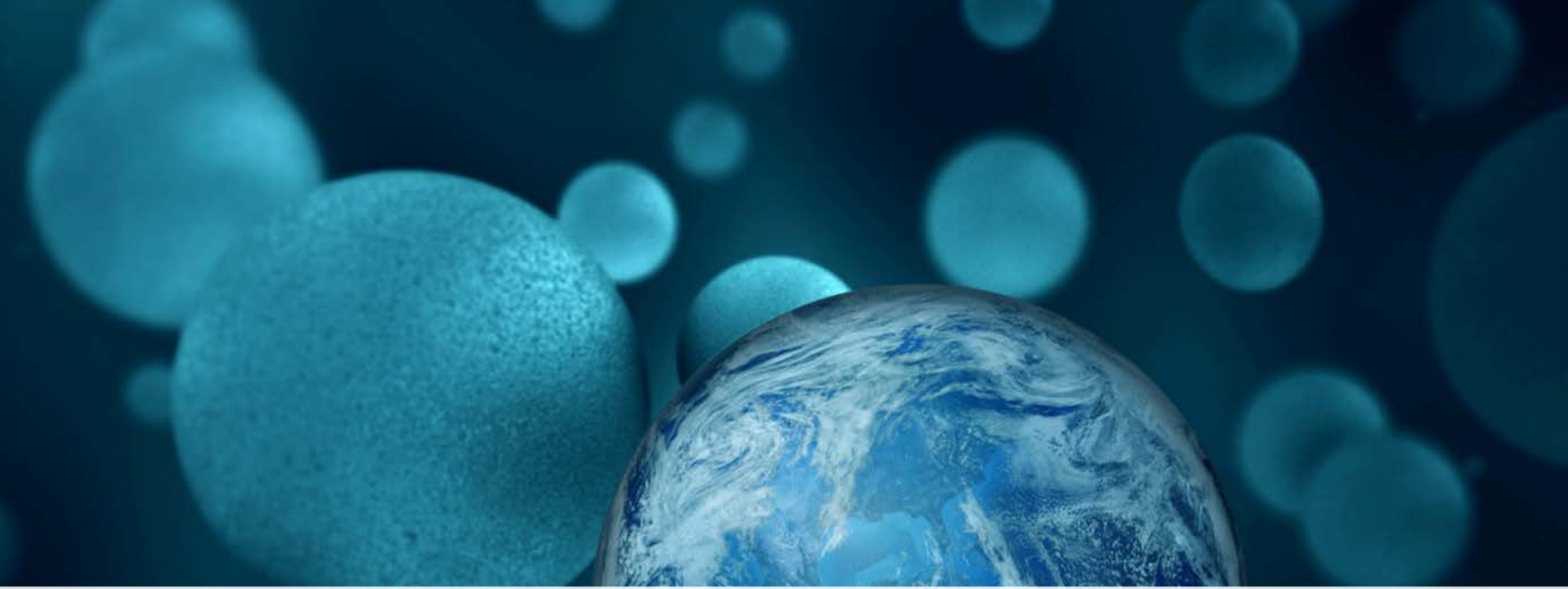

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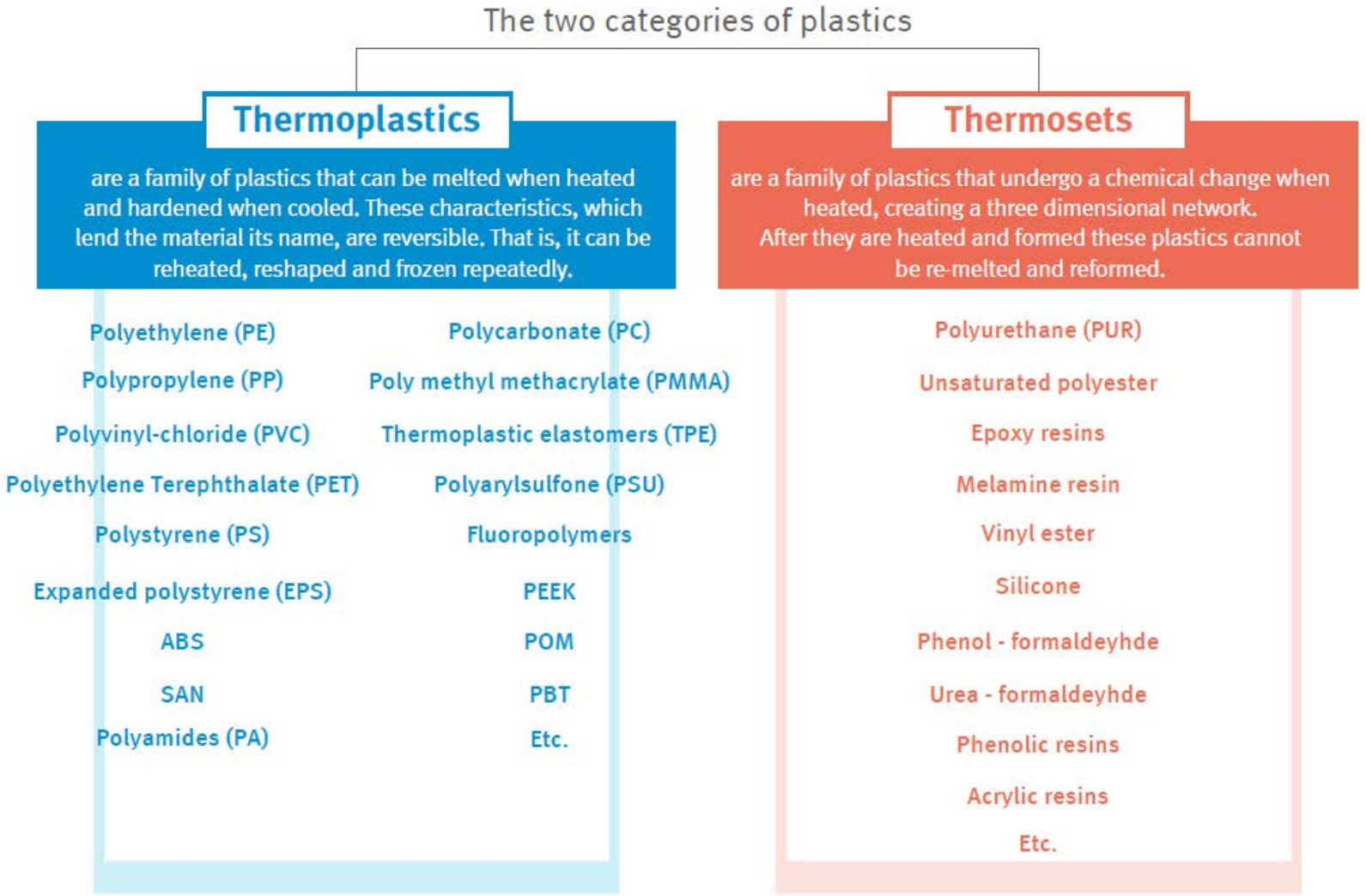
Pyrolysis-GC-Orbitrap MS - A Powerful Analytical Tool for Identification and Quantification of Microplastics in a Biological Matrix

Dr. Julian Renpenning
Regional Marketing Manager GC, GCMS and IOMS
Thermo Fisher Scientific

Microplastics in the Environment

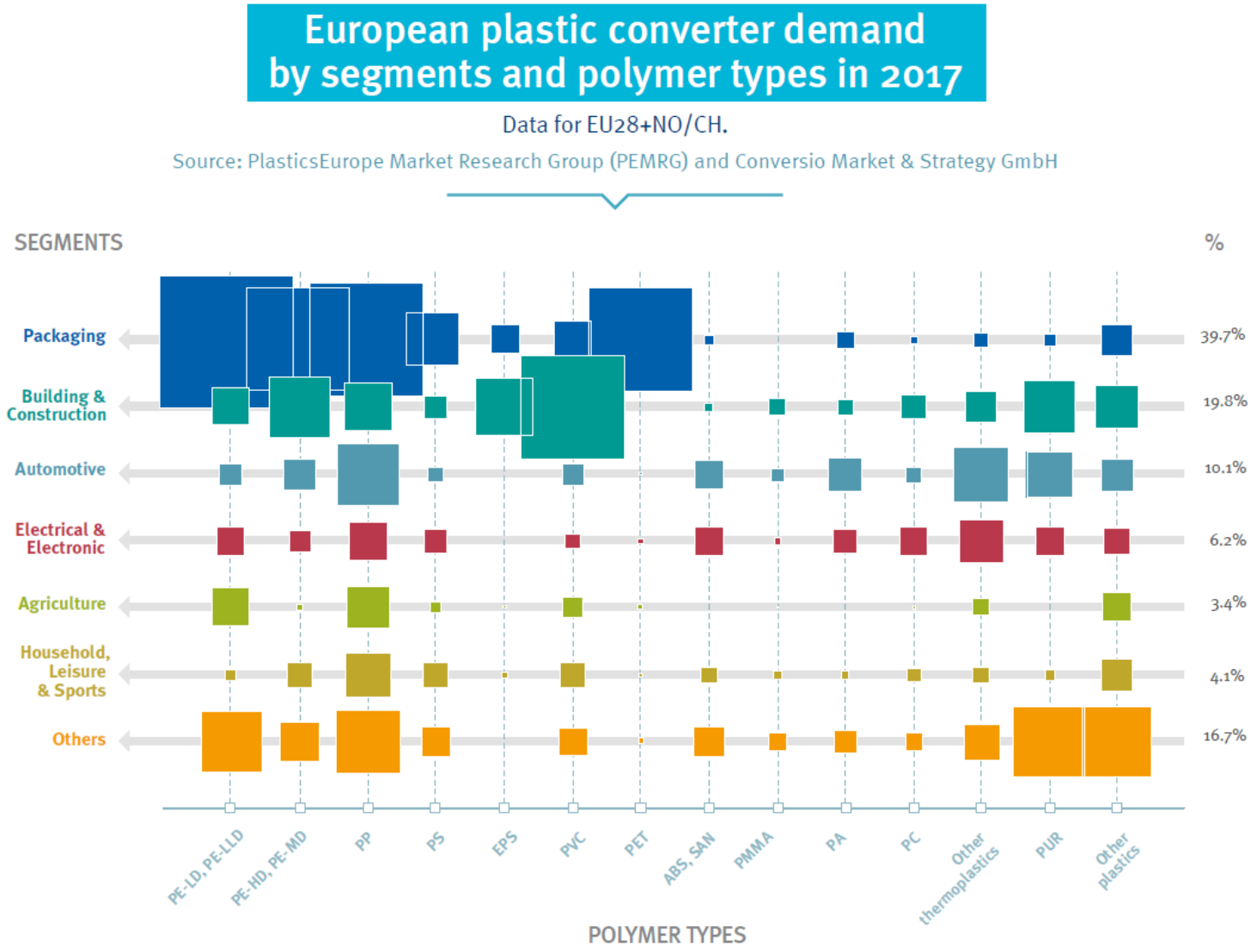
- Global plastics production increased by 620% since 1975
- Largest market sector is packaging with about 40% share only in the EU
- Plastics made up at least 10% of solid waste world wide
- Up to 12.7 million tons plastic waste enter the ocean world wide every year
- Single-use plastics making up approx. 40% of beach litter
- *Jambeck et al. 2015, Science Reports*

Plastic Polymers



Source: PlasticsEurope AISBL, www.plasticseurope.org

Plastic Polymers



Source: PlasticsEurope AISBL, www.plasticseurope.org

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Analytical Techniques

Techniques for microplastic analysis

- Fourier Transformation Infrared (FTIR) spectroscopy

- Raman spectroscopy and microscopy

- Pyrolysis – Gas Chromatography Mass Spectrometry (py-GC-MS)

Objectives

- Demonstrate the efficiency of pyrolysis GC coupled to a high-resolution mass spectrometry
- Qualitative and quantitative analysis of microplastics
- Benefit of a high resolution GC-MS system

thermoscientific

APPLICATION NOTE 10643

Pyrolysis-GC-Orbitrap MS - a powerful analytical tool for identification and quantification of microplastics in a biological matrix

Authors

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Keywords

Exactive GC, pyrolysis, microplastics, high resolution, Orbitrap technology, gas chromatography, fishmeal

Goal

The purpose of the experiments described in this work was to assess the applicability of pyrolysis-gas chromatography-Orbitrap™ mass spectrometry for the qualitative and quantitative analysis of plastic polymers in complex biological matrices.

Introduction

Plastics are synthetic organic polymers, commercially introduced on a large scale starting in the 1950s. Single-use plastics (grocery bags, food packaging, bottles, utensils) are persistent pollutants making up approximately 40% of beach litter[1]. This litter eventually ends up in the marine environment, with an estimated 8 million metric tons of plastic waste entering the oceans worldwide every year[2]. Most plastics have a very long degradation time, and for a timespan up to centuries they end up as macro-, micro- and nanoplastics through weathering. Due to their characteristics and additional content (monomeric residue, plasticizers, flame retardants etc.), micro- and nanoplastics can have complex toxicological effects on marine life through direct ingestion[3-5] and/or leachates[6]. This might represent a hazard for ecosystems and for human exposure through consumption and inhalation[7]. As this is an emerging field, there are limited studies on the identification

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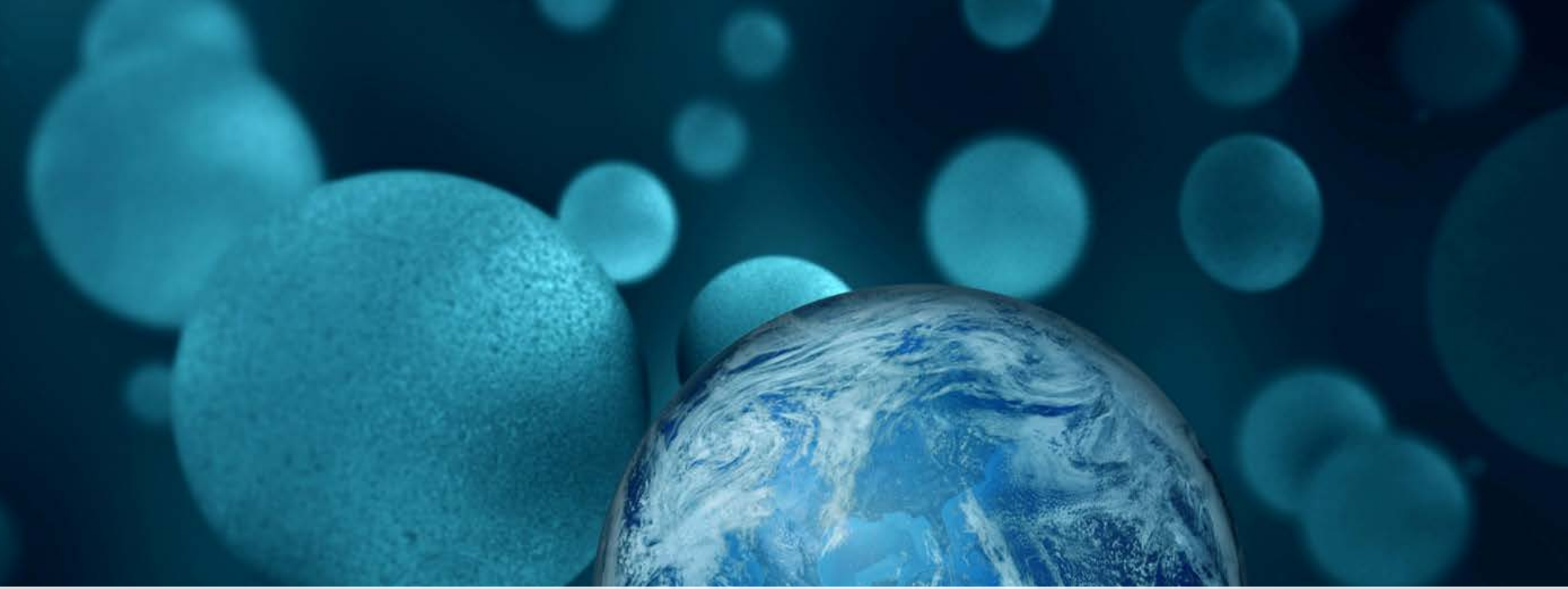

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Analytical Instrumentation

Instrumentation: Pyrolysis-GC-Orbitrap MS

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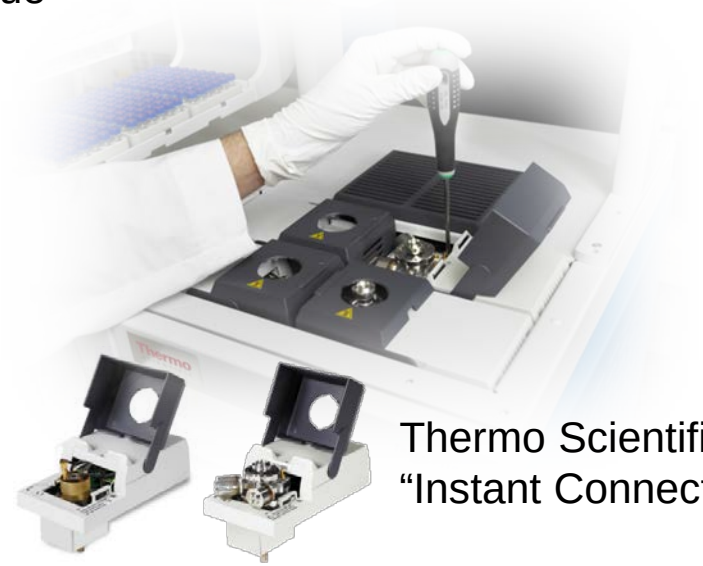
Thermo Scientific Trace 1310 GC

Thermo Scientific™ TRACE™ 1310: Unique modular injector and detector design

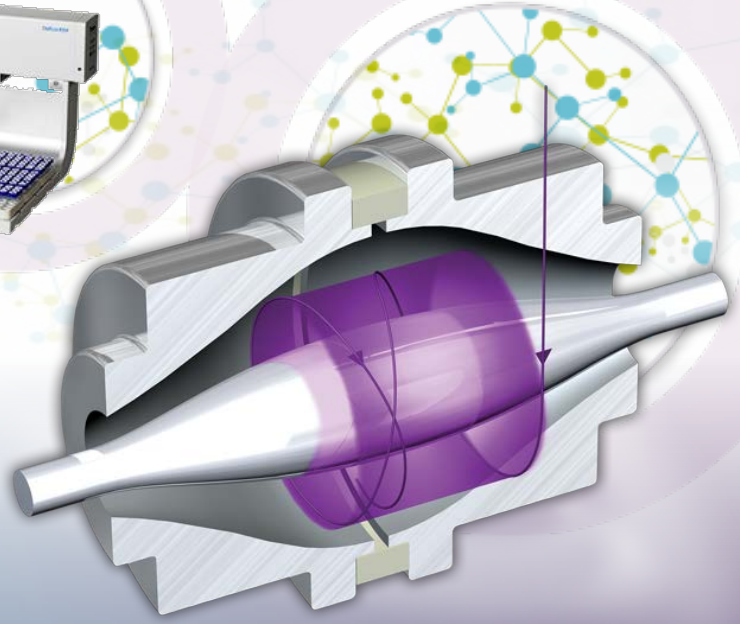


Thermo Scientific "Instant Connect" modules

Injectors	Detectors	Additional Options	Software drivers
Thermospray SSL	FID	MS NoVent Microfluidics	Chromeleon™ CDS
SSL	WLD	Auxiliary Oven	Xcalibur™
SSL backflush	ECD	Inj/Oven Cryo	TraceFinder
PTV	NPD	Aux carrier	
PTV backflush	FPD	Aux temperature	
OnColumn	PDD	D/A-converter (AOI)	
Gas Sampling Valve (GSV)	PFPD		
	MS		

Thermo Scientific™ Q Exactive™ GC Orbitrap™ GC-MS/MS system

Hybrid Quadrupole-Orbitrap GC-MS/MS System



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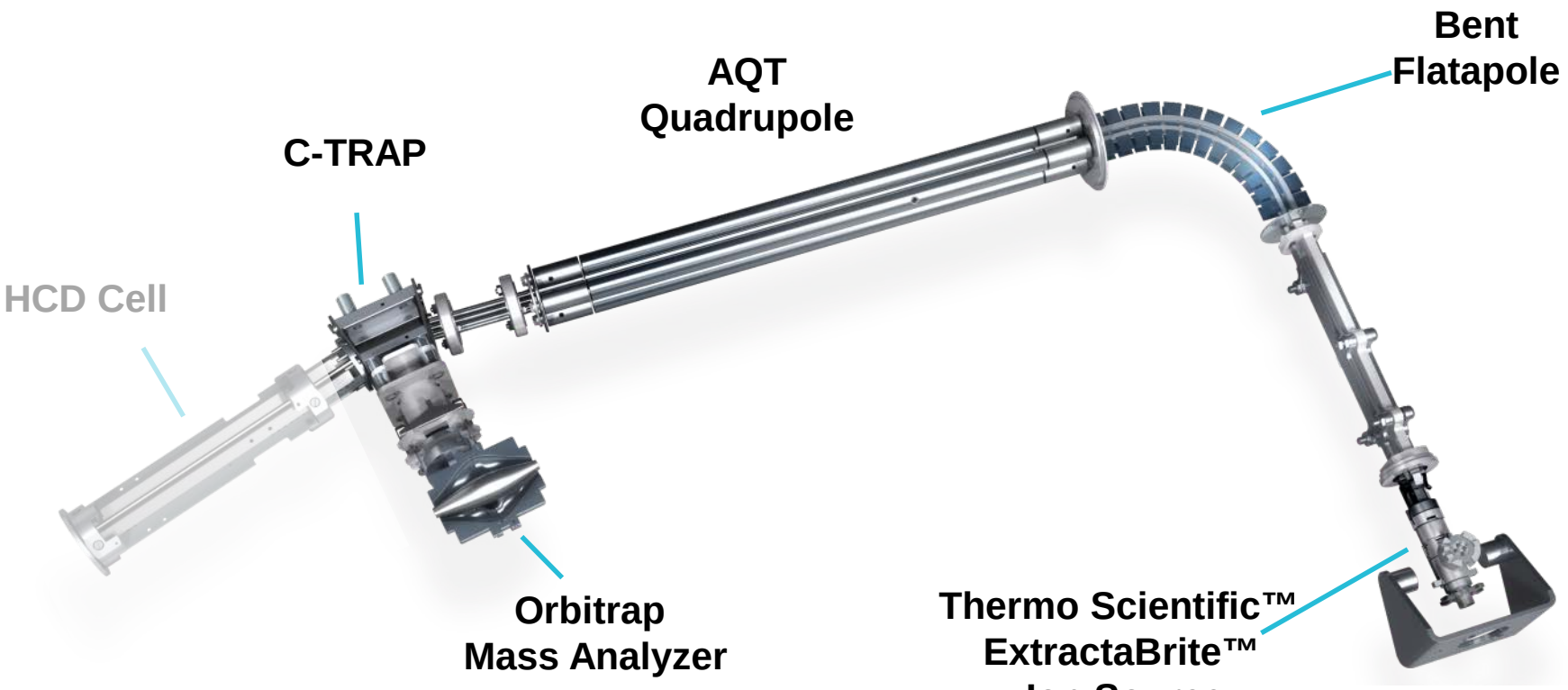
Q Exactive and Exactive GC



Source:	EI and CI (NCI/PCI)
Scan range	m/z 30-3000
Resolving power:	15/30/60/120K @ m/z 200
Acquisition :	non-targeted - full scan
	targeted - SIM, (MS/MS)
	combined NT/T - full scan + SIM

Exactive GC System Features

- Ultra high resolution up to 60.000
- Data aquisition rate of 7 Hz at 60k

- Mass Accuracy:
  - Internal: < 1 ppm RMS
  - External: < 3 ppm RMS

  Under conditions defined in 1 µL,
  100 fg/µL *octafluoronaphthalene*
  EI Full MS installation specification

- Vent free source and routine proof source
- Vent free column exchange
- PCI and NCI
- Very good system linearity

Frontier Lab's Multi-Shot Pyrolyzer

- **What is it?**
  - Sample introduction system for viscous liquids or solid organic materials into a GC or GC/MS
- **How does it work?**
  - Uses vertical micro furnace technology to thermally vaporize or decompose a sample into a gaseous state - reproducibly

EGA/PY-3030D
Double-Shot

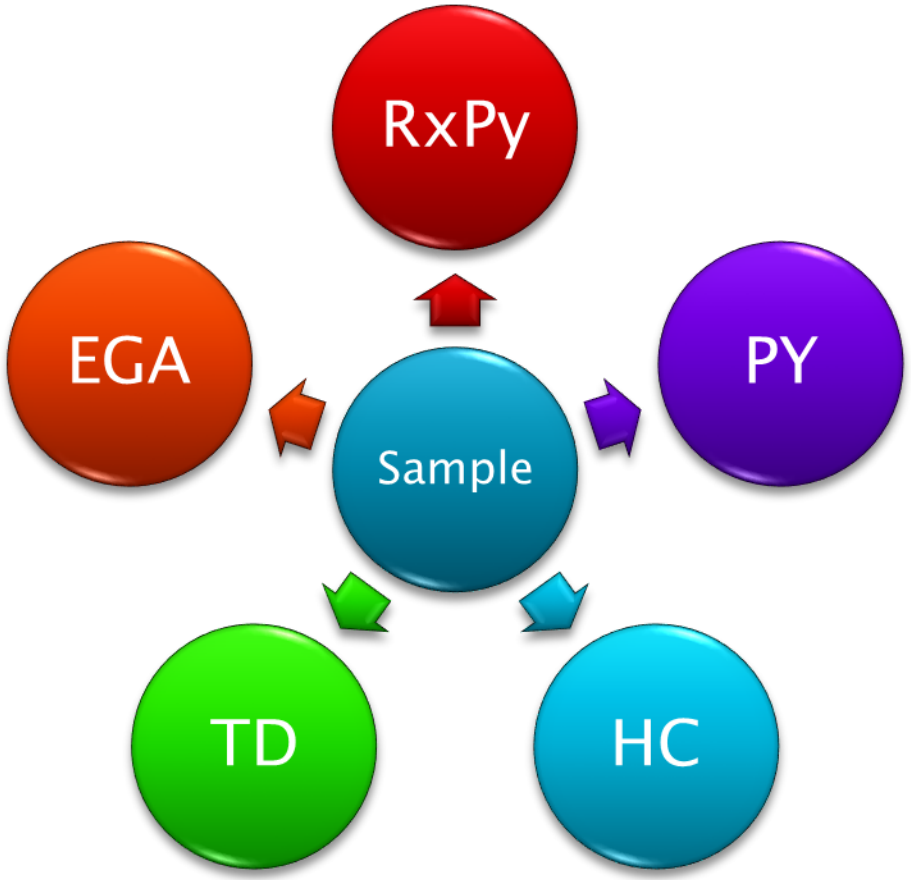
AS-1020E
Auto-Shot

Analytical Techniques

1. Single-Shot
2. Double-Shot
3. EGA
4. Heart-cut EGA

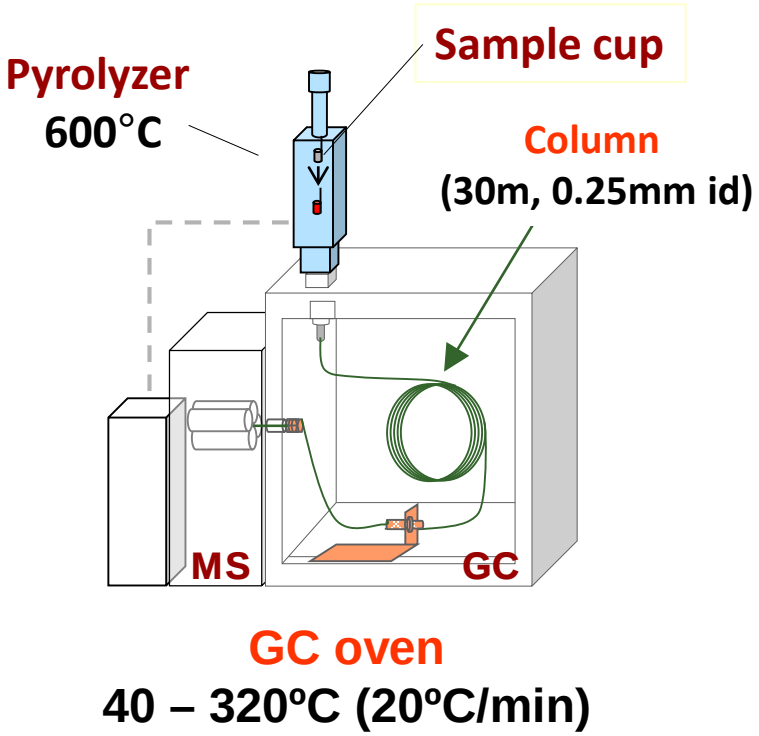
Programmable
(10 - 1050 ° C)

Techniques Used For Samples



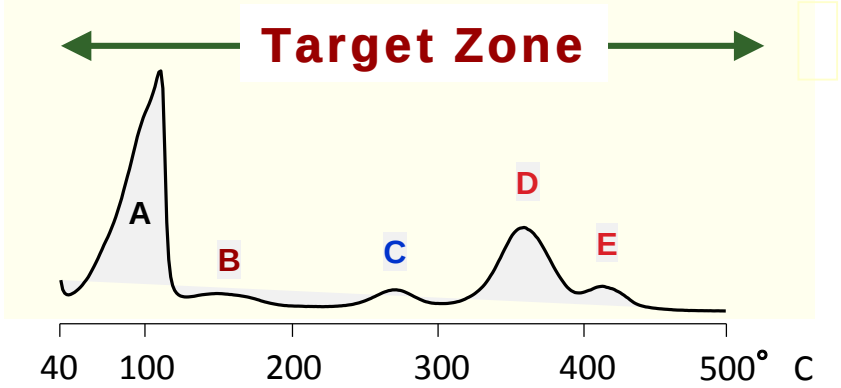
EGA	Evolved Gas Analysis
TD	Thermal Desorption
HC	Heart-Cutting
PY	Pyrolysis
RxPy	Reactive Pyrolysis

Single-Shot Py-GC/MS Information

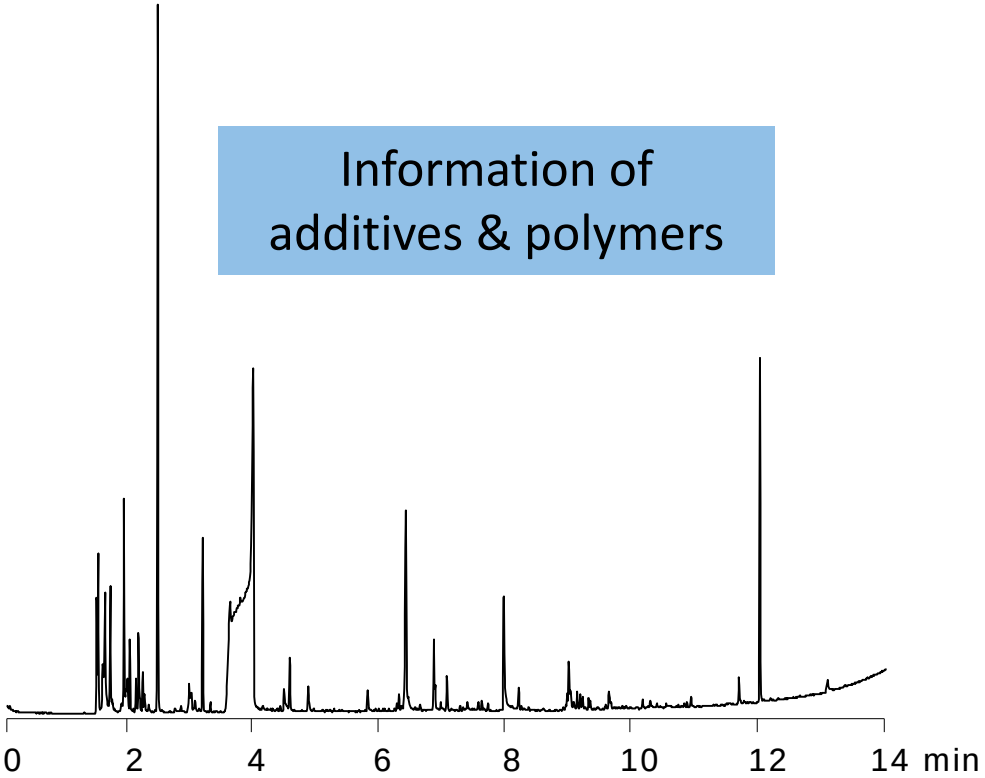


GC oven

40 – 320ºC (20ºC/min)



Information of additives & polymers



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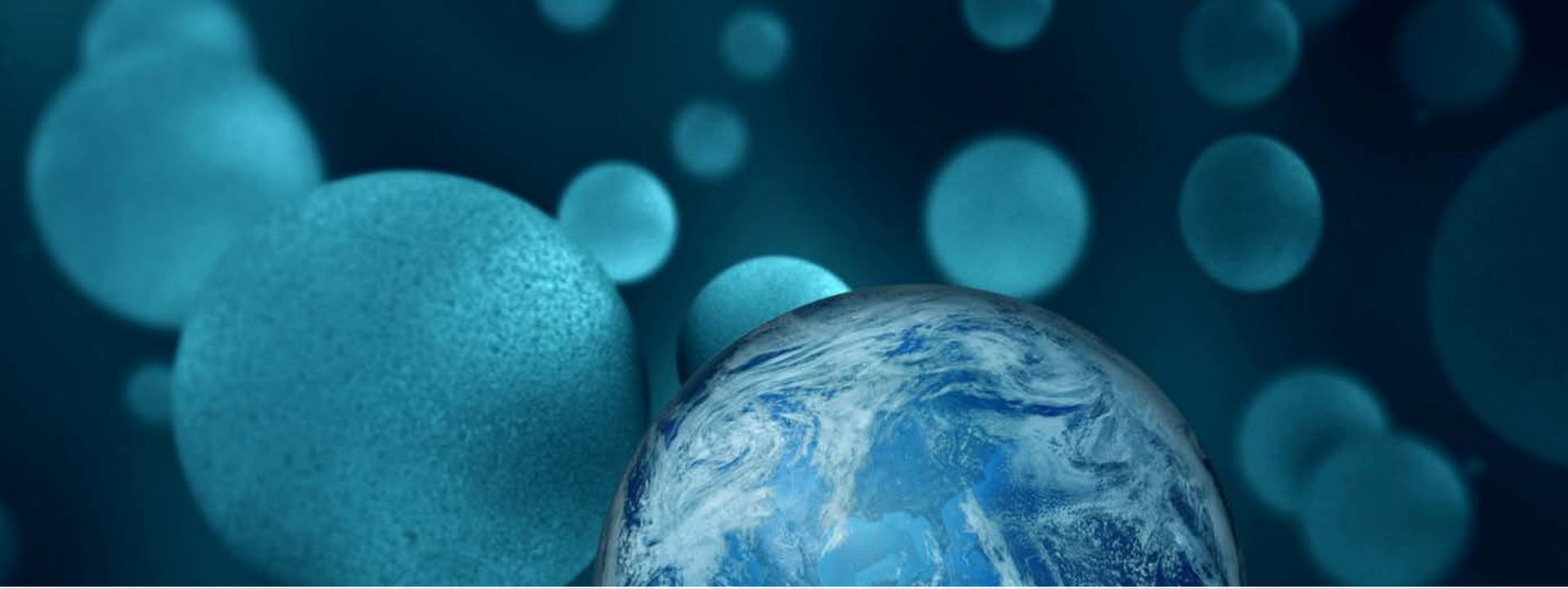

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Analysis of Microplastic and Microplastic in Spiked Fish

Experimental and Analytical Conditions

1. Polymer Standards
Aliquots of PMMA and PS standards (0.05 – 5µg) dissolved in ethyl acetate

2. Spiked Fishmeal
Analysis in decomposed fishmeal as a complex matrix. Fishmeal sample spiked with PMMA (2.5 µg) and PS (2.7 µg)

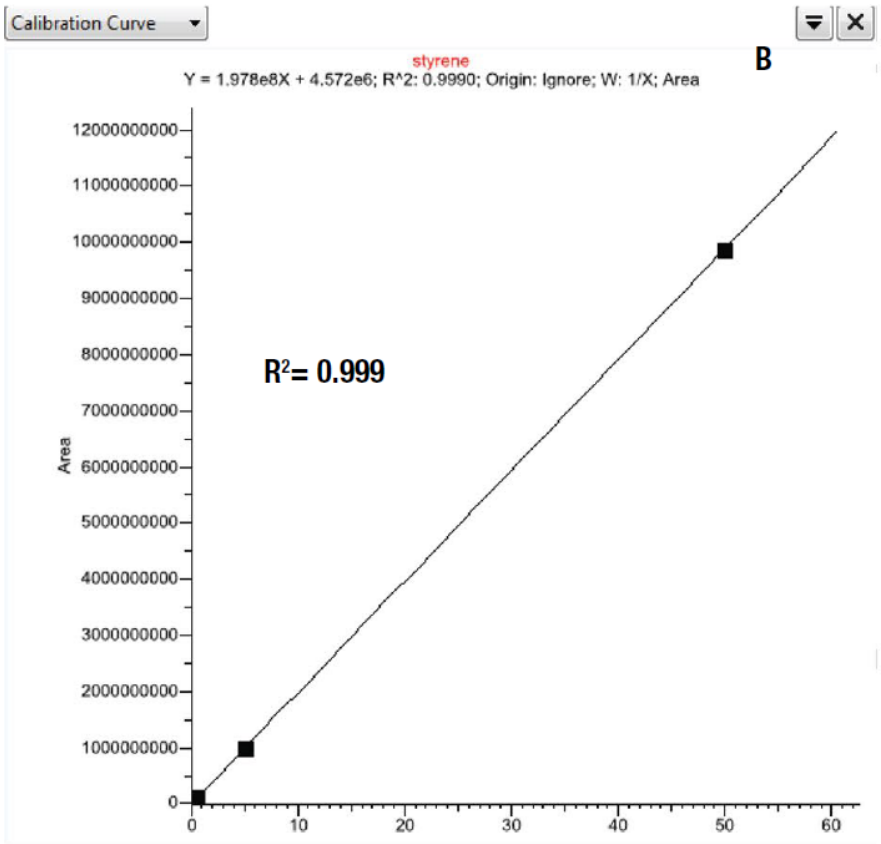
3. Polymer Mixture
Qualitative analysis of a PA, PC, PE, PMMA, PP, PS, PVC and PET polymer mixture (10-100 µg of each polymer) with TMAH as methylation agent.

Multi-Shot Pyrolyzer EGA/PY-3030D Parameters	
Oven Temp.:	600 °C
Interface Temp. :	300 °C
TRACE 1310 GC System Parameters	
Injector:	Thermo Scientific™ Instant Connect Thermospray (TSI)
Inlet:	270 °C
Carrier Gas:	He, 1.2 (mL/min)
Split Flow:	200 mL/min
Oven Temperature Program	
Temperature 1:	50 °C
Hold Time:	1 min
Temperature 2:	320 °C
Rate:	15 °C/min
Hold Time:	5 min
Exactive GC Orbitrap Mass Spectrometer Parameters	
Transfer Line:	320 °C
Ionization Type:	EI
Ion Source:	280 °C
Electron Energy:	70 eV
Emission Current:	20 µA
Acquisition Mode:	Full-scan, centroid
Mass Range:	50-650 Da
Resolving Power:	60,000 FWHM at *m/z* 200
Lockmass, Column Bleed:	207.03235 *m/z*

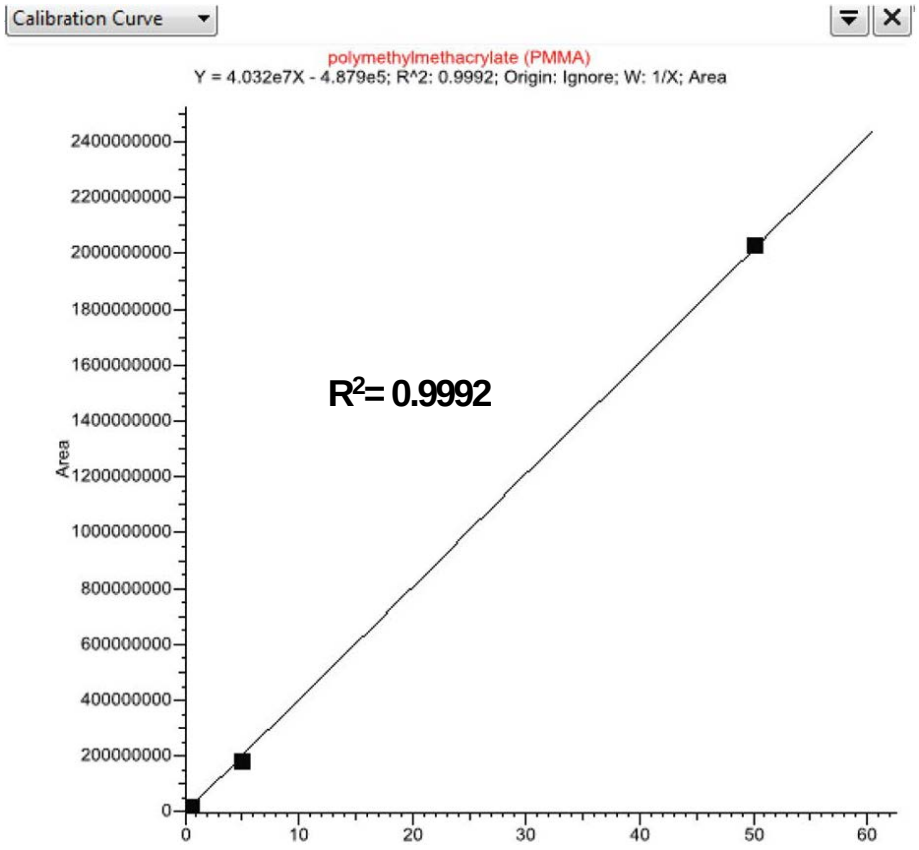
1. Polymer Standards - Sensitivity and Linearity

Analysis of standards with concentration of **0.05**, **0.5**, **5** and **50 µg**

Polystyrene (PS)



Polymethyl methacrylate (PMMA)



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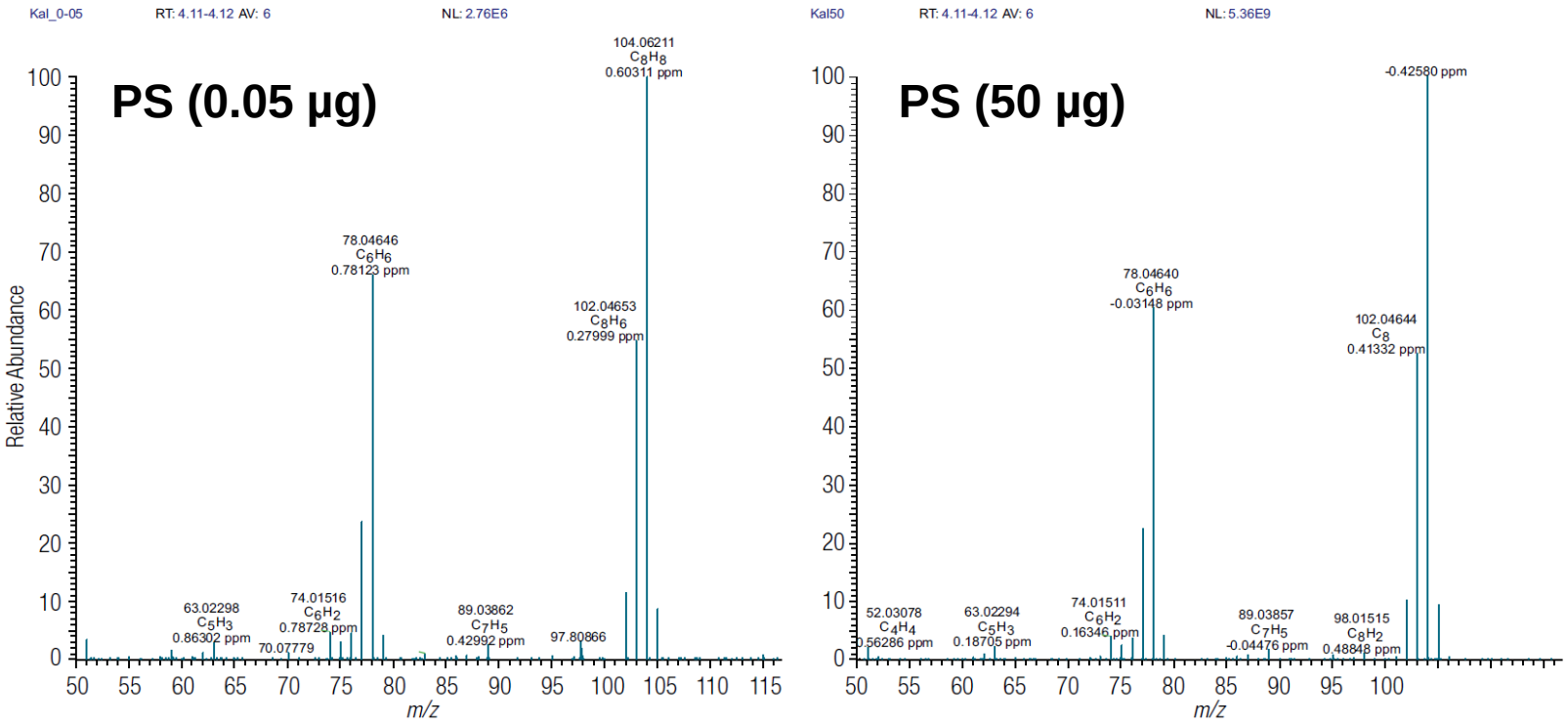
2. Spiked Fishmeal

Stability and mass accuracy irrespective of compound concentration



Accuracy of quantification for PS and PMMA

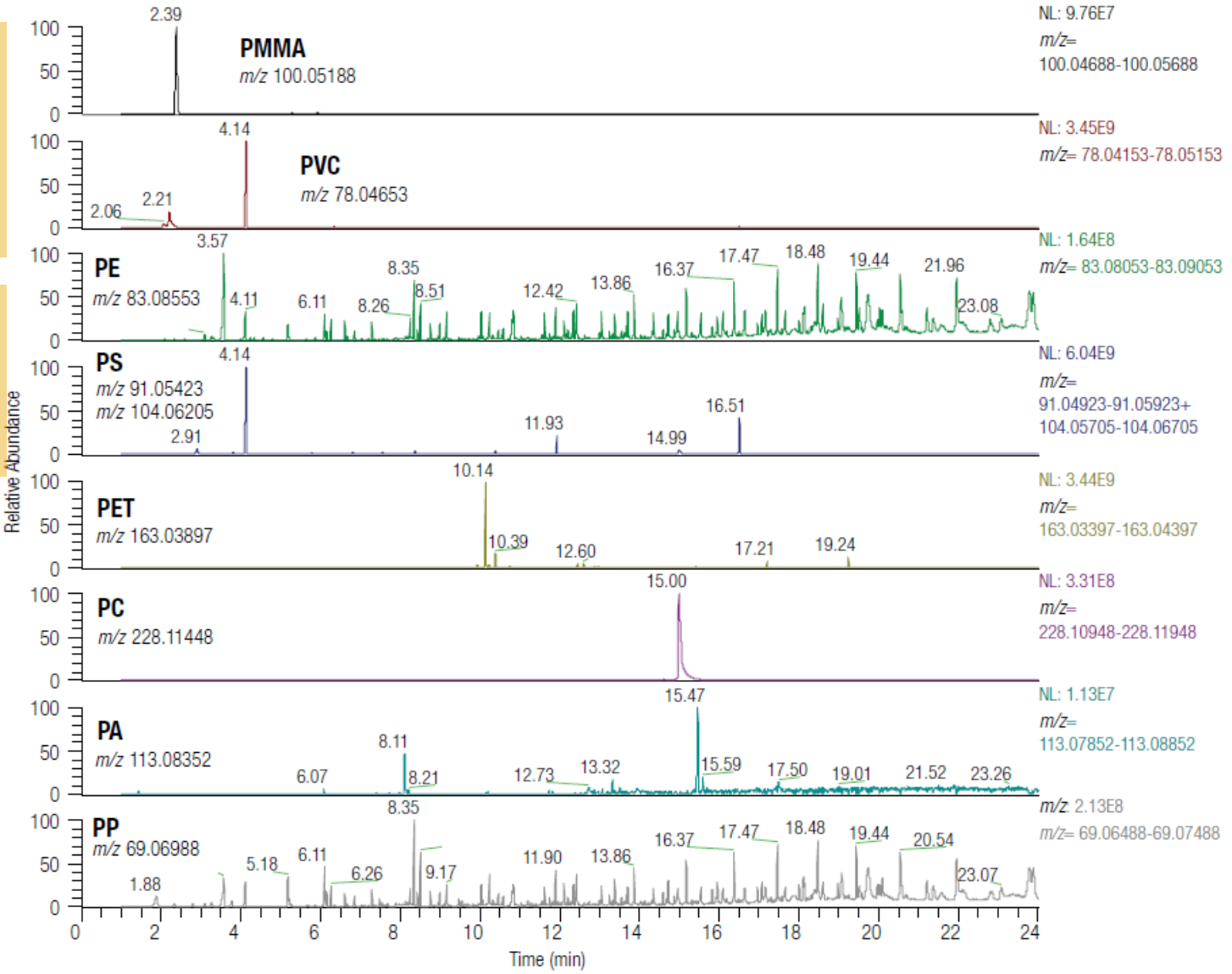
Compound	Spiked Amount (µg)	Measured Amount (µg)
Polystyrene (PS)	2.7	2.9
Polymethyl methacrylate (PMMA)	2.5	2.2

3. Polymer Mixture - Selectivity in High-Resolution

Selectively isolated m/z values corresponding to pyrolysis product of polymer

60,000 resolution

Extraction window ± 5 ppm



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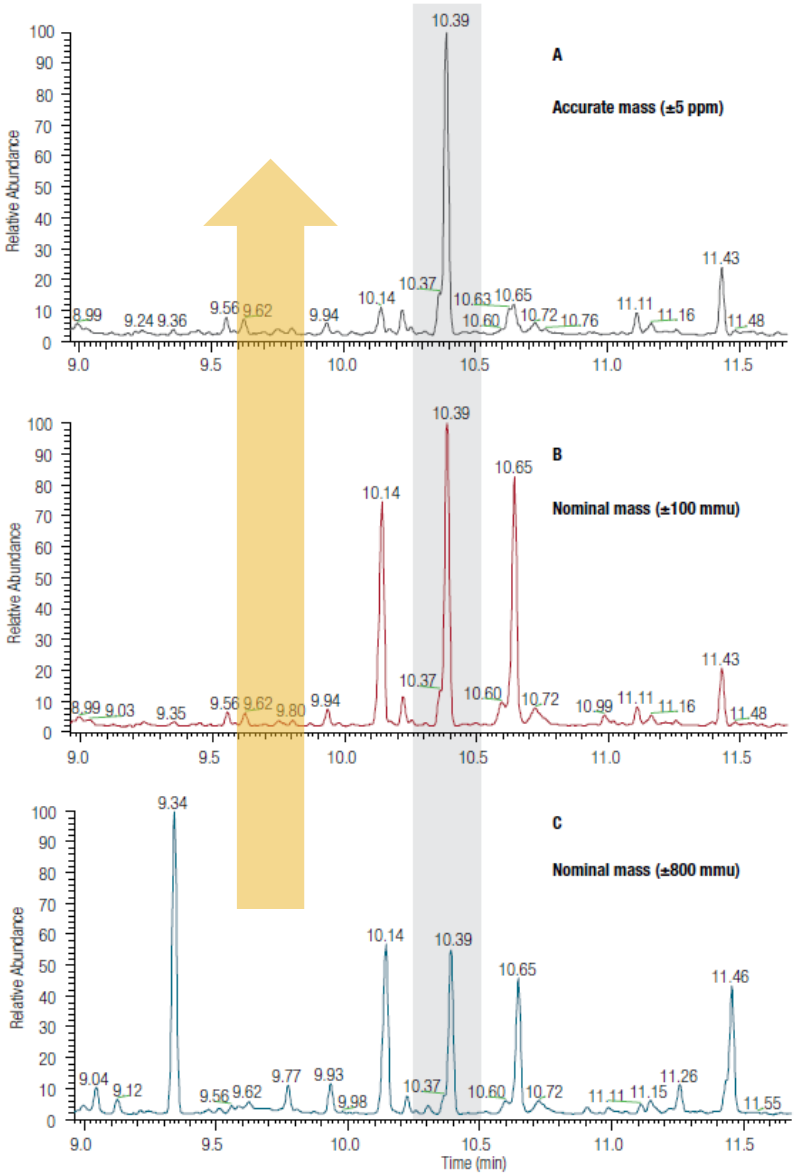
Benefit of High-Resolution and Accurate Mass Selectivity



- Full-scan accurate mass selectivity demonstrated for PS in a mixed sample containing PS, PA, PC, PE, PMMA, PP, PVC, and PET
- Accurate mass measurements enable confident detection (±5 ppm, A), whereas at nominal mass acquisitions additional interfering compounds can be detected

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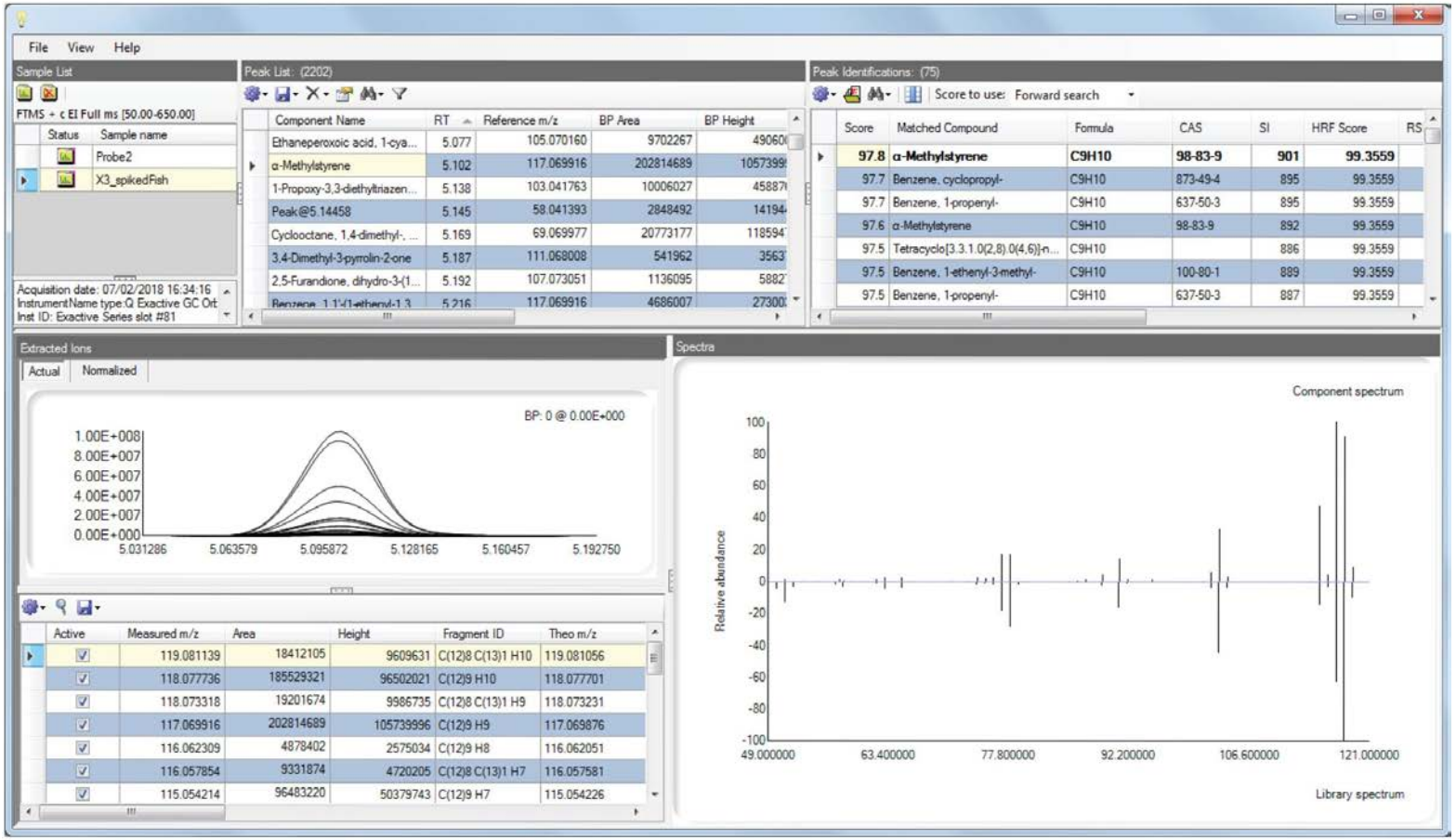
Non-Targeted Unknown Compound Identification

- With routine full-scan, high-resolution mode additional untargeted analysis of sample can be done with TraceFinder software
- Example: α-methylstyrene, a degradation product of polystyrene



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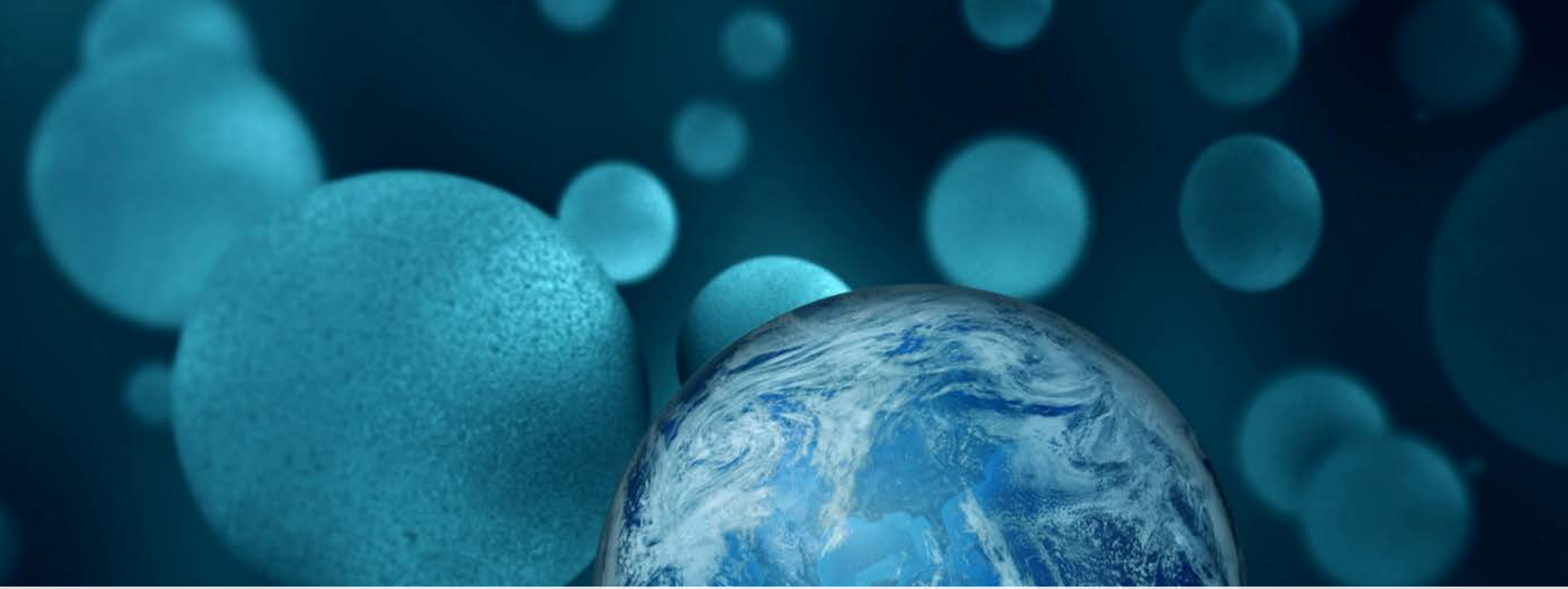

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Summary and Outlook

Summary

- py-GC-MS system in combination with pyrolysis a promising analytical technique that opens new possibilities in environmental microplastic analysis
- Exactive GC Orbitrap GC-MS system provides excellent linearity (0.05 – 50 µg) with accurate quantitative estimation of plastic polymer in real sample
- High resolving power facilitates sub-ppm accuracy at low and high concentrations -> confidential selectivity and identification of pyrolysis products
- Routine full-scan enables detection and identification of non-targeted and potentially unknown microplastic by-products during pyrolysis

Acknowledgement

www.shanalytik.de

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Thank you for your attention