Environmental

Identification of microplastics in water and food using pyrolysis GC with high resolution Orbitrap mass spectrometry

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Objective

The objective of this study was to demonstrate the utility of pyrolysis-gas chromatography-Orbitrap™ mass spectrometry for the detection and identification of common polymers in milk, meat and surface water samples.

Introduction

Microplastics are small particles made from synthetic polymers with a diameter typically ranging between 5 mm and 1 µm, whereas nanoparticles cover particles sizes of sub 1 µm. Two sources of microplastics can be recognized. The primary source is cosmetic and medical products, where microparticles—typically polypropylene, polyethylene, and polystyrene—were added deliberately. The secondary source is debris formed through the fragmentation of larger items made from synthetic polymers that typically enter the environment through inadequate disposal. The fragmentation occurs due to mechanical stress and atmospheric conditions. Some legal steps have been taken to limit the usage of microplastics in cosmetic products; however, secondary sources are considered the major contributor to microplastic pollution.

Today, microplastics are present in the terrestrial and aquatic environment and because of their small size they can easily migrate from the environment into the food chain. Microplastics may consist of not only the pure synthetic polymer but also include residuals of the monomer, plasticizers, flame retardants, and many other toxic additives that can have a negative impact on human health. Over time, microplastics may incorporate environmental contaminants such as trace metals.

Fourier Transform Infrared (FTIR) spectroscopy, Raman spectroscopy, and microscopy-based techniques are commonly applied to screen samples for the presence and identification of the chemical backbone of microplastic particles. However, especially for microscopy-based analysis, the number of samples that can be screened is limited. Pyrolysis gas chromatography mass spectrometry (py-GC-MS) presents a promising alternative for surveillance and identification of microplastics where throughput is critical. Furthermore, this analytical approach enables time-saving detection of bulk amounts of micro- and nanoplastics below the lower size limit of the microscopy techniques

Materials and methods

Sample preparation

Two sample types were investigated in this study, covering potential contamination in environmental waters and food related matrices. For the stormwater analysis, the sample (1 L total volume) was spiked with deuterated polystyrene (D5 -PS). The sample was filtered sequentially through Whatman™ 1 and 0.7 µm glass fiber filters (GFFs) to collect particulates (47 mm, GF/A and GF/F, Rowe Scientific, Wacol, Australia). The GFF was wrapped in aluminum foil (precleaned with acetone), dried in an orbital incubator at 50 ° C weighed in a pyrolysis cup (Eco-Cup LF, Frontier Laboratories, Japan) to which deuterated polystyrene (D^5-PS) was added. The milk and steak samples were freeze dried and milled with a grinder for 30 min using an overhead shaker at 140 rpm for 2 h to homogenize. After that, 1 g of each sample was spiked with D5-PS and extracted by pressurized liquid extraction in precleaned 5 mL ASE cells on a Thermo Scientific™ Dionex™ ASE™ 350 Accelerated Solvent Extractor. Extraction was performed with dichloromethane at 180 ° C and 1,500 psi with a heat and static time of 5 min using three extraction cycles. The extracts were weighed and 80 µL transferred to a pyrolysis cup. Analysis on Thermo Fisher Scientific™ Orbitrap Exploris™ GC 240 MS with Thermo Scientific TRACE™ 1310 GC.

Multi-Shot Pyrolyzer EGA/PY-3030D parameters	
Analysis type	Double-shot analysis
Thermal desorption	
Initial (°C)	100
Initial (min)	0
Rate (°C /min)	20
Final (°C)	300
Final (min)	1
Total time (min)	11
Pyrolysis	
Initial (°C)	650
Initial (min)	0.2
Interface temperature °C	320

Trace 1310 GC System parameters	
Injector type	SSL with an adapter kit for gas injection
Injection mode	Split
Temperature (°C)	300
Split ratio	200:1
Carrier gas (mL/min)	He, 1
Oven temperature program	
Temperature 1 (°C)	40
Hold time (min)	2
Rate (°C /min)	20
Temperature 2 (°C)	320
Hold time (min)	14

Orbitrap Exploris GC 240 MS parameters	
Transfer line temperature (°C)	300
Ionization type	EI
Ion source temperature (°C)	280
Electron energy (eV)	70
Emission current (µA)	50
Acquisition mode	Full scan
Mass range (*m/z*)	40–600
Resolving power setting	60,000
Lock masses (*m/z*)	133.01356; 207.03235; 225.04292; 281.05114; 299.06171; 355.06993

Table 1. Thermo Scientific™ Orbitrap Exploris™ GC 240 method parameters.

Results

An overlap of the TD total ion current chromatogram of the standard mix and the milk sample is shown in Figure 1. This comparison demonstrates that the TD stage removes a considerable quantity of chemical background from the sample data. In the first step of this study, a series of polymer standards were subjected to pyrolysis to find characteristic fragmentation products that can be used for polymer identification in real samples. For data processing, the resulting pyrograms were screened with Thermo Scientific™ Compound Discoverer™ software to find the known pyrolysis products. Compound Discoverer software can use both nominal as well as high resolution accurate mass (HRAM) spectral libraries (figure 3).

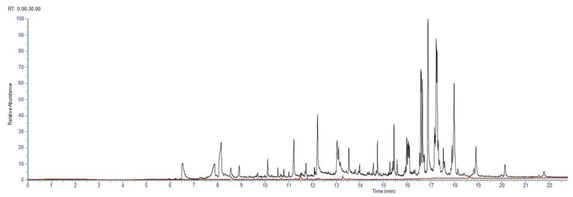


Figure 1. Total ion current chromatogram (*m/z* 40–600) obtained for a milk sample (black chromatogram) compared with a solvent standard of a mix of polymers (red chromatogram) after the TD step.

Polymer	Pyrolysis products
Polystyrene (PS)	Styrene; styrene dimer; styrene trimer; allylbenzene; α-methylstyrene; toluene
Polypropylene (PP)	2,4-dimethyl-1-heptane; 3-5-dimethyl-1-hexane
Polyvinyl chloride (PVC)	Benzene, naphthalene, fluorene
Polymethyl methacrylate (PMMA)	Methyl methacrylate
Polycarbonate (PC)	Bisphenol A
Polyethylene terephthalate (PET)	Vinyl benzoate

Table 2. Polymers and their characteristic pyrolysis products identified .

In the second step of this study, real samples (prepared as described above) were pyrolyzed to confirm the presence of microplastic particles and identify the polymer types if particles are present. During the data processing in Thermo Scientific™ Chromeleon™ CDS software, benzene, naphthalene, and fluorene were found in the stormwater sample. As can be seen in Table 4, these compounds are formed during the pyrolysis of PVC.

Figure 4 shows molecular ions of benzene, naphthalene, and fluorene in the standard mix and in the stormwater sample. It was concluded that PVC was present in the sample. Styrene, allylbenzene, α-methylstyrene, and toluene were detected in the pyrolysis chromatograms of milk and beef, indicating the possible presence of polystyrene. However, the most indicative polystyrene pyrolysis products, styrene dimer and styrene trimer, were not found. Therefore, the contamination with polystyrene could not be confirmed

Figure 3. The top spectrum is the deconvoluted spectrum, the bottom one from the library, α-methylstyrene (nominal mass library).

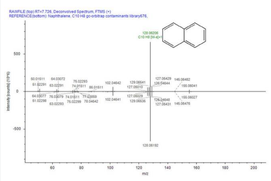
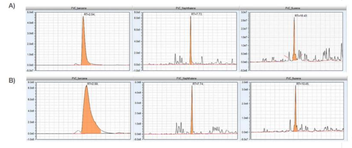


Figure 4. Identification of PVC, A) standard and B) stormwater sample.



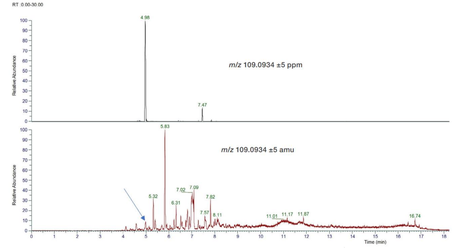


Figure 5. Extracted ion chromatogram of *m/z* 109.0934 for a spiked storm water sample. The upper chromatogram was obtained with a mass extraction window of ±5 ppm (HRAM approach); the bottom chromatogram was obtained with a mass extraction window of ±0.5 amu (simulation of a single quadrupole mass spectrometer). The blue arrow points to the deuterated styrene peak

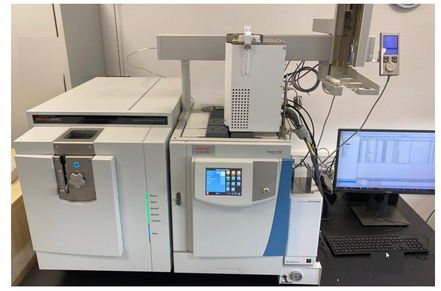


Figure 6. Orbitrap Exploris GC 240 with Frontier multi shot pyrolizer installed on GC.

Conclusions

.The work presented demonstrates:

- Py-GC-Orbitrap MS is an excellent tool for the confirmation of the presence and identity of microplastics in different sample types.
- High selectivity and sensitivity were achieved by using the unique characteristics of the Orbitrap mass spectrometer, in combination with a targeted screening approach using both Compound Discoverer software and Chromeleon software.
- The combination of automated sample analysis using the pyrolizer and targeted data processing enables an automated analysis of environmental samples.

Acknowledgements

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