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

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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

The two categories of plastics

**Thermoplastics**
- are a family of plastics that can be melted when heated and hardened when cooled. These characteristics, which lend the material its name, are reversible. That is, it can be reheated, reshaped and frozen repeatedly.
- Polyethylene (PE)
- Polypropylene (PP)
- Polyvinyl-chloride (PVC)
- Polyethylene Terephthalate (PET)
- Polystyrene (PS)
- Expanded polystyrene (EPS)
- ABS
- SAN
- Polyamides (PA)
- Polycarbonate (PC)
- Poly methyl methacrylate (PMMA)
- Thermoplastic elastomers (TPE)
- Polyarylsulfone (PSU)
- Fluoropolymers
- PEEK
- POM
- PBT
- Etc.

**Thermosets**
- are a family of plastics that undergo a chemical change when heated, creating a three dimensional network. After they are heated and formed these plastics cannot be re-melted and reformed.
- Polyurethane (PUR)
- Unsaturated polyester
- Epoxy resins
- Melamine resin
- Vinyl ester
- Silicone
- Phenol - formaldehyde
- Urea - formaldehyde
- Phenolic resins
- Acrylic resins
- Etc.

Source: PlasticsEurope AISBL, [www.plasticseurope.org](http://www.plasticseurope.org)
European plastic converter demand by segments and polymer types in 2017

Data for EU28+NO/CH.
Source: PlasticsEurope Market Research Group (PEMRG) and Conversio Market & Strategy GmbH

Source: PlasticsEurope AISBL, www.plasticseurope.org
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
Instrumentation: Pyrolysis-GC-Orbitrap MS
**Thermo Scientific™ TRACE™ 1310:** Unique modular injector and detector design

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<th>Detectors</th>
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<th>Software drivers</th>
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<td>PFPD</td>
<td>MS</td>
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Thermo Scientific™ Q Exactive™ GC Orbitrap™ GC-MS/MS system

Hybrid Quadrupole-Orbitrap GC-MS/MS System
**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 acquisition 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

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<th>Evolved Gas Analysis</th>
<th>Thermal Desorption</th>
<th>Heart–Cutting</th>
<th>Pyrolysis</th>
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<td>RxPy</td>
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Sample

EGA

TD

HC

PY

RxPy
Single-Shot Py-GC/MS Information

Pyrolyzer
600°C

Sample cup
Column
(30m, 0.25mm id)

MS
GC

GC oven
40 – 320°C (20°C/min)

Target Zone

Information of additives & polymers

40 100 200 300 400 500°C

0 2 4 6 8 10 12 14 min
Analysis of Microplastic and Microplastic in Spiked Fish
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.
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)

Polystyrene (PS):

- Calibration Curve:
  - $Y = 1.978e8X + 4.572e6\; R^2: 0.9999$;
  - Origin: Ignore; W: 1/X; Area
  - $R^2 = 0.999$

Polymethyl methacrylate (PMMA):

- Calibration Curve:
  - $Y = 4.032e7X - 4.879e5\; R^2: 0.9992$;
  - Origin: Ignore; W: 1/X; Area
  - $R^2 = 0.9992$
2. Spiked Fishmeal

Stability and mass accuracy irrespective of compound concentration

Accuracy of quantification for PS and PMMA

<table>
<thead>
<tr>
<th>Compound</th>
<th>Spiked Amount (µg)</th>
<th>Measured Amount (µg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polystyrene (PS)</td>
<td>2.7</td>
<td>2.9</td>
</tr>
<tr>
<td>Polymethyl methacrylate (PMMA)</td>
<td>2.5</td>
<td>2.2</td>
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</table>
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
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
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
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

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Thank you for your attention