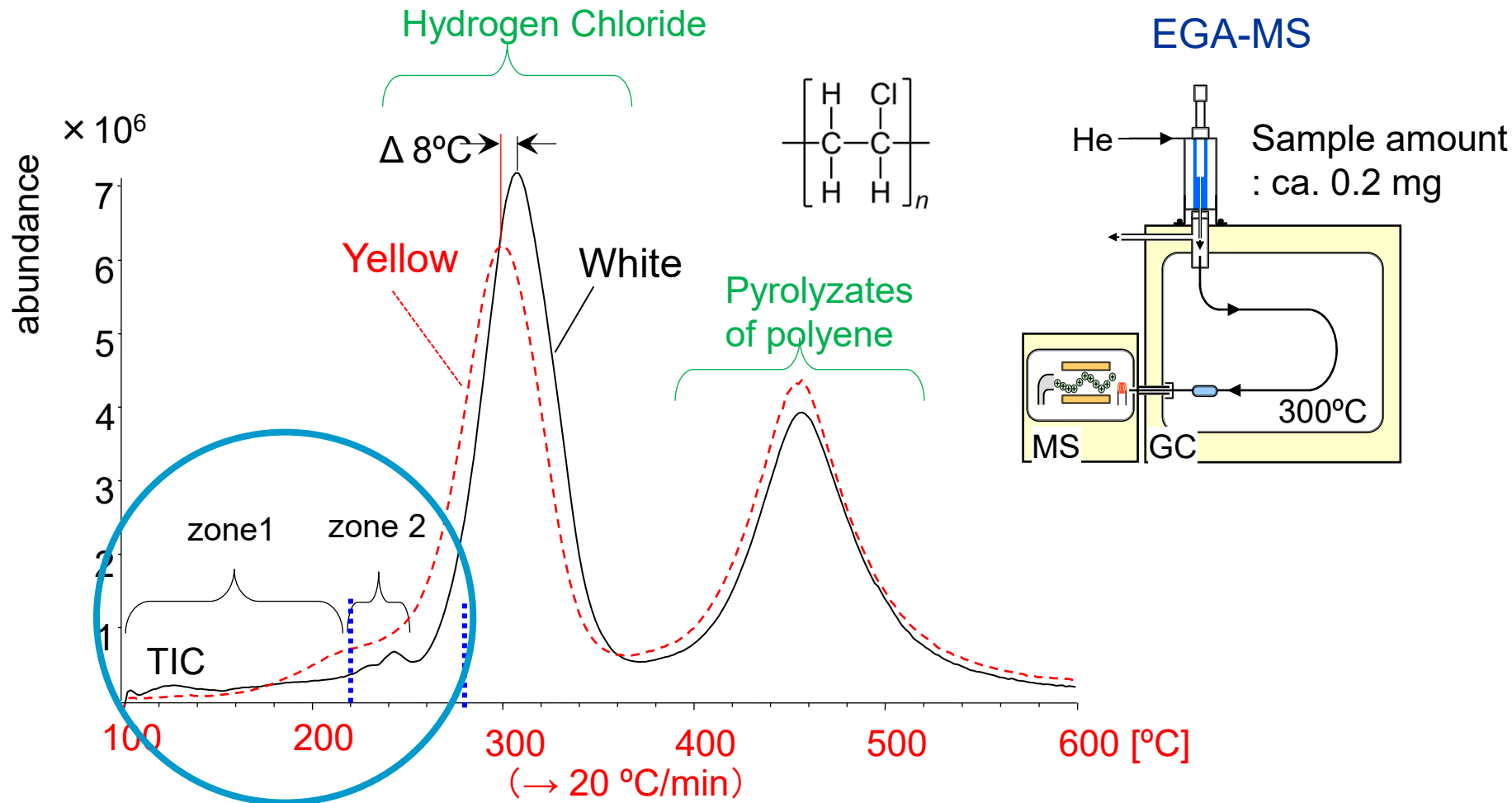
(slightly yellow)



Analytical methods

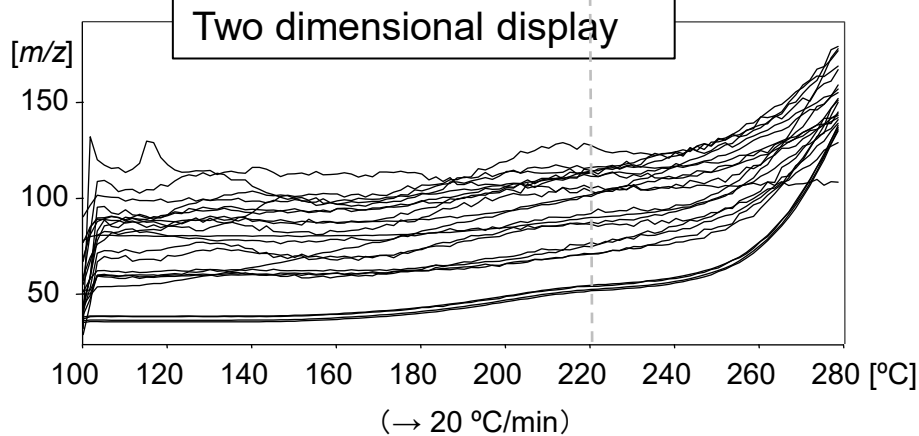
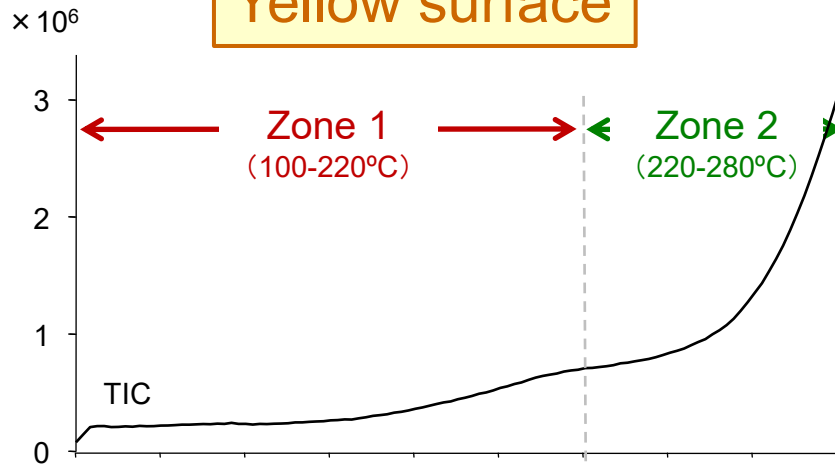
1. Evolved Gas-MS (EGA-MS)
2. Pyrolysis-**GC/MS** (**Py-GC/MS**)
3. Heart cutting **EGA-GC/MS** (**HC/EGA-GC/MS**)

EGA-MS curves of yellow and white sides of PVC

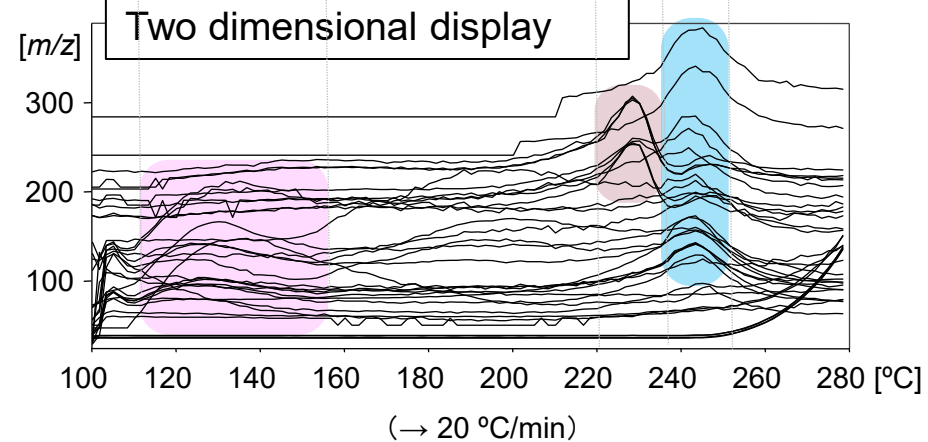
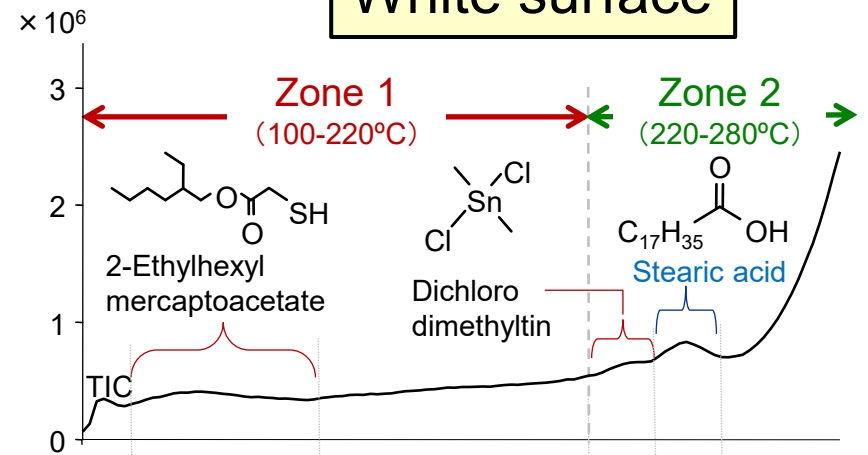


Two dimensional EGA curves of 100- 280°C

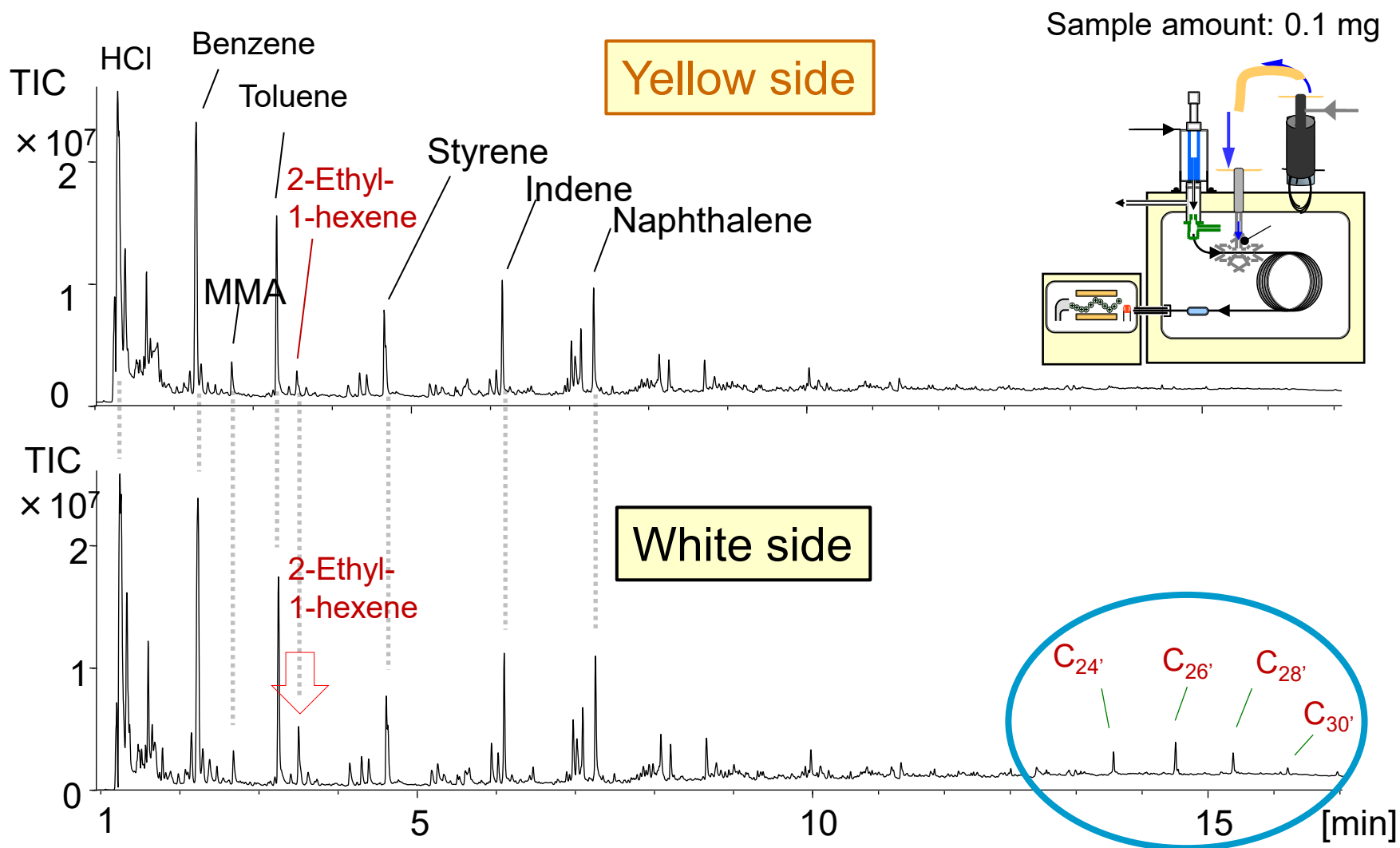
Yellow surface



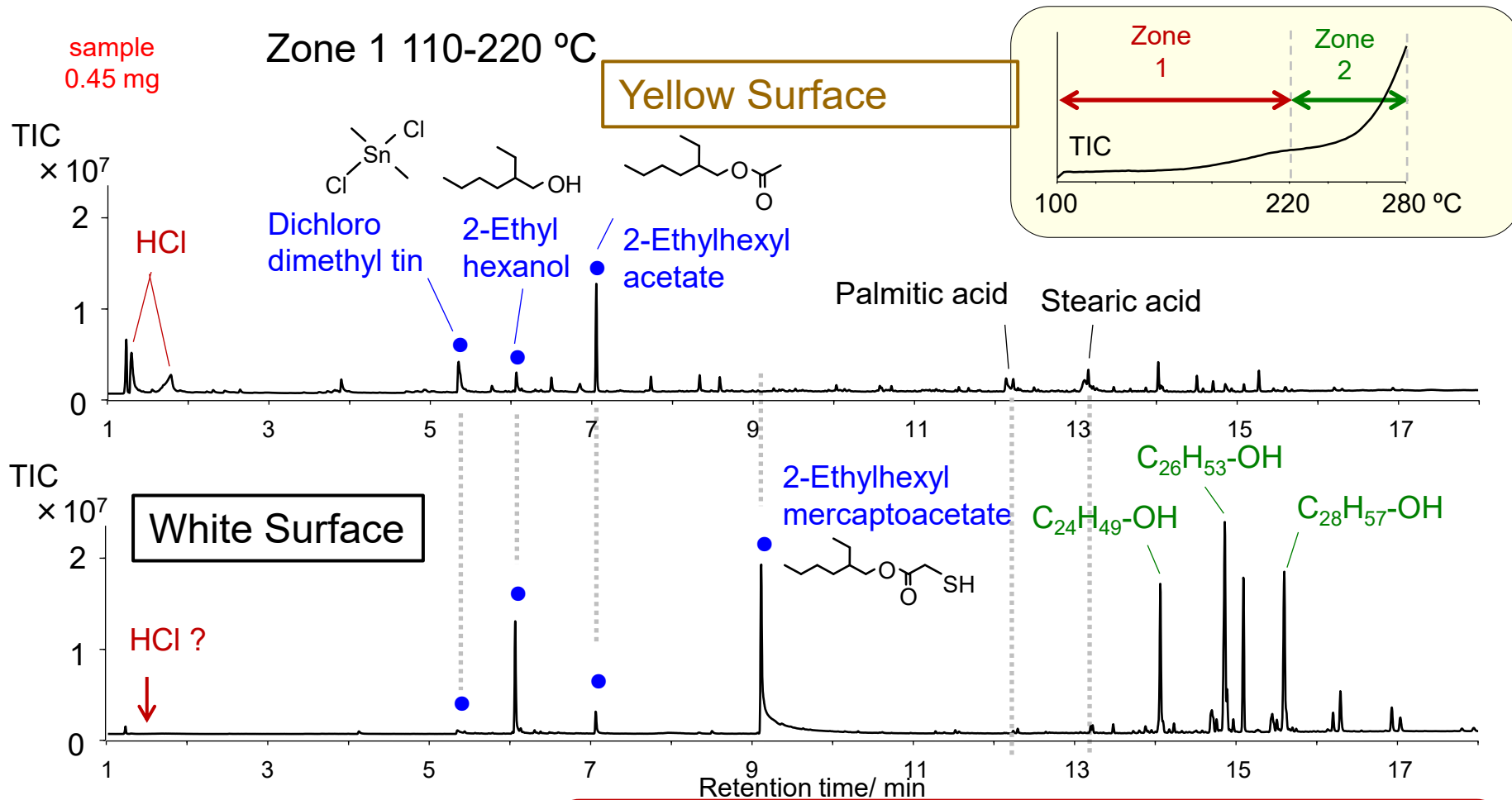
White surface



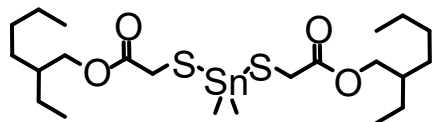
Pyrograms of yellow and white sides of PVC at 600°C



HC-GC/MS Chromatograms of Zone 1 (110-220 °C)



● ... Pyrolyzate of therm. Stabilizers
Methyl-tin-mercaptide



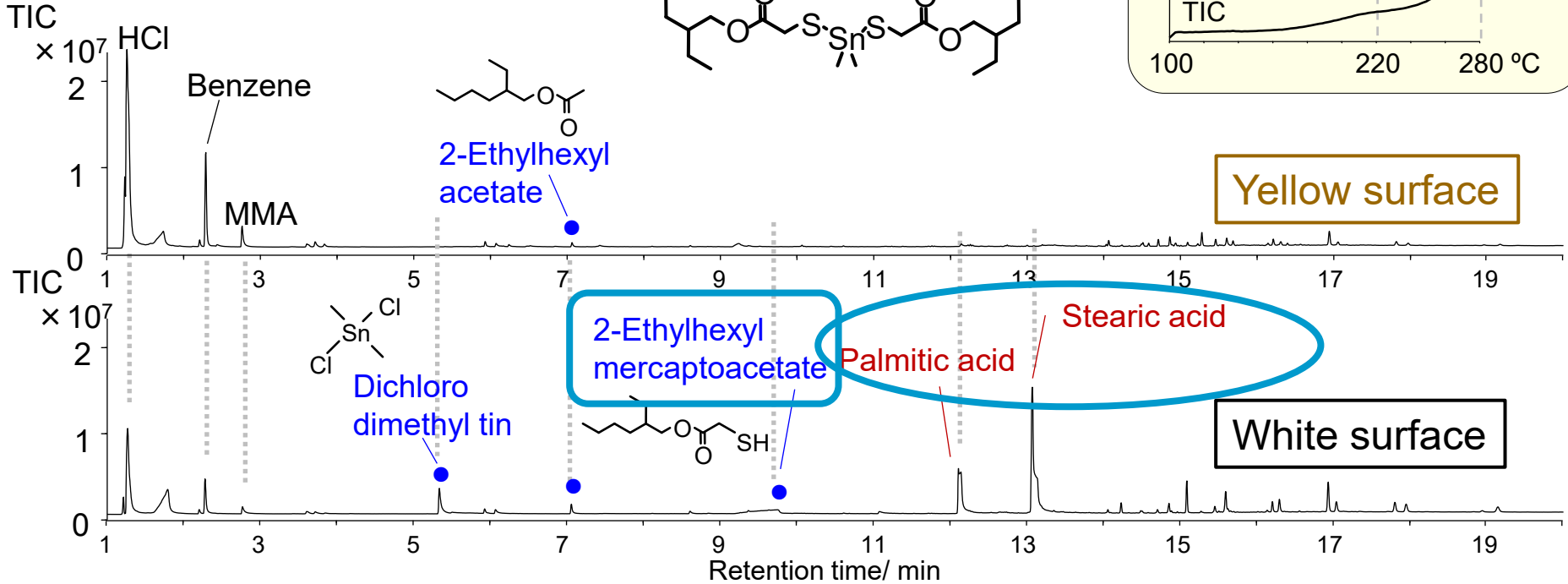
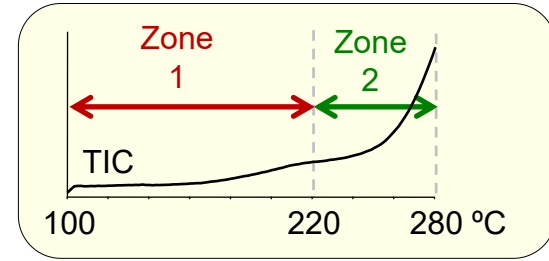
1. HCl could be detected on yellow surface only
2. Degree of degradation of therm. Stabilizers are different
3. Long chain alcohols from lubricants could be detected on white surface only

HC-GC/MS Chromatograms of Zone 2 (220-280 °C)

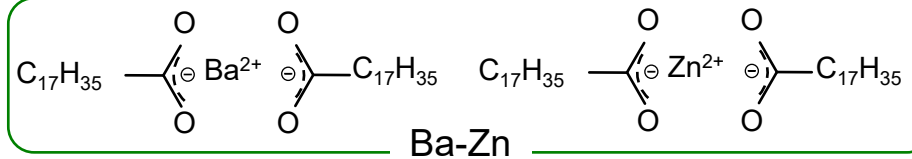
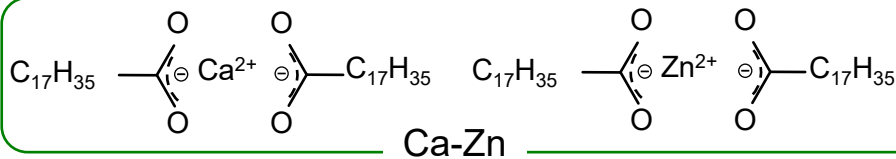
sample
0.45 mg

● ... Pyrolyzates of therm. Stabilizers
Methyl tin mercaptide

Zone 2 220-280 °C



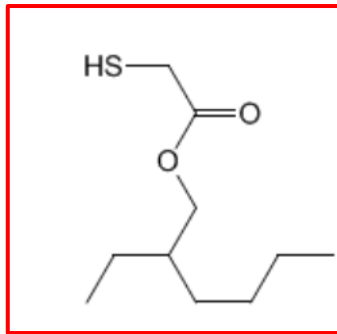
Peaks for stearic and palmitic acid are only observed on the white surface, indicating the presence of the stabilizer “metallic soap”.



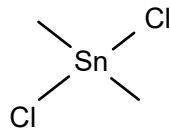
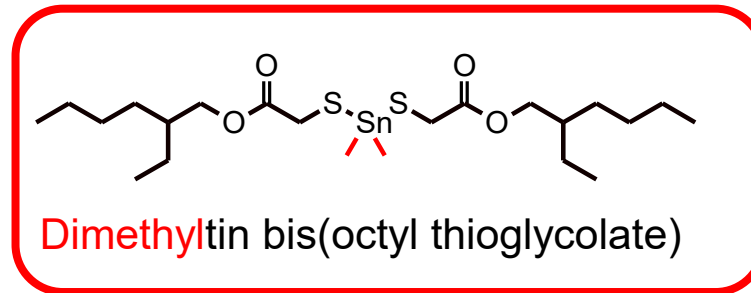
2-Ethylhexyl mercaptoacetate library search (F-SEARCH 3.8)

	Assignment	Polymer / Additive	Qual...
1	2-Ethylhexyl mercaptoacetate	Dimethyltin bis(octyl thioglycolate)	96
2	2-Ethylhexyl mercaptoacetate	Dibutyltin bis(octyl thioglycolate)	96
3	2-Ethylhexyl mercaptoacetate	Di-n-octyltin bis(octyl thioglycolate)	96
4	7-Methylpentadecane		86
5			...

2-Ethylhexyl mercaptoacetate



Pyrolyzate

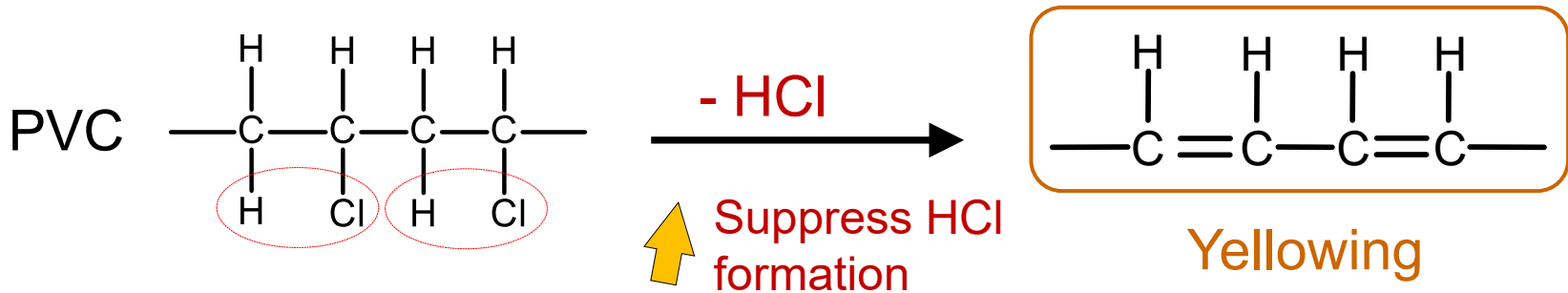


Dichloro dimethylzinn

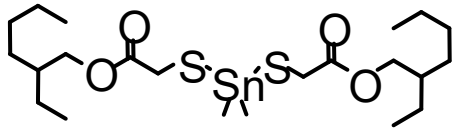
Methyltin mercaptide Basic information

Product Name:	Methyltin mercaptide
Synonyms:	2-ethylhexyl 10-ethyl-4-[[2-[(2-ethylhexyl)oxy]-2-oxoethyl]thio]-4-methyl-7-oxo-8-oxa-3,5-dithia-4-s-tannatetradecanoate; dimethyltin bis(2-ethylhexylmercaptoacetate); methyltin mercaptide; Methyl Tin Stabilizer; 2-ethylhexyl 2-[[2-(2-ethylhexoxy)-2-oxoethyl]sulfanyl-dimethylstannyl]sulfanylacetate; Methyltin Mercaptide stabiliser; Methyltin mercaptide (PVC heat stabilizers); 3-Oxa-3,5-dithia-4-stannatetradecanoic acid, 10-ethyl-4,4-dimethyl-7-oxo-, 2-ethylhexyl ester

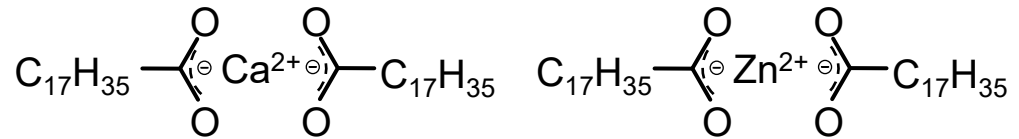
Yellowing of PVC back side



Thermal stabilizers



Dimethyltin bis(2-ethylhexyl thioglycolate)



Metal soap (Ca-Zn)

White side

Formation of HCl is suppressed by thermal stabilizers

Yellow side

Degradation and decrease of thermal stabilizers cause the formation of HCl in PVC backbone

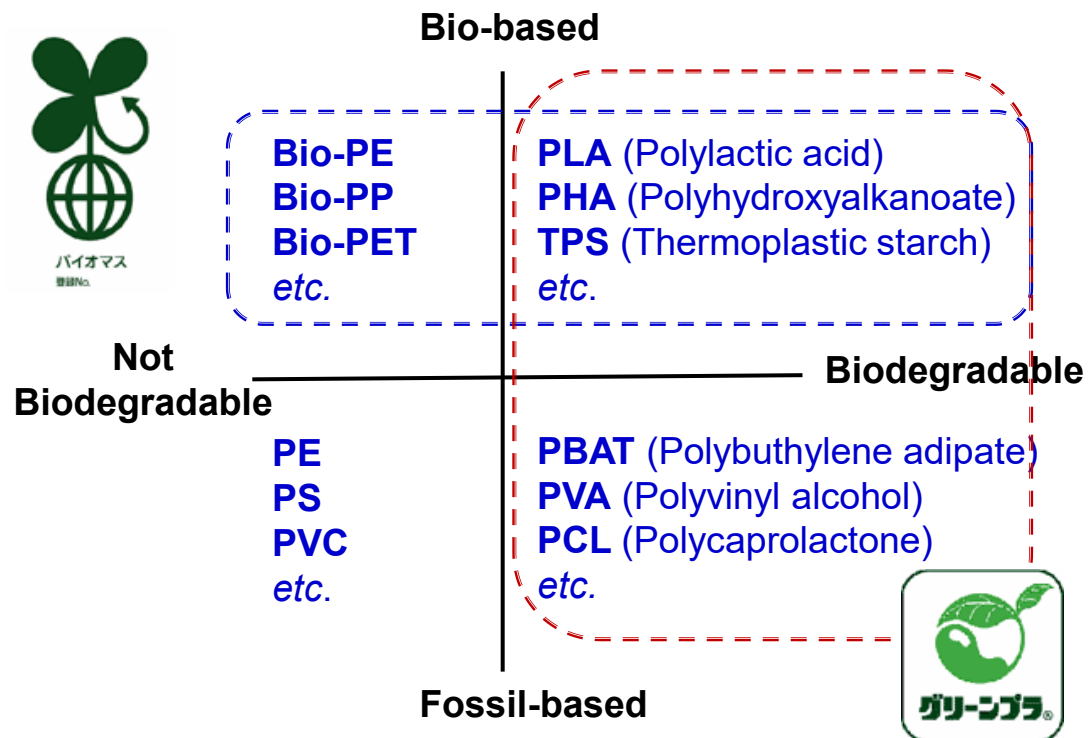
Yellowing can be ascribed to the formation of double bonds in PVC backbone

Analysis of (Bio-) Plastic Bags using Evolved Gas Analysis and Pyrolysis- GC/MS

Background and Objective

Recently, environmentally friendly “Bioplastics” have attracted much attention due to global plastic pollutions. Bioplastics are classified from the viewpoint of “bio-based” (*i.e.*, material source) and “biodegradable”, which are called as “Biomass Plastics” and “Green Plastics”, respectively in Japan.

It is interesting to examine the main constituents and additives of bioplastics, since they may cause contamination to the environment under aging process.



Material coordinate system of bioplastics

X. Zhao *et al.*, *Environ. Sci. Technol.*, 54 (2020) 4712.

Objective of this research:

Characterization of the main constituents and additives of commercially available conventional plastic and bioplastic bags using a pyrolysis-GC/MS system.

Experimental Sample

Sample: Plastic bags

Conventional STD

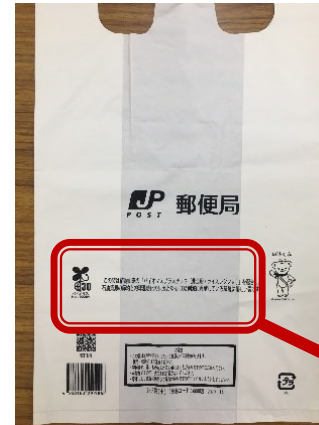


Biomass A BP-A



30 % biomass

Biomass B BP-B



30 % biomass



This bag contains a plant-derived [biomass plastic (non-edible / rice resin ®)] and is a kind of environmentally friendly bag that contributes to CO2 reduction, saving oil resources and global warming.

Green GP



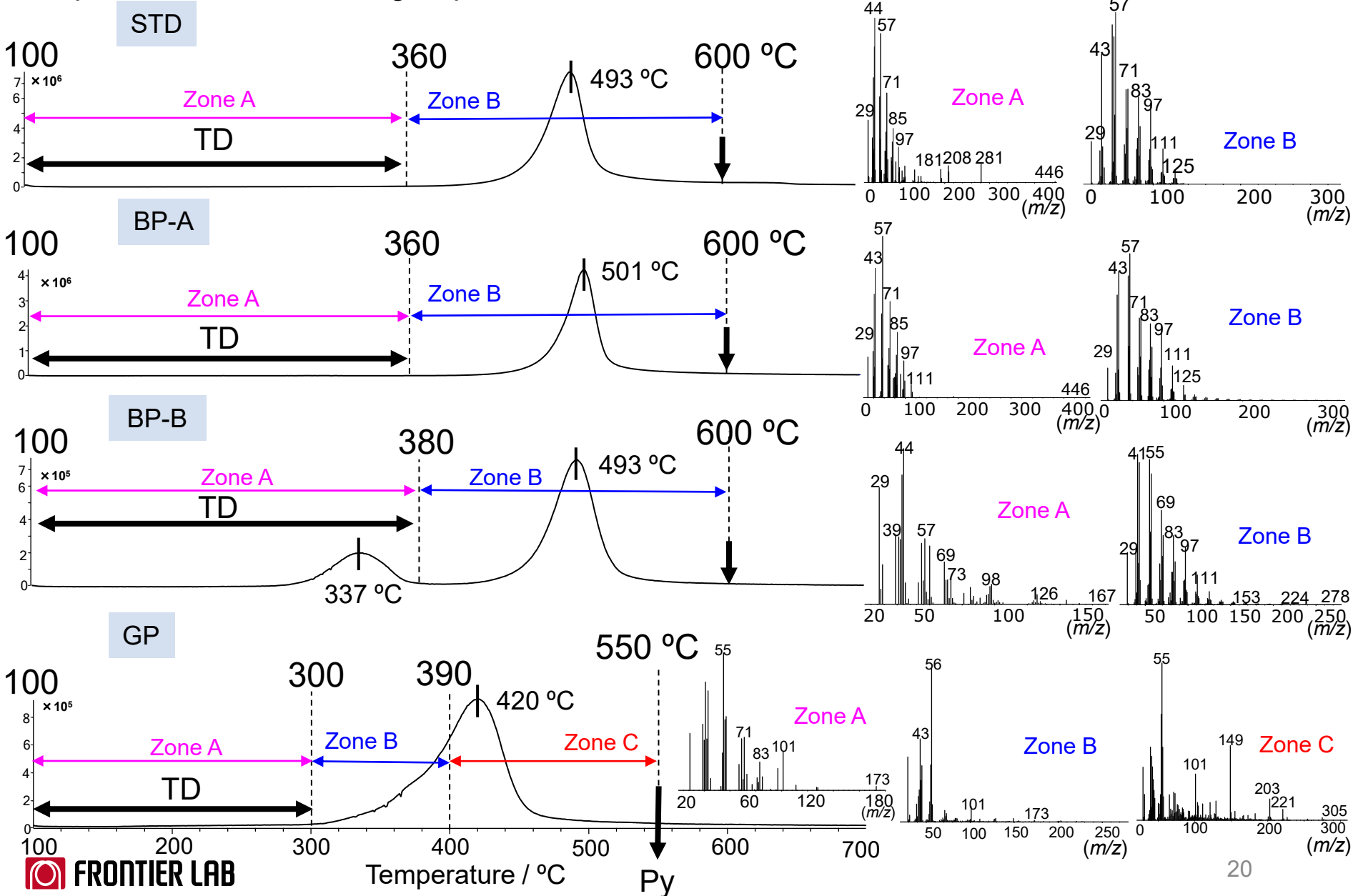
Biodegradable plastic: Decomposed by microorganism

Sample preparation method:

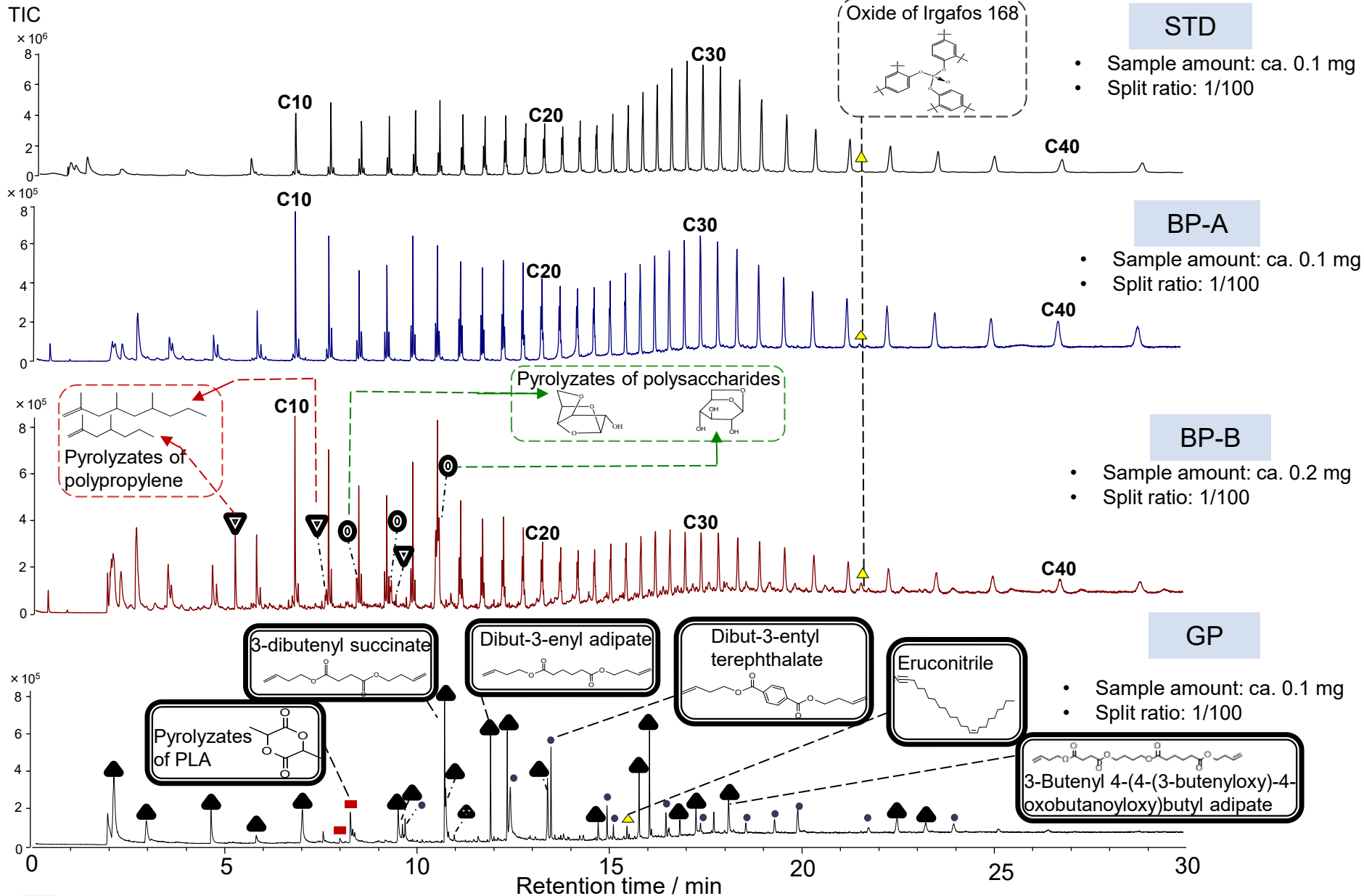
Portion of plastic bags without printed characters and patterns was cut and used for the measurements.

EGA-MS

Sample amount : ca. 0.2 mg; Split ratio:1/50



Py-GC/MS

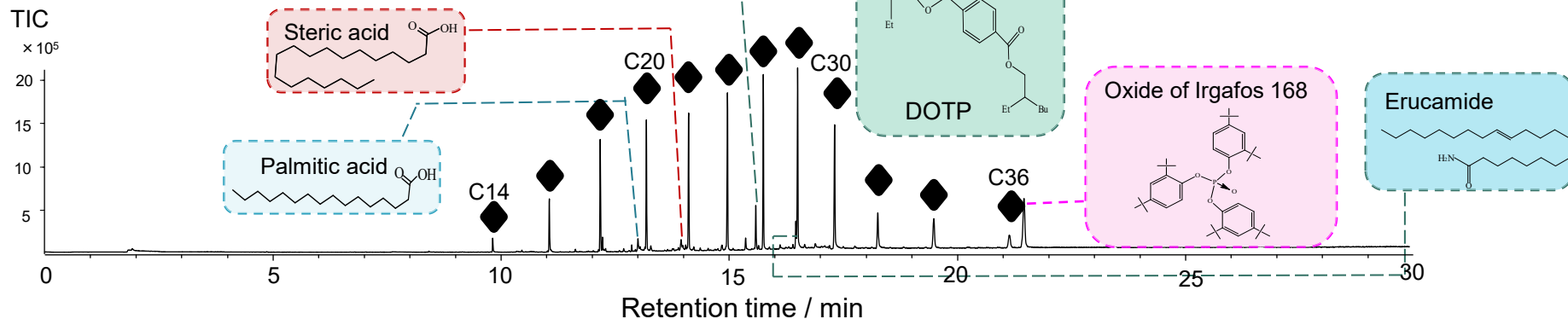


▼ Polypropylene; ● Polysaccharide; ▲ PBSA; ■ PLA; ● PBAT; ▲ Additive

TD-GC/MS; results I

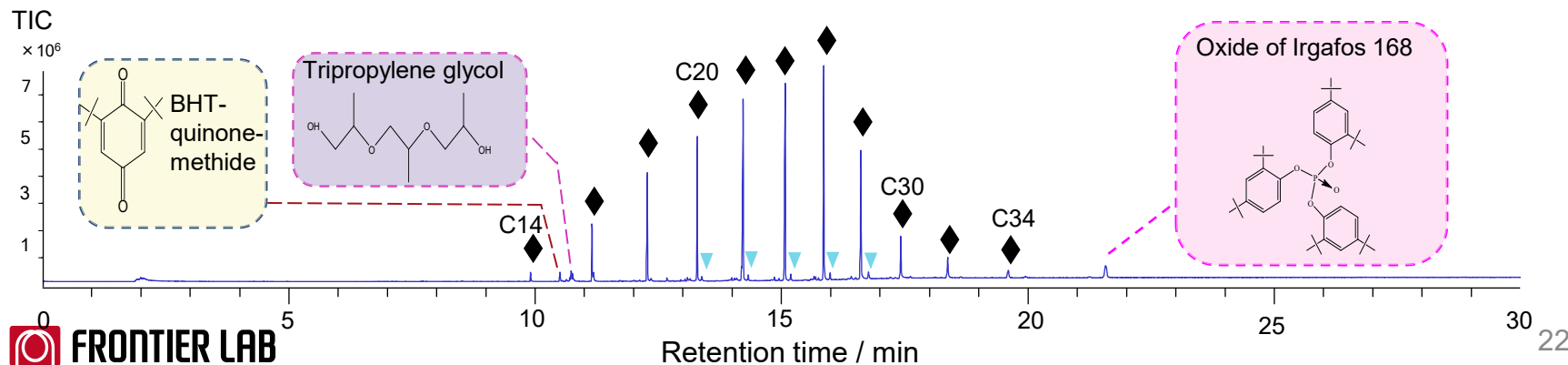
STD

- Furnace temp.: 100 - 40 °C/min -360 °C (1 min)
- Sample amount: ca. 1 mg
- Split ratio: 1/10



BP-A

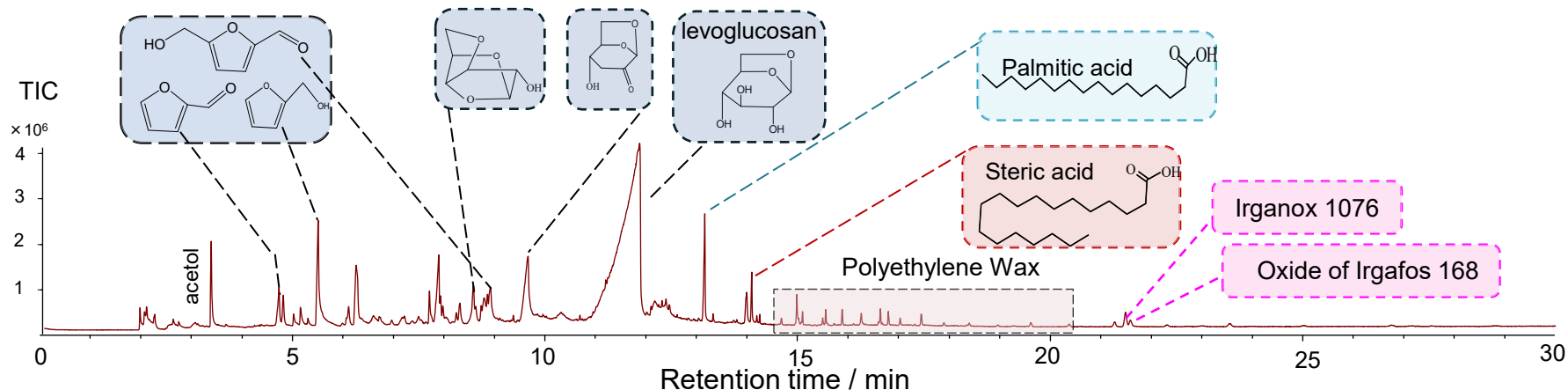
- Furnace temp.: 100 - 40 °C/min -360 °C (1 min)
- Sample amount: ca. 1 mg
- Split ratio: 1/10



TD-GC/MS; results II

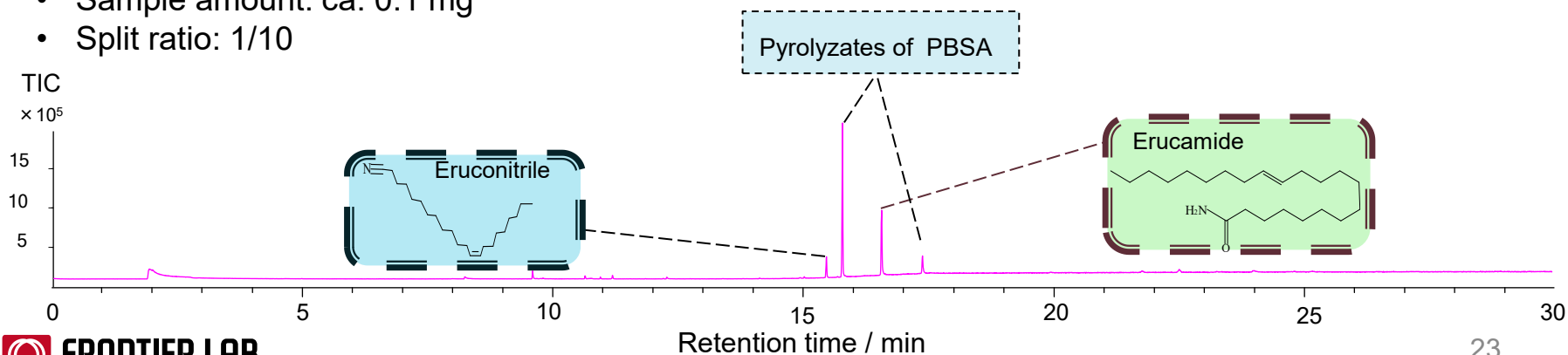
BP-B

- Furnace temp.: 100 - 40 °C/min -380 °C (1 min)
- Sample amount: ca. 1 mg
- Split ratio: 1/10



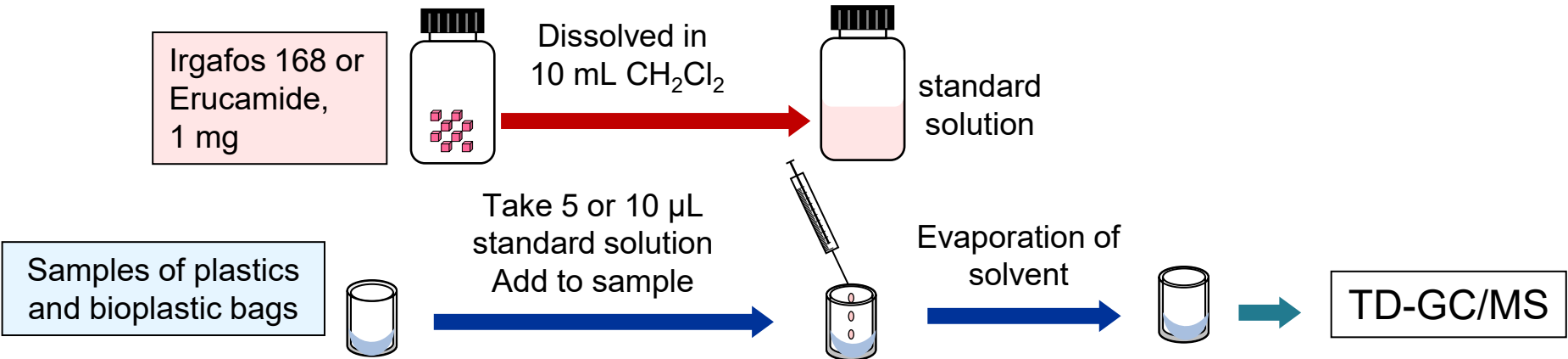
GP

- Furnace temp.: 100- 40 °C/min - 300 °C (1 min)
- Sample amount: ca. 0.1 mg
- Split ratio: 1/10

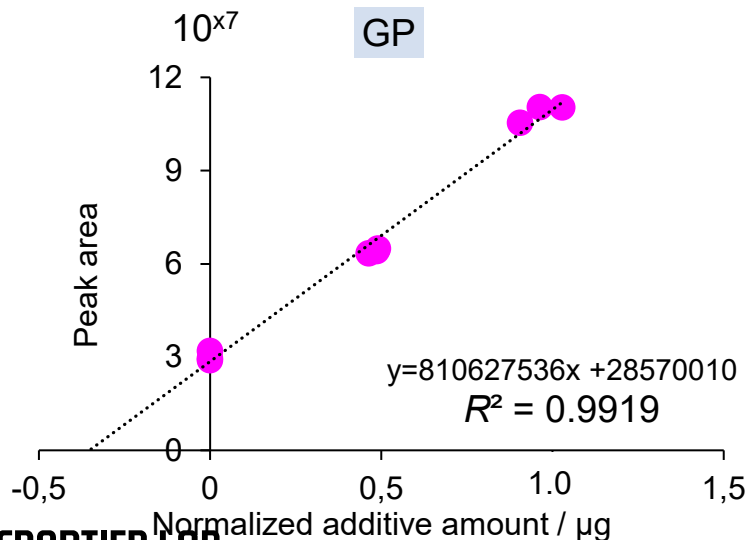


Quantitative analysis of additives

➤ Experimental procedures (standard addition method)

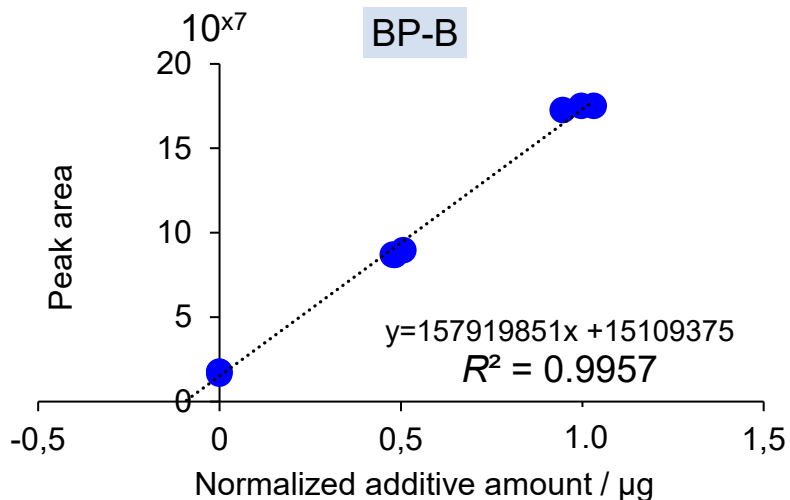
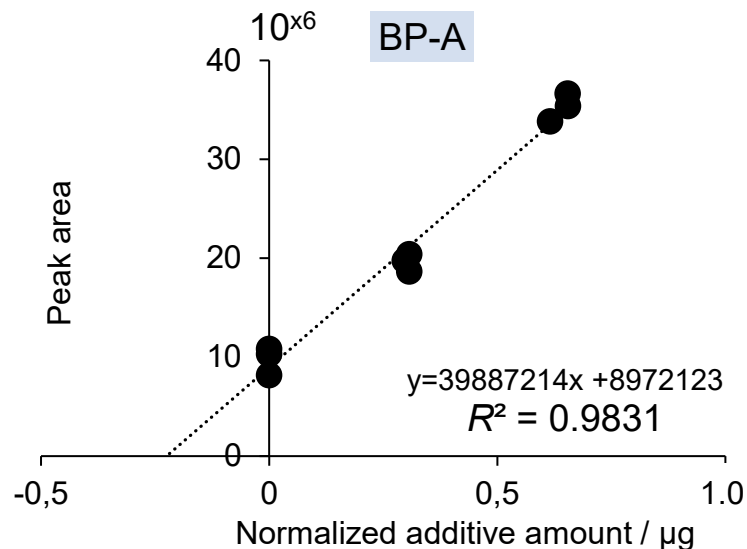
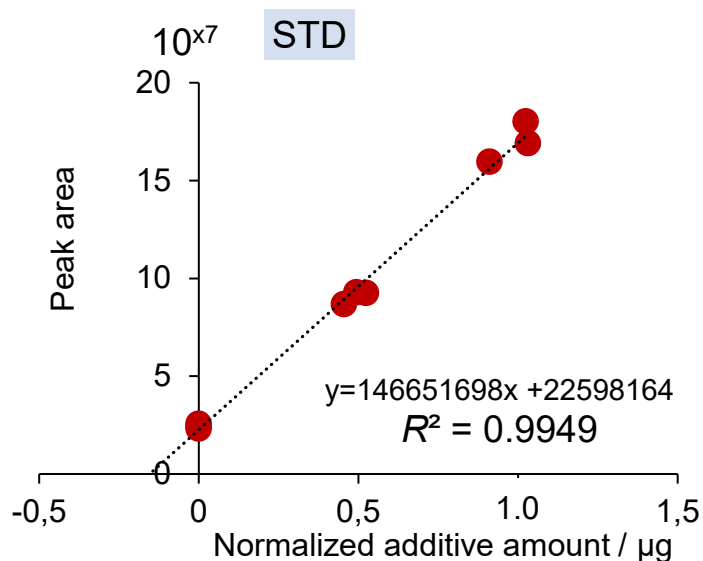


◆ Quantitative analysis of Erucamide (Lubricant)



Plastics type	Experiment sample amount	Determined amount of Erucamide
GP	ca. 0.5 mg	705 ppm

Quantitative analysis of Irgafos 168 (Anti-oxidant)



Plastics type	Experiment sample amount	Determined amounts of Irgafos 168
STD	ca. 0.5 mg	308 ppm
BP-A	ca. 0.8 mg	450 ppm
BP-B	ca. 1 mg	95 ppm

Conclusion

Polymer types and additives of commercially available plastic bags were analyzed by EGA-MS, TD-GC/MS and Py-GC/MS, and the results are summarized as follows:

Plastic bags	Polymer Types	Additives
Conventional plastics (STD)	PE	Irgafos 168 (308 ppm), Wax, Palmitic acid, Stearic acid, DOTP, Erucamide
Bio-based plastic A (BP-A)	PE	Irgafos 168 (450 ppm), Wax
Bio-based plastic B (BP-B)	PE, PP and Polysaccharides	Irgafos 168 (95 ppm), Palmitic acid, Stearic acid
Green plastic (GP)	PBSA, PLA and PBAT	Erucamide (705 ppm)

PE: polyethylene, PP: polypropylene, PBSA: poly (butylene succinate/ adipate), PLA: poly(lactic acid), PBAT: poly (butylene adipate-co-terephthalate), DOTP: Dioctyl terephthalate

Defect analysis of recycled ABS molded products using pyrolysis-GC/MS

BACKGROUND

Acrylonitrile butadiene styrene resin (ABS resin)

Good impact resistance and processability, widely used for home appliances and daily necessities.

Also used as a base (hair implantation base) for brushes.
→ When brushes are manufactured, the bristles are implanted in the holes at regular intervals.



Defects occurred in ABS brush base

Conventional good brushes have no problem with bristle implantation

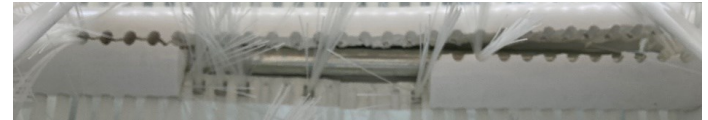
Switched to recycled material

→ During the process of implanting the brush bristles into the implantation holes, cracks often occurred.

Good products: Virgin material

Defective products: Recycled material

→ Defect occurred due to the recycled material used.



Goals, Analytical method, and Sample

Pyrolysis (Py)-GC/MS and energy dispersive X-ray analysis (SEM-EDX) were used to analyze the polymers and additives contained in the good and defective products of the ABS brush base, and the cause of the cracks in the defective product was investigated.

Analytical method and target

SEM-EDX Inorganics (target: antimony and bromine flame retardants)

SEM: Scanning electron microscope

Py-GC/MS Polymers, additives (organics)
(1) Evolved gas analysis (EGA)-MS
(2) Pyrolysis (Py)-GC/MS
(3) Thermal desorption (TD)-GC/MS

Sample

ABS brush base

Good



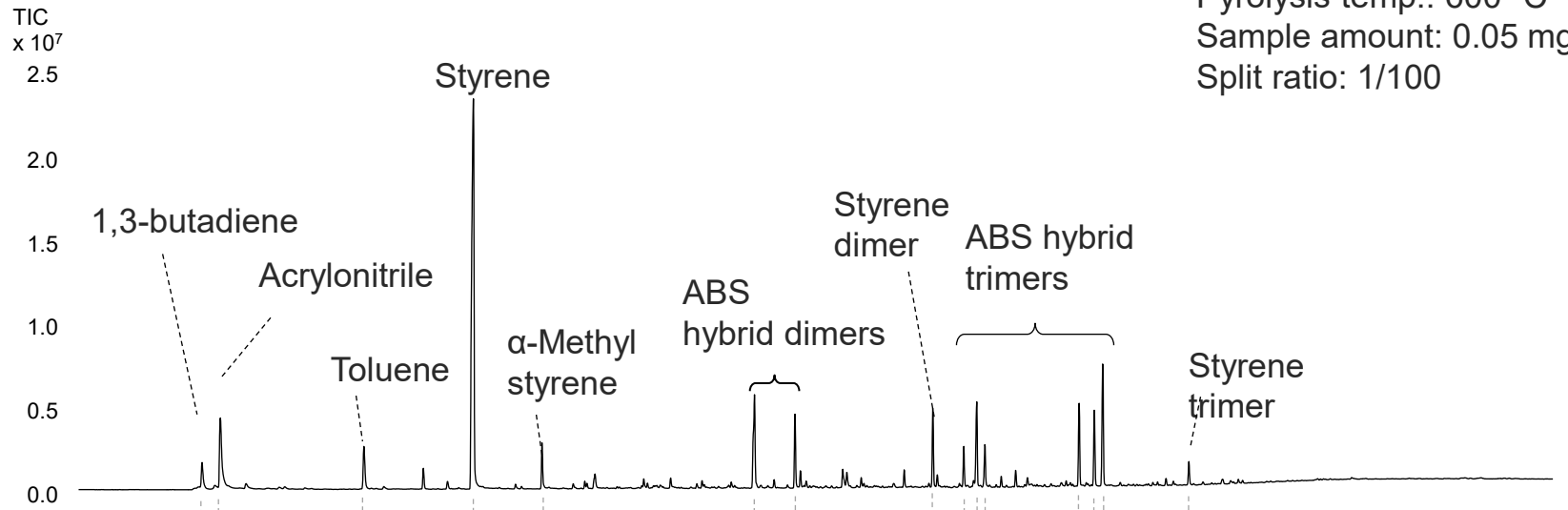
Defective



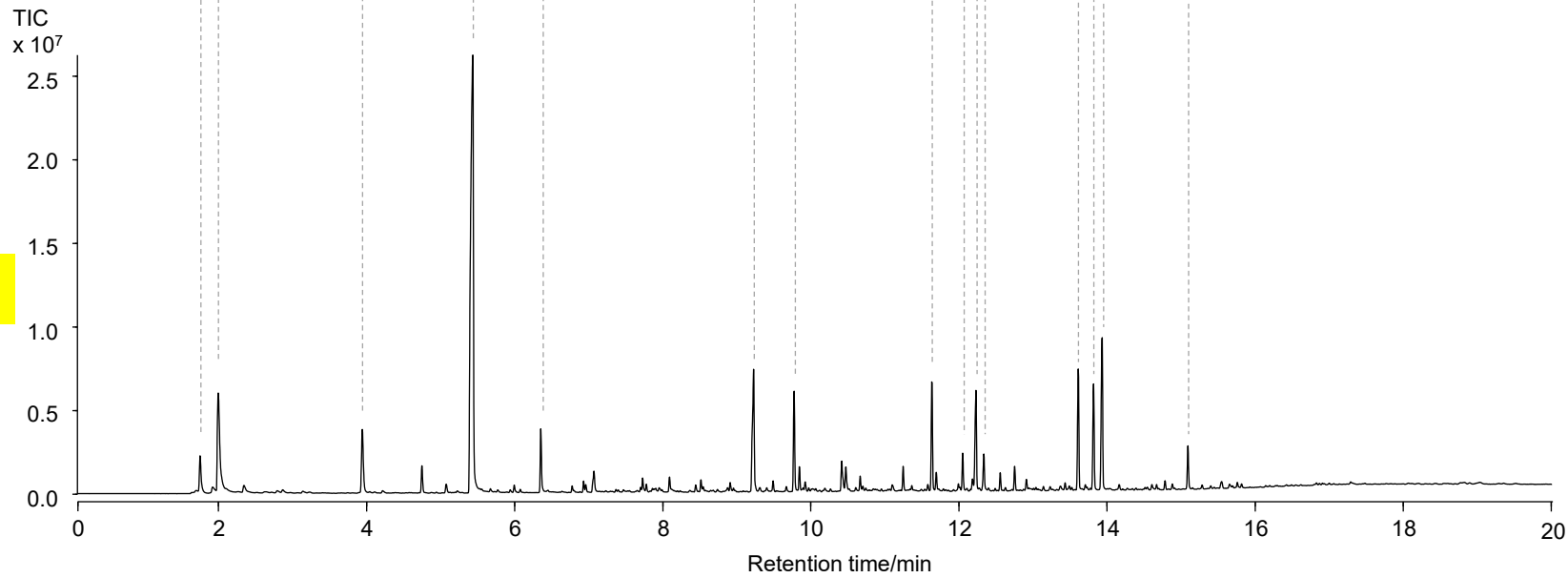
Pyrogram comparison

Pyrolysis temp.: 600 °C
Sample amount: 0.05 mg
Split ratio: 1/100

Good

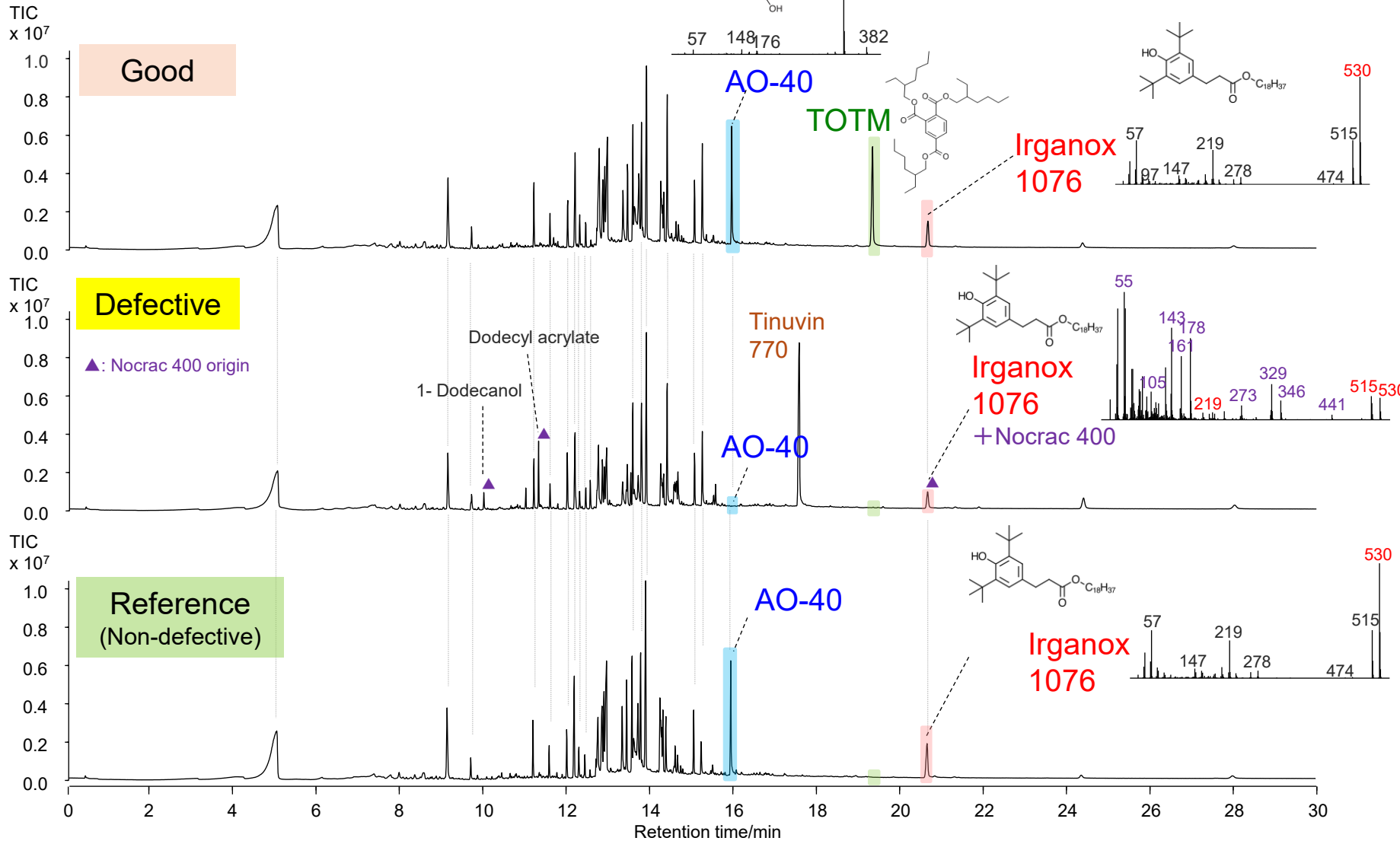


Defective



TD Chromatograms

TD temp.: 100-380 °C (20 °C/min, 1 min hold)
 Sample amount: 1.0 mg, Split ratio: 1/20



Quantitative results

[EIC peak area and reproducibility of good and defective products]

	AO-40		Irganox 1076	
	<i>m/z</i> 339 EIC peak area (<i>n</i> =3 average) (/ABS sample1 mg)	RSD [%]	<i>m/z</i> 530 EIC peak area (<i>n</i> =3 average) (/ABS sample1 mg)	RSD [%]
(a) Good	41,334,309	4.2	7,226,761	1.7
(b) Defective	273,266	19.4	295,432	1.2

[Quantitative results]

	AO-40		Irganox 1076	
	[µg]	[ppm]	[µg]	[ppm]
(a) Good	0.623	623	0.507	507
(b) Defective	0.004	4	0.021	21

Summary

		Good	Defective
EDX analysis		Antimony and bromine flame retardants not detected	
EGA-MS	Polymer	ABS	
	Thermal desorption / pyrolysis behavior	Almost the same evolved gas behavior	
	AO-40	○	x
	Irganox 1076	○	x
Py-GC/MS	Polymer	ABS	
	Comparison of pyrograms	No significant differences	
TD-GC/MS	Tinuvin 770	x	○
	Nocrac 400	x	○
	TOTM	○	x
	AO-40 [ppm]	623	4
	Irganox 1076 [ppm]	507	21

○: Detected
x: Not detected

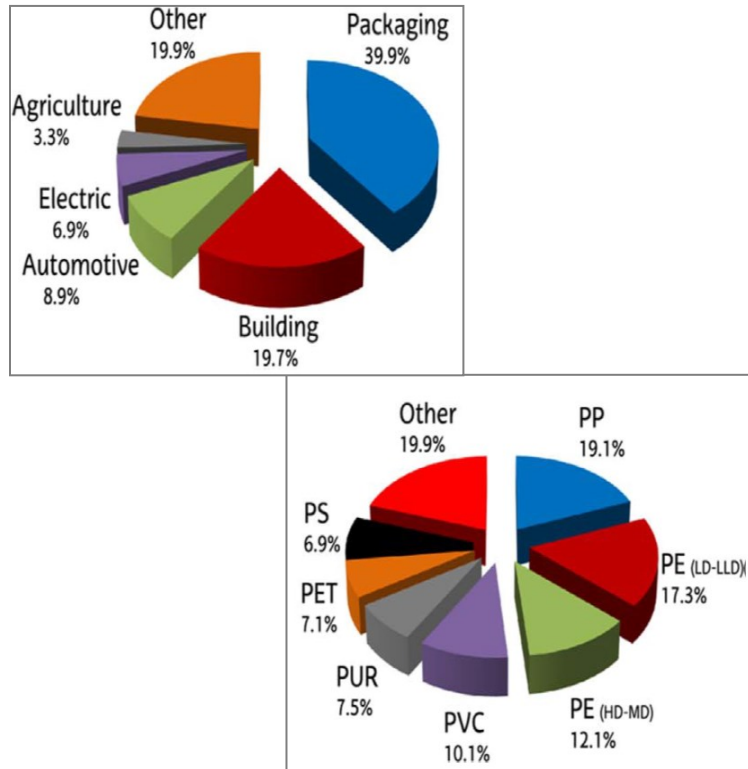
Microplastics



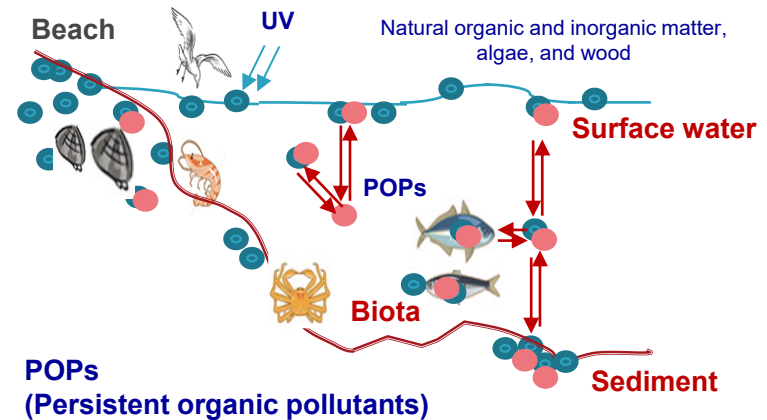
Background : What are microplastics (MNPs) ?

Types and uses of plastics in Europe

(Global annual production : 390 Mt in 2021)



Plastics – the Facts 2016. An analysis of European plastics production, demand and waste data; 2016.



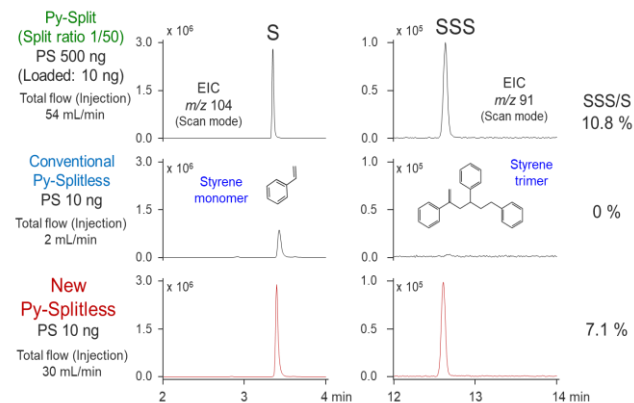
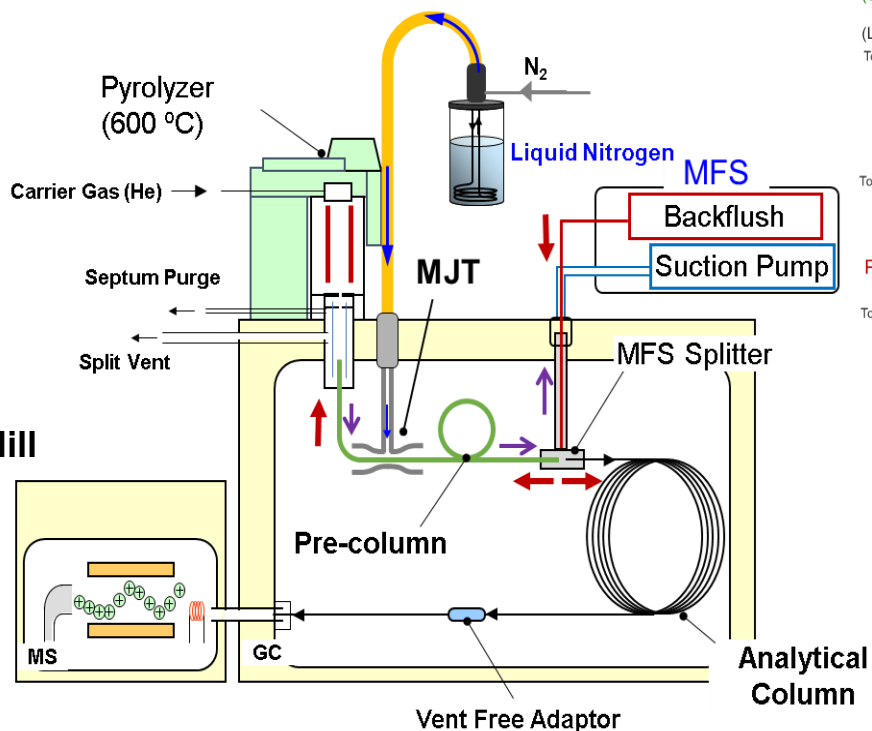
Microplastics: (1 μm - 5 mm)

- Primary - pellets and fibers
- Secondary - degraded pieces
- Damage to wildlife by ingestion

Nano-plastics: (< 1 μm)

- Impact on marine life by accidental ingestion
- Health effects by the concentration of POPs through the food chain

Micro-Furnace Pyrolysis-GC/MS for MP Analysis



- Combination with Single Q GC/MS system
- Need for Micro-Jet Cryo-Trap when using Splitless pyrolysis

Analytical software for microplastics analysis

F-Search MPs 2.1

Easily identify and quantify unknown microplastics (MPs)

- Quick identification of polymer types for unknown MPs by a sophisticated search program

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- Automatic creation of calibration curves and quick quantification
- Library for 12 commonly used polymers



Polyethylene (PE), Polypropylene (PP), Polystyrene (PS), Acrylonitrile–butadiene–styrene resin (ABS), Styrene–butadiene rubber (SBR), Polymethyl methacrylate (PMMA), Polycarbonate (PC), Polyvinyl chloride (PVC), Polyurethane (PU: MDI type), Polyethylene terephthalate (PET), Nylon–6 (N6), Nylon–6,6 (N66)

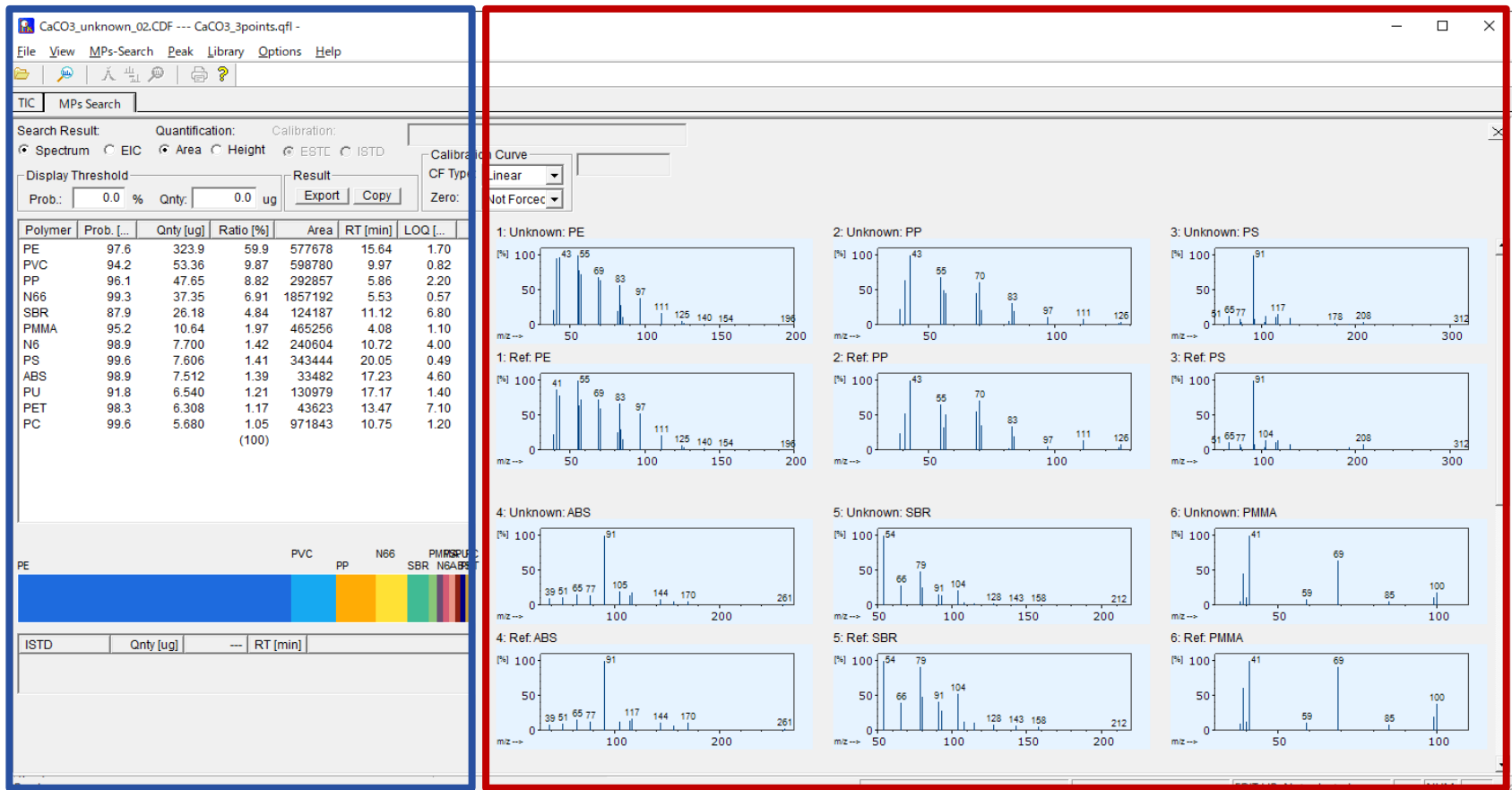
Analytical software for microplastics analysis

F-Search MPs 2.1

Result Window for Qualitative/quantitative analysis results

Qualitative/quantitative result

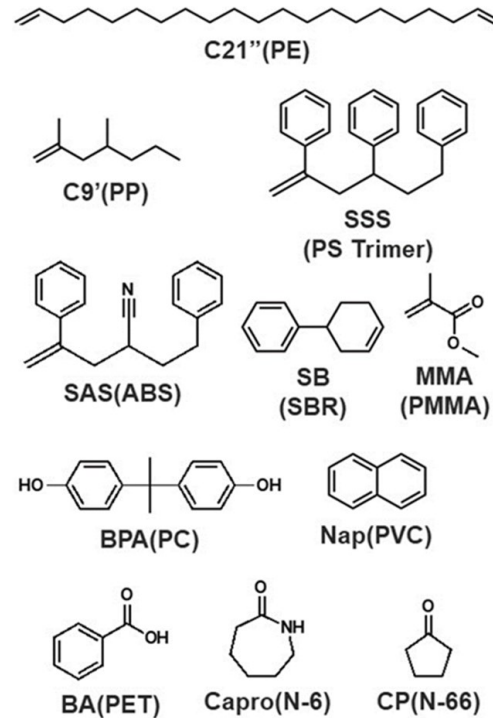
MS spectrum and peak shape



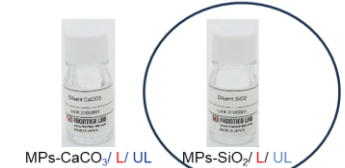
Analytical software for microplastics analysis

F-Search MPs 2.1 : Quantifier Compounds / SiO₂

#	Polymer	Characteristic Compound	Abbreviation*	Quant Ion (main m/z)	Confirm Ion (sub m/z)
1	PE	1,20-Heneicosadiene	C21''	82	292
2	PP	2,4-Dimethyl-1-heptene	C9	126	70
3	PS	Styrene trimer	SSS	91	212
4	ABS	2-Phenethyl-4-phenylpent-4-enitrile	SAS	170	91
5	SBR	4-Phenylcyclohexene	SB	104	158
6	PMMA	Methyl methacrylate	MMA	100	69
7	PC	Bisphenol A	BPA	213	228
8	PVC	Naphthalene	Naph	128	115
9	PET	Benzoic acid	BA	105	122
10	N-6	ε-Caprolactam	Capro	113	85
11	N-66	Cyclopentanone	CP	84	55



2 types of Polymer mixtures in inorganic diluents



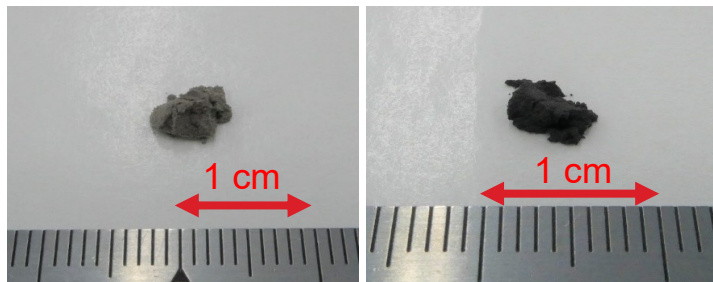
3 concentrations used: Std, Low and Ultra Low
Amount of each polymer contained in 4 mg of MPCs
The weight in the table below is a reference value.
Refer to the inspection sheet attached to the product.

PE	160 / 16 / 1.6 µg	PC	4 / 0.4 / 0.04 µg
PP	40 / 4 / 0.4 µg	PVC	40 / 4 / 0.4 µg
PS	8 / 0.8 / 0.08 µg	PU	4 / 0.4 / 0.04 µg
ABS	16 / 1.6 / 0.16 µg	PET	16 / 1.6 / 0.16 µg
SBR	16 / 1.6 / 0.16 µg	N6	5 / 0.5 / 0.05 µg
PMMA	8 / 0.8 / 0.08 µg	N66	18 / 1.8 / 0.18 µg

Analysis of micro plastics in marine sediment samples



Sediment samples after grinding



Offshore sediment sample

Coastal sediment sample

Samples were provided by Dr. Barbara Scholz-Böttcher, University of Oldenburg, ICBM.

Collected from coastal and offshore seabed surfaces of North Atlantic Bay of Biscay (Spain)

Aqueous sodium bromide solution (density: 1.46 g/mL) was added to the sample and stirred, then density separation was performed.

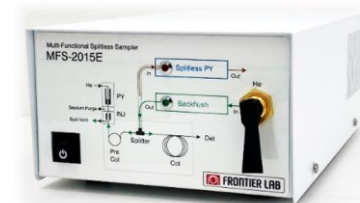
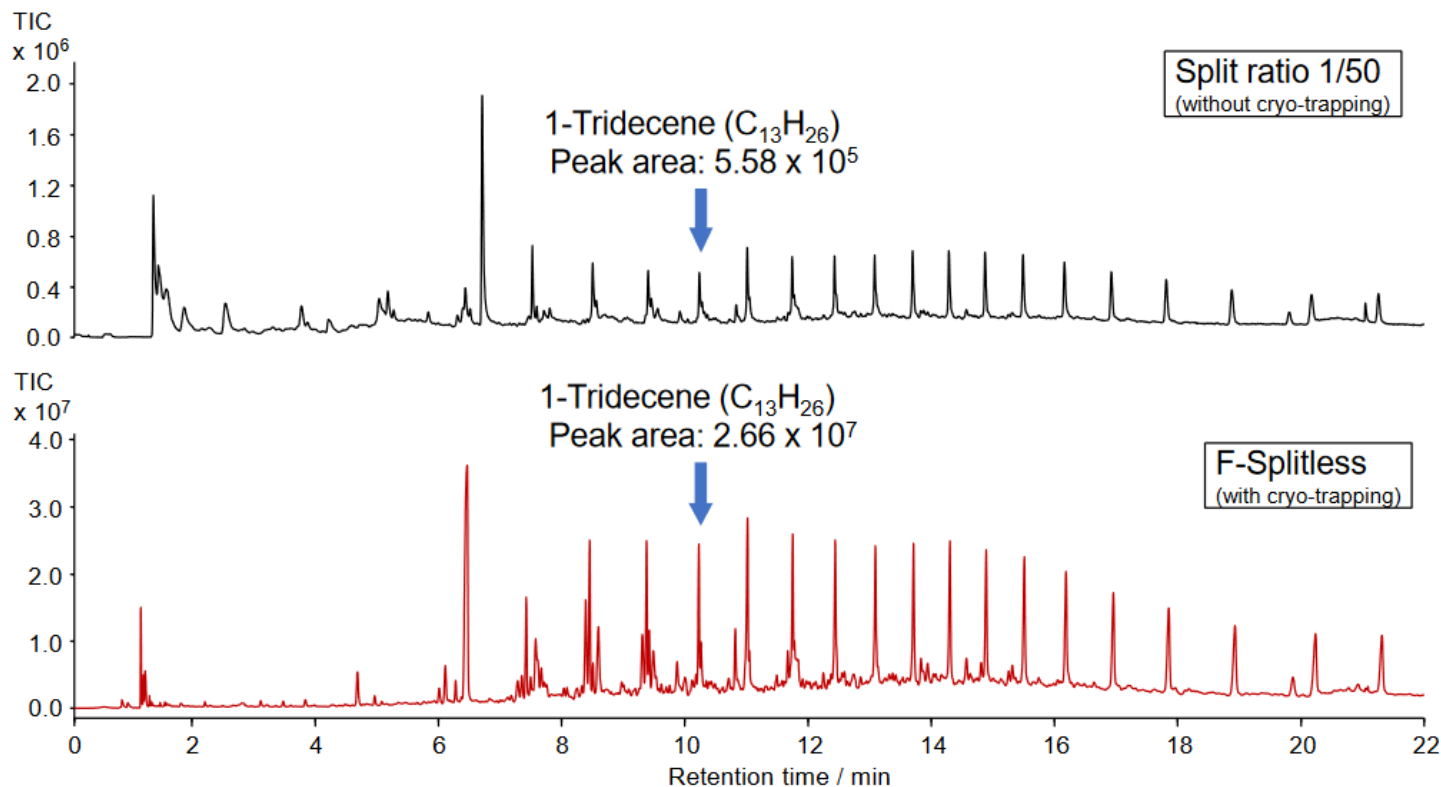
Rinsed with petroleum ether.

Organic substances other than MPs decomposed with hydrogen peroxide solution (32 %, 50 °C, 3 h)

Homogenized by grinding

4.0 mg of the sample was placed in a sample cup covered with quartz wool for measurement.

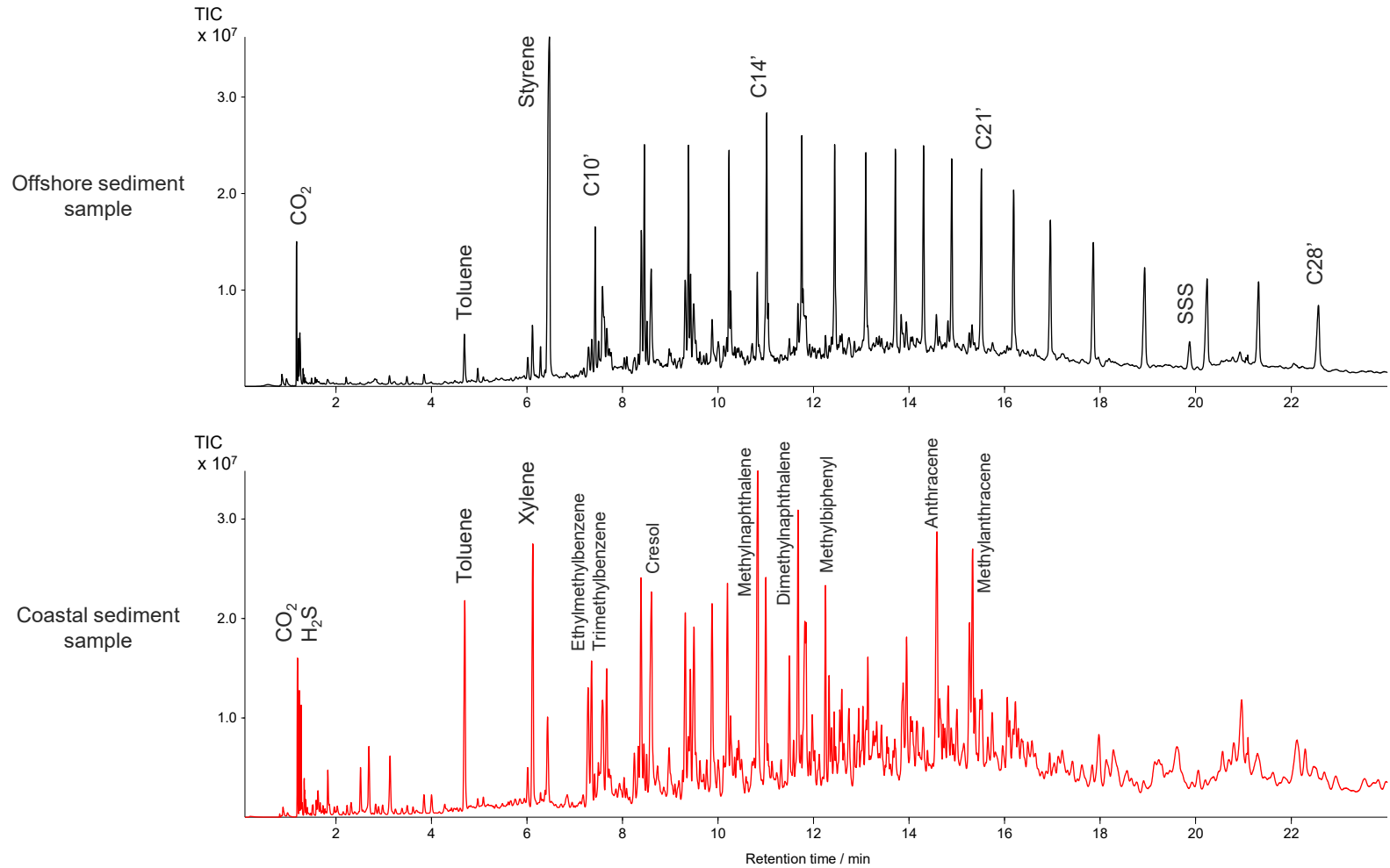
Analysis of micro plastics in marine sediment samples



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Offshore Sediment Sample

Analysis of micro plastics in marine sediment samples



Analysis of micro plastics in marine sediment samples

Offshore sediment sample
(Sample wt. 4.047 mg)

Polymer	Prob. [%]	Qty [ug]	Ratio [%]
PE	98.6	10.22	58.0
PP	90.4	0.23	1.3
PS	99.0	1.12	6.4
PMMA	99.9	0.15	0.9
PET	90.8	0.12	0.7
N66	87.1	0.25	1.4
SBR	51.5	0.67	3.8

Coastal sediment sample
(Sample wt. 4.046 mg)

Polymer	Prob. [%]	Qty [ug]	Ratio [%]
PE	99.1	3.83	12.0
PP	94.5	0.44	1.4
PMMA	99.8	0.26	0.8
N6	96.8	0.17	0.5
N66	72.5	0.33	1.0
SBR	36.8	1.66	5.2

The qualitative and quantitative analyses of MPs in the sediment samples were carried out by creating calibration curves using the Polymer/Silica mixture and F-Search MPs software in F-Splitless mode.

Summary

The use of a multifunctional pyrolyzer in combination with GC/MS, accessory modules (MFS, MJT, SS, AS) and polymer databases and search software (F-SEARCH, F-SEARCH MPs) enables combined thermal methods (EGA-MS, pyrolysis-GC/MS, TD-GC/MS, HC-EGA-GC/MS) for the reliable characterization of polymeric materials (also in the trace range) or identification and quantification of polymers, additives and impurities in order to meet today's new challenges in the laboratory due samples related to sustainability and environment.