Microplastic Analysis by Gas Chromatography-Mass Spectrometry (GC-MS)

PRESENTED BY

Ratimarth Bunlorm

GC GCMS Product Specialist

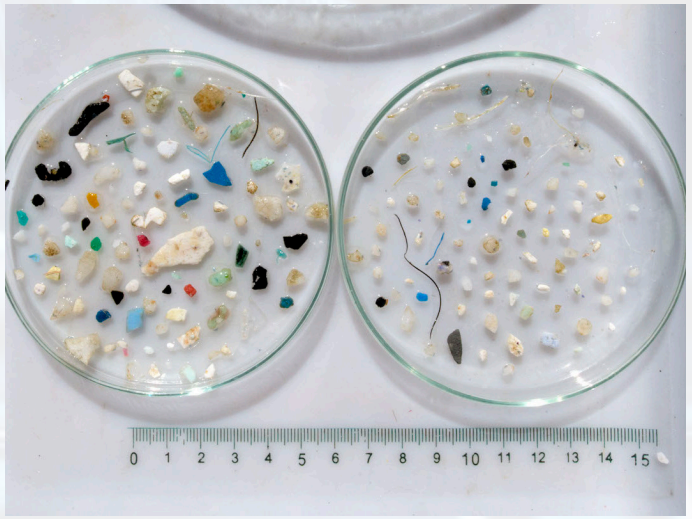
Topic

- Microplastics (MPs)
- Gas Chromatography – Mass Spectrometry (GC-MS)
- Microplastic Analysis by TD-GC/MS
- Microplastic Analysis by PY-GC/MS
- Q&A

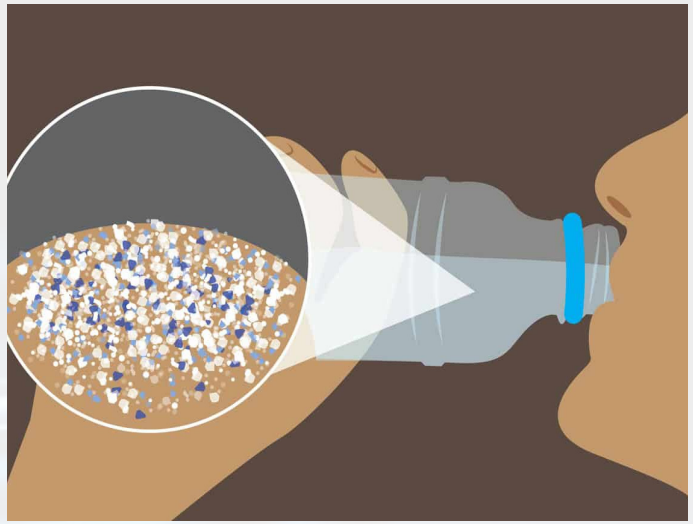
Microplastics (MPs)

Plastics are found throughout the environment

Microplastics are any type of plastic polymer less than 5 mm in length*



Due to their small size they can be easily ingested and accumulate in the human body.



*Source: NOAA

Regulatory & standards landscape

- **UN:** Commissioned a report - Legal Limits on Single-Use Plastics and Microplastics: A Global Review of National Laws and Regulations
- **Europe:** ECHA's Committee for Risk Assessment (RAC) currently in a consultation period. Expected to amend REACH Annex XV to include some MPs.
- **WHO:** Released report in 2019, covers risk to human health, identifies knowledge gaps, recommendations for management actions.
- **ISO/CD 24187:** "Principles for the development of standards for investigation procedures of plastics in environmental matrices and related materials"
- **ASTM WK67788:** New Test Method for Identification of Microplastic Particles and fibres in Municipal Wastewater using Pyrolysis-GC/MS.

Gas Chromatography – Mass Spectrometry

GC-MS

Gas Chromatography

- Gas Chromatography (GC) : Chromatography technique which gas is used as mobile phase

- Sample will be injected into the system, Injection port where all components are vaporized and swept into the column

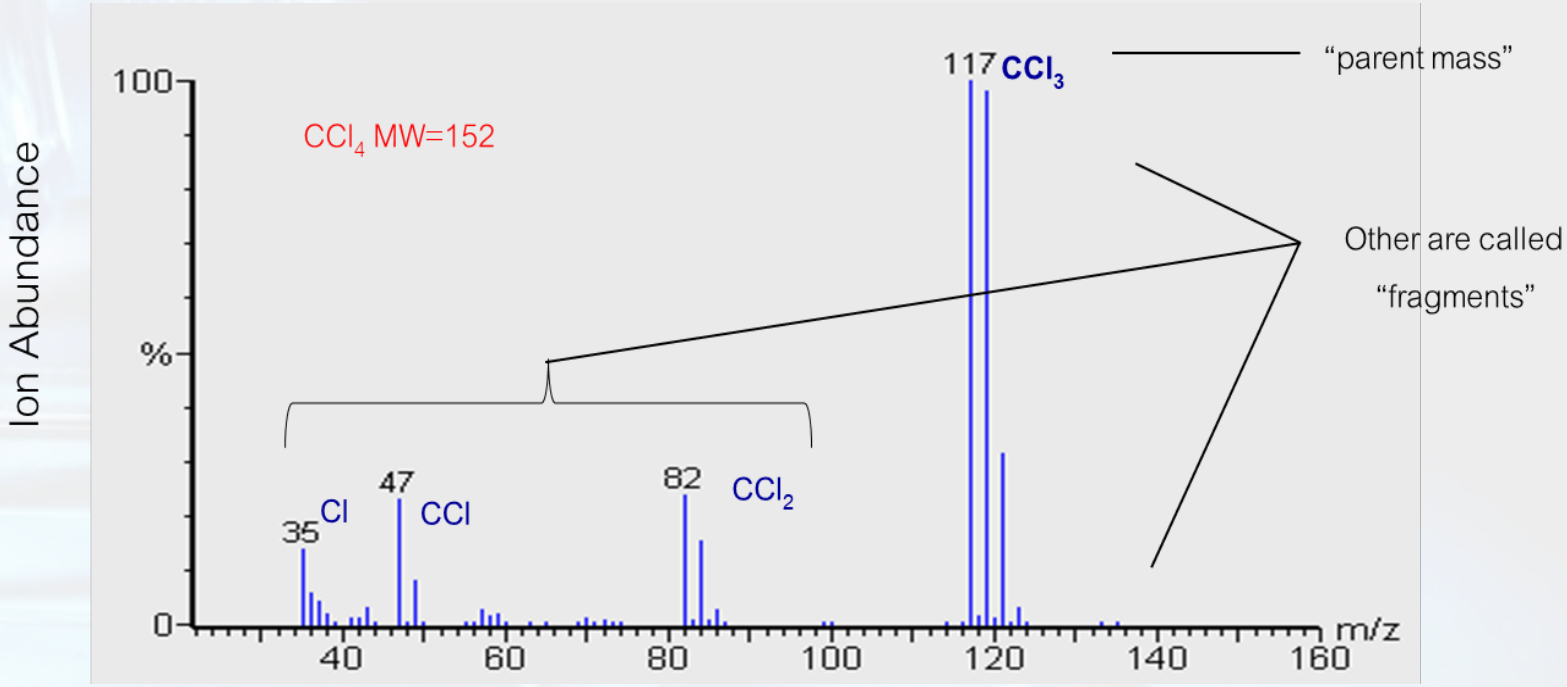
- Sample components will then be separated according to the interaction with stationary phase and eluted to detector.

Mass Spectrometry

- The production of ions that are subsequently separated or filtered according to their mass-to-charge (m/z) ratio and detected.
- The resulting mass spectrum is a plot of the (relative) abundance of the produced ions as a function of the m/z ratio."

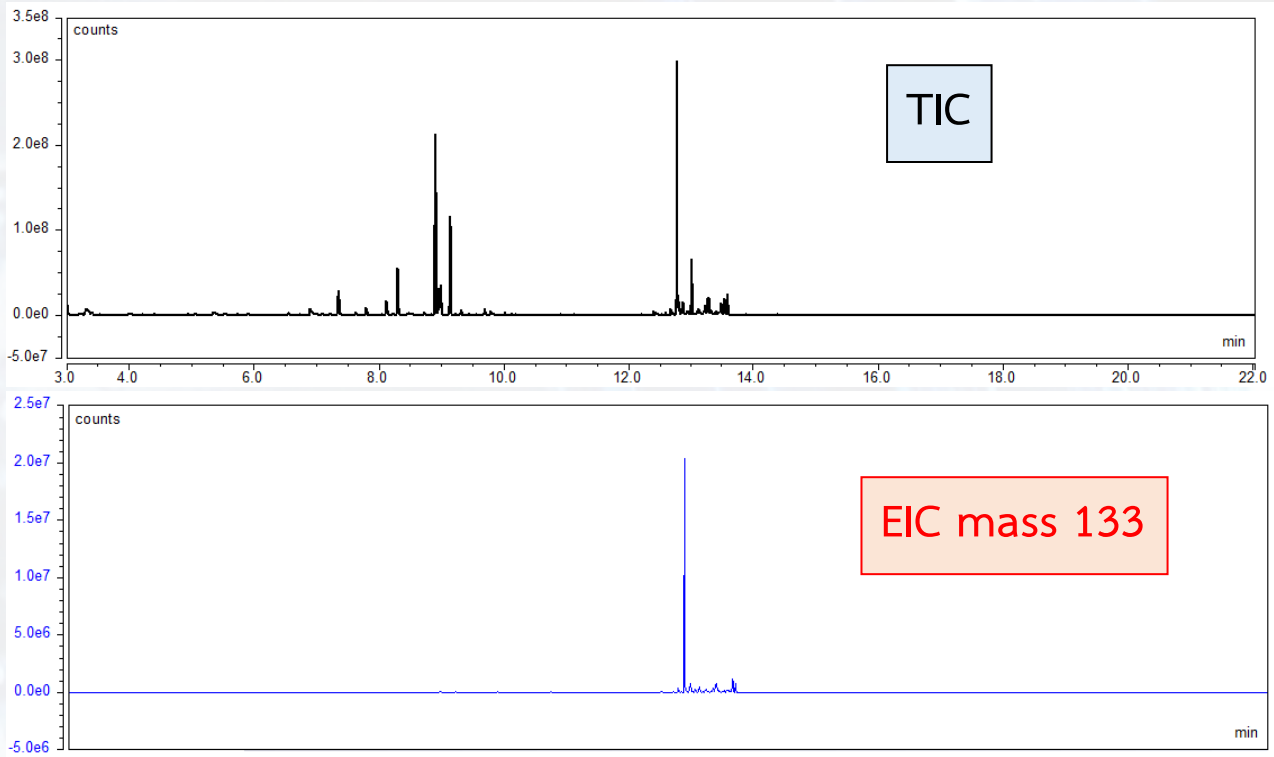
Characteristics of a Mass Spectrum

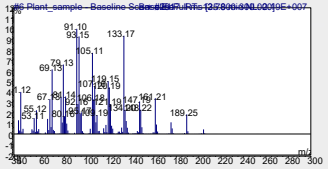
- Graph of Ion Intensity vs. m/z
- Ion Fragments detail structure and molecular weight of compound
- Example : Mass spectrum of Carbon Tetrachloride



Total Ion Chromatogram (TIC)

Extracted Ion Chromatogram (EIC), and Mass Spectrum





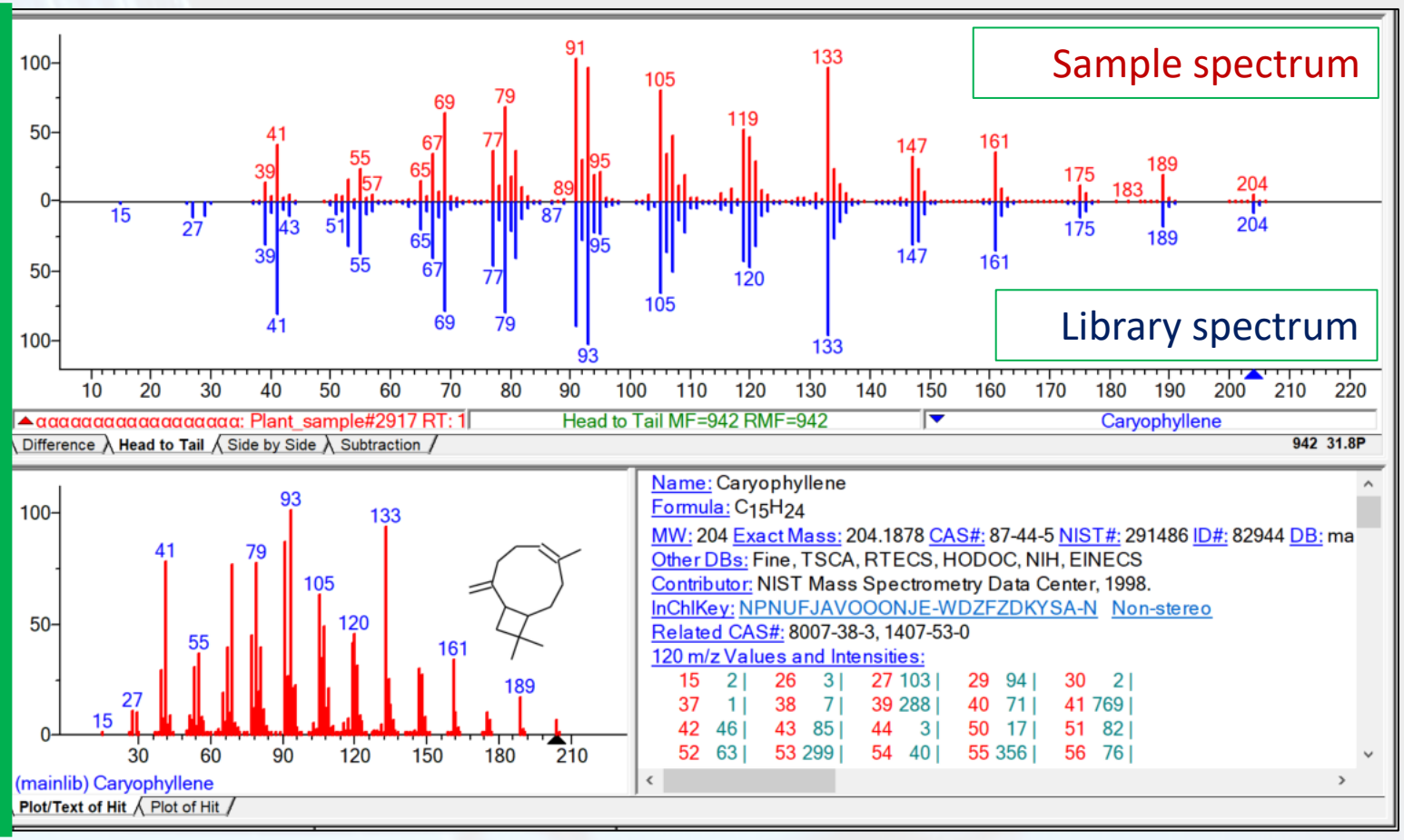
Spectrum peak at RT 12.7 min

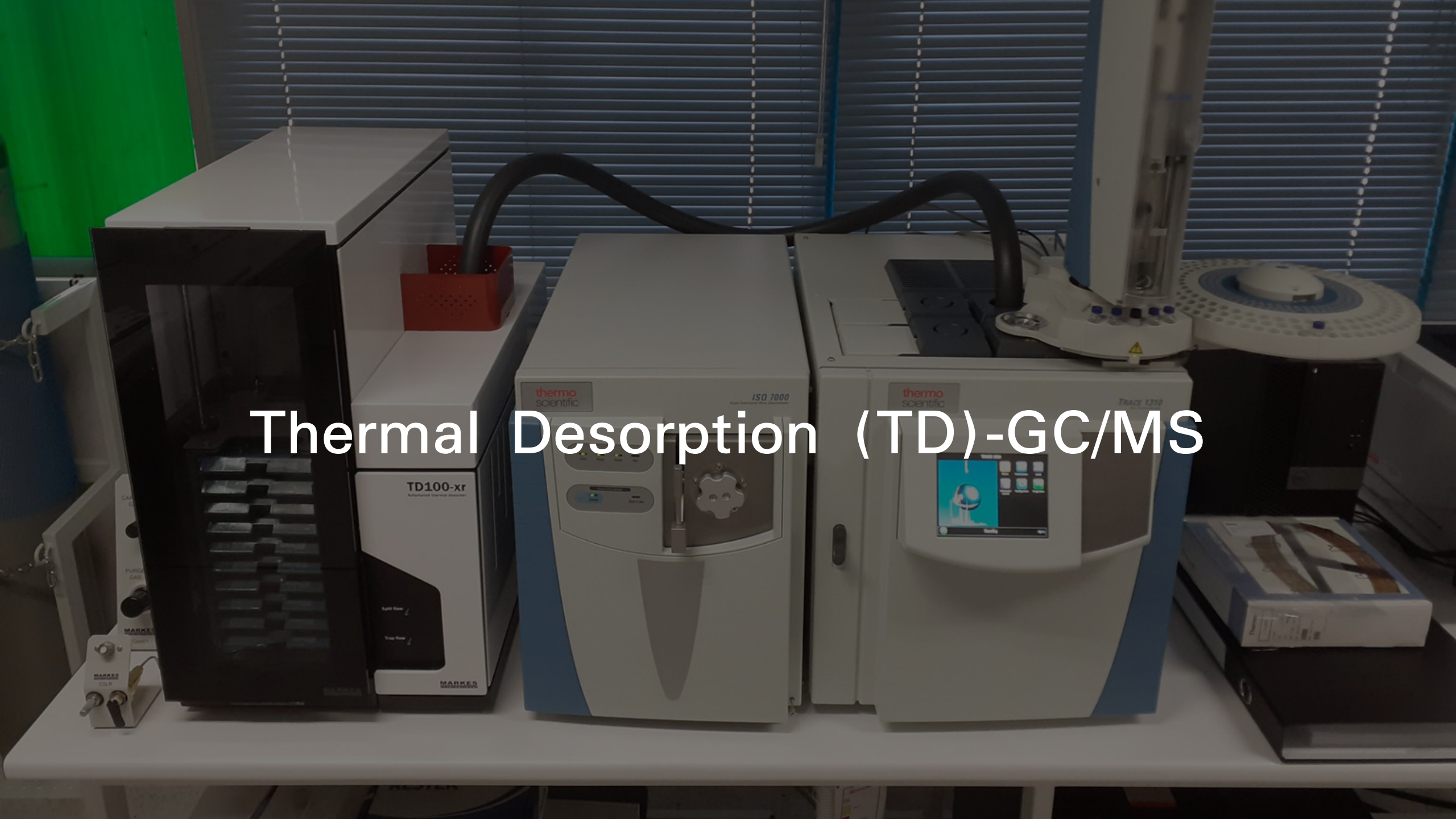
Library Search

GC/MS (EI) Library Search

#	Lib.	Match	Prob. (%)	Name
1	M	942	31.8	Caryophyllene
2	M	920	12.6	Bicyclo[5.2.0]nonane, 2-methylene-4,8,8-trimethyl-4-vi...
3	M	907	8.13	Bicyclo[7.2.0]undec-4-ene, 4,11,11-trimethyl-8-methyl...
4	M	889	4.19	Bicyclo[7.2.0]undec-4-ene, 4,11,11-trimethyl-8-methyl...
5	M	888	4.03	1R,3Z,9S-4,11,11-Trimethyl-8-methylenebicyclo[7.2.0...
6	M	876	2.68	Longifolene-(V4)
7	M	875	2.58	(1R,9R,E)-4,11,11-Trimethyl-8-methylenebicyclo[7.2.0...
8	M	873	2.38	(4aS,9aR)-3,5,5,9-Tetramethyl-2,4a,5,6,7,9a-hexahyd...
9	M	863	1.68	β-Longipinene
10	M	863	1.68	Bicyclo[5.3.0]decane, 2-methylene-5-(1-methylvinyl)-8...
11	M	861	1.55	Spiro[5.5]undec-2-ene, 3,7,7-trimethyl-11-methylene-, ...
12	M	861	1.55	Bicyclo[4.3.0]nonane, 7-methylene-2,4,4-trimethyl-2-vi...
13	M	860	1.49	Alloaromadendrene
14	M	858	1.37	Longifolene
15	M	853	1.10	1H-Cycloprop[e]azulene, decahydro-1,1,7-trimethyl-4-...
16	M	851	1.02	Cycloheptane, 4-methylene-1-methyl-2-(2-methyl-1-pr...
17	M	848	0.90	4,11,11-trimethyl-8-methylenebicyclo[7.2.0]undec-3-ene
18	M	846	0.83	(3R,4aS,5R)-4a,5-Dimethyl-3-(prop-1-en-2-yl)-1,2,3,4,...
19	M	846	0.83	1H-Benzocycloheptene, 2,4a,5,6,7,8,9,9a-octahydro-3...
20	M	844	0.76	Aciphyllene
21	M	844	0.76	(S,1Z,6Z)-8-Isopropyl-1-methyl-5-methylenecyclodec...
22	M	843	0.73	(-)-Tricyclo[6.2.1.0(4,11)]undec-5-ene, 1,5,9,9-tetramet...
23	M	843	0.73	Naphthalene, 1,2,3,5,6,7,8,8a-octahydro-1,8a-dimethy...
24	M	841	0.68	1,4-Methano-1H-indene, octahydro-4-methyl-8-methyl...

Names | Structures — InLib = -100, Hit List





Thermal Desorption（TD)-GC/MS

Thermal desorption (TD)

- Thermal desorption is arguably the world's most versatile, readily-automated injector mechanism for gas chromatography.

- An alternative to solvent extraction for measuring VOC and SVOC compounds in many different sample matrices – solids, liquids or gases

Thermal desorption Sampling

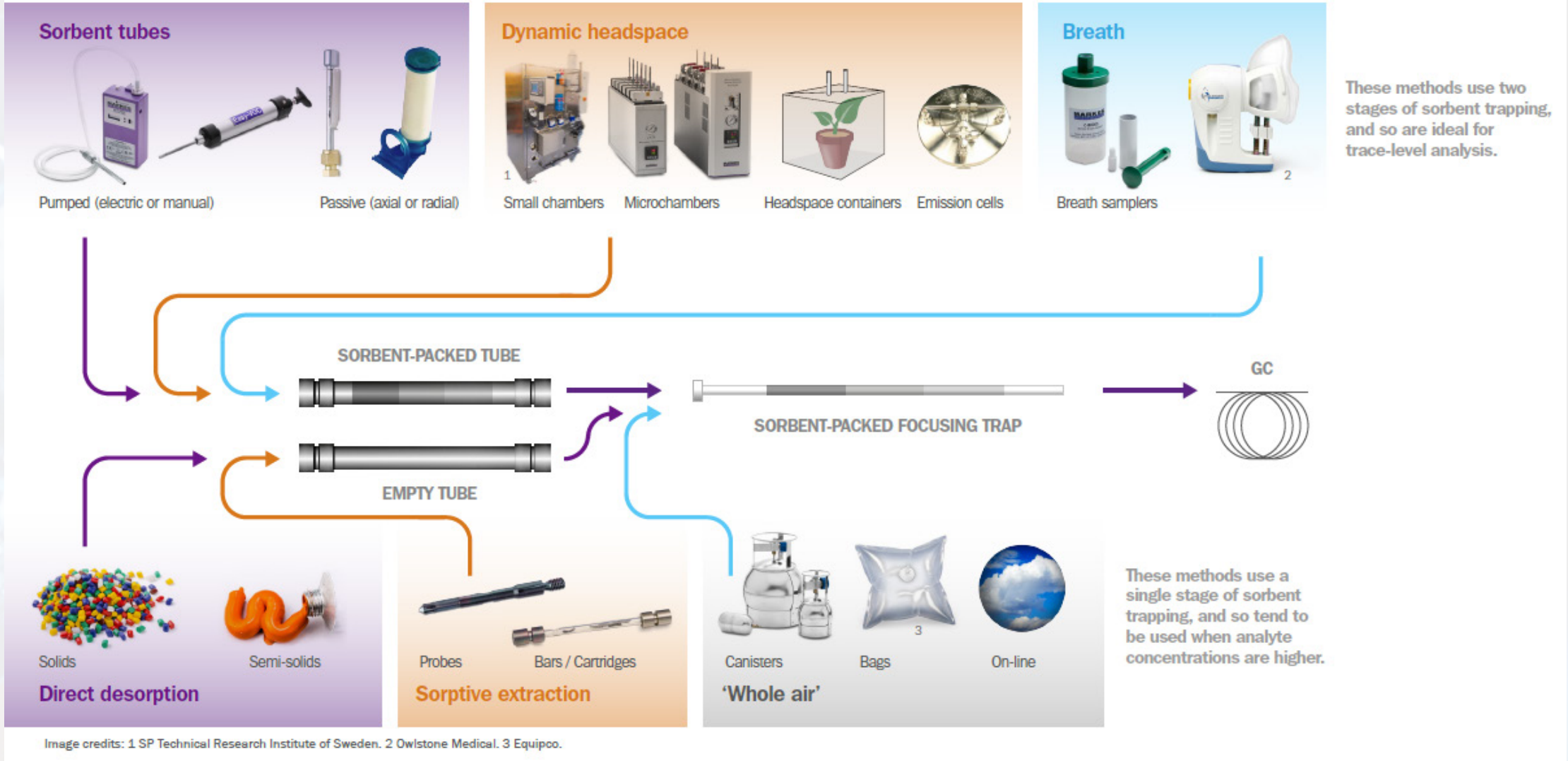
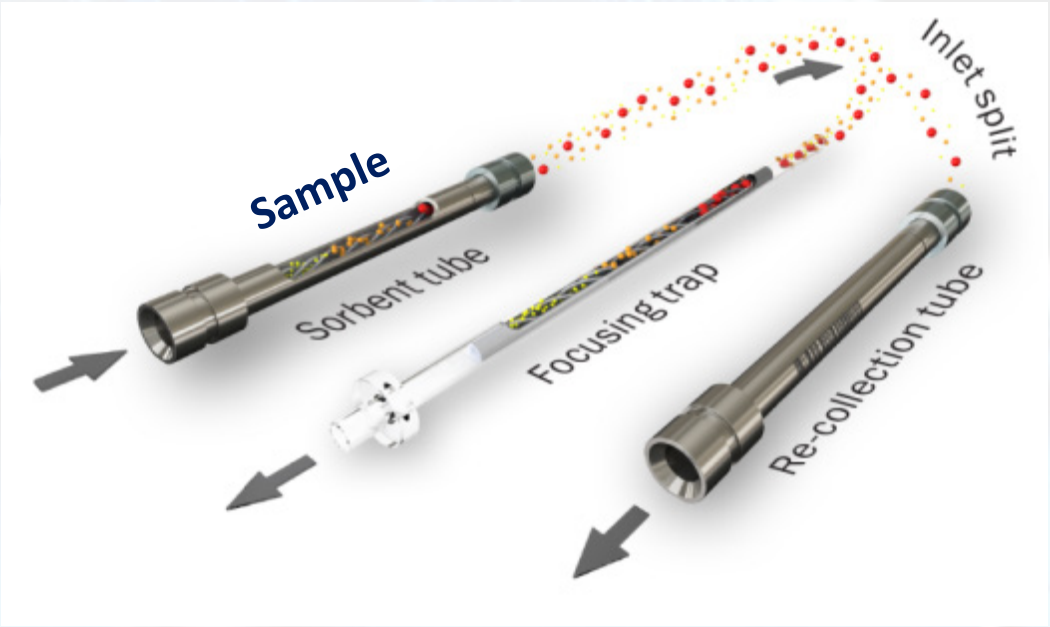


Image credits: 1 SP Technical Research Institute of Sweden. 2 Owlstone Medical. 3 Equipco.

The analytical thermal desorption process

Stage 1

- Tubes containing the sample materials or sampled sorbents are heated in a reverse flow of inert (carrier) gas, releasing the trapped compounds and sweeping them into an electrically-cooled, low thermal mass sorbent focusing trap, typically held at -30 to +30°C.

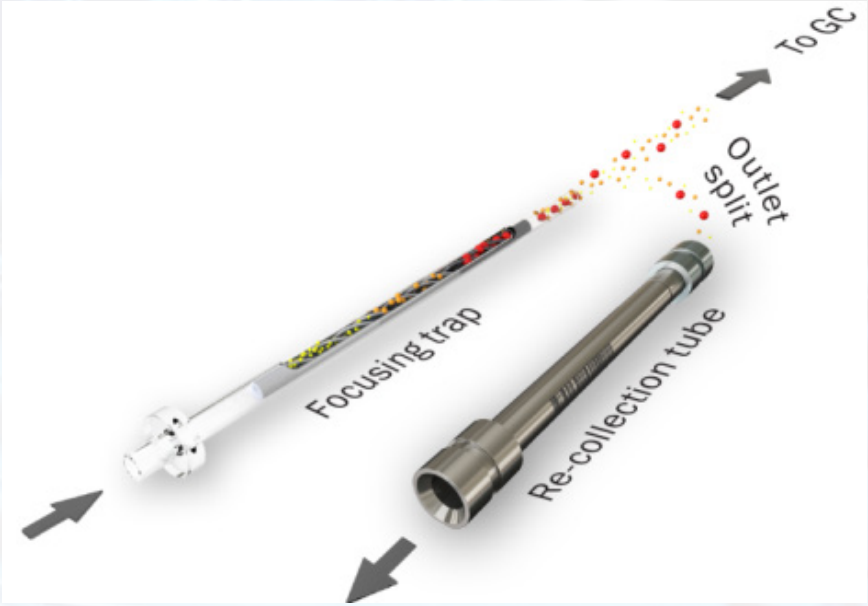


Optional 'inlet' split with re-collection

The analytical thermal desorption process

Stage 2

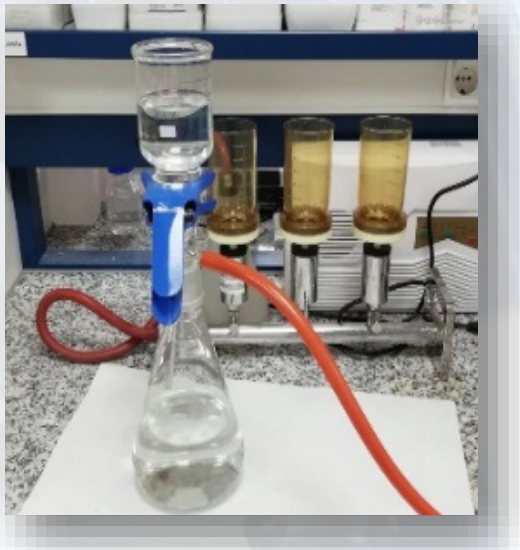
- Once the sample has been focussed onto the trap it is rapidly heated, at rates up to 100°C/s, in a reverse flow of carrier gas.
- Retained compounds are released and injected into the GC in a narrow band of vapour - delivering high sensitivity capillary GC performance.

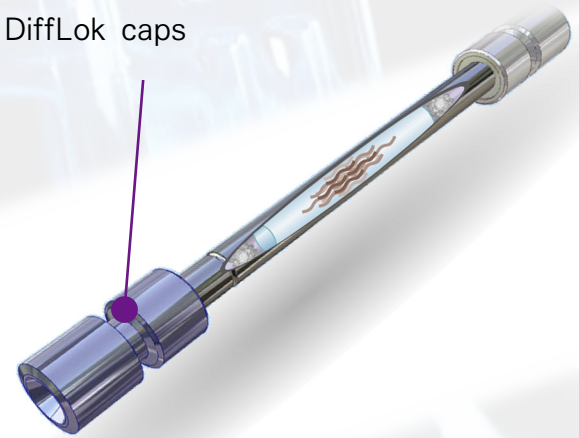


Optional 'outlet' split with re-collection

Microplastic Analysis by TD-GC/MS

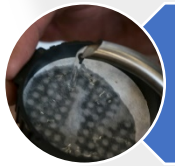
Sample Preparation for analysis MPs (PET) in drinker water





- Hundreds of mL to liters of water are filtered
- The filter is then washed with multiple reagents to remove organic matter
- Dried filter is then placed directly into an empty thermal desorption tube for analysis

Filtering
0.2µm quartz filter



Washing
with reagents

Drying
30min at 100˚C

Quick Preparation
filter into TD-tube

1 h
Sample
preparation
time

Direct Desorption at
320˚C

30 mins
analytical cycle

Workflow: TD-GC/MS analysis

- After trap desorption the compounds separate within the GC column and are detected and identified with the MS.
- This produces a chromatogram which can be used as a chemical fingerprint
- Marker compounds are identified using standards and peak areas can be used to create a calibration curve

TD-GC/MS system

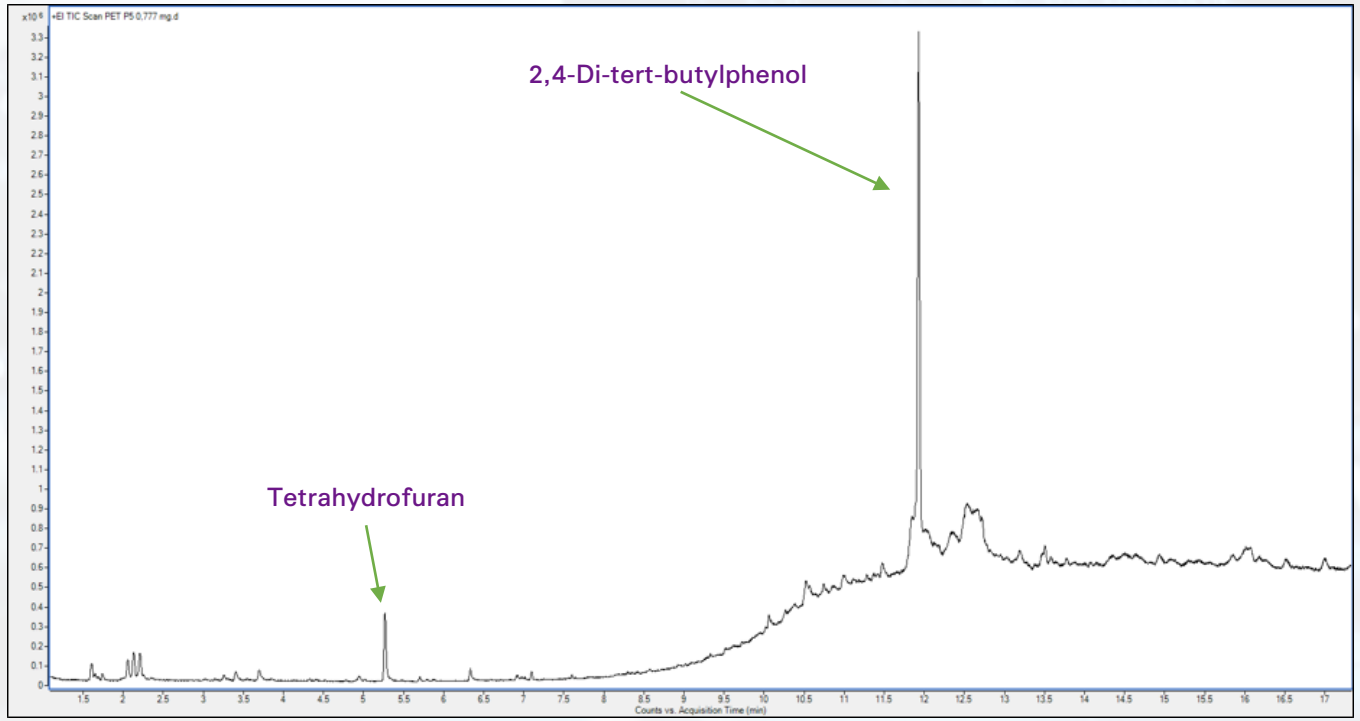
Polyethylene terephthalate (PET) in water

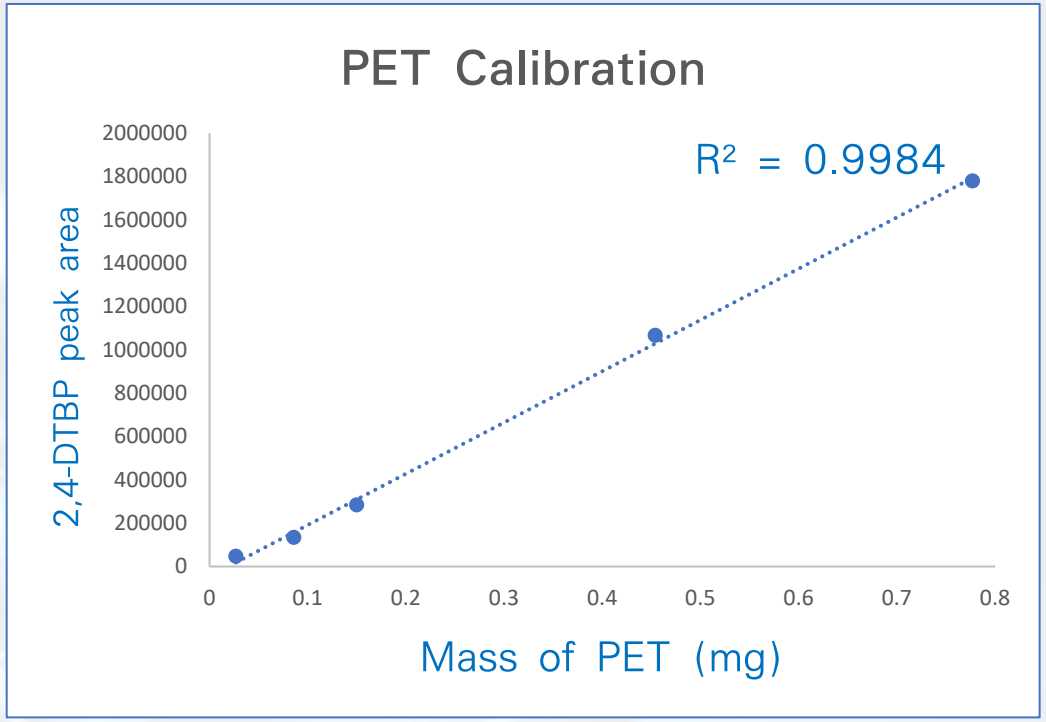
Identify marker compounds for PET by TD–GC–MS analysis of standard pellets.

- 2,4-di-tert-butylphenol (2,4-DTBP) used as quantitation marker
- Tetrahydrofuran is used to confirm presence of PET

Create calibration curve to quantify PET in samples

- Mass of PET vs DTBP peak area

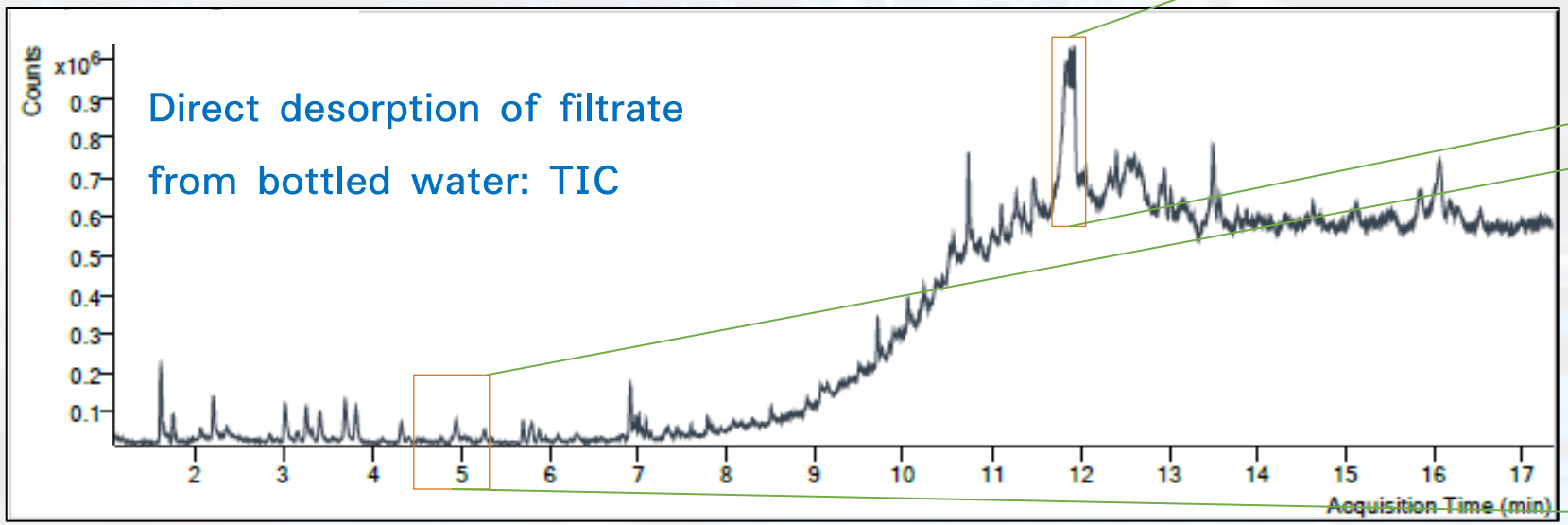


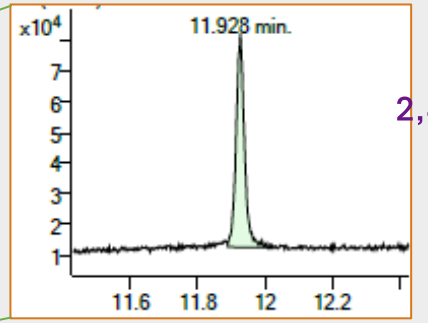


Microplastics in beverages: Case study

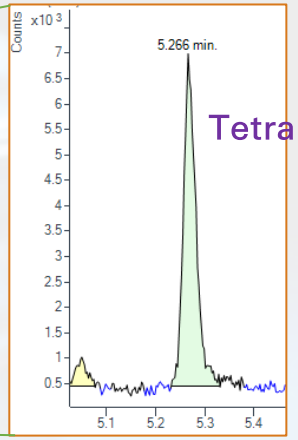
Bottled water sample analysis:

- Both the quantification and confirmation markers were identified
- Concentration of PET in a still water sample was quantified as 46 µg/L





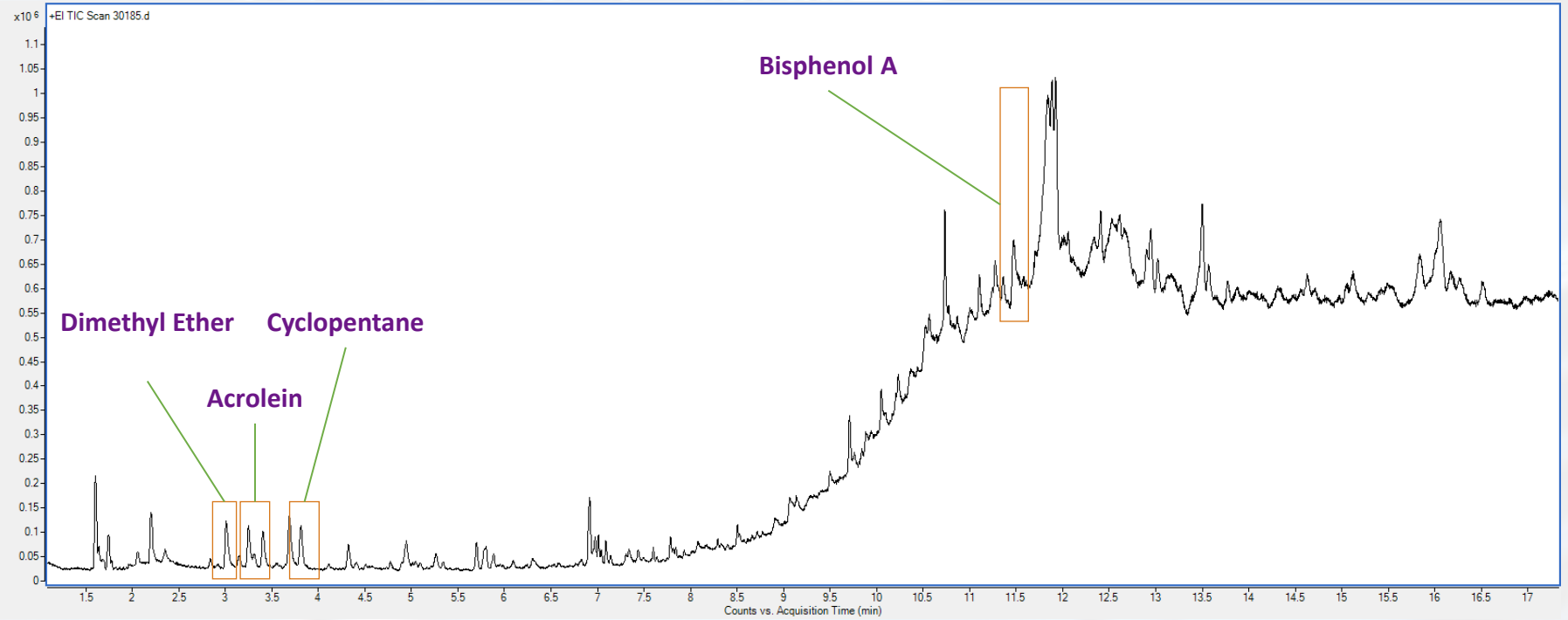
EIC
2,4-DTBP

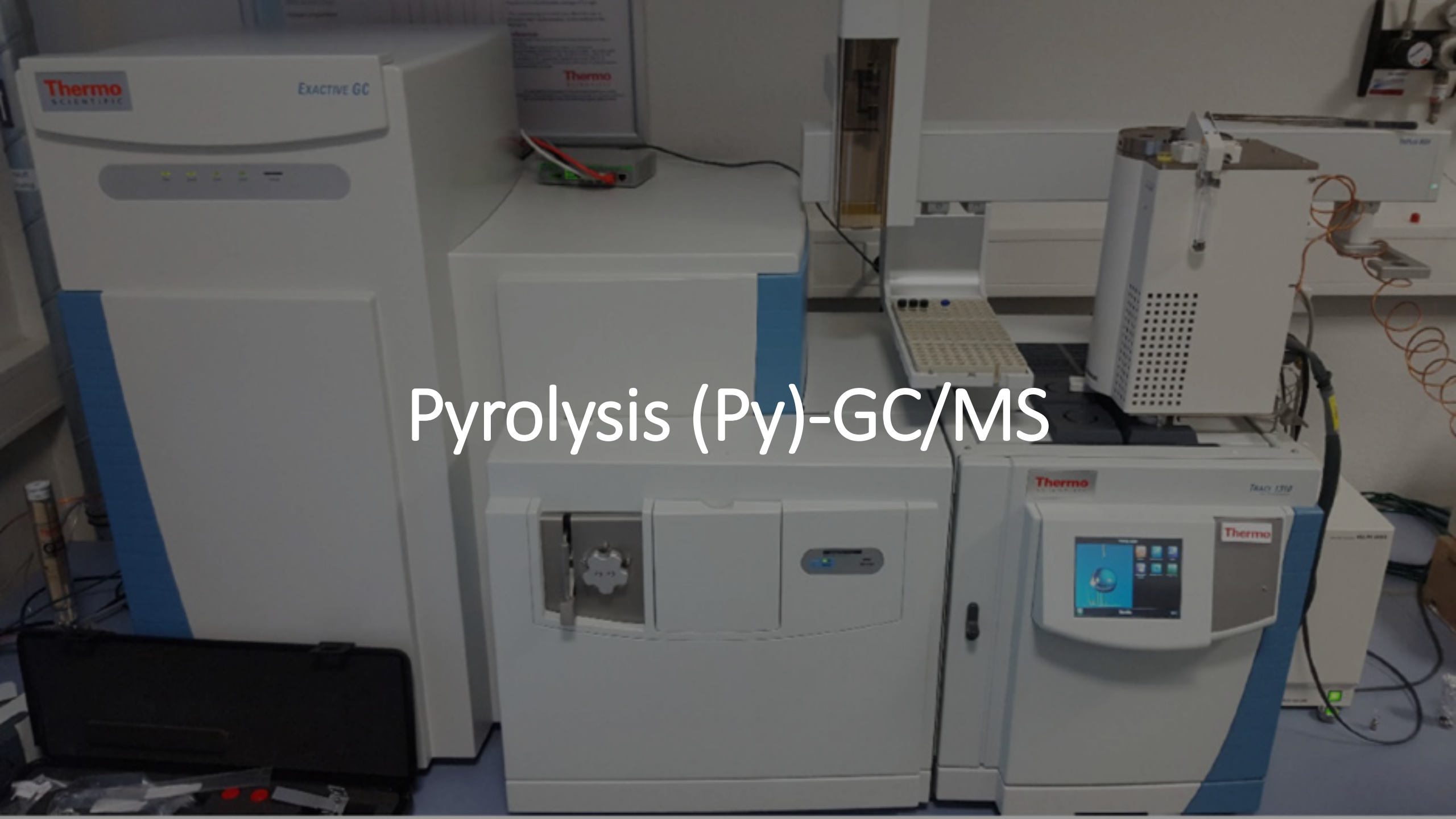


EIC
Tetrahydrofuran

Polyethylene terephthalate (PET) in water

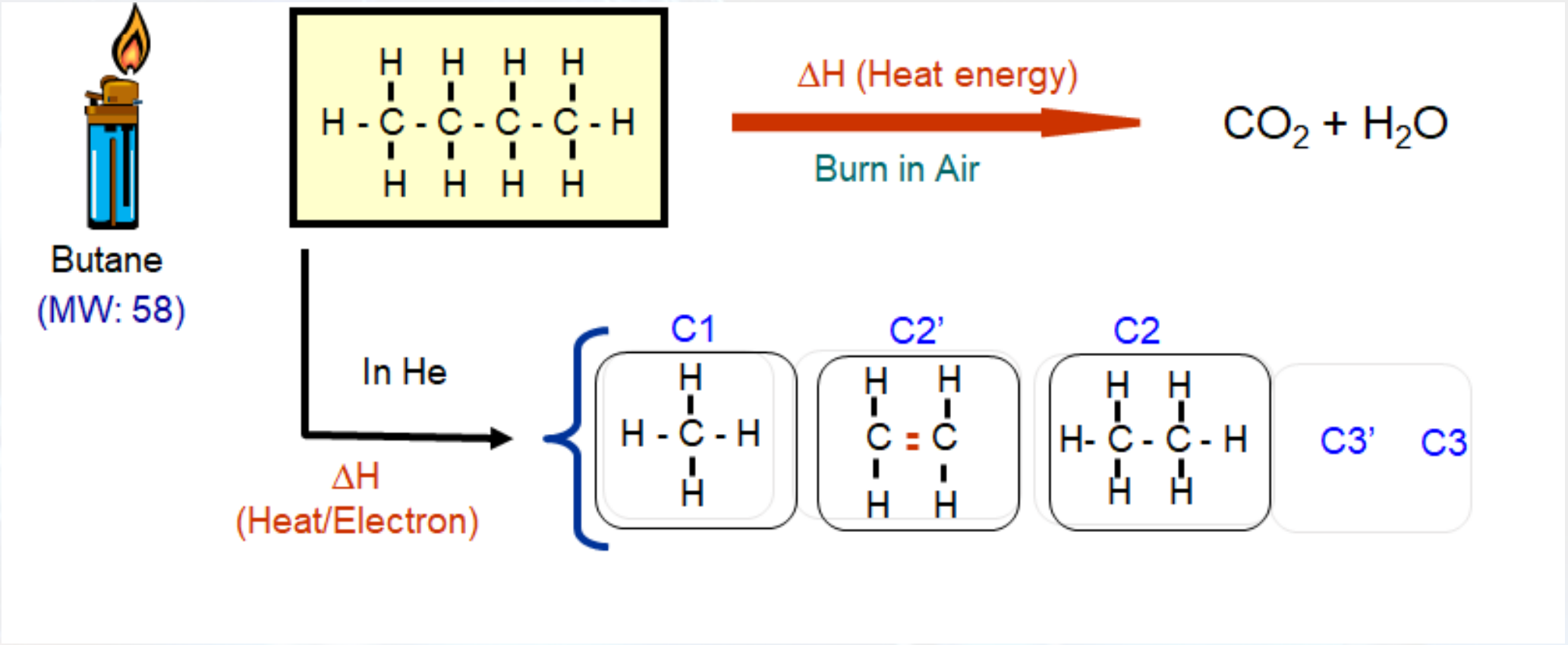
- In addition to markers for PET, a number of compounds used in the process of manufacturing plastics have been tentatively found including dimethyl ether, acrolein and cyclopentene and could assist with source profiling.
- Bisphenol A (BPA) is an additive found in plastics to help with hardening. Research suggests this may be an endocrine disruptor so it is a compound of interest in assessing toxicity.





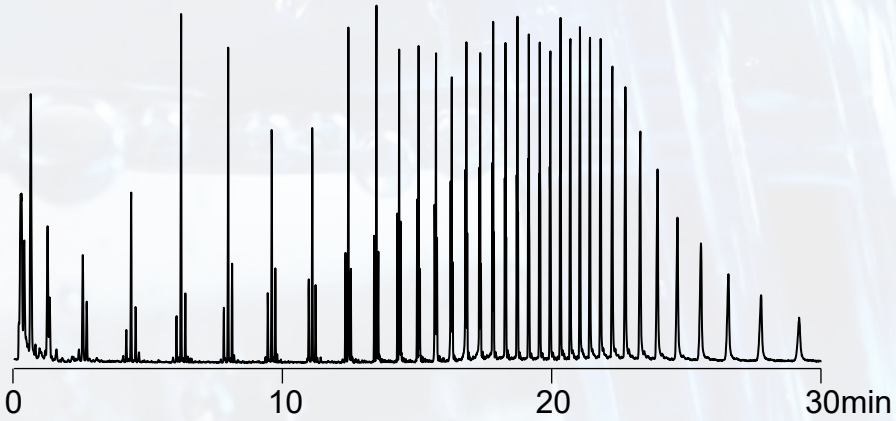
Pyrolysis (Py)-GC/MS

Pyrolysis and pyrolyzates of polymeric materials

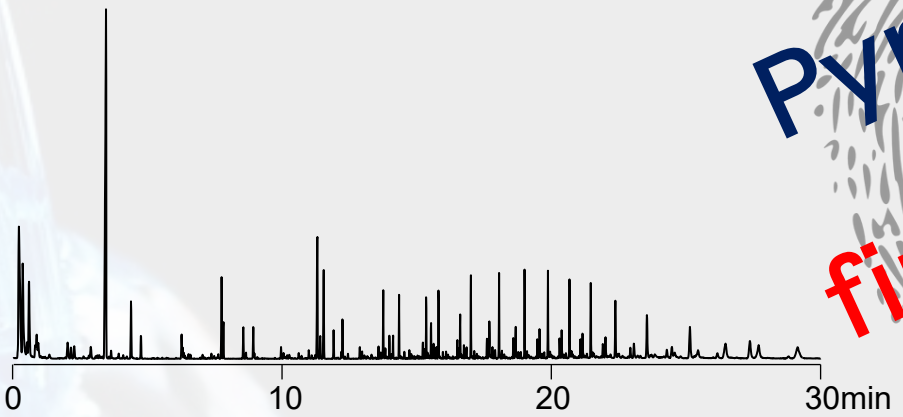


Pyrograms of typical polymers

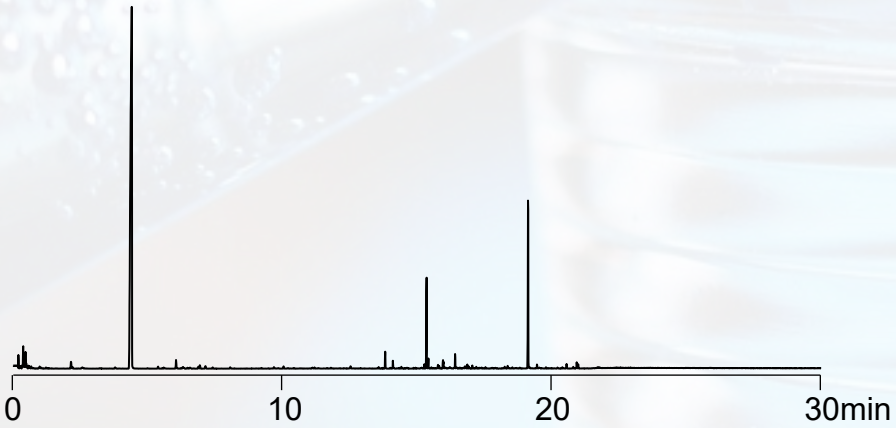
Polyethylene



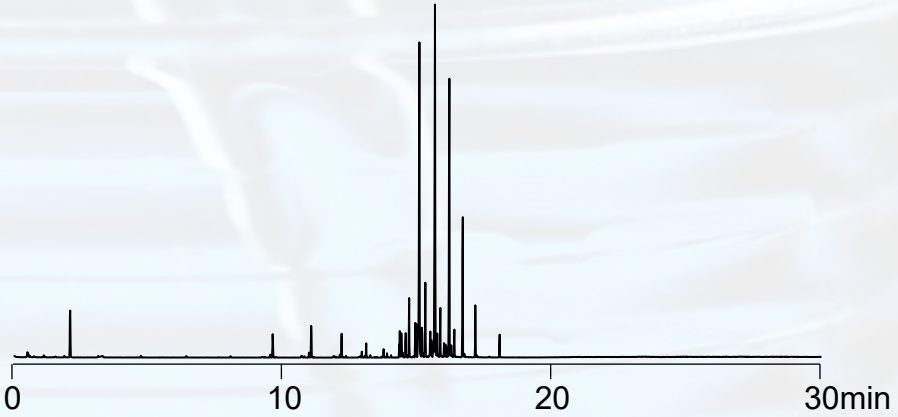
Polypropylene



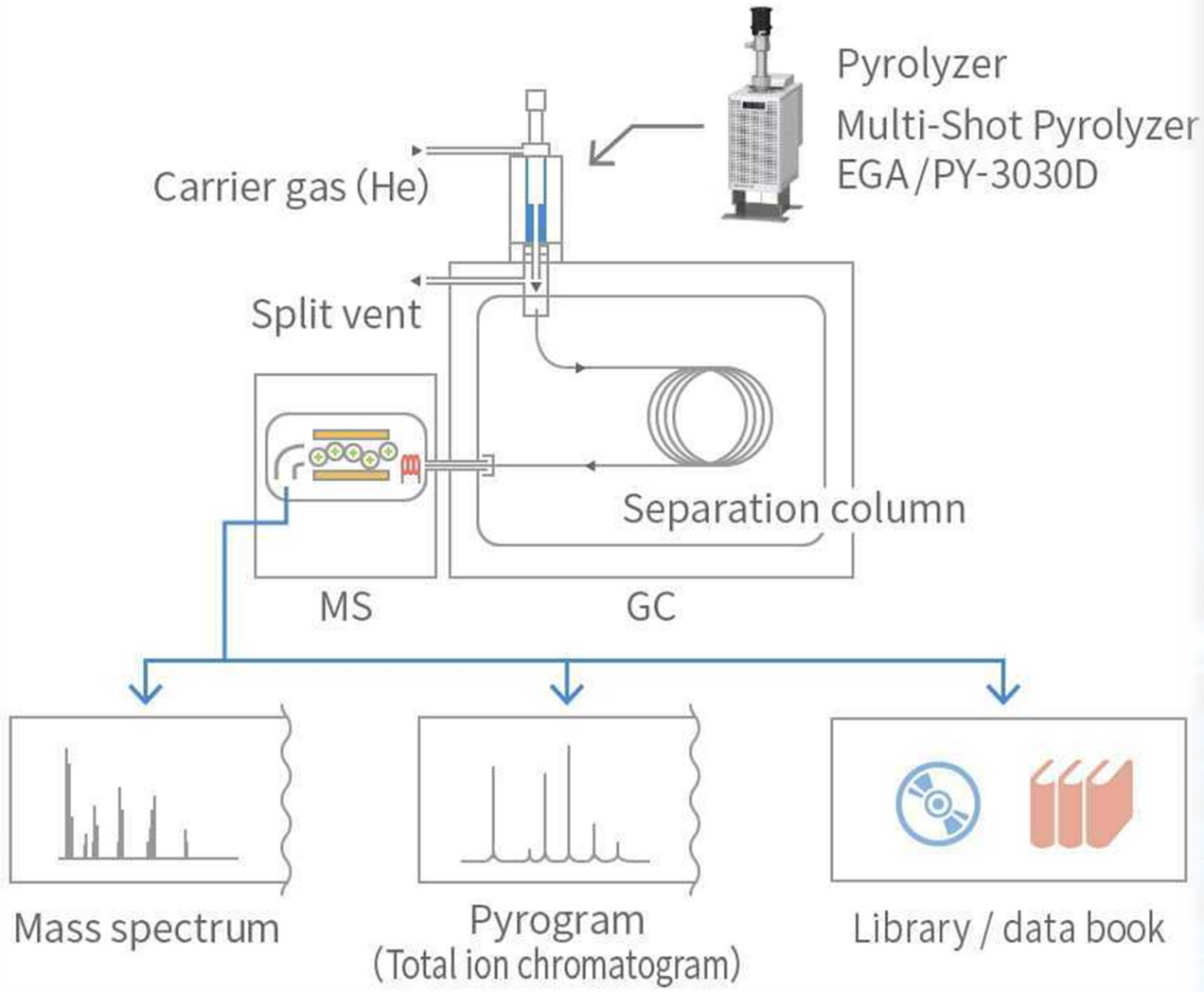
Polystyrene



Higher methacrylate copolymer

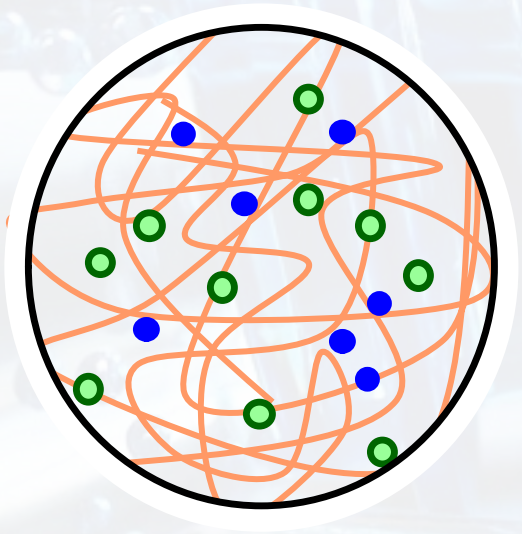


Configuration of pyrolysis-GC/MS system



Polymeric material and pyrolysis

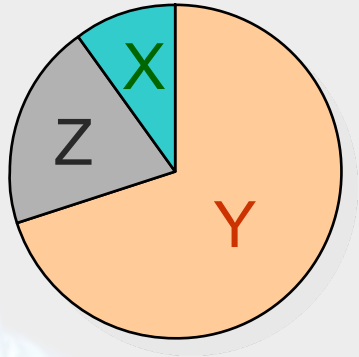
Pattern diagram of
typical polymeric material



: Additives

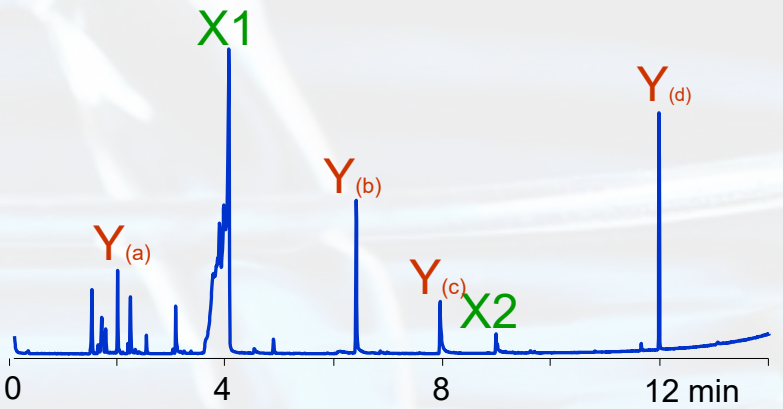
: Polymer

: Inorganics



X: Additives
Y: Polymer
Z: Inorganic

Pyrolysis (Single-Shot)

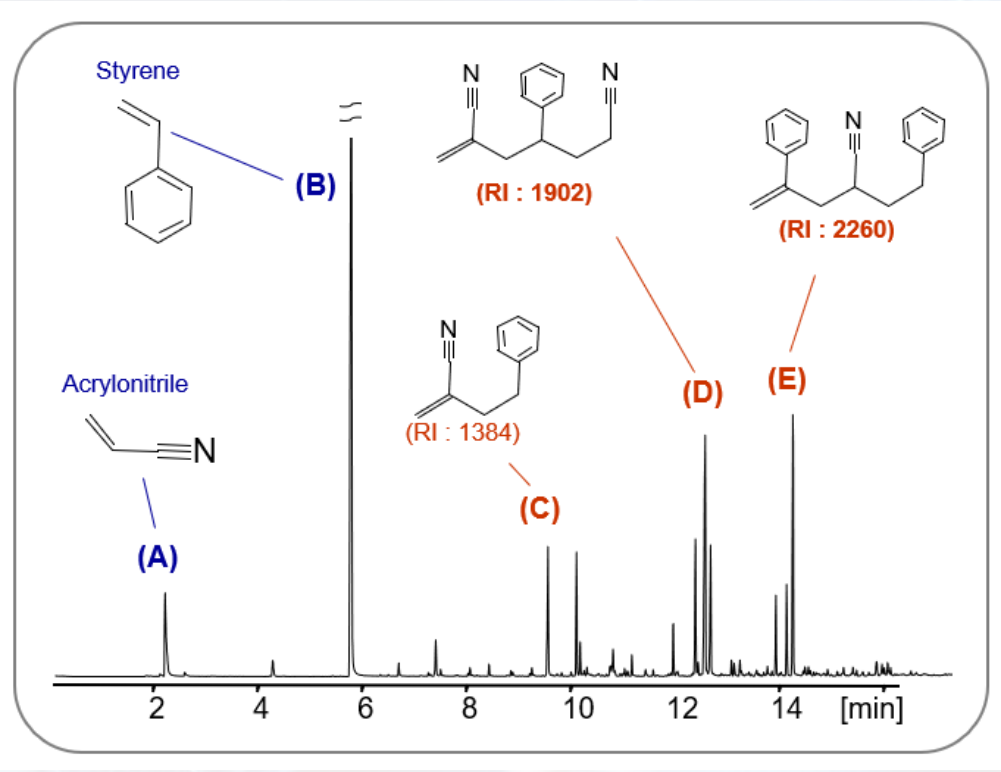


Mixed Information of polymer and volatiles

Sometimes difficult to interpret results !!

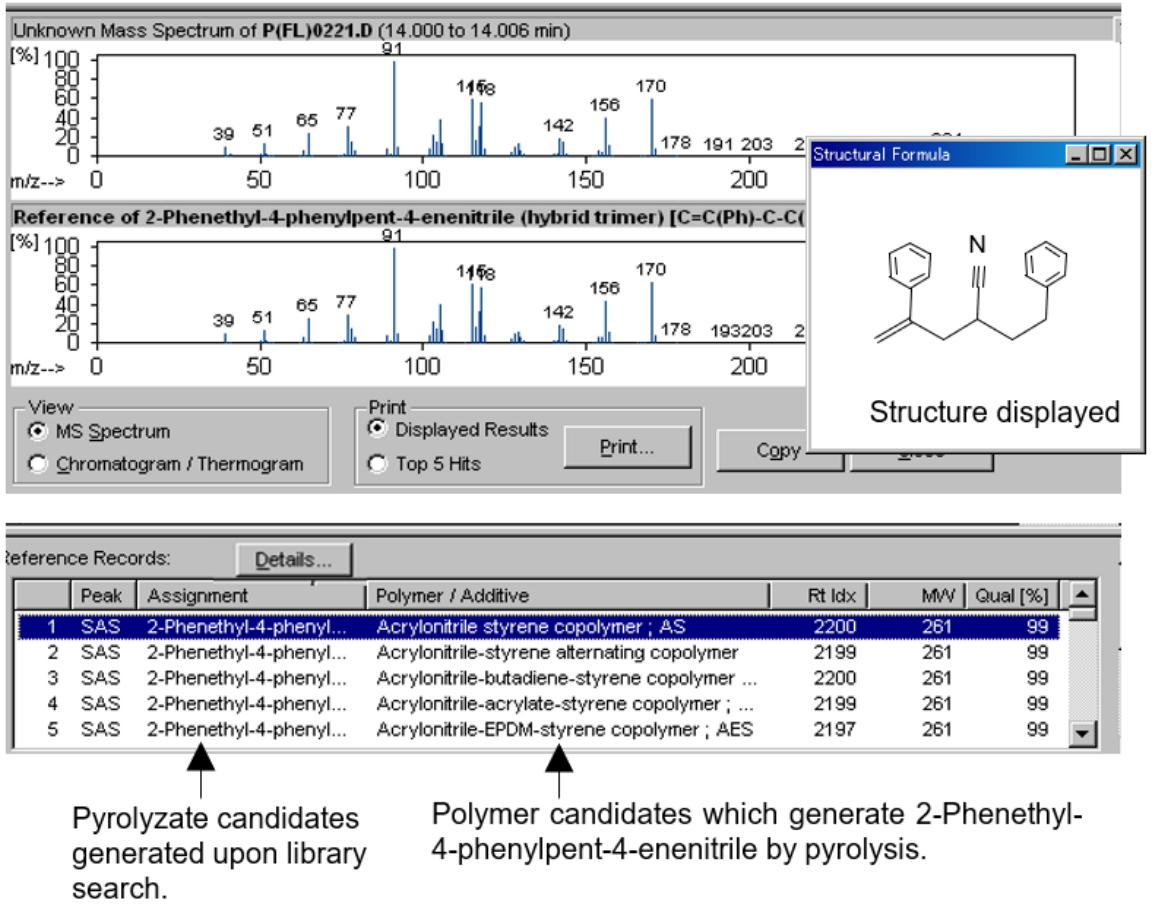
F-Search Software

Polymer search using pyrolyzates of pyrogram



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

Search result for peak (E)



F-Search Software

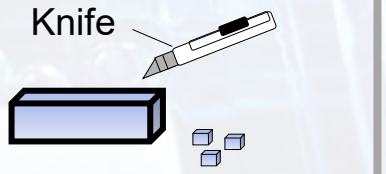
Specifications for F-Search System (Japanese patent 3801355, US patent 6444979)

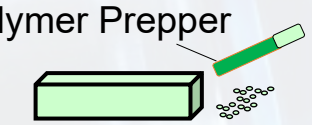
Product name (P/N)	F-Search "All-In-One" (PY-1110E-181)	Optional libraries (search software F-Search (Ver. 3.6) (PY-1111E-181) required)			
		EGA-MS18B (PY-1112E-181)	**PyGC-MS18B** (PY-1113E-181)	**Pyrolyzate-MS18B** (PY-1115E-181)	**ADD-MS16B** (PY-1114E-161)
Analytical technique	Package contains F-Search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

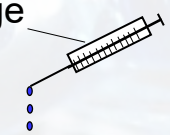
Microplastic Analysis by PY-GC/MS

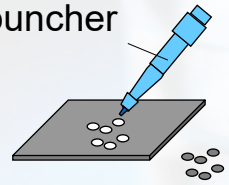
PY-Sample preparation

Step 1



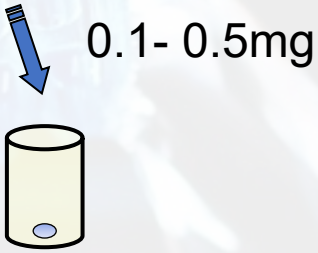






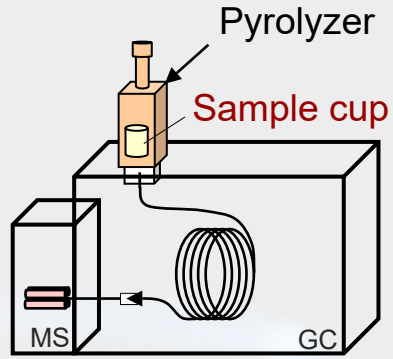
Step 2

Place a sample
in the sample cup



No solvent extraction

Step 3



Ready for Analysis !!

Sample Preparation Protocol for analysis MPs in environment sample

MPs in Sediment

Mass reduction by Sieving

↓

Density separation

(Ns_2WO_4, NaCl, NaI, $ZnCl_2$ aq soln.)

↓

MPs in Water

Sampling with a plankton net (ca. 0.3 mm)

↓

Mass reduction by Sieving

↓

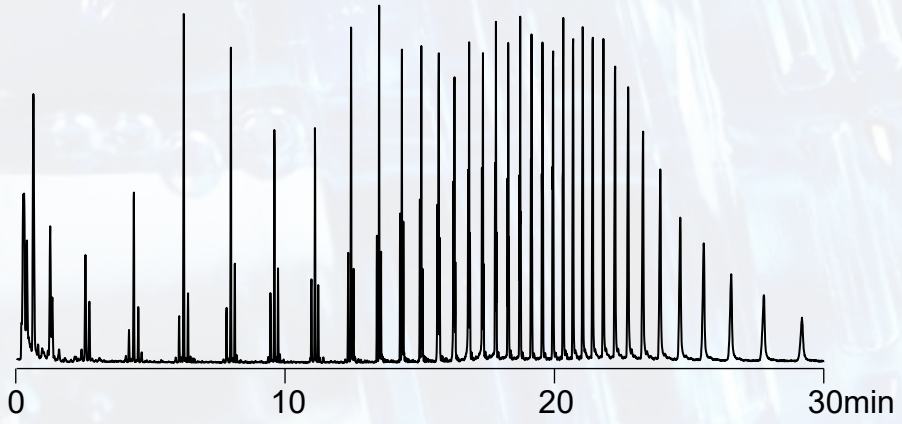
Remove of nature debris from the MPs surface (Chemical; H_2O_2, enzymatic)

Visual analysis (Shape, color, size, *etc.*) by Microscope

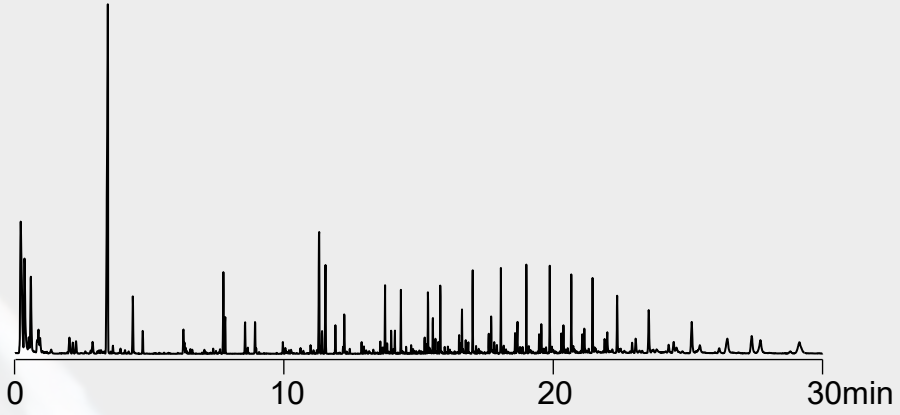
Identification of MPs by FTIR, Raman, PY-GC/MS, *etc.*

Pyrograms

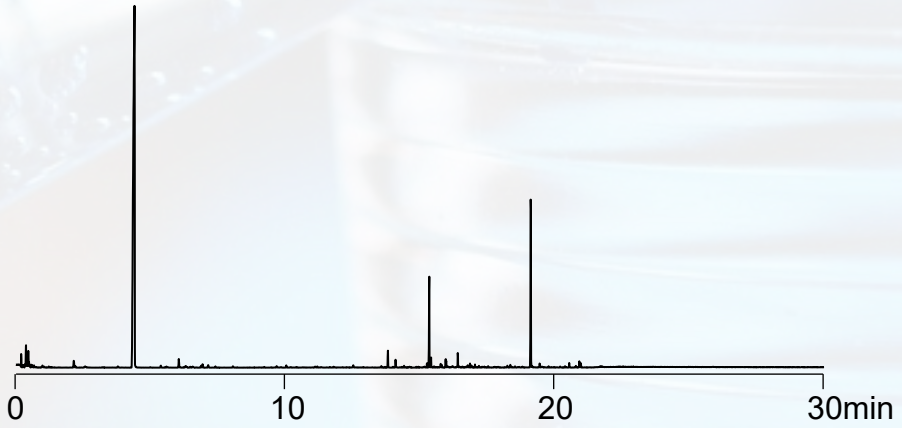
Polyethylene



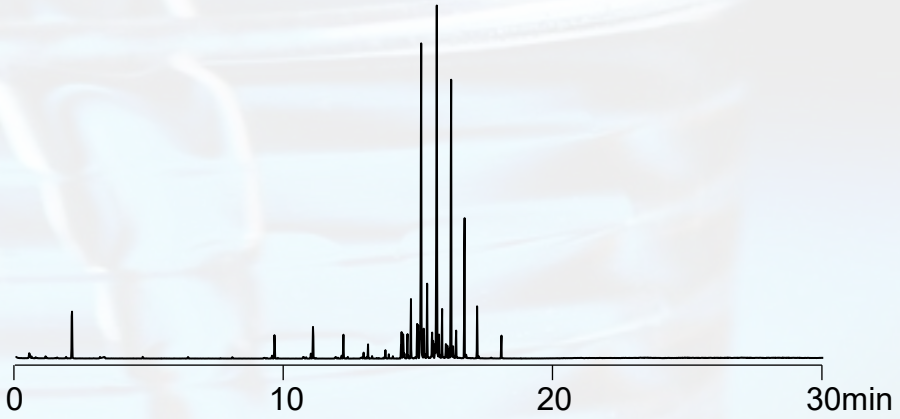
Polypropylene



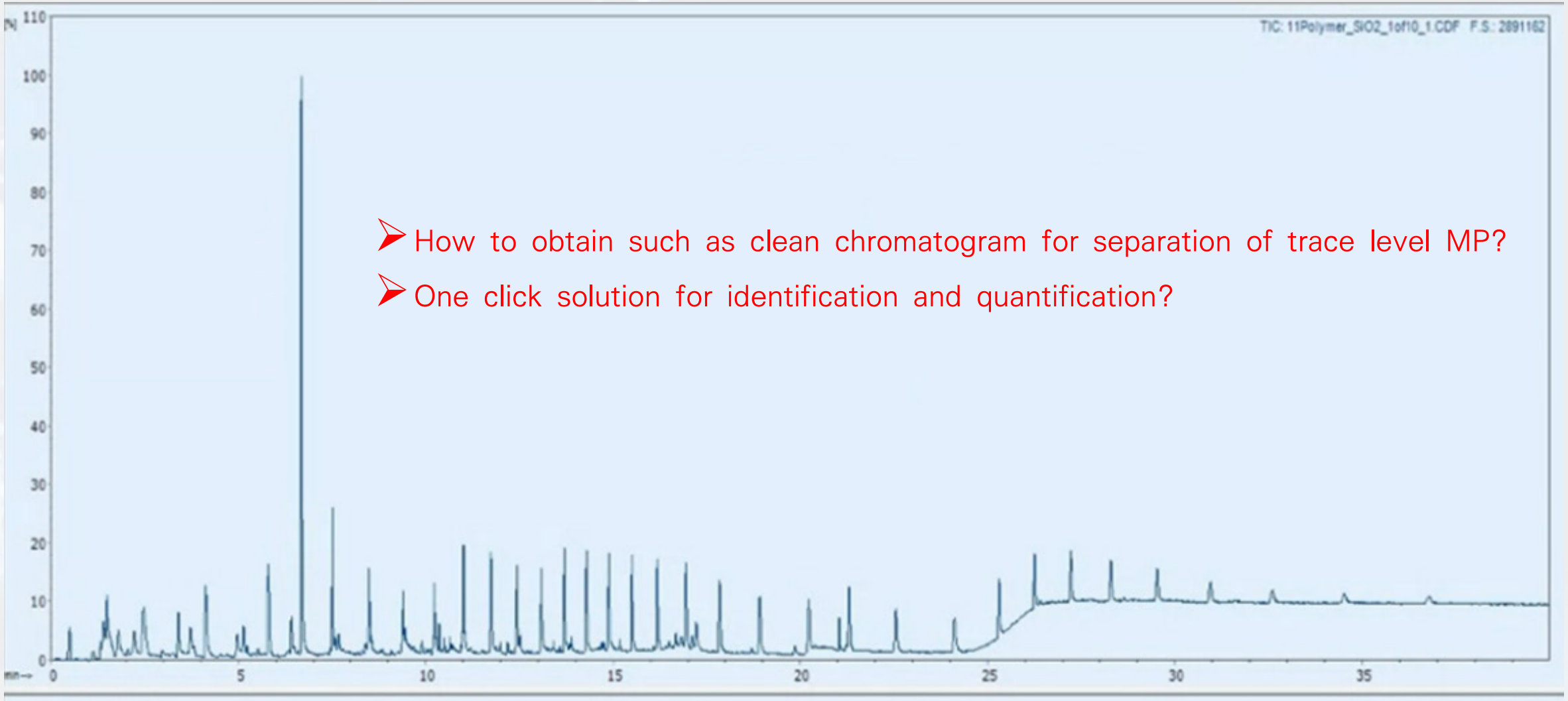
Polystyrene



Higher methacrylate copolymer

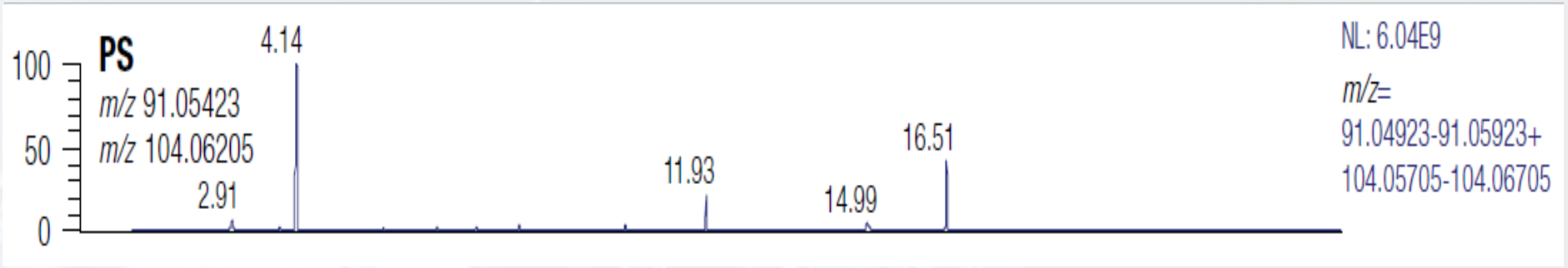


MPs (Mix of 12) Chromatogram

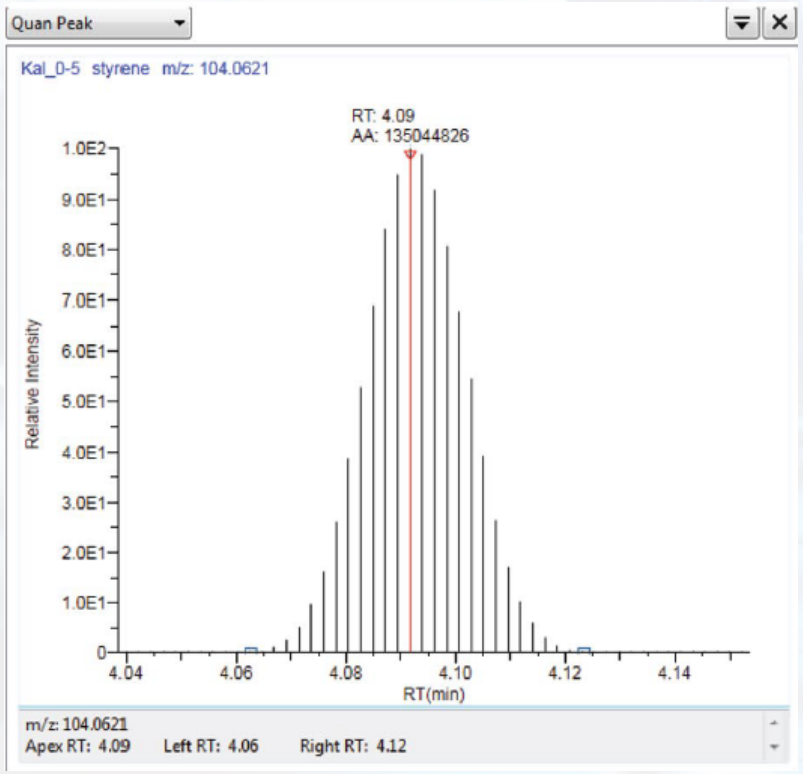


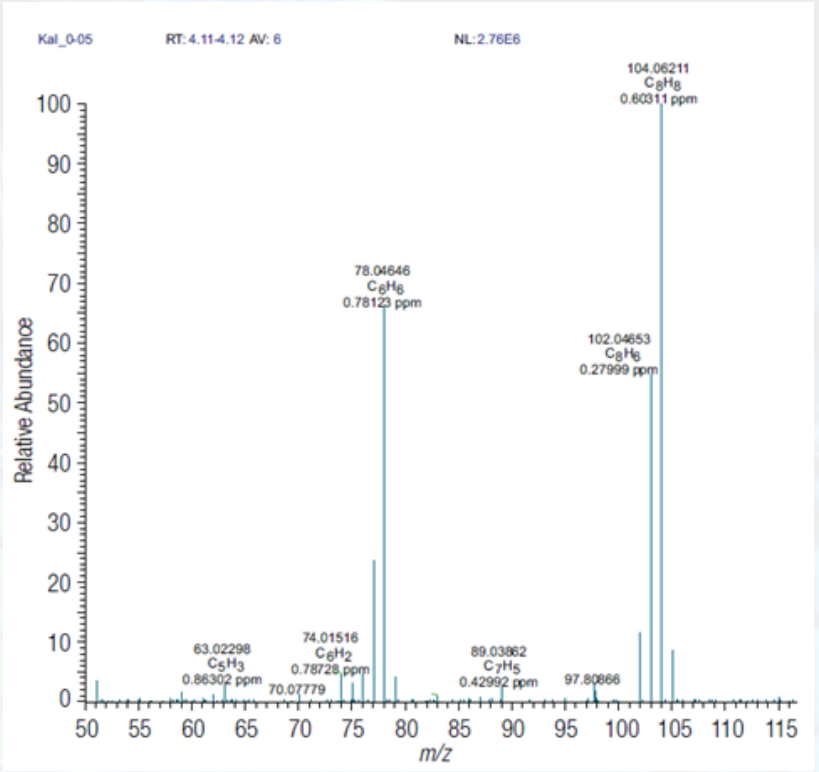
- How to obtain such as clean chromatogram for separation of trace level MP?
- One click solution for identification and quantification?

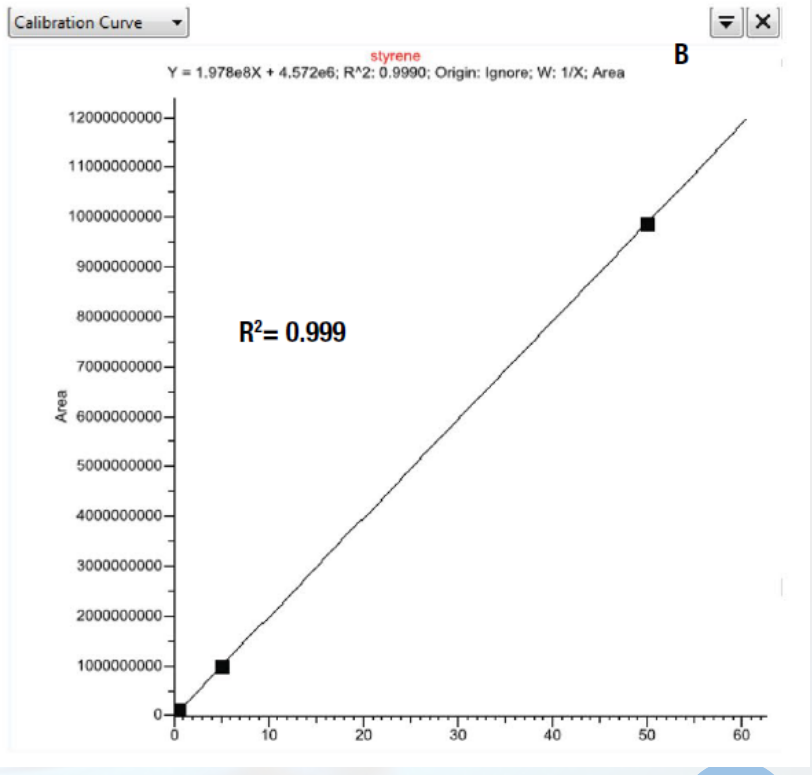
GC coupled to high-resolution, accurate-mass spectrometry



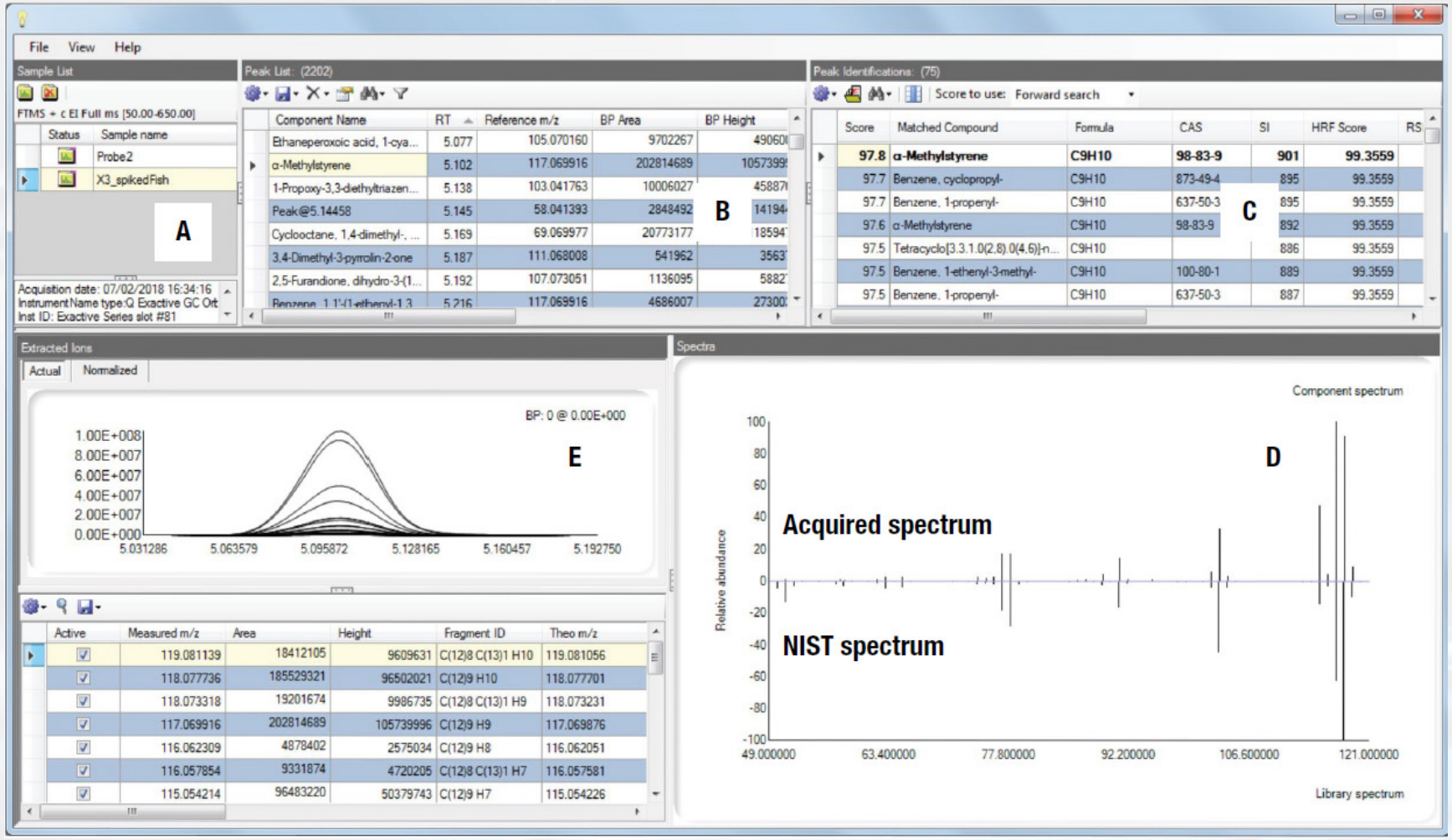
Thermo Scientific™ Exactive™ GC Orbitrap™







TraceFinder deconvolution



TraceFinder deconvolution browser showing **α-methylstyrene** (RT=5.1 min)

Tentative identification based on library (NIST) match (reverse search index, SI 901), fragment rationalization with a confidence score > 97% and mass accuracies of measured fragments

Samples processed (A), peaks detected (B), identified chemicals (C), acquired versus library spectra (D), and deconvoluted mass spectra for α-methylstyrene (E) are indicated.

F-search MPs 2.0 : Analytical software for microplastic analysis

*Japan Patent #6683335

Easily identify and quantify unknown microplastic (MPs)

- Quick identification of polymer types for unknown MPs by a patented search algorithm*
- Automatic creation of calibration curve and quick quantification
- Library for 12 commonly used polymers

Microplastic Calibration Standard (MPCS)

MPCS for calibration curve on MPs analysis

- Mixture of 12 polymers

  PE / PP / PS / ABS / SBR / PMMA

  PC / PVC / PU / PET / N6 / N66

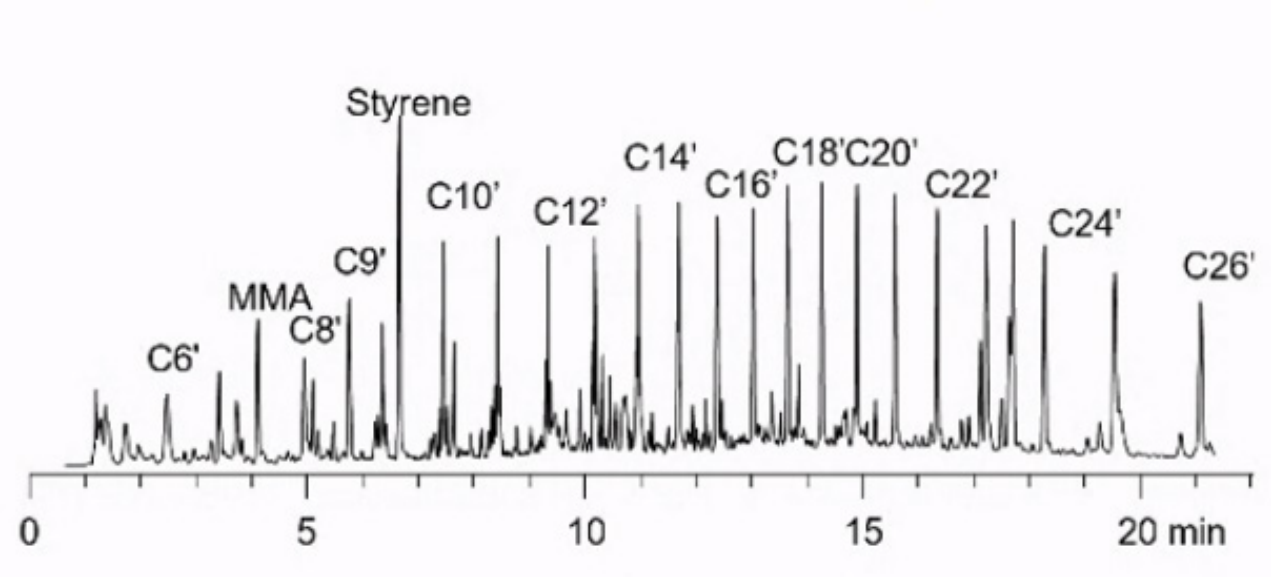
- Micro spatula contained

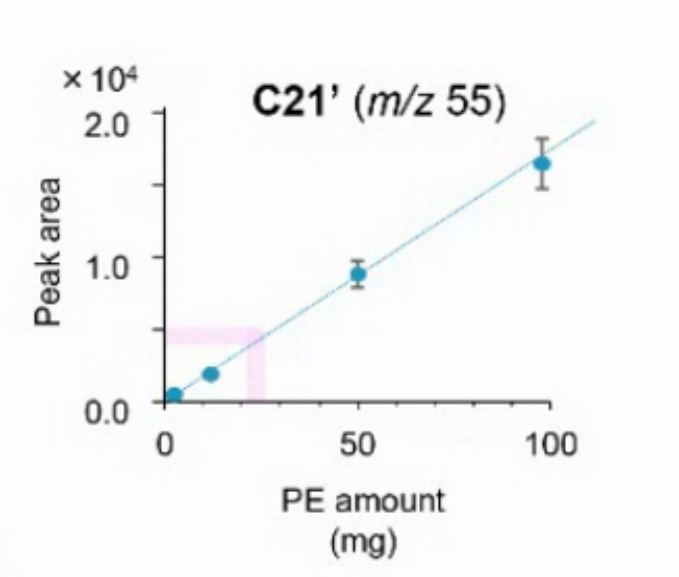
F-search MPs 2.0 Software

Automate qualification and quantification work

1. Search marker peaks for each polymer

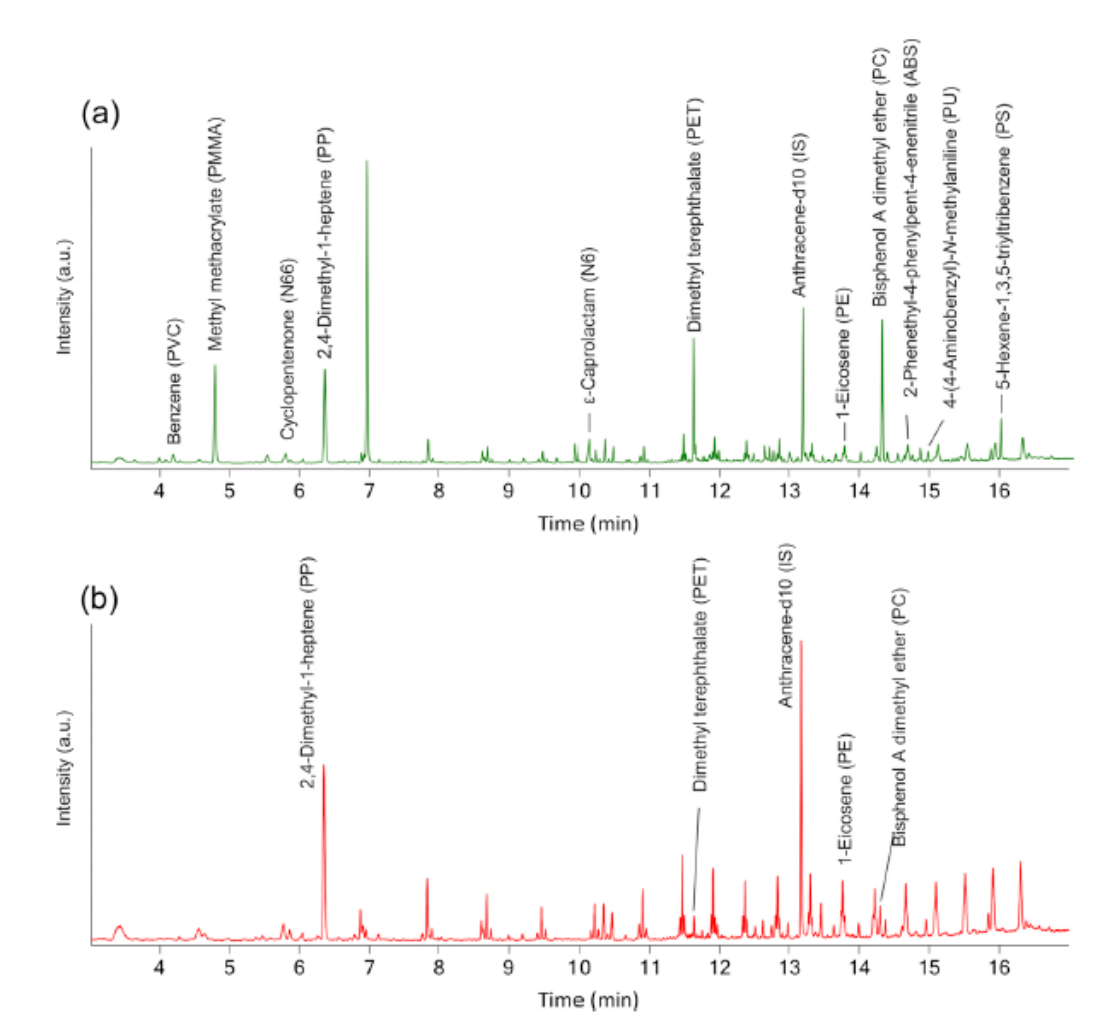
2. Quantify each polymer based on calibration curve





Pyrograms of the reference polymer mixture and the real marine microplastic sample

*K.Matsui et al. J. Anal. Appl. Pyrol. 149 (2020) 104834



Pyrograms of the reference polymer mixture (a) and of the real microplastic sample (b).

Results of Qual/Quant

Library Match Quality (%)

Plastic Name

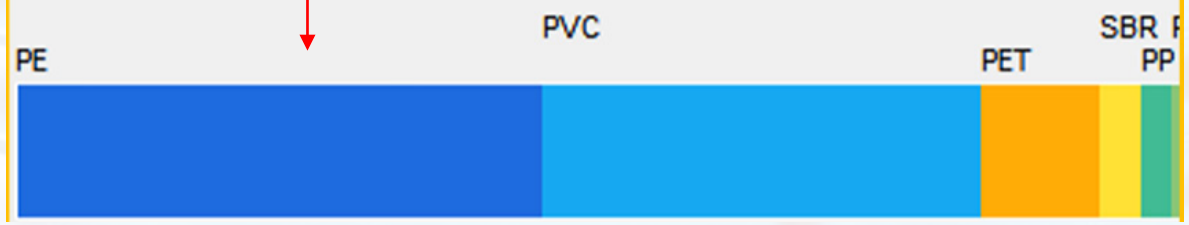
Quant Result (µg)

Relative Amount (%)

Peak Area

Polymer	Prob. [%]	Qnty [ug]	Ratio [%]	Area	RT [m...	LOQ [ug]
PE	99.5	11.20	42.5	31420	16.36	7.60
PVC	92.5	9.355	35.5	146285	10.57	2.70
PET	7.8	2.562	9.73	21353	14.10	1.20
SBR	18.8	0.917	3.48	7107	11.50	1.30
PP	89.9	0.691	2.62	4116	6.46	3.90
PS	98.2	0.601	2.28	75144	21.33	0.51
PMMA	99.2	0.375	1.42	39050	4.82	0.69
PU	96.1	0.276	1.05	81556	18.01	0.69
ABS	57.6	0.150	0.57	2697	18.02	0.76
N66	94.1	0.138	0.52	6349	6.23	0.55
N6	61.6	0.058	0.22	3745	11.50	0.23
PC	69.5	0.018	0.07	5027	11.24	0.67
			(100)			

Bar graph of Relative Amount (%)

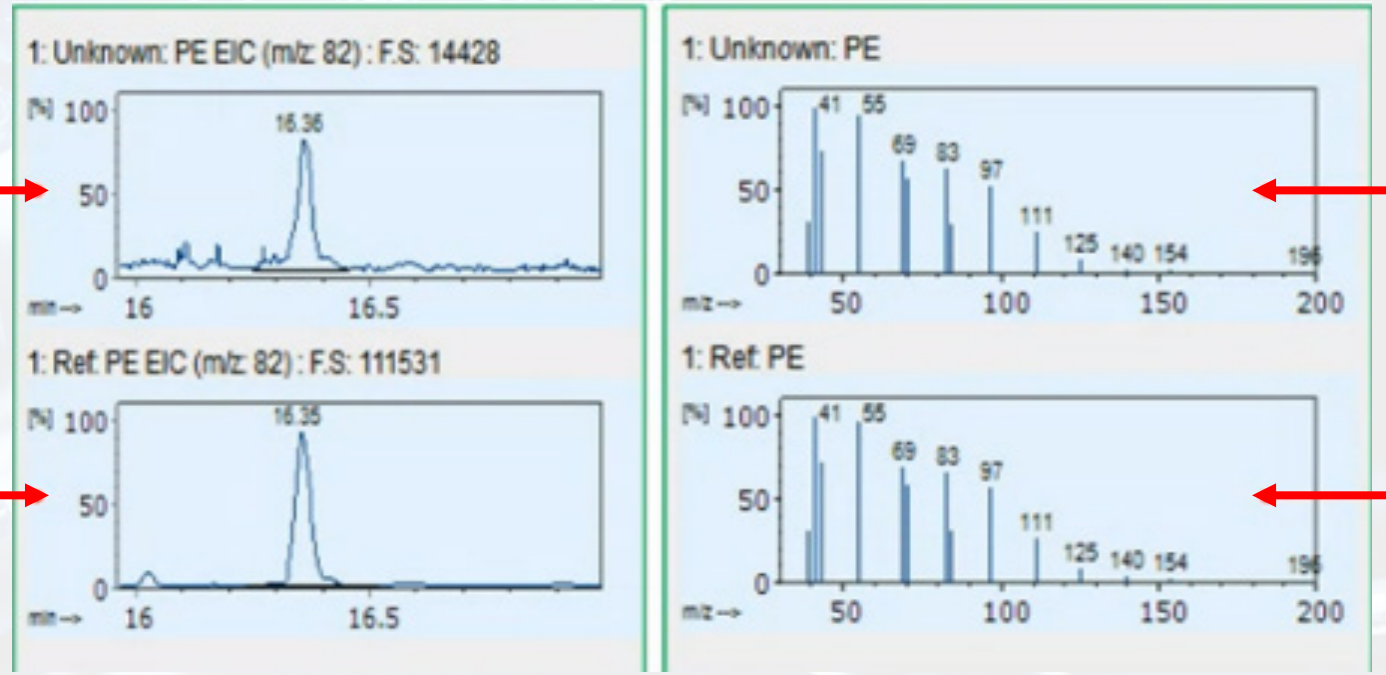


Confirmation of searching result

Peak shapes and Mass Spectrum

Marker peak of Sample

Marker peak of MPs Calibration standard



Summation mass spectrum of sample peak

Summation mass spectrum of Reference polymer in library

Each polymer has its own marker peaks and ions

Check peak shape, RT, Mass Spectrum, Integrated peak area

Conclusions

- GC/MS technique can analysis MPs in all particle size is only limited by the size of filter chosen
- TD-GC/MS and PY-GC/MS Simple sample preparation workflows that can be applied to wide ranging sample types. And large sample sizes for enhanced repeatability and sensitivity.
- TD-GC/MS technique can identification and quantification of MPs and provides simultaneous information on targets and non-targets compounds. Additional toxicity information and source profiling.
- Py–GC–MS technique provides detailed information about polymers, additives, and even contaminants.
- Py–GC/MS technique And Software F-Search MPs can identification and quantification of MPs is rapid and automated.

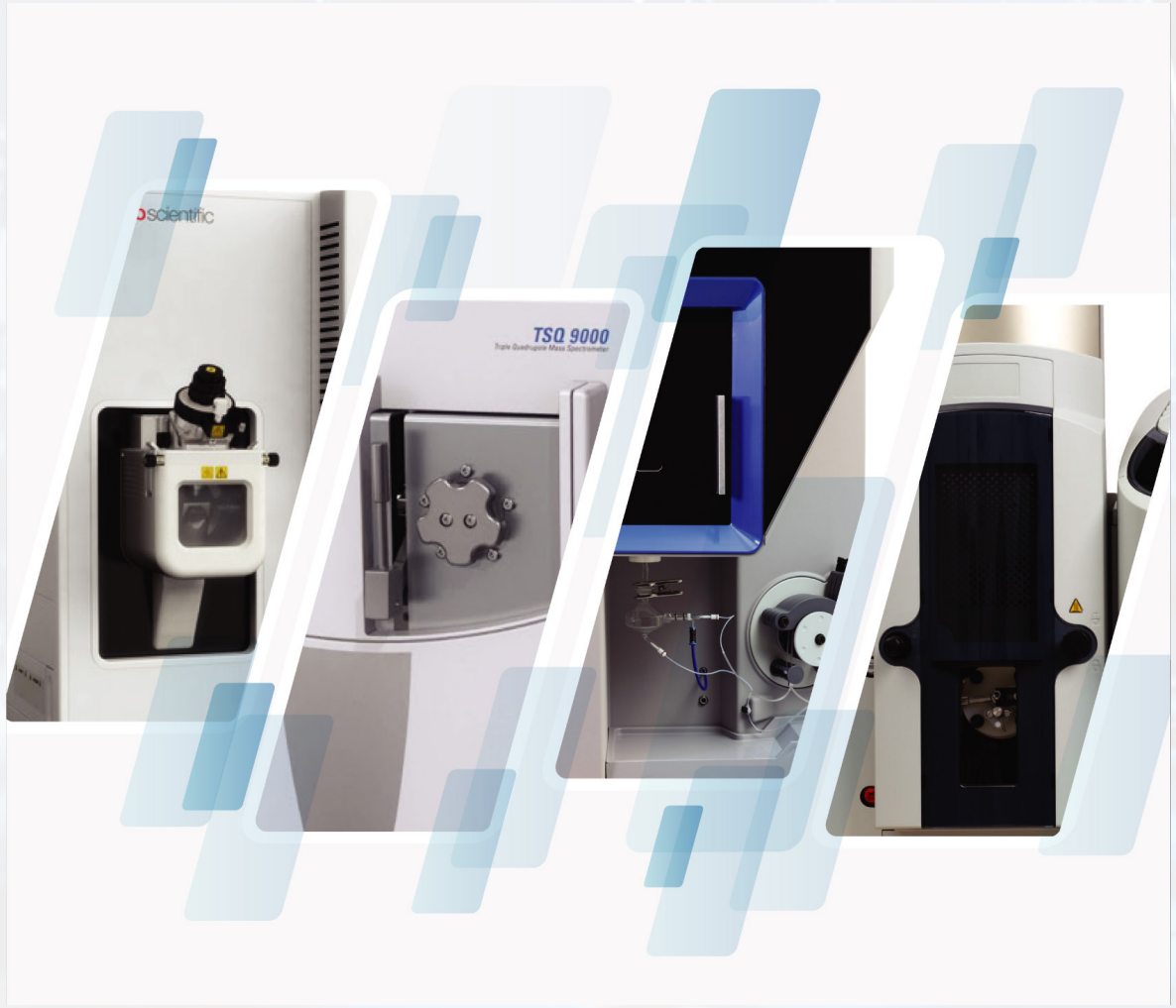
ติดตามกิจกรรมของทางบริษัทได้ที่

www.scispec.co.th

/scispec

@scispec

crm@scispec.co.th



ThermoFisher SCIENTIFIC

MARKES international

FRONTIER LAB

GAS

CTC Analytics

LC Tech
SAMPLE PREPARATION & ANALYSIS

908devices

YOUR SCIENTIFIC SPECIALIST